M_r = 484.61	F(000) = 524
Triclinic, $P\overline{1}$	D_x = 1.145 Mg m^{-3}
Hall symbol: -P 1	Mo $K\alpha$ radiation, λ = 0.71073 Å
a = 8.3154 (6) Å	Cell parameters from 4014 reflections
b = 12.5589 (8) Å	θ = 2.5–27.3°
c = 13.9410 (9) Å	μ = 0.08 mm^{-1}
α = 101.782 (1)°	T = 293 K
β = 97.529 (1)°	Block, colourless
γ = 94.156 (1)°	0.45 × 0.35 × 0.30 mm
V = 1405.52 (16) Å^3	

Data collection

Bruker SMART APEX diffractometer	4482 reflections with $I > 2\sigma(I)$
Radiation source: fine-focus sealed tube	R_{int} = 0.021
graphite	θ_{max} = 27.5°, θ_{min} = 1.7°
ω scans	h = −10→10
13784 measured reflections	k = −16→14
6428 independent reflections	l = −18→17

Refinement

Refinement on F^2	Primary atom site location: structure-invariant direct methods
Least-squares matrix: full	Secondary atom site location: difference Fourier map
$R[F^2 > 2\sigma(F^2)]$ = 0.060	Hydrogen site location: inferred from neighbouring sites
$wR(F^2)$ = 0.184	H-atom parameters constrained
S = 1.03	$w = 1/[\sigma^2(F_o^2) + (0.0989P)^2 + 0.2549P]$ where $P = (F_o^2 + 2F_c^2)/3$
6428 reflections	$(\Delta/\sigma)_{max}$ = 0.001
318 parameters	$\Delta\rho_{max}$ = 0.35 e Å^{-3}
0 restraints	$\Delta\rho_{min}$ = −0.19 e Å^{-3}

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å^2)

	x	y	z	U_{iso}*/U_{eq}
O1	0.54867 (16)	0.16145 (12)	0.44990 (9)	0.0584 (4)
O2	0.28231 (18)	0.17998 (13)	0.40617 (11)	0.0644 (4)
O3	0.22035 (16)	0.13010 (10)	0.58548 (10)	0.0537 (3)
O4	0.13940 (17)	0.83903 (11)	1.01874 (10)	0.0608 (4)
O5	0.4354 (2)	0.79162 (18)	1.21064 (11)	0.0891 (6)
O6	0.43525 (16)	0.77133 (14)	1.04833 (10)	0.0665 (4)
C1	0.6069 (3)	0.17993 (18)	0.35761 (14)	0.0571 (5)
C2	0.7872 (3)	0.1715 (3)	0.3802 (2)	0.1093 (12)
H2A	0.8337	0.2275	0.4369	0.164*

H2B	0.8384	0.1808	0.3242	0.164*
H2C	0.8044	0.1010	0.3939	0.164*
C3	0.5730 (4)	0.29242 (19)	0.34262 (19)	0.0811 (7)
H3A	0.6249	0.3465	0.3994	0.122*
H3B	0.4575	0.2972	0.3344	0.122*
H3C	0.6150	0.3051	0.2846	0.122*
C4	0.5265 (4)	0.0919 (2)	0.27129 (18)	0.0882 (8)
H4A	0.4108	0.0961	0.2625	0.132*
H4B	0.5486	0.0216	0.2839	0.132*
H4C	0.5685	0.1016	0.2124	0.132*
C5	0.3936 (2)	0.16414 (14)	0.46314 (13)	0.0459 (4)
C6	0.3813 (2)	0.14131 (16)	0.56480 (14)	0.0516 (4)
H6A	0.4307	0.0747	0.5700	0.062*
H6B	0.4434	0.2005	0.6146	0.062*
C7	0.1432 (2)	0.22212 (13)	0.61535 (12)	0.0424 (4)
C8	0.2100 (2)	0.32846 (15)	0.62278 (14)	0.0501 (4)
H8	0.3146	0.3418	0.6082	0.060*
C9	0.1196 (2)	0.41480 (14)	0.65211 (14)	0.0506 (4)
H9	0.1661	0.4860	0.6585	0.061*
C10	−0.0379 (2)	0.39793 (13)	0.67218 (12)	0.0429 (4)
C11	−0.0997 (2)	0.29071 (14)	0.66524 (12)	0.0432 (4)
H11	−0.2045	0.2775	0.6795	0.052*
C12	−0.0121 (2)	0.20183 (13)	0.63788 (12)	0.0423 (4)
C13	−0.0854 (3)	0.08640 (15)	0.63031 (16)	0.0593 (5)
H13A	−0.1955	0.0875	0.6441	0.089*
H13B	−0.0223	0.0540	0.6774	0.089*
H13C	−0.0851	0.0443	0.5646	0.089*
C14	−0.1407 (2)	0.49513 (14)	0.69162 (14)	0.0480 (4)
C15	−0.3066 (2)	0.46110 (18)	0.7189 (2)	0.0755 (7)
H15A	−0.3641	0.4036	0.6669	0.113*
H15B	−0.3691	0.5228	0.7274	0.113*
H15C	−0.2904	0.4356	0.7796	0.113*
C16	−0.1702 (3)	0.53592 (18)	0.59406 (15)	0.0711 (7)
H16A	−0.0673	0.5558	0.5749	0.107*
H16B	−0.2309	0.5985	0.6037	0.107*
H16C	−0.2308	0.4788	0.5429	0.107*
C17	−0.0548 (2)	0.58614 (13)	0.77766 (12)	0.0403 (4)
C18	−0.0610 (2)	0.69584 (13)	0.77638 (12)	0.0402 (4)
H18	−0.1110	0.7143	0.7192	0.048*
C19	0.0042 (2)	0.77945 (13)	0.85692 (12)	0.0420 (4)
C20	0.0800 (2)	0.75110 (14)	0.94170 (13)	0.0445 (4)
C21	0.0898 (2)	0.64272 (16)	0.94550 (14)	0.0522 (4)
H21	0.1415	0.6243	1.0023	0.063*
C22	0.0220 (2)	0.56143 (15)	0.86392 (14)	0.0494 (4)
H22	0.0281	0.4886	0.8671	0.059*
C23	−0.0095 (3)	0.89746 (16)	0.85277 (17)	0.0642 (6)
H23A	0.0977	0.9358	0.8633	0.096*
H23B	−0.0696	0.9303	0.9034	0.096*
H23C	−0.0651	0.9015	0.7890	0.096*

C24	0.1975 (2)	0.8205 (2)	1.11273 (14)	0.0632 (6)
H24A	0.1263	0.7618	1.1251	0.076*
H24B	0.1881	0.8857	1.1619	0.076*
C25	0.3708 (2)	0.79182 (16)	1.12921 (13)	0.0527 (5)
C26	0.6032 (2)	0.7409 (2)	1.04549 (17)	0.0702 (6)
C27	0.6246 (5)	0.6415 (3)	1.0903 (3)	0.1357 (14)
H27A	0.6150	0.6602	1.1595	0.203*
H27B	0.7303	0.6178	1.0827	0.203*
H27C	0.5419	0.5836	1.0572	0.203*
C28	0.7205 (4)	0.8347 (3)	1.1020 (3)	0.1313 (15)
H28A	0.7017	0.8982	1.0754	0.197*
H28B	0.8299	0.8172	1.0967	0.197*
H28C	0.7055	0.8493	1.1704	0.197*
C29	0.6096 (4)	0.7084 (4)	0.9371 (2)	0.1321 (15)
H29A	0.5931	0.7701	0.9073	0.198*
H29B	0.5257	0.6502	0.9072	0.198*
H29C	0.7142	0.6842	0.9270	0.198*

Atomic displacement parameters (Å^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
O1	0.0552 (8)	0.0840 (10)	0.0451 (7)	0.0226 (7)	0.0167 (6)	0.0235 (7)
O2	0.0593 (8)	0.0816 (10)	0.0560 (8)	0.0185 (7)	0.0039 (7)	0.0224 (7)
O3	0.0603 (8)	0.0434 (7)	0.0634 (8)	0.0169 (6)	0.0273 (6)	0.0100 (6)
O4	0.0636 (8)	0.0574 (8)	0.0506 (8)	0.0147 (6)	−0.0056 (6)	−0.0076 (6)
O5	0.0735 (11)	0.1484 (18)	0.0461 (9)	0.0218 (11)	0.0038 (7)	0.0219 (9)
O6	0.0487 (8)	0.1064 (12)	0.0437 (7)	0.0157 (7)	0.0103 (6)	0.0098 (7)
C1	0.0673 (12)	0.0676 (13)	0.0446 (10)	0.0186 (10)	0.0208 (9)	0.0193 (9)
C2	0.0730 (17)	0.195 (4)	0.093 (2)	0.048 (2)	0.0443 (15)	0.075 (2)
C3	0.113 (2)	0.0603 (14)	0.0764 (16)	0.0089 (13)	0.0251 (14)	0.0213 (12)
C4	0.136 (2)	0.0705 (15)	0.0585 (14)	0.0123 (15)	0.0343 (15)	0.0028 (11)
C5	0.0526 (10)	0.0408 (9)	0.0452 (9)	0.0152 (7)	0.0102 (8)	0.0055 (7)
C6	0.0563 (11)	0.0560 (11)	0.0490 (10)	0.0241 (9)	0.0171 (8)	0.0141 (8)
C7	0.0503 (9)	0.0407 (9)	0.0375 (8)	0.0122 (7)	0.0120 (7)	0.0055 (7)
C8	0.0454 (9)	0.0462 (10)	0.0595 (11)	0.0042 (8)	0.0177 (8)	0.0074 (8)
C9	0.0538 (10)	0.0344 (9)	0.0622 (11)	0.0019 (7)	0.0144 (8)	0.0049 (8)
C10	0.0462 (9)	0.0370 (8)	0.0426 (9)	0.0070 (7)	0.0067 (7)	0.0004 (7)
C11	0.0430 (9)	0.0422 (9)	0.0429 (9)	0.0042 (7)	0.0113 (7)	0.0029 (7)
C12	0.0540 (10)	0.0355 (8)	0.0372 (8)	0.0059 (7)	0.0112 (7)	0.0041 (6)
C13	0.0721 (13)	0.0401 (10)	0.0686 (13)	0.0044 (9)	0.0302 (10)	0.0066 (9)
C14	0.0489 (10)	0.0385 (9)	0.0524 (10)	0.0110 (7)	0.0031 (8)	0.0010 (7)
C15	0.0450 (11)	0.0517 (12)	0.119 (2)	0.0112 (9)	0.0138 (11)	−0.0087 (12)
C16	0.0976 (17)	0.0548 (12)	0.0504 (11)	0.0289 (11)	−0.0129 (11)	−0.0050 (9)
C17	0.0419 (8)	0.0387 (8)	0.0405 (8)	0.0093 (7)	0.0107 (7)	0.0048 (7)
C18	0.0458 (9)	0.0396 (9)	0.0369 (8)	0.0100 (7)	0.0101 (7)	0.0079 (6)
C19	0.0441 (9)	0.0388 (9)	0.0443 (9)	0.0086 (7)	0.0130 (7)	0.0061 (7)
C20	0.0413 (9)	0.0461 (9)	0.0428 (9)	0.0090 (7)	0.0075 (7)	−0.0005 (7)
C21	0.0564 (11)	0.0567 (11)	0.0432 (9)	0.0166 (8)	0.0007 (8)	0.0105 (8)

C22	0.0586 (11)	0.0391 (9)	0.0525 (10)	0.0141 (8)	0.0060 (8)	0.0129 (8)
C23	0.0833 (15)	0.0417 (10)	0.0646 (13)	0.0103 (10)	0.0068 (11)	0.0058 (9)
C24	0.0547 (11)	0.0802 (15)	0.0449 (10)	0.0143 (10)	0.0049 (8)	−0.0102 (9)
C25	0.0516 (10)	0.0627 (12)	0.0382 (9)	0.0016 (8)	0.0045 (8)	0.0010 (8)
C26	0.0450 (11)	0.0988 (18)	0.0643 (13)	0.0143 (11)	0.0131 (9)	0.0065 (12)
C27	0.140 (3)	0.116 (3)	0.163 (4)	0.069 (2)	0.040 (3)	0.029 (3)
C28	0.0605 (16)	0.132 (3)	0.174 (4)	−0.0194 (17)	0.0303 (19)	−0.027 (3)
C29	0.087 (2)	0.228 (5)	0.081 (2)	0.045 (2)	0.0380 (17)	0.007 (2)

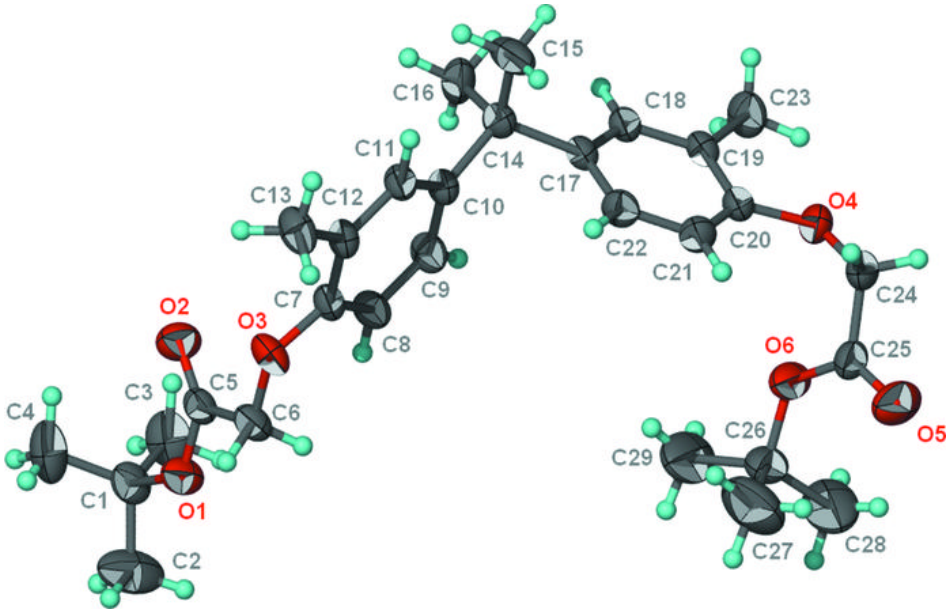
Geometric parameters (Å, °)

O1—C5	1.328 (2)	C13—H13C	0.96
O1—C1	1.488 (2)	C14—C15	1.533 (3)
O2—C5	1.194 (2)	C14—C17	1.534 (2)
O3—C7	1.379 (2)	C14—C16	1.545 (3)
O3—C6	1.409 (2)	C15—H15A	0.96
O4—C20	1.384 (2)	C15—H15B	0.96
O4—C24	1.407 (3)	C15—H15C	0.96
O5—C25	1.191 (2)	C16—H16A	0.96
O6—C25	1.298 (2)	C16—H16B	0.96
O6—C26	1.478 (2)	C16—H16C	0.96
C1—C4	1.502 (3)	C17—C18	1.386 (2)
C1—C2	1.507 (3)	C17—C22	1.389 (2)
C1—C3	1.511 (3)	C18—C19	1.391 (2)
C2—H2A	0.96	C18—H18	0.93
C2—H2B	0.96	C19—C20	1.389 (2)
C2—H2C	0.96	C19—C23	1.507 (3)
C3—H3A	0.96	C20—C21	1.381 (3)
C3—H3B	0.96	C21—C22	1.389 (3)
C3—H3C	0.96	C21—H21	0.93
C4—H4A	0.96	C22—H22	0.93
C4—H4B	0.96	C23—H23A	0.96
C4—H4C	0.96	C23—H23B	0.96
C5—C6	1.517 (3)	C23—H23C	0.96
C6—H6A	0.97	C24—C25	1.510 (3)
C6—H6B	0.97	C24—H24A	0.97
C7—C12	1.387 (2)	C24—H24B	0.97
C7—C8	1.387 (3)	C26—C28	1.488 (4)
C8—C9	1.388 (3)	C26—C29	1.492 (4)
C8—H8	0.93	C26—C27	1.517 (5)
C9—C10	1.385 (3)	C27—H27A	0.96
C9—H9	0.93	C27—H27B	0.96
C10—C11	1.386 (2)	C27—H27C	0.96
C10—C14	1.540 (2)	C28—H28A	0.96
C11—C12	1.392 (2)	C28—H28B	0.96
C11—H11	0.93	C28—H28C	0.96
C12—C13	1.509 (2)	C29—H29A	0.96
C13—H13A	0.96	C29—H29B	0.96
C13—H13B	0.96	C29—H29C	0.96

C5—O1—C1	122.52 (14)	C14—C15—H15B	109.5
C7—O3—C6	119.71 (14)	H15A—C15—H15B	109.5
C20—O4—C24	119.61 (16)	C14—C15—H15C	109.5
C25—O6—C26	123.23 (16)	H15A—C15—H15C	109.5
O1—C1—C4	109.56 (18)	H15B—C15—H15C	109.5
O1—C1—C2	101.98 (16)	C14—C16—H16A	109.5
C4—C1—C2	111.8 (2)	C14—C16—H16B	109.5
O1—C1—C3	109.83 (17)	H16A—C16—H16B	109.5
C4—C1—C3	111.7 (2)	C14—C16—H16C	109.5
C2—C1—C3	111.5 (2)	H16A—C16—H16C	109.5
C1—C2—H2A	109.5	H16B—C16—H16C	109.5
C1—C2—H2B	109.5	C18—C17—C22	117.09 (15)
H2A—C2—H2B	109.5	C18—C17—C14	121.98 (15)
C1—C2—H2C	109.5	C22—C17—C14	120.75 (15)
H2A—C2—H2C	109.5	C17—C18—C19	122.83 (15)
H2B—C2—H2C	109.5	C17—C18—H18	118.6
C1—C3—H3A	109.5	C19—C18—H18	118.6
C1—C3—H3B	109.5	C20—C19—C18	118.19 (15)
H3A—C3—H3B	109.5	C20—C19—C23	120.99 (16)
C1—C3—H3C	109.5	C18—C19—C23	120.81 (16)
H3A—C3—H3C	109.5	C21—C20—O4	124.86 (16)
H3B—C3—H3C	109.5	C21—C20—C19	120.66 (16)
C1—C4—H4A	109.5	O4—C20—C19	114.47 (15)
C1—C4—H4B	109.5	C20—C21—C22	119.52 (16)
H4A—C4—H4B	109.5	C20—C21—H21	120.2
C1—C4—H4C	109.5	C22—C21—H21	120.2
H4A—C4—H4C	109.5	C21—C22—C17	121.70 (16)
H4B—C4—H4C	109.5	C21—C22—H22	119.2
O2—C5—O1	127.28 (17)	C17—C22—H22	119.2
O2—C5—C6	125.41 (17)	C19—C23—H23A	109.5
O1—C5—C6	107.31 (15)	C19—C23—H23B	109.5
O3—C6—C5	113.92 (15)	H23A—C23—H23B	109.5
O3—C6—H6A	108.8	C19—C23—H23C	109.5
C5—C6—H6A	108.8	H23A—C23—H23C	109.5
O3—C6—H6B	108.8	H23B—C23—H23C	109.5
C5—C6—H6B	108.8	O4—C24—C25	116.98 (17)
H6A—C6—H6B	107.7	O4—C24—H24A	108.1
O3—C7—C12	114.91 (15)	C25—C24—H24A	108.1
O3—C7—C8	124.60 (16)	O4—C24—H24B	108.1
C12—C7—C8	120.48 (15)	C25—C24—H24B	108.1
C7—C8—C9	119.50 (17)	H24A—C24—H24B	107.3
C7—C8—H8	120.2	O5—C25—O6	126.65 (19)
C9—C8—H8	120.2	O5—C25—C24	120.14 (18)
C10—C9—C8	121.84 (16)	O6—C25—C24	113.20 (16)
C10—C9—H9	119.1	O6—C26—C28	109.1 (2)
C8—C9—H9	119.1	O6—C26—C29	102.79 (19)
C9—C10—C11	116.96 (15)	C28—C26—C29	116.1 (3)
C9—C10—C14	119.77 (15)	O6—C26—C27	109.7 (2)
C11—C10—C14	123.03 (15)	C28—C26—C27	110.2 (3)

C10—C11—C12	123.05 (16)	C29—C26—C27	108.5 (3)
C10—C11—H11	118.5	C26—C27—H27A	109.5
C12—C11—H11	118.5	C26—C27—H27B	109.5
C7—C12—C11	118.11 (15)	H27A—C27—H27B	109.5
C7—C12—C13	120.80 (15)	C26—C27—H27C	109.5
C11—C12—C13	121.08 (16)	H27A—C27—H27C	109.5
C12—C13—H13A	109.5	H27B—C27—H27C	109.5
C12—C13—H13B	109.5	C26—C28—H28A	109.5
H13A—C13—H13B	109.5	C26—C28—H28B	109.5
C12—C13—H13C	109.5	H28A—C28—H28B	109.5
H13A—C13—H13C	109.5	C26—C28—H28C	109.5
H13B—C13—H13C	109.5	H28A—C28—H28C	109.5
C15—C14—C17	106.90 (16)	H28B—C28—H28C	109.5
C15—C14—C10	111.80 (15)	C26—C29—H29A	109.5
C17—C14—C10	111.47 (14)	C26—C29—H29B	109.5
C15—C14—C16	108.36 (18)	H29A—C29—H29B	109.5
C17—C14—C16	111.53 (15)	C26—C29—H29C	109.5
C10—C14—C16	106.79 (15)	H29A—C29—H29C	109.5
C14—C15—H15A	109.5	H29B—C29—H29C	109.5
C5—O1—C1—C4	−62.9 (2)	C15—C14—C17—C18	−95.7 (2)
C5—O1—C1—C2	178.6 (2)	C10—C14—C17—C18	141.89 (16)
C5—O1—C1—C3	60.2 (3)	C16—C14—C17—C18	22.6 (2)
C1—O1—C5—O2	0.6 (3)	C15—C14—C17—C22	79.1 (2)
C1—O1—C5—C6	179.73 (16)	C10—C14—C17—C22	−43.3 (2)
C7—O3—C6—C5	−80.1 (2)	C16—C14—C17—C22	−162.58 (17)
O2—C5—C6—O3	5.4 (3)	C22—C17—C18—C19	−0.6 (3)
O1—C5—C6—O3	−173.69 (15)	C14—C17—C18—C19	174.44 (15)
C6—O3—C7—C12	−177.31 (15)	C17—C18—C19—C20	0.6 (3)
C6—O3—C7—C8	3.2 (3)	C17—C18—C19—C23	−178.41 (17)
O3—C7—C8—C9	178.89 (17)	C24—O4—C20—C21	−8.0 (3)
C12—C7—C8—C9	−0.6 (3)	C24—O4—C20—C19	170.98 (16)
C7—C8—C9—C10	−1.5 (3)	C18—C19—C20—C21	0.0 (3)
C8—C9—C10—C11	2.3 (3)	C23—C19—C20—C21	178.97 (18)
C8—C9—C10—C14	−172.32 (17)	C18—C19—C20—O4	−179.11 (15)
C9—C10—C11—C12	−1.1 (3)	C23—C19—C20—O4	−0.1 (2)
C14—C10—C11—C12	173.34 (16)	O4—C20—C21—C22	178.45 (17)
O3—C7—C12—C11	−177.78 (14)	C19—C20—C21—C22	−0.5 (3)
C8—C7—C12—C11	1.8 (3)	C20—C21—C22—C17	0.6 (3)
O3—C7—C12—C13	0.7 (2)	C18—C17—C22—C21	0.0 (3)
C8—C7—C12—C13	−179.79 (18)	C14—C17—C22—C21	−175.09 (17)
C10—C11—C12—C7	−0.9 (3)	C20—O4—C24—C25	82.9 (2)
C10—C11—C12—C13	−179.34 (17)	C26—O6—C25—O5	1.7 (4)
C9—C10—C14—C15	−176.28 (18)	C26—O6—C25—C24	−179.7 (2)
C11—C10—C14—C15	9.4 (3)	O4—C24—C25—O5	168.5 (2)
C9—C10—C14—C17	−56.7 (2)	O4—C24—C25—O6	−10.2 (3)
C11—C10—C14—C17	129.00 (18)	C25—O6—C26—C28	−65.1 (3)
C9—C10—C14—C16	65.4 (2)	C25—O6—C26—C29	171.0 (3)
C11—C10—C14—C16	−109.0 (2)	C25—O6—C26—C27	55.7 (3)

Fig. 1


C15
C16
C18
C23
C11
C14
C19
C13
C12
C17
O4
C10
C22
C20
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C24
O2
C7
C9
O3
C8
O6
C25
C3
C5
C4
C6
O5
C26
C29
C1
O1
C27
C28
C2

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4-[2-(2,2-Dimethyl-4,6-dioxo-1,3-dioxan-5-ylidene)hydrazin-1-yl]benzonitrile

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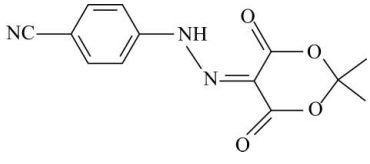
Key indicators: single-crystal X-ray study; T = 100 K; mean σ(C–C) = 0.002 Å; R factor = 0.038; wR factor = 0.108; data-to-parameter ratio = 13.8.

In the title compound, $C_{13}H_{11}N_3O_4$, the dioxane ring adopts an envelope conformation with the C atom bonded to the dimethyl group in the flap position [deviation = 0.613 (1) Å]. The nitrile group and the attached benzene ring are roughly coplanar [maximum deviation = 0.087 (1) Å]. An intramolecular N—H···O hydrogen bond involving the hydrazinyl group generates an S(6) ring. The N—N and C—N bond lengths indicate that the compound may be a mixture of the azo and hydrazone tautomeric forms but the presence of the N-bound H atom supports the hydrazone form. The crystal structure is stabilized by weak intermolecular C—H···O, C—H···N and C—H···π interactions.

Related literature

For the applications of related azo compounds, see: Branger *et al.* (1997); Buchel *et al.* (1995); Gale *et al.* (1998); Ikeda & Tsutsumi (1995); Kang *et al.* (2000); Karcı *et al.* (2004); Kim *et al.* (1995); Kobrakov *et al.* (2004); Natansohn *et al.* (1992); Rochon *et al.* (1995). For related hydrazone structures, see: Çolak *et al.* (2010); Pavlovic *et al.* (2009); Seferoğlu *et al.* (2008); Seferoğlu *et al.* (2009); Wojciechowski & Szymezak (2007).



Experimental

Crystal data

$C_{13}H_{11}N_3O_4$
M_r = 273.25
Monoclinic, $P2_1/n$
a = 9.7617 (2) Å
b = 11.0023 (2) Å
c = 11.4753 (3) Å
β = 93.796 (1)°
V = 1229.76 (5) Å^3
Z = 4
Mo $K\alpha$ radiation
μ = 0.11 mm^{-1}
T = 100 K
0.46 × 0.43 × 0.29 mm

Data collection

Bruker Kappa APEXII CCD area-detector diffractometer
Absorption correction: multi-scan (*SADABS*; Bruker, 2005)
T_{min} = 0.950, T_{max} = 0.968
11746 measured reflections
3098 independent reflections
2591 reflections with $I > 2\sigma(I)$
R_{int} = 0.029

Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.038
$wR(F^2)$ = 0.108
S = 1.04
3098 reflections
225 parameters
All H-atom parameters refined
$\Delta\rho_{max}$ = 0.38 e Å^{-3}
$\Delta\rho_{min}$ = −0.24 e Å^{-3}

Table 1
Hydrogen-bond geometry (Å, °).

*Cg*1 is the centroid of the C5–C10 ring.

D—H···A	D—H	H···A	D···A	D—H···A
N2—H2···O3	0.92 (2)	1.958 (16)	2.6674 (13)	132 (1)
C9—H9···N1^{i}	0.94 (2)	2.624 (15)	3.5320 (16)	164 (1)
C10—H10···N3^{ii}	0.99 (2)	2.485 (15)	3.3876 (16)	152 (1)
C12—H123···O2^{iii}	0.97 (2)	2.527 (17)	3.4454 (15)	159 (1)
C12—H122···*Cg*1^{iv}	0.98 (2)	2.491 (15)	3.4575 (13)	171 (1)

Symmetry codes: (i) $-x+\frac{3}{2}, y-\frac{1}{2}, -z+\frac{3}{2}$; (ii) $x-\frac{1}{2}, -y+\frac{1}{2}, z+\frac{1}{2}$; (iii) $-x, -y+1, -z+2$; (iv) $-x+\frac{3}{2}, y-\frac{1}{2}, -z+\frac{1}{2}$.

Data collection: *APEX2* (Bruker, 2007); cell refinement: *SAINT* (Bruker, 2007); data reduction: *SAINT* program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *ORTEP-3 for Windows* (Farrugia, 1997); software used to prepare material for publication: *WinGX* (Farrugia, 1999) and *PLATON* (Spek, 2009).

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Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: CI5104).

References

Branger, C., Lequan, M., Lequan, R. M., Large, M. & Kajzar, F. (1997). *Chem. Phys. Lett.* **272**, 265–270.
Bruker (2005). *SADABS*. Bruker AXS Inc. Madison, Wisconsin, USA.
Bruker (2007). *APEX2* and *SAINT*. Bruker AXS Inc. Madison, Wisconsin, USA.
Buchel, M., Sekkat, Z., Paul, S., Weichart, B., Menzel, H. & Knoll, W. (1995). *Langmuir*, **11**, 4460–4466.
Çolak, N., Aksakal, D., Andaç, Ö. & Büyükgüngör, O. (2010). *Acta Cryst.* E**66**, o1165–o1166.
Farrugia, L. J. (1997). *J. Appl. Cryst.* **30**, 565.

Farrugia, L. J. (1999). *J. Appl. Cryst.* **32**, 837–838.
Gale, P. A., Chen, Z., Drew, M. G. B., Heath, J. A. & Beer, P. D. (1998). *Polyhedron*, **4**, 405–412.
Ikeda, T. & Tsutsumi, O. (1995). *Science*, **268**, 1873–1875.
Kang, H. C., Lee, B. M., Yoon, J. & Yoon, M. (2000). *J. Colloid Interface Sci.* **231**, 255–264.
Karcı, F., Şener, İ. & Deligöz, H. (2004). *Dyes Pigments*, **62**, 131–140.
Kim, D. Y., Tripathy, S. K., Li, L. & Kumar, J. (1995). *Appl. Phys. Lett.* **66**, 1166–1168.
Kobrakov, K. I., Glyadyaeva, O. Yu., Stankevich, G. S. & Kovtun, L. G. (2004). *Fibre Chem.* **36**, 41–42.
Natansohn, A., Rochon, P., Gosselin, J. & Xie, S. (1992). *Macromolecules*, **25**, 2268–2273.
Pavlovic, G., Racane, L., Cicak, H. & Tralic-Kulenovic, V. (2009). *Dyes Pigments*, **83**, 354–362.
Rochon, P., Battalla, E. & Natansohn, A. (1995). *Appl. Phys. Lett.* **66**, 136–138.
Seferoğlu, Z., Ertan, N., Hökelek, T. & Şahin, E. (2008). *Dyes Pigments*, **77**, 614–625.
Seferoğlu, Z., Ertan, N., Kickelbick, G. & Hökelek, T. (2009). *Dyes Pigments*, **82**, 20–25.
Sheldrick, G. M. (2008). *Acta Cryst.* A**64**, 112–122.
Spek, A. L. (2009). *Acta Cryst.* D**65**, 148–155.
Wojciechowski, K. & Szymezak, A. (2007). *Dyes Pigments*, **75**, 45–51.

supplementary materials

Acta Cryst. (2010). E**66**, o1784-o1785 [**doi:10.1107/S1600536810024025**]

4-[2-(2,2-Dimethyl-4,6-dioxo-1,3-dioxan-5-ylidene)hydrazin-1-yl]benzonitrile

N. Çolak, Y. Yildirir, B. Tercan, E. Ermis and T. Hökelek

Comment

It has been known for many years that the azo compounds are widely used class of dyes due to their applications in various fields such as the dyeing of textile fibers, the coloring of different materials, colored plastics and electrochemical sensors (Kobrakov *et al.*, 2004; Karcı *et al.*, 2004; Gale *et al.*, 1998). Azo dyes have been attracting intensive interest for their potential use in optical data storage (Natansohn *et al.*, 1992), optical switching (Ikeda & Tsutsumi, 1995), polarization holography (Kim *et al.*, 1995; Rochon *et al.*, 1995), optical modulation (Buchel *et al.*, 1995), nonlinear optics (Branger *et al.*, 1997) and photolabile surfactants (Kang *et al.*, 2000).

The dyes may exist in two possible tautomeric forms, namely azo form and hydrazone form. The azo-hydrazone tautomerism is quite interesting from a theoretical and practical point of view because the two tautomers have different properties. Azo dyes are known to exist in the azo-hydrazone tautomeric forms (Çolak *et al.*, 2010; Pavlovic *et al.*, 2009; Seferoğlu *et al.*, 2009; Seferoğlu *et al.*, 2008; Wojciechowski & Szymezak, 2007). We herein report the crystal structure of the title compound, (I).

The title compound, (I), contains benzonitrile and 2,2-dimethyl-1,3-dioxane -4,6-dione groups connected *via* a hydrazinyl group (Fig. 1). In (I), N1—N2 [1.3082 (14) Å] bond length is between the N═N double bond [1.20–1.28 Å for a real azo compound] and N—N single bond [longer than 1.4 Å] lengths. The N1—C3 and N2—C5 bond lengths are 1.3116 (14) and 1.4075 (14) Å, respectively. The carbonyl O atoms O3 and O4 slightly deviate from the N1/C2–C4 plane by 0.255 (2) and 0.259 (2) Å, respectively. So, the title compound may exist both in azo and hydrazone tautomeric forms, and is mainly in the hydrazone tautomeric form. The C8—C13 [1.4418 (15) Å] bond length is longer for a $C(sp^2)$—$C(sp^1)$ bond, but in agreement with the previously reported value [1.442 (3) Å; Çolak *et al.*, 2010).

An intramolecular N2—H2···O3 hydrogen bond (Table 1) results in the formation of a nearly planar [with a maximum deviation of 0.056 (1) Å for atom C4] six-membered ring C (O3/N1/N2/H2/C3/C4), which is oriented with respect to the benzonitrile ring B (C5–C10) at a dihedral angle of 7.8 (43)°. Atoms N1, N2, N3 and C13 are displaced by -0.162 (2), 0.038 (2), 0.049 (2) and 0.028 (2) Å from the plane of ring B, respectively. The benzonitrile and hydrazinyl groups (4-hydrazinylbenzonitrile) are essentially coplanar [with a maximum deviation of -0.087 (1) Å for atom N1]. The dioxane ring A (O1/O2/C1–C4) is not planar having envelope conformation with atom C1 displaced by 0.613 (1) Å from the plane of the other ring atoms.

In the crystal structure, weak C—H···O and C—H···N hydrogen bonds (Table 1) may be effective in the stabilization of the crystal packing. There also exists a weak C—H···π interaction (Table 1).

Experimental

A hydrochloric acid solution (2.5 ml) of 4-aminobenzonitrile (1.18 g, 10 mmol) and an aqueous solution (10 ml) of sodium nitrite (0.69 g, 10 mmol) were mixed and stirred at 273 K for 1 h. To this solution, an ethanol solution (10 ml) of the coupling

component 2,2-dimethyl-1,3-dioxane-4,6-dione (1.44 g, 10 mmol) was added and the stirring was continued at 273 K for 4 h. The resulting product was filtered and washed with water, dried and crystallized from ethanol (yield 1.88 g, 69%; m.p. 440–442 K).

Refinement

H atoms were located in difference Fourier maps and refined isotropically.

Figures

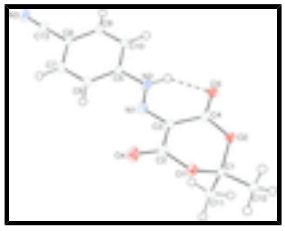


Fig. 1. The molecular structure of the title compound, with the atom-numbering scheme. Displacement ellipsoids are drawn at the 50% probability level. The dashed line indicates a hydrogen bond.

4-[2-(2,2-Dimethyl-4,6-dioxo-1,3-dioxan-5-ylidene)hydrazin-1-yl]benzonitrile

Crystal data

$C_{13}H_{11}N_3O_4$	$F(000) = 568$
$M_r = 273.25$	$D_x = 1.476$ Mg m^{-3}
Monoclinic, $P2_1/n$	Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å
Hall symbol: -P 2yn	Cell parameters from 4103 reflections
$a = 9.7617$ (2) Å	$\theta = 2.6$–$28.4°$
$b = 11.0023$ (2) Å	$\mu = 0.11$ mm^{-1}
$c = 11.4753$ (3) Å	$T = 100$ K
$\beta = 93.796$ (1)°	Block, yellow
$V = 1229.76$ (5) Å^3	0.46 × 0.43 × 0.29 mm
$Z = 4$	

Data collection

Bruker Kappa APEXII CCD area-detector diffractometer	3098 independent reflections
Radiation source: fine-focus sealed tube	2591 reflections with $I > 2\sigma(I)$
graphite	$R_{int} = 0.029$
φ and ω scans	$\theta_{max} = 28.5°$, $\theta_{min} = 2.6°$
Absorption correction: multi-scan (*SADABS*; Bruker, 2005)	$h = -13 \rightarrow 13$
$T_{min} = 0.950$, $T_{max} = 0.968$	$k = -14 \rightarrow 14$
11746 measured reflections	$l = -15 \rightarrow 8$

Refinement

Refinement on F^2	Primary atom site location: structure-invariant direct methods
Least-squares matrix: full	Secondary atom site location: difference Fourier map
$R[F^2 > 2\sigma(F^2)] = 0.038$	Hydrogen site location: inferred from neighbouring sites
$wR(F^2) = 0.108$	All H-atom parameters refined
$S = 1.04$	$w = 1/[\sigma^2(F_o^2) + (0.0626P)^2 + 0.2729P]$ where $P = (F_o^2 + 2F_c^2)/3$
3098 reflections	$(\Delta/\sigma)_{max} = 0.001$
225 parameters	$\Delta\rho_{max} = 0.38$ e Å^{-3}
0 restraints	$\Delta\rho_{min} = -0.24$ e Å^{-3}

Special details

Geometry. All e.s.d.'s (except the e.s.d. in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell e.s.d.'s are taken into account individually in the estimation of e.s.d.'s in distances, angles and torsion angles; correlations between e.s.d.'s in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell e.s.d.'s is used for estimating e.s.d.'s involving l.s. planes.

Refinement. Refinement of F^2 against ALL reflections. The weighted *R*-factor *wR* and goodness of fit *S* are based on F^2, conventional *R*-factors *R* are based on *F*, with *F* set to zero for negative F^2. The threshold expression of $F^2 > \sigma(F^2)$ is used only for calculating *R*-factors(gt) *etc*. and is not relevant to the choice of reflections for refinement. *R*-factors based on F^2 are statistically about twice as large as those based on *F*, and *R*- factors based on ALL data will be even larger.

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å^2)

	x	*y*	*z*	U_{iso}*/U_{eq}
O1	0.16363 (8)	0.74524 (7)	0.85585 (7)	0.0172 (2)
O2	0.17892 (8)	0.56739 (7)	0.97179 (7)	0.01470 (19)
O3	0.35656 (9)	0.44276 (8)	0.96914 (7)	0.0187 (2)
O4	0.32521 (9)	0.79574 (8)	0.73794 (8)	0.0249 (2)
N1	0.44403 (10)	0.56888 (9)	0.76510 (9)	0.0165 (2)
N2	0.51381 (10)	0.46953 (9)	0.78943 (9)	0.0159 (2)
H2	0.4942 (16)	0.4243 (15)	0.8538 (15)	0.028 (4)*
N3	1.03756 (11)	0.29578 (10)	0.47015 (10)	0.0232 (2)
C1	0.08704 (11)	0.64589 (10)	0.90176 (10)	0.0143 (2)
C2	0.27845 (12)	0.71950 (11)	0.79881 (10)	0.0172 (2)
C3	0.34022 (12)	0.59901 (10)	0.82608 (10)	0.0155 (2)
C4	0.29477 (11)	0.52812 (10)	0.92521 (10)	0.0144 (2)
C5	0.62374 (11)	0.43844 (10)	0.72180 (10)	0.0148 (2)
C6	0.64458 (13)	0.49922 (11)	0.61746 (10)	0.0173 (2)
H6	0.5852 (15)	0.5636 (14)	0.5904 (13)	0.020 (4)*
C7	0.75216 (13)	0.46401 (11)	0.55177 (10)	0.0175 (2)
H7	0.7668 (15)	0.5059 (14)	0.4788 (13)	0.024 (4)*
C8	0.83788 (12)	0.36875 (11)	0.59035 (10)	0.0155 (2)

C9	0.81720 (12)	0.30898 (11)	0.69557 (10)	0.0161 (2)
H9	0.8752 (14)	0.2457 (14)	0.7224 (12)	0.020 (4)*
C10	0.70992 (12)	0.34407 (11)	0.76131 (10)	0.0159 (2)
H10	0.6926 (14)	0.3023 (14)	0.8350 (13)	0.021 (4)*
C11	0.01442 (13)	0.57371 (11)	0.80405 (10)	0.0178 (2)
H111	0.0795 (15)	0.5338 (14)	0.7556 (13)	0.022 (4)*
H112	−0.0444 (15)	0.5101 (14)	0.8393 (13)	0.023 (4)*
H113	−0.0456 (15)	0.6270 (15)	0.7544 (14)	0.026 (4)*
C12	−0.00717 (13)	0.70098 (11)	0.98606 (10)	0.0169 (2)
H121	0.0494 (16)	0.7364 (15)	1.0534 (13)	0.026 (4)*
H122	−0.0616 (15)	0.7636 (14)	0.9446 (13)	0.021 (4)*
H123	−0.0673 (16)	0.6388 (16)	1.0133 (15)	0.035 (4)*
C13	0.94875 (12)	0.32918 (11)	0.52248 (10)	0.0177 (2)

Atomic displacement parameters (Å^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
O1	0.0168 (4)	0.0111 (4)	0.0244 (4)	0.0003 (3)	0.0057 (3)	0.0024 (3)
O2	0.0132 (4)	0.0139 (4)	0.0169 (4)	0.0027 (3)	0.0012 (3)	0.0015 (3)
O3	0.0164 (4)	0.0178 (4)	0.0220 (4)	0.0033 (3)	0.0011 (3)	0.0027 (3)
O4	0.0244 (5)	0.0191 (5)	0.0321 (5)	0.0004 (4)	0.0096 (4)	0.0083 (4)
N1	0.0144 (5)	0.0146 (5)	0.0204 (5)	−0.0002 (4)	0.0009 (4)	−0.0023 (4)
N2	0.0151 (5)	0.0149 (5)	0.0179 (5)	0.0004 (4)	0.0031 (4)	−0.0005 (4)
N3	0.0227 (6)	0.0233 (6)	0.0244 (5)	0.0003 (4)	0.0076 (4)	0.0001 (4)
C1	0.0135 (5)	0.0111 (5)	0.0182 (5)	0.0005 (4)	0.0010 (4)	0.0024 (4)
C2	0.0152 (6)	0.0159 (6)	0.0208 (5)	−0.0001 (4)	0.0025 (4)	−0.0003 (4)
C3	0.0143 (5)	0.0140 (5)	0.0184 (5)	−0.0005 (4)	0.0017 (4)	−0.0006 (4)
C4	0.0127 (5)	0.0135 (5)	0.0170 (5)	−0.0010 (4)	0.0008 (4)	−0.0027 (4)
C5	0.0119 (5)	0.0143 (5)	0.0182 (5)	−0.0024 (4)	0.0014 (4)	−0.0037 (4)
C6	0.0178 (6)	0.0137 (5)	0.0205 (5)	−0.0001 (4)	0.0014 (4)	0.0001 (4)
C7	0.0196 (6)	0.0155 (5)	0.0178 (5)	−0.0026 (4)	0.0039 (4)	0.0004 (4)
C8	0.0134 (5)	0.0155 (5)	0.0179 (5)	−0.0031 (4)	0.0028 (4)	−0.0022 (4)
C9	0.0137 (5)	0.0160 (5)	0.0185 (5)	0.0003 (4)	0.0001 (4)	−0.0002 (4)
C10	0.0144 (5)	0.0177 (5)	0.0155 (5)	−0.0026 (4)	0.0010 (4)	−0.0004 (4)
C11	0.0174 (6)	0.0170 (6)	0.0188 (5)	0.0019 (5)	−0.0009 (4)	−0.0015 (4)
C12	0.0162 (6)	0.0141 (5)	0.0207 (5)	0.0032 (4)	0.0037 (4)	0.0007 (4)
C13	0.0178 (6)	0.0167 (6)	0.0188 (5)	−0.0029 (4)	0.0024 (4)	0.0006 (4)

Geometric parameters (Å, °)

O1—C1	1.4435 (13)	C6—C7	1.3878 (16)
O1—C2	1.3645 (13)	C6—H6	0.954 (15)
O2—C1	1.4493 (13)	C7—C8	1.3949 (17)
O2—C4	1.3533 (13)	C7—H7	0.974 (15)
O3—C4	1.2081 (14)	C8—C9	1.4012 (16)
O4—C2	1.2009 (14)	C8—C13	1.4418 (15)
N1—N2	1.3082 (14)	C9—C10	1.3854 (15)
N1—C3	1.3116 (14)	C9—H9	0.936 (15)
N2—C5	1.4075 (14)	C10—H10	0.986 (15)

N2—H2	0.922 (17)	C11—C1	1.5117 (16)
N3—C13	1.1473 (15)	C11—H111	0.976 (15)
C1—C12	1.5055 (15)	C11—H113	0.984 (16)
C2—C3	1.4812 (16)	C11—H112	1.007 (16)
C3—C4	1.4718 (15)	C12—H122	0.975 (15)
C5—C6	1.3981 (16)	C12—H121	0.999 (16)
C5—C10	1.3932 (17)	C12—H123	0.967 (17)
C2—O1—C1	118.66 (9)	C7—C6—H6	119.7 (9)
C4—O2—C1	118.29 (8)	C6—C7—C8	119.80 (11)
N2—N1—C3	120.47 (10)	C6—C7—H7	119.6 (9)
N1—N2—C5	119.38 (10)	C8—C7—H7	120.6 (9)
N1—N2—H2	119.3 (10)	C7—C8—C9	120.56 (10)
C5—N2—H2	121.1 (10)	C7—C8—C13	120.76 (10)
O1—C1—O2	109.71 (9)	C9—C8—C13	118.68 (11)
O1—C1—C11	110.85 (9)	C8—C9—H9	120.9 (9)
O1—C1—C12	106.43 (9)	C10—C9—C8	119.72 (11)
O2—C1—C11	109.92 (9)	C10—C9—H9	119.4 (9)
O2—C1—C12	105.40 (9)	C5—C10—H10	119.5 (9)
C12—C1—C11	114.31 (10)	C9—C10—C5	119.50 (10)
O1—C2—C3	114.85 (10)	C9—C10—H10	121.0 (9)
O4—C2—O1	119.33 (11)	C1—C11—H111	111.6 (9)
O4—C2—C3	125.66 (11)	C1—C11—H113	110.4 (9)
N1—C3—C2	115.57 (10)	C1—C11—H112	108.6 (9)
N1—C3—C4	124.16 (11)	H111—C11—H112	109.0 (12)
C4—C3—C2	119.88 (10)	H111—C11—H113	108.9 (13)
O2—C4—C3	116.02 (10)	H113—C11—H112	108.3 (12)
O3—C4—O2	119.38 (10)	C1—C12—H121	108.9 (9)
O3—C4—C3	124.52 (10)	C1—C12—H122	107.9 (8)
C6—C5—N2	121.03 (11)	C1—C12—H123	109.4 (10)
C10—C5—N2	117.89 (10)	H121—C12—H123	110.0 (13)
C10—C5—C6	121.08 (10)	H122—C12—H121	110.9 (13)
C5—C6—H6	120.9 (9)	H122—C12—H123	109.6 (13)
C7—C6—C5	119.34 (11)	N3—C13—C8	178.56 (13)
C2—O1—C1—O2	51.23 (12)	O4—C2—C3—N1	−9.81 (19)
C2—O1—C1—C11	−70.35 (13)	O4—C2—C3—C4	163.35 (12)
C2—O1—C1—C12	164.79 (10)	N1—C3—C4—O2	−174.73 (10)
C1—O1—C2—O4	163.20 (11)	N1—C3—C4—O3	8.59 (19)
C1—O1—C2—C3	−21.07 (14)	C2—C3—C4—O2	12.73 (16)
C4—O2—C1—O1	−50.36 (12)	C2—C3—C4—O3	−163.95 (11)
C4—O2—C1—C12	−164.59 (9)	N2—C5—C6—C7	−178.47 (10)
C4—O2—C1—C11	71.77 (12)	C10—C5—C6—C7	0.62 (18)
C1—O2—C4—O3	−163.46 (10)	N2—C5—C10—C9	178.44 (10)
C1—O2—C4—C3	19.68 (14)	C6—C5—C10—C9	−0.67 (18)
C3—N1—N2—C5	179.24 (10)	C5—C6—C7—C8	0.05 (18)
N2—N1—C3—C2	173.80 (10)	C6—C7—C8—C9	−0.65 (18)
N2—N1—C3—C4	0.97 (18)	C6—C7—C8—C13	178.87 (11)
N1—N2—C5—C6	−11.37 (17)	C7—C8—C9—C10	0.60 (18)
N1—N2—C5—C10	169.52 (10)	C13—C8—C9—C10	−178.93 (11)

O1—C2—C3—N1	174.77 (10)	C8—C9—C10—C5	0.06 (17)
O1—C2—C3—C4	−12.07 (16)		

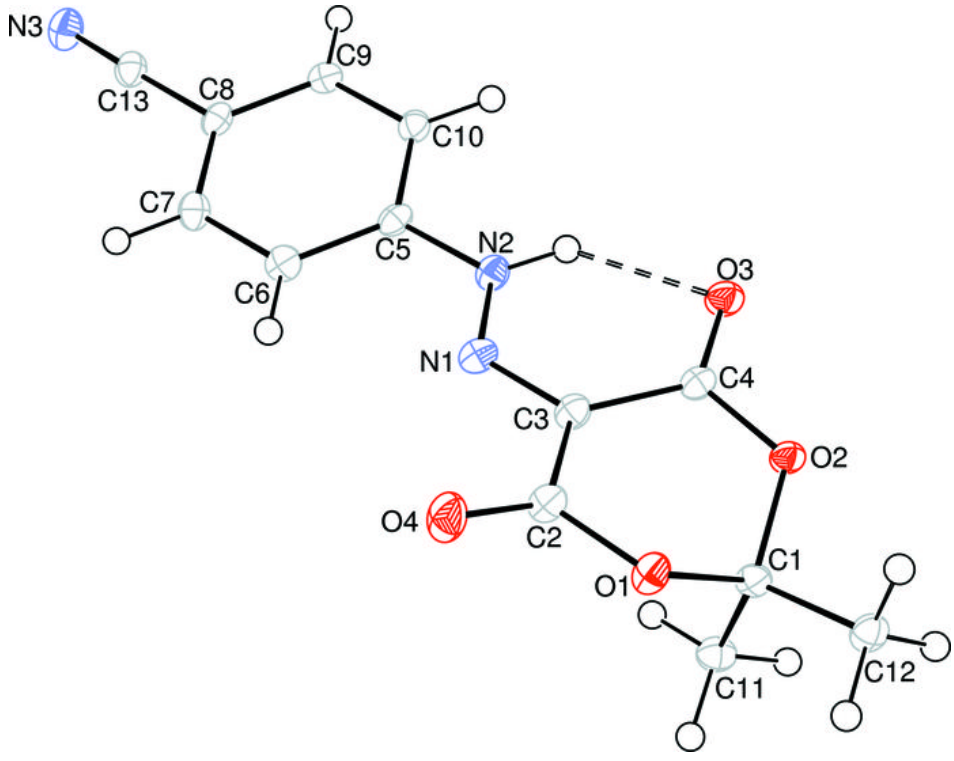
Hydrogen-bond geometry (Å, °)

Cg1 is the centroid of the C5–C10 ring.

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
N2—H2···O3	0.92 (2)	1.958 (16)	2.6674 (13)	132 (1)
C9—H9···N1^{i}	0.94 (2)	2.624 (15)	3.5320 (16)	164 (1)
C10—H10···N3^{ii}	0.99 (2)	2.485 (15)	3.3876 (16)	152 (1)
C12—H123···O2^{iii}	0.97 (2)	2.527 (17)	3.4454 (15)	159 (1)
C12—H122···Cg1^{iv}	0.98 (2)	2.491 (15)	3.4575 (13)	171 (1)

Symmetry codes: (i) −*x*+3/2, *y*−1/2, −*z*+3/2; (ii) *x*−1/2, −*y*+1/2, *z*+1/2; (iii) −*x*, −*y*+1, −*z*+2; (iv) −*x*+3/2, *y*−1/2, −*z*+1/2.

Fig. 1



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2-Chloro-4-nitro-1*H*-imidazole

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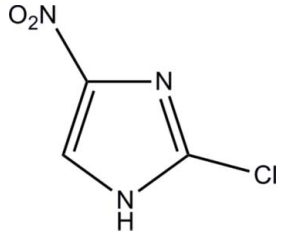
Key indicators: single-crystal X-ray study; T = 100 K; mean σ(C–C) = 0.002 Å; R factor = 0.037; wR factor = 0.097; data-to-parameter ratio = 16.8.

The molecule of the title compound, $C_3H_2ClN_3O_2$, is almost planar; the dihedral angle between the imidazole ring and the nitro group is 1.7 (2)°. In the crystal structure, pairs of intermolecular C—H···O hydrogen bonds link inversion-related molecules into dimers, generating $R_2^2(10)$ ring motifs. The dimers are interconnected into two-dimensional networks parallel to (102) *via* intermolecular N—H···N hydrogen bonds. Further stabilization is provided by short intermolecular Cl···O interactions [3.142 (2) and 3.1475 (19) Å].

Related literature

For general background to and applications of imidazole derivatives, see: Anuradha *et al.* (2006); Clark & Macquarrie (1996); Jadhav *et al.* (2008); Kolavi *et al.* (2006); Susanta *et al.* (2000). For graph-set descriptions of hydrogen-bond ring motifs, see: Bernstein *et al.* (1995). For related 4-nitroimidazole crystal structures, see: Ségalas *et al.* (1992); De Bondt *et al.* (1993). For the stability of the temperature controller used for the data collection, see: Cosier & Glazer (1986).



Experimental

Crystal data

$C_3H_2ClN_3O_2$
M_r = 147.53
Monoclinic, $P2_1/c$
a = 5.905 (2) Å
b = 10.033 (4) Å
c = 9.150 (3) Å
β = 105.180 (8)°
V = 523.2 (3) Å^3
Z = 4
Mo $K\alpha$ radiation
μ = 0.64 mm^{-1}
T = 100 K
0.29 × 0.19 × 0.04 mm

Data collection

Bruker APEXII DUO CCD area-detector diffractometer
Absorption correction: multi-scan (*SADABS*; Bruker, 2009)
T_{min} = 0.837, T_{max} = 0.977
5484 measured reflections
1509 independent reflections
1195 reflections with $I > 2\sigma(I)$
R_{int} = 0.037

Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.037
$wR(F^2)$ = 0.097
S = 1.11
1509 reflections
90 parameters
All H-atom parameters refined
$\Delta\rho_{max}$ = 0.42 e Å^{-3}
$\Delta\rho_{min}$ = −0.44 e Å^{-3}

Table 1
Hydrogen-bond geometry (Å, °).

D—H···A	D—H	H···A	D···A	D—H···A
N1—H1*N*1···N2^{i}	0.86 (3)	2.07 (3)	2.900 (2)	163 (2)
C2—H2···O1^{ii}	0.92 (3)	2.48 (3)	3.317 (3)	151 (2)

Symmetry codes: (i) $-x+1, y-\frac{1}{2}, -z+\frac{1}{2}$; (ii) $-x, -y+1, -z+1$.

Data collection: *APEX2* (Bruker, 2009); cell refinement: *SAINT* (Bruker, 2009); data reduction: *SAINT*; program(s) used to solve structure: *SHELXTL* (Sheldrick, 2008); program(s) used to refine structure: *SHELXTL*; molecular graphics: *SHELXTL*; software used to prepare material for publication: *SHELXTL* and *PLATON* (Spek, 2009).

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Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: CI5106).

References

Anuradha, V., Srinivas, P. V., Aparna, P. & Madhusudana, J. R. (2006). *Tetrahedron Lett.* **47**, 4933-4935.
Bernstein, J., Davis, R. E., Shimoni, L. & Chang, N.-L. (1995). *Angew. Chem. Int. Ed. Engl.* **34**, 1555–1573.
Bruker (2009). *APEX2*, *SAINT* and *SADABS*. Bruker AXS Inc., Madison, Wisconsin, USA.
Clark, J. H. & Macquarrie, J. (1996). *Chem. Soc. Rev.* **25**, 3445–3446.
Cosier, J. & Glazer, A. M. (1986). *J. Appl. Cryst.* **19**, 105–107.

‡ Thomson Reuters ResearcherID: A-3561-2009.
§ Thomson Reuters ResearcherID: C-7576-2009.

De Bondt, H. L., Ragia, E., Blaton, N. M., Peeters, O. M. & De Ranter, C. J. (1993). *Acta Cryst.* C**49**, 693–695.
Jadhav, V. B., Kulkarni, M. V. & Rasal, V. P. (2008). *Eur. J. Med. Chem.* **43**, 1721–1729.
Kolavi, G., Hegde, V., Khan, I. z7 Gadag, P. (2006). *Bioorg. Med. Chem.* **14**, 3069–3080.
Ségalas, I., Poitras, J. & Beauchamp, A. L. (1992). *Acta Cryst.* C**48**, 295–298.
Sheldrick, G. M. (2008). *Acta Cryst.* A**64**, 112–122.
Spek, A. L. (2009). *Acta Cryst.* D**65**, 148–155.
Susanta, S., Frederick, F. B. & Bimal, K. B. (2000). *Tetrahedron Lett.* **41**, 8017–8020.

supplementary materials

Acta Cryst. (2010). E**66**, o1828-o1829 [**doi:10.1107/S1600536810024542**]

2-Chloro-4-nitro-1*H*-imidazole

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Comment

The nitro aromatic compounds are used as key substrates for the preparation of useful materials such as dyes, pharmaceuticals, perfumes and plastics (Susanta *et al.*, 2000). Therefore, nitration of hydrocarbons particularly of aromatic compounds is probably one of the most widely studied organic reactions (Jadhav *et al.*, 2008). In addition, they have proven to be valuable reagents for the synthesis of complex target molecules (Kolavi *et al.*, 2006). Most of the substituted imidazoles are widely used in pharmaceutical ingredients (Clark & Macquarrie, 1996). The imidazole nucleus is one of the important heterocyclic groups due to its presence in a large number of bioactive pharmaceutical and agrochemicals (Anuradha *et al.*, 2006). It was also reported that a large number of compounds containing the imidazole ring possess some moderately useful activities. The environmentally friendly nitration reaction has been the focus of recent research.

In the title imidazole derivative, the 1*H*-imidazole ring with atom sequence C1/N1/C2/C3/N2 is essentially planar, with a maximum deviation of 0.003 (2) Å at atom N1. The nitro group is coplanar with the attached 1*H*-imidazole ring, as indicated by the dihedral angle of 1.7 (2)°. The geometric parameters agree well with those reported for related 4-nitroimidazole structures (Ségalas *et al.*, 1992; De Bondt *et al.*, 1993).

In the crystal structure, (Fig. 2), pairs of intermolecular C2—H2···O1 hydrogen bonds (Table 1) link inversion-related molecules into dimers, generating $R^2_2(10)$ hydrogen bond ring motifs (Bernstein *et al.*, 1995). These dimers are further interconnected into two-dimensional arrays parallel to the (102) plane *via* intermolecular N1—H1N1···N2 hydrogen bonds (Table 1). The interesting features of the crystal structure are the intermolecular short Cl···O interactions [$Cl1\cdots O1^{iii}$ = 3.143 (2) and $Cl1\cdots O2^{i}$ = 3.148 (2) Å; (i) 1-x, y-1/2, 1/2-z and (iii) 1+x, 3/2-y, z-1/2] which are shorter than the sum of the van der Waals radii of the relavant atoms and help to further stabilize the crystal structure.

Experimental

Nitronium tetrafluoroborate (1.42 g, 0.0107 mol) was dissolved in nitromethane (10 ml) and 2-chloroimidazole (1 g, 0.0097 mol) was then added in lot-wise. The reaction mixture was stirred at room temperature for 3 h. The reaction mixture was then neutrallized with an aqueous solution of sodium bicarbonate. The separated solid was then filtered. The crude product was purified by column chromatography using 60–120 silica gel. The fraction eluted at 10 % ethyl acetate in hexane was concentrated to afford the title compound as pale yellow single crystals (Yield 0.9 g, 62.93 %; *m.p.* 363–366 K).

Refinement

Atoms H1N1 and H2 were located in a difference Fourier map and allowed to refine freely [N1—H1N1 = 0.86 (3) and C2—H2A = 0.93 (3) Å].

Figures

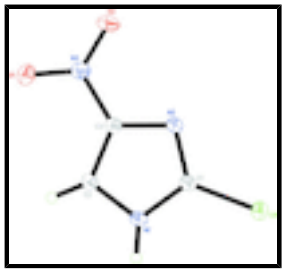


Fig. 1. The molecular structure of the title compound, showing 50% probability displacement ellipsoids for non-H atoms and the atom-numbering scheme.

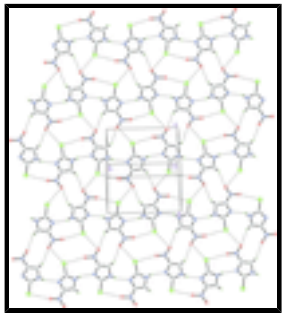


Fig. 2. The crystal structure of the title compound, showing a two-dimensional network. Intermolecular interactions are shown as dashed lines.

2-Chloro-4-nitro-1*H*-imidazole

Crystal data

$C_3H_2ClN_3O_2$	$F(000) = 296$
$M_r = 147.53$	$D_x = 1.873$ Mg m^{-3}
Monoclinic, $P2_1/c$	Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å
Hall symbol: -P 2ybc	Cell parameters from 2073 reflections
$a = 5.905$ (2) Å	$\theta = 3.6$–$30.0°$
$b = 10.033$ (4) Å	$\mu = 0.64$ mm^{-1}
$c = 9.150$ (3) Å	$T = 100$ K
$\beta = 105.180$ (8)°	Plate, yellow
$V = 523.2$ (3) Å^3	0.29 × 0.19 × 0.04 mm
$Z = 4$	

Data collection

Bruker APEXII DUO CCD area-detector diffractometer	1509 independent reflections
Radiation source: fine-focus sealed tube	1195 reflections with $I > 2\sigma(I)$
graphite	$R_{int} = 0.037$
φ and ω scans	$\theta_{max} = 30.0°$, $\theta_{min} = 3.1°$
Absorption correction: multi-scan (*SADABS*; Bruker, 2009)	$h = -6 \rightarrow 8$
$T_{min} = 0.837$, $T_{max} = 0.977$	$k = -13 \rightarrow 14$
5484 measured reflections	$l = -12 \rightarrow 12$

Refinement

Refinement on F^2	Primary atom site location: structure-invariant direct methods
Least-squares matrix: full	Secondary atom site location: difference Fourier map
$R[F^2 > 2\sigma(F^2)] = 0.037$	Hydrogen site location: inferred from neighbouring sites
$wR(F^2) = 0.097$	All H-atom parameters refined
$S = 1.11$	$w = 1/[\sigma^2(F_o^2) + (0.0453P)^2 + 0.1822P]$ where $P = (F_o^2 + 2F_c^2)/3$
1509 reflections	$(\Delta/\sigma)_{max} = 0.001$
90 parameters	$\Delta\rho_{max} = 0.42$ e Å^{-3}
0 restraints	$\Delta\rho_{min} = -0.44$ e Å^{-3}

Special details

Experimental. The crystal was placed in the cold stream of an Oxford Cryosystems Cobra open-flow nitrogen cryostat (Cosier & Glazer, 1986) operating at 100.0 (1)K.

Geometry. All esds (except the esd in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell esds are taken into account individually in the estimation of esds in distances, angles and torsion angles; correlations between esds in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell esds is used for estimating esds involving l.s. planes.

Refinement. Refinement of F^2 against ALL reflections. The weighted R-factor wR and goodness of fit S are based on F^2, conventional R-factors R are based on F, with F set to zero for negative F^2. The threshold expression of $F^2 > 2\text{sigma}(F^2)$ is used only for calculating R-factors(gt) etc. and is not relevant to the choice of reflections for refinement. R-factors based on F^2 are statistically about twice as large as those based on F, and R- factors based on ALL data will be even larger.

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å^2)

	x	*y*	*z*	U_{iso}*/U_{eq}
Cl1	0.72178 (8)	0.63986 (4)	0.10842 (5)	0.01869 (15)
O1	0.0169 (3)	0.65199 (14)	0.47907 (19)	0.0268 (4)
O2	0.1231 (3)	0.84048 (13)	0.40048 (18)	0.0250 (3)
N1	0.4713 (3)	0.49414 (15)	0.25596 (19)	0.0157 (3)
N2	0.4212 (3)	0.71387 (14)	0.26450 (18)	0.0151 (3)
N3	0.1318 (3)	0.71851 (16)	0.41138 (19)	0.0190 (3)
C1	0.5304 (3)	0.61677 (16)	0.2149 (2)	0.0149 (4)
C2	0.3104 (3)	0.51281 (17)	0.3371 (2)	0.0164 (4)
C3	0.2845 (3)	0.64762 (17)	0.3405 (2)	0.0150 (4)
H1N1	0.525 (4)	0.417 (3)	0.240 (3)	0.025 (6)*
H2	0.246 (4)	0.441 (3)	0.375 (3)	0.025 (6)*

Atomic displacement parameters (Å^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Cl1	0.0218 (2)	0.0162 (2)	0.0214 (3)	−0.00093 (16)	0.01140 (19)	0.00052 (17)

O1	0.0311 (8)	0.0228 (7)	0.0340 (9)	−0.0028 (6)	0.0221 (7)	−0.0015 (6)
O2	0.0308 (8)	0.0120 (6)	0.0351 (9)	0.0043 (5)	0.0140 (7)	−0.0022 (6)
N1	0.0193 (8)	0.0096 (7)	0.0196 (8)	0.0010 (6)	0.0078 (7)	−0.0003 (6)
N2	0.0179 (8)	0.0107 (6)	0.0184 (8)	0.0001 (5)	0.0075 (6)	0.0000 (6)
N3	0.0206 (8)	0.0151 (7)	0.0231 (9)	0.0008 (6)	0.0090 (7)	−0.0017 (6)
C1	0.0174 (9)	0.0113 (8)	0.0163 (9)	−0.0013 (6)	0.0053 (7)	−0.0004 (6)
C2	0.0186 (9)	0.0114 (8)	0.0208 (10)	−0.0010 (6)	0.0082 (8)	0.0001 (7)
C3	0.0167 (9)	0.0122 (8)	0.0170 (9)	−0.0007 (6)	0.0060 (7)	−0.0019 (7)

Geometric parameters (Å, °)

Cl1—C1	1.690 (2)	N2—C1	1.313 (2)
O1—N3	1.228 (2)	N2—C3	1.368 (2)
O2—N3	1.228 (2)	N3—C3	1.430 (2)
N1—C1	1.359 (2)	C2—C3	1.362 (2)
N1—C2	1.363 (3)	C2—H2	0.93 (3)
N1—H1N1	0.86 (3)		
C1—N1—C2	107.01 (15)	N2—C1—Cl1	124.11 (14)
C1—N1—H1N1	129.2 (17)	N1—C1—Cl1	122.87 (14)
C2—N1—H1N1	123.7 (17)	C3—C2—N1	104.32 (16)
C1—N2—C3	102.95 (15)	C3—C2—H2	135.0 (16)
O2—N3—O1	124.46 (17)	N1—C2—H2	120.7 (16)
O2—N3—C3	118.46 (16)	C2—C3—N2	112.71 (17)
O1—N3—C3	117.08 (16)	C2—C3—N3	126.29 (18)
N2—C1—N1	113.01 (17)	N2—C3—N3	120.99 (16)
C3—N2—C1—N1	−0.4 (2)	C1—N2—C3—C2	0.0 (2)
C3—N2—C1—Cl1	178.70 (15)	C1—N2—C3—N3	−179.05 (17)
C2—N1—C1—N2	0.6 (2)	O2—N3—C3—C2	−177.8 (2)
C2—N1—C1—Cl1	−178.52 (14)	O1—N3—C3—C2	1.9 (3)
C1—N1—C2—C3	−0.5 (2)	O2—N3—C3—N2	1.1 (3)
N1—C2—C3—N2	0.3 (2)	O1—N3—C3—N2	−179.10 (18)
N1—C2—C3—N3	179.32 (18)		

Hydrogen-bond geometry (Å, °)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
N1—H1N1···N2^{i}	0.86 (3)	2.07 (3)	2.900 (2)	163 (2)
C2—H2···O1^{ii}	0.92 (3)	2.48 (3)	3.317 (3)	151 (2)

Symmetry codes: (i) −*x*+1, *y*−1/2, −*z*+1/2; (ii) −*x*, −*y*+1, −*z*+1.

Fig. 1

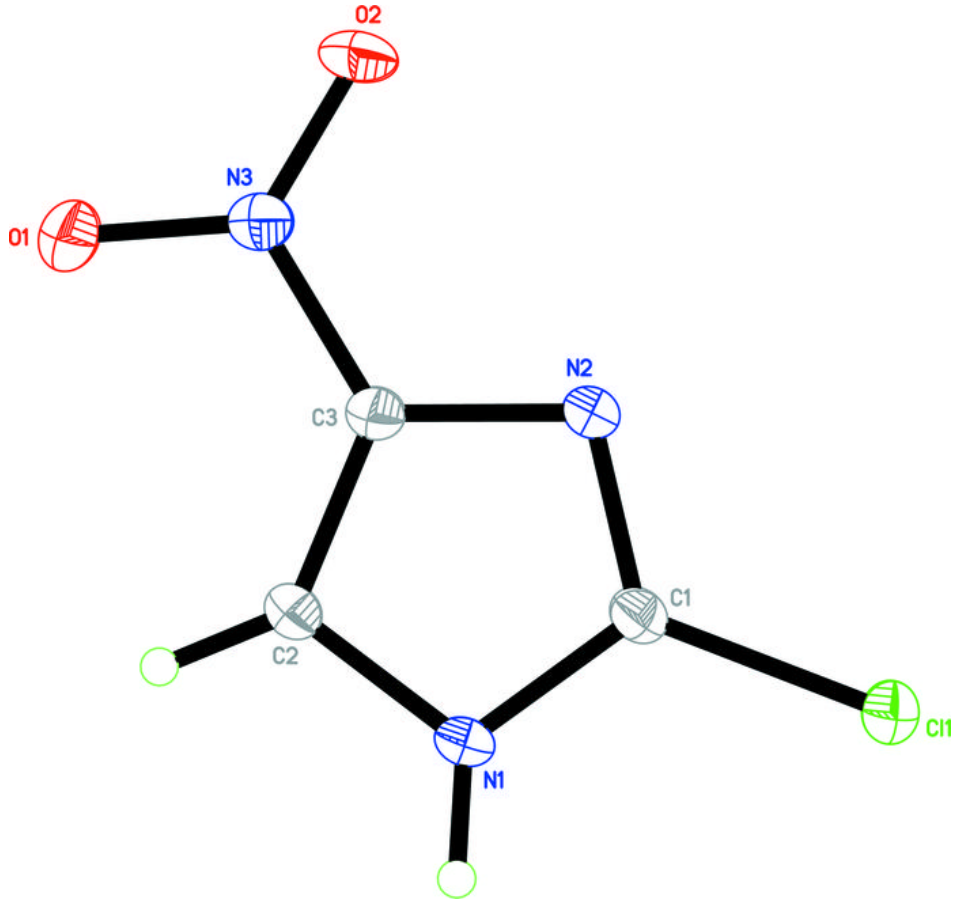
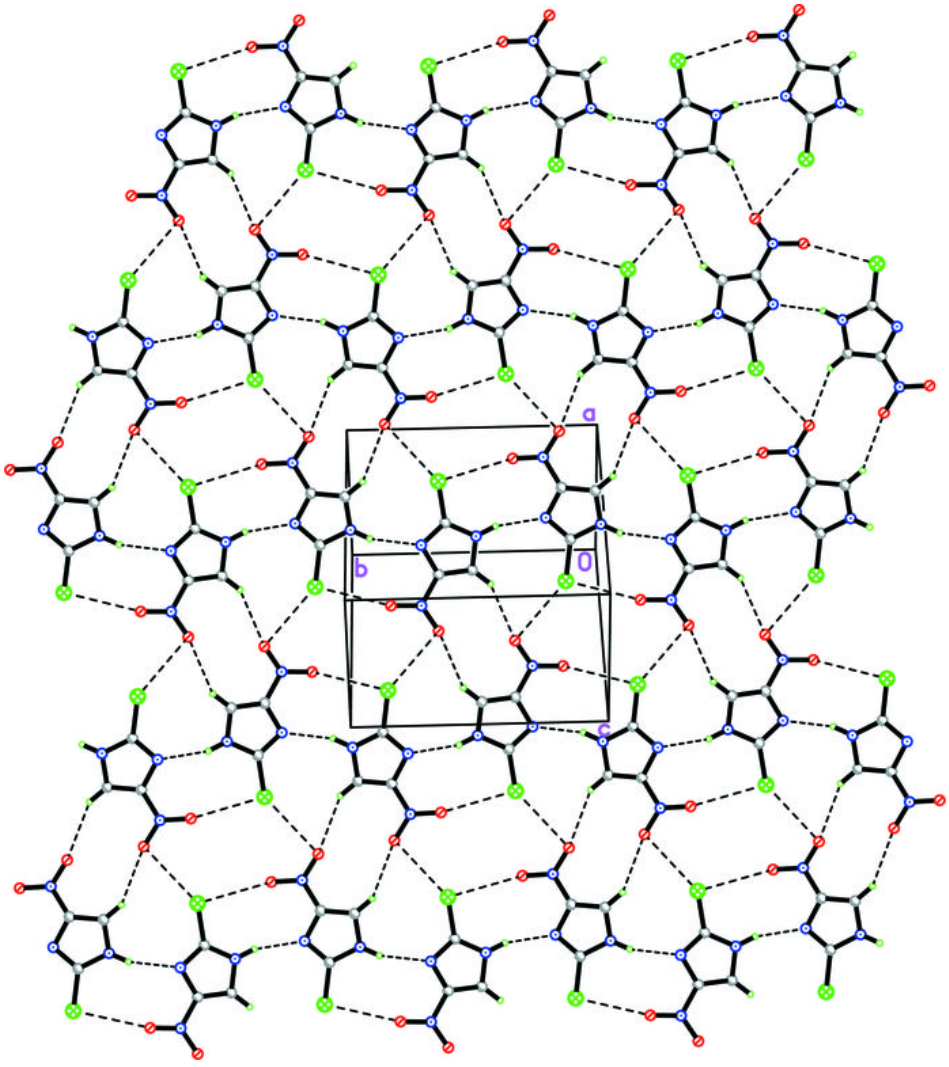


Fig. 2



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N-(4-Methylbenzoyl)benzenesulfonamide

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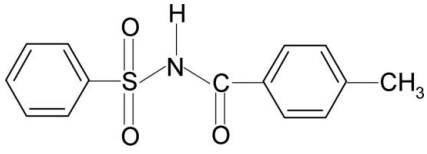
Key indicators: single-crystal X-ray study; T = 299 K; mean σ(C–C) = 0.002 Å; R factor = 0.038; wR factor = 0.109; data-to-parameter ratio = 15.0.

In the title compound, $C_{14}H_{13}NO_3S$, the conformation of the N—H bond in the C—SO_2—NH—C(O) segment is *anti* to the C=O bond. The dihedral angle between the sulfonyl benzene ring and the S—N—C—O segment (r.m.s. deviation = 0.039 Å) is 77.1 (1)° and that between the sulfonyl and benzoyl benzene rings is 71.9 (1)°.

Related literature

For background to our study of the effect of ring and side-chain substituents on the crystal structures of *N*-aromatic sulfonamides and for related structures, see: Gowda *et al.* (2009); Suchetan *et al.* (2009, 2010).



Experimental

Crystal data

$C_{14}H_{13}NO_3S$
M_r = 275.31
Triclinic, $P\overline{1}$
a = 5.5519 (6) Å
b = 10.541 (1) Å
c = 11.105 (1) Å
α = 85.654 (9)°
β = 83.667 (9)°
γ = 81.949 (9)°
V = 638.36 (11) Å^3
Z = 2
Mo $K\alpha$ radiation
μ = 0.26 mm^{-1}
T = 299 K
0.40 × 0.32 × 0.16 mm

Data collection

Oxford Diffraction Xcalibur diffractometer with a Sapphire CCD detector
Absorption correction: multi-scan (*CrysAlis RED*; Oxford Diffraction, 2009)
T_{min} = 0.904, T_{max} = 0.960
4293 measured reflections
2595 independent reflections
2207 reflections with $I > 2\sigma(I)$
R_{int} = 0.017

Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.038
$wR(F^2)$ = 0.109
S = 1.08
2595 reflections
173 parameters
H-atom parameters constrained
$\Delta\rho_{max}$ = 0.24 e Å^{-3}
$\Delta\rho_{min}$ = −0.30 e Å^{-3}

Data collection: *CrysAlis CCD* (Oxford Diffraction, 2009); cell refinement: *CrysAlis RED* (Oxford Diffraction, 2009); data reduction: *CrysAlis RED*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *PLATON* (Spek, 2009); software used to prepare material for publication: *SHELXL97*.

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Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: CI5108).

References

Gowda, B. T., Foro, S., Suchetan, P. A. & Fuess, H. (2009). *Acta Cryst.* E**65**, o2516.
Oxford Diffraction (2009). *CrysAlis CCD* and *CrysAlis RED*. Oxford Diffraction Ltd, Yarnton, England.
Sheldrick, G. M. (2008). *Acta Cryst.* A**64**, 112–122.
Spek, A. L. (2009). *Acta Cryst.* D**65**, 148–155.
Suchetan, P. A., Gowda, B. T., Foro, S. & Fuess, H. (2009). *Acta Cryst.* E**65**, o3156.
Suchetan, P. A., Gowda, B. T., Foro, S. & Fuess, H. (2010). *Acta Cryst.* E**66**, o1039.

supplementary materials

Acta Cryst. (2010). E**66**, o1772 [**doi:10.1107/S1600536810023974**]

N-(4-Methylbenzoyl)benzenesulfonamide

P. A. Suchetan, B. T. Gowda, S. Foro and H. Fuess

Comment

As a part of studying the effect of ring and the side chain substituents on the crystal structures of *N*-aromatic sulfonamides (Gowda *et al.*, 2009; Suchetan *et al.*, 2009, 2010), the crystal structure of *N*-(4-methylbenzoyl)benzenesulfonamide has been determined (Fig. 1). The conformation of the N—H bond in the C—SO_2—NH—C(O) segment is *anti* to the C═O bond, similar to those observed in *N*-(benzoyl)benzenesulfonamide (II) (Gowda *et al.*, 2009), *N*-(benzoyl)-4-methylbenzenesulfonamide (III) (Suchetan *et al.*, 2010) and *N*-(4-chlorobenzoyl)-benzenesulfonamide (IV) (Suchetan *et al.*, 2009).

The molecules are twisted at the S—N bonds with the C—SO_2—NH—C torsional angle of 67.4 (1)°, compared to the values of -66.9 (3)° in (II), 73.2 (2)° in (III) and 69.4 (2)° in (IV).

The dihedral angle between the sulfonyl-bound benzene ring and the S—N—C—O segment (r.m.s. deviation 0.039 Å) is 77.1 (1)°, compared to the values of 86.5 (1)° in (II), 76.5 (1)° in (III) and 75.7 (1)° in (IV).

The dihedral angle between the sulfonyl and the benzoyl benzene rings is 71.9 (1)°, compared to the values of 80.3 (1) in (II), 79.4 (1)° in (III), and 68.6 (1)° in (IV).

Experimental

The title compound was prepared by refluxing a mixture of 4-methylbenzoic acid, benzenesulfonamide and phosphorous oxy chloride for 3 h on a water bath. The resultant mixture was cooled and poured into ice cold water. The solid obtained was filtered, washed thoroughly with water and then dissolved in a sodium bicarbonate solution. The compound was later reprecipitated by acidifying the filtered solution with dilute HCl. It was filtered, dried and recrystallized. Colourless needle-shaped single crystals of the title compound used in X-ray diffraction studies were obtained by slow evaporation of its toluene solution at room temperature.

Refinement

H atoms were positioned with idealized geometry using a riding model with N–H = 0.86 Å, C–H = 0.93–0.96 Å and were refined with isotropic displacement parameters (set to 1.2 times of the U_{eq} of the parent atom).

Figures

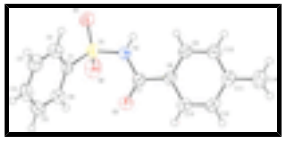


Fig. 1. Molecular structure of the title compound, showing the atom-labelling scheme. Displacement ellipsoids are drawn at the 50% probability level.

N-(4-Methylbenzoyl)benzenesulfonamide

Crystal data

$C_{14}H_{13}NO_3S$	$Z = 2$
$M_r = 275.31$	$F(000) = 288$
Triclinic, $P\overline{1}$	$D_x = 1.432$ Mg m^{-3}
Hall symbol: -P 1	Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å
$a = 5.5519$ (6) Å	Cell parameters from 2679 reflections
$b = 10.541$ (1) Å	$\theta = 2.6$–$27.7°$
$c = 11.105$ (1) Å	$\mu = 0.26$ mm^{-1}
$\alpha = 85.654$ (9)°	$T = 299$ K
$\beta = 83.667$ (9)°	Needle, colourless
$\gamma = 81.949$ (9)°	0.40 × 0.32 × 0.16 mm
$V = 638.36$ (11) Å^3	

Data collection

Oxford Diffraction Xcalibur diffractometer with a Sapphire CCD detector	2595 independent reflections
Radiation source: fine-focus sealed tube	2207 reflections with $I > 2\sigma(I)$
graphite	$R_{int} = 0.017$
Rotation method data acquisition using ω and φ scans	$\theta_{max} = 26.4°$, $\theta_{min} = 2.6°$
Absorption correction: multi-scan (*CrysAlis RED*; Oxford Diffraction, 2009)	$h = -6 \rightarrow 6$
$T_{min} = 0.904$, $T_{max} = 0.960$	$k = -13 \rightarrow 11$
4293 measured reflections	$l = -13 \rightarrow 12$

Refinement

Refinement on F^2	Primary atom site location: structure-invariant direct methods
Least-squares matrix: full	Secondary atom site location: difference Fourier map
$R[F^2 > 2\sigma(F^2)] = 0.038$	Hydrogen site location: inferred from neighbouring sites
$wR(F^2) = 0.109$	H-atom parameters constrained
$S = 1.08$	$w = 1/[\sigma^2(F_o^2) + (0.0564P)^2 + 0.1768P]$ where $P = (F_o^2 + 2F_c^2)/3$
2595 reflections	$(\Delta/\sigma)_{max} = 0.020$
173 parameters	$\Delta\rho_{max} = 0.24$ e Å^{-3}
0 restraints	$\Delta\rho_{min} = -0.30$ e Å^{-3}

Special details

Geometry. All e.s.d.'s (except the e.s.d. in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell e.s.d.'s are taken into account individually in the estimation of e.s.d.'s in distances, angles and torsion angles; correlations

between e.s.d.'s in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell e.s.d.'s is used for estimating e.s.d.'s involving l.s. planes.

Refinement. Refinement of F^2 against ALL reflections. The weighted *R*-factor *wR* and goodness of fit *S* are based on F^2, conventional *R*-factors *R* are based on *F*, with *F* set to zero for negative F^2. The threshold expression of $F^2 > \sigma(F^2)$ is used only for calculating *R*-factors(gt) *etc*. and is not relevant to the choice of reflections for refinement. *R*-factors based on F^2 are statistically about twice as large as those based on *F*, and *R*- factors based on ALL data will be even larger.

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å^2)

	x	*y*	*z*	U_{iso}*/U_{eq}
C1	0.0535 (3)	0.17087 (15)	0.37945 (14)	0.0370 (3)
C2	0.2512 (3)	0.07861 (18)	0.39763 (17)	0.0491 (4)
H2	0.3709	0.0944	0.4448	0.059*
C3	0.2687 (4)	−0.03734 (19)	0.34486 (19)	0.0557 (5)
H3	0.4008	−0.1001	0.3567	0.067*
C4	0.0919 (4)	−0.06031 (17)	0.27507 (18)	0.0514 (5)
H4	0.1050	−0.1383	0.2394	0.062*
C5	−0.1047 (4)	0.03194 (19)	0.25778 (17)	0.0517 (5)
H5	−0.2241	0.0157	0.2106	0.062*
C6	−0.1262 (3)	0.14869 (17)	0.31001 (16)	0.0439 (4)
H6	−0.2592	0.2110	0.2985	0.053*
C7	0.1508 (3)	0.45512 (14)	0.24545 (14)	0.0362 (3)
C8	0.2982 (3)	0.55415 (14)	0.18611 (13)	0.0345 (3)
C9	0.4790 (3)	0.60283 (16)	0.23892 (15)	0.0393 (4)
H9	0.5113	0.5748	0.3177	0.047*
C10	0.6111 (3)	0.69266 (17)	0.17506 (15)	0.0429 (4)
H10	0.7328	0.7235	0.2113	0.051*
C11	0.5653 (3)	0.73765 (16)	0.05771 (15)	0.0403 (4)
C12	0.3825 (3)	0.69012 (18)	0.00681 (16)	0.0471 (4)
H12	0.3477	0.7197	−0.0712	0.056*
C13	0.2508 (3)	0.60001 (17)	0.06897 (15)	0.0451 (4)
H13	0.1291	0.5695	0.0324	0.054*
C14	0.7134 (4)	0.83301 (19)	−0.01353 (19)	0.0553 (5)
H14A	0.8409	0.7882	−0.0661	0.066*
H14B	0.7844	0.8795	0.0415	0.066*
H14C	0.6090	0.8920	−0.0613	0.066*
N1	0.2026 (3)	0.40757 (13)	0.36175 (13)	0.0466 (4)
H1N	0.3319	0.4262	0.3887	0.056*
O1	0.1439 (3)	0.29602 (14)	0.55935 (12)	0.0705 (5)
O2	−0.2229 (3)	0.37520 (13)	0.45410 (13)	0.0618 (4)
O3	−0.0051 (2)	0.41356 (12)	0.19791 (11)	0.0493 (3)
S1	0.02709 (9)	0.31703 (4)	0.45017 (4)	0.04709 (17)

Atomic displacement parameters (Å^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
C1	0.0466 (9)	0.0344 (8)	0.0314 (8)	−0.0135 (7)	−0.0018 (6)	0.0008 (6)

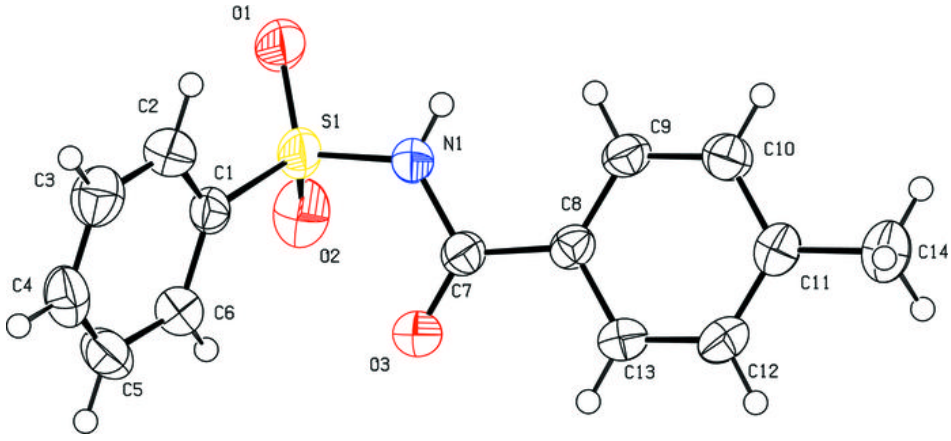
C2	0.0481 (10)	0.0518 (10)	0.0501 (10)	−0.0113 (8)	−0.0125 (8)	−0.0001 (8)
C3	0.0556 (11)	0.0452 (10)	0.0633 (12)	−0.0003 (8)	−0.0039 (9)	0.0008 (9)
C4	0.0641 (12)	0.0386 (9)	0.0524 (11)	−0.0164 (8)	0.0059 (9)	−0.0079 (8)
C5	0.0555 (11)	0.0545 (11)	0.0510 (11)	−0.0219 (9)	−0.0081 (8)	−0.0105 (8)
C6	0.0453 (9)	0.0427 (9)	0.0453 (9)	−0.0096 (7)	−0.0076 (7)	−0.0014 (7)
C7	0.0448 (9)	0.0310 (8)	0.0330 (8)	−0.0035 (6)	−0.0065 (6)	−0.0027 (6)
C8	0.0391 (8)	0.0319 (8)	0.0313 (8)	−0.0004 (6)	−0.0035 (6)	−0.0018 (6)
C9	0.0429 (9)	0.0439 (9)	0.0313 (8)	−0.0054 (7)	−0.0071 (6)	0.0016 (6)
C10	0.0417 (9)	0.0476 (9)	0.0408 (9)	−0.0092 (7)	−0.0061 (7)	−0.0030 (7)
C11	0.0419 (9)	0.0359 (8)	0.0397 (8)	0.0000 (7)	0.0026 (7)	−0.0005 (6)
C12	0.0571 (11)	0.0495 (10)	0.0342 (8)	−0.0070 (8)	−0.0097 (7)	0.0074 (7)
C13	0.0524 (10)	0.0494 (10)	0.0366 (9)	−0.0127 (8)	−0.0145 (7)	0.0030 (7)
C14	0.0585 (12)	0.0500 (11)	0.0552 (11)	−0.0114 (9)	0.0036 (9)	0.0053 (9)
N1	0.0680 (10)	0.0420 (8)	0.0359 (7)	−0.0246 (7)	−0.0154 (7)	0.0053 (6)
O1	0.1269 (14)	0.0621 (9)	0.0333 (7)	−0.0439 (9)	−0.0218 (7)	0.0059 (6)
O2	0.0745 (10)	0.0493 (8)	0.0565 (8)	−0.0036 (7)	0.0148 (7)	−0.0111 (6)
O3	0.0544 (7)	0.0519 (7)	0.0459 (7)	−0.0172 (6)	−0.0166 (6)	0.0056 (5)
S1	0.0756 (3)	0.0393 (2)	0.0295 (2)	−0.0204 (2)	−0.00330 (19)	−0.00178 (16)

Geometric parameters (Å, °)

C1—C6	1.381 (2)	C9—C10	1.384 (2)
C1—C2	1.382 (3)	C9—H9	0.93
C1—S1	1.7626 (16)	C10—C11	1.391 (2)
C2—C3	1.382 (3)	C10—H10	0.93
C2—H2	0.93	C11—C12	1.383 (2)
C3—C4	1.373 (3)	C11—C14	1.510 (2)
C3—H3	0.93	C12—C13	1.377 (2)
C4—C5	1.376 (3)	C12—H12	0.93
C4—H4	0.93	C13—H13	0.93
C5—C6	1.385 (3)	C14—H14A	0.96
C5—H5	0.93	C14—H14B	0.96
C6—H6	0.93	C14—H14C	0.96
C7—O3	1.209 (2)	N1—S1	1.6529 (15)
C7—N1	1.395 (2)	N1—H1N	0.86
C7—C8	1.487 (2)	O1—S1	1.4257 (14)
C8—C9	1.391 (2)	O2—S1	1.4340 (15)
C8—C13	1.393 (2)		
C6—C1—C2	121.09 (16)	C9—C10—C11	121.20 (16)
C6—C1—S1	119.75 (13)	C9—C10—H10	119.4
C2—C1—S1	119.13 (13)	C11—C10—H10	119.4
C3—C2—C1	119.19 (17)	C12—C11—C10	117.86 (15)
C3—C2—H2	120.4	C12—C11—C14	120.74 (16)
C1—C2—H2	120.4	C10—C11—C14	121.39 (16)
C4—C3—C2	120.29 (18)	C13—C12—C11	121.56 (16)
C4—C3—H3	119.9	C13—C12—H12	119.2
C2—C3—H3	119.9	C11—C12—H12	119.2
C3—C4—C5	120.12 (17)	C12—C13—C8	120.55 (16)
C3—C4—H4	119.9	C12—C13—H13	119.7

C5—C4—H4	119.9	C8—C13—H13	119.7
C4—C5—C6	120.56 (17)	C11—C14—H14A	109.5
C4—C5—H5	119.7	C11—C14—H14B	109.5
C6—C5—H5	119.7	H14A—C14—H14B	109.5
C1—C6—C5	118.75 (17)	C11—C14—H14C	109.5
C1—C6—H6	120.6	H14A—C14—H14C	109.5
C5—C6—H6	120.6	H14B—C14—H14C	109.5
O3—C7—N1	119.51 (15)	C7—N1—S1	123.07 (12)
O3—C7—C8	123.77 (14)	C7—N1—H1N	118.5
N1—C7—C8	116.70 (14)	S1—N1—H1N	118.5
C9—C8—C13	118.37 (15)	O1—S1—O2	119.65 (10)
C9—C8—C7	124.69 (14)	O1—S1—N1	103.47 (8)
C13—C8—C7	116.93 (14)	O2—S1—N1	109.71 (8)
C10—C9—C8	120.45 (15)	O1—S1—C1	109.18 (9)
C10—C9—H9	119.8	O2—S1—C1	108.24 (8)
C8—C9—H9	119.8	N1—S1—C1	105.73 (8)
C6—C1—C2—C3	0.2 (3)	C10—C11—C12—C13	−0.7 (3)
S1—C1—C2—C3	178.30 (14)	C14—C11—C12—C13	177.89 (17)
C1—C2—C3—C4	0.1 (3)	C11—C12—C13—C8	0.2 (3)
C2—C3—C4—C5	−0.3 (3)	C9—C8—C13—C12	0.8 (3)
C3—C4—C5—C6	0.2 (3)	C7—C8—C13—C12	−178.80 (16)
C2—C1—C6—C5	−0.4 (3)	O3—C7—N1—S1	−12.2 (2)
S1—C1—C6—C5	−178.42 (13)	C8—C7—N1—S1	168.97 (11)
C4—C5—C6—C1	0.2 (3)	C7—N1—S1—O1	−177.83 (14)
O3—C7—C8—C9	−179.72 (16)	C7—N1—S1—O2	−49.07 (16)
N1—C7—C8—C9	−0.9 (2)	C7—N1—S1—C1	67.44 (15)
O3—C7—C8—C13	−0.1 (2)	C6—C1—S1—O1	149.92 (14)
N1—C7—C8—C13	178.70 (15)	C2—C1—S1—O1	−28.17 (17)
C13—C8—C9—C10	−1.3 (2)	C6—C1—S1—O2	18.16 (16)
C7—C8—C9—C10	178.29 (15)	C2—C1—S1—O2	−159.93 (14)
C8—C9—C10—C11	0.8 (3)	C6—C1—S1—N1	−99.34 (14)
C9—C10—C11—C12	0.2 (3)	C2—C1—S1—N1	82.58 (15)
C9—C10—C11—C14	−178.37 (16)		

Fig. 1



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4-Chloro-*N*-(3-chlorobenzoyl)benzenesulfonamide monohydrate

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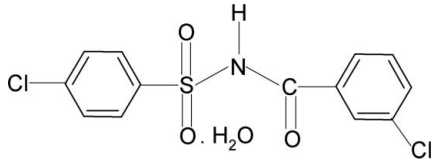
Key indicators: single-crystal X-ray study; T = 299 K; mean σ(C–C) = 0.005 Å; R factor = 0.066; wR factor = 0.184; data-to-parameter ratio = 12.6.

In the title compound, $C_{13}H_9Cl_2NO_3S\cdot H_2O$, the conformation of the C=O bond is *syn* to the *meta*-Cl group in the benzoyl ring. The molecules are twisted at the S—N bond with a C—S—N—C torsion angle of 72.9 (2)°. The dihedral angle between the sulfonyl benzene ring and the S—NH—C—O segment is 77.8 (1)° and that between the sulfonyl and benzoyl benzene rings is 80.5 (1)°. In the crystal, molecules are linked into a two-dimensional network parallel to (100) by N—H···O and O—H···O hydrogen bonds.

Related literature

For background to our study of the effect of ring and side-chain substituents on the crystal structures of *N*-aromatic sulfonamides and for related structures, see: Gowda *et al.* (2009, 2010); Suchetan *et al.* (2010*a*,*b*).



Experimental

Crystal data

$C_{13}H_9Cl_2NO_3S\cdot H_2O$
M_r = 348.19
Monoclinic, $C2/c$
a = 46.909 (3) Å
b = 4.9469 (5) Å
c = 12.919 (1) Å
β = 95.938 (9)°
V = 2981.8 (4) Å^3
Z = 8
Mo $K\alpha$ radiation
μ = 0.59 mm^{-1}
T = 299 K
0.30 × 0.14 × 0.10 mm

Data collection

Oxford Diffraction Xcalibur diffractometer with a Sapphire CCD detector
Absorption correction: multi-scan (*CrysAlis RED*; Oxford Diffraction, 2009)
T_{min} = 0.843, T_{max} = 0.944
7848 measured reflections
2511 independent reflections
2027 reflections with $I > 2\sigma(I)$
R_{int} = 0.094

Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.066
$wR(F^2)$ = 0.184
S = 1.01
2511 reflections
199 parameters
3 restraints
H atoms treated by a mixture of independent and constrained refinement
$\Delta\rho_{max}$ = 0.49 e Å^{-3}
$\Delta\rho_{min}$ = −0.48 e Å^{-3}

Table 1
Hydrogen-bond geometry (Å, °).

D—H···A	D—H	H···A	D···A	D—H···A
N1—H1*N*···O4^{i}	0.83 (2)	1.98 (2)	2.805 (4)	175 (3)
O4—H41···O2^{ii}	0.83 (2)	2.17 (3)	2.944 (3)	154 (4)
O4—H42···O1	0.85 (2)	2.32 (4)	3.035 (4)	142 (5)
O4—H42···O3	0.85 (2)	2.27 (4)	2.952 (3)	137 (5)

Symmetry codes: (i) $x, -y+1, z-\frac{1}{2}$; (ii) $x, -y+2, z+\frac{1}{2}$.

Data collection: *CrysAlis CCD* (Oxford Diffraction, 2009); cell refinement: *CrysAlis RED* (Oxford Diffraction, 2009); data reduction: *CrysAlis RED*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *PLATON* (Spek, 2009); software used to prepare material for publication: *SHELXL97*.

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Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: CI5109).

References

Gowda, B. T., Foro, S., Suchetan, P. A. & Fuess, H. (2009). *Acta Cryst.* E**65**, o2750.
Gowda, B. T., Foro, S., Suchetan, P. A. & Fuess, H. (2010). *Acta Cryst.* E**66**, o1467.
Oxford Diffraction (2009). *CrysAlis CCD* and *CrysAlis RED*. Oxford Diffraction Ltd, Yarnton, England.
Sheldrick, G. M. (2008). *Acta Cryst.* A**64**, 112–122.
Spek, A. L. (2009). *Acta Cryst.* D**65**, 148–155.
Suchetan, P. A., Gowda, B. T., Foro, S. & Fuess, H. (2010*a*). *Acta Cryst.* E**66**, o766.
Suchetan, P. A., Gowda, B. T., Foro, S. & Fuess, H. (2010*b*). *Acta Cryst.* E**66**, o1253.

supplementary materials

Acta Cryst. (2010). E**66**, o1773 [**doi:10.1107/S1600536810023962**]

4-Chloro-*N*-(3-chlorobenzoyl)benzenesulfonamide monohydrate

P. A. Suchetan, B. T. Gowda, S. Foro and H. Fuess

Comment

As a part of studying the effect of ring and the side chain substituents on the crystal structures of *N*-aromatic sulfonamides (Gowda *et al.*, 2009, 2010; Suchetan *et al.*, 2010*a,b*), the structure of 4-chloro-*N*-(3-Chlorobenzoyl)benzenesulfonamide monohydrate (I) has been determined (Fig.1).

The conformation of the N—H bond in the C—SO_2—NH—C(O) segment is *anti* to the C═O bond, similar to those observed in *N*-(3-chlorobenzoyl)-benzenesulfonamide (II) (Gowda *et al.*, 2009), *N*-(benzoyl)-4-chlorobenzenesulfonamide (III) (Suchetan *et al.*, 2010*a*), 4-chloro-*N*-(2-chlorobenzoyl)benzenesulfonamide (IV) (Gowda *et al.*, 2010), and *N*-(4-chlorobenzoyl)-4- chlorobenzenesulfonamide (V) (Suchetan *et al.*, 2010*b*).

Further, the conformation of the C═O bond in the C—SO_2—NH—C(O) segment of (I) is *syn* to the *meta*-Cl in the benzoyl ring, similar to that observed between the C═O bond and *ortho*-Cl in (IV), but contrary to the *anti* conformation observed between the C═O bond and *meta*-Cl in (II).

The molecules are twisted at the S—N bond with the C1—S1—N1—C7 torsional angle of 72.9 (2)°, compared to those of 65.3 (2)° in (II), -70.0 (2)°, 61.3 (2)° in the two independent molecules of (III), 65.7 (2)° in (IV) and 67.5 (3)° in (V).

The dihedral angles between the sulfonyl benzene ring and the S/N/C/O plane is 77.8 (1)°, compared to the values of 89.9 (1)° in (II), 72.0 (1)° & 77.3 (1)° in the two molecules of (III), 88.5 (1)° in (IV) and 79.0 (1)° in (V).

Furthermore, the dihedral angle between the sulfonyl and the benzoyl benzene rings is 80.5 (1)°, compared to the values of 87.5 (1)° in (II), 62.8 (1)° (molecule 1) and 78.6 (1)° (molecule 2) of (III), 58.0 (1)° in (IV) and 85.6 (1)° in (V)

The molecules are linked into a two-dimensional network (Fig.2) parallel to the (100) by N—H···O and O—H···O hydrogen bonds (Table 1).

Experimental

The title compound was prepared by refluxing a mixture of 3-chlorobenzoic acid, 4-chlorobenzenesulfonamide and phosphorous oxy chloride for 3 h on a water bath. The resultant mixture was cooled and poured into ice cold water. The solid obtained was filtered, washed thoroughly with water and then dissolved in sodium bicarbonate solution. The compound was later reprecipitated by acidifying the filtered solution with dilute HCl. It was filtered, dried and recrystallized. Long needle like colourless single crystals of the title compound used in X-ray diffraction studies were obtained by slow evaporation of its toluene solution at room temperature.

Refinement

The H atom of the NH group and the H atoms of the water molecule were located in a difference map and later restrained to N–H = 0.86 (2) %A and to O–H = 0.85 (2) %A. The other H atoms were positioned with idealized geometry using a riding model with C–H = 0.93 Å. All H atoms were refined with isotropic displacement parameters (set to 1.2 times of the U_{eq} of the parent atom).

Figures

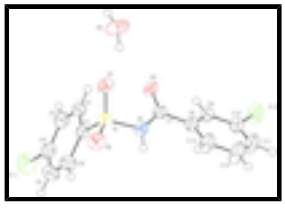


Fig. 1. Molecular structure of the title compound, showing the atom-labelling scheme. Displacement ellipsoids are drawn at the 50% probability level.

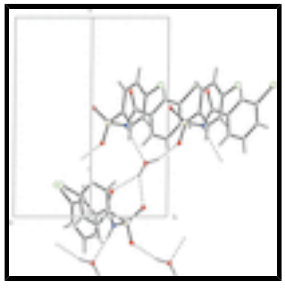


Fig. 2. Part of the crystal packing in the title compound, showing hydrogen bonds (dashed lines) involving the water molecules.

4-Chloro-*N*-(3-chlorobenzoyl)benzenesulfonamide monohydrate

Crystal data

$C_{13}H_9Cl_2NO_3S·H_2O$	$F(000) = 1424$
$M_r = 348.19$	$D_x = 1.551$ Mg m^{-3}
Monoclinic, *C*2/*c*	Mo *K*α radiation, λ = 0.71073 Å
Hall symbol: -C 2yc	Cell parameters from 3786 reflections
$a = 46.909$ (3) Å	θ = 27.9–2.6°
$b = 4.9469$ (5) Å	μ = 0.59 mm^{-1}
$c = 12.919$ (1) Å	$T = 299$ K
β = 95.938 (9)°	Long needle, colourless
$V = 2981.8$ (4) Å^3	0.30 × 0.14 × 0.10 mm
$Z = 8$	

Data collection

Oxford Diffraction Xcalibur diffractometer with a Sapphire CCD detector	2511 independent reflections
Radiation source: fine-focus sealed tube	2027 reflections with $I > 2\sigma(I)$
graphite	$R_{int} = 0.094$
Rotation method data acquisition using ω and φ scans	$\theta_{max} = 25.4°$, $\theta_{min} = 2.6°$

Absorption correction: multi-scan (*CrysAlis RED*; Oxford Diffraction, 2009)	$h = -56 \rightarrow 55$
$T_{min} = 0.843$, $T_{max} = 0.944$	$k = -5 \rightarrow 5$
7848 measured reflections	$l = -15 \rightarrow 15$

Refinement

Refinement on F^2	Primary atom site location: structure-invariant direct methods
Least-squares matrix: full	Secondary atom site location: difference Fourier map
$R[F^2 > 2\sigma(F^2)] = 0.066$	Hydrogen site location: inferred from neighbouring sites
$wR(F^2) = 0.184$	H atoms treated by a mixture of independent and constrained refinement
$S = 1.01$	$w = 1/[\sigma^2(F_o^2) + (0.1432P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
2511 reflections	$(\Delta/\sigma)_{max} = 0.008$
199 parameters	$\Delta\rho_{max} = 0.49$ e Å^{-3}
3 restraints	$\Delta\rho_{min} = -0.48$ e Å^{-3}

Special details

Geometry. All e.s.d.'s (except the e.s.d. in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell e.s.d.'s are taken into account individually in the estimation of e.s.d.'s in distances, angles and torsion angles; correlations between e.s.d.'s in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell e.s.d.'s is used for estimating e.s.d.'s involving l.s. planes.

Refinement. Refinement of F^2 against ALL reflections. The weighted *R*-factor *wR* and goodness of fit *S* are based on F^2, conventional *R*-factors *R* are based on *F*, with *F* set to zero for negative F^2. The threshold expression of $F^2 > \sigma(F^2)$ is used only for calculating *R*-factors(gt) *etc*. and is not relevant to the choice of reflections for refinement. *R*-factors based on F^2 are statistically about twice as large as those based on *F*, and *R*- factors based on ALL data will be even larger.

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å^2)

	x	*y*	*z*	U_{iso}*/U_{eq}
Cl1	0.23824 (2)	−0.1411 (2)	0.15914 (10)	0.0751 (4)
Cl2	0.030813 (19)	−0.4014 (2)	0.16022 (8)	0.0636 (4)
S1	0.145674 (14)	0.62369 (12)	−0.02750 (5)	0.0330 (3)
O1	0.13859 (4)	0.8302 (4)	0.04597 (17)	0.0413 (5)
O2	0.15376 (5)	0.6968 (4)	−0.13059 (16)	0.0478 (6)
O3	0.10727 (4)	0.3795 (4)	0.12809 (15)	0.0433 (6)
N1	0.11762 (5)	0.4252 (5)	−0.04251 (18)	0.0348 (6)
H1N	0.1192 (7)	0.357 (6)	−0.1005 (17)	0.042*
C1	0.17257 (6)	0.4165 (5)	0.0259 (2)	0.0332 (6)
C2	0.17479 (6)	0.3855 (6)	0.1325 (2)	0.0398 (7)
H2	0.1630	0.4779	0.1740	0.048*
C3	0.19519 (7)	0.2122 (7)	0.1723 (2)	0.0456 (7)
H3	0.1976	0.1796	0.2436	0.055*

C4	0.21297 (6)	0.0798 (6)	0.1065 (3)	0.0453 (8)
C5	0.21165 (7)	0.1130 (7)	0.0002 (3)	0.0544 (9)
H5	0.2240	0.0242	−0.0404	0.065*
C6	0.19104 (7)	0.2844 (7)	−0.0406 (2)	0.0476 (8)
H6	0.1888	0.3170	−0.1119	0.057*
C7	0.10191 (6)	0.3242 (5)	0.0382 (2)	0.0340 (6)
C8	0.07754 (6)	0.1437 (5)	0.0091 (2)	0.0363 (7)
C9	0.06672 (5)	−0.0221 (6)	0.0866 (2)	0.0375 (6)
H9	0.0754	−0.0138	0.1546	0.045*
C10	0.04422 (6)	−0.1911 (6)	0.0642 (3)	0.0428 (7)
C11	0.03190 (7)	−0.1960 (8)	−0.0333 (3)	0.0600 (10)
H11	0.0163	−0.3092	−0.0514	0.072*
C12	0.04251 (8)	−0.0290 (9)	−0.1094 (3)	0.0681 (11)
H12	0.0335	−0.0357	−0.1770	0.082*
C13	0.06525 (7)	0.1418 (7)	−0.0887 (3)	0.0516 (9)
H13	0.0718	0.2507	−0.1399	0.062*
O4	0.12309 (7)	0.8386 (5)	0.26833 (19)	0.0640 (7)
H41	0.1273 (10)	0.997 (5)	0.287 (4)	0.096*
H42	0.1245 (11)	0.760 (10)	0.211 (2)	0.096*

Atomic displacement parameters (Å^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Cl1	0.0623 (6)	0.0664 (7)	0.0913 (9)	0.0265 (4)	−0.0185 (6)	−0.0069 (5)
Cl2	0.0642 (6)	0.0712 (6)	0.0563 (6)	−0.0273 (4)	0.0111 (5)	0.0027 (4)
S1	0.0396 (4)	0.0302 (4)	0.0291 (4)	−0.0026 (2)	0.0029 (3)	0.0016 (2)
O1	0.0499 (11)	0.0297 (10)	0.0434 (11)	−0.0007 (8)	0.0003 (9)	−0.0043 (9)
O2	0.0608 (13)	0.0483 (12)	0.0340 (11)	−0.0061 (10)	0.0041 (10)	0.0097 (10)
O3	0.0485 (11)	0.0524 (13)	0.0282 (11)	−0.0123 (9)	0.0004 (9)	−0.0059 (8)
N1	0.0377 (12)	0.0387 (12)	0.0269 (12)	−0.0045 (10)	−0.0023 (10)	−0.0021 (10)
C1	0.0328 (13)	0.0335 (13)	0.0335 (15)	−0.0047 (11)	0.0042 (11)	−0.0027 (11)
C2	0.0350 (14)	0.0480 (16)	0.0357 (16)	0.0033 (12)	0.0011 (12)	−0.0058 (12)
C3	0.0426 (15)	0.0536 (17)	0.0388 (15)	0.0045 (14)	−0.0035 (13)	−0.0015 (15)
C4	0.0371 (15)	0.0411 (15)	0.055 (2)	0.0041 (12)	−0.0075 (14)	−0.0033 (14)
C5	0.0468 (17)	0.060 (2)	0.057 (2)	0.0109 (15)	0.0100 (16)	−0.0134 (16)
C6	0.0504 (17)	0.0571 (18)	0.0363 (15)	0.0051 (15)	0.0089 (13)	−0.0062 (15)
C7	0.0363 (13)	0.0347 (13)	0.0301 (14)	0.0027 (11)	−0.0017 (11)	−0.0032 (11)
C8	0.0324 (13)	0.0362 (14)	0.0388 (15)	0.0003 (11)	−0.0035 (12)	−0.0020 (11)
C9	0.0337 (14)	0.0455 (16)	0.0326 (14)	−0.0021 (12)	−0.0003 (12)	−0.0046 (12)
C10	0.0372 (15)	0.0464 (16)	0.0450 (17)	−0.0074 (12)	0.0051 (13)	−0.0039 (14)
C11	0.0472 (18)	0.075 (2)	0.054 (2)	−0.0219 (17)	−0.0127 (16)	−0.0065 (19)
C12	0.061 (2)	0.090 (3)	0.047 (2)	−0.023 (2)	−0.0225 (18)	0.005 (2)
C13	0.0528 (18)	0.062 (2)	0.0375 (17)	−0.0116 (15)	−0.0075 (15)	0.0068 (14)
O4	0.111 (2)	0.0504 (14)	0.0298 (12)	0.0019 (14)	0.0024 (13)	0.0003 (11)

Geometric parameters (Å, °)

Cl1—C4	1.701 (3)	C5—C6	1.351 (4)
Cl2—C10	1.782 (3)	C5—H5	0.93

S1—O1	1.456 (2)	C6—H6	0.93
S1—O2	1.467 (2)	C7—C8	1.468 (4)
S1—N1	1.637 (2)	C8—C13	1.333 (4)
S1—C1	1.714 (3)	C8—C9	1.427 (4)
O3—C7	1.195 (3)	C9—C10	1.354 (4)
N1—C7	1.428 (4)	C9—H9	0.93
N1—H1N	0.833 (18)	C10—C11	1.331 (5)
C1—C2	1.379 (4)	C11—C12	1.413 (6)
C1—C6	1.438 (4)	C11—H11	0.93
C2—C3	1.347 (4)	C12—C13	1.365 (5)
C2—H2	0.93	C12—H12	0.93
C3—C4	1.412 (5)	C13—H13	0.93
C3—H3	0.93	O4—H41	0.83 (2)
C4—C5	1.379 (5)	O4—H42	0.85 (2)
O1—S1—O2	121.10 (13)	C5—C6—H6	119.9
O1—S1—N1	105.25 (13)	C1—C6—H6	119.9
O2—S1—N1	108.69 (12)	O3—C7—N1	123.9 (2)
O1—S1—C1	111.44 (13)	O3—C7—C8	117.9 (3)
O2—S1—C1	105.30 (14)	N1—C7—C8	118.2 (2)
N1—S1—C1	103.79 (12)	C13—C8—C9	120.7 (3)
C7—N1—S1	126.36 (17)	C13—C8—C7	119.7 (3)
C7—N1—H1N	128 (2)	C9—C8—C7	119.6 (2)
S1—N1—H1N	102 (2)	C10—C9—C8	122.1 (3)
C2—C1—C6	123.9 (3)	C10—C9—H9	119.0
C2—C1—S1	116.4 (2)	C8—C9—H9	119.0
C6—C1—S1	119.7 (2)	C11—C10—C9	117.8 (3)
C3—C2—C1	115.5 (3)	C11—C10—Cl2	119.9 (2)
C3—C2—H2	122.3	C9—C10—Cl2	122.4 (2)
C1—C2—H2	122.3	C10—C11—C12	119.9 (3)
C2—C3—C4	120.4 (3)	C10—C11—H11	120.1
C2—C3—H3	119.8	C12—C11—H11	120.1
C4—C3—H3	119.8	C13—C12—C11	123.3 (3)
C5—C4—C3	125.2 (3)	C13—C12—H12	118.3
C5—C4—Cl1	115.6 (3)	C11—C12—H12	118.3
C3—C4—Cl1	119.2 (3)	C8—C13—C12	116.3 (3)
C6—C5—C4	114.8 (3)	C8—C13—H13	121.9
C6—C5—H5	122.6	C12—C13—H13	121.9
C4—C5—H5	122.6	H41—O4—H42	130 (5)
C5—C6—C1	120.2 (3)		
O1—S1—N1—C7	−44.3 (2)	S1—C1—C6—C5	−177.6 (3)
O2—S1—N1—C7	−175.4 (2)	S1—N1—C7—O3	1.7 (4)
C1—S1—N1—C7	72.9 (2)	S1—N1—C7—C8	−178.91 (19)
O1—S1—C1—C2	27.9 (3)	O3—C7—C8—C13	159.3 (3)
O2—S1—C1—C2	161.0 (2)	N1—C7—C8—C13	−20.1 (4)
N1—S1—C1—C2	−84.9 (2)	O3—C7—C8—C9	−18.9 (4)
O1—S1—C1—C6	−152.8 (2)	N1—C7—C8—C9	161.7 (2)
O2—S1—C1—C6	−19.7 (3)	C13—C8—C9—C10	1.5 (5)
N1—S1—C1—C6	94.4 (2)	C7—C8—C9—C10	179.7 (3)

C6—C1—C2—C3	−2.2 (4)	C8—C9—C10—C11	−1.0 (5)
S1—C1—C2—C3	177.0 (2)	C8—C9—C10—Cl2	179.3 (2)
C1—C2—C3—C4	1.1 (4)	C9—C10—C11—C12	0.3 (6)
C2—C3—C4—C5	0.5 (5)	Cl2—C10—C11—C12	179.9 (3)
C2—C3—C4—Cl1	−179.2 (2)	C10—C11—C12—C13	0.1 (7)
C3—C4—C5—C6	−1.1 (5)	C9—C8—C13—C12	−1.1 (5)
Cl1—C4—C5—C6	178.6 (2)	C7—C8—C13—C12	−179.3 (3)
C4—C5—C6—C1	0.1 (5)	C11—C12—C13—C8	0.4 (6)
C2—C1—C6—C5	1.6 (5)		

Hydrogen-bond geometry (Å, °)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
N1—H1N···O4^{i}	0.83 (2)	1.98 (2)	2.805 (4)	175 (3)
O4—H41···O2^{ii}	0.83 (2)	2.17 (3)	2.944 (3)	154 (4)
O4—H42···O1	0.85 (2)	2.32 (4)	3.035 (4)	142 (5)
O4—H42···O3	0.85 (2)	2.27 (4)	2.952 (3)	137 (5)

Symmetry codes: (i) *x*, −*y*+1, *z*−1/2; (ii) *x*, −*y*+2, *z*+1/2.

Fig. 1

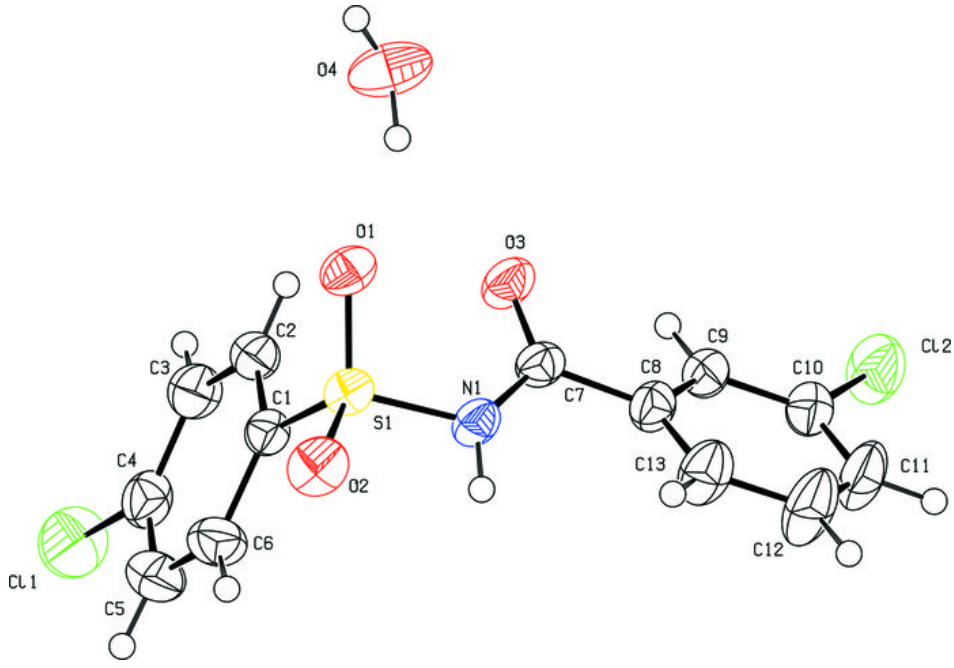
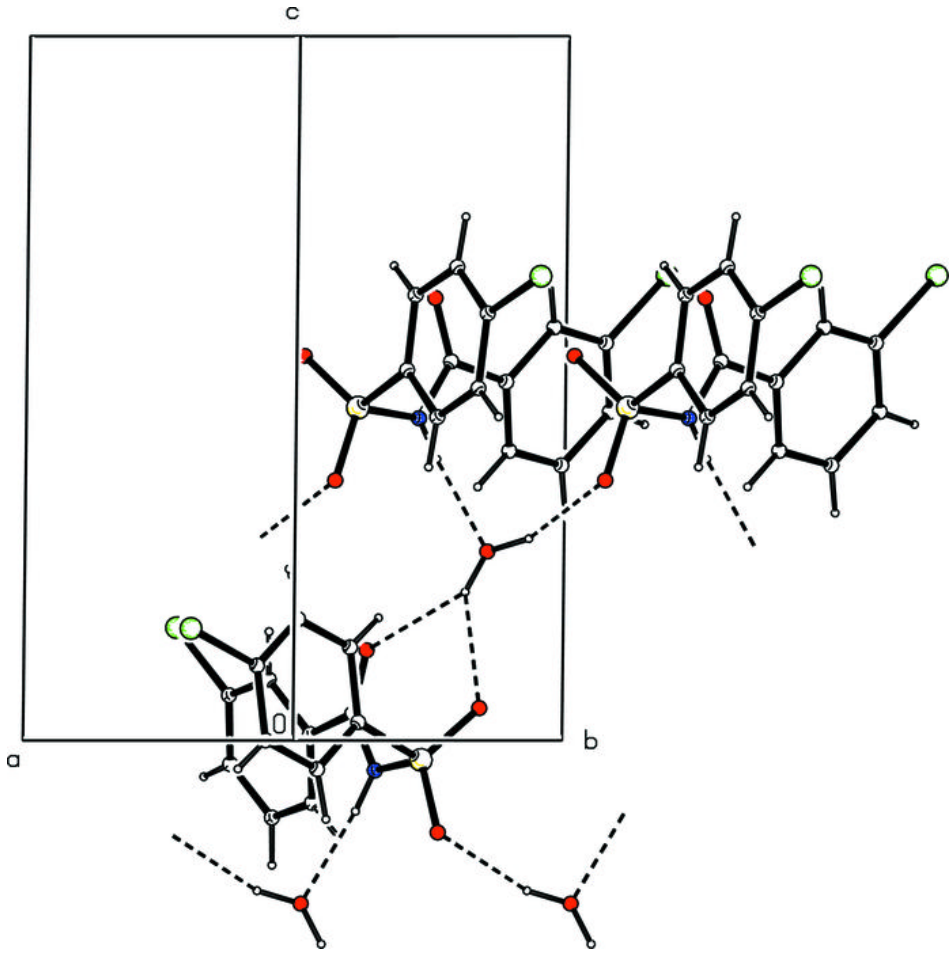


Fig. 2



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1,5-Dimethyl-3-propargyl-1*H*-1,5-benzodiazepine-2,4(3*H*,5*H*)-dione

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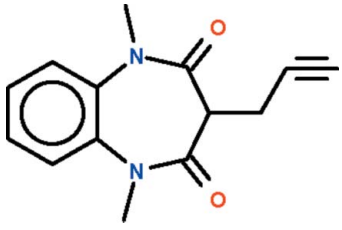
Key indicators: single-crystal X-ray study; T = 293 K; mean σ(C–C) = 0.004 Å; R factor = 0.038; wR factor = 0.105; data-to-parameter ratio = 10.6.

The asymmetric unit of the title compound, $C_{14}H_{14}N_2O_2$, comprises two independent molecules, which slightly differ in the orientation of the propargyl chain. In both molecules, the diazepine ring adopts a boat conformation with the propargyl-bearing C atom as the prow and the C atoms at the ring junction as the stern. The carbonyl O atom of one independent molecule is hydrogen bonded to the acetylenic H atom of the other independent molecule. In the crystal, symmetry-related molecules are linked together by C—H···O hydrogen bonds, forming a ribbon-like structure along the c axis.

Related literature

For a related structure, see: Jabli *et al.* (2009).



Experimental

Crystal data

$C_{14}H_{14}N_2O_2$
M_r = 242.27
Monoclinic, *Cc*
a = 16.0768 (3) Å
b = 17.1087 (3) Å
c = 8.9530 (2) Å
β = 93.701 (1)°
V = 2457.42 (8) Å^3
Z = 8
Mo $K\alpha$ radiation
μ = 0.09 mm^{-1}
T = 293 K
0.40 × 0.30 × 0.05 mm

Data collection

Bruker X8 APEXII area-detector diffractometer
21953 measured reflections
3580 independent reflections
2637 reflections with $I > 2\sigma(I)$
R_{int} = 0.049

Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.038
$wR(F^2)$ = 0.105
S = 1.06
3580 reflections
337 parameters
4 restraints
H atoms treated by a mixture of independent and constrained refinement
$\Delta\rho_{max}$ = 0.22 e Å^{-3}
$\Delta\rho_{min}$ = −0.19 e Å^{-3}

Table 1
Hydrogen-bond geometry (Å, °).

D—H···A	D—H	H···A	D···A	D—H···A
C13—H13···O4	0.93 (3)	2.44 (3)	3.366 (3)	172 (3)
C8—H8···O2^{i}	0.98	2.56	3.536 (3)	175
C19—H19···O1^{i}	0.93	2.49	3.374 (3)	160

Symmetry code: (i) $x, -y+1, z+\frac{1}{2}$.

Data collection: *APEX2* (Bruker, 2008); cell refinement: *SAINT* (Bruker, 2008); data reduction: *SAINT*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *X-SEED* (Barbour, 2001); software used to prepare material for publication: *publCIF* (Westrip, 2010).

The authors thank Université Mohammed V-Agdal and the University of Malaya for supporting this study.

Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: CI5110).

References

Barbour, L. J. (2001). *J. Supramol. Chem.* **1**, 189–191.
Bruker (2008). *APEX2* and *SAINT*. Bruker AXS Inc., Madison, Wisconsin, USA.
Jabli, H., Ouazzani Chahdi, F., Garrigues, B., Essassi, E. M. & Ng, S. W. (2009). *Acta Cryst.* E**65**, o3149.
Sheldrick, G. M. (2008). *Acta Cryst.* A**64**, 112–122.
Westrip, S. P. (2010). *J. Appl. Cryst.* **43**. Submitted.

supplementary materials

Acta Cryst. (2010). E**66**, o1797 [**doi:10.1107/S1600536810024219**]

1,5-Dimethyl-3-propargyl-1*H*-1,5-benzodiazepine-2,4(3*H*,5*H*)-dione

R. Dardouri, F. Ouazzani Chahdi, N. Saffon, E. M. Essassi and S. W. Ng

Comment

We recently reported the crystal stucture of 1,5-dibenzyl-3-propargyl-1,5-benzodiazepine-2,4-dione, a compound readily synthesized by reacting the disubstituted 1,5-benzodiazepine-2,4-dione with propargyl bromide (Jabli *et al.*, 2009). The background to the study of such compounds is given in other reports. Replacing the benzyl unit by a methyl unit in the present study gives a compoound having a diazepine ring system (Scheme I, Fig. 1). This ring adopts a boat conformation (with the propargyl-bearing C atom as the prow and the fused-ring C atoms as the stern). There are two independent molecules; the acetylenic H-atom of one molecule forms a hydrogen to the carbonyl O-atom of the other independent molecule.

Experimental

To a solution of potassium *t*-butoxide (0.42 g, 3.6 mmol) in DMF (15 ml) was added 1,5-dimethyl-1,5-benzodiazepine-2,4-dione (0.50 g, 2.4 mmol) and propargyl bromide (0.26 ml, 2.87 mmol). Stirring was continued for 24 h. The reaction was monitored by thin layer chromatography. On completion of the reaction, the mixture was filtered; crystals were obtained when the solvent was allowed to evaporate.

Refinement

The acetylenic H atoms were located in a difference Fourier map and were refined with C–H distances restrained to 0.93 (1) Å; their U_{iso} parameters were freely refined. The remaining H atoms were placed in calculated positions (C–H = 0.93–0.98 Å) and were included in the refinement in the riding-model approximation, with U_{iso}(H) set to 1.2–1.5U_{eq}(C). In the absence of significant anomalous scattering effects, 3266 Friedel pairs were averaged.

Figures

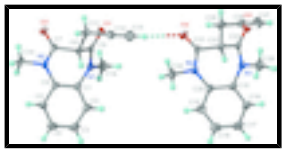


Fig. 1. Thermal ellipsoid plot (Barbour, 2001) of the two independent molecules of $C_{14}H_{14}N_2O_2$ at the 50% probability level shown as a hydrogen-bonded dimer; H atoms are drawn as spheres of arbitrary radius. The dashed line denotes a hydrogen bond.

1,5-Dimethyl-3-propargyl-1*H*-1,5-benzodiazepine- 2,4(3*H*,5*H*)-dione

Crystal data

$C_{14}H_{14}N_2O_2$	$F(000) = 1024$
$M_r = 242.27$	$D_x = 1.310$ Mg m^{-3}
Monoclinic, *Cc*	Mo *K*α radiation, λ = 0.71073 Å
Hall symbol: C -2yc	Cell parameters from 5448 reflections

a = 16.0768 (3) Å	θ = 2.5–29.4°
b = 17.1087 (3) Å	μ = 0.09 mm^{-1}
c = 8.9530 (2) Å	T = 293 K
β = 93.701 (1)°	Plate, colourless
V = 2457.42 (8) Å^3	0.40 × 0.30 × 0.05 mm
Z = 8	

Data collection

Bruker X8 APEXII area-detector diffractometer	2637 reflections with $I > 2\sigma(I)$
Radiation source: fine-focus sealed tube	R_{int} = 0.049
graphite	θ_{max} = 30.0°, θ_{min} = 2.8°
φ and ω scans	h = −22→22
21953 measured reflections	k = −24→23
3580 independent reflections	l = −12→12

Refinement

Refinement on F^2	Primary atom site location: structure-invariant direct methods
Least-squares matrix: full	Secondary atom site location: difference Fourier map
$R[F^2 > 2\sigma(F^2)]$ = 0.038	Hydrogen site location: inferred from neighbouring sites
$wR(F^2)$ = 0.105	H atoms treated by a mixture of independent and constrained refinement
S = 1.06	$w = 1/[\sigma^2(F_o^2) + (0.0514P)^2 + 0.5357P]$ where $P = (F_o^2 + 2F_c^2)/3$
3580 reflections	$(\Delta/\sigma)_{max}$ = 0.001
337 parameters	$\Delta\rho_{max}$ = 0.22 e Å^{-3}
4 restraints	$\Delta\rho_{min}$ = −0.19 e Å^{-3}

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å^2)

	x	y	z	U_{iso}*/U_{eq}
O1	0.50007 (11)	0.33109 (11)	0.5000 (2)	0.0339 (4)
O2	0.34014 (11)	0.41769 (12)	0.21819 (19)	0.0332 (4)
O3	0.99978 (11)	0.63153 (11)	0.9419 (2)	0.0363 (4)
O4	0.78408 (12)	0.58439 (13)	0.74162 (19)	0.0380 (5)
N1	0.39120 (12)	0.33841 (12)	0.6473 (2)	0.0268 (4)
N2	0.26570 (12)	0.39080 (12)	0.4189 (2)	0.0253 (4)
N3	0.91197 (13)	0.68624 (13)	1.1007 (2)	0.0293 (5)
N4	0.75177 (12)	0.65404 (14)	0.9454 (2)	0.0298 (5)
C1	0.31443 (15)	0.37280 (14)	0.6847 (3)	0.0251 (5)
C2	0.29827 (17)	0.38043 (16)	0.8365 (3)	0.0318 (6)
H2	0.3393	0.3670	0.9099	0.038*
C3	0.22235 (19)	0.40758 (17)	0.8778 (3)	0.0382 (6)
H3	0.2124	0.4121	0.9786	0.046*

C4	0.16095 (18)	0.42805 (17)	0.7692 (3)	0.0384 (6)
H4	0.1091	0.4449	0.7969	0.046*
C5	0.17692 (16)	0.42341 (15)	0.6190 (3)	0.0308 (5)
H5	0.1359	0.4385	0.5467	0.037*
C6	0.25334 (15)	0.39661 (13)	0.5746 (3)	0.0240 (5)
C7	0.33523 (15)	0.41709 (14)	0.3543 (3)	0.0242 (5)
C8	0.40776 (14)	0.44186 (14)	0.4628 (2)	0.0232 (5)
H8	0.3882	0.4782	0.5375	0.028*
C9	0.43852 (14)	0.36629 (14)	0.5383 (3)	0.0250 (5)
C10	0.19504 (16)	0.36807 (17)	0.3156 (3)	0.0329 (6)
H10A	0.2141	0.3334	0.2408	0.049*
H10B	0.1711	0.4139	0.2682	0.049*
H10C	0.1537	0.3421	0.3704	0.049*
C11	0.47672 (15)	0.48013 (16)	0.3774 (3)	0.0295 (5)
H11A	0.4954	0.4434	0.3040	0.035*
H11B	0.4540	0.5255	0.3239	0.035*
C12	0.54896 (16)	0.50462 (16)	0.4769 (3)	0.0324 (5)
C13	0.60798 (19)	0.5229 (2)	0.5539 (4)	0.0446 (7)
H13	0.6549 (15)	0.537 (2)	0.614 (4)	0.062 (11)*
C14	0.42070 (18)	0.26755 (16)	0.7274 (3)	0.0373 (6)
H14A	0.4325	0.2277	0.6563	0.056*
H14B	0.3784	0.2493	0.7898	0.056*
H14C	0.4704	0.2794	0.7884	0.056*
C15	0.83776 (15)	0.68259 (15)	1.1784 (3)	0.0279 (5)
C16	0.84147 (18)	0.69589 (16)	1.3331 (3)	0.0343 (6)
H16	0.8919	0.7095	1.3829	0.041*
C17	0.7709 (2)	0.68902 (17)	1.4124 (3)	0.0404 (7)
H17	0.7745	0.6968	1.5154	0.049*
C18	0.6949 (2)	0.67062 (18)	1.3391 (3)	0.0429 (7)
H18	0.6477	0.6658	1.3932	0.052*
C19	0.68919 (17)	0.65948 (16)	1.1858 (3)	0.0357 (6)
H19	0.6378	0.6481	1.1369	0.043*
C20	0.75997 (16)	0.66527 (14)	1.1039 (3)	0.0278 (5)
C21	0.79742 (15)	0.60039 (16)	0.8740 (3)	0.0281 (5)
C22	0.87014 (15)	0.56424 (15)	0.9697 (3)	0.0274 (5)
H22	0.8497	0.5453	1.0640	0.033*
C23	0.93407 (15)	0.62914 (15)	1.0034 (3)	0.0272 (5)
C24	0.67961 (17)	0.68895 (18)	0.8601 (3)	0.0386 (6)
H24A	0.6957	0.7049	0.7634	0.058*
H24B	0.6605	0.7336	0.9131	0.058*
H24C	0.6356	0.6511	0.8484	0.058*
C25	0.90761 (17)	0.49596 (16)	0.8873 (3)	0.0330 (6)
H25A	0.8631	0.4621	0.8477	0.040*
H25B	0.9365	0.5159	0.8034	0.040*
C26	0.96610 (17)	0.45014 (16)	0.9847 (3)	0.0326 (6)
C27	1.01106 (19)	0.41189 (19)	1.0637 (4)	0.0445 (7)
H27	1.043 (2)	0.3804 (19)	1.130 (4)	0.070 (12)*
C28	0.97458 (18)	0.74656 (18)	1.1443 (4)	0.0426 (7)
H28A	1.0095	0.7556	1.0630	0.064*

H28B	1.0082	0.7291	1.2305	0.064*
H28C	0.9468	0.7942	1.1679	0.064*

Atomic displacement parameters (Å^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
O1	0.0256 (9)	0.0397 (10)	0.0365 (11)	0.0051 (8)	0.0020 (7)	−0.0001 (8)
O2	0.0345 (9)	0.0472 (11)	0.0175 (9)	−0.0022 (8)	−0.0014 (7)	0.0014 (8)
O3	0.0284 (10)	0.0455 (11)	0.0350 (11)	−0.0010 (8)	0.0007 (8)	−0.0021 (9)
O4	0.0363 (10)	0.0558 (13)	0.0210 (10)	−0.0022 (9)	−0.0054 (8)	−0.0026 (8)
N1	0.0276 (10)	0.0311 (10)	0.0210 (10)	0.0018 (8)	−0.0029 (8)	0.0052 (9)
N2	0.0234 (10)	0.0323 (11)	0.0197 (10)	−0.0023 (8)	−0.0022 (8)	−0.0003 (8)
N3	0.0267 (10)	0.0350 (12)	0.0254 (11)	−0.0037 (8)	−0.0038 (8)	−0.0050 (9)
N4	0.0256 (10)	0.0398 (12)	0.0233 (11)	−0.0010 (8)	−0.0030 (8)	0.0021 (9)
C1	0.0275 (12)	0.0277 (12)	0.0202 (11)	−0.0040 (9)	0.0019 (9)	0.0009 (10)
C2	0.0372 (13)	0.0376 (14)	0.0204 (12)	−0.0069 (11)	0.0008 (10)	0.0013 (10)
C3	0.0507 (16)	0.0403 (15)	0.0249 (13)	−0.0065 (12)	0.0139 (12)	−0.0015 (12)
C4	0.0376 (15)	0.0383 (15)	0.0411 (16)	−0.0005 (12)	0.0161 (12)	−0.0007 (13)
C5	0.0272 (12)	0.0342 (13)	0.0312 (13)	−0.0017 (10)	0.0034 (10)	0.0002 (11)
C6	0.0256 (11)	0.0261 (11)	0.0202 (11)	−0.0039 (9)	0.0015 (9)	0.0003 (9)
C7	0.0244 (11)	0.0288 (12)	0.0194 (11)	0.0038 (9)	−0.0003 (8)	0.0019 (9)
C8	0.0243 (11)	0.0293 (12)	0.0162 (10)	−0.0010 (9)	0.0022 (8)	−0.0013 (9)
C9	0.0230 (11)	0.0309 (12)	0.0202 (11)	−0.0016 (9)	−0.0056 (9)	−0.0008 (9)
C10	0.0276 (13)	0.0400 (15)	0.0295 (14)	−0.0048 (11)	−0.0102 (10)	−0.0004 (11)
C11	0.0279 (12)	0.0380 (14)	0.0227 (12)	−0.0040 (10)	0.0017 (9)	0.0037 (10)
C12	0.0308 (13)	0.0374 (13)	0.0296 (13)	−0.0036 (11)	0.0060 (11)	0.0054 (11)
C13	0.0379 (15)	0.0542 (19)	0.0412 (17)	−0.0145 (14)	−0.0016 (13)	0.0030 (14)
C14	0.0414 (15)	0.0365 (15)	0.0335 (14)	0.0051 (12)	−0.0019 (11)	0.0121 (12)
C15	0.0316 (13)	0.0288 (13)	0.0231 (12)	0.0016 (10)	−0.0010 (10)	−0.0013 (10)
C16	0.0438 (15)	0.0345 (14)	0.0238 (13)	0.0031 (11)	−0.0047 (11)	−0.0013 (11)
C17	0.0598 (18)	0.0374 (15)	0.0244 (13)	0.0026 (13)	0.0047 (13)	0.0006 (12)
C18	0.0497 (17)	0.0412 (17)	0.0401 (17)	−0.0037 (13)	0.0199 (14)	0.0010 (13)
C19	0.0337 (14)	0.0384 (15)	0.0356 (15)	−0.0055 (11)	0.0056 (12)	−0.0004 (12)
C20	0.0317 (12)	0.0284 (12)	0.0233 (12)	−0.0028 (10)	0.0011 (10)	0.0004 (10)
C21	0.0254 (11)	0.0374 (13)	0.0210 (12)	−0.0078 (10)	−0.0016 (9)	0.0018 (10)
C22	0.0312 (12)	0.0335 (13)	0.0170 (11)	−0.0003 (10)	−0.0016 (9)	0.0007 (10)
C23	0.0250 (11)	0.0353 (13)	0.0202 (12)	0.0019 (9)	−0.0056 (9)	0.0023 (10)
C24	0.0291 (13)	0.0506 (17)	0.0351 (15)	0.0009 (12)	−0.0066 (11)	0.0030 (13)
C25	0.0422 (14)	0.0367 (14)	0.0197 (12)	−0.0012 (11)	−0.0007 (11)	−0.0029 (10)
C26	0.0341 (13)	0.0362 (14)	0.0279 (13)	−0.0034 (11)	0.0051 (10)	−0.0044 (11)
C27	0.0344 (15)	0.0495 (18)	0.0488 (19)	−0.0012 (13)	−0.0036 (13)	0.0078 (14)
C28	0.0351 (14)	0.0497 (17)	0.0423 (17)	−0.0121 (13)	−0.0030 (12)	−0.0113 (14)

Geometric parameters (Å, °)

O1—C9	1.226 (3)	C11—C12	1.478 (4)
O2—C7	1.226 (3)	C11—H11A	0.97
O3—C23	1.223 (3)	C11—H11B	0.97
O4—C21	1.222 (3)	C12—C13	1.179 (4)

N1—C9	1.361 (3)	C13—H13	0.93 (3)
N1—C1	1.427 (3)	C14—H14A	0.96
N1—C14	1.472 (3)	C14—H14B	0.96
N2—C7	1.367 (3)	C14—H14C	0.96
N2—C6	1.424 (3)	C15—C16	1.401 (3)
N2—C10	1.470 (3)	C15—C20	1.411 (3)
N3—C23	1.371 (3)	C16—C17	1.381 (4)
N3—C15	1.421 (3)	C16—H16	0.93
N3—C28	1.476 (3)	C17—C18	1.385 (4)
N4—C21	1.360 (3)	C17—H17	0.93
N4—C20	1.430 (3)	C18—C19	1.383 (4)
N4—C24	1.473 (3)	C18—H18	0.93
C1—C6	1.406 (3)	C19—C20	1.397 (4)
C1—C2	1.406 (4)	C19—H19	0.93
C2—C3	1.379 (4)	C21—C22	1.535 (3)
C2—H2	0.93	C22—C25	1.526 (4)
C3—C4	1.385 (4)	C22—C23	1.530 (3)
C3—H3	0.93	C22—H22	0.98
C4—C5	1.388 (4)	C24—H24A	0.96
C4—H4	0.93	C24—H24B	0.96
C5—C6	1.393 (4)	C24—H24C	0.96
C5—H5	0.93	C25—C26	1.468 (4)
C7—C8	1.528 (3)	C25—H25A	0.97
C8—C9	1.526 (3)	C25—H25B	0.97
C8—C11	1.534 (3)	C26—C27	1.177 (4)
C8—H8	0.98	C27—H27	0.93 (3)
C10—H10A	0.96	C28—H28A	0.96
C10—H10B	0.96	C28—H28B	0.96
C10—H10C	0.96	C28—H28C	0.96
C9—N1—C1	123.77 (19)	N1—C14—H14A	109.5
C9—N1—C14	117.4 (2)	N1—C14—H14B	109.5
C1—N1—C14	118.8 (2)	H14A—C14—H14B	109.5
C7—N2—C6	124.09 (19)	N1—C14—H14C	109.5
C7—N2—C10	116.2 (2)	H14A—C14—H14C	109.5
C6—N2—C10	118.88 (19)	H14B—C14—H14C	109.5
C23—N3—C15	122.7 (2)	C16—C15—C20	118.8 (2)
C23—N3—C28	117.8 (2)	C16—C15—N3	119.6 (2)
C15—N3—C28	118.7 (2)	C20—C15—N3	121.6 (2)
C21—N4—C20	122.6 (2)	C17—C16—C15	120.7 (2)
C21—N4—C24	117.4 (2)	C17—C16—H16	119.7
C20—N4—C24	118.6 (2)	C15—C16—H16	119.7
C6—C1—C2	119.1 (2)	C16—C17—C18	120.3 (3)
C6—C1—N1	122.0 (2)	C16—C17—H17	119.9
C2—C1—N1	118.8 (2)	C18—C17—H17	119.9
C3—C2—C1	120.8 (2)	C17—C18—C19	120.1 (3)
C3—C2—H2	119.6	C17—C18—H18	120.0
C1—C2—H2	119.6	C19—C18—H18	120.0
C2—C3—C4	120.0 (3)	C18—C19—C20	120.5 (3)
C2—C3—H3	120.0	C18—C19—H19	119.8

C4—C3—H3	120.0	C20—C19—H19	119.8
C3—C4—C5	119.8 (3)	C19—C20—C15	119.6 (2)
C3—C4—H4	120.1	C19—C20—N4	119.1 (2)
C5—C4—H4	120.1	C15—C20—N4	121.3 (2)
C4—C5—C6	121.1 (3)	O4—C21—N4	122.7 (2)
C4—C5—H5	119.4	O4—C21—C22	122.1 (2)
C6—C5—H5	119.4	N4—C21—C22	115.1 (2)
C5—C6—C1	119.0 (2)	C25—C22—C23	111.7 (2)
C5—C6—N2	118.9 (2)	C25—C22—C21	110.40 (19)
C1—C6—N2	122.1 (2)	C23—C22—C21	107.2 (2)
O2—C7—N2	122.0 (2)	C25—C22—H22	109.2
O2—C7—C8	122.3 (2)	C23—C22—H22	109.2
N2—C7—C8	115.7 (2)	C21—C22—H22	109.2
C9—C8—C7	105.00 (19)	O3—C23—N3	121.9 (2)
C9—C8—C11	111.0 (2)	O3—C23—C22	121.6 (2)
C7—C8—C11	110.36 (19)	N3—C23—C22	116.4 (2)
C9—C8—H8	110.1	N4—C24—H24A	109.5
C7—C8—H8	110.1	N4—C24—H24B	109.5
C11—C8—H8	110.1	H24A—C24—H24B	109.5
O1—C9—N1	121.8 (2)	N4—C24—H24C	109.5
O1—C9—C8	122.4 (2)	H24A—C24—H24C	109.5
N1—C9—C8	115.7 (2)	H24B—C24—H24C	109.5
N2—C10—H10A	109.5	C26—C25—C22	112.3 (2)
N2—C10—H10B	109.5	C26—C25—H25A	109.1
H10A—C10—H10B	109.5	C22—C25—H25A	109.1
N2—C10—H10C	109.5	C26—C25—H25B	109.1
H10A—C10—H10C	109.5	C22—C25—H25B	109.1
H10B—C10—H10C	109.5	H25A—C25—H25B	107.9
C12—C11—C8	112.7 (2)	C27—C26—C25	178.0 (3)
C12—C11—H11A	109.1	C26—C27—H27	176 (3)
C8—C11—H11A	109.1	N3—C28—H28A	109.5
C12—C11—H11B	109.1	N3—C28—H28B	109.5
C8—C11—H11B	109.1	H28A—C28—H28B	109.5
H11A—C11—H11B	107.8	N3—C28—H28C	109.5
C13—C12—C11	178.1 (3)	H28A—C28—H28C	109.5
C12—C13—H13	180 (3)	H28B—C28—H28C	109.5
C9—N1—C1—C6	44.7 (3)	C23—N3—C15—C16	131.1 (3)
C14—N1—C1—C6	−133.7 (3)	C28—N3—C15—C16	−38.5 (3)
C9—N1—C1—C2	−137.7 (2)	C23—N3—C15—C20	−48.5 (3)
C14—N1—C1—C2	43.9 (3)	C28—N3—C15—C20	142.0 (3)
C6—C1—C2—C3	2.9 (4)	C20—C15—C16—C17	2.7 (4)
N1—C1—C2—C3	−174.9 (2)	N3—C15—C16—C17	−176.9 (3)
C1—C2—C3—C4	−0.3 (4)	C15—C16—C17—C18	−1.5 (4)
C2—C3—C4—C5	−1.9 (4)	C16—C17—C18—C19	−0.4 (4)
C3—C4—C5—C6	1.6 (4)	C17—C18—C19—C20	1.1 (4)
C4—C5—C6—C1	1.0 (4)	C18—C19—C20—C15	0.0 (4)
C4—C5—C6—N2	178.2 (2)	C18—C19—C20—N4	−179.5 (3)
C2—C1—C6—C5	−3.2 (3)	C16—C15—C20—C19	−1.9 (4)
N1—C1—C6—C5	174.4 (2)	N3—C15—C20—C19	177.7 (2)

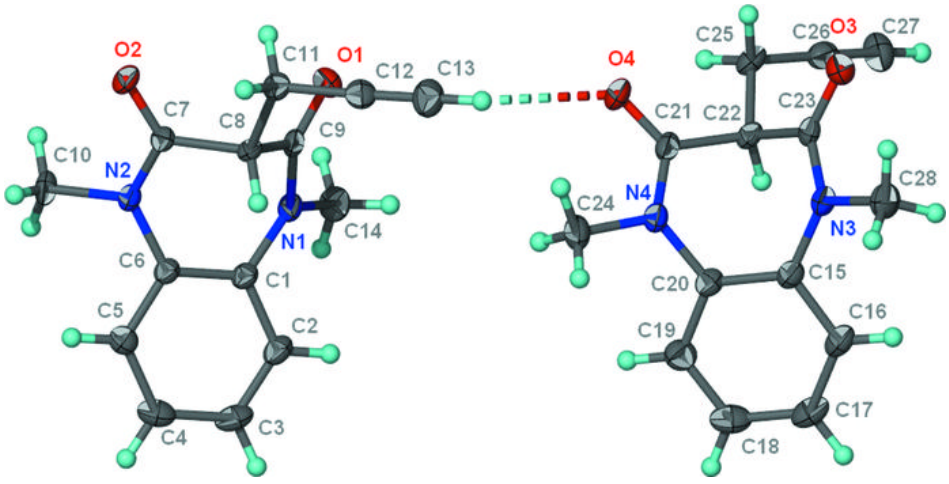
C2—C1—C6—N2	179.8 (2)	C16—C15—C20—N4	177.6 (2)
N1—C1—C6—N2	−2.6 (3)	N3—C15—C20—N4	−2.8 (4)
C7—N2—C6—C5	133.8 (2)	C21—N4—C20—C19	−124.8 (3)
C10—N2—C6—C5	−35.1 (3)	C24—N4—C20—C19	41.7 (3)
C7—N2—C6—C1	−49.2 (3)	C21—N4—C20—C15	55.7 (3)
C10—N2—C6—C1	141.9 (2)	C24—N4—C20—C15	−137.8 (2)
C6—N2—C7—O2	−173.0 (2)	C20—N4—C21—O4	171.5 (2)
C10—N2—C7—O2	−3.8 (3)	C24—N4—C21—O4	4.8 (4)
C6—N2—C7—C8	9.9 (3)	C20—N4—C21—C22	−11.6 (3)
C10—N2—C7—C8	179.0 (2)	C24—N4—C21—C22	−178.2 (2)
O2—C7—C8—C9	−109.3 (3)	O4—C21—C22—C25	−12.3 (3)
N2—C7—C8—C9	67.9 (3)	N4—C21—C22—C25	170.7 (2)
O2—C7—C8—C11	10.4 (3)	O4—C21—C22—C23	109.5 (3)
N2—C7—C8—C11	−172.4 (2)	N4—C21—C22—C23	−67.4 (3)
C1—N1—C9—O1	−173.1 (2)	C15—N3—C23—O3	−177.0 (2)
C14—N1—C9—O1	5.3 (3)	C28—N3—C23—O3	−7.4 (4)
C1—N1—C9—C8	4.2 (3)	C15—N3—C23—C22	6.0 (3)
C14—N1—C9—C8	−177.4 (2)	C28—N3—C23—C22	175.6 (2)
C7—C8—C9—O1	100.1 (2)	C25—C22—C23—O3	14.7 (3)
C11—C8—C9—O1	−19.1 (3)	C21—C22—C23—O3	−106.3 (3)
C7—C8—C9—N1	−77.2 (2)	C25—C22—C23—N3	−168.3 (2)
C11—C8—C9—N1	163.55 (19)	C21—C22—C23—N3	70.7 (3)
C9—C8—C11—C12	−63.5 (3)	C23—C22—C25—C26	72.0 (3)
C7—C8—C11—C12	−179.5 (2)	C21—C22—C25—C26	−168.9 (2)

Hydrogen-bond geometry (Å, °)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
C13—H13···O4	0.93 (3)	2.44 (3)	3.366 (3)	172 (3)
C8—H8···O2^{i}	0.98	2.56	3.536 (3)	175
C19—H19···O1^{i}	0.93	2.49	3.374 (3)	160

Symmetry codes: (i) *x*, −*y*+1, *z*+1/2.

Fig. 1


O2
C11
O1
C12
C13
O4
C25
C26
O3
C27
C7
C8
C9
C21
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C23
C10
N2
C24
N4
C28
N1
C14
N3
C6
C1
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C5
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C18

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8-Methyl-2-[4-(trifluoromethyl)phenyl]-8*H*-pyrazolo[4,3-*e*][1,2,4]triazolo[1,5-*c*]-pyrimidin-5-amine methanol disolvate

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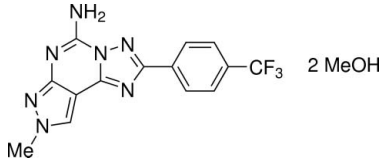
Key indicators: single-crystal X-ray study; T = 223 K; mean σ(C–C) = 0.002 Å; R factor = 0.054; wR factor = 0.145; data-to-parameter ratio = 15.3.

In the title compound, $C_{14}H_{10}F_3N_7\cdot 2CH_4O$, the heterocyclic ring system is essentially planar (r.m.s. deviation = 0.009 Å) and makes a dihedral angle of 6.91 (8)° with the attached benzene ring. In the crystal, the main molecules form centrosymmetric $R_2^2(8)$ dimers *via* pairs of N—H···N hydrogen bonds between the amino groups and pyrimidine N atoms. One of the independent methanol molecules and its inversion equivalent are linked to the dimers *via* O—H···N and N—H···O hydrogen bonds, forming $R_4^4(16)$ graph-set motifs. The dimers along with the hydrogen-bonded methanol molecules are stacked along the *a* axis, with π–π interactions between the pyrazole and triazole rings [centroid–centroid distance = 3.4953 (10) Å].

Related literature

For reviews on pyrazolo[4,3-*e*][1,2,4]triazolo[1,5-*c*]pyrimidine adenosine receptor antagonists, see: Baraldi *et al.* (2006); Cacciari *et al.* (2007). For the general method used for the synthesis of the title compound, see: Dolzhenko *et al.* (2009); Cheong *et al.* (2010). For the crystal structures of related pyrazolo[4,3-*e*][1,2,4]triazolo[1,5-*c*]pyrimidines, see: Ferretti *et al.* (2006); Mezheritsky *et al.* (2004); Tyurin *et al.* (2005); Xiao & Shi (2007). For graph-set analysis of hydrogen bonding, see: Bernstein *et al.* (1995).



Experimental

Crystal data

$C_{14}H_{10}F_3N_7\cdot 2CH_4O$
M_r = 397.37
Monoclinic, $P2_1/n$
a = 4.6179 (3) Å
b = 17.1149 (10) Å
c = 22.7627 (13) Å
β = 94.323 (1)°
V = 1793.93 (19) Å^3
Z = 4
Mo $K\alpha$ radiation
μ = 0.12 mm^{-1}
T = 223 K
0.58 × 0.32 × 0.12 mm

Data collection

Bruker SMART APEX CCD diffractometer
Absorption correction: multi-scan (*SADABS*; Sheldrick, 2001)
T_{min} = 0.932, T_{max} = 0.985
12385 measured reflections
4076 independent reflections
3538 reflections with $I > 2\sigma(I)$
R_{int} = 0.027

Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.054
$wR(F^2)$ = 0.145
S = 1.05
4076 reflections
266 parameters
H atoms treated by a mixture of independent and constrained refinement
$\Delta\rho_{max}$ = 0.35 e Å^{-3}
$\Delta\rho_{min}$ = −0.21 e Å^{-3}

Table 1
Hydrogen-bond geometry (Å, °).

D—H···A	D—H	H···A	D···A	D—H···A
O1*S*—H1*S*···N2^{i}	0.83	2.05	2.877 (2)	175
O2*S*—H2*S*···N6	0.83	2.04	2.853 (2)	165
N7—H7*A*···O1*S*	0.85 (2)	2.46 (2)	3.050 (2)	128 (2)
N7—H7*B*···N3^{i}	0.89 (2)	2.09 (3)	2.979 (2)	179 (2)

Symmetry code: (i) $-x, -y+1, -z$.

Data collection: *SMART* (Bruker, 2001); cell refinement: *SAINT* (Bruker, 2001); data reduction: *SAINT*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *SHELXTL* (Sheldrick, 2008); software used to prepare material for publication: *SHELXTL*.

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Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: CI5111).

References

Baraldi, P. G., Tabrizi, M. A., Romagnoli, R., El-Kashef, H., Preti, D., Bovero, A., Fruttarolo, F., Gordaliza, M. & Borea, P. A. (2006). *Curr. Org. Chem.* **10**, 259–275.
Bernstein, J., Davis, R. E., Shimoni, L. & Chang, N.-L. (1995). *Angew. Chem. Int. Ed. Engl.* **34**, 1555–1573.
Bruker (2001). *SMART* and *SAINT*. Bruker AXS GmbH, Karlsruhe, Germany.
Cacciari, B., Bolcato, C., Spalluto, G., Klotz, K.-N., Bacilieri, M., Deflorian, F. & Moro, S. (2007). *Purinergic Signal.* **3**, 183–193.
Cheong, S. L., Dolzhenko, A., Kachler, S., Paoletta, S., Federico, S., Cacciari, B., Dolzhenko, A., Klotz, K.-N., Moro, S., Spalluto, G. & Pastorin, G. (2010). *J. Med. Chem.* **53**, 3361–3375.
Dolzhenko, A. V., Pastorin, G., Dolzhenko, A. V. & Chui, W. K. (2009). *Tetrahedron Lett.* **50**, 5617–5621.
Ferretti, V., Pretto, L., Tabrizi, M. A. & Gilli, P. (2006). *Acta Cryst.* B**62**, 634–641.

Mezheritsky, V. V., Minkin, V. I., Minyaeva, L. G., Tyurin, R. G., Krasnikov, V. V., Vorobyev, E. V. & Starikova, Z. A. (2004). *ARKIVOC*, pp. 9–17.
Sheldrick, G. M. (2001). *SADABS*. University of Göttingen, Germany.
Sheldrick, G. M. (2008). *Acta Cryst.* A**64**, 112–122.
Tyurin, R. V., Vorob'ev, E. V., Minyaeva, L. G., Krasnikov, V. V. & Mezheritskii, V. V. (2005). *Russ. J. Org. Chem.* **41**, 916–921.
Xiao, L.-X. & Shi, D.-Q. (2007). *Acta Cryst.* E**63**, o3613.

supplementary materials

Acta Cryst. (2010). E**66**, o1835-o1836 [**doi:10.1107/S1600536810024591**]

8-Methyl-2-[4-(trifluoromethyl)phenyl]-8*H*-pyrazolo[4,3-*e*][1,2,4]triazolo[1,5-*c*]pyrimidin-5-amine methanol disolvate

A. V. Dolzhenko, G. K. Tan, A. V. Dolzhenko, L. L. Koh and G. Pastorin

Comment

Pyrazolo[4,3-*e*][1,2,4]triazolo[1,5-*c*]pyrimidine system has been recognized as an excellent template for the construction of new adenosine receptor antagonists (Baraldi *et al.*, 2006; Cacciari *et al.*, 2007). However, information on the structure of this heterocyclic system is limited (Ferretti *et al.*, 2006; Mezheritsky *et al.*, 2004; Tyurin *et al.*, 2005; Xiao & Shi, 2007). In continuation of our works on the development of new pyrazolo[4,3-*e*][1,2,4]triazolo[1,5-*c*]pyrimidine adenosine receptor antagonists (Dolzhenko *et al.*, 2009; Cheong *et al.*, 2010), we report here the molecular and crystal structure of 8-methyl-2-(4-trifluoromethylphenyl)-8*H*-pyrazolo[4,3-*e*][1,2,4]triazolo[1,5-*c*]pyrimidin-5-amine.

The compound crystallizes with two methanol solvent molecules. The heterocyclic ring system is essentially planar with an r.m.s. deviation of 0.009 Å. The phenyl ring makes a dihedral angle of 6.91 (8)° with the pyrazolo[4,3-*e*][1,2,4]triazolo[1,5-*c*]pyrimidine core. The trifluoromethyl group C atom, C13, is located 0.130 (3) Å above the C7—C12 mean plane.

In the crystal, molecules of 8-methyl-2-(4-trifluoromethylphenyl)-8*H*-pyrazolo[4,3-*e*][1,2,4]triazolo[1,5-*c*]pyrimidin-5-amine form centrosymmetric inversion dimers (Fig. 2). The pyrimidine N3 atom is connected with amino group N7—H7B of the pair molecule by intermolecular N···H—N hydrogen bond making $R_2^2(8)$ graph-set motif (Bernstein *et al.*,1995). Methanol hydroxy group O1S—H1S also links the heterocyclic molecules in the dimer by the N—H···O—H···N hydrogen bond array with amino group N7—H7A and N2 of the pyrazole ring making $R_4^4(16)$ graph-set motif. Another methanol molecule forms the O—H···N hydrogen bond with N6 of the triazole ring. The dimers are stacked along the *a* axis, with π–π interactions between pyrazole and triazole rings [centroid-to-centroid distance = 3.4953 (10) Å] (Fig. 2).

Experimental

8-Methyl-2-(4-trifluoromethylphenyl)-8*H*-pyrazolo[4,3-*e*][1,2,4]triazolo][1,5-*c*]pyrimidin-5-amine was prepared from 8-methyl-2-(4-trifluoromethylphenyl)-8*H*-pyrazolo[4,3-*e*][1,2,4]triazolo][1,5-*c*]pyrimidine (Dolzhenko *et al.*, 2009) similarly to the described method (Cheong *et al.*, 2010). The detail procedure will be reported elsewhere. The crystals suitable for crystallographic analysis were grown by recrystallization from methanol. m.p. 573 K.

Refinement

All C-bound H atoms were positioned geometrically and included in the refinement in riding-motion approximation [0.94 Å for CH of aromatic systems, 0.97 Å for methyl groups, and 0.83 Å for hydroxyl groups; $U_{iso}(H) = 1.2U_{eq}(C_{Ar})$ and $U_{iso}(H) = 1.5U_{eq}(O,C_{Me})$] while the amino group H atoms were located in a difference map and refined freely.

Figures

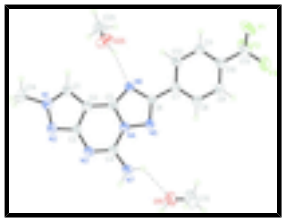


Fig. 1. The asymmetric unit of the title compound, showing the atomic numbering scheme. Displacement ellipsoids are drawn at the 50% probability level.

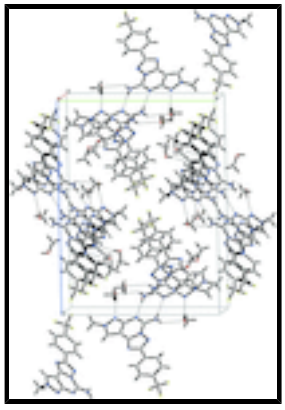


Fig. 2. Crystal packing of the title compound, viewed along the *a* axis.

8-Methyl-2-[4-(trifluoromethyl)phenyl]-8*H*-pyrazolo[4,3-*e*][1,2,4]triazolo[1,5-*c*]pyrimidin-5-amine methanol disolvate

Crystal data

$C_{14}H_{10}F_3N_7 \cdot 2CH_4O$	$F(000) = 824$
$M_r = 397.37$	$D_x = 1.471$ Mg m^{-3}
Monoclinic, $P2_1/n$	Melting point: 573 K
Hall symbol: -P 2yn	Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å
$a = 4.6179$ (3) Å	Cell parameters from 4421 reflections
$b = 17.1149$ (10) Å	$\theta = 2.4$–$27.2°$
$c = 22.7627$ (13) Å	$\mu = 0.12$ mm^{-1}
$\beta = 94.323$ (1)°	$T = 223$ K
$V = 1793.93$ (19) Å^3	Block, colourless
$Z = 4$	0.58 × 0.32 × 0.12 mm

Data collection

Bruker SMART APEX CCD diffractometer	4076 independent reflections
Radiation source: fine-focus sealed tube	3538 reflections with $I > 2\sigma(I)$
graphite	$R_{int} = 0.027$
φ and ω scans	$\theta_{max} = 27.5°$, $\theta_{min} = 1.5°$
Absorption correction: multi-scan (*SADABS*; Sheldrick, 2001)	$h = -5 \rightarrow 5$
$T_{min} = 0.932$, $T_{max} = 0.985$	$k = -21 \rightarrow 22$

12385 measured reflections	$l = -23 \rightarrow 29$

Refinement

Refinement on F^2	Primary atom site location: structure-invariant direct methods
Least-squares matrix: full	Secondary atom site location: difference Fourier map
$R[F^2 > 2\sigma(F^2)] = 0.054$	Hydrogen site location: inferred from neighbouring sites
$wR(F^2) = 0.145$	H atoms treated by a mixture of independent and constrained refinement
$S = 1.05$	$w = 1/[\sigma^2(F_o^2) + (0.0746P)^2 + 0.7421P]$ where $P = (F_o^2 + 2F_c^2)/3$
4076 reflections	$(\Delta/\sigma)_{max} = 0.001$
266 parameters	$\Delta\rho_{max} = 0.35$ e Å^{-3}
0 restraints	$\Delta\rho_{min} = -0.21$ e Å^{-3}

Special details

Geometry. All e.s.d.'s (except the e.s.d. in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell e.s.d.'s are taken into account individually in the estimation of e.s.d.'s in distances, angles and torsion angles; correlations between e.s.d.'s in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell e.s.d.'s is used for estimating e.s.d.'s involving l.s. planes.

Refinement. Refinement of F^2 against ALL reflections. The weighted *R*-factor *wR* and goodness of fit *S* are based on F^2, conventional *R*-factors *R* are based on *F*, with *F* set to zero for negative F^2. The threshold expression of $F^2 > 2\sigma(F^2)$ is used only for calculating *R*-factors(gt) *etc*. and is not relevant to the choice of reflections for refinement. *R*-factors based on F^2 are statistically about twice as large as those based on *F*, and *R*- factors based on ALL data will be even larger.

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å^2)

	x	*y*	*z*	U_{iso}*/U_{eq}
O1S	0.5063 (3)	0.68580 (11)	0.08136 (7)	0.0581 (4)
H1S	0.4507	0.6882	0.0459	0.087*
C1S	0.8079 (5)	0.68768 (18)	0.08766 (13)	0.0684 (7)
H1S1	0.8735	0.7415	0.0887	0.103*
H1S2	0.8852	0.6611	0.0546	0.103*
H1S3	0.8756	0.6617	0.1240	0.103*
C2S	0.1594 (6)	0.15803 (13)	0.27649 (11)	0.0581 (6)
H2S1	0.2028	0.1917	0.3103	0.087*
H2S2	0.1779	0.1038	0.2887	0.087*
H2S3	−0.0374	0.1678	0.2602	0.087*
F1	1.4952 (3)	0.39342 (8)	0.43457 (6)	0.0616 (4)
F2	1.2039 (3)	0.48312 (8)	0.45616 (5)	0.0550 (4)
F3	1.5562 (3)	0.50993 (9)	0.40469 (6)	0.0642 (4)
N1	−0.3122 (3)	0.23144 (9)	0.07561 (7)	0.0362 (3)
N2	−0.2997 (3)	0.29563 (9)	0.04026 (7)	0.0375 (4)
N3	−0.0193 (3)	0.41222 (8)	0.04749 (6)	0.0365 (4)

N4	0.3019 (3)	0.41895 (8)	0.13254 (6)	0.0296 (3)
N5	0.5146 (3)	0.45421 (8)	0.16847 (6)	0.0309 (3)
N6	0.3934 (3)	0.33542 (8)	0.20487 (6)	0.0286 (3)
N7	0.2815 (4)	0.51915 (10)	0.06445 (8)	0.0461 (4)
H7A	0.402 (5)	0.5454 (13)	0.0863 (10)	0.044 (6)*
H7B	0.204 (5)	0.5402 (14)	0.0312 (11)	0.052 (6)*
C1	−0.1317 (4)	0.23497 (10)	0.12400 (8)	0.0343 (4)
H1	−0.1081	0.1971	0.1539	0.041*
C2	0.0145 (4)	0.30557 (9)	0.12153 (7)	0.0301 (4)
C3	−0.0985 (4)	0.34097 (10)	0.06864 (7)	0.0322 (4)
C4	0.1813 (4)	0.45034 (10)	0.07964 (7)	0.0336 (4)
C5	0.2331 (4)	0.34778 (9)	0.15530 (7)	0.0276 (3)
C6	0.5597 (4)	0.40191 (9)	0.21105 (7)	0.0269 (3)
C7	0.7738 (3)	0.41460 (9)	0.26155 (7)	0.0274 (3)
C8	0.9154 (4)	0.48630 (10)	0.26875 (7)	0.0326 (4)
H8	0.8786	0.5261	0.2407	0.039*
C9	1.1098 (4)	0.49892 (10)	0.31706 (8)	0.0343 (4)
H9	1.2041	0.5474	0.3221	0.041*
C10	1.1650 (4)	0.43965 (10)	0.35808 (7)	0.0307 (4)
C11	1.0299 (4)	0.36786 (10)	0.35067 (8)	0.0343 (4)
H11	1.0710	0.3277	0.3782	0.041*
C12	0.8337 (4)	0.35550 (10)	0.30243 (8)	0.0331 (4)
H12	0.7407	0.3068	0.2974	0.040*
C13	1.3561 (4)	0.45625 (11)	0.41268 (8)	0.0368 (4)
C14	−0.5043 (5)	0.16731 (12)	0.05670 (10)	0.0464 (5)
H14A	−0.4241	0.1396	0.0245	0.070*
H14B	−0.6940	0.1879	0.0436	0.070*
H14C	−0.5229	0.1317	0.0894	0.070*
O2S	0.3553 (4)	0.17366 (9)	0.23347 (8)	0.0626 (5)
H2S	0.3819	0.2215	0.2314	0.094*

Atomic displacement parameters (Å^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
O1S	0.0507 (9)	0.0792 (12)	0.0434 (8)	−0.0125 (8)	−0.0029 (7)	−0.0038 (8)
C1S	0.0505 (14)	0.0805 (18)	0.0727 (17)	0.0068 (12)	−0.0050 (12)	−0.0207 (14)
C2S	0.0740 (16)	0.0445 (12)	0.0554 (13)	0.0039 (11)	0.0027 (12)	0.0023 (10)
F1	0.0664 (9)	0.0601 (8)	0.0537 (8)	0.0231 (7)	−0.0252 (6)	−0.0033 (6)
F2	0.0506 (7)	0.0806 (9)	0.0333 (6)	0.0123 (6)	0.0006 (5)	−0.0145 (6)
F3	0.0544 (8)	0.0857 (10)	0.0502 (7)	−0.0294 (7)	−0.0117 (6)	0.0062 (7)
N1	0.0395 (8)	0.0307 (8)	0.0381 (8)	−0.0050 (6)	0.0010 (6)	−0.0035 (6)
N2	0.0428 (9)	0.0336 (8)	0.0348 (8)	−0.0033 (6)	−0.0047 (6)	−0.0025 (6)
N3	0.0491 (9)	0.0286 (7)	0.0300 (7)	−0.0014 (6)	−0.0081 (6)	0.0023 (6)
N4	0.0391 (8)	0.0237 (7)	0.0254 (7)	−0.0008 (5)	−0.0027 (5)	−0.0003 (5)
N5	0.0385 (8)	0.0260 (7)	0.0273 (7)	−0.0014 (6)	−0.0036 (6)	−0.0018 (5)
N6	0.0343 (7)	0.0250 (7)	0.0264 (7)	0.0006 (5)	0.0011 (5)	0.0003 (5)
N7	0.0665 (12)	0.0316 (8)	0.0369 (9)	−0.0117 (8)	−0.0177 (8)	0.0086 (7)
C1	0.0389 (9)	0.0310 (9)	0.0332 (9)	−0.0026 (7)	0.0030 (7)	−0.0004 (7)

C2	0.0350 (9)	0.0278 (8)	0.0274 (8)	0.0001 (6)	0.0019 (6)	−0.0020 (6)
C3	0.0382 (9)	0.0286 (8)	0.0292 (8)	0.0018 (7)	−0.0014 (7)	−0.0029 (6)
C4	0.0441 (10)	0.0277 (8)	0.0279 (8)	0.0018 (7)	−0.0037 (7)	0.0018 (6)
C5	0.0335 (8)	0.0232 (7)	0.0264 (7)	0.0026 (6)	0.0040 (6)	−0.0013 (6)
C6	0.0322 (8)	0.0234 (7)	0.0253 (7)	0.0024 (6)	0.0031 (6)	−0.0008 (6)
C7	0.0295 (8)	0.0277 (8)	0.0252 (7)	0.0032 (6)	0.0029 (6)	−0.0008 (6)
C8	0.0402 (9)	0.0272 (8)	0.0299 (8)	−0.0004 (7)	−0.0010 (7)	0.0052 (6)
C9	0.0374 (9)	0.0300 (8)	0.0349 (9)	−0.0041 (7)	−0.0011 (7)	−0.0002 (7)
C10	0.0281 (8)	0.0361 (9)	0.0279 (8)	0.0051 (7)	0.0022 (6)	−0.0005 (7)
C11	0.0398 (9)	0.0312 (9)	0.0314 (8)	0.0042 (7)	−0.0016 (7)	0.0068 (7)
C12	0.0394 (9)	0.0252 (8)	0.0344 (9)	−0.0010 (7)	0.0000 (7)	0.0021 (6)
C13	0.0350 (9)	0.0426 (10)	0.0323 (9)	0.0037 (7)	0.0002 (7)	−0.0005 (7)
C14	0.0476 (11)	0.0386 (10)	0.0526 (12)	−0.0119 (9)	0.0009 (9)	−0.0091 (8)
O2S	0.0839 (12)	0.0294 (7)	0.0764 (11)	0.0002 (8)	0.0186 (9)	0.0034 (7)

Geometric parameters (Å, °)

O1S—C1S	1.390 (3)	N7—C4	1.321 (2)
O1S—H1S	0.83	N7—H7A	0.85 (2)
C1S—H1S1	0.97	N7—H7B	0.89 (2)
C1S—H1S2	0.97	C1—C2	1.387 (2)
C1S—H1S3	0.97	C1—H1	0.94
C2S—O2S	1.408 (3)	C2—C3	1.412 (2)
C2S—H2S1	0.97	C2—C5	1.419 (2)
C2S—H2S2	0.97	C6—C7	1.475 (2)
C2S—H2S3	0.97	C7—C12	1.388 (2)
F1—C13	1.330 (2)	C7—C8	1.394 (2)
F2—C13	1.338 (2)	C8—C9	1.383 (2)
F3—C13	1.325 (2)	C8—H8	0.94
N1—C1	1.331 (2)	C9—C10	1.389 (2)
N1—N2	1.366 (2)	C9—H9	0.94
N1—C14	1.456 (2)	C10—C11	1.382 (3)
N2—C3	1.339 (2)	C10—C13	1.496 (2)
N3—C4	1.310 (2)	C11—C12	1.386 (2)
N3—C3	1.371 (2)	C11—H11	0.94
N4—N5	1.3698 (19)	C12—H12	0.94
N4—C5	1.370 (2)	C14—H14A	0.97
N4—C4	1.396 (2)	C14—H14B	0.97
N5—C6	1.324 (2)	C14—H14C	0.97
N6—C5	1.319 (2)	O2S—H2S	0.83
N6—C6	1.374 (2)		
C1S—O1S—H1S	109.5	N6—C5—N4	109.56 (14)
O1S—C1S—H1S1	109.5	N6—C5—C2	135.39 (15)
O1S—C1S—H1S2	109.5	N4—C5—C2	115.05 (14)
H1S1—C1S—H1S2	109.5	N5—C6—N6	115.41 (14)
O1S—C1S—H1S3	109.5	N5—C6—C7	122.01 (14)
H1S1—C1S—H1S3	109.5	N6—C6—C7	122.58 (14)
H1S2—C1S—H1S3	109.5	C12—C7—C8	119.65 (15)
O2S—C2S—H2S1	109.5	C12—C7—C6	120.21 (15)

O2S—C2S—H2S2	109.5	C8—C7—C6	120.14 (14)
H2S1—C2S—H2S2	109.5	C9—C8—C7	120.09 (15)
O2S—C2S—H2S3	109.5	C9—C8—H8	120.0
H2S1—C2S—H2S3	109.5	C7—C8—H8	120.0
H2S2—C2S—H2S3	109.5	C8—C9—C10	119.71 (16)
C1—N1—N2	113.54 (14)	C8—C9—H9	120.1
C1—N1—C14	127.47 (16)	C10—C9—H9	120.1
N2—N1—C14	118.95 (15)	C11—C10—C9	120.58 (16)
C3—N2—N1	103.90 (14)	C11—C10—C13	120.16 (16)
C4—N3—C3	116.28 (14)	C9—C10—C13	119.11 (16)
N5—N4—C5	110.01 (13)	C10—C11—C12	119.62 (15)
N5—N4—C4	124.55 (14)	C10—C11—H11	120.2
C5—N4—C4	125.41 (14)	C12—C11—H11	120.2
C6—N5—N4	101.84 (13)	C11—C12—C7	120.34 (16)
C5—N6—C6	103.18 (13)	C11—C12—H12	119.8
C4—N7—H7A	123.1 (15)	C7—C12—H12	119.8
C4—N7—H7B	117.2 (15)	F3—C13—F1	106.84 (16)
H7A—N7—H7B	119 (2)	F3—C13—F2	105.89 (16)
N1—C1—C2	106.40 (15)	F1—C13—F2	105.45 (15)
N1—C1—H1	126.8	F3—C13—C10	113.04 (15)
C2—C1—H1	126.8	F1—C13—C10	113.31 (15)
C1—C2—C3	104.97 (15)	F2—C13—C10	111.71 (14)
C1—C2—C5	138.58 (16)	N1—C14—H14A	109.5
C3—C2—C5	116.45 (15)	N1—C14—H14B	109.5
N2—C3—N3	122.67 (15)	H14A—C14—H14B	109.5
N2—C3—C2	111.18 (15)	N1—C14—H14C	109.5
N3—C3—C2	126.15 (15)	H14A—C14—H14C	109.5
N3—C4—N7	122.99 (16)	H14B—C14—H14C	109.5
N3—C4—N4	120.64 (15)	C2S—O2S—H2S	109.5
N7—C4—N4	116.37 (16)		

C1—N1—N2—C3	0.3 (2)	C1—C2—C5—N6	0.6 (4)
C14—N1—N2—C3	−177.53 (16)	C3—C2—C5—N6	−178.44 (18)
C5—N4—N5—C6	−0.34 (17)	C1—C2—C5—N4	−179.5 (2)
C4—N4—N5—C6	−178.42 (15)	C3—C2—C5—N4	1.4 (2)
N2—N1—C1—C2	−0.4 (2)	N4—N5—C6—N6	0.51 (18)
C14—N1—C1—C2	177.22 (17)	N4—N5—C6—C7	−179.41 (14)
N1—C1—C2—C3	0.29 (19)	C5—N6—C6—N5	−0.49 (19)
N1—C1—C2—C5	−178.9 (2)	C5—N6—C6—C7	179.44 (14)
N1—N2—C3—N3	179.97 (16)	N5—C6—C7—C12	−174.11 (16)
N1—N2—C3—C2	−0.1 (2)	N6—C6—C7—C12	6.0 (2)
C4—N3—C3—N2	−179.75 (17)	N5—C6—C7—C8	6.4 (2)
C4—N3—C3—C2	0.3 (3)	N6—C6—C7—C8	−173.47 (15)
C1—C2—C3—N2	−0.1 (2)	C12—C7—C8—C9	−1.4 (3)
C5—C2—C3—N2	179.25 (15)	C6—C7—C8—C9	178.09 (16)
C1—C2—C3—N3	179.81 (17)	C7—C8—C9—C10	0.5 (3)
C5—C2—C3—N3	−0.8 (3)	C8—C9—C10—C11	0.8 (3)
C3—N3—C4—N7	179.18 (18)	C8—C9—C10—C13	−174.85 (16)
C3—N3—C4—N4	−0.5 (3)	C9—C10—C11—C12	−1.2 (3)
N5—N4—C4—N3	179.14 (16)	C13—C10—C11—C12	174.37 (16)

C5—N4—C4—N3	1.3 (3)	C10—C11—C12—C7	0.4 (3)
N5—N4—C4—N7	−0.6 (3)	C8—C7—C12—C11	0.9 (3)
C5—N4—C4—N7	−178.36 (17)	C6—C7—C12—C11	−178.53 (16)
C6—N6—C5—N4	0.23 (17)	C11—C10—C13—F3	154.07 (17)
C6—N6—C5—C2	−179.89 (18)	C9—C10—C13—F3	−30.3 (2)
N5—N4—C5—N6	0.06 (19)	C11—C10—C13—F1	32.3 (2)
C4—N4—C5—N6	178.13 (15)	C9—C10—C13—F1	−152.04 (17)
N5—N4—C5—C2	−179.84 (14)	C11—C10—C13—F2	−86.6 (2)
C4—N4—C5—C2	−1.8 (2)	C9—C10—C13—F2	89.0 (2)

Hydrogen-bond geometry (Å, °)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
O1S—H1S···N2^{i}	0.83	2.05	2.877 (2)	175
O2S—H2S···N6	0.83	2.04	2.853 (2)	165
N7—H7A···O1S	0.85 (2)	2.46 (2)	3.050 (2)	128 (2)
N7—H7B···N3^{i}	0.89 (2)	2.09 (3)	2.979 (2)	179 (2)

Symmetry codes: (i) −*x*, −*y*+1, −*z*.

Fig. 1

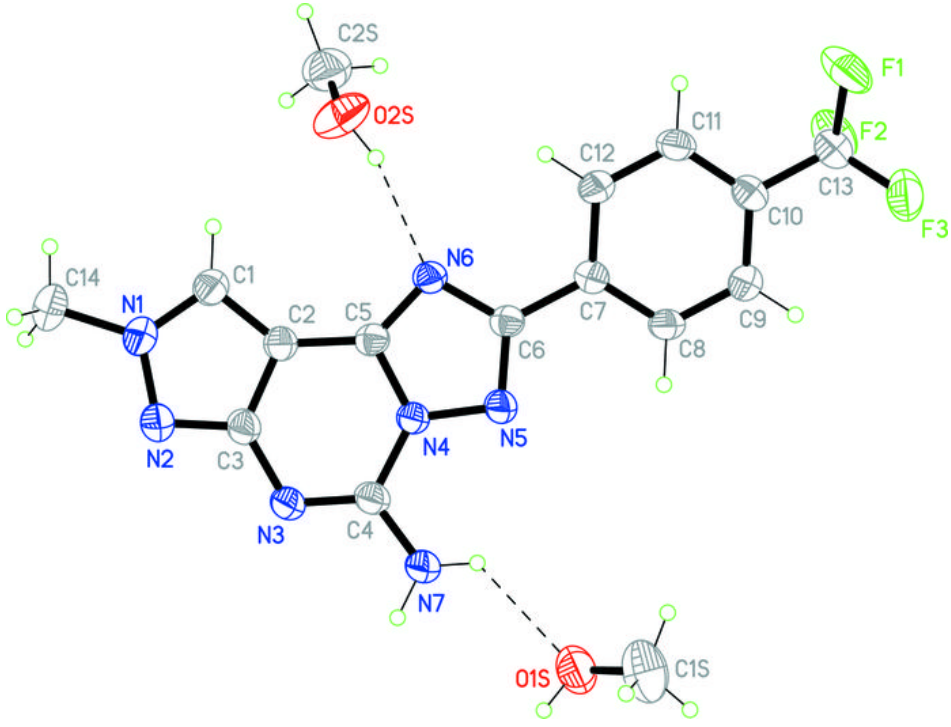
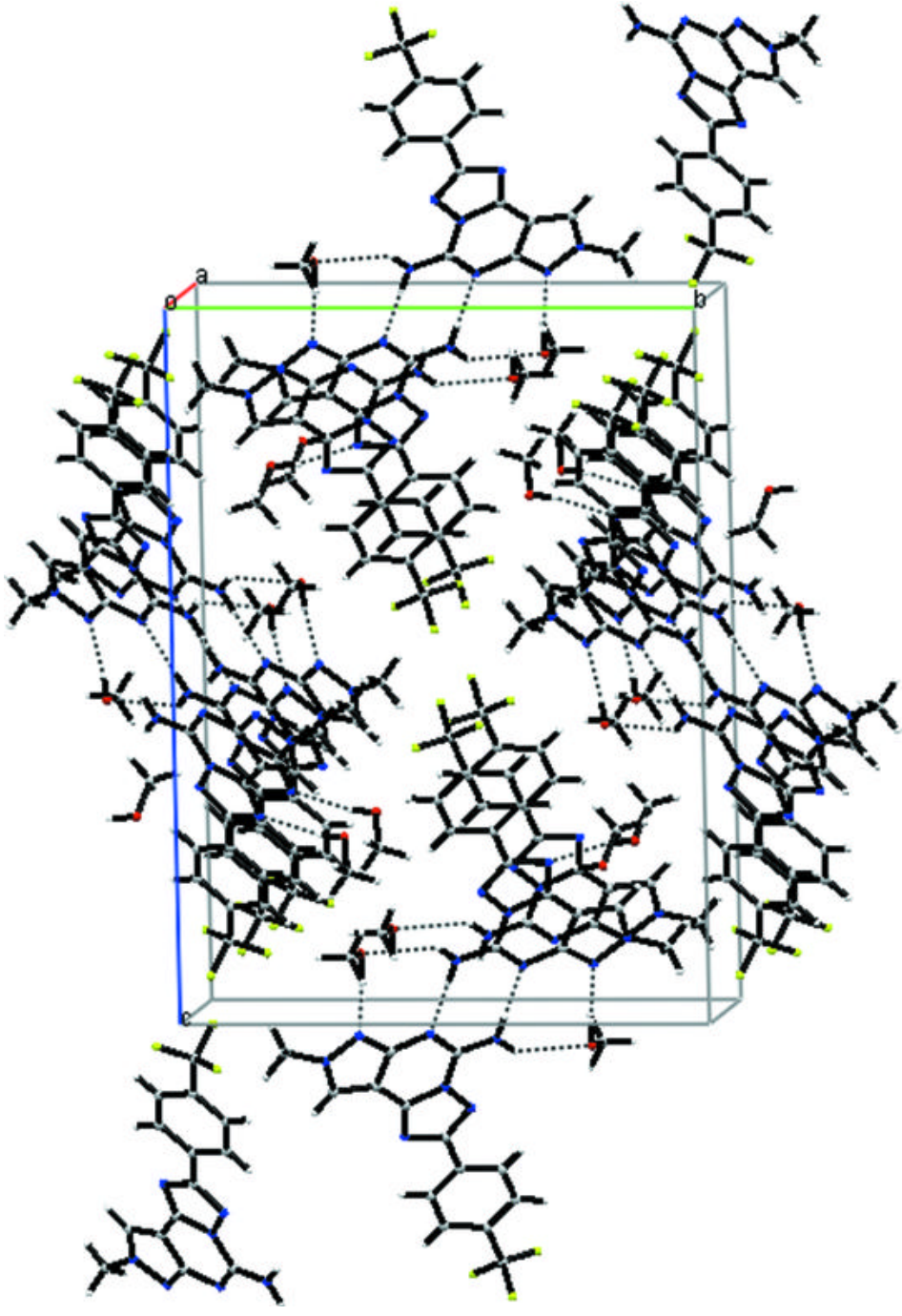

C2S
O2S
F1
F2
F3
C11
C12
C13
C10
N6
C14
C1
N1
C2
C5
C7
C9
C6
C8
N2
C3
N4
N5
N3
C4
N7
O1S
C1S

Fig. 2



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1,3-Diallyl-1*H*-anthra[1,2-*d*]imidazole-2,6,11(3*H*)-trione

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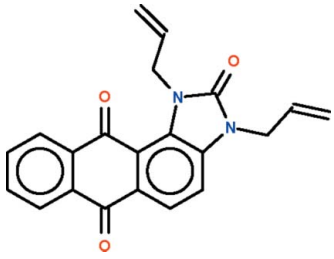
Key indicators: single-crystal X-ray study; T = 293 K; mean σ(C–C) = 0.002 Å; R factor = 0.049; wR factor = 0.153; data-to-parameter ratio = 20.4.

In the title compound, $C_{21}H_{16}N_2O_3$, the fused-ring system (r.m.s. deviation = 0.067 Å) is slightly buckled at the carbonyl C atom of the anthracenyl ring system [deviation = 0.177 (1) Å] that is closer to an allyl substituent. The two allyl units lie on the same side of the fused-ring plane but are oriented in opposite directions, with N—C—C—C torsion angles of 126.9 (2) and 116.7 (2)°. In the crystal, the molecules are linked into chains propagating along the *b* axis by C—H···O hydrogen bonds.

Related literature

For a related structure, see: Guimarães *et al.* (2009).



Experimental

Crystal data

$C_{21}H_{16}N_2O_3$
M_r = 344.36
Monoclinic, $P2_1/c$
a = 7.8539 (2) Å
b = 11.5822 (3) Å
c = 18.1455 (4) Å
β = 93.537 (1)°
V = 1647.47 (7) Å^3
Z = 4
Mo $K\alpha$ radiation
μ = 0.09 mm^{-1}
T = 293 K
0.40 × 0.35 × 0.20 mm

Data collection

Bruker X8 APEXII area-detector diffractometer
22612 measured reflections
4806 independent reflections **4805 in *Refinement?***
3053 reflections with $I > 2\sigma(I)$
R_{int} = 0.039

Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.049
$wR(F^2)$ = 0.153
S = 1.02
4805 reflections
236 parameters
H-atom parameters constrained
$\Delta\rho_{max}$ = 0.31 e Å^{-3}
$\Delta\rho_{min}$ = −0.22 e Å^{-3}

Table 1
Hydrogen-bond geometry (Å, °).

D—H···A	D—H	H···A	D···A	D—H···A
C13—H13···O3^{i}	0.93	2.49	3.406 (2)	168
C16—H16*B*···O3^{i}	0.97	2.42	3.362 (2)	165

Symmetry code: (i) $-x+1, y+\frac{1}{2}, -z+\frac{1}{2}$.

Data collection: *APEX2* (Bruker, 2008); cell refinement: *SAINT* (Bruker, 2008); data reduction: *SAINT*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *X-SEED* (Barbour, 2001); software used to prepare material for publication: *publCIF* (Westrip, 2010).

The authors thank Université Mohammed V-Agdal and the University of Malaya for supporting this study.

Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: CI5112).

References

Barbour, L. J. (2001). *J. Supramol. Chem.* **1**, 189–191.
Bruker (2008). *APEX2* and *SAINT*. Bruker AXS Inc., Madison, Wisconsin, USA.
Guimarães, T. T., Da Silva Júnior, E. N., Carvalho, C. E. M., De Simone, C. A. & Pinto, A. V. (2009). *Acta Cryst.* E**65**, o1063.
Sheldrick, G. M. (2008). *Acta Cryst.* A**64**, 112–122.
Westrip, S. P. (2010). *J. Appl. Cryst.* **43**. Submitted.

supplementary materials

Acta Cryst. (2010). E**66**, o1851 [**doi:10.1107/S1600536810024748**]

1,3-Diallyl-1*H*-anthra[1,2-*d*]imidazole-2,6,11(3*H*)-trione

Z. Afrakssou, Y. K. Rodi, H. Zouihri, E. M. Essassi and S. W. Ng

Comment

An imidazol-one such as 1*H*-anthra[2,1-*d*]imidazole-2,6,11(3*H*)-trione, in which the five-membered ring is fused with an anthraquinone system, alkyl halides under catalytic conditions to yield di-*N*,*N*'-substituted derivatives that serve as starting reagents for the synthesis of other drugs. The anthraquinone system itself is found in a large number of pigments and dyes. The title compound (Scheme I, Fig. 1) is a deep orange material that may be useful as an organic fluorophone.

The title molecule features four rings that are fused together (r.m.s. deviation 0.067 Å). The fused-ring system is slightly buckled at that carbonyl C-atom, C3, of the anthracenyl system [0.177 (1) Å] that is closer to an allyl substituent. The pendant allyl units lie on the same side of the fused-ring plane but are oriented in opposite directions. The crystal packing is stabilized by C—H···O hydrogen bonds (Table 1).

Experimental

To a solution of 1*H*-anthra[2,1-*d*]imidazole-2,6,11(3*H*)-trione (1.00 g, 0.38 mmol), potassium carbonate (1.56 g,11 mmol) and tetra *n*-butyl ammonium bromide (0.12 g, 0.38 mmol) in DMF (20 ml)) was added allyl bromide (0.77 ml, 11 mmol). Stirring was continued at room temperature for 24 h. The mixture was filtered and the solvent removed. The residue was extracted with water. The organic compound was chromatographed on a column of silica gel with ethyl acetate-hexane (1/1) as eluent. Orange crystals were isolated when the solvent was allowed to evaporate.

Refinement

H atoms were placed in calculated positions (C–H = 0.93–0.97 Å) and were included in the refinement in the riding model approximation, with U(H) set to 1.2U_{eq}(C).

Figures

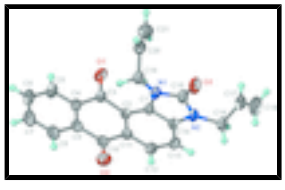


Fig. 1. Displacement ellipsoid plot (Barbour, 2001) of $C_{21}H_{16}N_2O_3$ at the 50% probability leve. H atoms are drawn as spheres of arbitrary radii.

1,3-Diallyl-1*H*-anthra[1,2-*d*]imidazole-2,6,11(3*H*)-trione

Crystal data

$C_{21}H_{16}N_2O_3$ $F(000) = 720$

M_r = 344.36	D_x = 1.388 Mg m^{-3}
Monoclinic, $P2_1/c$	Mo $K\alpha$ radiation, λ = 0.71073 Å
Hall symbol: -P 2ybc	Cell parameters from 4815 reflections
a = 7.8539 (2) Å	θ = 2.2–29.4°
b = 11.5822 (3) Å	μ = 0.09 mm^{-1}
c = 18.1455 (4) Å	T = 293 K
β = 93.537 (1)°	Block, orange
V = 1647.47 (7) Å^3	0.40 × 0.35 × 0.20 mm
Z = 4	

Data collection

Bruker X8 APEXII area-detector diffractometer	3053 reflections with $I > 2\sigma(I)$
Radiation source: fine-focus sealed tube	R_{int} = 0.039
graphite	θ_{max} = 30.0°, θ_{min} = 2.1°
φ and ω scans	h = −11→11
22612 measured reflections	k = −16→16
4806 independent reflections	l = −25→25

Refinement

Refinement on F^2	Secondary atom site location: difference Fourier map
Least-squares matrix: full	Hydrogen site location: inferred from neighbouring sites
$R[F^2 > 2\sigma(F^2)]$ = 0.049	H-atom parameters constrained
$wR(F^2)$ = 0.153	$w = 1/[\sigma^2(F_o^2) + (0.0755P)^2 + 0.2066P]$ where $P = (F_o^2 + 2F_c^2)/3$
S = 1.02	$(\Delta/\sigma)_{max}$ = 0.001
4805 reflections	$\Delta\rho_{max}$ = 0.31 e Å^{-3}
236 parameters	$\Delta\rho_{min}$ = −0.22 e Å^{-3}
0 restraints	Extinction correction: *SHELXL97* (Sheldrick, 2008), $Fc^*=kFc[1+0.001xFc^2\lambda^3/\sin(2\theta)]^{-1/4}$
Primary atom site location: structure-invariant direct methods	Extinction coefficient: 0.0033 (11)

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å^2)

	x	y	z	U_{iso}*/U_{eq}
O1	0.14067 (16)	0.31774 (10)	0.53905 (6)	0.0588 (3)
O2	0.23915 (17)	0.77316 (10)	0.53322 (7)	0.0623 (3)
O3	0.44816 (18)	0.19062 (10)	0.30395 (6)	0.0633 (4)
N1	0.35081 (16)	0.29295 (10)	0.40381 (6)	0.0405 (3)
N2	0.42897 (16)	0.38962 (10)	0.30579 (6)	0.0422 (3)
C1	0.32994 (17)	0.40923 (11)	0.41903 (7)	0.0342 (3)
C2	0.27111 (16)	0.47213 (11)	0.47863 (7)	0.0342 (3)
C3	0.18650 (18)	0.41799 (12)	0.54058 (7)	0.0387 (3)

C4	0.14672 (17)	0.49192 (13)	0.60472 (8)	0.0408 (3)
C5	0.0848 (2)	0.43992 (15)	0.66656 (9)	0.0532 (4)
H5	0.0729	0.3601	0.6683	0.064*
C6	0.0408 (2)	0.50686 (19)	0.72553 (9)	0.0635 (5)
H6	−0.0001	0.4719	0.7671	0.076*
C7	0.0572 (2)	0.62479 (19)	0.72301 (10)	0.0649 (5)
H7	0.0265	0.6693	0.7627	0.078*
C8	0.1187 (2)	0.67763 (16)	0.66225 (10)	0.0557 (4)
H8	0.1301	0.7575	0.6610	0.067*
C9	0.16416 (18)	0.61104 (13)	0.60235 (8)	0.0427 (3)
C10	0.22782 (18)	0.66824 (13)	0.53631 (8)	0.0428 (3)
C11	0.27960 (17)	0.59389 (12)	0.47464 (7)	0.0372 (3)
C12	0.3362 (2)	0.64983 (13)	0.41289 (8)	0.0443 (3)
H12	0.3403	0.7301	0.4122	0.053*
C13	0.38660 (19)	0.58851 (12)	0.35255 (8)	0.0437 (3)
H13	0.4219	0.6261	0.3108	0.052*
C14	0.38263 (17)	0.47023 (12)	0.35652 (7)	0.0368 (3)
C15	0.4124 (2)	0.28065 (13)	0.33395 (8)	0.0451 (4)
C16	0.4861 (2)	0.40982 (14)	0.23155 (7)	0.0462 (4)
H16A	0.5829	0.3603	0.2237	0.055*
H16B	0.5234	0.4893	0.2277	0.055*
C17	0.3483 (2)	0.38657 (17)	0.17310 (9)	0.0595 (5)
H17	0.3070	0.3114	0.1688	0.071*
C18	0.2826 (3)	0.4620 (2)	0.12858 (11)	0.0851 (7)
H18A	0.3206	0.5380	0.1312	0.102*
H18B	0.1969	0.4409	0.0935	0.102*
C19	0.3537 (2)	0.18926 (12)	0.45100 (8)	0.0431 (3)
H19A	0.3615	0.2133	0.5023	0.052*
H19B	0.4552	0.1448	0.4424	0.052*
C20	0.2018 (2)	0.11366 (14)	0.43818 (8)	0.0498 (4)
H20	0.0939	0.1461	0.4403	0.060*
C21	0.2140 (3)	0.00335 (17)	0.42404 (11)	0.0695 (5)
H21A	0.3207	−0.0307	0.4217	0.083*
H21B	0.1158	−0.0411	0.4163	0.083*

Atomic displacement parameters (Å^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
O1	0.0796 (8)	0.0408 (6)	0.0591 (7)	−0.0081 (6)	0.0298 (6)	−0.0009 (5)
O2	0.0821 (9)	0.0354 (6)	0.0711 (8)	−0.0067 (6)	0.0191 (6)	−0.0114 (5)
O3	0.1046 (10)	0.0388 (6)	0.0494 (7)	0.0101 (6)	0.0285 (6)	−0.0027 (5)
N1	0.0577 (7)	0.0304 (6)	0.0343 (6)	0.0046 (5)	0.0110 (5)	0.0026 (4)
N2	0.0573 (7)	0.0374 (6)	0.0330 (6)	0.0023 (5)	0.0113 (5)	0.0013 (5)
C1	0.0386 (7)	0.0309 (6)	0.0332 (6)	0.0013 (5)	0.0033 (5)	0.0014 (5)
C2	0.0356 (7)	0.0342 (7)	0.0327 (6)	0.0008 (5)	0.0021 (5)	0.0006 (5)
C3	0.0418 (7)	0.0374 (7)	0.0373 (7)	0.0022 (6)	0.0067 (6)	0.0014 (6)
C4	0.0381 (7)	0.0484 (8)	0.0363 (7)	0.0042 (6)	0.0048 (6)	−0.0015 (6)
C5	0.0589 (10)	0.0575 (10)	0.0447 (8)	0.0056 (8)	0.0151 (7)	0.0033 (7)

C6	0.0697 (11)	0.0793 (13)	0.0434 (9)	0.0053 (10)	0.0189 (8)	−0.0030 (9)
C7	0.0712 (12)	0.0783 (14)	0.0465 (9)	0.0071 (10)	0.0143 (8)	−0.0192 (9)
C8	0.0608 (10)	0.0552 (10)	0.0518 (9)	0.0046 (8)	0.0077 (8)	−0.0152 (8)
C9	0.0399 (7)	0.0472 (8)	0.0409 (7)	0.0030 (6)	0.0024 (6)	−0.0077 (6)
C10	0.0443 (8)	0.0376 (8)	0.0466 (8)	−0.0008 (6)	0.0034 (6)	−0.0079 (6)
C11	0.0395 (7)	0.0330 (7)	0.0392 (7)	0.0004 (5)	0.0028 (6)	−0.0015 (5)
C12	0.0560 (9)	0.0311 (7)	0.0462 (8)	−0.0028 (6)	0.0064 (7)	0.0023 (6)
C13	0.0548 (9)	0.0366 (7)	0.0404 (7)	−0.0025 (6)	0.0087 (6)	0.0061 (6)
C14	0.0408 (7)	0.0361 (7)	0.0339 (7)	0.0010 (6)	0.0052 (5)	0.0013 (5)
C15	0.0618 (9)	0.0382 (8)	0.0365 (7)	0.0053 (7)	0.0123 (7)	0.0003 (6)
C16	0.0564 (9)	0.0479 (8)	0.0360 (7)	−0.0006 (7)	0.0158 (6)	0.0019 (6)
C17	0.0686 (11)	0.0708 (12)	0.0406 (8)	−0.0083 (9)	0.0168 (8)	−0.0026 (8)
C18	0.0780 (14)	0.131 (2)	0.0468 (10)	0.0076 (13)	0.0107 (9)	0.0108 (12)
C19	0.0573 (9)	0.0331 (7)	0.0394 (7)	0.0057 (6)	0.0076 (6)	0.0057 (6)
C20	0.0611 (10)	0.0430 (8)	0.0458 (8)	0.0004 (7)	0.0067 (7)	0.0062 (7)
C21	0.0869 (13)	0.0486 (10)	0.0739 (13)	−0.0104 (10)	0.0114 (10)	−0.0024 (9)

Geometric parameters (Å, °)

O1—C3	1.2154 (18)	C8—H8	0.93
O2—C10	1.2200 (18)	C9—C10	1.483 (2)
O3—C15	1.2170 (17)	C10—C11	1.4884 (19)
N1—C1	1.3867 (16)	C11—C12	1.3908 (19)
N1—C15	1.3918 (18)	C12—C13	1.383 (2)
N1—C19	1.4742 (17)	C12—H12	0.93
N2—C15	1.3708 (19)	C13—C14	1.372 (2)
N2—C14	1.3757 (17)	C13—H13	0.93
N2—C16	1.4647 (17)	C16—C17	1.493 (2)
C1—C2	1.4056 (18)	C16—H16A	0.97
C1—C14	1.4194 (18)	C16—H16B	0.97
C2—C11	1.4139 (19)	C17—C18	1.277 (3)
C2—C3	1.4800 (18)	C17—H17	0.93
C3—C4	1.4934 (19)	C18—H18A	0.93
C4—C9	1.387 (2)	C18—H18B	0.93
C4—C5	1.388 (2)	C19—C20	1.486 (2)
C5—C6	1.382 (2)	C19—H19A	0.97
C5—H5	0.93	C19—H19B	0.97
C6—C7	1.373 (3)	C20—C21	1.308 (2)
C6—H6	0.93	C20—H20	0.93
C7—C8	1.375 (3)	C21—H21A	0.93
C7—H7	0.93	C21—H21B	0.93
C8—C9	1.397 (2)		
C1—N1—C15	109.44 (11)	C2—C11—C10	121.50 (12)
C1—N1—C19	132.32 (11)	C13—C12—C11	121.32 (13)
C15—N1—C19	116.86 (11)	C13—C12—H12	119.3
C15—N2—C14	109.90 (11)	C11—C12—H12	119.3
C15—N2—C16	122.09 (12)	C14—C13—C12	117.55 (13)
C14—N2—C16	128.00 (12)	C14—C13—H13	121.2
N1—C1—C2	134.84 (12)	C12—C13—H13	121.2

N1—C1—C14	106.28 (11)	C13—C14—N2	129.39 (13)
C2—C1—C14	118.87 (12)	C13—C14—C1	123.19 (13)
C1—C2—C11	117.30 (12)	N2—C14—C1	107.40 (12)
C1—C2—C3	123.31 (12)	O3—C15—N2	126.33 (14)
C11—C2—C3	119.10 (12)	O3—C15—N1	126.71 (14)
O1—C3—C2	122.25 (13)	N2—C15—N1	106.95 (12)
O1—C3—C4	119.32 (13)	N2—C16—C17	112.01 (13)
C2—C3—C4	118.31 (12)	N2—C16—H16A	109.2
C9—C4—C5	119.78 (14)	C17—C16—H16A	109.2
C9—C4—C3	121.35 (13)	N2—C16—H16B	109.2
C5—C4—C3	118.81 (14)	C17—C16—H16B	109.2
C6—C5—C4	119.96 (17)	H16A—C16—H16B	107.9
C6—C5—H5	120.0	C18—C17—C16	125.0 (2)
C4—C5—H5	120.0	C18—C17—H17	117.5
C7—C6—C5	120.24 (17)	C16—C17—H17	117.5
C7—C6—H6	119.9	C17—C18—H18A	120.0
C5—C6—H6	119.9	C17—C18—H18B	120.0
C6—C7—C8	120.54 (16)	H18A—C18—H18B	120.0
C6—C7—H7	119.7	N1—C19—C20	113.92 (13)
C8—C7—H7	119.7	N1—C19—H19A	108.8
C7—C8—C9	119.83 (18)	C20—C19—H19A	108.8
C7—C8—H8	120.1	N1—C19—H19B	108.8
C9—C8—H8	120.1	C20—C19—H19B	108.8
C4—C9—C8	119.64 (15)	H19A—C19—H19B	107.7
C4—C9—C10	120.54 (13)	C21—C20—C19	122.60 (17)
C8—C9—C10	119.81 (15)	C21—C20—H20	118.7
O2—C10—C9	120.76 (13)	C19—C20—H20	118.7
O2—C10—C11	121.17 (14)	C20—C21—H21A	120.0
C9—C10—C11	118.07 (13)	C20—C21—H21B	120.0
C12—C11—C2	121.62 (13)	H21A—C21—H21B	120.0
C12—C11—C10	116.87 (13)		
C15—N1—C1—C2	178.83 (15)	C1—C2—C11—C10	−177.23 (12)
C19—N1—C1—C2	−15.3 (3)	C3—C2—C11—C10	8.7 (2)
C15—N1—C1—C14	−0.69 (16)	O2—C10—C11—C12	−1.9 (2)
C19—N1—C1—C14	165.13 (14)	C9—C10—C11—C12	179.00 (13)
N1—C1—C2—C11	176.13 (15)	O2—C10—C11—C2	178.30 (14)
C14—C1—C2—C11	−4.39 (18)	C9—C10—C11—C2	−0.8 (2)
N1—C1—C2—C3	−10.1 (2)	C2—C11—C12—C13	0.1 (2)
C14—C1—C2—C3	169.38 (12)	C10—C11—C12—C13	−179.75 (14)
C1—C2—C3—O1	−10.6 (2)	C11—C12—C13—C14	−1.6 (2)
C11—C2—C3—O1	163.09 (14)	C12—C13—C14—N2	−178.38 (14)
C1—C2—C3—C4	173.42 (12)	C12—C13—C14—C1	−0.1 (2)
C11—C2—C3—C4	−12.91 (19)	C15—N2—C14—C13	176.95 (15)
O1—C3—C4—C9	−166.55 (14)	C16—N2—C14—C13	−3.9 (3)
C2—C3—C4—C9	9.6 (2)	C15—N2—C14—C1	−1.58 (16)
O1—C3—C4—C5	10.9 (2)	C16—N2—C14—C1	177.55 (14)
C2—C3—C4—C5	−172.99 (13)	N1—C1—C14—C13	−177.27 (13)
C9—C4—C5—C6	0.0 (2)	C2—C1—C14—C13	3.1 (2)
C3—C4—C5—C6	−177.51 (15)	N1—C1—C14—N2	1.38 (15)

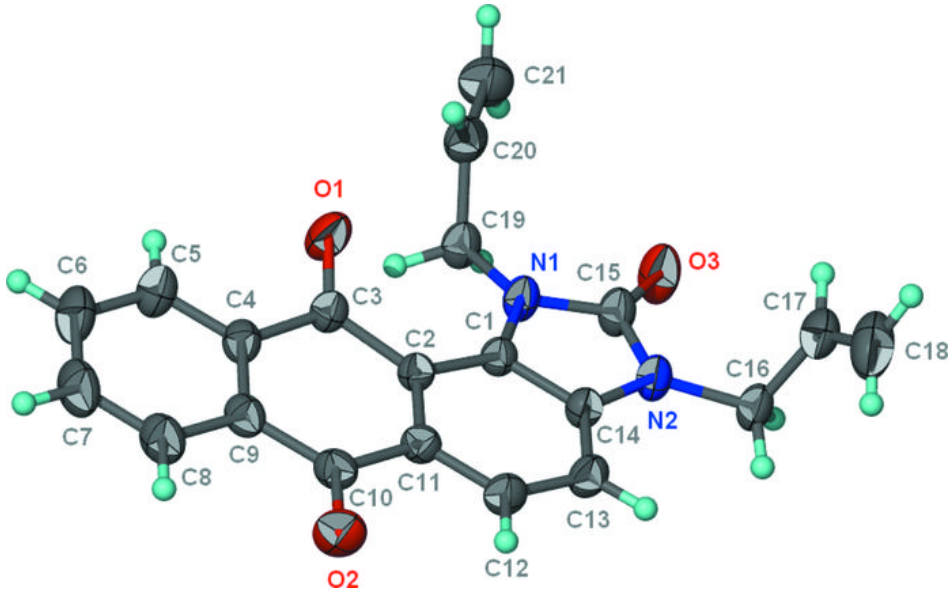
C4—C5—C6—C7	0.4 (3)	C2—C1—C14—N2	−178.24 (12)
C5—C6—C7—C8	−0.5 (3)	C14—N2—C15—O3	−177.54 (17)
C6—C7—C8—C9	0.3 (3)	C16—N2—C15—O3	3.3 (3)
C5—C4—C9—C8	−0.2 (2)	C14—N2—C15—N1	1.15 (17)
C3—C4—C9—C8	177.27 (14)	C16—N2—C15—N1	−178.04 (13)
C5—C4—C9—C10	−179.13 (14)	C1—N1—C15—O3	178.43 (16)
C3—C4—C9—C10	−1.7 (2)	C19—N1—C15—O3	10.1 (3)
C7—C8—C9—C4	0.0 (2)	C1—N1—C15—N2	−0.26 (18)
C7—C8—C9—C10	178.99 (15)	C19—N1—C15—N2	−168.54 (12)
C4—C9—C10—O2	178.08 (14)	C15—N2—C16—C17	76.63 (19)
C8—C9—C10—O2	−0.9 (2)	C14—N2—C16—C17	−102.40 (18)
C4—C9—C10—C11	−2.8 (2)	N2—C16—C17—C18	116.73 (19)
C8—C9—C10—C11	178.24 (14)	C1—N1—C19—C20	109.60 (18)
C1—C2—C11—C12	2.9 (2)	C15—N1—C19—C20	−85.41 (17)
C3—C2—C11—C12	−171.10 (13)	N1—C19—C20—C21	126.87 (17)

Hydrogen-bond geometry (Å, °)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
C13—H13···O3^{i}	0.93	2.49	3.406 (2)	168
C16—H16B···O3^{i}	0.97	2.42	3.362 (2)	165

Symmetry codes: (i) −*x*+1, *y*+1/2, −*z*+1/2.

Fig. 1


C21
C20
O1
C19
C6
C5
N1
C15
O3
C17
C4
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C1
C18
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N2
C7
C14
C9
C8
C11
C10
C13
C12
O2

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3-Benzyl-6-bromo-2-(2-furyl)-3*H*-imidazo[4,5-*b*]pyridine

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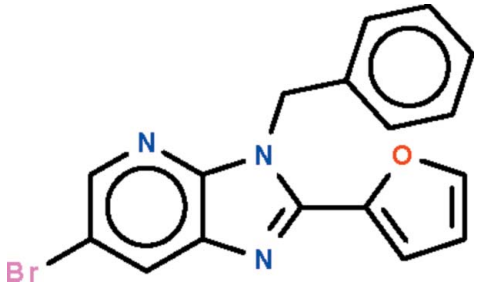
Key indicators: single-crystal X-ray study; T = 293 K; mean σ(C–C) = 0.005 Å; R factor = 0.031; wR factor = 0.110; data-to-parameter ratio = 13.1.

In the title molecule, $C_{17}H_{12}BrN_3O$, the imidazopyridine ring system is almost coplanar with the furan ring [dihedral angle = 2.0 (3)°]. The benzyl phenyl ring is oriented at dihedral angles of 85.2 (2) and 85.5 (1)°, respectively, with respect to the furan ring and the imidazopyridine ring system. In the crystal, molecules are linked into chains propagating along the *b* axis by C—H···N hydrogen bonds. Adjacent chains are linked *via* short Br···Br contacts [3.493 (1) Å].

Related literature

For a related structure, see: Ouzidan *et al.* (2010).



Experimental

Crystal data

$C_{17}H_{12}BrN_3O$
M_r = 354.21
Monoclinic, $P2_1/c$
a = 15.8422 (3) Å
b = 5.4747 (1) Å
c = 18.4243 (3) Å
β = 111.509 (1)°
V = 1486.68 (5) Å^3
Z = 4
Mo $K\alpha$ radiation
μ = 2.77 mm^{-1}
T = 293 K
0.25 × 0.25 × 0.10 mm

Data collection

Bruker X8 APEXII area-detector diffractometer
Absorption correction: multi-scan (*SADABS*; Sheldrick, 1996)
T_{min} = 0.544, T_{max} = 0.769
19471 measured reflections
2614 independent reflections
2105 reflections with $I > 2\sigma(I)$
R_{int} = 0.036

Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.031
$wR(F^2)$ = 0.110
S = 0.97
2614 reflections
199 parameters
H-atom parameters constrained
$\Delta\rho_{max}$ = 0.33 e Å^{-3}
$\Delta\rho_{min}$ = −0.44 e Å^{-3}

Table 1
Hydrogen-bond geometry (Å, °).

D—H···A	D—H	H···A	D···A	D—H···A
C3—H3···N3^{i}	0.93	2.51	3.399 (4)	160

Symmetry code: (i) $-x+1, y+\frac{1}{2}, -z+\frac{1}{2}$.

Data collection: *APEX2* (Bruker, 2008); cell refinement: *SAINT* (Bruker, 2008); data reduction: *SAINT*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *X-SEED* (Barbour, 2001); software used to prepare material for publication: *publCIF* (Westrip, 2010).

The authors thank Université Mohammed V-Agdal and the University of Malaya for supporting this study.

Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: CI5113).

References

Barbour, L. J. (2001). *J. Supramol. Chem.* **1**, 189–191.
Bruker (2008). *APEX2* and *SAINT*. Bruker AXS Inc., Madison, Wisconsin, USA..
Ouzidan, Y., Obbade, S., Capet, F., Essassi, E. M. & Ng, S. W. (2010). *Acta Cryst.* E**66**, o946.
Sheldrick, G. M. (1996). *SADABS*. University of Göttingen, Germany.
Sheldrick, G. M. (2008). *Acta Cryst.* A**64**, 112–122.
Westrip, S. P. (2010). *J. Appl. Cryst.* **43**. Submitted.

supplementary materials

Acta Cryst. (2010). E**66**, o1874 [**doi:10.1107/S160053681002475X**]

3-Benzyl-6-bromo-2-(2-furyl)-3*H*-imidazo[4,5-*b*]pyridine

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Comment

The imidazo[4,5-*b*]pyridine unit is an important heterocyclic nucleus found in a large number of molecules in medicinal chemistry. Heterocycles derived from such compounds posess useful medicinal properties. Owing to their importance, strategies have been developed for their synthesis. The most popular synthetic approach involves the cyclocondensation of 2,3-pyridinediamine with carboxylic acid derivatives or on condensation with aldehydes. An earlier study reported the crystal structure of 4-benzyl-6-bromo-2-phenyl-4*H*-imidazo[4,5-*b*]pyridine (Ouzidan *et al.*, 2010), which was synthesized by using a much more convenient route. The synthesis is extended to the title compound.

In the title molecule (Scheme and Fig. 1), the imidazopyridine ring system is almost coplanar with the furan ring at the 2-position of the five-membered ring [dihedral angle = 2.0 (3) °]. The molecules are linked into chains along the *b* axis by C—H···N hydrogen bonds (Table 1). The adjacent chains are linked via short Br···Br contacts [3.493 (1) Å].

Experimental

6-Bromo-2-furyl-3*H*-imidazo[4,5-*b*]pyridine (0.30 g, 1.13 mmol) was dissolved in DMF (15 ml). Potassium carbonate (0.2 g, 1,48 mmol), tetra-*n*-butylammonium bromide (0.04 g, 0.1 mmol) and benzyl chloride (0.15 ml, 1.36 mmol) were added. Stirring was continued at room temperature for 12 h. The mixture was filtered and the solvent removed under reduced pressure. The residue was chromatographed on a column of silica gel with ethyl acetate-hexane (1/2) as eluent. The compound was recrystallized from chloroform to give orange crystals.

Refinement

H atoms were placed in calculated positions (C–H = 0.93–0.97 Å) and were included in the refinement in the riding model approximation, with U(H) set to 1.2U_{eq}(C).

Figures

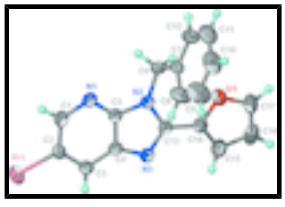


Fig. 1. Displacement ellipsoid plot (Barbour, 2001) of the molecule of $C_{17}H_{12}BrN_3O$ at the 50% probability level. H atoms are shown as spheres of arbitrary radii.

3-Benzyl-6-bromo-2-(2-furyl)-3*H*-imidazo[4,5-*b*]pyridine

Crystal data

$C_{17}H_{12}BrN_3O$	$F(000) = 712$
$M_r = 354.21$	$D_x = 1.583$ Mg m^{-3}
Monoclinic, $P2_1/c$	Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å
Hall symbol: -P 2ybc	Cell parameters from 5830 reflections
$a = 15.8422$ (3) Å	$\theta = 2.7$–$23.3°$
$b = 5.4747$ (1) Å	$\mu = 2.77$ mm^{-1}
$c = 18.4243$ (3) Å	$T = 293$ K
$\beta = 111.509$ (1)°	Prism, orange
$V = 1486.68$ (5) Å^3	0.25 × 0.25 × 0.10 mm
$Z = 4$	

Data collection

Bruker X8 APEXII area-detector diffractometer	2614 independent reflections
Radiation source: fine-focus sealed tube	2105 reflections with $I > 2\sigma(I)$
graphite	$R_{int} = 0.036$
φ and ω scans	$\theta_{max} = 25.0°$, $\theta_{min} = 2.8°$
Absorption correction: multi-scan (*SADABS*; Sheldrick, 1996)	$h = -17\rightarrow18$
$T_{min} = 0.544$, $T_{max} = 0.769$	$k = -6\rightarrow5$
19471 measured reflections	$l = -21\rightarrow18$

Refinement

Refinement on F^2	Primary atom site location: structure-invariant direct methods
Least-squares matrix: full	Secondary atom site location: difference Fourier map
$R[F^2 > 2\sigma(F^2)] = 0.031$	Hydrogen site location: inferred from neighbouring sites
$wR(F^2) = 0.110$	H-atom parameters constrained
$S = 0.97$	$w = 1/[\sigma^2(F_o^2) + (0.0848P)^2 + 0.0891P]$ where $P = (F_o^2 + 2F_c^2)/3$
2614 reflections	$(\Delta/\sigma)_{max} = 0.001$
199 parameters	$\Delta\rho_{max} = 0.33$ e Å^{-3}
0 restraints	$\Delta\rho_{min} = -0.44$ e Å^{-3}

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å^2)

	x	*y*	*z*	U_{iso}*/U_{eq}
Br1	0.47189 (2)	1.27997 (6)	0.426257 (19)	0.05859 (18)
O1	0.21672 (14)	0.1051 (4)	0.11117 (12)	0.0605 (6)

N1	0.28026 (15)	0.7379 (4)	0.34628 (14)	0.0407 (6)
N2	0.26035 (13)	0.4610 (4)	0.23929 (12)	0.0362 (5)
N3	0.37245 (14)	0.6006 (4)	0.20155 (13)	0.0415 (5)
C1	0.33253 (18)	0.9234 (5)	0.38466 (16)	0.0437 (6)
H1	0.3214	0.9916	0.4265	0.052*
C2	0.40263 (16)	1.0193 (5)	0.36533 (15)	0.0399 (6)
C3	0.42374 (17)	0.9297 (5)	0.30393 (15)	0.0400 (6)
H3	0.4701	0.9949	0.2904	0.048*
C4	0.37115 (19)	0.7370 (4)	0.26428 (18)	0.0364 (6)
C5	0.30126 (16)	0.6536 (5)	0.28810 (15)	0.0347 (6)
C6	0.18408 (17)	0.3215 (5)	0.24445 (16)	0.0398 (6)
H6A	0.1851	0.3335	0.2973	0.048*
H6B	0.1923	0.1509	0.2344	0.048*
C7	0.09249 (16)	0.4032 (4)	0.18891 (15)	0.0373 (6)
C8	0.0798 (2)	0.6091 (6)	0.1437 (2)	0.0660 (9)
H8	0.1294	0.7050	0.1467	0.079*
C9	−0.0063 (3)	0.6757 (7)	0.0935 (3)	0.0863 (13)
H9	−0.0139	0.8138	0.0623	0.104*
C10	−0.0799 (2)	0.5399 (7)	0.0897 (2)	0.0752 (10)
H10	−0.1375	0.5839	0.0556	0.090*
C11	−0.0687 (2)	0.3409 (8)	0.1356 (2)	0.0706 (10)
H11	−0.1190	0.2505	0.1340	0.085*
C12	0.0171 (2)	0.2703 (5)	0.1851 (2)	0.0549 (8)
H12	0.0239	0.1319	0.2160	0.066*
C13	0.30648 (16)	0.4385 (5)	0.18846 (15)	0.0369 (6)
C14	0.2871 (2)	0.2623 (4)	0.12615 (18)	0.0428 (7)
C15	0.3289 (2)	0.2287 (6)	0.0754 (2)	0.0587 (9)
H15	0.3787	0.3147	0.0737	0.070*
C16	0.2825 (2)	0.0376 (6)	0.02513 (19)	0.0651 (9)
H16	0.2956	−0.0266	−0.0163	0.078*
C17	0.2169 (3)	−0.0318 (6)	0.04850 (19)	0.0683 (9)
H17	0.1761	−0.1570	0.0257	0.082*

Atomic displacement parameters (Å^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Br1	0.0540 (3)	0.0519 (2)	0.0593 (3)	−0.00676 (12)	0.00831 (18)	−0.01181 (13)
O1	0.0659 (14)	0.0602 (13)	0.0594 (14)	−0.0183 (11)	0.0276 (11)	−0.0162 (10)
N1	0.0330 (13)	0.0534 (13)	0.0395 (14)	0.0029 (9)	0.0176 (11)	−0.0003 (10)
N2	0.0268 (11)	0.0449 (11)	0.0378 (13)	−0.0025 (9)	0.0130 (9)	−0.0003 (9)
N3	0.0317 (12)	0.0538 (14)	0.0424 (13)	−0.0020 (10)	0.0175 (10)	−0.0037 (10)
C1	0.0380 (15)	0.0519 (15)	0.0416 (16)	0.0036 (12)	0.0150 (12)	−0.0047 (12)
C2	0.0330 (14)	0.0416 (13)	0.0391 (16)	0.0017 (11)	0.0061 (12)	−0.0006 (11)
C3	0.0296 (14)	0.0464 (14)	0.0440 (16)	−0.0006 (11)	0.0135 (12)	0.0030 (11)
C4	0.0281 (15)	0.0436 (14)	0.0396 (17)	0.0007 (10)	0.0147 (13)	0.0028 (11)
C5	0.0253 (13)	0.0419 (13)	0.0361 (15)	0.0025 (10)	0.0101 (11)	0.0027 (11)
C6	0.0345 (15)	0.0458 (14)	0.0414 (16)	−0.0046 (11)	0.0165 (13)	0.0047 (11)
C7	0.0288 (13)	0.0408 (13)	0.0437 (16)	−0.0052 (10)	0.0152 (12)	−0.0047 (11)

C8	0.0388 (17)	0.063 (2)	0.086 (2)	−0.0040 (14)	0.0108 (17)	0.0219 (17)
C9	0.062 (2)	0.069 (2)	0.102 (3)	0.0088 (19)	−0.001 (2)	0.025 (2)
C10	0.0368 (19)	0.089 (3)	0.083 (3)	0.0077 (17)	0.0013 (17)	−0.012 (2)
C11	0.0350 (19)	0.093 (3)	0.081 (3)	−0.0156 (17)	0.0181 (19)	−0.015 (2)
C12	0.0417 (19)	0.0643 (19)	0.061 (2)	−0.0119 (13)	0.0216 (16)	0.0033 (14)
C13	0.0291 (13)	0.0446 (13)	0.0366 (15)	0.0046 (10)	0.0116 (11)	0.0011 (11)
C14	0.0353 (16)	0.0481 (15)	0.0427 (18)	0.0018 (11)	0.0117 (13)	−0.0002 (11)
C15	0.053 (2)	0.074 (2)	0.054 (2)	−0.0036 (14)	0.0244 (18)	−0.0152 (15)
C16	0.076 (2)	0.070 (2)	0.049 (2)	0.0112 (18)	0.0221 (17)	−0.0105 (15)
C17	0.091 (3)	0.0550 (18)	0.054 (2)	−0.0113 (18)	0.0199 (19)	−0.0155 (15)

Geometric parameters (Å, °)

Br1—C2	1.897 (3)	C7—C8	1.372 (4)
O1—C14	1.355 (3)	C7—C12	1.377 (4)
O1—C17	1.378 (4)	C8—C9	1.387 (5)
N1—C5	1.317 (3)	C8—H8	0.93
N1—C1	1.337 (3)	C9—C10	1.362 (5)
N2—C5	1.383 (3)	C9—H9	0.93
N2—C13	1.388 (3)	C10—C11	1.351 (5)
N2—C6	1.462 (3)	C10—H10	0.93
N3—C13	1.324 (3)	C11—C12	1.385 (5)
N3—C4	1.382 (4)	C11—H11	0.93
C1—C2	1.388 (4)	C12—H12	0.93
C1—H1	0.93	C13—C14	1.444 (4)
C2—C3	1.382 (4)	C14—C15	1.341 (5)
C3—C4	1.376 (4)	C15—C16	1.412 (4)
C3—H3	0.93	C15—H15	0.93
C4—C5	1.408 (4)	C16—C17	1.317 (5)
C6—C7	1.505 (4)	C16—H16	0.93
C6—H6A	0.97	C17—H17	0.93
C6—H6B	0.97		
C14—O1—C17	105.2 (2)	C7—C8—C9	120.7 (3)
C5—N1—C1	113.9 (2)	C7—C8—H8	119.7
C5—N2—C13	105.62 (19)	C9—C8—H8	119.7
C5—N2—C6	123.9 (2)	C10—C9—C8	120.3 (4)
C13—N2—C6	130.5 (2)	C10—C9—H9	119.8
C13—N3—C4	105.2 (2)	C8—C9—H9	119.8
N1—C1—C2	123.4 (3)	C11—C10—C9	119.6 (3)
N1—C1—H1	118.3	C11—C10—H10	120.2
C2—C1—H1	118.3	C9—C10—H10	120.2
C3—C2—C1	122.2 (2)	C10—C11—C12	120.6 (3)
C3—C2—Br1	119.38 (19)	C10—C11—H11	119.7
C1—C2—Br1	118.46 (19)	C12—C11—H11	119.7
C4—C3—C2	115.2 (2)	C7—C12—C11	120.6 (3)
C4—C3—H3	122.4	C7—C12—H12	119.7
C2—C3—H3	122.4	C11—C12—H12	119.7
C3—C4—N3	131.8 (2)	N3—C13—N2	113.1 (2)
C3—C4—C5	118.4 (3)	N3—C13—C14	121.1 (2)

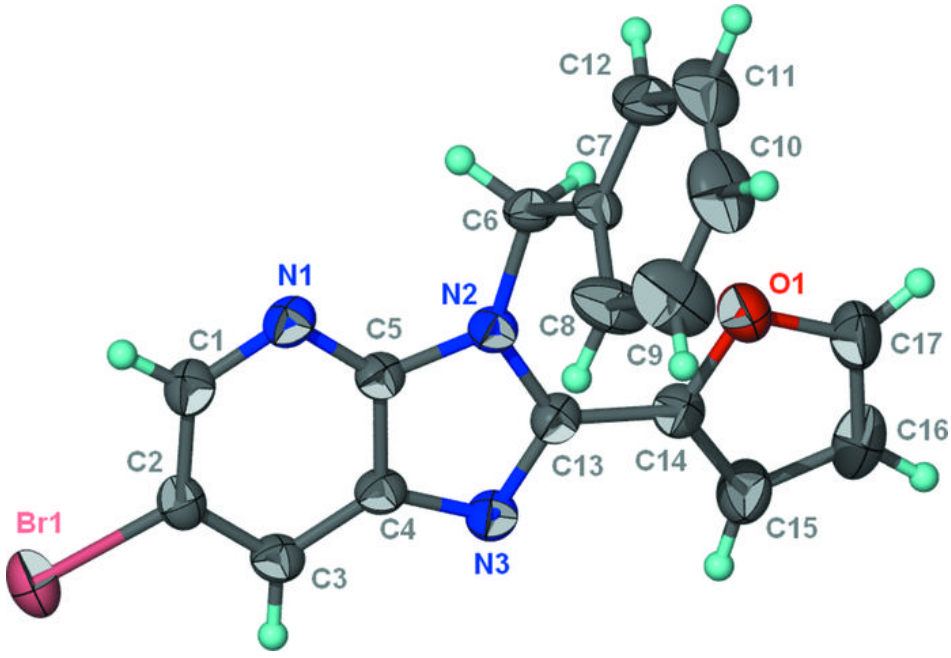
N3—C4—C5	109.9 (2)	N2—C13—C14	125.8 (2)
N1—C5—N2	126.8 (2)	C15—C14—O1	110.5 (3)
N1—C5—C4	127.0 (2)	C15—C14—C13	129.1 (3)
N2—C5—C4	106.2 (2)	O1—C14—C13	120.3 (3)
N2—C6—C7	114.5 (2)	C14—C15—C16	106.7 (3)
N2—C6—H6A	108.6	C14—C15—H15	126.6
C7—C6—H6A	108.6	C16—C15—H15	126.6
N2—C6—H6B	108.6	C17—C16—C15	106.4 (3)
C7—C6—H6B	108.6	C17—C16—H16	126.8
H6A—C6—H6B	107.6	C15—C16—H16	126.8
C8—C7—C12	118.1 (3)	C16—C17—O1	111.2 (3)
C8—C7—C6	123.2 (2)	C16—C17—H17	124.4
C12—C7—C6	118.6 (2)	O1—C17—H17	124.4
C5—N1—C1—C2	0.0 (4)	C6—C7—C8—C9	−180.0 (3)
N1—C1—C2—C3	0.2 (4)	C7—C8—C9—C10	1.4 (7)
N1—C1—C2—Br1	−179.2 (2)	C8—C9—C10—C11	0.7 (7)
C1—C2—C3—C4	−0.8 (4)	C9—C10—C11—C12	−1.7 (6)
Br1—C2—C3—C4	178.56 (19)	C8—C7—C12—C11	1.3 (5)
C2—C3—C4—N3	−179.3 (3)	C6—C7—C12—C11	179.1 (3)
C2—C3—C4—C5	1.2 (4)	C10—C11—C12—C7	0.7 (6)
C13—N3—C4—C3	179.7 (3)	C4—N3—C13—N2	0.5 (3)
C13—N3—C4—C5	−0.7 (3)	C4—N3—C13—C14	179.9 (2)
C1—N1—C5—N2	178.7 (2)	C5—N2—C13—N3	0.0 (3)
C1—N1—C5—C4	0.4 (4)	C6—N2—C13—N3	179.7 (2)
C13—N2—C5—N1	−179.0 (2)	C5—N2—C13—C14	−179.4 (2)
C6—N2—C5—N1	1.3 (4)	C6—N2—C13—C14	0.3 (4)
C13—N2—C5—C4	−0.4 (3)	C17—O1—C14—C15	0.7 (4)
C6—N2—C5—C4	179.9 (2)	C17—O1—C14—C13	179.1 (3)
C3—C4—C5—N1	−1.1 (4)	N3—C13—C14—C15	1.2 (5)
N3—C4—C5—N1	179.3 (2)	N2—C13—C14—C15	−179.5 (3)
C3—C4—C5—N2	−179.7 (2)	N3—C13—C14—O1	−176.9 (2)
N3—C4—C5—N2	0.7 (3)	N2—C13—C14—O1	2.4 (4)
C5—N2—C6—C7	96.8 (3)	O1—C14—C15—C16	−0.3 (4)
C13—N2—C6—C7	−82.8 (3)	C13—C14—C15—C16	−178.5 (3)
N2—C6—C7—C8	−7.5 (4)	C14—C15—C16—C17	−0.3 (4)
N2—C6—C7—C12	174.8 (2)	C15—C16—C17—O1	0.7 (4)
C12—C7—C8—C9	−2.3 (5)	C14—O1—C17—C16	−0.8 (4)

Hydrogen-bond geometry (Å, °)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
C3—H3···N3^{i}	0.93	2.51	3.399 (4)	160

Symmetry codes: (i) −*x*+1, *y*+1/2, −*z*+1/2.

Fig. 1


C12
C11
C7
C10
C6
N1
N2
O1
C1
C5
C8
C9
C17
C16
C2
C13
C14
Br1
C4
C15
C3
N3

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Methyl 2,6-bis[(5-chloro-4,6-dimethoxypyrimidin-2-yl)oxy]benzoate

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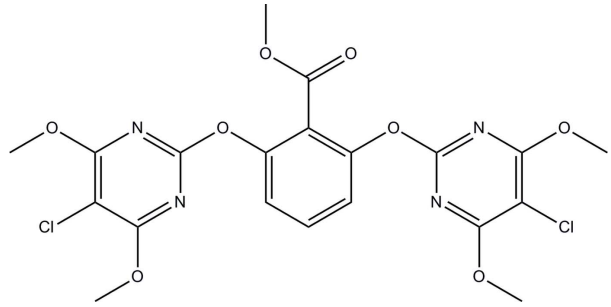
Key indicators: single-crystal X-ray study; T = 100 K; mean σ(C–C) = 0.002 Å; R factor = 0.040; wR factor = 0.129; data-to-parameter ratio = 25.8.

In the title compound, $C_{20}H_{18}Cl_2N_4O_8$, the two pyrimidine rings are inclined at dihedral angles of 66.68 (5) and 71.91 (6)° with respect to the central benzene ring. In the crystal structure, intermolecular C—H···N hydrogen bonds link neighbouring molecules into a ribbon-like structure along the b axis. The ribbons are interconnected into a two-dimensional network parallel to the bc plane by short intermolecular Cl···Cl [3.4427 (6) Å] and Cl···O [3.1420 (9) and 3.1750 (11) Å] interactions. The crystal structure is further stabilized by intermolecular π–π interactions [centroid–centroid distance 3.4552 (8) Å] involving the pyrimidine rings.

Related literature

For general background to and applications of the title compound, see: Koichiro *et al.* (1988, 1998); He *et al.* (2007); Li *et al.* (2006); Gerorge (1983). For graph-set descriptions of hydrogen-bonded ring motifs, see: Bernstein *et al.* (1995). For a closely related structure, see: Li & Luo (2006). For the stability of the temperature controller used for the data collection, see: Cosier & Glazer (1986).



Experimental

Crystal data

$C_{20}H_{18}Cl_2N_4O_8$
M_r = 513.28
Monoclinic, $C2/c$
a = 29.354 (3) Å
b = 8.0485 (8) Å
c = 22.5923 (19) Å
β = 123.014 (2)°
V = 4475.7 (7) Å^3
Z = 8
Mo $K\alpha$ radiation
μ = 0.35 mm^{-1}
T = 100 K
0.58 × 0.31 × 0.16 mm

Data collection

Bruker APEXII DUO CCD area-detector diffractometer
Absorption correction: multi-scan (*SADABS*; Bruker, 2009)
T_{min} = 0.825, T_{max} = 0.948
22170 measured reflections
8040 independent reflections
6824 reflections with $I > 2\sigma(I)$
R_{int} = 0.023

Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.040
$wR(F^2)$ = 0.129
S = 1.08
8040 reflections
312 parameters
H-atom parameters constrained
$\Delta\rho_{max}$ = 0.71 e Å^{-3}
$\Delta\rho_{min}$ = −0.55 e Å^{-3}

Table 1
Hydrogen-bond geometry (Å, °).

D—H···A	D—H	H···A	D···A	D—H···A
C16—H16A···N1^{i}	0.96	2.58	3.5018 (19)	161
C20—H20A···N3^{ii}	0.96	2.59	3.5148 (19)	161

Symmetry codes: (i) $x, y-1, z$; (ii) $x, y+1, z$.

Data collection: *APEX2* (Bruker, 2009); cell refinement: *SAINT* (Bruker, 2009); data reduction: *SAINT*; program(s) used to solve structure: *SHELXTL* (Sheldrick, 2008); program(s) used to refine structure: *SHELXTL*; molecular graphics: *SHELXTL*; software used to prepare material for publication: *SHELXTL* and *PLATON* (Spek, 2009).

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‡ Thomson Reuters ResearcherID: A-3561-2009.
§ Thomson Reuters ResearcherID: C-7576-2009.

Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: CI5115).

References

Bernstein, J., Davis, R. E., Shimoni, L. & Chang, N.-L. (1995). *Angew. Chem. Int. Ed. Engl.* **34**, 1555–1573.

Bruker (2009). *APEX2*, *SAINT* and *SADABS*. Bruker AXS Inc., Madison, Wisconsin, USA.

Cosier, J. & Glazer, A. M. (1986). *J. Appl. Cryst.* **19**, 105–107.

Gerorge, L. (1983). US Patent No. 4 394 506.

He, Y.-Z., Li, Y.-X., Zhu, X.-L., Xi, Z., Niu, C., Wan, J., Zhang, L. & Yang, G.-F. (2007). *J. Chem. Inf. Model.* **47**, 2335–2344.

Koichiro, S., Shoji, K., Yasubumi, T., Takeshige, M. & Ryo, Y. (1988). Jpn Patent No. JP 88 132 167; Chem. Abstr. (1998), 112, 216956.

Koichiro, S., Shoji, K., Yasubumi, T., Takeshige, M. & Ryo, Y. (1998). *Chem. Abstr.* **112**, 216956.

Li, Y.-X. & Luo, Y.-P. (2006). *Acta Cryst.* E**62**, o1323–o1325.

Li, Y.-X., Luo, Y.-P., Xi, Z., Niu, C., He, Y.-Z. & Yang, G.-F. (2006). *J. Agric. Food Chem.* **54**, 9135–9139.

Sheldrick, G. M. (2008). *Acta Cryst.* A**64**, 112–122.

Spek, A. L. (2009). *Acta Cryst.* D**65**, 148–155.

supplementary materials

Acta Cryst. (2010). E**66**, o1869-o1870 [**doi:10.1107/S1600536810024785**]

Methyl 2,6-bis[(5-chloro-4,6-dimethoxypyrimidin-2-yl)oxy]benzoate

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Comment

Methyl-2,6-bis[(5-bromo-4,6-dimethoxypyrimidin-2-yl)oxy]benzoate is a derivative of herbicide showing excellent herbicidal effects on annual and perennial weeds and high-safety crops, especially rice and wheat and is applied to paddy fields, ploughed fields and non-agricultural land (Koichiro *et al.*, 1988, 1998). Most sulphonylurea herbicides and all pyrimidinyl-benzoate herbicides (He *et al.*, 2007) such as nicofulfuron, amidosulfuron, halopyrazosulfuron, ethoxysulfuron, pyriminobac-methyl and pyriftalid, possess 4,6-dimethoxypyrimidin-2-yl groups (Li *et al.*, 2006), while sulfometuron-methyl, a kind of sulfonylurea, contains 4,6-dimethylpyrimidin-2-yl groups, which suggests that the two disubstituted pyrimidin-2-yl groups possess high biological activity (Gerorge, 1983).

In the title compound (Fig. 1), the two pyrimidine rings (C1-C4/N1/N2 and C11-C14/N3/N4) are essentially planar, with maximum deviations of 0.011 (1) and 0.007 (1) Å, respectively, at atoms N1 and N4. The central phenyl ring is inclined at dihedral angles of 66.68 (5) and 71.91 (6)°, respectively, with respect to the C1-C4/N1/N2 and C11-C14/N3/N4 pyrimidine rings. The bond lengths and angles are consistent with a closely related structure (Li & Luo, 2006).

In the crystal structure, intermolecular C16—H16A···N1 and C20—H20A···N3 hydrogen bonds (Table 1) link neighbouring molecules into a ribbon-like structure containing $R^2_2(26)$ ring motifs (Fig. 2, Bernstein *et al.*, 1995), along the *b* axis. The interesting features of the crystal structure are the intermolecular short Cl···Cl [Cl1···Cl2^{iii} = 3.4427 (6) Å; (iii) 1/2-x2, y-1/2, 1/2-z] and Cl···O [Cl1···O8^{iii} = 3.1750 (11) and Cl2···O1^{iv} = 3.1420 (9) Å; (iv) x, 2-y, z+1/2] interactions, which are shorter than the sum of the van der Waals radii of the relevant atoms, interconnecting the ribbons into two-dimensional networks parallel to the *bc* plane. The crystal structure is further stabilized by weak intermolecular π–π interactions [*Cg*1···*Cg*1^{v} = 3.4552 (8) Å; (v) -x, y, -z+1/2; *Cg*1 is the centroid of C11-C14/N3/N4 pyrimidine ring].

Experimental

To a stirred solution of methyl-2,6-dihydroxybenzoate (0.50 g, 0.0026 mol) in acetonitrile (10 ml) was added potassium carbonate (1.00 g, 0.0070 mol) and 5-chloro-4,6-dimethoxy-2-(methylsulfonyl)pyrimidine (1.58 g, 0.0050 mol). The reaction mixture was heated to reflux for 4 h. Mass analysis showed completion of the reaction. The reaction mixture was filtered and the filtrate was concentrated. The residue was recrystallized using dichloromethane to obtain the title compound (yield: 67 %, m.p. 427–430 K).

Refinement

All H atoms were placed in the calculated positions, with C–H = 0.93–0.96 Å, and refined using a riding model with U_{iso} = 1.2 or 1.5 U_{eq}(C). The rotating group model was used for the methyl groups.

Figures

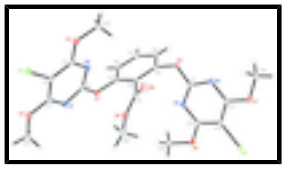


Fig. 1. The molecular structure of the title compound, showing 30 % probability displacement ellipsoids for non-H atoms and the atom-numbering scheme.

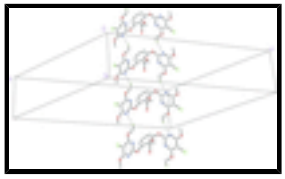


Fig. 2. Part of the crystal structure, viewed along an arbitrary axis, showing a molecular ribbon. H atoms not involved in hydrogen bonds (dashed lines) have been omitted for clarity.

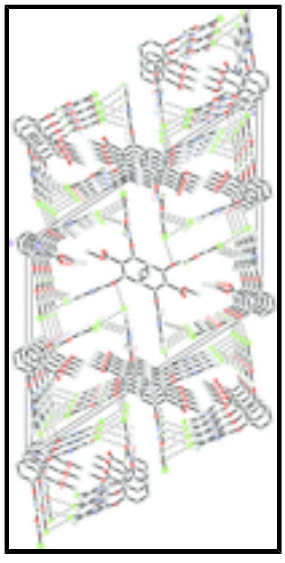


Fig. 3. The crystal structure of the title compound, viewed along the *b* axis, showing two-dimensional networks parallel to the *bc* plane. H atoms not involved in intermolecular interactions (dashed lines) have been omitted for clarity.

Methyl 2,6-bis[(5-chloro-4,6-dimethoxypyrimidin-2-yl)oxy]benzoate

Crystal data

$C_{20}H_{18}Cl_2N_4O_8$	$F(000) = 2112$
$M_r = 513.28$	$D_x = 1.523$ Mg m^{-3}
Monoclinic, *C*2/*c*	Mo *K*α radiation, λ = 0.71073 Å
Hall symbol: -C 2yc	Cell parameters from 9948 reflections
a = 29.354 (3) Å	θ = 2.7–32.6°
b = 8.0485 (8) Å	μ = 0.35 mm^{-1}
c = 22.5923 (19) Å	*T* = 100 K
β = 123.014 (2)°	Block, colourless
V = 4475.7 (7) Å^3	0.58 × 0.31 × 0.16 mm
Z = 8	

Data collection

Bruker APEXII DUO CCD area-detector	8040 independent reflections

diffractometer

Radiation source: fine-focus sealed tube

graphite

φ and ω scans

Absorption correction: multi-scan (*SADABS*; Bruker, 2009)

T_{min} = 0.825, T_{max} = 0.948

22170 measured reflections

6824 reflections with $I > 2\sigma(I)$

R_{int} = 0.023

θ_{max} = 32.6°, θ_{min} = 1.7°

h = −44→43

k = −12→12

l = −34→34

Refinement

Refinement on F^2

Least-squares matrix: full

$R[F^2 > 2\sigma(F^2)]$ = 0.040

$wR(F^2)$ = 0.129

S = 1.08

8040 reflections

312 parameters

0 restraints

Primary atom site location: structure-invariant direct methods

Secondary atom site location: difference Fourier map

Hydrogen site location: inferred from neighbouring sites

H-atom parameters constrained

$w = 1/[\sigma^2(F_o^2) + (0.0781P)^2 + 1.9869P]$ where $P = (F_o^2 + 2F_c^2)/3$

$(\Delta/\sigma)_{max}$ = 0.001

$\Delta\rho_{max}$ = 0.71 e Å^{-3}

$\Delta\rho_{min}$ = −0.55 e Å^{-3}

Special details

Experimental. The crystal was placed in the cold stream of an Oxford Cryosystems Cobra open-flow nitrogen cryostat (Cosier & Glazer, 1986) operating at 100.0 (1)K.

Geometry. All esds (except the esd in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell esds are taken into account individually in the estimation of esds in distances, angles and torsion angles; correlations between esds in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell esds is used for estimating esds involving l.s. planes.

Refinement. Refinement of F^2 against ALL reflections. The weighted R-factor wR and goodness of fit S are based on F^2, conventional R-factors R are based on F, with F set to zero for negative F^2. The threshold expression of $F^2 > 2$sigma(F^2) is used only for calculating R-factors(gt) etc. and is not relevant to the choice of reflections for refinement. R-factors based on F^2 are statistically about twice as large as those based on F, and R- factors based on ALL data will be even larger.

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å^2)

	x	*y*	*z*	U_{iso}*/U_{eq}
Cl1	0.307309 (11)	0.57598 (4)	0.096234 (18)	0.02454 (8)
Cl2	0.082300 (12)	0.91419 (4)	0.399331 (14)	0.01982 (8)
O1	0.11797 (3)	0.91625 (11)	0.04367 (4)	0.01529 (16)
O2	0.04987 (3)	0.57525 (11)	0.15715 (4)	0.01615 (16)
O3	0.28912 (4)	0.93539 (12)	0.08837 (5)	0.02288 (19)
O4	0.20796 (3)	0.42435 (11)	0.07368 (5)	0.01987 (17)
O5	0.16660 (4)	0.88991 (14)	0.18631 (5)	0.0263 (2)
O6	0.16179 (4)	0.62171 (15)	0.20959 (5)	0.0296 (2)

O7	0.07442 (4)	0.55550 (12)	0.37357 (4)	0.01848 (17)
O8	0.07019 (4)	1.06655 (11)	0.27317 (4)	0.01907 (17)
N1	0.20277 (4)	0.92889 (13)	0.06785 (5)	0.01634 (18)
N2	0.16079 (4)	0.66706 (13)	0.05757 (5)	0.01477 (17)
N3	0.06228 (4)	0.56256 (13)	0.26376 (5)	0.01535 (18)
N4	0.06122 (4)	0.82430 (13)	0.21320 (5)	0.01471 (17)
C1	0.24667 (4)	0.84915 (16)	0.07879 (6)	0.0167 (2)
C2	0.25047 (4)	0.67647 (16)	0.08112 (6)	0.0171 (2)
C3	0.20559 (4)	0.58939 (15)	0.07043 (5)	0.0152 (2)
C4	0.16281 (4)	0.83107 (15)	0.05732 (5)	0.01390 (19)
C5	0.07753 (4)	0.82779 (14)	0.04464 (5)	0.01343 (18)
C6	0.02637 (4)	0.83115 (16)	−0.01690 (5)	0.0172 (2)
H6A	0.0207	0.8867	−0.0565	0.021*
C7	−0.01650 (4)	0.75105 (17)	−0.01925 (6)	0.0206 (2)
H7A	−0.0510	0.7533	−0.0605	0.025*
C8	−0.00804 (4)	0.66766 (16)	0.03972 (6)	0.0179 (2)
H8A	−0.0366	0.6133	0.0382	0.022*
C9	0.04341 (4)	0.66658 (15)	0.10068 (5)	0.01393 (18)
C10	0.08739 (4)	0.74658 (14)	0.10524 (5)	0.01335 (18)
C11	0.05844 (4)	0.66055 (15)	0.21417 (5)	0.01376 (18)
C12	0.06937 (4)	0.64190 (16)	0.32011 (5)	0.01463 (19)
C13	0.07199 (4)	0.81463 (15)	0.32568 (5)	0.01496 (19)
C14	0.06775 (4)	0.90169 (15)	0.26965 (5)	0.01476 (19)
C15	0.28520 (6)	1.11370 (19)	0.08786 (9)	0.0296 (3)
H15A	0.3151	1.1619	0.0877	0.044*
H15B	0.2863	1.1497	0.1291	0.044*
H15C	0.2516	1.1484	0.0464	0.044*
C16	0.16177 (5)	0.33858 (18)	0.06581 (8)	0.0262 (3)
H16A	0.1695	0.2218	0.0735	0.039*
H16B	0.1306	0.3562	0.0190	0.039*
H16C	0.1545	0.3807	0.0997	0.039*
C17	0.14212 (4)	0.74193 (17)	0.17246 (6)	0.0187 (2)
C18	0.22073 (7)	0.8981 (3)	0.24900 (9)	0.0473 (5)
H18A	0.2353	1.0076	0.2534	0.071*
H18B	0.2435	0.8182	0.2456	0.071*
H18C	0.2194	0.8740	0.2897	0.071*
C19	0.07186 (6)	0.37652 (18)	0.36714 (6)	0.0226 (2)
H19A	0.0735	0.3285	0.4072	0.034*
H19B	0.1019	0.3373	0.3653	0.034*
H19C	0.0384	0.3449	0.3247	0.034*
C20	0.07386 (7)	1.15252 (18)	0.21994 (7)	0.0286 (3)
H20A	0.0771	1.2698	0.2292	0.043*
H20B	0.0418	1.1311	0.1743	0.043*
H20C	0.1052	1.1140	0.2209	0.043*

Atomic displacement parameters (Å^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}

Cl1	0.01660 (12)	0.02313 (16)	0.03475 (16)	0.00517 (10)	0.01454 (11)	0.00213 (12)
Cl2	0.02636 (14)	0.02056 (15)	0.01647 (12)	−0.00313 (10)	0.01420 (10)	−0.00502 (9)
O1	0.0144 (3)	0.0143 (4)	0.0208 (3)	0.0030 (3)	0.0119 (3)	0.0037 (3)
O2	0.0246 (4)	0.0139 (4)	0.0150 (3)	−0.0023 (3)	0.0141 (3)	−0.0023 (3)
O3	0.0179 (4)	0.0186 (4)	0.0352 (5)	0.0000 (3)	0.0164 (3)	0.0014 (4)
O4	0.0170 (3)	0.0131 (4)	0.0280 (4)	0.0012 (3)	0.0113 (3)	−0.0011 (3)
O5	0.0220 (4)	0.0305 (5)	0.0185 (4)	−0.0102 (4)	0.0060 (3)	−0.0027 (4)
O6	0.0222 (4)	0.0338 (6)	0.0234 (4)	0.0043 (4)	0.0064 (3)	0.0104 (4)
O7	0.0266 (4)	0.0176 (4)	0.0158 (3)	−0.0012 (3)	0.0144 (3)	0.0008 (3)
O8	0.0267 (4)	0.0131 (4)	0.0175 (3)	0.0004 (3)	0.0121 (3)	−0.0015 (3)
N1	0.0160 (4)	0.0151 (5)	0.0205 (4)	0.0010 (3)	0.0116 (3)	0.0012 (3)
N2	0.0148 (4)	0.0142 (4)	0.0162 (3)	0.0020 (3)	0.0090 (3)	0.0003 (3)
N3	0.0185 (4)	0.0154 (5)	0.0155 (4)	−0.0007 (3)	0.0114 (3)	−0.0009 (3)
N4	0.0179 (4)	0.0139 (4)	0.0139 (3)	0.0006 (3)	0.0097 (3)	−0.0008 (3)
C1	0.0146 (4)	0.0176 (5)	0.0190 (4)	−0.0001 (4)	0.0100 (3)	0.0005 (4)
C2	0.0141 (4)	0.0174 (5)	0.0206 (4)	0.0033 (4)	0.0100 (3)	0.0008 (4)
C3	0.0153 (4)	0.0142 (5)	0.0156 (4)	0.0023 (4)	0.0081 (3)	0.0002 (4)
C4	0.0135 (4)	0.0156 (5)	0.0140 (4)	0.0023 (4)	0.0083 (3)	0.0011 (4)
C5	0.0142 (4)	0.0135 (5)	0.0155 (4)	0.0013 (4)	0.0100 (3)	−0.0001 (4)
C6	0.0165 (4)	0.0212 (6)	0.0144 (4)	0.0016 (4)	0.0088 (3)	0.0019 (4)
C7	0.0154 (4)	0.0270 (7)	0.0167 (4)	−0.0003 (4)	0.0071 (3)	0.0010 (4)
C8	0.0162 (4)	0.0211 (6)	0.0182 (4)	−0.0024 (4)	0.0105 (4)	−0.0020 (4)
C9	0.0178 (4)	0.0133 (5)	0.0137 (4)	−0.0001 (4)	0.0105 (3)	−0.0011 (4)
C10	0.0144 (4)	0.0136 (5)	0.0130 (4)	0.0007 (3)	0.0081 (3)	−0.0009 (3)
C11	0.0146 (4)	0.0154 (5)	0.0136 (4)	−0.0007 (4)	0.0092 (3)	−0.0020 (4)
C12	0.0146 (4)	0.0177 (5)	0.0135 (4)	−0.0005 (4)	0.0089 (3)	0.0000 (4)
C13	0.0171 (4)	0.0161 (5)	0.0139 (4)	−0.0004 (4)	0.0099 (3)	−0.0025 (4)
C14	0.0153 (4)	0.0142 (5)	0.0149 (4)	0.0006 (4)	0.0083 (3)	−0.0013 (4)
C15	0.0243 (6)	0.0186 (6)	0.0490 (8)	−0.0024 (5)	0.0220 (6)	0.0008 (6)
C16	0.0207 (5)	0.0153 (6)	0.0407 (7)	−0.0013 (4)	0.0155 (5)	−0.0015 (5)
C17	0.0161 (4)	0.0242 (6)	0.0156 (4)	−0.0012 (4)	0.0085 (3)	0.0002 (4)
C18	0.0290 (7)	0.0602 (13)	0.0281 (7)	−0.0201 (8)	−0.0003 (6)	−0.0017 (7)
C19	0.0323 (6)	0.0183 (6)	0.0214 (5)	−0.0017 (5)	0.0173 (4)	0.0016 (5)
C20	0.0497 (8)	0.0162 (6)	0.0220 (5)	0.0018 (6)	0.0209 (5)	0.0020 (5)

Geometric parameters (Å, °)

Cl1—C2	1.7126 (11)	C5—C6	1.3834 (14)
Cl2—C13	1.7187 (11)	C5—C10	1.3978 (14)
O1—C4	1.3621 (12)	C6—C7	1.3889 (16)
O1—C5	1.3944 (13)	C6—H6A	0.93
O2—C11	1.3569 (12)	C7—C8	1.3881 (16)
O2—C9	1.3929 (13)	C7—H7A	0.93
O3—C1	1.3370 (14)	C8—C9	1.3824 (14)
O3—C15	1.4393 (18)	C8—H8A	0.93
O4—C3	1.3301 (14)	C9—C10	1.3952 (14)
O4—C16	1.4436 (15)	C10—C17	1.4934 (15)
O5—C17	1.3370 (16)	C12—C13	1.3943 (17)
O5—C18	1.4432 (17)	C13—C14	1.3918 (15)

O6—C17	1.2023 (16)	C15—H15A	0.96
O7—C12	1.3301 (13)	C15—H15B	0.96
O7—C19	1.4457 (16)	C15—H15C	0.96
O8—C14	1.3288 (14)	C16—H16A	0.96
O8—C20	1.4415 (15)	C16—H16B	0.96
N1—C4	1.3224 (14)	C16—H16C	0.96
N1—C1	1.3365 (14)	C18—H18A	0.96
N2—C4	1.3215 (16)	C18—H18B	0.96
N2—C3	1.3372 (14)	C18—H18C	0.96
N3—C11	1.3238 (14)	C19—H19A	0.96
N3—C12	1.3353 (13)	C19—H19B	0.96
N4—C11	1.3214 (16)	C19—H19C	0.96
N4—C14	1.3360 (13)	C20—H20A	0.96
C1—C2	1.3930 (18)	C20—H20B	0.96
C2—C3	1.3923 (15)	C20—H20C	0.96
C4—O1—C5	117.72 (9)	N3—C11—O2	112.86 (10)
C11—O2—C9	117.70 (9)	O7—C12—N3	119.87 (11)
C1—O3—C15	116.92 (10)	O7—C12—C13	117.78 (9)
C3—O4—C16	116.97 (9)	N3—C12—C13	122.35 (10)
C17—O5—C18	115.74 (13)	C14—C13—C12	116.54 (9)
C12—O7—C19	117.10 (9)	C14—C13—Cl2	121.81 (9)
C14—O8—C20	117.10 (9)	C12—C13—Cl2	121.61 (8)
C4—N1—C1	114.76 (11)	O8—C14—N4	119.85 (10)
C4—N2—C3	115.27 (9)	O8—C14—C13	118.24 (10)
C11—N3—C12	114.78 (10)	N4—C14—C13	121.92 (11)
C11—N4—C14	115.29 (9)	O3—C15—H15A	109.5
N1—C1—O3	120.02 (11)	O3—C15—H15B	109.5
N1—C1—C2	122.37 (10)	H15A—C15—H15B	109.5
O3—C1—C2	117.60 (10)	O3—C15—H15C	109.5
C3—C2—C1	116.54 (10)	H15A—C15—H15C	109.5
C3—C2—Cl1	121.59 (10)	H15B—C15—H15C	109.5
C1—C2—Cl1	121.87 (9)	O4—C16—H16A	109.5
O4—C3—N2	119.63 (10)	O4—C16—H16B	109.5
O4—C3—C2	118.50 (10)	H16A—C16—H16B	109.5
N2—C3—C2	121.87 (11)	O4—C16—H16C	109.5
N2—C4—N1	129.15 (10)	H16A—C16—H16C	109.5
N2—C4—O1	117.63 (9)	H16B—C16—H16C	109.5
N1—C4—O1	113.22 (10)	O6—C17—O5	124.13 (11)
C6—C5—O1	116.19 (9)	O6—C17—C10	124.84 (12)
C6—C5—C10	121.70 (9)	O5—C17—C10	111.03 (10)
O1—C5—C10	122.04 (9)	O5—C18—H18A	109.5
C5—C6—C7	119.62 (10)	O5—C18—H18B	109.5
C5—C6—H6A	120.2	H18A—C18—H18B	109.5
C7—C6—H6A	120.2	O5—C18—H18C	109.5
C8—C7—C6	120.21 (10)	H18A—C18—H18C	109.5
C8—C7—H7A	119.9	H18B—C18—H18C	109.5
C6—C7—H7A	119.9	O7—C19—H19A	109.5
C9—C8—C7	119.10 (10)	O7—C19—H19B	109.5
C9—C8—H8A	120.4	H19A—C19—H19B	109.5

C7—C8—H8A	120.4	O7—C19—H19C	109.5
C8—C9—O2	116.45 (9)	H19A—C19—H19C	109.5
C8—C9—C10	122.36 (10)	H19B—C19—H19C	109.5
O2—C9—C10	121.14 (9)	O8—C20—H20A	109.5
C9—C10—C5	117.01 (9)	O8—C20—H20B	109.5
C9—C10—C17	120.20 (9)	H20A—C20—H20B	109.5
C5—C10—C17	122.79 (9)	O8—C20—H20C	109.5
N4—C11—N3	129.10 (10)	H20A—C20—H20C	109.5
N4—C11—O2	118.04 (9)	H20B—C20—H20C	109.5
C4—N1—C1—O3	178.40 (10)	C8—C9—C10—C17	179.84 (11)
C4—N1—C1—C2	−1.96 (15)	O2—C9—C10—C17	−2.78 (16)
C15—O3—C1—N1	1.42 (16)	C6—C5—C10—C9	0.94 (16)
C15—O3—C1—C2	−178.24 (11)	O1—C5—C10—C9	177.93 (10)
N1—C1—C2—C3	0.85 (16)	C6—C5—C10—C17	−179.62 (11)
O3—C1—C2—C3	−179.50 (10)	O1—C5—C10—C17	−2.62 (17)
N1—C1—C2—Cl1	−179.21 (8)	C14—N4—C11—N3	−1.47 (16)
O3—C1—C2—Cl1	0.44 (15)	C14—N4—C11—O2	177.68 (9)
C16—O4—C3—N2	−2.55 (15)	C12—N3—C11—N4	0.79 (16)
C16—O4—C3—C2	177.03 (10)	C12—N3—C11—O2	−178.39 (9)
C4—N2—C3—O4	178.15 (10)	C9—O2—C11—N4	−1.34 (13)
C4—N2—C3—C2	−1.42 (14)	C9—O2—C11—N3	177.94 (9)
C1—C2—C3—O4	−178.62 (10)	C19—O7—C12—N3	0.01 (14)
Cl1—C2—C3—O4	1.43 (14)	C19—O7—C12—C13	−179.72 (10)
C1—C2—C3—N2	0.95 (15)	C11—N3—C12—O7	−179.16 (9)
Cl1—C2—C3—N2	−178.99 (8)	C11—N3—C12—C13	0.55 (14)
C3—N2—C4—N1	0.15 (16)	O7—C12—C13—C14	178.67 (9)
C3—N2—C4—O1	179.26 (9)	N3—C12—C13—C14	−1.04 (15)
C1—N1—C4—N2	1.52 (16)	O7—C12—C13—Cl2	0.85 (14)
C1—N1—C4—O1	−177.62 (9)	N3—C12—C13—Cl2	−178.87 (8)
C5—O1—C4—N2	12.29 (13)	C20—O8—C14—N4	−9.19 (15)
C5—O1—C4—N1	−168.46 (9)	C20—O8—C14—C13	170.99 (11)
C4—O1—C5—C6	−121.76 (11)	C11—N4—C14—O8	−179.01 (10)
C4—O1—C5—C10	61.09 (13)	C11—N4—C14—C13	0.81 (14)
O1—C5—C6—C7	−177.67 (11)	C12—C13—C14—O8	−179.86 (10)
C10—C5—C6—C7	−0.51 (18)	Cl2—C13—C14—O8	−2.04 (14)
C5—C6—C7—C8	−0.20 (19)	C12—C13—C14—N4	0.31 (15)
C6—C7—C8—C9	0.43 (19)	Cl2—C13—C14—N4	178.14 (8)
C7—C8—C9—O2	−177.46 (11)	C18—O5—C17—O6	2.3 (2)
C7—C8—C9—C10	0.03 (18)	C18—O5—C17—C10	−177.92 (13)
C11—O2—C9—C8	−110.10 (11)	C9—C10—C17—O6	41.16 (17)
C11—O2—C9—C10	72.38 (13)	C5—C10—C17—O6	−138.26 (13)
C8—C9—C10—C5	−0.70 (16)	C9—C10—C17—O5	−138.63 (11)
O2—C9—C10—C5	176.68 (10)	C5—C10—C17—O5	41.94 (15)

Hydrogen-bond geometry (Å, °)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
C16—H16A···N1^{i}	0.96	2.58	3.5018 (19)	161

C20—H20A···N3^{ii}	0.96	2.59	3.5148 (19)	161

Symmetry codes: (i) *x*, *y*−1, *z*; (ii) *x*, *y*+1, *z*.

Fig. 1

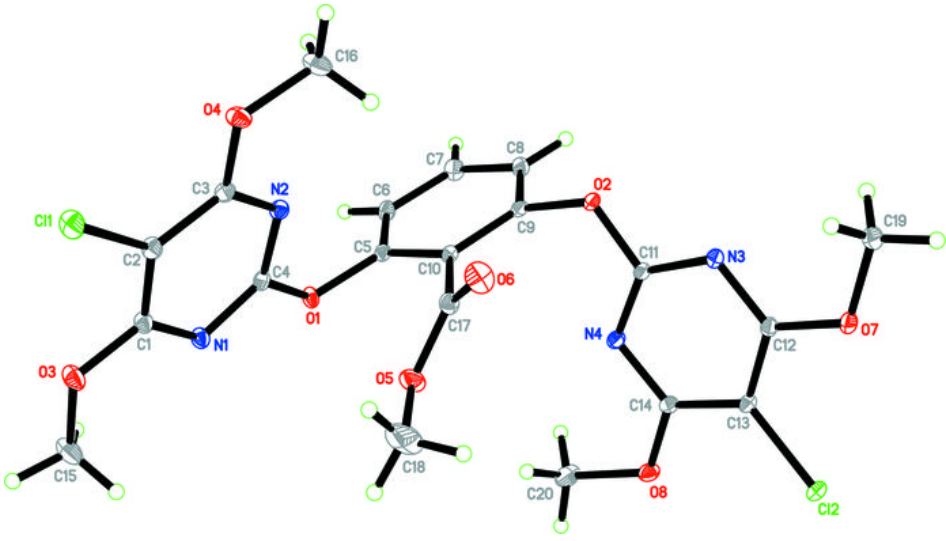


Fig. 2

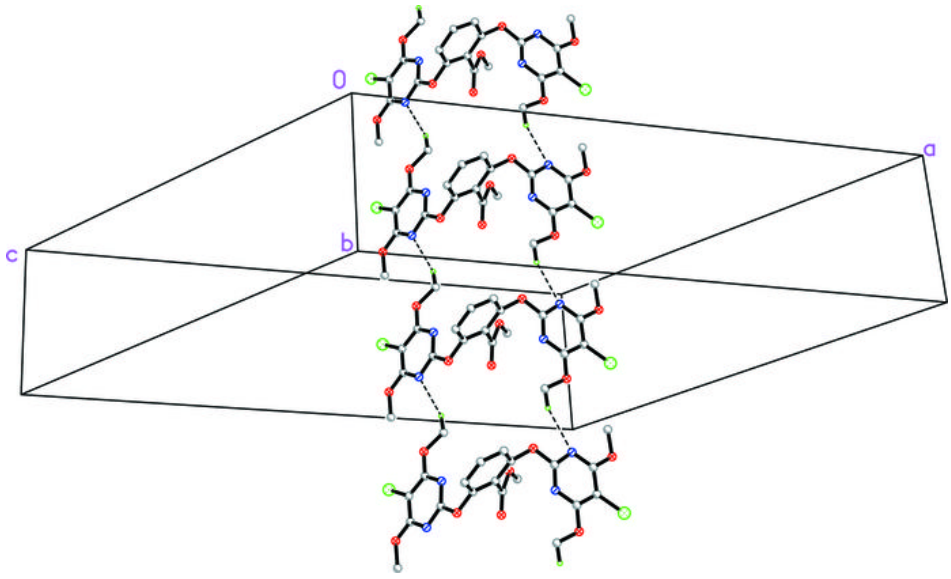
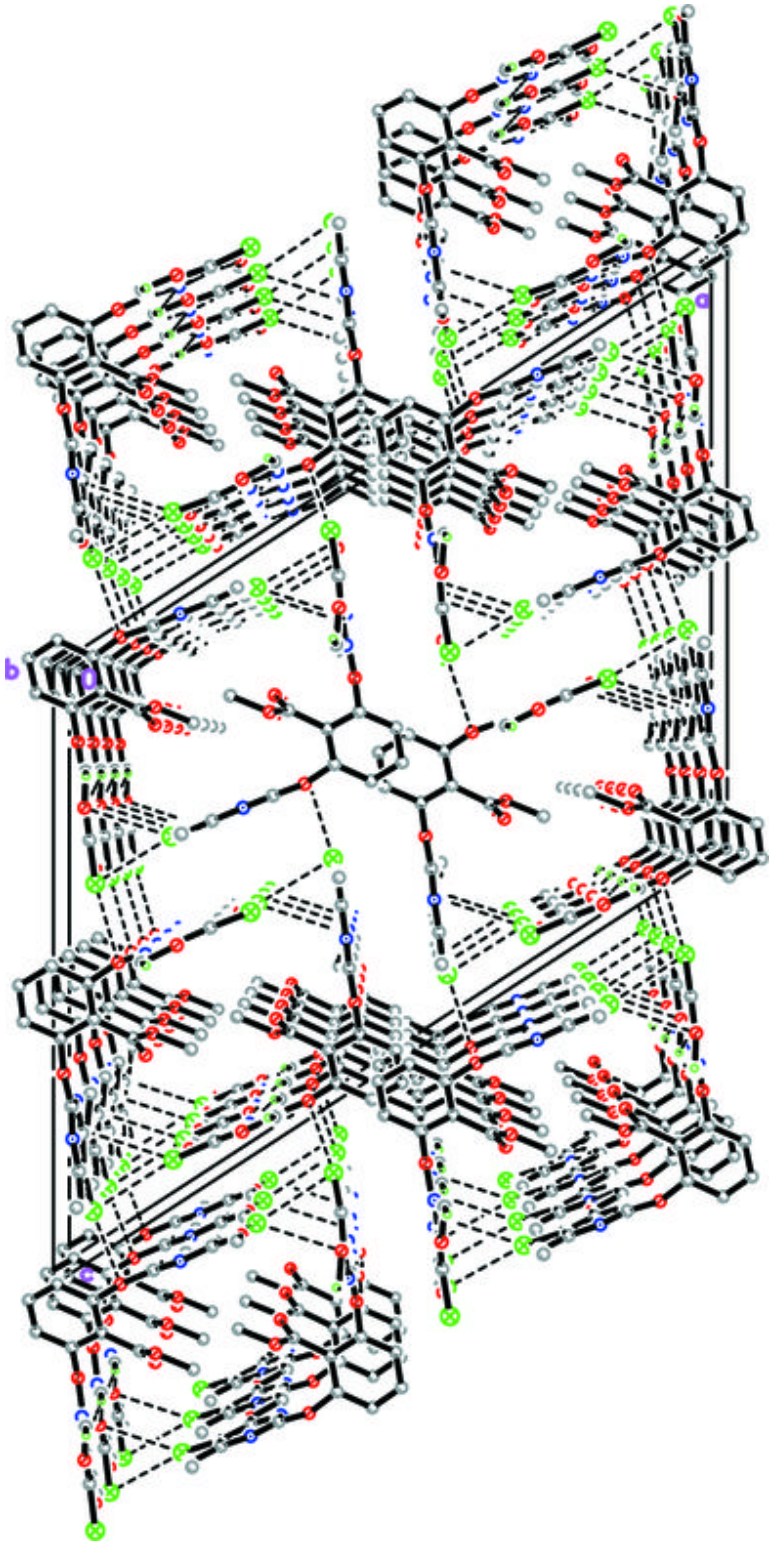


Fig. 3



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3-(4-Fluorophenylsulfinyl)-5-iodo-2-methyl-1-benzofuran

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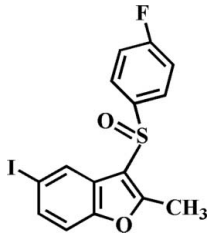
Key indicators: single-crystal X-ray study; T = 173 K; mean σ(C–C) = 0.003 Å; R factor = 0.029; wR factor = 0.077; data-to-parameter ratio = 18.1.

In the title compound, $C_{15}H_{10}FIO_2S$, the O atom and the 4-fluorophenyl group of the 4-fluorophenylsulfinyl substituent are located on opposite sides of the plane through the benzofuran fragment; the 4-fluorophenyl ring is nearly perpendicular to this plane, making a dihedral angle of 83.37 (7)°. The crystal structure is stabilized by weak intermolecular C—H···O hydrogen bonds and an I···O interaction [I···O = 3.255 (2) Å]. The crystal structure also exhibits intermolecular C—F···π interactions [3.068 (2) Å], and aromatic π–π interactions between the furan and benzene rings of neighbouring benzofuran fragments [centroid–centroid distance = 3.636 (2) Å].

Related literature

For the crystal structures of similar 3-(4-fluorophenylsulfinyl)-2-methyl-1-benzofuran derivatives, see: Choi *et al.* (2010*a*,*b*,*c*). For the pharmacological activity of benzofuran compounds, see: Aslam *et al.* (2006); Galal *et al.* (2009); Khan *et al.* (2005). For natural products with benzofuran rings, see: Akgul & Anil (2003); Soekamto *et al.* (2003). For a review of halogen bonding, see: Politzer *et al.* (2007).



Experimental

Crystal data

$C_{15}H_{10}FIO_2S$
M_r = 400.19
Monoclinic, $P2_1/c$
a = 13.1665 (4) Å
b = 11.4338 (4) Å
c = 9.9296 (3) Å
β = 107.181 (1)°
V = 1428.13 (8) Å^3
Z = 4
Mo $K\alpha$ radiation
μ = 2.40 mm^{-1}
T = 173 K
0.27 × 0.24 × 0.20 mm

Data collection

Bruker SMART APEXII CCD diffractometer
Absorption correction: multi-scan (*SADABS*; Bruker, 2009)
T_{min} = 0.565, T_{max} = 0.648
12825 measured reflections
3297 independent reflections
2990 reflections with $I > 2\sigma(I)$
R_{int} = 0.031

Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.029
$wR(F^2)$ = 0.077
S = 1.11
3297 reflections
182 parameters
H-atom parameters constrained
$\Delta\rho_{max}$ = 0.58 e Å^{-3}
$\Delta\rho_{min}$ = −1.56 e Å^{-3}

Table 1
Hydrogen-bond geometry (Å, °).

D—H···A	D—H	H···A	D···A	D—H···A
C5—H5···O1^{i}	0.93	2.55	3.472 (3)	170
C9—H9C···O2^{ii}	0.96	2.53	3.277 (3)	135

Symmetry codes: (i) $-x+2, y-\frac{1}{2}, -z+\frac{3}{2}$; (ii) $x, -y+\frac{3}{2}, z+\frac{1}{2}$.

Data collection: *APEX2* (Bruker, 2009); cell refinement: *SAINT* (Bruker, 2009); data reduction: *SAINT*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *ORTEP-3* (Farrugia, 1997) and *DIAMOND* (Brandenburg, 1998); software used to prepare material for publication: *SHELXL97*.

Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: CS2129).

References

Akgul, Y. Y. & Anil, H. (2003). *Phytochemistry*, **63**, 939–943.
Aslam, S. N., Stevenson, P. C., Phythian, S. J., Veitch, N. C. & Hall, D. R. (2006). *Tetrahedron*, **62**, 4214–4226.
Brandenburg, K. (1998). *DIAMOND*. Crystal Impact GmbH, Bonn, Germany.
Bruker (2009). *APEX2*. *SADABS* and *SAINT*. Bruker AXS Inc., Madison, Wisconsin, USA.
Choi, H. D., Seo, P. J., Son, B. W. & Lee, U. (2010*a*). *Acta Cryst.* E**66**, o472.
Choi, H. D., Seo, P. J., Son, B. W. & Lee, U. (2010*b*). *Acta Cryst.* E**66**, o543.
Choi, H. D., Seo, P. J., Son, B. W. & Lee, U. (2010*c*). *Acta Cryst.* E**66**, o564.
Farrugia, L. J. (1997). *J. Appl. Cryst.* **30**, 565.
Galal, S. A., Abd El-All, A. S., Abdallah, M. M. & El-Diwani, H. I. (2009). *Bioorg. Med. Chem. Lett.* **19**, 2420–2428.
Khan, M. W., Alam, M. J., Rashid, M. A. & Chowdhury, R. (2005). *Bioorg. Med. Chem.* **13**, 4796–4805.
Politzer, P., Lane, P., Concha, M. C., Ma, Y. & Murray, J. S. (2007). *J. Mol. Model.*, **13**, 305–311.
Sheldrick, G. M. (2008). *Acta Cryst.* A**64**, 112–122.
Soekamto, N. H., Achmad, S. A., Ghisalberti, E. L., Hakim, E. H. & Syah, Y. M. (2003). *Phytochemistry*, **64**, 831–834.

supplementary materials

Acta Cryst. (2010). E**66**, o1876 [**doi:10.1107/S1600536810024931**]

3-(4-Fluorophenylsulfinyl)-5-iodo-2-methyl-1-benzofuran

H. D. Choi, P. J. Seo, B. W. Son and U. Lee

Comment

Molecules containing benzofuran skeleton show variouspharmacological properties such as antifungal (Aslam *et al.*, 2006), antitumor and antiviral (Galal *et al.*., 2009), antimicrobial (Khan *et al.*., 2005) activity, and these compounds widely occur in nature (Akgul & Anil, 2003; Soekamto *et al.*., 2003). As a part of our ongoing studies of the effect of side chain substituents on the solid state structures of 3-(4-fluorophenylsulfinyl)-2-methyl-1-benzofuran analogues (Choi *et al.*., 2010*a,b,c*), we report the crystal structure of the title compound (Fig. 1).

The benzofuran unit is essentially planar, with a mean deviation of 0.008 (2) Å from the least-squares plane defined by the nine constituent atoms. The 4-fluorophenyl ring is almost perpendicular to the plane of the benzofuran fragment [83.37 (7)°] and is tilted slightly towards it. The crystal packing (Fig. 2) is stabilized by weak intermolecular C—H···O hydrogen bonds; the first one between the benzene H atom and the furan O atom with a C5—H5···O1^{i}, and the second one between the methyl H atom and the oxygen of the S═O unit, with a C9—H9C···O2^{ii}, respectively (Table 1). The molecular packing (Fig. 2) is also stabilized by an I···O halogen bonding between the iodine and the oxygen of the S═O unit [I···O2^{v} = 3.255 (2) Å; C4—I···O2^{v} = 164.42 (8)°] (Politzer *et al.*, 2007). The crystal packing (Fig. 3) also exhibits intermolecular C—F···π interactions between the fluorine and the benzene ring of an adjacent benzofuran system, with a C13—F···Cg2^{vii} distance of 3.068 (2) Å (Cg2 is the centroid of the C2–C7 benzene ring), and aromatic π–π interactions between the furan and the benzene rings of the adjacent benzofuran systems, with a Cg1···Cg2^{viii} distance of 3.636 (2) Å (Cg1 is the centroid of the C1/C2/C7/O1/C8 furan ring).

Experimental

77% 3-Chloroperoxybenzoic acid (166 mg, 1.0 mmol) was added in small portions to a stirred solution of 3-(4-fluorophenyl-sulfanyl)–5-iodo-2-methyl-1-benzofuran (346 mg, 0.9 mmol) in dichloromethane (30 mL) at 273 K. After being stirred at room temperature for 3h, the mixture was washed with saturated sodium bicarbonate solution and the organic layer was separated, dried over magnesium sulfate, filtered and concentrated at reduced pressure. The residue was purified by column chromatography (hexane–ethyl acetate, 1:1 v/v) to afford the title compound as a colorless solid [yield 77%, m.p. 428–429 K; R_f = 0.64 (hexane–ethyl acetate, 1:1 v/v)]. Single crystals suitable for X-ray diffraction were prepared by slow evaporation of a solution of the title compound in benzene at room temperature.

Refinement

All H atoms were positioned geometrically and refined using a riding model, with C—H = 0.93 Å for aryl and 0.96 Å for methyl H atoms. U_{iso}(H) = 1.2U_{eq}(C) for aryl and 1.5U_{eq}(C) for methyl H atoms.

Figures

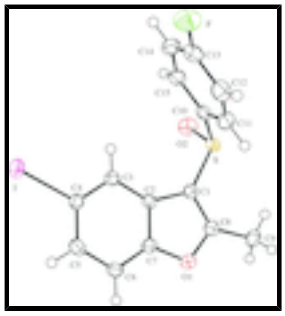


Fig. 1. The molecular structure of the title compound with the atom numbering scheme. Displacement ellipsoids are drawn at the 50% probability level. H atoms are presented as a small spheres of arbitrary radius.

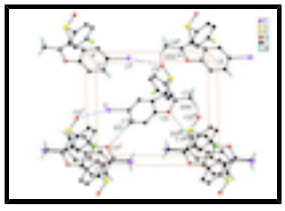


Fig. 2. C—H···O and I···O interactions (dotted lines) in the crystal structure of the title compound. [Symmetry codes: (i) - *x* + 2, *y* - 1/2, - *z* + 3/2; (ii) *x*, - *y* + 3/2, *z* + 1/2; (iii) - *x* + 2, *y* + 1/2, - *z* + 3/2; (iv) *x*, - *y* + 3/2, *z* - 1/2; (v) *x*, - *y* + 1/2, *z* + 1/2; (vi) *x*, - *y* + 1/2, *z* - 1/2.]

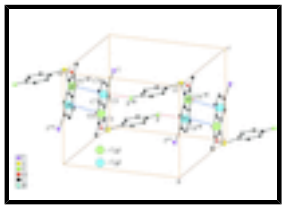


Fig. 3. C—F···π and π–π interactions (dotted lines) in the crystal structure of the title compound. Cg denotes the ring centroid. [Symmetry codes: (vii) - *x* + 1, - *y* +1 , - *z* + 1; (viii) - *x* + 2, - *y* + 1, - *z* + 1.]

3-(4-Fluorophenylsulfinyl)-5-iodo-2-methyl-1-benzofuran

Crystal data

$C_{15}H_{10}FIO_2S$	$F(000)$ = 776
M_r = 400.19	D_x = 1.861 Mg m^{-3}
Monoclinic, $P2_1/c$	Mo $K\alpha$ radiation, λ = 0.71073 Å
Hall symbol: -P 2ybc	Cell parameters from 8763 reflections
a = 13.1665 (4) Å	θ = 2.4–27.6°
b = 11.4338 (4) Å	μ = 2.40 mm^{-1}
c = 9.9296 (3) Å	T = 173 K
β = 107.181 (1)°	Block, colourless
V = 1428.13 (8) Å^3	0.27 × 0.24 × 0.20 mm
Z = 4	

Data collection

Bruker SMART APEXII CCD diffractometer	3297 independent reflections
Radiation source: rotating anode	2990 reflections with $I > 2\sigma(I)$
graphite multilayer	R_{int} = 0.031
Detector resolution: 10.0 pixels mm^{-1}	θ_{max} = 27.6°, θ_{min} = 1.6°
φ and ω scans	h = −15→17

Absorption correction: multi-scan (*SADABS*; Bruker, 2009)
T_{min} = 0.565, T_{max} = 0.648
12825 measured reflections

k = −14→14
l = −12→12

Refinement

Refinement on F^2
Least-squares matrix: full
$R[F^2 > 2\sigma(F^2)]$ = 0.029
$wR(F^2)$ = 0.077
S = 1.11
3297 reflections
182 parameters
0 restraints

Primary atom site location: structure-invariant direct methods
Secondary atom site location: difference Fourier map
Hydrogen site location: difference Fourier map
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.0381P)^2 + 1.2193P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max}$ = 0.57 e Å^{-3}
$\Delta\rho_{min}$ = −1.56 e Å^{-3}

Special details

Geometry. All esds (except the esd in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell esds are taken into account individually in the estimation of esds in distances, angles and torsion angles; correlations between esds in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell esds is used for estimating esds involving l.s. planes.

Refinement. Refinement of F^2 against ALL reflections. The weighted R-factor wR and goodness of fit S are based on F^2, conventional R-factors R are based on F, with F set to zero for negative F^2. The threshold expression of $F^2 > 2$sigma(F^2) is used only for calculating R-factors(gt) etc. and is not relevant to the choice of reflections for refinement. R-factors based on F^2 are statistically about twice as large as those based on F, and R- factors based on ALL data will be even larger.

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å^2)

	x	*y*	*z*	U_{iso}*/U_{eq}
I	0.774810 (15)	0.162106 (16)	0.53507 (2)	0.03259 (8)
S	0.70499 (5)	0.67499 (6)	0.22747 (6)	0.02368 (14)
F	0.31812 (15)	0.49689 (19)	0.3339 (2)	0.0480 (5)
O1	0.94047 (15)	0.67042 (15)	0.57609 (19)	0.0249 (4)
O2	0.71831 (16)	0.60325 (19)	0.10757 (19)	0.0318 (4)
C1	0.8028 (2)	0.6377 (2)	0.3837 (2)	0.0213 (5)
C2	0.82677 (18)	0.5281 (2)	0.4598 (2)	0.0195 (5)
C3	0.78672 (19)	0.4142 (2)	0.4425 (2)	0.0219 (5)
H3	0.7309	0.3931	0.3643	0.026*
C4	0.8338 (2)	0.3340 (2)	0.5469 (3)	0.0233 (5)
C5	0.9195 (2)	0.3625 (2)	0.6643 (3)	0.0263 (5)
H5	0.9488	0.3058	0.7318	0.032*
C6	0.9608 (2)	0.4746 (2)	0.6804 (3)	0.0259 (5)
H6	1.0184	0.4951	0.7567	0.031*
C7	0.91229 (19)	0.5544 (2)	0.5777 (2)	0.0214 (5)

C8	0.8732 (2)	0.7187 (2)	0.4571 (3)	0.0229 (5)
C9	0.8903 (2)	0.8441 (2)	0.4345 (3)	0.0292 (6)
H9A	0.8451	0.8675	0.3436	0.044*
H9B	0.9632	0.8567	0.4387	0.044*
H9C	0.8735	0.8896	0.5064	0.044*
C10	0.59180 (19)	0.6152 (2)	0.2691 (2)	0.0226 (5)
C11	0.5564 (2)	0.6657 (2)	0.3746 (3)	0.0298 (6)
H11	0.5945	0.7263	0.4293	0.036*
C12	0.4639 (2)	0.6250 (3)	0.3973 (3)	0.0330 (6)
H12	0.4393	0.6570	0.4679	0.040*
C13	0.4092 (2)	0.5362 (3)	0.3133 (3)	0.0310 (6)
C14	0.4427 (2)	0.4850 (3)	0.2094 (3)	0.0315 (6)
H14	0.4039	0.4247	0.1549	0.038*
C15	0.5360 (2)	0.5251 (2)	0.1870 (3)	0.0267 (5)
H15	0.5607	0.4916	0.1173	0.032*

Atomic displacement parameters (Å^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
I	0.03251 (12)	0.02096 (12)	0.04268 (13)	0.00056 (6)	0.00859 (9)	0.00097 (7)
S	0.0267 (3)	0.0237 (3)	0.0189 (3)	0.0016 (2)	0.0038 (2)	0.0032 (2)
F	0.0320 (9)	0.0613 (13)	0.0562 (11)	−0.0066 (9)	0.0216 (8)	−0.0055 (10)
O1	0.0236 (9)	0.0244 (10)	0.0240 (8)	−0.0017 (7)	0.0031 (7)	−0.0028 (7)
O2	0.0364 (10)	0.0411 (12)	0.0203 (8)	−0.0014 (9)	0.0122 (8)	−0.0030 (8)
C1	0.0214 (11)	0.0211 (12)	0.0208 (11)	0.0004 (9)	0.0056 (9)	0.0009 (9)
C2	0.0191 (11)	0.0211 (12)	0.0182 (10)	0.0021 (9)	0.0055 (8)	0.0003 (9)
C3	0.0219 (11)	0.0216 (12)	0.0208 (11)	0.0012 (9)	0.0043 (9)	−0.0012 (9)
C4	0.0250 (12)	0.0193 (13)	0.0258 (12)	0.0005 (9)	0.0079 (10)	−0.0022 (9)
C5	0.0293 (13)	0.0265 (13)	0.0215 (11)	0.0076 (11)	0.0050 (10)	0.0024 (10)
C6	0.0243 (12)	0.0286 (14)	0.0206 (11)	0.0034 (10)	0.0004 (9)	−0.0028 (10)
C7	0.0206 (11)	0.0230 (12)	0.0207 (10)	0.0009 (9)	0.0064 (9)	−0.0027 (9)
C8	0.0231 (12)	0.0247 (13)	0.0220 (11)	0.0013 (10)	0.0085 (9)	−0.0013 (9)
C9	0.0294 (14)	0.0238 (14)	0.0353 (14)	−0.0034 (10)	0.0111 (11)	−0.0010 (10)
C10	0.0234 (12)	0.0233 (13)	0.0183 (10)	0.0050 (10)	0.0017 (9)	0.0027 (9)
C11	0.0339 (15)	0.0285 (15)	0.0256 (12)	0.0020 (11)	0.0067 (11)	−0.0051 (10)
C12	0.0354 (15)	0.0368 (16)	0.0295 (13)	0.0068 (13)	0.0138 (11)	−0.0024 (12)
C13	0.0221 (12)	0.0380 (16)	0.0324 (13)	0.0038 (11)	0.0074 (10)	0.0035 (12)
C14	0.0272 (13)	0.0327 (15)	0.0319 (13)	−0.0027 (11)	0.0045 (11)	−0.0071 (11)
C15	0.0260 (12)	0.0295 (14)	0.0225 (11)	0.0034 (10)	0.0039 (10)	−0.0049 (10)

Geometric parameters (Å, °)

I—C4	2.104 (2)	C6—C7	1.376 (4)
I—O2^{i}	3.255 (2)	C6—H6	0.9300
S—O2	1.4981 (19)	C8—C9	1.478 (4)
S—C1	1.751 (2)	C9—H9A	0.9600
S—C10	1.795 (3)	C9—H9B	0.9600
F—C13	1.351 (3)	C9—H9C	0.9600

O1—C8	1.366 (3)	C10—C15	1.383 (4)
O1—C7	1.379 (3)	C10—C11	1.391 (4)
C1—C8	1.360 (4)	C11—C12	1.383 (4)
C1—C2	1.449 (3)	C11—H11	0.9300
C2—C3	1.396 (3)	C12—C13	1.375 (4)
C2—C7	1.396 (3)	C12—H12	0.9300
C3—C4	1.386 (3)	C13—C14	1.368 (4)
C3—H3	0.9300	C14—C15	1.389 (4)
C4—C5	1.401 (4)	C14—H14	0.9300
C5—C6	1.383 (4)	C15—H15	0.9300
C5—H5	0.9300		
C4—I—O2^{i}	164.42 (8)	C1—C8—C9	133.5 (2)
O2—S—C1	110.03 (12)	O1—C8—C9	115.8 (2)
O2—S—C10	105.95 (12)	C8—C9—H9A	109.5
C1—S—C10	98.44 (11)	C8—C9—H9B	109.5
C8—O1—C7	106.94 (19)	H9A—C9—H9B	109.5
C8—C1—C2	107.5 (2)	C8—C9—H9C	109.5
C8—C1—S	121.0 (2)	H9A—C9—H9C	109.5
C2—C1—S	131.48 (19)	H9B—C9—H9C	109.5
C3—C2—C7	119.1 (2)	C15—C10—C11	121.0 (3)
C3—C2—C1	136.5 (2)	C15—C10—S	118.73 (19)
C7—C2—C1	104.4 (2)	C11—C10—S	120.1 (2)
C4—C3—C2	117.1 (2)	C12—C11—C10	119.3 (3)
C4—C3—H3	121.4	C12—C11—H11	120.3
C2—C3—H3	121.4	C10—C11—H11	120.3
C3—C4—C5	122.8 (2)	C13—C12—C11	118.6 (3)
C3—C4—I	120.02 (19)	C13—C12—H12	120.7
C5—C4—I	117.21 (19)	C11—C12—H12	120.7
C6—C5—C4	120.3 (2)	F—C13—C14	118.1 (3)
C6—C5—H5	119.9	F—C13—C12	118.9 (3)
C4—C5—H5	119.9	C14—C13—C12	123.0 (3)
C7—C6—C5	116.6 (2)	C13—C14—C15	118.5 (3)
C7—C6—H6	121.7	C13—C14—H14	120.8
C5—C6—H6	121.7	C15—C14—H14	120.8
C6—C7—O1	125.4 (2)	C10—C15—C14	119.5 (2)
C6—C7—C2	124.1 (2)	C10—C15—H15	120.2
O1—C7—C2	110.5 (2)	C14—C15—H15	120.2
C1—C8—O1	110.7 (2)		

Symmetry codes: (i) *x*, −*y*+1/2, *z*+1/2.

Hydrogen-bond geometry (Å, °)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
C5—H5···O1^{ii}	0.93	2.55	3.472 (3)	170
C9—H9C···O2^{iii}	0.96	2.53	3.277 (3)	135

Symmetry codes: (ii) −*x*+2, *y*−1/2, −*z*+3/2; (iii) *x*, −*y*+3/2, *z*+1/2.

Fig. 1

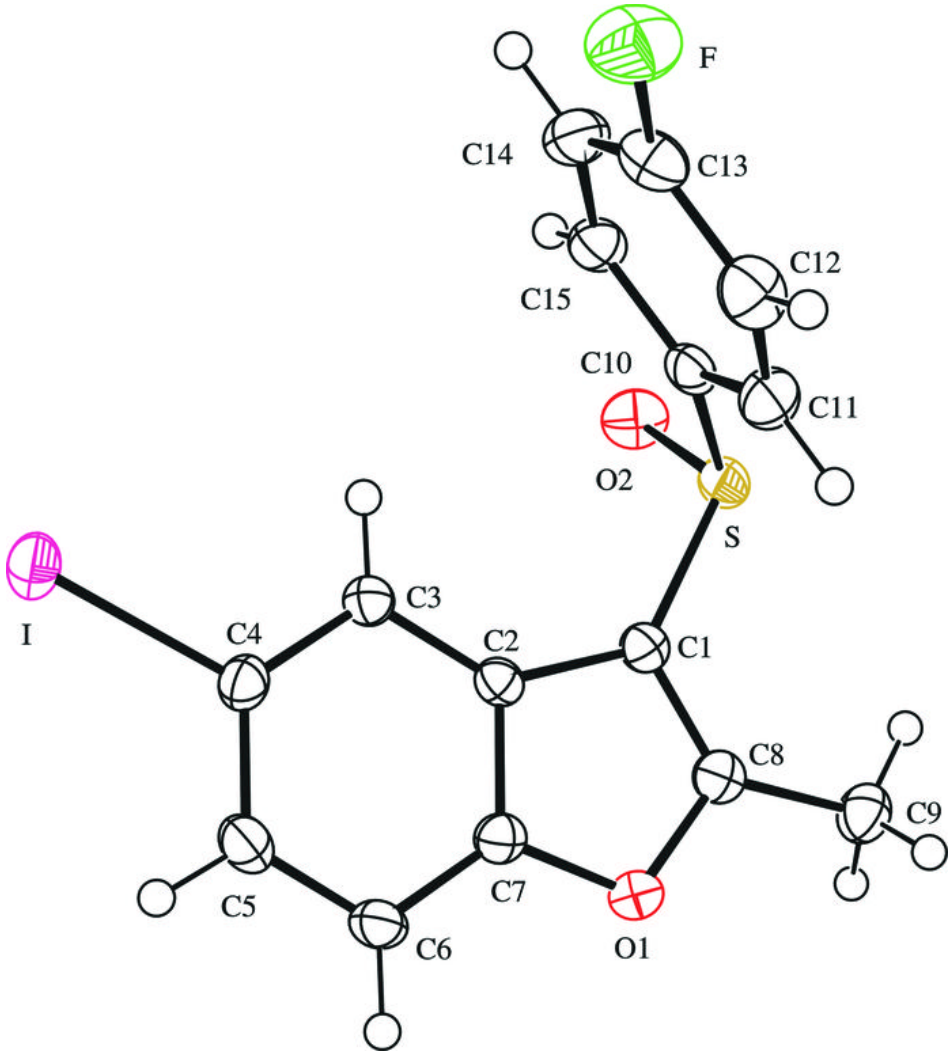


Fig. 2

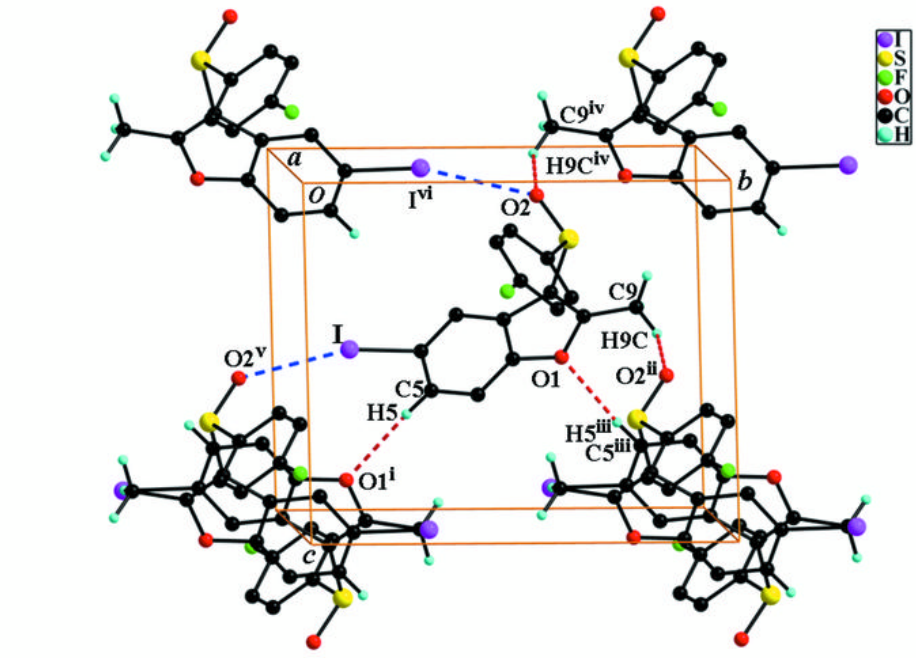
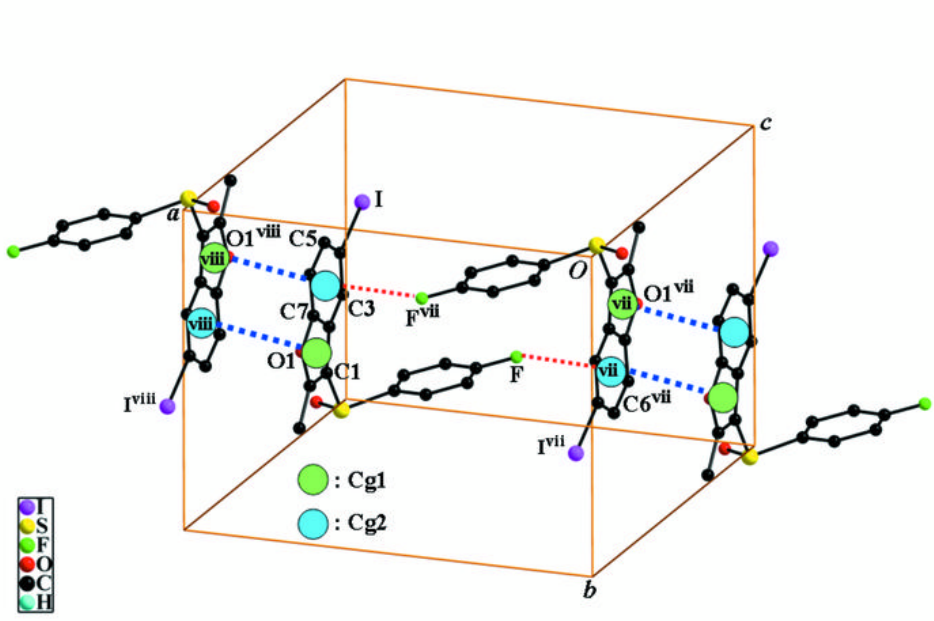

I
S
F
O
C
H
a
o
b
c
C9iv
H9Civ
Ivi
O2
C9
H9C
O2ii
O1
I
O2v
C5
H5
O1i
H5iii
C5iii

Fig. 3


a
c
b
I
O1viii
C5
viii
C7
C3
Fvii
O
O1vii
vii
viii
O1
C1
F
Iviii
C6vii
Ivii
: Cg1
: Cg2
I
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F
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H

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(2*R**,6*S**)-*tert*-Butyl 2,6-bis(hydroxymethyl)morpholine-4-carboxylate

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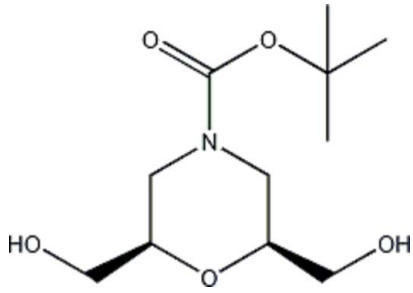
Key indicators: single-crystal X-ray study; T = 293 K; mean σ(C–C) = 0.004 Å; disorder in main residue; R factor = 0.066; wR factor = 0.199; data-to-parameter ratio = 14.3.

In the title compound, $C_{11}H_{21}NO_5$, the H atoms of the hydroxy groups are disordered over two positions, each in a 1:1 ratio. In the crystal, intermolecular O—H···O hydrogen bonds link pairs of molecules into centrosymmetric dimers. Weak intermolecular O—H···O interactions further link these dimers into chains extended in the [100] direction.

Related literature

For details of the synthesis of 2,6-disubstituted morpholines, see: Dave & Sasaki (2004); Lupi *et al.* (2004).



Experimental

Crystal data

$C_{11}H_{21}NO_5$
M_r = 247.29
Monoclinic, $C2/c$
a = 21.909 (3) Å
b = 5.6643 (8) Å
c = 22.510 (3) Å
β = 107.612 (3)°
V = 2662.5 (7) Å^3
Z = 8
Mo $K\alpha$ radiation
μ = 0.10 mm^{-1}
T = 293 K
0.45 × 0.34 × 0.21 mm

Data collection

Bruker SMART CCD area-detector diffractometer
6675 measured reflections
2476 independent reflections
1699 reflections with $I > 2\sigma(I)$
R_{int} = 0.086

Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.066
$wR(F^2)$ = 0.199
S = 1.06
2476 reflections
173 parameters
4 restraints
H atoms treated by a mixture of independent and constrained refinement
$\Delta\rho_{max}$ = 0.53 e Å^{-3}
$\Delta\rho_{min}$ = −0.38 e Å^{-3}

Table 1
Hydrogen-bond geometry (Å, °).

D—H···A	D—H	H···A	D···A	D—H···A
O3—H3D···O3^{i}	0.82 (3)	2.02 (3)	2.809 (4)	164 (6)
O2—H2E···O3^{i}	0.86 (3)	1.99 (3)	2.849 (3)	176 (5)
O2—H2D···O4^{ii}	0.82 (4)	2.48 (5)	3.269 (4)	163 (6)

Symmetry codes: (i) $-x+1, -y+3, -z$; (ii) $-x+\frac{1}{2}, -y+\frac{5}{2}, -z$.

Data collection: *SMART* (Bruker, 2002); cell refinement: *SAINT* (Bruker, 2002); data reduction: *SAINT*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *SHELXTL* (Sheldrick, 2008); software used to prepare material for publication: *SHELXTL*.

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Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: CV2712).

References

Bruker (2002). *SMART* and *SAINT*. Bruker AXS Inc., Madison, Wisconsin, USA.
Dave, R. & Sasaki, N. A. (2004). *Org. Lett.* **6**, 15–18.
Lupi, V., Albanese, D., Landini, D., Scaletti, D. & Penso, M. (2004). *Tetrahedron*, **60**, 11709–11718.
Sheldrick, G. M. (2008). *Acta Cryst.* A**64**, 112–122.

supplementary materials

Acta Cryst. (2010). E**66**, o1623 [**doi:10.1107/S1600536810017599**]

(2*R**,6*S**)-*tert*-Butyl 2,6-bis(hydroxymethyl)morpholine-4-carboxylate

Q. Chen, B. Li and G. Xia

Comment

Morpholine and its derivatives have been widely investigated (Lupi *et al.*, 2004; Dave &Sasaki, 2004) due to their importance in the search of new therapeutically and biologically active compounds. In the present paper, we report the crystal structure of the title compound, (I).

In (I) (Fig. 1), the H atoms of two hydroxy groups are disordered over two positions each in a ratio 1:1. In the crystal, intermolecular O—H···O hydrogen bonds (Table 1) link two molecules into centrosymmetric dimer. Weak intermolecular O—H···O interactions [O···O 3.269 (4) Å] (Table 1) link further these dimers into chains extended in direction [100].

Experimental

A mixture of (*S*)-(+)-benzyl glycidyl ether(9.84 g,60 mmol) and benzylamine(3.21 g,30 mmol) was heated with stirring at 60 centidegrees for 16 h. After being cooled to room temperature, an oil crude product (A) was obtained. Under ice-bath cooling, compound A (4.36 g,10 mmol) was dissolved in dry tetrahydrofuran (90 mL), 60% NaOH (1.0 g,25 mmol) was added over 15 minutes. The reaction mixture was stirred at 0 centidegrees for 30 minutes.Then a solution of TsCl(1.9 g,10 mmol) in dry THF(10 mL) was added dropwise over 30 minutes. After 10 min the solution was allowed to react at rt for 30 minutes and then heated at 50 centidegree until complete (usually about 2 h). After addition of an appropriate volume of 100 mL water, the aqueous layer was extracted three times with ethyl ether (30 mL). The combined organic layers were dried over anhydrous sodium sulfate and the solvent was removed and gave a yellow oil product(II). A solution of product II(2.09,5 mm mol) and acetic acid(10 mL) in methanol (30 mL) was treated with 10%Pd/C(200 mg) and then hydrogenated until complete(24 h). The catalyst was filtered and the solvent removed under reduced pressure.The pure product(III) was obtained. Product III was reacted with Boc anhydride to gave the target product. The target product was recrystallized from dry ether. Colourless crystals suitable for single crystal X-ray diffraction were obtained.

Refinement

H atoms bonded to O2 and O3 were each positioned in two possible idealized positions with occupancies fixed to 0.5, and were isotropically refined with the O—H bond length restrained to 0.82 (3) Å. C-bound H atoms were geometrically positioned (C—H = 0.96-0.98 Å) and treated as riding, with U_{iso}(H)=1.2-1.5 U_{eq}(C).

Figures

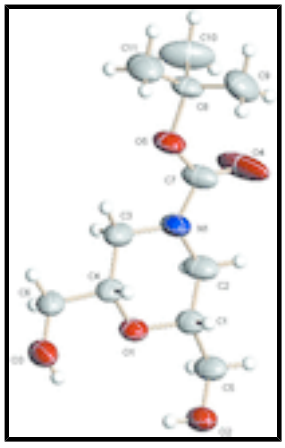


Fig. 1. The molecular structure of (I) showing the atomic numbering and 30% probability displacement ellipsoids. For each of two disordered H atoms (bound to O2 and O3) only one position is shown.

(2*R**,6*S**)-*tert*-Butyl 2,6-bis(hydroxymethyl)morpholine-4-carboxylate

Crystal data

$C_{11}H_{21}NO_5$	$F(000) = 1072$
$M_r = 247.29$	$D_x = 1.234$ Mg m^{-3}
Monoclinic, *C*2/*c*	Mo *K*α radiation, λ = 0.71073 Å
a = 21.909 (3) Å	Cell parameters from 1734 reflections
b = 5.6643 (8) Å	θ = 4.6–44.5°
c = 22.510 (3) Å	μ = 0.10 mm^{-1}
β = 107.612 (3)°	*T* = 293 K
V = 2662.5 (7) Å^3	Prismatic, colourless
Z = 8	0.45 × 0.34 × 0.21 mm

Data collection

Bruker SMART CCD area-detector diffractometer	1699 reflections with $I > 2\sigma(I)$
Radiation source: fine-focus sealed tube	$R_{int} = 0.086$
graphite	$\theta_{max} = 25.5°$, $\theta_{min} = 1.9°$
φ and ω scans	*h* = −26→25
6675 measured reflections	*k* = −6→6
2476 independent reflections	*l* = −27→19

Refinement

Refinement on F^2	Primary atom site location: structure-invariant direct methods
Least-squares matrix: full	Secondary atom site location: difference Fourier map
$R[F^2 > 2\sigma(F^2)] = 0.066$	Hydrogen site location: inferred from neighbouring sites

$wR(F^2) = 0.199$	H atoms treated by a mixture of independent and constrained refinement
$S = 1.06$	$w = 1/[\sigma^2(F_o^2) + (0.0978P)^2 + 0.9544P]$ where $P = (F_o^2 + 2F_c^2)/3$
2476 reflections	$(\Delta/\sigma)_{max} = 0.028$
173 parameters	$\Delta\rho_{max} = 0.53$ e Å^{-3}
4 restraints	$\Delta\rho_{min} = -0.38$ e Å^{-3}

Special details

Geometry. All esds (except the esd in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell esds are taken into account individually in the estimation of esds in distances, angles and torsion angles; correlations between esds in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell esds is used for estimating esds involving l.s. planes.

Refinement. Geometry. All esds (except the esd in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell esds are taken into account individually in the estimation of esds in distances, angles and torsion angles; correlations between esds in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell esds is used for estimating esds involving l.s. planes. Refinement. Refinement of F2 against ALL reflections. The weighted *R*-factor wR and goodness of fit *S* are based on F2, conventional *R*-factors *R* are based on *F*, with *F* set to zero for negative F2. The threshold expression of F2 > σ(F2) is used only for calculating *R*-factors(gt) etc. and is not relevant to the choice of reflections for refinement. *R*-factors based on F2 are statistically about twice as large as those based on *F*, and *R*- factors based on ALL data will be even larger.

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å^2)

	x	*y*	*z*	U_{iso}*/U_{eq}	Occ. (<1)
O1	0.41734 (8)	1.2127 (3)	0.00900 (7)	0.0487 (5)	
O2	0.33480 (10)	1.4453 (4)	−0.09361 (9)	0.0668 (6)	
O3	0.53146 (9)	1.4619 (4)	0.06357 (9)	0.0638 (6)	
O4	0.28864 (15)	0.7185 (5)	0.10144 (10)	0.1312 (14)	
O5	0.38194 (9)	0.7747 (3)	0.17686 (8)	0.0598 (6)	
N1	0.36921 (10)	0.9179 (4)	0.08274 (10)	0.0584 (6)	
C1	0.34976 (12)	1.1868 (5)	−0.00456 (11)	0.0503 (7)	
H1	0.3335	1.3098	0.0172	0.060*	
C2	0.33469 (15)	0.9479 (5)	0.01673 (12)	0.0650 (8)	
H2A	0.2890	0.9344	0.0102	0.078*	
H2B	0.3472	0.8254	−0.0074	0.078*	
C3	0.43769 (13)	0.9642 (5)	0.09948 (13)	0.0622 (8)	
H3A	0.4584	0.8401	0.0829	0.075*	
H3B	0.4558	0.9643	0.1445	0.075*	
C4	0.44998 (11)	1.1985 (4)	0.07397 (10)	0.0477 (6)	
H4	0.4348	1.3251	0.0956	0.057*	
C5	0.32122 (14)	1.2194 (5)	−0.07387 (12)	0.0623 (8)	
H5A	0.3381	1.0993	−0.0953	0.075*	
H5B	0.2752	1.1985	−0.0851	0.075*	
C6	0.51984 (12)	1.2342 (5)	0.08203 (12)	0.0566 (7)	
H6A	0.5442	1.2103	0.1254	0.068*	
H6B	0.5341	1.1185	0.0573	0.068*	

C7	0.34176 (15)	0.7944 (5)	0.11901 (12)	0.0621 (8)	
C8	0.36300 (13)	0.6503 (5)	0.22584 (11)	0.0527 (7)	
C9	0.30285 (16)	0.7518 (6)	0.23374 (18)	0.0880 (11)	
H9A	0.3061	0.9208	0.2358	0.132*	
H9B	0.2968	0.6926	0.2715	0.132*	
H9C	0.2670	0.7071	0.1989	0.132*	
C10	0.3569 (2)	0.3929 (6)	0.21181 (18)	0.1117 (15)	
H10A	0.3211	0.3662	0.1753	0.168*	
H10B	0.3503	0.3098	0.2465	0.168*	
H10C	0.3953	0.3367	0.2045	0.168*	
C11	0.41842 (16)	0.7042 (7)	0.28251 (14)	0.0860 (11)	
H11A	0.4570	0.6392	0.2773	0.129*	
H11B	0.4108	0.6357	0.3186	0.129*	
H11C	0.4230	0.8721	0.2878	0.129*	
H2E	0.3751 (10)	1.474 (9)	−0.083 (2)	0.050 (15)*	0.50
H3E	0.5706 (11)	1.495 (9)	0.074 (3)	0.056 (16)*	0.50
H2D	0.303 (2)	1.529 (11)	−0.104 (3)	0.09 (3)*	0.50
H3D	0.507 (2)	1.477 (10)	0.0285 (13)	0.055 (16)*	0.50

Atomic displacement parameters (Å^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
O1	0.0563 (11)	0.0596 (11)	0.0309 (9)	−0.0055 (8)	0.0143 (8)	0.0060 (7)
O2	0.0609 (14)	0.0802 (15)	0.0548 (12)	−0.0088 (12)	0.0109 (11)	0.0241 (11)
O3	0.0524 (12)	0.0870 (15)	0.0460 (12)	−0.0197 (10)	0.0059 (10)	0.0093 (10)
O4	0.147 (2)	0.169 (3)	0.0511 (13)	−0.123 (2)	−0.0095 (14)	0.0263 (15)
O5	0.0710 (12)	0.0721 (12)	0.0389 (10)	−0.0173 (9)	0.0205 (9)	0.0112 (8)
N1	0.0625 (14)	0.0725 (15)	0.0412 (12)	−0.0083 (11)	0.0172 (10)	0.0176 (11)
C1	0.0550 (15)	0.0575 (16)	0.0366 (13)	−0.0072 (12)	0.0113 (12)	0.0049 (11)
C2	0.083 (2)	0.0706 (19)	0.0403 (15)	−0.0186 (15)	0.0171 (14)	0.0078 (13)
C3	0.0615 (17)	0.0780 (19)	0.0519 (16)	0.0106 (14)	0.0243 (14)	0.0236 (14)
C4	0.0539 (15)	0.0601 (15)	0.0305 (12)	0.0048 (11)	0.0149 (11)	0.0068 (11)
C5	0.0687 (17)	0.0713 (18)	0.0415 (15)	−0.0159 (14)	0.0084 (13)	0.0121 (13)
C6	0.0551 (16)	0.0737 (19)	0.0406 (14)	0.0023 (13)	0.0143 (12)	0.0147 (13)
C7	0.086 (2)	0.0583 (16)	0.0398 (15)	−0.0304 (15)	0.0167 (14)	0.0014 (12)
C8	0.0714 (17)	0.0535 (15)	0.0382 (14)	−0.0117 (12)	0.0242 (13)	0.0085 (11)
C9	0.084 (2)	0.101 (3)	0.096 (3)	−0.0023 (18)	0.053 (2)	0.019 (2)
C10	0.212 (5)	0.0526 (19)	0.087 (3)	−0.011 (2)	0.070 (3)	0.0050 (19)
C11	0.087 (2)	0.119 (3)	0.0514 (18)	−0.0166 (19)	0.0197 (17)	0.0188 (18)

Geometric parameters (Å, °)

O1—C4	1.422 (3)	C3—H3A	0.9700
O1—C1	1.426 (3)	C3—H3B	0.9700
O2—C5	1.415 (3)	C4—C6	1.499 (3)
O2—H2E	0.858 (19)	C4—H4	0.9800
O2—H2D	0.82 (2)	C5—H5A	0.9700
O3—C6	1.402 (3)	C5—H5B	0.9700
O3—H3E	0.84 (2)	C6—H6A	0.9700

O3—H3D	0.817 (19)	C6—H6B	0.9700
O4—C7	1.191 (4)	C8—C10	1.489 (4)
O5—C7	1.338 (3)	C8—C9	1.497 (4)
O5—C8	1.470 (3)	C8—C11	1.503 (4)
N1—C7	1.347 (3)	C9—H9A	0.9600
N1—C3	1.456 (3)	C9—H9B	0.9600
N1—C2	1.459 (3)	C9—H9C	0.9600
C1—C2	1.505 (4)	C10—H10A	0.9600
C1—C5	1.506 (3)	C10—H10B	0.9600
C1—H1	0.9800	C10—H10C	0.9600
C2—H2A	0.9700	C11—H11A	0.9600
C2—H2B	0.9700	C11—H11B	0.9600
C3—C4	1.502 (4)	C11—H11C	0.9600
C4—O1—C1	112.38 (18)	C1—C5—H5A	109.2
C5—O2—H2E	112 (3)	O2—C5—H5B	109.2
C5—O2—H2D	112 (5)	C1—C5—H5B	109.2
H2E—O2—H2D	134 (6)	H5A—C5—H5B	107.9
C6—O3—H3E	113 (4)	O3—C6—C4	111.0 (2)
C6—O3—H3D	105 (4)	O3—C6—H6A	109.4
H3E—O3—H3D	125 (6)	C4—C6—H6A	109.4
C7—O5—C8	121.21 (19)	O3—C6—H6B	109.4
C7—N1—C3	123.4 (2)	C4—C6—H6B	109.4
C7—N1—C2	119.3 (2)	H6A—C6—H6B	108.0
C3—N1—C2	114.8 (2)	O4—C7—O5	125.6 (2)
O1—C1—C2	109.8 (2)	O4—C7—N1	123.9 (3)
O1—C1—C5	106.7 (2)	O5—C7—N1	110.5 (2)
C2—C1—C5	112.2 (2)	O5—C8—C10	109.7 (2)
O1—C1—H1	109.4	O5—C8—C9	111.3 (2)
C2—C1—H1	109.4	C10—C8—C9	112.0 (3)
C5—C1—H1	109.4	O5—C8—C11	101.6 (2)
N1—C2—C1	109.5 (2)	C10—C8—C11	112.1 (3)
N1—C2—H2A	109.8	C9—C8—C11	109.6 (3)
C1—C2—H2A	109.8	C8—C9—H9A	109.5
N1—C2—H2B	109.8	C8—C9—H9B	109.5
C1—C2—H2B	109.8	H9A—C9—H9B	109.5
H2A—C2—H2B	108.2	C8—C9—H9C	109.5
N1—C3—C4	110.5 (2)	H9A—C9—H9C	109.5
N1—C3—H3A	109.5	H9B—C9—H9C	109.5
C4—C3—H3A	109.6	C8—C10—H10A	109.5
N1—C3—H3B	109.6	C8—C10—H10B	109.5
C4—C3—H3B	109.5	H10A—C10—H10B	109.5
H3A—C3—H3B	108.1	C8—C10—H10C	109.5
O1—C4—C6	107.10 (19)	H10A—C10—H10C	109.5
O1—C4—C3	110.5 (2)	H10B—C10—H10C	109.5
C6—C4—C3	111.5 (2)	C8—C11—H11A	109.5
O1—C4—H4	109.2	C8—C11—H11B	109.5
C6—C4—H4	109.2	H11A—C11—H11B	109.5
C3—C4—H4	109.2	C8—C11—H11C	109.5
O2—C5—C1	112.0 (2)	H11A—C11—H11C	109.5

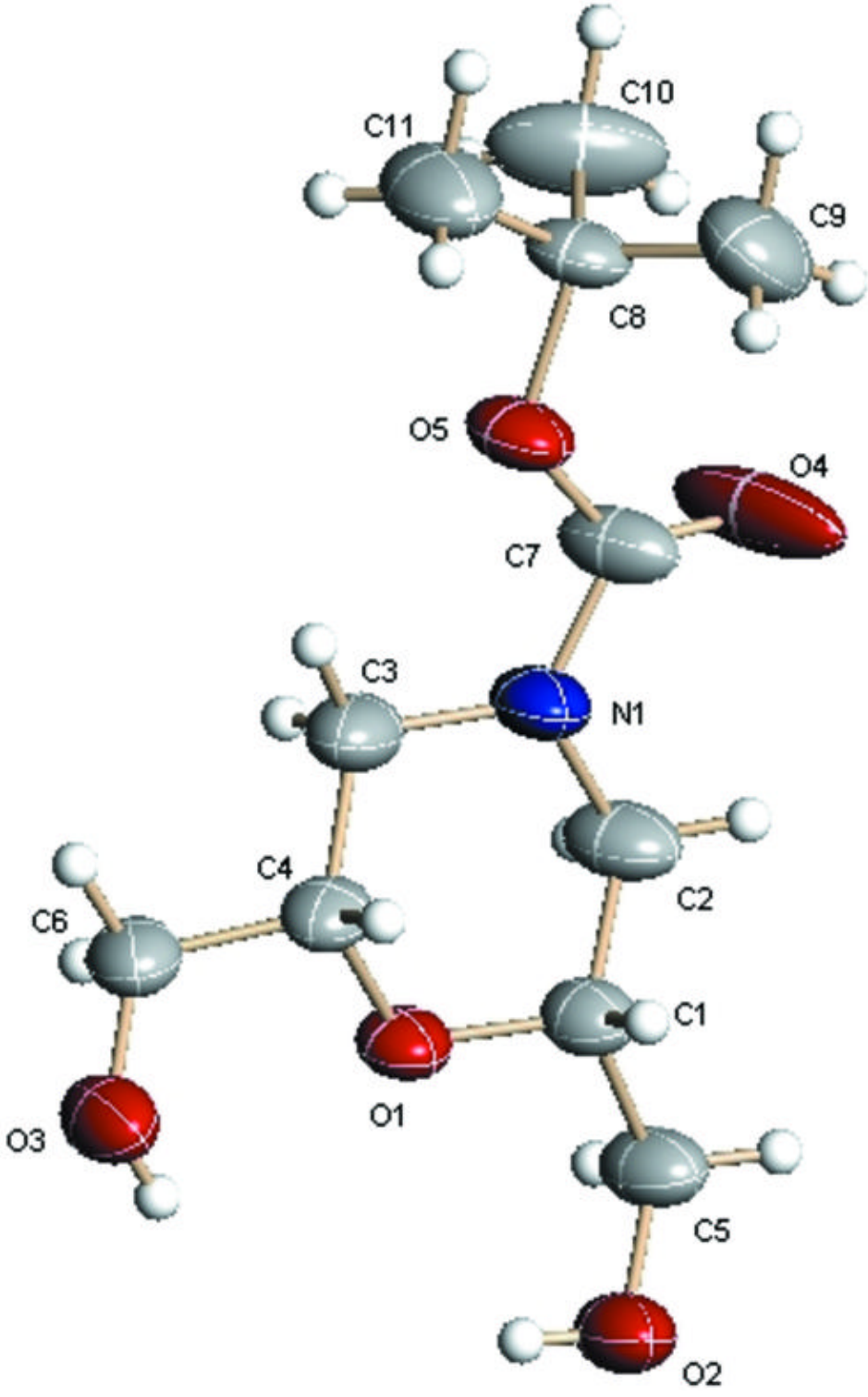
O2—C5—H5A	109.2	H11B—C11—H11C	109.5
C4—O1—C1—C2	−61.4 (3)	C2—C1—C5—O2	179.3 (2)
C4—O1—C1—C5	176.8 (2)	O1—C4—C6—O3	64.6 (3)
C7—N1—C2—C1	145.5 (3)	C3—C4—C6—O3	−174.3 (2)
C3—N1—C2—C1	−52.0 (3)	C8—O5—C7—O4	0.4 (5)
O1—C1—C2—N1	55.4 (3)	C8—O5—C7—N1	179.1 (2)
C5—C1—C2—N1	173.9 (2)	C3—N1—C7—O4	−165.7 (3)
C7—N1—C3—C4	−147.9 (3)	C2—N1—C7—O4	−4.8 (5)
C2—N1—C3—C4	50.5 (3)	C3—N1—C7—O5	15.6 (4)
C1—O1—C4—C6	−178.62 (19)	C2—N1—C7—O5	176.5 (2)
C1—O1—C4—C3	59.7 (3)	C7—O5—C8—C10	68.9 (4)
N1—C3—C4—O1	−52.3 (3)	C7—O5—C8—C9	−55.7 (3)
N1—C3—C4—C6	−171.3 (2)	C7—O5—C8—C11	−172.3 (3)
O1—C1—C5—O2	−60.5 (3)		

Hydrogen-bond geometry (Å, °)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
O3—H3D···O3^{i}	0.82 (3)	2.02 (3)	2.809 (4)	164 (6)
O2—H2E···O3^{i}	0.86 (3)	1.99 (3)	2.849 (3)	176 (5)
O2—H2D···O4^{ii}	0.82 (4)	2.48 (5)	3.269 (4)	163 (6)

Symmetry codes: (i) −*x*+1, −*y*+3, −*z*; (ii) −*x*+1/2, −*y*+5/2, −*z*.

Fig. 1



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8b,8c-Diphenyl-2,6-bis(4-pyridylmethyl)-perhydro-2,3a,4a,6,7a,8a-hexaazacyclopenta[*def*]fluorene-4,8-dithione chloroform solvate

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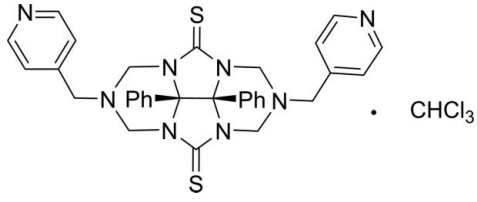
Key indicators: single-crystal X-ray study; T = 294 K; mean σ(C–C) = 0.008 Å; R factor = 0.062; wR factor = 0.210; data-to-parameter ratio = 13.7.

In the thioglycoluril system of the title compound, $C_{32}H_{30}N_8S_2\cdot CHCl_3$, the two pyridine rings are roughly parallel, forming a dihedral angle of 7.2 (1)°, and the distance between the centroids of the two phenyl rings is 3.951 (5) Å. The chloroform solvent molecule is linked to the main molecule *via* a weak C—H···N hydrogen bond.

Related literature

For applications of glycoluril derivatives, see: Rowan *et al.* (1999). For the preparation of the title compound, see: Broan *et al.* (1989); Li *et al.* (2008).



Experimental

Crystal data

$C_{32}H_{30}N_8S_2\cdot CHCl_3$ M_r = 710.13
Triclinic, $P\overline{1}$
a = 9.5381 (6) Å
b = 12.1712 (8) Å
c = 14.8765 (9) Å
α = 100.978 (1)°
β = 91.699 (1)°
γ = 98.500 (1)°
V = 1673.81 (18) Å^3
Z = 2
Mo $K\alpha$ radiation
μ = 0.44 mm^{-1}
T = 294 K
0.20 × 0.10 × 0.10 mm

Data collection

Bruker SMART APEX CCD area-detector diffractometer
11061 measured reflections
5690 independent reflections
2136 reflections with $I > 2\sigma(I)$
R_{int} = 0.109

Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.062
$wR(F^2)$ = 0.210
S = 0.85
5690 reflections
415 parameters
H-atom parameters constrained
$\Delta\rho_{max}$ = 0.47 e Å^{-3}
$\Delta\rho_{min}$ = −0.39 e Å^{-3}

Table 1
Hydrogen-bond geometry (Å, °).

D—H···A	D—H	H···A	D···A	D—H···A
C33—H33···N8^{i}	0.98	2.33	3.168 (9)	142 (8)

Symmetry code: (i) $-x+2, -y+1, -z+1$.

Data collection: *SMART* (Bruker, 1997); cell refinement: *SAINT* (Bruker, 1999); data reduction: *SAINT*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *SHELXTL* (Sheldrick, 2008); software used to prepare material for publication: *SHELXTL*.

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Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: CV2714).

References

Broan, C. J., Butler, A. R., Reed, D. & Sadler, I. H. (1989). *J. Chem. Soc. Perkin Trans. 2*, pp. 731–740.
Bruker (1997). *SMART*. Bruker AXS Inc., Madison, Wisconsin, USA.
Bruker (1999). *SAINT*. Bruker AXS Inc., Madison, Wisconsin, USA.
Li, Y. T., Meng, X. G., Cao, L. P., Wang, Y. Z., Yin, G. D., Gao, M., Wen, L. L. & Wu, A. X. (2008). *Cryst. Growth Des.* **8**, 1645–1653.
Rowan, A. E., Elemans, J. A. A. W. & Nolte, R. J. M. (1999). *Acc. Chem. Res.* **32**, 995–1006.
Sheldrick, G. M. (2008). *Acta Cryst.* A**64**, 112–122.

supplementary materials

Acta Cryst. (2010). E**66**, o1524 [**doi:10.1107/S1600536810020040**]

8b,8c-Diphenyl-2,6-bis(4-pyridylmethyl)perhydro-2,3a,4a,6,7a,8a-hexaazacyclopenta[*def*]fluorene-4,8-dithione chloroform solvate

C. Deng, W. Shu and D. Zhang

Comment

Recently, molecular clips based on concave glycoluril unit have been widely investigated in supramolecular chemistry (Rowan *et al.*, 1999). We report here the structure of the title compound (Fig. 1), which is a derivative of thioglycoluril with two pyridine units. We believe the title compound would offer the possibility in construction of coordination framework with novel patterns (Li *et al.*, 2008). The crystal packing exhibits weak intermolecular C—H···N hydrogen bond (Table 1) between the chloroform solvent molecule and the main molecule.

Experimental

The title compound was synthesized according to the literature (Broan *et al.*, 1989; Li *et al.*, 2008). Crystals of (I) suitable for X-ray diffraction were grown by slow evaporation of a chloroform-methanol (1:2) solution of the title compound under 293 K.

Refinement

All H atoms were positioned in geometrically idealized positions and constrained to ride on their parent atoms, with C—H distances in the range 0.93-0.98 Å and $U_{iso}(H) = 1.2\text{-}1.5U_{eq}(C)$. The low ratio observed/unique reflections (0.38) was mainly caused by poor quality of the crystal selected for measurements.

Figures

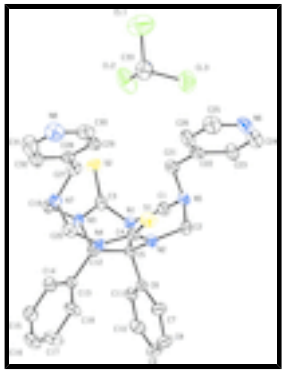


Fig. 1. A view of (I), showing the atom-labelling scheme, with displacement ellipsoids drawn at the 30% probability level.

8b,8c-Diphenyl-2,6-bis(4-pyridylmethyl)perhydro-2,3a,4a,6,7a,8a- hexaazacyclopenta[*def*]fluorene-4,8-dithione chloroform solvate

Crystal data

$C_{32}H_{30}N_8S_2{\cdot}CHCl_3$	V = 1673.81 (18) Å^3
M_r = 710.13	Z = 2
Triclinic, $P\overline{1}$	$F(000)$ = 736
Hall symbol: -P 1	D_x = 1.409 Mg m^{-3}
a = 9.5381 (6) Å	Mo $K\alpha$ radiation, λ = 0.71073 Å
b = 12.1712 (8) Å	μ = 0.44 mm^{-1}
c = 14.8765 (9) Å	T = 294 K
α = 100.978 (1)°	Block, colourless
β = 91.699 (1)°	0.20 × 0.10 × 0.10 mm
γ = 98.500 (1)°	

Data collection

Bruker SMART APEX CCD area-detector diffractometer	2136 reflections with $I > 2\sigma(I)$
Radiation source: fine-focus sealed tube	R_{int} = 0.109
graphite	θ_{max} = 25.0°, θ_{min} = 1.7°
phi and ω scans	h = −11→11
11061 measured reflections	k = −14→13
5690 independent reflections	l = −17→17

Refinement

Refinement on F^2	Primary atom site location: structure-invariant direct methods
Least-squares matrix: full	Secondary atom site location: difference Fourier map
$R[F^2 > 2\sigma(F^2)]$ = 0.062	Hydrogen site location: inferred from neighbouring sites
$wR(F^2)$ = 0.210	H-atom parameters constrained
S = 0.85	$w = 1/[\sigma^2(F_o^2) + (0.1041P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
5690 reflections	$(\Delta/\sigma)_{max}$ = 0.001
415 parameters	$\Delta\rho_{max}$ = 0.47 e Å^{-3}
0 restraints	$\Delta\rho_{min}$ = −0.39 e Å^{-3}

Special details

Geometry. All esds (except the esd in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell esds are taken into account individually in the estimation of esds in distances, angles and torsion angles; correlations between esds in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell esds is used for estimating esds involving l.s. planes.

Refinement. Refinement of F^2 against ALL reflections. The weighted *R*-factor wR and goodness of fit *S* are based on F^2, conventional *R*-factors *R* are based on *F*, with *F* set to zero for negative F^2. The threshold expression of $F^2 > \sigma(F^2)$ is used only for calculating *R*-factors(gt) etc. and is not relevant to the choice of reflections for refinement. *R*-factors based on F^2 are statistically about twice as large as those based on *F*, and *R*- factors based on ALL data will be even larger. Because of the poor quality of crystal, the ratio of Observed/Unique Reflections is 38%.

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å^2)

	x	*y*	*z*	U_{iso}*/U_{eq}
C1	0.4638 (5)	0.4696 (4)	0.1361 (4)	0.0426 (14)
H1A	0.4056	0.4515	0.0790	0.051*
H1B	0.4486	0.5435	0.1685	0.051*
C2	0.6423 (6)	0.3623 (4)	0.0735 (4)	0.0461 (15)
H2A	0.7434	0.3659	0.0658	0.055*
H2B	0.5934	0.3385	0.0133	0.055*
C3	0.4314 (5)	0.4077 (4)	0.2860 (4)	0.0395 (14)
C4	0.6795 (5)	0.2382 (4)	0.1877 (4)	0.0391 (14)
C5	0.4489 (5)	0.2700 (4)	0.1553 (3)	0.0295 (12)
C6	0.3463 (5)	0.2069 (4)	0.0750 (3)	0.0344 (13)
C7	0.3908 (6)	0.1281 (5)	0.0063 (4)	0.0518 (16)
H7	0.4868	0.1222	0.0040	0.062*
C8	0.2952 (6)	0.0585 (5)	−0.0584 (4)	0.0565 (17)
H8	0.3262	0.0045	−0.1031	0.068*
C9	0.1541 (7)	0.0688 (5)	−0.0572 (4)	0.0590 (17)
H9	0.0895	0.0223	−0.1014	0.071*
C10	0.1082 (6)	0.1478 (5)	0.0096 (4)	0.0546 (16)
H10	0.0125	0.1551	0.0104	0.065*
C11	0.2042 (6)	0.2160 (4)	0.0753 (4)	0.0436 (15)
H11	0.1725	0.2690	0.1205	0.052*
C12	0.4498 (5)	0.2132 (4)	0.2406 (3)	0.0322 (13)
C13	0.3367 (5)	0.1100 (4)	0.2397 (3)	0.0351 (13)
C14	0.2062 (6)	0.1236 (5)	0.2759 (4)	0.0567 (17)
H14	0.1877	0.1954	0.3020	0.068*
C15	0.1037 (7)	0.0290 (6)	0.2726 (4)	0.0675 (19)
H15	0.0167	0.0376	0.2975	0.081*
C16	0.1289 (7)	−0.0762 (6)	0.2335 (5)	0.077 (2)
H16	0.0588	−0.1389	0.2304	0.093*
C17	0.2577 (7)	−0.0896 (5)	0.1986 (5)	0.072 (2)
H17	0.2765	−0.1614	0.1730	0.086*
C18	0.3601 (6)	0.0048 (5)	0.2017 (4)	0.0570 (17)
H18	0.4470	−0.0045	0.1770	0.068*
C19	0.4813 (6)	0.2929 (4)	0.4068 (3)	0.0455 (15)
H19A	0.4783	0.3621	0.4511	0.055*
H19B	0.4162	0.2327	0.4245	0.055*
C20	0.6388 (6)	0.1716 (4)	0.3368 (4)	0.0469 (15)
H20A	0.5837	0.1033	0.3497	0.056*
H20B	0.7376	0.1611	0.3364	0.056*
C21	0.7120 (6)	0.5325 (5)	0.1933 (4)	0.0530 (16)

H21A	0.7130	0.4839	0.2379	0.064*
H21B	0.6786	0.6012	0.2227	0.064*
C22	0.8592 (6)	0.5619 (4)	0.1653 (4)	0.0482 (16)
C23	0.8900 (6)	0.6050 (5)	0.0882 (4)	0.0577 (17)
H23	0.8157	0.6157	0.0505	0.069*
C24	1.0254 (7)	0.6325 (5)	0.0652 (5)	0.068 (2)
H24	1.0400	0.6619	0.0124	0.081*
C25	1.1118 (7)	0.5806 (6)	0.1887 (5)	0.073 (2)
H25	1.1882	0.5730	0.2261	0.088*
C26	0.9754 (8)	0.5499 (6)	0.2152 (5)	0.075 (2)
H26	0.9635	0.5204	0.2682	0.090*
C27	0.7389 (6)	0.3621 (5)	0.4180 (4)	0.0481 (15)
H27A	0.7105	0.4275	0.4570	0.058*
H27B	0.7554	0.3804	0.3582	0.058*
C28	0.8721 (5)	0.3375 (4)	0.4579 (4)	0.0384 (14)
C29	1.0046 (6)	0.3720 (4)	0.4278 (4)	0.0505 (16)
H29	1.0126	0.4087	0.3784	0.061*
C30	1.1231 (6)	0.3516 (5)	0.4715 (5)	0.0576 (18)
H30	1.2098	0.3761	0.4491	0.069*
C31	0.9976 (8)	0.2679 (6)	0.5694 (5)	0.084 (2)
H31	0.9927	0.2311	0.6189	0.101*
C32	0.8720 (7)	0.2838 (6)	0.5309 (5)	0.0676 (19)
H32	0.7865	0.2582	0.5542	0.081*
C33	0.6754 (7)	0.8554 (6)	0.3853 (5)	0.076 (2)
H33	0.6949	0.7839	0.4001	0.091*
Cl1	0.7802 (3)	0.9693 (2)	0.4618 (2)	0.1451 (11)
Cl2	0.4992 (2)	0.86364 (19)	0.39764 (19)	0.1222 (10)
Cl3	0.7234 (2)	0.86119 (18)	0.27531 (15)	0.1061 (8)
N1	0.4182 (4)	0.3843 (3)	0.1924 (3)	0.0370 (11)
N2	0.5961 (4)	0.2785 (3)	0.1304 (3)	0.0380 (12)
N3	0.4351 (4)	0.3080 (3)	0.3151 (3)	0.0349 (11)
N4	0.5925 (4)	0.1866 (3)	0.2456 (3)	0.0342 (11)
N5	0.6126 (5)	0.4746 (4)	0.1154 (3)	0.0446 (12)
N6	1.1383 (6)	0.6195 (4)	0.1144 (5)	0.0697 (17)
N7	0.6238 (4)	0.2652 (3)	0.4087 (3)	0.0388 (11)
N8	1.1278 (6)	0.3010 (5)	0.5420 (5)	0.0756 (17)
S1	0.85378 (14)	0.24229 (12)	0.18583 (10)	0.0545 (5)
S2	0.43168 (16)	0.53272 (12)	0.35358 (10)	0.0527 (5)

Atomic displacement parameters (Å^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
C1	0.042 (3)	0.042 (3)	0.044 (3)	0.002 (3)	0.006 (3)	0.013 (3)
C2	0.042 (3)	0.056 (4)	0.040 (3)	0.002 (3)	0.015 (3)	0.009 (3)
C3	0.026 (3)	0.050 (4)	0.046 (4)	0.009 (3)	0.014 (3)	0.012 (3)
C4	0.038 (3)	0.028 (3)	0.046 (3)	0.004 (3)	0.014 (3)	−0.006 (2)
C5	0.025 (3)	0.032 (3)	0.031 (3)	0.006 (2)	0.004 (2)	0.003 (2)
C6	0.039 (3)	0.032 (3)	0.032 (3)	0.001 (2)	0.010 (3)	0.006 (2)

C7	0.039 (3)	0.055 (4)	0.052 (4)	−0.002 (3)	0.013 (3)	−0.009 (3)
C8	0.047 (4)	0.063 (4)	0.047 (4)	0.000 (3)	0.006 (3)	−0.012 (3)
C9	0.061 (4)	0.058 (4)	0.046 (4)	−0.009 (3)	−0.003 (3)	−0.005 (3)
C10	0.034 (3)	0.055 (4)	0.072 (5)	−0.003 (3)	−0.002 (3)	0.014 (3)
C11	0.042 (3)	0.040 (3)	0.046 (4)	0.002 (3)	0.014 (3)	0.005 (3)
C12	0.026 (3)	0.032 (3)	0.037 (3)	0.001 (2)	0.007 (2)	0.005 (2)
C13	0.035 (3)	0.038 (3)	0.034 (3)	−0.002 (3)	0.000 (3)	0.015 (2)
C14	0.050 (4)	0.060 (4)	0.054 (4)	−0.006 (3)	0.018 (3)	0.007 (3)
C15	0.046 (4)	0.090 (5)	0.058 (4)	−0.019 (4)	0.009 (3)	0.013 (4)
C16	0.066 (5)	0.066 (5)	0.091 (5)	−0.026 (4)	0.008 (4)	0.020 (4)
C17	0.066 (5)	0.038 (4)	0.104 (6)	−0.006 (3)	−0.002 (4)	0.007 (4)
C18	0.044 (4)	0.039 (4)	0.083 (5)	−0.007 (3)	0.009 (3)	0.009 (3)
C19	0.053 (4)	0.047 (3)	0.036 (3)	0.006 (3)	0.014 (3)	0.008 (3)
C20	0.038 (3)	0.039 (3)	0.066 (4)	0.008 (3)	0.008 (3)	0.013 (3)
C21	0.050 (4)	0.047 (4)	0.053 (4)	−0.010 (3)	0.012 (3)	0.002 (3)
C22	0.039 (4)	0.040 (3)	0.060 (4)	−0.006 (3)	0.006 (3)	0.004 (3)
C23	0.041 (4)	0.067 (4)	0.066 (4)	0.001 (3)	0.012 (3)	0.022 (3)
C24	0.055 (4)	0.070 (5)	0.086 (5)	0.008 (4)	0.010 (4)	0.034 (4)
C25	0.034 (4)	0.101 (6)	0.083 (5)	0.000 (4)	−0.019 (4)	0.026 (5)
C26	0.065 (5)	0.082 (5)	0.077 (5)	−0.017 (4)	0.012 (4)	0.032 (4)
C27	0.051 (4)	0.048 (4)	0.044 (4)	0.008 (3)	0.002 (3)	0.005 (3)
C28	0.030 (3)	0.040 (3)	0.040 (3)	0.003 (3)	−0.006 (3)	0.000 (3)
C29	0.040 (4)	0.047 (4)	0.057 (4)	−0.007 (3)	0.009 (3)	0.002 (3)
C30	0.025 (3)	0.064 (4)	0.075 (5)	0.006 (3)	−0.008 (3)	−0.006 (4)
C31	0.069 (5)	0.110 (6)	0.084 (6)	0.004 (5)	−0.016 (5)	0.056 (5)
C32	0.042 (4)	0.085 (5)	0.078 (5)	−0.004 (4)	0.007 (4)	0.031 (4)
C33	0.083 (5)	0.081 (5)	0.075 (5)	0.032 (4)	0.004 (4)	0.029 (4)
Cl1	0.178 (3)	0.1084 (19)	0.139 (2)	0.0305 (19)	−0.036 (2)	0.0012 (17)
Cl2	0.0895 (16)	0.1205 (19)	0.178 (2)	0.0245 (14)	0.0594 (16)	0.0679 (17)
Cl3	0.1197 (18)	0.1078 (16)	0.0969 (16)	0.0181 (14)	0.0459 (14)	0.0292 (12)
N1	0.041 (3)	0.034 (2)	0.034 (3)	0.003 (2)	0.012 (2)	0.0037 (19)
N2	0.029 (3)	0.039 (3)	0.044 (3)	−0.001 (2)	0.013 (2)	0.005 (2)
N3	0.033 (2)	0.038 (3)	0.032 (3)	0.003 (2)	0.011 (2)	0.0018 (19)
N4	0.028 (2)	0.032 (2)	0.040 (3)	0.0028 (19)	0.003 (2)	0.0026 (19)
N5	0.041 (3)	0.044 (3)	0.046 (3)	−0.004 (2)	0.011 (2)	0.010 (2)
N6	0.062 (4)	0.056 (3)	0.090 (5)	−0.003 (3)	0.027 (4)	0.017 (3)
N7	0.030 (2)	0.043 (3)	0.042 (3)	0.003 (2)	0.002 (2)	0.008 (2)
N8	0.057 (4)	0.079 (4)	0.095 (5)	0.019 (3)	−0.005 (4)	0.021 (4)
S1	0.0312 (8)	0.0584 (10)	0.0680 (11)	0.0046 (7)	0.0157 (8)	−0.0022 (8)
S2	0.0588 (10)	0.0434 (9)	0.0501 (9)	0.0087 (8)	0.0122 (8)	−0.0072 (7)

Geometric parameters (Å, °)

C1—N5	1.456 (6)	C18—H18	0.9300
C1—N1	1.479 (6)	C19—N7	1.449 (6)
C1—H1A	0.9700	C19—N3	1.474 (6)
C1—H1B	0.9700	C19—H19A	0.9700
C2—N5	1.462 (6)	C19—H19B	0.9700
C2—N2	1.472 (6)	C20—N7	1.434 (6)

C2—H2A	0.9700	C20—N4	1.466 (7)
C2—H2B	0.9700	C20—H20A	0.9700
C3—N1	1.366 (6)	C20—H20B	0.9700
C3—N3	1.368 (6)	C21—N5	1.471 (7)
C3—S2	1.656 (5)	C21—C22	1.488 (7)
C4—N2	1.355 (6)	C21—H21A	0.9700
C4—N4	1.386 (6)	C21—H21B	0.9700
C4—S1	1.657 (5)	C22—C26	1.357 (8)
C5—N2	1.457 (5)	C22—C23	1.372 (8)
C5—N1	1.470 (5)	C23—C24	1.356 (8)
C5—C6	1.527 (7)	C23—H23	0.9300
C5—C12	1.557 (7)	C24—N6	1.329 (8)
C6—C11	1.376 (6)	C24—H24	0.9300
C6—C7	1.385 (6)	C25—N6	1.300 (8)
C7—C8	1.373 (7)	C25—C26	1.390 (8)
C7—H7	0.9300	C25—H25	0.9300
C8—C9	1.370 (7)	C26—H26	0.9300
C8—H8	0.9300	C27—N7	1.469 (6)
C9—C10	1.374 (7)	C27—C28	1.481 (7)
C9—H9	0.9300	C27—H27A	0.9700
C10—C11	1.377 (7)	C27—H27B	0.9700
C10—H10	0.9300	C28—C32	1.369 (8)
C11—H11	0.9300	C28—C29	1.386 (7)
C12—N4	1.448 (6)	C29—C30	1.365 (8)
C12—N3	1.467 (5)	C29—H29	0.9300
C12—C13	1.528 (6)	C30—N8	1.316 (8)
C13—C18	1.350 (7)	C30—H30	0.9300
C13—C14	1.391 (6)	C31—N8	1.348 (8)
C14—C15	1.389 (8)	C31—C32	1.368 (9)
C14—H14	0.9300	C31—H31	0.9300
C15—C16	1.361 (8)	C32—H32	0.9300
C15—H15	0.9300	C33—Cl2	1.711 (6)
C16—C17	1.367 (8)	C33—Cl3	1.724 (7)
C16—H16	0.9300	C33—Cl1	1.772 (8)
C17—C18	1.386 (7)	C33—H33	0.9800
C17—H17	0.9300		
N5—C1—N1	112.5 (4)	N7—C20—H20A	108.9
N5—C1—H1A	109.1	N4—C20—H20A	108.9
N1—C1—H1A	109.1	N7—C20—H20B	108.9
N5—C1—H1B	109.1	N4—C20—H20B	108.9
N1—C1—H1B	109.1	H20A—C20—H20B	107.7
H1A—C1—H1B	107.8	N5—C21—C22	112.7 (4)
N5—C2—N2	111.2 (4)	N5—C21—H21A	109.0
N5—C2—H2A	109.4	C22—C21—H21A	109.0
N2—C2—H2A	109.4	N5—C21—H21B	109.0
N5—C2—H2B	109.4	C22—C21—H21B	109.0
N2—C2—H2B	109.4	H21A—C21—H21B	107.8
H2A—C2—H2B	108.0	C26—C22—C23	114.0 (6)
N1—C3—N3	108.0 (4)	C26—C22—C21	122.6 (6)

N1—C3—S2	126.4 (4)	C23—C22—C21	123.4 (6)
N3—C3—S2	125.4 (4)	C24—C23—C22	122.0 (6)
N2—C4—N4	108.0 (4)	C24—C23—H23	119.0
N2—C4—S1	126.5 (4)	C22—C23—H23	119.0
N4—C4—S1	125.4 (5)	N6—C24—C23	123.4 (6)
N2—C5—N1	108.9 (4)	N6—C24—H24	118.3
N2—C5—C6	111.8 (3)	C23—C24—H24	118.3
N1—C5—C6	112.8 (4)	N6—C25—C26	123.5 (7)
N2—C5—C12	103.1 (4)	N6—C25—H25	118.2
N1—C5—C12	103.9 (3)	C26—C25—H25	118.2
C6—C5—C12	115.6 (4)	C22—C26—C25	121.4 (6)
C11—C6—C7	118.3 (5)	C22—C26—H26	119.3
C11—C6—C5	120.8 (4)	C25—C26—H26	119.3
C7—C6—C5	120.4 (4)	N7—C27—C28	111.6 (4)
C8—C7—C6	120.9 (5)	N7—C27—H27A	109.3
C8—C7—H7	119.5	C28—C27—H27A	109.3
C6—C7—H7	119.5	N7—C27—H27B	109.3
C9—C8—C7	120.0 (5)	C28—C27—H27B	109.3
C9—C8—H8	120.0	H27A—C27—H27B	108.0
C7—C8—H8	120.0	C32—C28—C29	115.7 (6)
C8—C9—C10	119.9 (6)	C32—C28—C27	121.4 (5)
C8—C9—H9	120.0	C29—C28—C27	122.8 (5)
C10—C9—H9	120.0	C30—C29—C28	119.3 (6)
C9—C10—C11	119.8 (5)	C30—C29—H29	120.3
C9—C10—H10	120.1	C28—C29—H29	120.3
C11—C10—H10	120.1	N8—C30—C29	126.9 (6)
C6—C11—C10	121.0 (5)	N8—C30—H30	116.5
C6—C11—H11	119.5	C29—C30—H30	116.5
C10—C11—H11	119.5	N8—C31—C32	125.7 (7)
N4—C12—N3	109.6 (4)	N8—C31—H31	117.2
N4—C12—C13	112.3 (4)	C32—C31—H31	117.2
N3—C12—C13	112.3 (3)	C31—C32—C28	120.0 (6)
N4—C12—C5	103.0 (3)	C31—C32—H32	120.0
N3—C12—C5	101.7 (4)	C28—C32—H32	120.0
C13—C12—C5	116.9 (4)	Cl2—C33—Cl3	112.1 (4)
C18—C13—C14	119.0 (5)	Cl2—C33—Cl1	109.7 (4)
C18—C13—C12	120.8 (4)	Cl3—C33—Cl1	108.3 (4)
C14—C13—C12	120.2 (4)	Cl2—C33—H33	108.9
C15—C14—C13	119.3 (5)	Cl3—C33—H33	108.9
C15—C14—H14	120.4	Cl1—C33—H33	108.9
C13—C14—H14	120.4	C3—N1—C5	111.1 (4)
C16—C15—C14	120.8 (6)	C3—N1—C1	123.0 (4)
C16—C15—H15	119.6	C5—N1—C1	114.7 (3)
C14—C15—H15	119.6	C4—N2—C5	112.7 (4)
C15—C16—C17	119.8 (6)	C4—N2—C2	126.8 (4)
C15—C16—H16	120.1	C5—N2—C2	116.3 (4)
C17—C16—H16	120.1	C3—N3—C12	113.4 (4)
C16—C17—C18	119.5 (6)	C3—N3—C19	127.7 (4)
C16—C17—H17	120.3	C12—N3—C19	114.3 (4)

C18—C17—H17	120.3	C4—N4—C12	111.8 (4)
C13—C18—C17	121.6 (5)	C4—N4—C20	124.5 (4)
C13—C18—H18	119.2	C12—N4—C20	113.6 (4)
C17—C18—H18	119.2	C1—N5—C2	110.7 (4)
N7—C19—N3	111.8 (4)	C1—N5—C21	113.8 (4)
N7—C19—H19A	109.3	C2—N5—C21	113.6 (4)
N3—C19—H19A	109.3	C25—N6—C24	115.7 (6)
N7—C19—H19B	109.3	C20—N7—C19	111.5 (4)
N3—C19—H19B	109.3	C20—N7—C27	114.4 (4)
H19A—C19—H19B	107.9	C19—N7—C27	115.4 (4)
N7—C20—N4	113.5 (4)	C30—N8—C31	112.4 (6)
N2—C5—C6—C11	−162.1 (4)	C12—C5—N1—C3	12.7 (5)
N1—C5—C6—C11	−38.9 (6)	N2—C5—N1—C1	48.5 (6)
C12—C5—C6—C11	80.4 (6)	C6—C5—N1—C1	−76.3 (5)
N2—C5—C6—C7	26.4 (7)	C12—C5—N1—C1	157.8 (4)
N1—C5—C6—C7	149.6 (4)	N5—C1—N1—C3	87.6 (5)
C12—C5—C6—C7	−91.1 (5)	N5—C1—N1—C5	−52.9 (6)
C11—C6—C7—C8	−1.8 (8)	N4—C4—N2—C5	8.2 (5)
C5—C6—C7—C8	170.0 (5)	S1—C4—N2—C5	−175.2 (3)
C6—C7—C8—C9	1.8 (9)	N4—C4—N2—C2	163.9 (4)
C7—C8—C9—C10	−0.8 (10)	S1—C4—N2—C2	−19.5 (7)
C8—C9—C10—C11	−0.3 (9)	N1—C5—N2—C4	108.8 (4)
C7—C6—C11—C10	0.7 (8)	C6—C5—N2—C4	−125.8 (4)
C5—C6—C11—C10	−171.0 (5)	C12—C5—N2—C4	−1.1 (5)
C9—C10—C11—C6	0.4 (9)	N1—C5—N2—C2	−49.6 (5)
N2—C5—C12—N4	−5.9 (4)	C6—C5—N2—C2	75.7 (5)
N1—C5—C12—N4	−119.5 (4)	C12—C5—N2—C2	−159.5 (4)
C6—C5—C12—N4	116.3 (4)	N5—C2—N2—C4	−101.2 (5)
N2—C5—C12—N3	107.6 (4)	N5—C2—N2—C5	53.7 (6)
N1—C5—C12—N3	−6.0 (4)	N1—C3—N3—C12	10.3 (5)
C6—C5—C12—N3	−130.1 (4)	S2—C3—N3—C12	−173.6 (3)
N2—C5—C12—C13	−129.7 (4)	N1—C3—N3—C19	164.3 (4)
N1—C5—C12—C13	116.7 (4)	S2—C3—N3—C19	−19.6 (7)
C6—C5—C12—C13	−7.4 (5)	N4—C12—N3—C3	106.3 (5)
N4—C12—C13—C18	−31.2 (7)	C13—C12—N3—C3	−128.0 (4)
N3—C12—C13—C18	−155.3 (5)	C5—C12—N3—C3	−2.2 (5)
C5—C12—C13—C18	87.6 (6)	N4—C12—N3—C19	−51.3 (5)
N4—C12—C13—C14	150.7 (5)	C13—C12—N3—C19	74.4 (5)
N3—C12—C13—C14	26.6 (7)	C5—C12—N3—C19	−159.8 (4)
C5—C12—C13—C14	−90.4 (5)	N7—C19—N3—C3	−101.1 (5)
C18—C13—C14—C15	0.4 (9)	N7—C19—N3—C12	52.7 (5)
C12—C13—C14—C15	178.6 (5)	N2—C4—N4—C12	−12.5 (5)
C13—C14—C15—C16	−0.9 (10)	S1—C4—N4—C12	170.8 (3)
C14—C15—C16—C17	1.4 (11)	N2—C4—N4—C20	−155.4 (4)
C15—C16—C17—C18	−1.5 (11)	S1—C4—N4—C20	27.9 (6)
C14—C13—C18—C17	−0.5 (9)	N3—C12—N4—C4	−96.3 (4)
C12—C13—C18—C17	−178.6 (5)	C13—C12—N4—C4	138.1 (4)
C16—C17—C18—C13	1.1 (10)	C5—C12—N4—C4	11.3 (5)
N5—C21—C22—C26	−139.0 (6)	N3—C12—N4—C20	50.8 (5)

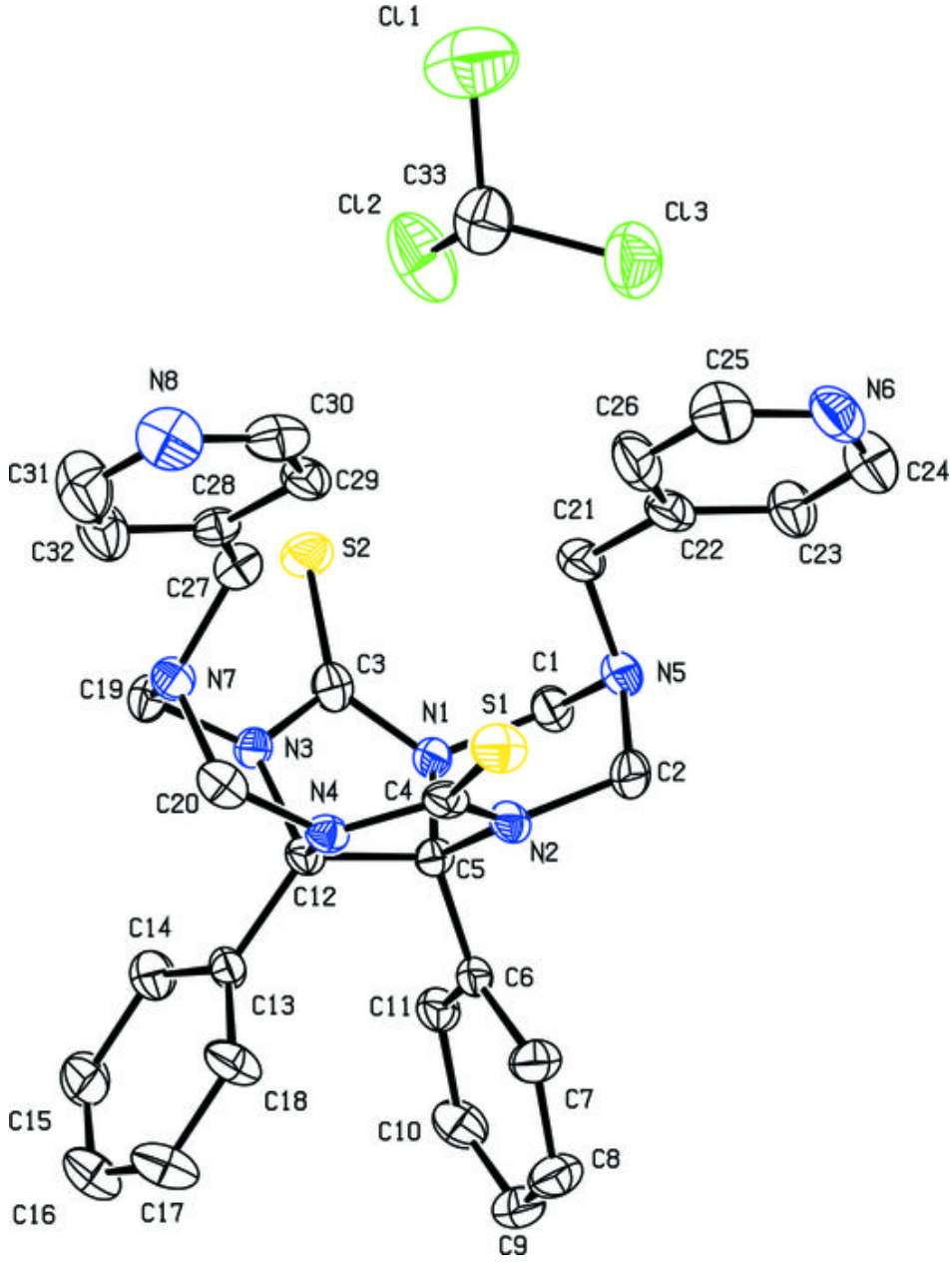
N5—C21—C22—C23	42.0 (7)	C13—C12—N4—C20	−74.8 (5)
C26—C22—C23—C24	0.0 (9)	C5—C12—N4—C20	158.5 (4)
C21—C22—C23—C24	179.1 (5)	N7—C20—N4—C4	89.0 (5)
C22—C23—C24—N6	0.5 (10)	N7—C20—N4—C12	−53.3 (5)
C23—C22—C26—C25	0.7 (9)	N1—C1—N5—C2	53.9 (6)
C21—C22—C26—C25	−178.4 (5)	N1—C1—N5—C21	−75.5 (6)
N6—C25—C26—C22	−2.0 (11)	N2—C2—N5—C1	−53.5 (6)
N7—C27—C28—C32	−43.3 (7)	N2—C2—N5—C21	76.0 (5)
N7—C27—C28—C29	140.3 (5)	C22—C21—N5—C1	−165.7 (4)
C32—C28—C29—C30	−0.2 (8)	C22—C21—N5—C2	66.4 (6)
C27—C28—C29—C30	176.3 (5)	C26—C25—N6—C24	2.3 (10)
C28—C29—C30—N8	−0.1 (9)	C23—C24—N6—C25	−1.6 (10)
N8—C31—C32—C28	0.0 (12)	N4—C20—N7—C19	52.5 (6)
C29—C28—C32—C31	0.3 (9)	N4—C20—N7—C27	−80.7 (5)
C27—C28—C32—C31	−176.3 (6)	N3—C19—N7—C20	−51.7 (5)
N3—C3—N1—C5	−14.4 (5)	N3—C19—N7—C27	81.0 (5)
S2—C3—N1—C5	169.5 (3)	C28—C27—N7—C20	−72.7 (5)
N3—C3—N1—C1	−156.2 (4)	C28—C27—N7—C19	155.9 (4)
S2—C3—N1—C1	27.7 (6)	C29—C30—N8—C31	0.4 (9)
N2—C5—N1—C3	−96.7 (5)	C32—C31—N8—C30	−0.3 (11)
C6—C5—N1—C3	138.6 (4)		

Hydrogen-bond geometry (Å, °)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
C33—H33···N8^{i}	0.98	2.33	3.168 (9)	142 (8)

Symmetry codes: (i) −*x*+2, −*y*+1, −*z*+1.

Fig. 1


Cl1
C33
Cl2
Cl3
N8
C30
C31
C28
C29
C32
S2
C27
C25
N6
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C24
C21
C22
C23
C19
N7
C3
C1
N5
S1
N1
N3
C2
C20
N4
C4
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C5
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C9

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1-Benzylpiperazine-1,4-diium bis(perchlorate) monohydrate

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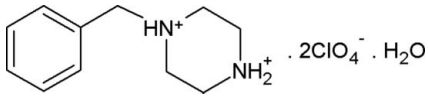
Key indicators: single-crystal X-ray study; T = 293 K; mean σ(C–C) = 0.004 Å; disorder in main residue; R factor = 0.066; wR factor = 0.240; data-to-parameter ratio = 23.1.

In the title compound, $C_{11}H_{18}N_2^{2+}\cdot 2ClO_4^-\cdot H_2O$, one perchlorate anion is disordered over two orientations in a 0.66 (3):0.34 (3) ratio. Intermolecular O—H···O, N—H···O and C—H···O hydrogen bonds link the cations, anions and water molecules into ribbons extending along [100].

Related literature

For general background to the properties of perchlorate salts containing organic cations, see: Czarnecki *et al.* (1994); Czupinski *et al.* (2002, 2006). For related structures, see: Antolini *et al.* (1982); Place & Willett (1988).



Experimental

Crystal data

$C_{11}H_{18}N_2^{2+}\cdot 2ClO_4^-\cdot H_2O$
M_r = 395.19
Triclinic, $P\overline{1}$
a = 8.6632 (6) Å
b = 10.0197 (8) Å
c = 10.8831 (7) Å
α = 70.184 (7)°
β = 83.946 (6)°
γ = 70.560 (7)°
V = 838.05 (12) Å^3
Z = 2
Mo $K\alpha$ radiation
μ = 0.44 mm^{-1}
T = 293 K
0.53 × 0.40 × 0.25 mm

Data collection

Oxford Diffraction Xcalibur Atlas Gemini ultra diffractometer
Absorption correction: analytical (*CrysAlis PRO*; Oxford Diffraction, 2006)
T_{min} = 0.832, T_{max} = 0.907
32031 measured reflections
5885 independent reflections
3882 reflections with $I > 2\sigma(I)$
R_{int} = 0.045

Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.066
$wR(F^2)$ = 0.240
S = 1.12
5885 reflections
255 parameters
40 restraints
H-atom parameters constrained
$\Delta\rho_{max}$ = 1.04 e Å^{-3}
$\Delta\rho_{min}$ = −0.88 e Å^{-3}

Table 1
Hydrogen-bond geometry (Å, °).

D—H···A	D—H	H···A	D···A	D—H···A
O9—H91···O4A^{i}	0.81	2.27	2.942 (11)	141
O9—H92···O5^{ii}	0.82	2.06	2.869 (6)	170
N16—H161···O8	0.90	2.15	2.964 (3)	151
N19—H191···O9^{iii}	0.89	1.92	2.750 (4)	155
N19—H192···O1A^{iv}	0.89	2.08	2.907 (10)	154
C17—H172···O6^{v}	0.97	2.48	3.446 (5)	172
C20—H201···O7^{iv}	0.95	2.49	3.406 (4)	160
C21—H212···O3A	0.96	2.48	3.130 (15)	125

Symmetry codes: (i) $-x+1, -y, -z+1$; (ii) $x+1, y-1, z$; (iii) $x, y+1, z$; (iv) $-x, -y+1, -z+1$; (v) $x+1, y, z$.

Data collection: *CrysAlis PRO* (Oxford Diffraction, 2006); cell refinement: *CrysAlis PRO*; data reduction: *CrysAlis PRO*; program(s) used to solve structure: *SIR97* (Altomare *et al.*, 1999); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *CAMERON* (Watkin *et al.*, 1996); software used to prepare material for publication: *SHELXL97*.

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Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: CV2717).

References

Altomare, A., Burla, M. C., Camalli, M., Cascarano, G. L., Giacovazzo, C., Guagliardi, A., Moliterni, A. G. G., Polidori, G. & Spagna, R. (1999). *J. Appl. Cryst.* **32**, 115–119.
Antolini, L., Menabue, L., Pellacani, G. C., Monica, S. & Giuseppe, M. (1982). *Inorg. Chim. Acta*, **58**, 193–200.
Czarnecki, P., Nawrocik, W., Pajaxk, Z. & Nawrocik, J. (1994). *J. Phys. Condens. Matter*, **6**, 4955–4960.
Czupinski, O., Bator, G., Ciunik, Z., Jakubas, R., Medycki, W. & Wiergiel, J. S. (2002). *J. Phys. Condens. Matter*, **14**, 8497–8512.
Czupinski, O., Wojtas, M., Zaleski, J., Jakubas, R. & Medycki, W. (2006). *J. Phys. Condens. Matter*, **88**, 3307–3324.
Oxford Diffraction (2006). *CrysAlis PRO*. Oxford Diffraction Ltd, Abingdon, England.
Place, H. & Willett, R. D. (1988). *Acta Cryst.* C**44**, 34–38.
Sheldrick, G. M. (2008). *Acta Cryst.* A**64**, 112–122.
Watkin, D. J., Prout, C. K. & Pearce, L. J. (1996). *CAMERON*. Chemical Crystallography Laboratory, Oxford, England.

supplementary materials

Acta Cryst. (2010). E**66**, o1722 [**doi:10.1107/S1600536810023123**]

1-Benzylpiperazine-1,4-diium bis(perchlorate) monohydrate

K. Kaabi, M. El Glaoui, E. Jeanneau, M. Rzaigui and C. Ben Nasr

Comment

Chemists and physicists of the solid state have shown an increasing interest in the study of perchlorate salts containing organic cations in recent years owing to their great interesting properties such as ferroelectric and dielectric behaviours. (Czarnecki *et al.*, 1994; Czupinski *et al.*, 2002; Czupinski *et al.*, 2006). Here, we report the synthesis and the crystal structure of the title compound (I), $[C_{11}H_{18}N_2]^{2+}.2ClO_4^-.H_2O$.

The crystal structure of (I) (Fig.1), contains two ClO_4^- anions, a 1-benzylpiperazine-1,4-diium dication and a water molecule. In its atomic arrangement, the ClO_4^- anions are associated per pair *via* O—H···O hydrogen bonds generated by a water molecule to form $[Cl_2O_8H_2O]^{2-}$ entities. The 1-benzylpiperazine-1,4-diium dications are associated to these entities and connected them through N—H···O and C—H···O hydrogen bonds, leading to the formation of three dimensional network. As expected, the ClO_4 anion has typical tetrahedral geometry where the Cl—O bond lengths and O—Cl—O angles are not equal to one another but very with the environment around the O atoms. In the title compound, the Cl—O bond lengths vary from 1.382 (12) Å to 1.437 (7) Å for $Cl1O_4$ anion and from 1.374 (3) Å to 1.484 (4) Å for $Cl2O_4$anion. The O—Cl—O angles range from 104.2 (14) ° to 119.3 (15) ° for the first anion and from 103.1 (2) °. to 118.4 (2) ° for the second one. These values clearly indicate that the coordination geometry of the Cl atom can be regarded as being a distorted tetrahedron. However, for $Cl2O_4$ tetrahedron all the oxygen atoms are involved in hydrogen bonds, while only three oxygen atoms acts as acceptors of hydrogen bonds for the $Cl1O_4$ tetrahedron.

Refinement

All H atoms were located in a difference map, but those attached to carbon atoms were repositioned geometrically. The H atoms were initially refined with soft restraints on the bond lengths and angles to regularize their geometry (C—H in the range 0.93–0.98, N—H in the range 0.86–0.89 N—H to 0.86 O—H = 0.82 Å) and U_{iso}(H) (in the range 1.2–1.5 times U_{eq} of the parent atom), after which the positions were refined with riding constraints. The rotational disorder observed for one perchlorate anion (with Cl1) was modelized using two superimposed molecules with partial occupancies. The molecules were then refined with restraints on the Cl—O bonds, O—Cl—O angles and displacement parameters of the oxygen atoms

Figures

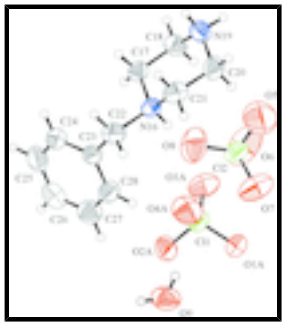


Fig. 1. View of (I), showing 50% probability displacement ellipsoids and arbitrary spheres for the H atoms. For the disordered perchlorate anion, only major part is shown.

1-Benzylpiperazine-1,4-diium bis(perchlorate) monohydrate

Crystal data

$C_{11}H_{18}N_2^{2+}\cdot 2ClO_4^-\cdot H_2O$	$Z = 2$
$M_r = 395.19$	$F(000) = 412.000$
Triclinic, $P\bar{1}$	$D_x = 1.566$ Mg m^{-3}
Hall symbol: -P 1	Mo $K\alpha$ radiation, $\lambda = 0.7107$ Å
$a = 8.6632$ (6) Å	Cell parameters from 13879 reflections
$b = 10.0197$ (8) Å	$\theta = 3.5$–$32.9°$
$c = 10.8831$ (7) Å	$\mu = 0.44$ mm^{-1}
$\alpha = 70.184$ (7)°	$T = 293$ K
$\beta = 83.946$ (6)°	Plate, colourless
$\gamma = 70.560$ (7)°	0.53 × 0.40 × 0.25 mm
$V = 838.05$ (12) Å^3	

Data collection

Oxford Diffraction Xcalibur Atlas Gemini ultra diffractometer	5885 independent reflections
Radiation source: Enhance (Mo) X-ray Source	3882 reflections with $I > 2\sigma(I)$
graphite	$R_{int} = 0.045$
Detector resolution: 10.4685 pixels mm^{-1}	$\theta_{max} = 33.0°$, $\theta_{min} = 3.5°$
ω/2\ scans	$h = -13\rightarrow13$
Absorption correction: analytical (*CrysAlis PRO*; Oxford Diffraction, 2006)	$k = -15\rightarrow15$
$T_{min} = 0.832$, $T_{max} = 0.907$	$l = -15\rightarrow16$
32031 measured reflections	

Refinement

Refinement on F^2	Secondary atom site location: difference Fourier map
Least-squares matrix: full	Hydrogen site location: inferred from neighbouring sites
$R[F^2 > 2\sigma(F^2)] = 0.066$	H-atom parameters constrained

$wR(F^2) = 0.240$	$w = 1/[\sigma^2(F_o^2) + (0.15P)^2 + 0.05P]$ where $P = (F_o^2 + 2F_c^2)/3$
$S = 1.12$	$(\Delta/\sigma)_{max} < 0.001$
5885 reflections	$\Delta\rho_{max} = 1.04$ e Å^{-3}
255 parameters	$\Delta\rho_{min} = -0.88$ e Å^{-3}
40 restraints	Extinction correction: *SHELXL97* (Sheldrick, 2008), $Fc^*=kFc[1+0.001xFc^2\lambda^3/\sin(2\theta)]^{-1/4}$
Primary atom site location: structure-invariant direct methods	Extinction coefficient: 0.062 (11)

Special details

Geometry. All e.s.d.'s (except the e.s.d. in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell e.s.d.'s are taken into account individually in the estimation of e.s.d.'s in distances, angles and torsion angles; correlations between e.s.d.'s in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell e.s.d.'s is used for estimating e.s.d.'s involving l.s. planes.

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å^2)

	x	*y*	*z*	U_{iso}*/U_{eq}	Occ. (<1)
N16	0.2509 (2)	0.3896 (2)	0.78548 (16)	0.0377 (4)	
H161	0.1556	0.3721	0.7879	0.045*	
N19	0.1505 (3)	0.7088 (2)	0.6477 (2)	0.0507 (5)	
H191	0.2431	0.7311	0.6393	0.061*	
H192	0.0729	0.7939	0.6086	0.061*	
C17	0.2348 (3)	0.5002 (3)	0.8544 (2)	0.0419 (4)	
H171	0.2003	0.4603	0.9431	0.050*	
H172	0.3416	0.5114	0.8562	0.050*	
C18	0.1106 (3)	0.6496 (3)	0.7878 (2)	0.0490 (5)	
H181	0.1085	0.7216	0.8271	0.059*	
H182	0.0026	0.6393	0.7937	0.059*	
C20	0.1645 (4)	0.5982 (3)	0.5795 (2)	0.0560 (6)	
H201	0.1960	0.6349	0.4910	0.067*	
H202	0.0599	0.5802	0.5822	0.067*	
C21	0.2923 (4)	0.4523 (3)	0.6457 (2)	0.0502 (6)	
H211	0.3980	0.4667	0.6411	0.060*	
H212	0.3022	0.3805	0.6022	0.060*	
C22	0.3782 (3)	0.2403 (3)	0.8511 (3)	0.0480 (5)	
H221	0.3960	0.1769	0.7969	0.058*	
H222	0.4798	0.2588	0.8566	0.058*	
C23	0.3262 (3)	0.1631 (2)	0.9849 (2)	0.0423 (5)	
C24	0.3844 (4)	0.1675 (3)	1.0962 (3)	0.0563 (6)	
H241	0.4594	0.2183	1.0883	0.068*	
C25	0.3348 (4)	0.0959 (3)	1.2180 (3)	0.0658 (8)	
H251	0.3758	0.1010	1.2910	0.079*	
C26	0.2275 (4)	0.0170 (3)	1.2299 (3)	0.0629 (7)	
H261	0.1933	−0.0309	1.3131	0.075*	
C27	0.1682 (4)	0.0116 (3)	1.1200 (3)	0.0606 (7)	

H271	0.0944	−0.0426	1.1291	0.073*	
C28	0.2175 (3)	0.0838 (3)	0.9975 (2)	0.0496 (5)	
H281	0.1822	0.0763	0.9236	0.059*	
Cl1	0.19840 (7)	0.07672 (7)	0.62088 (5)	0.0459 (2)	
O1A	0.0878 (13)	0.0586 (10)	0.5438 (9)	0.071 (2)	0.66 (3)
O2A	0.2349 (11)	−0.0512 (9)	0.7360 (6)	0.0630 (17)	0.66 (3)
O3A	0.1333 (19)	0.2126 (12)	0.6492 (15)	0.095 (4)	0.66 (3)
O4A	0.3513 (9)	0.0646 (13)	0.5527 (11)	0.086 (3)	0.66 (3)
O1B	0.122 (3)	0.082 (3)	0.510 (2)	0.101 (7)	0.34 (3)
O2B	0.190 (4)	−0.047 (2)	0.724 (2)	0.105 (6)	0.34 (3)
O3B	0.099 (2)	0.2007 (17)	0.660 (2)	0.064 (4)	0.34 (3)
O4B	0.3506 (16)	0.098 (2)	0.585 (2)	0.080 (3)	0.34 (3)
Cl2	−0.23663 (8)	0.44332 (8)	0.79535 (8)	0.0570 (2)	
O5	−0.2245 (5)	0.5724 (5)	0.6812 (5)	0.1421 (15)	
O6	−0.3698 (4)	0.5028 (5)	0.8630 (4)	0.1273 (13)	
O7	−0.2735 (4)	0.3526 (4)	0.7389 (3)	0.0951 (9)	
O8	−0.0873 (3)	0.3889 (4)	0.8630 (3)	0.0991 (10)	
O9	0.4548 (3)	−0.2670 (3)	0.5678 (3)	0.0757 (7)	
H91	0.4625	−0.1874	0.5194	0.114*	
H92	0.5408	−0.3200	0.6072	0.114*	

Atomic displacement parameters (Å^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
N16	0.0336 (8)	0.0422 (9)	0.0420 (9)	−0.0174 (7)	0.0030 (7)	−0.0149 (7)
N19	0.0463 (11)	0.0441 (10)	0.0544 (11)	−0.0149 (8)	−0.0041 (9)	−0.0050 (8)
C17	0.0433 (11)	0.0430 (10)	0.0421 (10)	−0.0128 (9)	−0.0001 (8)	−0.0181 (9)
C18	0.0464 (12)	0.0436 (11)	0.0537 (12)	−0.0111 (9)	0.0049 (10)	−0.0162 (10)
C20	0.0661 (17)	0.0639 (15)	0.0410 (11)	−0.0303 (13)	−0.0058 (11)	−0.0096 (10)
C21	0.0606 (15)	0.0569 (14)	0.0429 (11)	−0.0285 (12)	0.0128 (10)	−0.0222 (10)
C22	0.0369 (10)	0.0437 (11)	0.0629 (14)	−0.0112 (9)	0.0065 (10)	−0.0200 (10)
C23	0.0362 (10)	0.0365 (9)	0.0527 (11)	−0.0076 (8)	−0.0031 (9)	−0.0154 (8)
C24	0.0560 (14)	0.0472 (12)	0.0656 (15)	−0.0145 (11)	−0.0176 (12)	−0.0147 (11)
C25	0.077 (2)	0.0540 (15)	0.0563 (15)	−0.0025 (14)	−0.0229 (14)	−0.0163 (12)
C26	0.0640 (17)	0.0517 (14)	0.0544 (14)	−0.0049 (12)	0.0031 (12)	−0.0081 (11)
C27	0.0546 (15)	0.0554 (14)	0.0694 (17)	−0.0229 (12)	0.0045 (13)	−0.0132 (13)
C28	0.0476 (12)	0.0539 (13)	0.0515 (12)	−0.0201 (10)	−0.0020 (10)	−0.0177 (10)
Cl1	0.0433 (3)	0.0519 (3)	0.0484 (3)	−0.0204 (2)	−0.0019 (2)	−0.0177 (2)
O1A	0.079 (4)	0.062 (3)	0.078 (3)	−0.032 (3)	−0.033 (3)	−0.010 (3)
O2A	0.073 (4)	0.065 (3)	0.044 (2)	−0.030 (2)	−0.007 (2)	0.0004 (17)
O3A	0.123 (8)	0.077 (4)	0.112 (6)	−0.038 (4)	−0.016 (5)	−0.050 (4)
O4A	0.074 (3)	0.085 (5)	0.088 (5)	−0.039 (3)	0.015 (3)	−0.005 (3)
O1B	0.088 (10)	0.134 (16)	0.104 (11)	−0.017 (9)	−0.025 (9)	−0.078 (10)
O2B	0.130 (15)	0.093 (10)	0.125 (12)	−0.088 (11)	0.070 (9)	−0.047 (8)
O3B	0.060 (6)	0.054 (5)	0.071 (6)	0.003 (5)	−0.005 (4)	−0.029 (5)
O4B	0.060 (5)	0.094 (7)	0.116 (9)	−0.047 (5)	0.029 (5)	−0.057 (7)
Cl2	0.0410 (3)	0.0587 (4)	0.0838 (5)	−0.0185 (3)	−0.0003 (3)	−0.0358 (3)
O5	0.122 (3)	0.127 (3)	0.160 (3)	−0.076 (2)	−0.022 (2)	0.018 (2)

O6	0.0690 (18)	0.192 (3)	0.159 (3)	−0.029 (2)	0.0164 (18)	−0.120 (3)
O7	0.111 (2)	0.112 (2)	0.1031 (19)	−0.0633 (19)	0.0164 (17)	−0.0613 (18)
O8	0.0527 (14)	0.133 (3)	0.103 (2)	−0.0300 (15)	−0.0070 (13)	−0.0256 (19)
O9	0.0635 (14)	0.0607 (12)	0.1013 (17)	−0.0305 (11)	0.0107 (12)	−0.0167 (12)

Geometric parameters (Å, °)

N16—C21	1.491 (3)	C24—C25	1.377 (4)
N16—C17	1.499 (3)	C24—H241	0.9313
N16—C22	1.519 (3)	C25—C26	1.379 (5)
N16—H161	0.8954	C25—H251	0.9269
N19—C18	1.486 (3)	C26—C27	1.374 (5)
N19—C20	1.498 (4)	C26—H261	0.9388
N19—H191	0.8898	C27—C28	1.384 (4)
N19—H192	0.8904	C27—H271	0.9459
C17—C18	1.510 (3)	C28—H281	0.9242
C17—H171	0.9685	Cl1—O2B	1.382 (12)
C17—H172	0.9713	Cl1—O4B	1.398 (11)
C18—H181	0.9500	Cl1—O1B	1.409 (12)
C18—H182	0.9681	Cl1—O3A	1.416 (8)
C20—C21	1.503 (4)	Cl1—O2A	1.427 (5)
C20—H201	0.9532	Cl1—O3B	1.430 (10)
C20—H202	0.9768	Cl1—O1A	1.430 (6)
C21—H211	0.9671	Cl1—O4A	1.437 (7)
C21—H212	0.9645	Cl2—O6	1.374 (3)
C22—C23	1.500 (3)	Cl2—O7	1.386 (3)
C22—H221	0.9721	Cl2—O8	1.405 (3)
C22—H222	0.9695	Cl2—O5	1.484 (4)
C23—C24	1.380 (3)	O9—H91	0.8131
C23—C28	1.390 (3)	O9—H92	0.8189
C21—N16—C17	109.70 (17)	N16—C22—H222	108.0
C21—N16—C22	110.81 (18)	H221—C22—H222	108.4
C17—N16—C22	111.48 (17)	C24—C23—C28	118.9 (2)
C21—N16—H161	107.9	C24—C23—C22	121.7 (2)
C17—N16—H161	109.9	C28—C23—C22	119.3 (2)
C22—N16—H161	107.0	C25—C24—C23	120.8 (3)
C18—N19—C20	110.79 (19)	C25—C24—H241	120.0
C18—N19—H191	110.7	C23—C24—H241	119.2
C20—N19—H191	110.0	C24—C25—C26	120.0 (3)
C18—N19—H192	110.1	C24—C25—H251	118.8
C20—N19—H192	109.1	C26—C25—H251	121.1
H191—N19—H192	106.1	C27—C26—C25	119.9 (3)
N16—C17—C18	111.57 (19)	C27—C26—H261	120.3
N16—C17—H171	108.2	C25—C26—H261	119.7
C18—C17—H171	109.2	C26—C27—C28	120.1 (3)
N16—C17—H172	108.2	C26—C27—H271	119.3
C18—C17—H172	110.4	C28—C27—H271	120.5
H171—C17—H172	109.2	C27—C28—C23	120.2 (2)
N19—C18—C17	111.1 (2)	C27—C28—H281	120.4

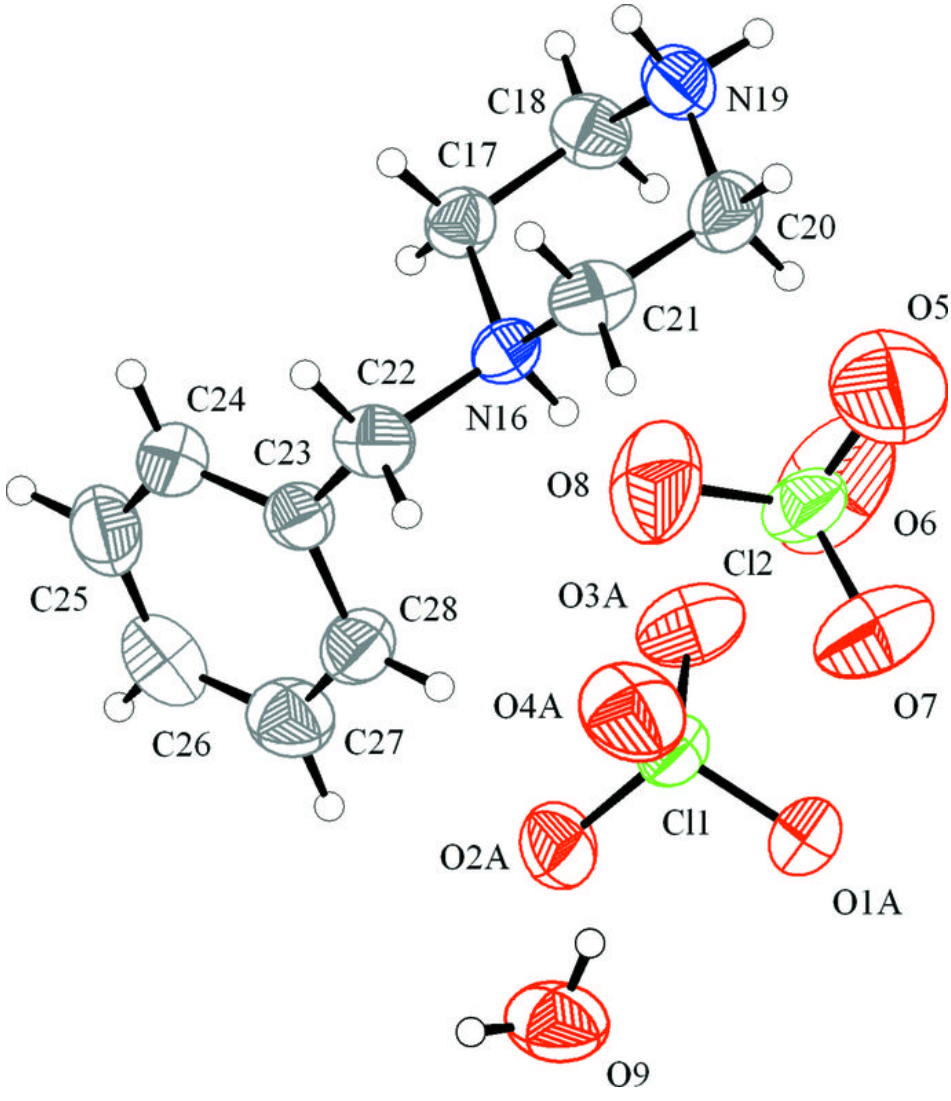
N19—C18—H181	107.3	C23—C28—H281	119.4
C17—C18—H181	111.0	O2B—Cl1—O4B	119.3 (15)
N19—C18—H182	108.7	O2B—Cl1—O1B	109.0 (11)
C17—C18—H182	109.9	O4B—Cl1—O1B	109.0 (12)
H181—C18—H182	108.7	O3A—Cl1—O2A	112.5 (8)
N19—C20—C21	110.0 (2)	O2B—Cl1—O3B	104.2 (14)
N19—C20—H201	110.1	O4B—Cl1—O3B	107.6 (11)
C21—C20—H201	108.4	O1B—Cl1—O3B	107.0 (13)
N19—C20—H202	110.0	O3A—Cl1—O1A	111.9 (7)
C21—C20—H202	108.6	O2A—Cl1—O1A	107.1 (4)
H201—C20—H202	109.7	O3A—Cl1—O4A	112.7 (6)
N16—C21—C20	111.0 (2)	O2A—Cl1—O4A	104.5 (5)
N16—C21—H211	109.0	O1A—Cl1—O4A	107.8 (6)
C20—C21—H211	110.0	O6—Cl2—O7	109.7 (2)
N16—C21—H212	109.1	O6—Cl2—O8	114.0 (2)
C20—C21—H212	110.5	O7—Cl2—O8	118.4 (2)
H211—C21—H212	107.1	O6—Cl2—O5	104.5 (3)
C23—C22—N16	111.90 (18)	O7—Cl2—O5	103.1 (2)
C23—C22—H221	109.6	O8—Cl2—O5	105.4 (2)
N16—C22—H221	108.8	H91—O9—H92	111.3
C23—C22—H222	110.1		

Hydrogen-bond geometry (Å, °)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
O9—H91···O4A^{i}	0.81	2.27	2.942 (11)	141
O9—H92···O5^{ii}	0.82	2.06	2.869 (6)	170
N16—H161···O8	0.90	2.15	2.964 (3)	151
N19—H191···O9^{iii}	0.89	1.92	2.750 (4)	155
N19—H192···O1A^{iv}	0.89	2.08	2.907 (10)	154
C17—H172···O6^{v}	0.97	2.48	3.446 (5)	172
C20—H201···O7^{iv}	0.95	2.49	3.406 (4)	160
C21—H212···O3A	0.96	2.48	3.130 (15)	125

Symmetry codes: (i) −*x*+1, −*y*, −*z*+1; (ii) *x*+1, *y*−1, *z*; (iii) *x*, *y*+1, *z*; (iv) −*x*, −*y*+1, −*z*+1; (v) *x*+1, *y*, *z*.

Fig. 1


C18
N19
C17
C20
C21
O5
C22
C24
N16
C23
O8
O6
Cl2
C25
C28
O3A
O4A
O7
C26
C27
Cl1
O2A
O1A
O9

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2,2′,6,6′-Tetraethyl-4,4′-methylenedibenzonitrile

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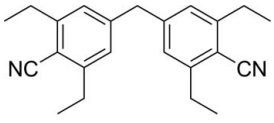
Key indicators: single-crystal X-ray study; T = 290 K; mean σ(C–C) = 0.002 Å; R factor = 0.038; wR factor = 0.111; data-to-parameter ratio = 17.6.

The asymmetric unit of the title compound, $C_{23}H_{26}N_2$, contains one half-molecule, which is completed by the operation of a crystallographic twofold axis. In the molecule, the two benzene rings form a dihedral angle of 77.09 (7)°.

Related literature

For applications of aromatic nitriles, see: Debasree *et al.* (2009); Lal Dhar *et al.* (2009); Ren *et al.* (2009); Zhou *et al.* (2009). For the preparation of the title compound, see: Donald *et al.* (1955).



Experimental

Crystal data

$C_{23}H_{26}N_2$ M_r = 330.46
Monoclinic, $C2/c$
a = 16.016 (3) Å
b = 9.3218 (19) Å
c = 13.977 (3) Å
β = 115.55 (3)°
V = 1882.6 (7) Å^3
Z = 4
Mo $K\alpha$ radiation
μ = 0.07 mm^{-1}
T = 290 K
0.16 × 0.10 × 0.10 mm

Data collection

Bruker SMART 4K CCD area-detector diffractometer
8636 measured reflections
2055 independent reflections
1405 reflections with $I > 2\sigma(I)$
R_{int} = 0.028

Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.038
$wR(F^2)$ = 0.111
S = 1.16
2055 reflections
117 parameters
H-atom parameters constrained
$\Delta\rho_{max}$ = 0.24 e Å^{-3}
$\Delta\rho_{min}$ = −0.20 e Å^{-3}

Data collection: *SMART* (Bruker, 1997); cell refinement: *SAINT* (Bruker, 1999); data reduction: *SAINT*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *SHELXTL* (Sheldrick, 2008); software used to prepare material for publication: *SHELXTL*.

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Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: CV2718).

References

Bruker (1997). *SMART*. Bruker AXS Inc., Madison, Wisconsin, USA.
Bruker (1999). *SAINT*. Bruker AXS Inc., Madison, Wisconsin, USA.
Debasree, S., Amit, S. & Brindaban, C. R. (2009). *Tetrahedron Lett.* **50**, 6088–6091.
Donald, L. V., Jonthan, L. H. & Henry, C. W. (1955). *J. Org. Chem.* **20**, 797–802.
Lal Dhar, S. Y., Vishnu, P. S. & Rajesh, P. (2009). *Tetrahedron Lett.* **50**, 5532–5535.
Ren, Y., Wang, W., Zhao, S., Tian, X., Wang, J., Yin, W. & Cheng, L. (2009). *Tetrahedron Lett.* **50**, 4595–4597.
Sheldrick, G. M. (2008). *Acta Cryst.* A**64**, 112–122.
Zhou, K. J., Daniele, A., Shoubhik, D. & Matthias, B. (2009). *Org. Lett.* **11**, 2461–2464.

supplementary materials

Acta Cryst. (2010). E**66**, o1523 [**doi:10.1107/S1600536810020052**]

2,2',6,6'-Tetraethyl-4,4'-methylenedibenzonitrile

J. Yuan and Y. Zhu

Comment

Aromatic nitriles are important intermediates in the synthesis of pharmaceuticals, agrochemicals, herbicides, dyes and pigments, and serve as precursors for many useful compounds including benzoic acid derivatives, benzylamines, benzaldehydes, and heterocycles (Debasree *et al.*, 2009; Lal Dhar *et al.*, 2009; Ren *et al.*, 2009; Zhou *et al.*, 2009).

In this paper, we report the synthesis and crystal structure of the title compound (Fig. 1). In the molecule, two benzene rings form a dihedral angle of 77.09 (7)°, and N···N separation is 11.67 (3)Å. The crystal packing doesn't exhibit hydrogen bonds or classical interactions.

Experimental

The title compound has been synthesized following the known procedure (Donald *et al.*, 1955). To an ice-bath cooled solution of 4,4'-methylenebis(2,6-diethylaniline) and sodium nitrite in water was added dropwise concentrated hydrogen chloride, keeping the temperature at 0-5^{o}C for 30 minutes. Then added potassium iodide into the mixed solution, and the white solid bis(3,5-diethyl-4-iodophenyl)methane was obtained. It reacted with cyanocopper in DMF solution at 180^{o}C for 1 hour, then the title compound was obtained. X-ray quality crystal of the title compound was obtained by slow evaporation from chloroform solution at room temperature.

Figures

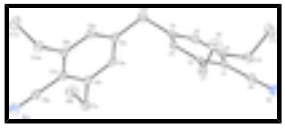


Fig. 1. A view of (I), showing the atom-labelling scheme and 40% probability displacement ellipsoids [symmetry code: (a) -x, y, 1/2-z]. H atoms omitted for clarity.

2,2',6,6'-Tetraethyl-4,4'-methylenedibenzonitrile

Crystal data

$C_{23}H_{26}N_2$	$F(000) = 712$
$M_r = 330.46$	$D_x = 1.166$ Mg m^{-3}
Monoclinic, $C2/c$	Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å
Hall symbol: -C 2yc	Cell parameters from 2049 reflections
$a = 16.016$ (3) Å	$\theta = 2.2$–$23.2°$
$b = 9.3218$ (19) Å	$\mu = 0.07$ mm^{-1}
$c = 13.977$ (3) Å	$T = 290$ K
$\beta = 115.55$ (3)°	Block, colourless
$V = 1882.6$ (7) Å^3	0.16 × 0.10 × 0.10 mm

$Z = 4$

Data collection

Bruker SMART 4K CCD area-detector diffractometer	1405 reflections with $I > 2\sigma(I)$
Radiation source: fine-focus sealed tube	$R_{int} = 0.028$
graphite	$\theta_{max} = 27.0°$, $\theta_{min} = 3.2°$
phi and ω scans	$h = -20 \rightarrow 20$
8636 measured reflections	$k = -11 \rightarrow 11$
2055 independent reflections	$l = -17 \rightarrow 17$

Refinement

Refinement on F^2	Secondary atom site location: difference Fourier map
Least-squares matrix: full	Hydrogen site location: inferred from neighbouring sites
$R[F^2 > 2\sigma(F^2)] = 0.038$	H-atom parameters constrained
$wR(F^2) = 0.111$	$w = 1/[\sigma^2(F_o^2) + (0.0506P)^2 + 0.6433P]$ where $P = (F_o^2 + 2F_c^2)/3$
$S = 1.16$	$(\Delta/\sigma)_{max} = 0.003$
2055 reflections	$\Delta\rho_{max} = 0.24$ e Å^{-3}
117 parameters	$\Delta\rho_{min} = -0.20$ e Å^{-3}
0 restraints	Extinction correction: *SHELXL97* (Sheldrick, 2008), $Fc^* = kFc[1+0.001xFc^2\lambda^3/\sin(2\theta)]^{-1/4}$
Primary atom site location: structure-invariant direct methods	Extinction coefficient: 0.0066 (13)

Special details

Geometry. All esds (except the esd in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell esds are taken into account individually in the estimation of esds in distances, angles and torsion angles; correlations between esds in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell esds is used for estimating esds involving l.s. planes.

Refinement. Refinement of F^2 against ALL reflections. The weighted *R*-factor wR and goodness of fit *S* are based on F^2, conventional *R*-factors *R* are based on *F*, with *F* set to zero for negative F^2. The threshold expression of $F^2 > \sigma(F^2)$ is used only for calculating *R*-factors(gt) etc. and is not relevant to the choice of reflections for refinement. *R*-factors based on F^2 are statistically about twice as large as those based on *F*, and *R*- factors based on ALL data will be even larger.

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å^2)

	x	*y*	*z*	U_{iso}*/U_{eq}
C1	0.15377 (8)	0.06614 (13)	0.12294 (10)	0.0215 (3)
C2	0.17923 (8)	0.06280 (13)	0.23286 (10)	0.0214 (3)
C3	0.12805 (8)	0.14471 (13)	0.27126 (10)	0.0217 (3)
H3	0.1444	0.1449	0.3437	0.026*
C4	0.05275 (8)	0.22672 (14)	0.20424 (10)	0.0222 (3)

C5	0.02799 (8)	0.22437 (14)	0.09566 (10)	0.0239 (3)
H5	−0.0233	0.2768	0.0504	0.029*
C6	0.07756 (8)	0.14604 (14)	0.05298 (10)	0.0227 (3)
C7	0.26297 (9)	−0.01923 (15)	0.30817 (10)	0.0254 (3)
H7A	0.2723	−0.1023	0.2721	0.030*
H7B	0.2524	−0.0530	0.3677	0.030*
C8	0.34907 (10)	0.07400 (17)	0.34864 (13)	0.0379 (4)
H8A	0.3615	0.1031	0.2902	0.057*
H8B	0.4008	0.0205	0.3984	0.057*
H8C	0.3394	0.1574	0.3829	0.057*
C9	0.20907 (9)	−0.01286 (15)	0.08264 (10)	0.0251 (3)
C10	0.05135 (9)	0.15086 (15)	−0.06463 (10)	0.0277 (3)
H10A	−0.0150	0.1648	−0.1028	0.033*
H10B	0.0664	0.0595	−0.0865	0.033*
C11	0.10057 (11)	0.26976 (19)	−0.09430 (12)	0.0392 (4)
H11A	0.0849	0.3607	−0.0742	0.059*
H11B	0.0817	0.2684	−0.1695	0.059*
H11C	0.1662	0.2554	−0.0580	0.059*
C12	0.0000	0.3165 (2)	0.2500	0.0265 (4)
H12	0.0432	0.3778	0.3053	0.032*
N1	0.25510 (9)	−0.07416 (14)	0.05233 (10)	0.0370 (3)

Atomic displacement parameters (Å^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
C1	0.0215 (6)	0.0215 (7)	0.0221 (6)	−0.0050 (5)	0.0099 (5)	−0.0016 (5)
C2	0.0203 (6)	0.0210 (7)	0.0229 (6)	−0.0039 (5)	0.0094 (5)	0.0005 (5)
C3	0.0223 (6)	0.0245 (7)	0.0183 (6)	−0.0037 (5)	0.0088 (5)	0.0003 (5)
C4	0.0203 (6)	0.0215 (6)	0.0263 (7)	−0.0048 (5)	0.0113 (5)	−0.0001 (5)
C5	0.0199 (6)	0.0241 (7)	0.0246 (7)	−0.0025 (5)	0.0066 (5)	0.0033 (5)
C6	0.0226 (6)	0.0235 (7)	0.0203 (6)	−0.0075 (5)	0.0077 (5)	0.0002 (5)
C7	0.0275 (7)	0.0270 (7)	0.0212 (7)	0.0034 (6)	0.0101 (6)	0.0026 (5)
C8	0.0263 (7)	0.0374 (9)	0.0385 (9)	0.0013 (6)	0.0031 (6)	0.0020 (7)
C9	0.0283 (7)	0.0266 (7)	0.0201 (6)	−0.0042 (6)	0.0102 (6)	−0.0004 (5)
C10	0.0273 (7)	0.0327 (8)	0.0195 (7)	−0.0039 (6)	0.0066 (6)	0.0002 (6)
C11	0.0393 (8)	0.0505 (10)	0.0266 (8)	−0.0096 (7)	0.0132 (7)	0.0069 (7)
C12	0.0255 (9)	0.0243 (10)	0.0309 (10)	0.000	0.0132 (8)	0.000
N1	0.0443 (7)	0.0378 (7)	0.0333 (7)	0.0020 (6)	0.0209 (6)	−0.0010 (6)

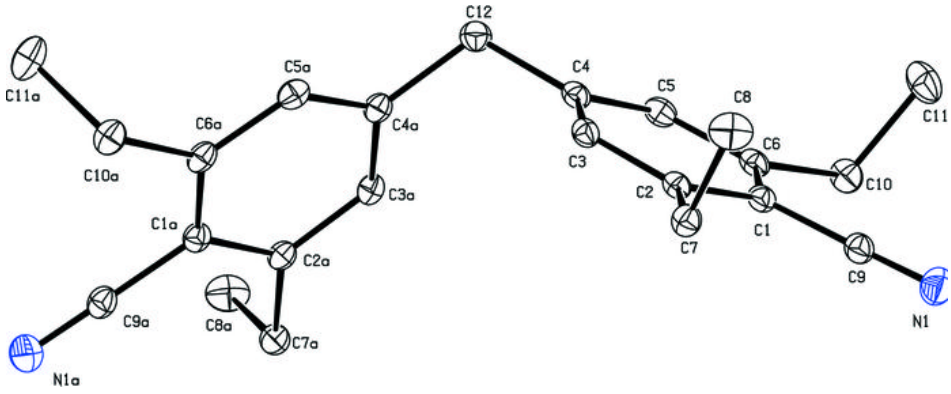
Geometric parameters (Å, °)

C1—C6	1.4040 (18)	C7—H7B	0.9700
C1—C2	1.4096 (18)	C8—H8A	0.9600
C1—C9	1.4402 (18)	C8—H8B	0.9600
C2—C3	1.3865 (18)	C8—H8C	0.9600
C2—C7	1.5079 (18)	C9—N1	1.1486 (17)
C3—C4	1.3935 (18)	C10—C11	1.5178 (19)
C3—H3	0.9300	C10—H10A	0.9700
C4—C5	1.3935 (18)	C10—H10B	0.9700

C4—C12	1.5129 (16)	C11—H11A	0.9600
C5—C6	1.3885 (19)	C11—H11B	0.9600
C5—H5	0.9300	C11—H11C	0.9600
C6—C10	1.5115 (18)	C12—C4^{i}	1.5130 (16)
C7—C8	1.5179 (19)	C12—H12	0.9700
C7—H7A	0.9700		
C6—C1—C2	121.79 (11)	H7A—C7—H7B	108.0
C6—C1—C9	119.69 (11)	C7—C8—H8A	109.5
C2—C1—C9	118.51 (11)	C7—C8—H8B	109.5
C3—C2—C1	117.92 (11)	H8A—C8—H8B	109.5
C3—C2—C7	120.36 (11)	C7—C8—H8C	109.5
C1—C2—C7	121.61 (11)	H8A—C8—H8C	109.5
C2—C3—C4	121.78 (12)	H8B—C8—H8C	109.5
C2—C3—H3	119.1	N1—C9—C1	178.28 (14)
C4—C3—H3	119.1	C6—C10—C11	112.67 (11)
C5—C4—C3	118.74 (12)	C6—C10—H10A	109.1
C5—C4—C12	121.37 (11)	C11—C10—H10A	109.1
C3—C4—C12	119.89 (10)	C6—C10—H10B	109.1
C6—C5—C4	121.96 (12)	C11—C10—H10B	109.1
C6—C5—H5	119.0	H10A—C10—H10B	107.8
C4—C5—H5	119.0	C10—C11—H11A	109.5
C5—C6—C1	117.78 (11)	C10—C11—H11B	109.5
C5—C6—C10	120.63 (12)	H11A—C11—H11B	109.5
C1—C6—C10	121.57 (12)	C10—C11—H11C	109.5
C2—C7—C8	111.18 (11)	H11A—C11—H11C	109.5
C2—C7—H7A	109.4	H11B—C11—H11C	109.5
C8—C7—H7A	109.4	C4—C12—C4^{i}	112.85 (15)
C2—C7—H7B	109.4	C4—C12—H12	109.0
C8—C7—H7B	109.4		
C6—C1—C2—C3	−1.79 (18)	C4—C5—C6—C10	−177.34 (11)
C9—C1—C2—C3	177.02 (11)	C2—C1—C6—C5	0.88 (18)
C6—C1—C2—C7	−177.97 (11)	C9—C1—C6—C5	−177.92 (11)
C9—C1—C2—C7	0.85 (18)	C2—C1—C6—C10	179.15 (11)
C1—C2—C3—C4	0.93 (18)	C9—C1—C6—C10	0.35 (18)
C7—C2—C3—C4	177.15 (11)	C3—C2—C7—C8	−86.55 (15)
C2—C3—C4—C5	0.80 (18)	C1—C2—C7—C8	89.53 (15)
C2—C3—C4—C12	−178.92 (11)	C5—C6—C10—C11	89.82 (15)
C3—C4—C5—C6	−1.77 (19)	C1—C6—C10—C11	−88.39 (15)
C12—C4—C5—C6	177.94 (12)	C5—C4—C12—C4^{i}	112.50 (12)
C4—C5—C6—C1	0.94 (18)	C3—C4—C12—C4^{i}	−67.79 (10)

Symmetry codes: (i) −*x*, *y*, −*z*+1/2.

Fig. 1


C12
C11a
C5a
C4
C5
C8
C11
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C4a
C3
C6
C10a
C2
C10
C3a
C1a
C7
C1
C2a
C9
C9a
C8a
N1
C7a
N1a

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Diethyl 7,8,18,19-tetramethyl-2,13-dioxo-hexacyclo[10.10.2.0^{3,24}.0^{5,10}.0^{14,23}.0^{16,21}]-tetracosa-5,7,9,16,18,20-hexaene-23,24-dicarboxylate

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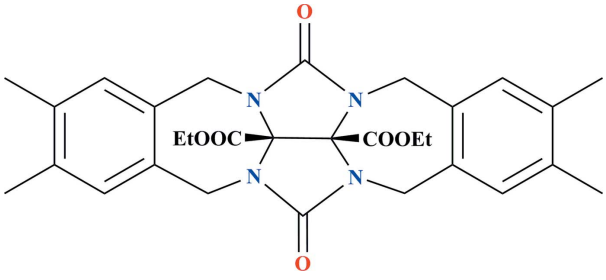
Key indicators: single-crystal X-ray study; T = 298 K; mean σ(C–C) = 0.003 Å; disorder in main residue; R factor = 0.047; wR factor = 0.116; data-to-parameter ratio = 17.0.

The asymmetric unit of the title compound, $C_{30}H_{34}N_4O_6$, contains two independent molecules. In one independent molecule, the two ethoxycarbonyl groups are each disordered over two conformations with occupancy ratios of 0.586 (2):0.414 (2) and 0.508 (2):0.492 (2). The crystal packing exhibits weak intermolecular C—H···O hydrogen bonds.

Related literature

For the preparation and the crystal engineering studies on the title compound, see: Wang *et al.* (2006). For glycoluril and its derivatives, see: Freeman *et al.* (1981); Rebek (2005); Rowan *et al.* (1999); Wu *et al.* (2002).



Experimental

Crystal data

$C_{30}H_{34}N_4O_6$
M_r = 546.61
Monoclinic, $P2_1/c$
a = 23.4988 (12) Å
b = 11.6005 (6) Å
c = 21.2685 (11) Å
β = 107.145 (1)°
V = 5540.1 (5) Å^3
Z = 8
Mo $K\alpha$ radiation
μ = 0.09 mm^{-1}
T = 298 K
0.16 × 0.12 × 0.10 mm

Data collection

Bruker SMART 4K CCD area-detector diffractometer
67299 measured reflections
13767 independent reflections
6896 reflections with $I > 2\sigma(I)$
R_{int} = 0.052

Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.047
$wR(F^2)$ = 0.116
S = 0.86
13767 reflections
809 parameters
20 restraints
H-atom parameters constrained
$\Delta\rho_{max}$ = 0.17 e Å^{-3}
$\Delta\rho_{min}$ = −0.18 e Å^{-3}

Table 1
Hydrogen-bond geometry (Å, °).

D—H···A	D—H	H···A	D···A	D—H···A
C9A—H9A1···O2B^{i}	0.97	2.31	3.205 (2)	153
C22B—H22A···O1A^{ii}	0.97	2.41	3.375 (2)	178
C29B—H29A···O1B^{iii}	0.96	2.53	3.441 (3)	160

Symmetry codes: (i) $x, y+1, z$; (ii) $x, -y+\frac{3}{2}, z+\frac{1}{2}$; (iii) $-x+1, y+\frac{1}{2}, -z+\frac{3}{2}$.

Data collection: *SMART* (Bruker, 1997); cell refinement: *SAINT* (Bruker, 1999); data reduction: *SAINT*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *SHELXTL* (Sheldrick, 2008); software used to prepare material for publication: *SHELXTL*.

The authors thank Profressor An-Xin Wu for helpful discussions and Dr Xiang-Gao Meng for the X-ray data collection.

Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: CV2719).

References

Bruker (1997). *SMART*. Bruker AXS Inc., Madison, Wisconsin, USA.
Bruker (1999). *SAINT*. Bruker AXS Inc., Madison, Wisconsin,USA.
Freeman, W. A., Mock, W. L. & Shih, N. Y. (1981). *J. Am. Chem. Soc.* **103**, 7367–7368.
Rebek, J. Jr (2005). *Angew. Chem. Int. Ed.* **44**, 2068–2078.
Rowan, A. E., Elemans, J. A. A. W. & Nolte, R. J. M. (1999). *Acc. Chem. Res.* **32**, 995–1006
Sheldrick, G. M. (2008). *Acta Cryst.* A**64**, 112–122.
Wang, Z., Zhou, B., Chen, Y., Yin, G., Li, Y., Wu, A. & Isaacs, L. (2006). *J. Org. Chem.* **71**, 4502–4508.
Wu, A., Fettinger, J. C. & Isaacs, L. (2002). *Tetrahedron*, **58**, 9769–9777.

supplementary materials

Acta Cryst. (2010). E**66**, o1681 [**doi:10.1107/S1600536810022038**]

Diethyl 7,8,18,19-tetramethyl-2,13-dioxohexacyclo[10.10.2.0^{3,24}.0^{5,10}.0^{14,23}.0^{16,21}]tetracosa-5,7,9,16,18,20-hexaene-23,24-dicarboxylate

J. Wang, J. Xiang and L. Cao

Comment

Glycoluril and its derivatives are widely used as building blocks for studies of self-assembly in homogeneous solution (Freeman *et al.*, 1981; Rebek, 2005; Rowan *et al.*, 1999; Wu *et al.*, 2002). As a part of our ongoing investigation into glycoluril derivatives (Wang *et al.*, 2006), here we report the structure of the title compound (I) (Fig. 1).

The asymmetric unit of (I) contains two independent molecules. In one independent molecule, two ethoxy carbonyl groups are disordered over two conformations each with ratios 0.586 (2)/0.414 (2) and 0.508 (2)/0.492 (2), respectively. The crystal packing exhibits weak intermolecular C—H···O hydrogen bonds (Table 1).

Experimental

The title compound was synthesized according to the reported method (Wang *et al.*; 2006). Crystals of (I) suitable for X-ray diffraction were grown by slow evaporation of a dichloromethane-methanol (4:1) solution of the title compound under 293 K.

Refinement

All H-atoms were positioned geometrically and constrained to ride on their parent atoms, with d(C—H) = 0.97 Å, Uĩso~ = 1.2U~eq~ (C) for CH~2~ and d(C—H) = 0.96 Å, Uĩso~ = 1.5U~eq~ (C) for CH~3~ atoms. In one independent molecule, two ethoxy carbonyl groups were treated as disordered over two conformations. The occupancies of the disordered positions C15A/ C15', C16A/ C16', O3A/O3' and O4A/O4' were refined to 0.508 (2) / 0.492 (2), while those for C19A/ C19', C20A/ C20', O5A/O5' and O6A/O6' were refined to 0.414 (2) / 0.586 (2).

Figures

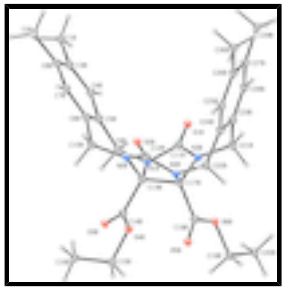


Fig. 1. A view of (I), showing one independent molecule with the atom-labelling scheme and 30% probability displacement ellipsoids.

Diethyl 7,8,18,19-tetramethyl-2,13- dioxohexacyclo[10.10.2.0^{3,24}.0^{5,10}.0^{14,23}.0^{16,21}]tetracosa- 5,7,9,16,18,20-hexaene-23,24-dicarboxylate

Crystal data

$C_{30}H_{34}N_4O_6$	$F(000) = 2320$
$M_r = 546.61$	$D_x = 1.311$ Mg m^{-3}
Monoclinic, $P2_1/c$	Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å
Hall symbol: -P 2ybc	Cell parameters from 8852 reflections
$a = 23.4988$ (12) Å	$\theta = 2.3$–$22.3°$
$b = 11.6005$ (6) Å	$\mu = 0.09$ mm^{-1}
$c = 21.2685$ (11) Å	$T = 298$ K
$\beta = 107.145$ (1)°	Block, colourless
$V = 5540.1$ (5) Å^3	0.16 × 0.12 × 0.10 mm
$Z = 8$	

Data collection

Bruker SMART 4K CCD area-detector diffractometer	6896 reflections with $I > 2\sigma(I)$
Radiation source: fine-focus sealed tube	$R_{int} = 0.052$
graphite	$\theta_{max} = 28.3°$, $\theta_{min} = 1.8°$
phi and ω scans	$h = -31\rightarrow31$
67299 measured reflections	$k = -15\rightarrow15$
13767 independent reflections	$l = -28\rightarrow28$

Refinement

Refinement on F^2	Primary atom site location: structure-invariant direct methods
Least-squares matrix: full	Secondary atom site location: difference Fourier map
$R[F^2 > 2\sigma(F^2)] = 0.047$	Hydrogen site location: inferred from neighbouring sites
$wR(F^2) = 0.116$	H-atom parameters constrained
$S = 0.86$	$w = 1/[\sigma^2(F_o^2) + (0.0539P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
13767 reflections	$(\Delta/\sigma)_{max} = 0.002$
809 parameters	$\Delta\rho_{max} = 0.17$ e Å^{-3}
20 restraints	$\Delta\rho_{min} = -0.18$ e Å^{-3}

Special details

Geometry. All e.s.d.'s (except the e.s.d. in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell e.s.d.'s are taken into account individually in the estimation of e.s.d.'s in distances, angles and torsion angles; correlations between e.s.d.'s in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell e.s.d.'s is used for estimating e.s.d.'s involving l.s. planes.

Refinement. Refinement of F^2 against ALL reflections. The weighted *R*-factor *wR* and goodness of fit *S* are based on F^2, conventional *R*-factors *R* are based on *F*, with *F* set to zero for negative F^2. The threshold expression of $F^2 > \sigma(F^2)$ is used only for calculating *R*-factors(gt) *etc*. and is not relevant to the choice of reflections for refinement. *R*-factors based on F^2 are statistically about twice as large as those based on *F*, and *R*- factors based on ALL data will be even larger.

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å^2)

	x	*y*	*z*	U_{iso}*/U_{eq}	Occ. (<1)
O1A	0.18810 (5)	1.18390 (11)	0.17156 (6)	0.0609 (3)	
O2A	0.13366 (5)	0.74461 (11)	0.24984 (6)	0.0633 (4)	
N1A	0.18396 (6)	1.08832 (11)	0.26470 (7)	0.0445 (3)	
N2A	0.15077 (6)	0.91667 (12)	0.30754 (7)	0.0454 (3)	
N3A	0.10001 (6)	1.11326 (12)	0.18400 (7)	0.0479 (4)	
N4A	0.08583 (6)	0.91354 (12)	0.20740 (7)	0.0494 (4)	
C1A	0.42409 (8)	0.89433 (17)	0.27568 (10)	0.0669 (6)	
H1A1	0.4500	0.8318	0.2953	0.100*	
H1A2	0.4435	0.9662	0.2910	0.100*	
H1A3	0.4150	0.8903	0.2287	0.100*	
C2A	0.38198 (9)	0.67344 (17)	0.32156 (10)	0.0693 (6)	
H2A1	0.3824	0.6491	0.2785	0.104*	
H2A2	0.3633	0.6153	0.3408	0.104*	
H2A3	0.4221	0.6851	0.3488	0.104*	
C3A	0.36724 (7)	0.88602 (16)	0.29477 (8)	0.0489 (4)	
C4A	0.33249 (7)	0.98434 (15)	0.29049 (8)	0.0483 (4)	
H4A	0.3451	1.0521	0.2753	0.058*	
C5A	0.28011 (7)	0.98636 (14)	0.30767 (8)	0.0423 (4)	
C6A	0.26109 (7)	0.88475 (15)	0.33059 (8)	0.0439 (4)	
C7A	0.29503 (7)	0.78633 (15)	0.33343 (8)	0.0483 (4)	
H7A	0.2820	0.7181	0.3476	0.058*	
C8A	0.34788 (7)	0.78424 (15)	0.31616 (8)	0.0486 (4)	
C9A	0.24609 (7)	1.09810 (14)	0.30318 (8)	0.0479 (4)	
H9A1	0.2482	1.1235	0.3473	0.058*	
H9A2	0.2650	1.1565	0.2835	0.058*	
C10A	0.20665 (7)	0.88039 (16)	0.35484 (9)	0.0528 (5)	
H10C	0.2019	0.8020	0.3683	0.063*	
H10D	0.2139	0.9289	0.3936	0.063*	
C11A	0.16072 (8)	1.13303 (14)	0.20341 (9)	0.0459 (4)	
C12A	0.12450 (7)	0.84661 (17)	0.25404 (9)	0.0482 (4)	
C13A	0.13984 (7)	1.03574 (15)	0.29051 (8)	0.0451 (4)	
C14A	0.13113 (9)	1.1126 (2)	0.34619 (10)	0.0588 (5)	
C15A	0.1006 (6)	1.1414 (7)	0.4389 (5)	0.081 (3)	0.508 (14)
H15C	0.0701	1.1979	0.4195	0.098*	0.508 (14)
H15D	0.1374	1.1816	0.4604	0.098*	0.508 (14)
C16A	0.0821 (7)	1.0681 (10)	0.4872 (5)	0.107 (3)	0.508 (14)
H16G	0.0433	1.0367	0.4667	0.160*	0.508 (14)
H16H	0.0811	1.1141	0.5243	0.160*	0.508 (14)
H16I	0.1101	1.0064	0.5016	0.160*	0.508 (14)
O3A	0.1475 (4)	1.2123 (5)	0.3507 (6)	0.077 (2)	0.508 (14)

O4A	0.1090 (5)	1.0641 (9)	0.3884 (5)	0.067 (2)	0.508 (14)
C16'	0.0627 (3)	1.1133 (12)	0.4607 (7)	0.101 (4)	0.492 (14)
H16F	0.0413	1.1644	0.4264	0.151*	0.492 (14)
H16E	0.0634	1.1449	0.5027	0.151*	0.492 (14)
H16D	0.0432	1.0395	0.4552	0.151*	0.492 (14)
C15'	0.1248 (3)	1.0992 (11)	0.4576 (4)	0.074 (2)	0.492 (14)
H15E	0.1438	1.1742	0.4617	0.088*	0.492 (14)
H15F	0.1471	1.0520	0.4943	0.088*	0.492 (14)
O3'	0.1234 (6)	1.2148 (7)	0.3406 (6)	0.107 (3)	0.492 (14)
O4'	0.1264 (5)	1.0456 (9)	0.3960 (4)	0.063 (2)	0.492 (14)
C17A	0.08463 (7)	1.03234 (15)	0.22728 (8)	0.0476 (4)	
C18A	0.02543 (9)	1.0647 (2)	0.23998 (11)	0.0618 (5)	
C19A	−0.0582 (5)	0.9725 (15)	0.2662 (6)	0.076 (3)	0.414 (14)
H19D	−0.0841	0.9105	0.2440	0.091*	0.414 (14)
H19C	−0.0782	1.0451	0.2514	0.091*	0.414 (14)
C20A	−0.0465 (6)	0.961 (2)	0.3392 (5)	0.125 (6)	0.414 (14)
H20A	−0.0268	0.8892	0.3537	0.187*	0.414 (14)
H20B	−0.0836	0.9631	0.3495	0.187*	0.414 (14)
H20C	−0.0217	1.0236	0.3610	0.187*	0.414 (14)
O5A	0.0137 (4)	1.1627 (7)	0.2523 (6)	0.083 (2)	0.414 (14)
O6A	−0.0033 (5)	0.9682 (9)	0.2497 (6)	0.076 (3)	0.414 (14)
C19'	−0.0466 (4)	1.0092 (8)	0.2890 (5)	0.072 (2)	0.586 (14)
H19E	−0.0799	1.0184	0.2496	0.087*	0.586 (14)
H19F	−0.0427	1.0790	0.3151	0.087*	0.586 (14)
C20'	−0.0562 (4)	0.9078 (7)	0.3277 (5)	0.084 (2)	0.586 (14)
H20D	−0.0629	0.8403	0.3003	0.126*	0.586 (14)
H20E	−0.0903	0.9213	0.3428	0.126*	0.586 (14)
H20F	−0.0217	0.8964	0.3648	0.126*	0.586 (14)
O5'	−0.0028 (4)	1.1489 (7)	0.2157 (5)	0.108 (2)	0.586 (14)
O6'	0.0079 (3)	0.9872 (6)	0.2718 (4)	0.0645 (18)	0.586 (14)
C21A	0.06619 (8)	1.11686 (16)	0.11404 (9)	0.0600 (5)	
H21C	0.0758	1.1880	0.0955	0.072*	
H21D	0.0241	1.1192	0.1105	0.072*	
C22A	0.04665 (8)	0.87020 (17)	0.14544 (9)	0.0606 (5)	
H22C	0.0068	0.8994	0.1397	0.073*	
H22D	0.0450	0.7868	0.1477	0.073*	
C23A	0.07681 (8)	1.01776 (17)	0.07294 (9)	0.0543 (5)	
C24A	0.06599 (7)	0.90349 (17)	0.08606 (9)	0.0542 (5)	
C25A	0.07319 (8)	0.81895 (18)	0.04264 (10)	0.0629 (5)	
H25A	0.0651	0.7428	0.0507	0.075*	
C26A	0.09188 (8)	0.8428 (2)	−0.01213 (10)	0.0657 (6)	
C27A	0.10430 (9)	0.9561 (2)	−0.02375 (10)	0.0689 (6)	
C28A	0.09629 (8)	1.04109 (19)	0.01882 (9)	0.0661 (5)	
H28A	0.1044	1.1172	0.0106	0.079*	
C29A	0.12856 (11)	0.9883 (3)	−0.08023 (11)	0.1068 (9)	
H29D	0.1298	1.0707	−0.0838	0.160*	
H29E	0.1032	0.9569	−0.1205	0.160*	
H29F	0.1680	0.9576	−0.0721	0.160*	
C30A	0.09864 (10)	0.7452 (2)	−0.05647 (11)	0.0939 (8)	

H30D	0.0744	0.7602	−0.1006	0.141*
H30F	0.0862	0.6743	−0.0413	0.141*
H30E	0.1396	0.7391	−0.0557	0.141*
O1B	0.43937 (5)	0.04574 (12)	0.71998 (6)	0.0632 (4)
O2B	0.28886 (5)	0.12011 (11)	0.46037 (6)	0.0611 (3)
O3B	0.23181 (6)	−0.17082 (13)	0.54130 (7)	0.0830 (5)
O4B	0.27176 (5)	−0.20261 (11)	0.64928 (6)	0.0589 (3)
O5B	0.18946 (6)	0.03919 (13)	0.62346 (7)	0.0790 (4)
O6B	0.26075 (5)	0.05723 (12)	0.71918 (6)	0.0662 (4)
N1B	0.36696 (6)	−0.07053 (12)	0.65219 (6)	0.0456 (3)
N2B	0.32046 (6)	−0.02124 (13)	0.53878 (6)	0.0471 (4)
N3B	0.34505 (6)	0.11166 (13)	0.66635 (6)	0.0463 (4)
N4B	0.26966 (6)	0.12751 (12)	0.56039 (6)	0.0454 (3)
C1B	0.59664 (8)	−0.2226 (2)	0.59397 (11)	0.0791 (6)
H1B1	0.6071	−0.2400	0.6401	0.119*
H1B2	0.6215	−0.1614	0.5868	0.119*
H1B3	0.6023	−0.2899	0.5702	0.119*
C2B	0.53769 (9)	−0.16490 (19)	0.45324 (10)	0.0748 (6)
H2B1	0.5753	−0.1265	0.4699	0.112*
H2B2	0.5147	−0.1274	0.4137	0.112*
H2B3	0.5442	−0.2439	0.4438	0.112*
C3B	0.53237 (8)	−0.18567 (15)	0.57005 (10)	0.0544 (5)
C4B	0.49900 (8)	−0.17902 (14)	0.61356 (9)	0.0514 (4)
H4B	0.5180	−0.1931	0.6578	0.062*
C5B	0.43871 (7)	−0.15249 (14)	0.59491 (8)	0.0460 (4)
C6B	0.41070 (8)	−0.12653 (14)	0.52904 (9)	0.0478 (4)
C7B	0.44481 (8)	−0.12908 (14)	0.48547 (9)	0.0530 (5)
H7B	0.4267	−0.1091	0.4418	0.064*
C8B	0.50443 (8)	−0.15993 (15)	0.50415 (10)	0.0535 (5)
C9B	0.40622 (8)	−0.16434 (16)	0.64638 (9)	0.0536 (5)
H9B1	0.3828	−0.2345	0.6372	0.064*
H9B2	0.4358	−0.1743	0.6888	0.064*
C10B	0.34481 (8)	−0.10271 (16)	0.50137 (8)	0.0548 (5)
H10A	0.3372	−0.0734	0.4569	0.066*
H10B	0.3235	−0.1751	0.4986	0.066*
C11B	0.38948 (8)	0.03153 (16)	0.68311 (8)	0.0466 (4)
C12B	0.29294 (7)	0.07911 (16)	0.51412 (8)	0.0458 (4)
C13B	0.31232 (7)	−0.05049 (15)	0.60153 (8)	0.0450 (4)
C14B	0.26692 (8)	−0.14919 (16)	0.59342 (10)	0.0539 (5)
C15B	0.23022 (9)	−0.2983 (2)	0.64711 (10)	0.0754 (6)
H15A	0.1907	−0.2761	0.6203	0.091*
H15B	0.2282	−0.3137	0.6912	0.091*
C16B	0.24875 (11)	−0.4051 (2)	0.61965 (12)	0.0959 (8)
H16A	0.2461	−0.3930	0.5742	0.144*
H16B	0.2230	−0.4675	0.6232	0.144*
H16C	0.2891	−0.4237	0.6438	0.144*
C17B	0.29055 (7)	0.06692 (15)	0.62221 (8)	0.0451 (4)
C18B	0.24006 (9)	0.05387 (16)	0.65443 (10)	0.0536 (5)
C19B	0.21676 (9)	0.0420 (2)	0.75488 (11)	0.0920 (8)

H19A	0.1838	0.0950	0.7381	0.110*
H19B	0.2013	−0.0360	0.7490	0.110*
C20B	0.24566 (12)	0.0646 (2)	0.82460 (11)	0.0992 (8)
H20G	0.2768	0.0093	0.8414	0.149*
H20H	0.2169	0.0585	0.8484	0.149*
H20I	0.2623	0.1409	0.8298	0.149*
C21B	0.35170 (8)	0.23038 (15)	0.68850 (8)	0.0552 (5)
H21A	0.3859	0.2363	0.7273	0.066*
H21B	0.3168	0.2530	0.7009	0.066*
C22B	0.25941 (7)	0.25230 (15)	0.55949 (9)	0.0539 (5)
H22A	0.2378	0.2704	0.5907	0.065*
H22B	0.2345	0.2742	0.5161	0.065*
C23B	0.35967 (8)	0.31235 (15)	0.63671 (8)	0.0486 (4)
C24B	0.31593 (8)	0.32328 (15)	0.57615 (8)	0.0488 (4)
C25B	0.32564 (9)	0.39956 (16)	0.53058 (9)	0.0572 (5)
H25B	0.2965	0.4073	0.4903	0.069*
C26B	0.37723 (9)	0.46536 (16)	0.54247 (10)	0.0595 (5)
C27B	0.42118 (8)	0.45323 (15)	0.60225 (10)	0.0554 (5)
C28B	0.41137 (8)	0.37727 (15)	0.64819 (9)	0.0529 (5)
H28B	0.4406	0.3694	0.6884	0.063*
C29B	0.47928 (9)	0.51749 (17)	0.61727 (11)	0.0770 (6)
H29A	0.5019	0.5041	0.6622	0.116*
H29B	0.4716	0.5985	0.6105	0.116*
H29C	0.5014	0.4909	0.5887	0.116*
C30B	0.38487 (11)	0.5469 (2)	0.48971 (11)	0.0910 (7)
H30A	0.4128	0.5147	0.4695	0.136*
H30B	0.3994	0.6198	0.5093	0.136*
H30C	0.3472	0.5578	0.4570	0.136*

Atomic displacement parameters (Å^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
O1A	0.0681 (8)	0.0636 (8)	0.0582 (8)	−0.0060 (7)	0.0300 (7)	0.0106 (7)
O2A	0.0638 (8)	0.0445 (8)	0.0857 (10)	−0.0010 (7)	0.0284 (7)	0.0005 (7)
N1A	0.0429 (8)	0.0496 (9)	0.0438 (8)	−0.0020 (7)	0.0170 (7)	0.0057 (7)
N2A	0.0436 (8)	0.0477 (9)	0.0480 (9)	0.0007 (7)	0.0182 (7)	0.0055 (7)
N3A	0.0464 (9)	0.0530 (9)	0.0445 (9)	0.0031 (7)	0.0137 (7)	0.0044 (7)
N4A	0.0472 (9)	0.0493 (9)	0.0520 (9)	−0.0025 (7)	0.0151 (7)	−0.0024 (7)
C1A	0.0556 (12)	0.0763 (14)	0.0759 (14)	0.0014 (10)	0.0303 (11)	0.0031 (11)
C2A	0.0734 (14)	0.0653 (14)	0.0774 (14)	0.0149 (11)	0.0349 (12)	0.0068 (11)
C3A	0.0444 (10)	0.0584 (12)	0.0435 (10)	−0.0022 (9)	0.0125 (8)	−0.0014 (9)
C4A	0.0465 (10)	0.0502 (11)	0.0491 (11)	−0.0080 (9)	0.0154 (9)	0.0007 (8)
C5A	0.0428 (10)	0.0462 (10)	0.0376 (9)	−0.0026 (8)	0.0113 (8)	−0.0022 (8)
C6A	0.0431 (10)	0.0512 (11)	0.0376 (9)	0.0001 (8)	0.0123 (8)	0.0022 (8)
C7A	0.0536 (11)	0.0471 (11)	0.0445 (10)	−0.0025 (9)	0.0150 (9)	0.0054 (8)
C8A	0.0493 (11)	0.0541 (12)	0.0429 (10)	0.0053 (9)	0.0146 (8)	0.0014 (8)
C9A	0.0463 (10)	0.0500 (11)	0.0476 (10)	−0.0056 (8)	0.0141 (8)	−0.0017 (8)
C10A	0.0523 (11)	0.0596 (12)	0.0500 (11)	0.0023 (9)	0.0207 (9)	0.0126 (9)

C11A	0.0516 (11)	0.0429 (10)	0.0481 (11)	0.0023 (8)	0.0226 (9)	−0.0012 (8)
C12A	0.0424 (10)	0.0516 (12)	0.0590 (12)	−0.0040 (9)	0.0278 (9)	0.0033 (10)
C13A	0.0453 (10)	0.0485 (11)	0.0453 (10)	0.0009 (8)	0.0195 (8)	0.0017 (8)
C14A	0.0588 (13)	0.0670 (15)	0.0558 (13)	0.0052 (13)	0.0251 (10)	−0.0033 (12)
C15A	0.098 (7)	0.091 (6)	0.070 (5)	−0.001 (4)	0.046 (5)	−0.029 (4)
C16A	0.122 (9)	0.148 (9)	0.064 (5)	0.013 (5)	0.049 (6)	−0.004 (4)
O3A	0.088 (4)	0.048 (3)	0.109 (5)	−0.001 (2)	0.053 (4)	−0.018 (3)
O4A	0.074 (6)	0.074 (3)	0.068 (3)	−0.010 (3)	0.044 (4)	−0.015 (2)
C16'	0.090 (5)	0.125 (9)	0.099 (8)	0.006 (5)	0.047 (5)	−0.036 (6)
C15'	0.075 (5)	0.091 (7)	0.060 (4)	−0.009 (3)	0.027 (4)	−0.014 (3)
O3'	0.173 (9)	0.084 (4)	0.080 (4)	0.052 (4)	0.060 (6)	0.002 (3)
O4'	0.066 (5)	0.087 (4)	0.046 (3)	−0.005 (3)	0.034 (3)	−0.012 (2)
C17A	0.0428 (10)	0.0525 (11)	0.0505 (11)	0.0024 (8)	0.0184 (9)	0.0008 (9)
C18A	0.0478 (12)	0.0689 (15)	0.0725 (15)	0.0086 (11)	0.0235 (11)	0.0072 (13)
C19A	0.048 (5)	0.108 (9)	0.085 (7)	0.003 (4)	0.038 (5)	0.008 (5)
C20A	0.065 (5)	0.23 (2)	0.081 (6)	−0.023 (10)	0.028 (5)	0.033 (9)
O5A	0.071 (4)	0.070 (3)	0.122 (6)	0.018 (2)	0.050 (4)	−0.003 (4)
O6A	0.056 (4)	0.098 (5)	0.086 (6)	−0.005 (3)	0.038 (4)	−0.004 (3)
C19'	0.052 (4)	0.094 (5)	0.082 (6)	0.012 (3)	0.038 (4)	0.008 (4)
C20'	0.060 (5)	0.086 (4)	0.115 (6)	−0.003 (3)	0.041 (4)	0.025 (3)
O5'	0.089 (4)	0.109 (4)	0.150 (6)	0.050 (3)	0.071 (4)	0.057 (4)
O6'	0.046 (3)	0.070 (3)	0.088 (4)	0.0134 (19)	0.036 (3)	0.025 (3)
C21A	0.0614 (12)	0.0628 (13)	0.0524 (12)	0.0090 (10)	0.0114 (10)	0.0075 (10)
C22A	0.0513 (11)	0.0633 (13)	0.0652 (13)	−0.0107 (9)	0.0143 (10)	−0.0087 (10)
C23A	0.0453 (10)	0.0653 (13)	0.0478 (11)	0.0060 (9)	0.0068 (9)	0.0010 (10)
C24A	0.0407 (10)	0.0660 (14)	0.0523 (12)	−0.0004 (9)	0.0080 (9)	−0.0042 (10)
C25A	0.0504 (12)	0.0681 (14)	0.0630 (13)	0.0014 (10)	0.0058 (10)	−0.0080 (11)
C26A	0.0478 (11)	0.0940 (17)	0.0493 (12)	0.0139 (11)	0.0050 (10)	−0.0123 (12)
C27A	0.0582 (13)	0.0947 (18)	0.0524 (13)	0.0076 (12)	0.0142 (10)	−0.0006 (12)
C28A	0.0643 (13)	0.0793 (15)	0.0513 (12)	0.0026 (11)	0.0117 (10)	0.0072 (11)
C29A	0.112 (2)	0.151 (3)	0.0690 (16)	0.0029 (18)	0.0449 (15)	−0.0001 (16)
C30A	0.0838 (16)	0.117 (2)	0.0767 (16)	0.0254 (15)	0.0166 (13)	−0.0248 (14)
O1B	0.0422 (7)	0.0888 (10)	0.0525 (8)	−0.0113 (7)	0.0046 (6)	0.0012 (7)
O2B	0.0693 (8)	0.0764 (9)	0.0379 (7)	0.0098 (7)	0.0162 (6)	0.0073 (6)
O3B	0.0718 (9)	0.0992 (12)	0.0616 (9)	−0.0304 (8)	−0.0060 (8)	0.0069 (8)
O4B	0.0554 (8)	0.0702 (9)	0.0515 (8)	−0.0185 (6)	0.0164 (6)	0.0035 (7)
O5B	0.0440 (8)	0.1239 (13)	0.0725 (10)	−0.0137 (8)	0.0222 (7)	−0.0035 (9)
O6B	0.0534 (8)	0.1029 (11)	0.0513 (8)	0.0017 (7)	0.0292 (7)	0.0122 (7)
N1B	0.0379 (8)	0.0579 (9)	0.0410 (8)	−0.0008 (7)	0.0115 (7)	0.0014 (7)
N2B	0.0475 (8)	0.0596 (10)	0.0356 (8)	0.0057 (7)	0.0143 (7)	0.0016 (7)
N3B	0.0423 (8)	0.0590 (10)	0.0383 (8)	−0.0057 (7)	0.0129 (7)	−0.0020 (7)
N4B	0.0412 (8)	0.0561 (10)	0.0398 (8)	0.0019 (7)	0.0135 (7)	0.0012 (7)
C1B	0.0537 (13)	0.0992 (18)	0.0872 (16)	0.0014 (12)	0.0252 (12)	−0.0178 (13)
C2B	0.0789 (15)	0.0823 (15)	0.0762 (15)	−0.0032 (12)	0.0431 (12)	−0.0137 (12)
C3B	0.0504 (11)	0.0492 (11)	0.0664 (13)	−0.0030 (9)	0.0216 (10)	−0.0132 (10)
C4B	0.0500 (11)	0.0502 (11)	0.0535 (11)	−0.0012 (9)	0.0145 (9)	−0.0032 (9)
C5B	0.0477 (10)	0.0437 (10)	0.0482 (11)	−0.0008 (8)	0.0166 (9)	−0.0007 (8)
C6B	0.0522 (11)	0.0453 (10)	0.0475 (11)	−0.0007 (8)	0.0170 (9)	−0.0062 (8)
C7B	0.0673 (13)	0.0488 (11)	0.0470 (11)	−0.0003 (9)	0.0229 (10)	−0.0071 (8)

C8B	0.0611 (12)	0.0443 (11)	0.0622 (13)	−0.0059 (9)	0.0293 (10)	−0.0128 (9)
C9B	0.0479 (10)	0.0641 (12)	0.0482 (11)	0.0050 (9)	0.0132 (9)	0.0087 (9)
C10B	0.0584 (12)	0.0650 (13)	0.0406 (10)	0.0036 (10)	0.0139 (9)	−0.0066 (9)
C11B	0.0409 (10)	0.0682 (13)	0.0334 (9)	−0.0075 (10)	0.0153 (8)	0.0048 (9)
C12B	0.0392 (10)	0.0614 (12)	0.0352 (10)	−0.0035 (9)	0.0087 (8)	−0.0008 (9)
C13B	0.0380 (9)	0.0580 (11)	0.0381 (10)	−0.0041 (8)	0.0100 (8)	0.0013 (8)
C14B	0.0461 (11)	0.0640 (13)	0.0482 (12)	−0.0051 (9)	0.0088 (9)	0.0003 (10)
C15B	0.0674 (13)	0.0936 (17)	0.0682 (14)	−0.0333 (12)	0.0246 (11)	0.0037 (12)
C16B	0.112 (2)	0.0737 (17)	0.0967 (19)	−0.0279 (15)	0.0226 (16)	−0.0022 (14)
C17B	0.0378 (9)	0.0603 (11)	0.0389 (10)	−0.0037 (8)	0.0139 (8)	0.0000 (8)
C18B	0.0462 (11)	0.0665 (13)	0.0525 (12)	−0.0008 (10)	0.0215 (10)	0.0026 (10)
C19B	0.0712 (15)	0.150 (2)	0.0721 (16)	0.0005 (15)	0.0476 (13)	0.0227 (15)
C20B	0.134 (2)	0.109 (2)	0.0802 (18)	0.0127 (16)	0.0710 (17)	0.0114 (14)
C21B	0.0626 (12)	0.0641 (13)	0.0420 (10)	−0.0079 (10)	0.0202 (9)	−0.0094 (9)
C22B	0.0473 (11)	0.0665 (13)	0.0497 (11)	0.0079 (9)	0.0172 (9)	0.0000 (9)
C23B	0.0567 (11)	0.0522 (11)	0.0412 (10)	−0.0011 (9)	0.0211 (9)	−0.0074 (8)
C24B	0.0518 (11)	0.0520 (11)	0.0455 (11)	0.0042 (9)	0.0190 (9)	−0.0049 (9)
C25B	0.0654 (13)	0.0560 (12)	0.0503 (11)	0.0063 (10)	0.0173 (10)	0.0013 (9)
C26B	0.0751 (14)	0.0485 (12)	0.0605 (13)	−0.0005 (10)	0.0285 (11)	0.0000 (10)
C27B	0.0637 (12)	0.0450 (11)	0.0616 (13)	−0.0013 (9)	0.0249 (11)	−0.0067 (9)
C28B	0.0603 (12)	0.0511 (11)	0.0478 (11)	0.0000 (9)	0.0167 (9)	−0.0068 (9)
C29B	0.0784 (15)	0.0599 (14)	0.0920 (16)	−0.0143 (11)	0.0240 (13)	0.0021 (12)
C30B	0.1126 (19)	0.0788 (16)	0.0806 (16)	−0.0167 (14)	0.0272 (14)	0.0201 (13)

Geometric parameters (Å, °)

O1A—C11A	1.2160 (18)	C27A—C28A	1.388 (3)
O2A—C12A	1.211 (2)	C27A—C29A	1.520 (3)
N1A—C11A	1.359 (2)	C28A—H28A	0.9300
N1A—C13A	1.4435 (19)	C29A—H29D	0.9600
N1A—C9A	1.452 (2)	C29A—H29E	0.9600
N2A—C12A	1.386 (2)	C29A—H29F	0.9600
N2A—C13A	1.432 (2)	C30A—H30D	0.9600
N2A—C10A	1.461 (2)	C30A—H30F	0.9600
N3A—C11A	1.382 (2)	C30A—H30E	0.9600
N3A—C17A	1.434 (2)	O1B—C11B	1.2143 (19)
N3A—C21A	1.466 (2)	O2B—C12B	1.2155 (19)
N4A—C12A	1.371 (2)	O3B—C14B	1.197 (2)
N4A—C17A	1.444 (2)	O4B—C14B	1.315 (2)
N4A—C22A	1.457 (2)	O4B—C15B	1.470 (2)
C1A—C3A	1.509 (2)	O5B—C18B	1.189 (2)
C1A—H1A1	0.9600	O6B—C18B	1.319 (2)
C1A—H1A2	0.9600	O6B—C19B	1.463 (2)
C1A—H1A3	0.9600	N1B—C11B	1.382 (2)
C2A—C8A	1.501 (2)	N1B—C13B	1.431 (2)
C2A—H2A1	0.9600	N1B—C9B	1.455 (2)
C2A—H2A2	0.9600	N2B—C12B	1.360 (2)
C2A—H2A3	0.9600	N2B—C13B	1.4434 (19)
C3A—C8A	1.389 (2)	N2B—C10B	1.457 (2)

C3A—C4A	1.390 (2)	N3B—C11B	1.365 (2)
C4A—C5A	1.383 (2)	N3B—C17B	1.443 (2)
C4A—H4A	0.9300	N3B—C21B	1.449 (2)
C5A—C6A	1.398 (2)	N4B—C12B	1.379 (2)
C5A—C9A	1.511 (2)	N4B—C17B	1.443 (2)
C6A—C7A	1.384 (2)	N4B—C22B	1.467 (2)
C6A—C10A	1.515 (2)	C1B—C3B	1.507 (3)
C7A—C8A	1.395 (2)	C1B—H1B1	0.9600
C7A—H7A	0.9300	C1B—H1B2	0.9600
C9A—H9A1	0.9700	C1B—H1B3	0.9600
C9A—H9A2	0.9700	C2B—C8B	1.512 (2)
C10A—H10C	0.9700	C2B—H2B1	0.9600
C10A—H10D	0.9700	C2B—H2B2	0.9600
C13A—C14A	1.543 (2)	C2B—H2B3	0.9600
C13A—C17A	1.570 (2)	C3B—C4B	1.380 (2)
C14A—O3'	1.200 (7)	C3B—C8B	1.394 (3)
C14A—O3A	1.213 (6)	C4B—C5B	1.388 (2)
C14A—O4A	1.291 (7)	C4B—H4B	0.9300
C14A—O4'	1.346 (7)	C5B—C6B	1.394 (2)
C15A—O4A	1.456 (7)	C5B—C9B	1.514 (2)
C15A—C16A	1.494 (8)	C6B—C7B	1.393 (2)
C15A—H15C	0.9700	C6B—C10B	1.511 (2)
C15A—H15D	0.9700	C7B—C8B	1.386 (2)
C16A—H16G	0.9600	C7B—H7B	0.9300
C16A—H16H	0.9600	C9B—H9B1	0.9700
C16A—H16I	0.9600	C9B—H9B2	0.9700
C16'—C15'	1.490 (8)	C10B—H10A	0.9700
C16'—H16F	0.9600	C10B—H10B	0.9700
C16'—H16E	0.9600	C13B—C14B	1.540 (2)
C16'—H16D	0.9600	C13B—C17B	1.563 (2)
C15'—O4'	1.461 (7)	C15B—C16B	1.488 (3)
C15'—H15E	0.9700	C15B—H15A	0.9700
C15'—H15F	0.9700	C15B—H15B	0.9700
C17A—C18A	1.540 (2)	C16B—H16A	0.9600
C18A—O5'	1.208 (5)	C16B—H16B	0.9600
C18A—O5A	1.216 (6)	C16B—H16C	0.9600
C18A—O6'	1.264 (5)	C17B—C18B	1.543 (2)
C18A—O6A	1.355 (8)	C19B—C20B	1.461 (3)
C19A—O6A	1.434 (8)	C19B—H19A	0.9700
C19A—C20A	1.500 (9)	C19B—H19B	0.9700
C19A—H19D	0.9700	C20B—H20G	0.9600
C19A—H19C	0.9700	C20B—H20H	0.9600
C20A—H20A	0.9600	C20B—H20I	0.9600
C20A—H20B	0.9600	C21B—C23B	1.508 (2)
C20A—H20C	0.9600	C21B—H21A	0.9700
C19'—O6'	1.455 (6)	C21B—H21B	0.9700
C19'—C20'	1.491 (7)	C22B—C24B	1.513 (2)
C19'—H19E	0.9700	C22B—H22A	0.9700
C19'—H19F	0.9700	C22B—H22B	0.9700

C20'—H20D	0.9600	C23B—C28B	1.388 (2)
C20'—H20E	0.9600	C23B—C24B	1.397 (2)
C20'—H20F	0.9600	C24B—C25B	1.380 (2)
C21A—C23A	1.509 (2)	C25B—C26B	1.391 (3)
C21A—H21C	0.9700	C25B—H25B	0.9300
C21A—H21D	0.9700	C26B—C27B	1.389 (3)
C22A—C24A	1.513 (2)	C26B—C30B	1.519 (3)
C22A—H22C	0.9700	C27B—C28B	1.385 (2)
C22A—H22D	0.9700	C27B—C29B	1.505 (3)
C23A—C28A	1.385 (2)	C28B—H28B	0.9300
C23A—C24A	1.394 (3)	C29B—H29A	0.9600
C24A—C25A	1.391 (2)	C29B—H29B	0.9600
C25A—C26A	1.389 (3)	C29B—H29C	0.9600
C25A—H25A	0.9300	C30B—H30A	0.9600
C26A—C27A	1.385 (3)	C30B—H30B	0.9600
C26A—C30A	1.512 (3)	C30B—H30C	0.9600
C11A—N1A—C13A	113.29 (14)	C27A—C29A—H29D	109.5
C11A—N1A—C9A	124.30 (14)	C27A—C29A—H29E	109.5
C13A—N1A—C9A	122.28 (13)	H29D—C29A—H29E	109.5
C12A—N2A—C13A	110.77 (14)	C27A—C29A—H29F	109.5
C12A—N2A—C10A	119.25 (15)	H29D—C29A—H29F	109.5
C13A—N2A—C10A	120.65 (14)	H29E—C29A—H29F	109.5
C11A—N3A—C17A	110.49 (14)	C26A—C30A—H30D	109.5
C11A—N3A—C21A	120.08 (14)	C26A—C30A—H30F	109.5
C17A—N3A—C21A	120.43 (14)	H30D—C30A—H30F	109.5
C12A—N4A—C17A	113.23 (14)	C26A—C30A—H30E	109.5
C12A—N4A—C22A	124.49 (15)	H30D—C30A—H30E	109.5
C17A—N4A—C22A	122.17 (14)	H30F—C30A—H30E	109.5
C3A—C1A—H1A1	109.5	C14B—O4B—C15B	116.61 (14)
C3A—C1A—H1A2	109.5	C18B—O6B—C19B	116.05 (15)
H1A1—C1A—H1A2	109.5	C11B—N1B—C13B	110.60 (14)
C3A—C1A—H1A3	109.5	C11B—N1B—C9B	121.18 (14)
H1A1—C1A—H1A3	109.5	C13B—N1B—C9B	120.54 (14)
H1A2—C1A—H1A3	109.5	C12B—N2B—C13B	112.36 (13)
C8A—C2A—H2A1	109.5	C12B—N2B—C10B	124.30 (14)
C8A—C2A—H2A2	109.5	C13B—N2B—C10B	122.21 (14)
H2A1—C2A—H2A2	109.5	C11B—N3B—C17B	112.89 (14)
C8A—C2A—H2A3	109.5	C11B—N3B—C21B	124.17 (15)
H2A1—C2A—H2A3	109.5	C17B—N3B—C21B	122.92 (14)
H2A2—C2A—H2A3	109.5	C12B—N4B—C17B	110.61 (14)
C8A—C3A—C4A	118.43 (15)	C12B—N4B—C22B	119.41 (14)
C8A—C3A—C1A	122.93 (16)	C17B—N4B—C22B	120.20 (13)
C4A—C3A—C1A	118.65 (16)	C3B—C1B—H1B1	109.5
C5A—C4A—C3A	123.22 (16)	C3B—C1B—H1B2	109.5
C5A—C4A—H4A	118.4	H1B1—C1B—H1B2	109.5
C3A—C4A—H4A	118.4	C3B—C1B—H1B3	109.5
C4A—C5A—C6A	118.58 (15)	H1B1—C1B—H1B3	109.5
C4A—C5A—C9A	119.55 (15)	H1B2—C1B—H1B3	109.5
C6A—C5A—C9A	121.85 (14)	C8B—C2B—H2B1	109.5

C7A—C6A—C5A	118.13 (15)	C8B—C2B—H2B2	109.5
C7A—C6A—C10A	119.43 (15)	H2B1—C2B—H2B2	109.5
C5A—C6A—C10A	122.39 (15)	C8B—C2B—H2B3	109.5
C6A—C7A—C8A	123.30 (16)	H2B1—C2B—H2B3	109.5
C6A—C7A—H7A	118.3	H2B2—C2B—H2B3	109.5
C8A—C7A—H7A	118.3	C4B—C3B—C8B	118.02 (17)
C3A—C8A—C7A	118.31 (16)	C4B—C3B—C1B	120.04 (18)
C3A—C8A—C2A	122.26 (16)	C8B—C3B—C1B	121.92 (17)
C7A—C8A—C2A	119.43 (16)	C3B—C4B—C5B	123.67 (17)
N1A—C9A—C5A	113.18 (13)	C3B—C4B—H4B	118.2
N1A—C9A—H9A1	108.9	C5B—C4B—H4B	118.2
C5A—C9A—H9A1	108.9	C4B—C5B—C6B	118.33 (16)
N1A—C9A—H9A2	108.9	C4B—C5B—C9B	117.57 (15)
C5A—C9A—H9A2	108.9	C6B—C5B—C9B	123.85 (15)
H9A1—C9A—H9A2	107.8	C7B—C6B—C5B	118.06 (16)
N2A—C10A—C6A	115.70 (13)	C7B—C6B—C10B	117.99 (16)
N2A—C10A—H10C	108.4	C5B—C6B—C10B	123.84 (15)
C6A—C10A—H10C	108.4	C8B—C7B—C6B	123.10 (17)
N2A—C10A—H10D	108.4	C8B—C7B—H7B	118.5
C6A—C10A—H10D	108.4	C6B—C7B—H7B	118.5
H10C—C10A—H10D	107.4	C7B—C8B—C3B	118.72 (17)
O1A—C11A—N1A	126.20 (16)	C7B—C8B—C2B	119.80 (18)
O1A—C11A—N3A	125.68 (16)	C3B—C8B—C2B	121.48 (18)
N1A—C11A—N3A	108.10 (14)	N1B—C9B—C5B	117.44 (14)
O2A—C12A—N4A	126.46 (18)	N1B—C9B—H9B1	107.9
O2A—C12A—N2A	125.99 (18)	C5B—C9B—H9B1	107.9
N4A—C12A—N2A	107.54 (16)	N1B—C9B—H9B2	107.9
N2A—C13A—N1A	114.10 (13)	C5B—C9B—H9B2	107.9
N2A—C13A—C14A	114.70 (15)	H9B1—C9B—H9B2	107.2
N1A—C13A—C14A	108.67 (14)	N2B—C10B—C6B	115.36 (14)
N2A—C13A—C17A	103.51 (13)	N2B—C10B—H10A	108.4
N1A—C13A—C17A	100.93 (12)	C6B—C10B—H10A	108.4
C14A—C13A—C17A	114.13 (14)	N2B—C10B—H10B	108.4
O3'—C14A—O4A	114.8 (7)	C6B—C10B—H10B	108.4
O3A—C14A—O4A	122.9 (7)	H10A—C10B—H10B	107.5
O3'—C14A—O4'	127.2 (7)	O1B—C11B—N3B	126.51 (18)
O3A—C14A—O4'	125.9 (8)	O1B—C11B—N1B	125.81 (18)
O3'—C14A—C13A	123.0 (6)	N3B—C11B—N1B	107.65 (15)
O3A—C14A—C13A	120.1 (5)	O2B—C12B—N2B	126.48 (16)
O4A—C14A—C13A	117.0 (5)	O2B—C12B—N4B	125.03 (17)
O4'—C14A—C13A	109.3 (5)	N2B—C12B—N4B	108.48 (14)
O4A—C15A—C16A	106.7 (7)	N1B—C13B—N2B	113.60 (13)
O4A—C15A—H15C	110.4	N1B—C13B—C14B	113.69 (14)
C16A—C15A—H15C	110.4	N2B—C13B—C14B	110.33 (14)
O4A—C15A—H15D	110.4	N1B—C13B—C17B	103.02 (13)
C16A—C15A—H15D	110.4	N2B—C13B—C17B	101.48 (13)
H15C—C15A—H15D	108.6	C14B—C13B—C17B	113.95 (13)
C14A—O4A—C15A	114.5 (8)	O3B—C14B—O4B	126.18 (17)
C15'—C16'—H16F	109.5	O3B—C14B—C13B	121.69 (17)

C15'—C16'—H16E	109.5	O4B—C14B—C13B	112.13 (15)
H16F—C16'—H16E	109.5	O4B—C15B—C16B	111.87 (17)
C15'—C16'—H16D	109.5	O4B—C15B—H15A	109.2
H16F—C16'—H16D	109.5	C16B—C15B—H15A	109.2
H16E—C16'—H16D	109.5	O4B—C15B—H15B	109.2
O4'—C15'—C16'	111.8 (7)	C16B—C15B—H15B	109.2
O4'—C15'—H15E	109.3	H15A—C15B—H15B	107.9
C16'—C15'—H15E	109.3	C15B—C16B—H16A	109.5
O4'—C15'—H15F	109.3	C15B—C16B—H16B	109.5
C16'—C15'—H15F	109.3	H16A—C16B—H16B	109.5
H15E—C15'—H15F	107.9	C15B—C16B—H16C	109.5
C14A—O4'—C15'	119.3 (8)	H16A—C16B—H16C	109.5
N3A—C17A—N4A	113.99 (13)	H16B—C16B—H16C	109.5
N3A—C17A—C18A	111.39 (15)	N3B—C17B—N4B	114.56 (13)
N4A—C17A—C18A	112.37 (15)	N3B—C17B—C18B	113.43 (14)
N3A—C17A—C13A	103.45 (13)	N4B—C17B—C18B	110.67 (14)
N4A—C17A—C13A	101.09 (13)	N3B—C17B—C13B	101.25 (12)
C18A—C17A—C13A	113.87 (15)	N4B—C17B—C13B	102.69 (13)
O5'—C18A—O6'	125.4 (5)	C18B—C17B—C13B	113.46 (14)
O5A—C18A—O6'	114.8 (6)	O5B—C18B—O6B	125.66 (16)
O5'—C18A—O6A	119.9 (7)	O5B—C18B—C17B	122.84 (17)
O5A—C18A—O6A	125.8 (7)	O6B—C18B—C17B	111.46 (16)
O5'—C18A—C17A	122.2 (4)	C20B—C19B—O6B	108.48 (18)
O5A—C18A—C17A	122.6 (5)	C20B—C19B—H19A	110.0
O6'—C18A—C17A	112.0 (4)	O6B—C19B—H19A	110.0
O6A—C18A—C17A	110.0 (5)	C20B—C19B—H19B	110.0
O6A—C19A—C20A	110.2 (8)	O6B—C19B—H19B	110.0
O6A—C19A—H19D	109.6	H19A—C19B—H19B	108.4
C20A—C19A—H19D	109.6	C19B—C20B—H20G	109.5
O6A—C19A—H19C	109.6	C19B—C20B—H20H	109.5
C20A—C19A—H19C	109.6	H20G—C20B—H20H	109.5
H19D—C19A—H19C	108.1	C19B—C20B—H20I	109.5
C18A—O6A—C19A	122.3 (10)	H20G—C20B—H20I	109.5
O6'—C19'—C20'	106.8 (6)	H20H—C20B—H20I	109.5
O6'—C19'—H19E	110.4	N3B—C21B—C23B	112.75 (14)
C20'—C19'—H19E	110.4	N3B—C21B—H21A	109.0
O6'—C19'—H19F	110.4	C23B—C21B—H21A	109.0
C20'—C19'—H19F	110.4	N3B—C21B—H21B	109.0
H19E—C19'—H19F	108.6	C23B—C21B—H21B	109.0
C19'—C20'—H20D	109.5	H21A—C21B—H21B	107.8
C19'—C20'—H20E	109.5	N4B—C22B—C24B	113.86 (14)
H20D—C20'—H20E	109.5	N4B—C22B—H22A	108.8
C19'—C20'—H20F	109.5	C24B—C22B—H22A	108.8
H20D—C20'—H20F	109.5	N4B—C22B—H22B	108.8
H20E—C20'—H20F	109.5	C24B—C22B—H22B	108.8
C18A—O6'—C19'	117.4 (6)	H22A—C22B—H22B	107.7
N3A—C21A—C23A	115.69 (15)	C28B—C23B—C24B	118.74 (16)
N3A—C21A—H21C	108.4	C28B—C23B—C21B	120.28 (16)
C23A—C21A—H21C	108.4	C24B—C23B—C21B	120.97 (16)

N3A—C21A—H21D	108.4	C25B—C24B—C23B	118.46 (17)
C23A—C21A—H21D	108.4	C25B—C24B—C22B	120.00 (16)
H21C—C21A—H21D	107.4	C23B—C24B—C22B	121.53 (16)
N4A—C22A—C24A	113.69 (14)	C24B—C25B—C26B	122.67 (18)
N4A—C22A—H22C	108.8	C24B—C25B—H25B	118.7
C24A—C22A—H22C	108.8	C26B—C25B—H25B	118.7
N4A—C22A—H22D	108.8	C27B—C26B—C25B	118.94 (17)
C24A—C22A—H22D	108.8	C27B—C26B—C30B	121.43 (19)
H22C—C22A—H22D	107.7	C25B—C26B—C30B	119.61 (19)
C28A—C23A—C24A	118.49 (18)	C28B—C27B—C26B	118.48 (17)
C28A—C23A—C21A	118.96 (18)	C28B—C27B—C29B	119.65 (18)
C24A—C23A—C21A	122.52 (17)	C26B—C27B—C29B	121.84 (18)
C25A—C24A—C23A	118.19 (18)	C27B—C28B—C23B	122.69 (17)
C25A—C24A—C22A	119.97 (18)	C27B—C28B—H28B	118.7
C23A—C24A—C22A	121.84 (17)	C23B—C28B—H28B	118.7
C26A—C25A—C24A	123.2 (2)	C27B—C29B—H29A	109.5
C26A—C25A—H25A	118.4	C27B—C29B—H29B	109.5
C24A—C25A—H25A	118.4	H29A—C29B—H29B	109.5
C27A—C26A—C25A	118.32 (19)	C27B—C29B—H29C	109.5
C27A—C26A—C30A	122.2 (2)	H29A—C29B—H29C	109.5
C25A—C26A—C30A	119.4 (2)	H29B—C29B—H29C	109.5
C26A—C27A—C28A	118.79 (19)	C26B—C30B—H30A	109.5
C26A—C27A—C29A	121.4 (2)	C26B—C30B—H30B	109.5
C28A—C27A—C29A	119.7 (2)	H30A—C30B—H30B	109.5
C23A—C28A—C27A	123.0 (2)	C26B—C30B—H30C	109.5
C23A—C28A—H28A	118.5	H30A—C30B—H30C	109.5
C27A—C28A—H28A	118.5	H30B—C30B—H30C	109.5
C8A—C3A—C4A—C5A	1.3 (3)	N4A—C22A—C24A—C23A	−53.5 (2)
C1A—C3A—C4A—C5A	−179.06 (16)	C23A—C24A—C25A—C26A	1.5 (3)
C3A—C4A—C5A—C6A	0.1 (2)	C22A—C24A—C25A—C26A	−178.75 (16)
C3A—C4A—C5A—C9A	178.31 (15)	C24A—C25A—C26A—C27A	0.4 (3)
C4A—C5A—C6A—C7A	−1.5 (2)	C24A—C25A—C26A—C30A	179.80 (17)
C9A—C5A—C6A—C7A	−179.68 (15)	C25A—C26A—C27A—C28A	−1.4 (3)
C4A—C5A—C6A—C10A	175.81 (15)	C30A—C26A—C27A—C28A	179.23 (18)
C9A—C5A—C6A—C10A	−2.3 (2)	C25A—C26A—C27A—C29A	176.23 (18)
C5A—C6A—C7A—C8A	1.7 (2)	C30A—C26A—C27A—C29A	−3.1 (3)
C10A—C6A—C7A—C8A	−175.76 (15)	C24A—C23A—C28A—C27A	1.4 (3)
C4A—C3A—C8A—C7A	−1.2 (2)	C21A—C23A—C28A—C27A	−176.58 (17)
C1A—C3A—C8A—C7A	179.18 (16)	C26A—C27A—C28A—C23A	0.5 (3)
C4A—C3A—C8A—C2A	179.21 (16)	C29A—C27A—C28A—C23A	−177.18 (19)
C1A—C3A—C8A—C2A	−0.5 (3)	C8B—C3B—C4B—C5B	2.6 (3)
C6A—C7A—C8A—C3A	−0.3 (3)	C1B—C3B—C4B—C5B	−176.01 (17)
C6A—C7A—C8A—C2A	179.36 (16)	C3B—C4B—C5B—C6B	−2.7 (3)
C11A—N1A—C9A—C5A	−106.97 (17)	C3B—C4B—C5B—C9B	171.81 (16)
C13A—N1A—C9A—C5A	77.30 (18)	C4B—C5B—C6B—C7B	0.2 (2)
C4A—C5A—C9A—N1A	126.93 (16)	C9B—C5B—C6B—C7B	−173.89 (16)
C6A—C5A—C9A—N1A	−54.9 (2)	C4B—C5B—C6B—C10B	176.46 (16)
C12A—N2A—C10A—C6A	71.0 (2)	C9B—C5B—C6B—C10B	2.3 (3)
C13A—N2A—C10A—C6A	−72.5 (2)	C5B—C6B—C7B—C8B	2.3 (3)

C7A—C6A—C10A—N2A	−124.46 (17)	C10B—C6B—C7B—C8B	−174.17 (16)
C5A—C6A—C10A—N2A	58.2 (2)	C6B—C7B—C8B—C3B	−2.4 (3)
C13A—N1A—C11A—O1A	178.27 (16)	C6B—C7B—C8B—C2B	177.66 (16)
C9A—N1A—C11A—O1A	2.2 (3)	C4B—C3B—C8B—C7B	0.0 (3)
C13A—N1A—C11A—N3A	−0.24 (18)	C1B—C3B—C8B—C7B	178.54 (17)
C9A—N1A—C11A—N3A	−176.31 (14)	C4B—C3B—C8B—C2B	179.91 (16)
C17A—N3A—C11A—O1A	168.77 (16)	C1B—C3B—C8B—C2B	−1.5 (3)
C21A—N3A—C11A—O1A	21.5 (3)	C11B—N1B—C9B—C5B	−76.6 (2)
C17A—N3A—C11A—N1A	−12.71 (18)	C13B—N1B—C9B—C5B	70.0 (2)
C21A—N3A—C11A—N1A	−159.99 (14)	C4B—C5B—C9B—N1B	134.07 (16)
C17A—N4A—C12A—O2A	179.59 (16)	C6B—C5B—C9B—N1B	−51.8 (2)
C22A—N4A—C12A—O2A	3.3 (3)	C12B—N2B—C10B—C6B	120.76 (17)
C17A—N4A—C12A—N2A	0.43 (18)	C13B—N2B—C10B—C6B	−72.4 (2)
C22A—N4A—C12A—N2A	−175.90 (14)	C7B—C6B—C10B—N2B	−135.78 (16)
C13A—N2A—C12A—O2A	167.42 (16)	C5B—C6B—C10B—N2B	48.0 (2)
C10A—N2A—C12A—O2A	20.6 (2)	C17B—N3B—C11B—O1B	−179.01 (15)
C13A—N2A—C12A—N4A	−13.43 (17)	C21B—N3B—C11B—O1B	2.8 (3)
C10A—N2A—C12A—N4A	−160.29 (13)	C17B—N3B—C11B—N1B	−0.94 (17)
C12A—N2A—C13A—N1A	−89.10 (16)	C21B—N3B—C11B—N1B	−179.15 (13)
C10A—N2A—C13A—N1A	57.23 (19)	C13B—N1B—C11B—O1B	−166.92 (15)
C12A—N2A—C13A—C14A	144.62 (15)	C9B—N1B—C11B—O1B	−17.4 (2)
C10A—N2A—C13A—C14A	−69.05 (19)	C13B—N1B—C11B—N3B	14.99 (17)
C12A—N2A—C13A—C17A	19.63 (16)	C9B—N1B—C11B—N3B	164.52 (13)
C10A—N2A—C13A—C17A	165.96 (13)	C13B—N2B—C12B—O2B	−174.47 (16)
C11A—N1A—C13A—N2A	121.71 (15)	C10B—N2B—C12B—O2B	−6.5 (3)
C9A—N1A—C13A—N2A	−62.13 (19)	C13B—N2B—C12B—N4B	5.16 (18)
C11A—N1A—C13A—C14A	−108.92 (16)	C10B—N2B—C12B—N4B	173.16 (14)
C9A—N1A—C13A—C14A	67.24 (19)	C17B—N4B—C12B—O2B	−170.80 (16)
C11A—N1A—C13A—C17A	11.40 (17)	C22B—N4B—C12B—O2B	−24.8 (2)
C9A—N1A—C13A—C17A	−172.44 (14)	C17B—N4B—C12B—N2B	9.56 (18)
N2A—C13A—C14A—O3'	177.6 (8)	C22B—N4B—C12B—N2B	155.54 (14)
N1A—C13A—C14A—O3'	48.6 (9)	C11B—N1B—C13B—N2B	87.41 (16)
C17A—C13A—C14A—O3'	−63.2 (9)	C9B—N1B—C13B—N2B	−62.35 (19)
N2A—C13A—C14A—O3A	147.2 (6)	C11B—N1B—C13B—C14B	−145.31 (14)
N1A—C13A—C14A—O3A	18.2 (6)	C9B—N1B—C13B—C14B	64.94 (19)
C17A—C13A—C14A—O3A	−93.6 (6)	C11B—N1B—C13B—C17B	−21.49 (16)
N2A—C13A—C14A—O4A	−29.2 (7)	C9B—N1B—C13B—C17B	−171.25 (13)
N1A—C13A—C14A—O4A	−158.3 (6)	C12B—N2B—C13B—N1B	−125.86 (15)
C17A—C13A—C14A—O4A	90.0 (7)	C10B—N2B—C13B—N1B	65.85 (19)
N2A—C13A—C14A—O4'	−9.8 (6)	C12B—N2B—C13B—C14B	105.12 (16)
N1A—C13A—C14A—O4'	−138.9 (6)	C10B—N2B—C13B—C14B	−63.17 (19)
C17A—C13A—C14A—O4'	109.4 (6)	C12B—N2B—C13B—C17B	−16.01 (17)
O3'—C14A—O4A—C15A	−23.4 (12)	C10B—N2B—C13B—C17B	175.70 (13)
O3A—C14A—O4A—C15A	4.9 (12)	C15B—O4B—C14B—O3B	0.4 (3)
O4'—C14A—O4A—C15A	110 (3)	C15B—O4B—C14B—C13B	179.78 (15)
C13A—C14A—O4A—C15A	−178.7 (6)	N1B—C13B—C14B—O3B	−149.65 (17)
C16A—C15A—O4A—C14A	−173.2 (15)	N2B—C13B—C14B—O3B	−20.7 (2)
O3'—C14A—O4'—C15'	−14.9 (14)	C17B—C13B—C14B—O3B	92.7 (2)
O3A—C14A—O4'—C15'	17.5 (12)	N1B—C13B—C14B—O4B	30.9 (2)

O4A—C14A—O4'—C15'	−70 (2)	N2B—C13B—C14B—O4B	159.89 (14)
C13A—C14A—O4'—C15'	172.9 (6)	C17B—C13B—C14B—O4B	−86.73 (18)
C16'—C15'—O4'—C14A	97.1 (17)	C14B—O4B—C15B—C16B	78.0 (2)
C11A—N3A—C17A—N4A	−89.73 (17)	C11B—N3B—C17B—N4B	−121.39 (15)
C21A—N3A—C17A—N4A	57.41 (19)	C21B—N3B—C17B—N4B	56.85 (19)
C11A—N3A—C17A—C18A	141.83 (15)	C11B—N3B—C17B—C18B	110.21 (16)
C21A—N3A—C17A—C18A	−71.0 (2)	C21B—N3B—C17B—C18B	−71.54 (19)
C11A—N3A—C17A—C13A	19.10 (17)	C11B—N3B—C17B—C13B	−11.69 (16)
C21A—N3A—C17A—C13A	166.24 (14)	C21B—N3B—C17B—C13B	166.55 (13)
C12A—N4A—C17A—N3A	121.29 (15)	C12B—N4B—C17B—N3B	90.12 (17)
C22A—N4A—C17A—N3A	−62.3 (2)	C22B—N4B—C17B—N3B	−55.55 (19)
C12A—N4A—C17A—C18A	−110.77 (17)	C12B—N4B—C17B—C18B	−140.11 (14)
C22A—N4A—C17A—C18A	65.7 (2)	C22B—N4B—C17B—C18B	74.22 (18)
C12A—N4A—C17A—C13A	11.01 (16)	C12B—N4B—C17B—C13B	−18.71 (16)
C22A—N4A—C17A—C13A	−172.56 (14)	C22B—N4B—C17B—C13B	−164.38 (13)
N2A—C13A—C17A—N3A	−135.92 (13)	N1B—C13B—C17B—N3B	19.17 (15)
N1A—C13A—C17A—N3A	−17.62 (15)	N2B—C13B—C17B—N3B	−98.63 (13)
C14A—C13A—C17A—N3A	98.73 (16)	C14B—C13B—C17B—N3B	142.81 (14)
N2A—C13A—C17A—N4A	−17.70 (15)	N1B—C13B—C17B—N4B	137.80 (12)
N1A—C13A—C17A—N4A	100.60 (13)	N2B—C13B—C17B—N4B	20.01 (14)
C14A—C13A—C17A—N4A	−143.05 (15)	C14B—C13B—C17B—N4B	−98.55 (15)
N2A—C13A—C17A—C18A	103.02 (16)	N1B—C13B—C17B—C18B	−102.72 (15)
N1A—C13A—C17A—C18A	−138.68 (15)	N2B—C13B—C17B—C18B	139.49 (14)
C14A—C13A—C17A—C18A	−22.3 (2)	C14B—C13B—C17B—C18B	20.9 (2)
N3A—C17A—C18A—O5'	−0.4 (8)	C19B—O6B—C18B—O5B	−0.4 (3)
N4A—C17A—C18A—O5'	−129.7 (8)	C19B—O6B—C18B—C17B	−178.18 (17)
C13A—C17A—C18A—O5'	116.2 (8)	N3B—C17B—C18B—O5B	165.61 (18)
N3A—C17A—C18A—O5A	−45.0 (8)	N4B—C17B—C18B—O5B	35.2 (2)
N4A—C17A—C18A—O5A	−174.3 (7)	C13B—C17B—C18B—O5B	−79.6 (2)
C13A—C17A—C18A—O5A	71.5 (7)	N3B—C17B—C18B—O6B	−16.5 (2)
N3A—C17A—C18A—O6'	172.4 (5)	N4B—C17B—C18B—O6B	−146.88 (15)
N4A—C17A—C18A—O6'	43.1 (5)	C13B—C17B—C18B—O6B	98.31 (17)
C13A—C17A—C18A—O6'	−71.1 (5)	C18B—O6B—C19B—C20B	−171.94 (18)
N3A—C17A—C18A—O6A	148.5 (6)	C11B—N3B—C21B—C23B	101.56 (18)
N4A—C17A—C18A—O6A	19.2 (6)	C17B—N3B—C21B—C23B	−76.48 (19)
C13A—C17A—C18A—O6A	−95.0 (6)	C12B—N4B—C22B—C24B	−66.68 (19)
O5'—C18A—O6A—C19A	−33.7 (11)	C17B—N4B—C22B—C24B	76.02 (18)
O5A—C18A—O6A—C19A	10.6 (12)	N3B—C21B—C23B—C28B	−118.73 (17)
O6'—C18A—O6A—C19A	77 (2)	N3B—C21B—C23B—C24B	60.3 (2)
C17A—C18A—O6A—C19A	176.6 (7)	C28B—C23B—C24B—C25B	−0.9 (2)
C20A—C19A—O6A—C18A	−97 (2)	C21B—C23B—C24B—C25B	−179.94 (16)
O5'—C18A—O6'—C19'	−9.7 (9)	C28B—C23B—C24B—C22B	177.98 (15)
O5A—C18A—O6'—C19'	32.2 (8)	C21B—C23B—C24B—C22B	−1.0 (2)
O6A—C18A—O6'—C19'	−93 (2)	N4B—C22B—C24B—C25B	118.61 (18)
C17A—C18A—O6'—C19'	177.9 (5)	N4B—C22B—C24B—C23B	−60.3 (2)
C20'—C19'—O6'—C18A	−178.2 (12)	C23B—C24B—C25B—C26B	0.3 (3)
C11A—N3A—C21A—C23A	71.3 (2)	C22B—C24B—C25B—C26B	−178.62 (16)
C17A—N3A—C21A—C23A	−72.7 (2)	C24B—C25B—C26B—C27B	0.7 (3)
C12A—N4A—C22A—C24A	−107.15 (19)	C24B—C25B—C26B—C30B	179.62 (18)

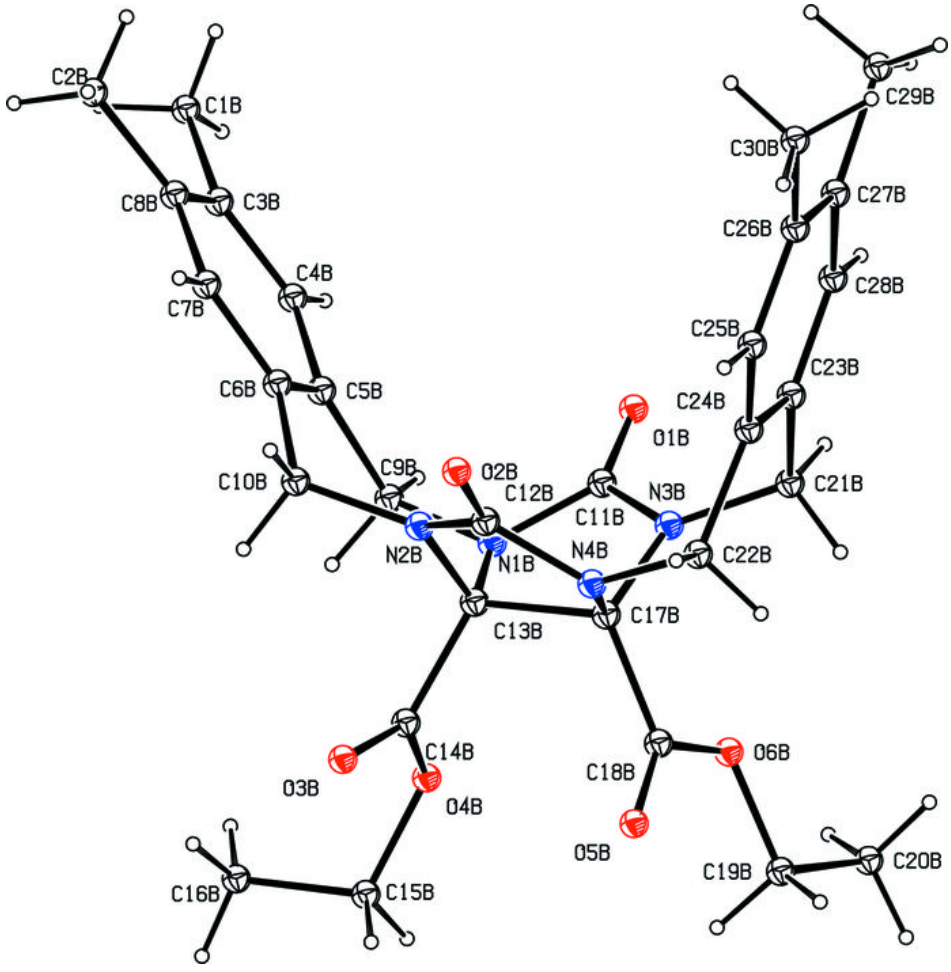
C17A—N4A—C22A—C24A	76.8 (2)	C25B—C26B—C27B—C28B	−1.1 (3)
N3A—C21A—C23A—C28A	−122.71 (18)	C30B—C26B—C27B—C28B	−179.96 (18)
N3A—C21A—C23A—C24A	59.4 (2)	C25B—C26B—C27B—C29B	177.13 (17)
C28A—C23A—C24A—C25A	−2.4 (3)	C30B—C26B—C27B—C29B	−1.7 (3)
C21A—C23A—C24A—C25A	175.58 (16)	C26B—C27B—C28B—C23B	0.5 (3)
C28A—C23A—C24A—C22A	177.89 (16)	C29B—C27B—C28B—C23B	−177.79 (16)
C21A—C23A—C24A—C22A	−4.2 (3)	C24B—C23B—C28B—C27B	0.6 (3)
N4A—C22A—C24A—C25A	126.78 (18)	C21B—C23B—C28B—C27B	179.57 (16)

Hydrogen-bond geometry (Å, °)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
C9A—H9A1···O2B^{i}	0.97	2.31	3.205 (2)	153
C22B—H22A···O1A^{ii}	0.97	2.41	3.375 (2)	178
C29B—H29A···O1B^{iii}	0.96	2.53	3.441 (3)	160

Symmetry codes: (i) *x*, *y*+1, *z*; (ii) *x*, −*y*+3/2, *z*+1/2; (iii) −*x*+1, *y*+1/2, −*z*+3/2.

Fig. 1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C28B
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O3B
O4B
C16B
C15B
C18B
O6B
O5B
C19B
C20B

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Bis[*N*,*N*-bis(2-hydroxyethyl)glycinato]-cobalt(II)

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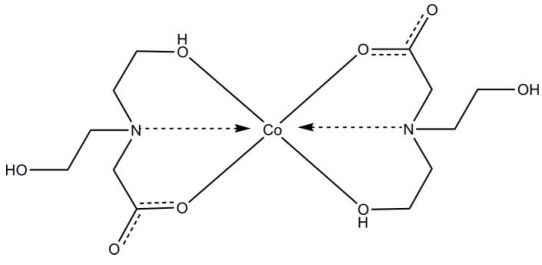
Key indicators: single-crystal X-ray study; T = 293 K; mean σ(C–C) = 0.006 Å; R factor = 0.057; wR factor = 0.159; data-to-parameter ratio = 17.2.

The asymmetric unit of the title compound, $[Co(C_6H_{12}NO_4)_2]$, contains one half-molecule with the Co^{II} ion situated on an inversion center. Intermolecular O—H···O hydrogen bonds generate a three-dimensional hydrogen-bonding network, which consolidates the crystal packing.

Related literature

For related structures, see: Ammar *et al.* (2001); Chuklanova *et al.* (1981); Thakuria & Das (2007).



Experimental

Crystal data

$[Co(C_6H_{12}NO_4)_2]$
M_r = 383.26
Monoclinic, $P2_1/c$
a = 9.932 (2) Å
b = 11.388 (2) Å
c = 7.4477 (15) Å
β = 110.12 (3)°
V = 791.0 (3) Å^3
Z = 2
Mo $K\alpha$ radiation
μ = 1.13 mm^{-1}
T = 293 K
0.20 × 0.18 × 0.18 mm

Data collection

Rigaku SCXmini diffractometer
Absorption correction: multi-scan (*ABSCOR*; Higashi, 1995)
T_{min} = 0.736, T_{max} = 1.000
8129 measured reflections
1819 independent reflections
1357 reflections with $I > 2\sigma(I)$
R_{int} = 0.072

Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.057
$wR(F^2)$ = 0.159
S = 1.00
1819 reflections
106 parameters
H-atom parameters constrained
$\Delta\rho_{max}$ = 0.48 e Å^{-3}
$\Delta\rho_{min}$ = −0.36 e Å^{-3}

Table 1
Hydrogen-bond geometry (Å, °).

D—H···A	D—H	H···A	D···A	D—H···A
O2—H12···O3^{i}	0.85	1.79	2.632 (4)	171
O1—H11···O3^{ii}	0.85	1.89	2.744 (4)	178

Symmetry codes: (i) $-x+1, y-\frac{1}{2}, -z+\frac{3}{2}$; (ii) $-x, y-\frac{1}{2}, -z+\frac{1}{2}$.

Data collection: *SCXmini Benchtop Crystallography System Software* (Rigaku, 2006); cell refinement: *PROCESS-AUTO* (Rigaku, 1998); data reduction: *PROCESS-AUTO*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *ORTEPIII* (Burnett & Johnson, 1996) and *PLATON* (Spek, 2009); software used to prepare material for publication: *SHELXTL* (Sheldrick, 2008).

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Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: CV2723).

References

Ammar, M. K., Amor, F. B., Driss, A. & Jouini, T. (2001). *Z. Kristallogr. New Cryst. Struct.* **216**, 631–633.
Burnett, M. N. & Johnson, C. K. (1996). *ORTEPIII*. Report ORNL-6895. Oak Ridge National Laboratory, Tennessee, USA.
Chuklanova, E. B., Polynova, T. N., Porai-Koshits, M. A. & Babeshkina, G. K. (1981). *Koord. Khim.* **7**, 944–951.
Higashi, T. (1995). *ABSCOR*. Rigaku Corporation, Tokyo, Japan.
Rigaku (1998). *PROCESS-AUTO*. Rigaku Americas Corporation, The Woodlands, Texas, USA.
Rigaku (2006). *SCXmini Benchtop Crystallography System Software*. Rigaku Americas Corporation, The Woodlands, Texas, USA.
Sheldrick, G. M. (2008). *Acta Cryst.* A**64**, 112–122.
Spek, A. L. (2009). *Acta Cryst.* D**65**, 148–155.
Thakuria, H. & Das, G. (2007). *Polyhedron*, **26**, 149–153.

supplementary materials

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Bis[*N*,*N*-bis(2-hydroxyethyl)glycinato]cobalt(II)

J.-P. Zhao and F.-C. Liu

Comment

As a contribution to a structural study of ML_2 complexes, where *L* = N,N-bis(2-hydroxyethyl)glycinato ligand, and M = Cu (Ammar *et al.*, 2001; Thakuria & Das, 2007) and Ni (Chuklanova *et al.*, 1981), herewith we report the crystal structure of the title compound CoL_2 (I).

In (I) (Fig. 1), the Co(II) ions are located on the inversion centers and are coordinated by two *L* ligands forming an octahedral enviromental geometry with four oxygen and two nitrogen atoms. The bond lengths are: Co1—N1 = 2.172 (3) Å, Co1—O2 = 2.088 (3) Å and Co1—O4 = 2.046 (2) Å. Though ML_2 complexes (M = Co, Ni, Cu) have similar structures, there are some differences. The Co and Ni centers are in a regular octahedron coordinated geometry, while the Cu center has an elongated octahedral coordination with two hydroxy atoms in axial positions.

Intermolecular O—H···O hydrogen bonds (Table 1) generate three-dimensional hydrogen-bonding network, which consolidate the crystal packing (Fig. 2).

Experimental

A mixture of Co(II) nitrate (1.0mmol), Dy(III)nitrate (0.5mmol) and N,N-bis(2-hydroxyethyl)glycine, (1 mmol), in 10 ml solvent wITH DMF:MeOH = 1:1 was sealed in a Teflon-lined stainless-steel Parr bomb that was heated at 413 K for 48 h. Red crystals of the title complex were collected after the bomb was allowed to cool to room temperature.Yield 20% based on metal salt.

Refinement

C-bound H atoms were included in calculated positions and treated as riding on their parent atoms, with C—H = 0.93Å and U_{iso}(H) = 1.2U_{eq}(C). Hydroxy H atoms were located on difference Fourier maps, but placed in idealized positions (O—H = 0.85Å) and refined as riding, with U_{iso}(H) = 1.2U_{eq}(O).

Figures

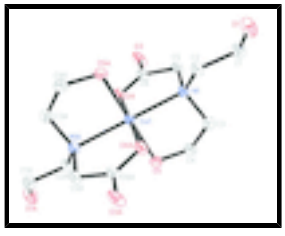


Fig. 1. The molecular structure of the title complex. Displacement ellipsoids are drawn at the 30% probability level. H atom have been omitted for clarity. Symmetry code: (A) -x+1, -y-1, -z+1.

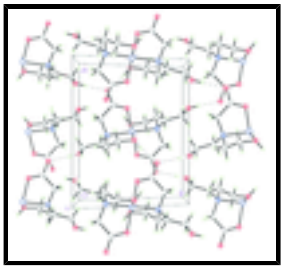


Fig. 2. A portion of the crystal packing viewed down the *c* axis. Dashed lines denote O—H···O hydrogen bonds.

Bis[*N*,*N*-bis(2-hydroxyethyl)glycinato]cobalt(II)

Crystal data

$[Co(C_6H_{12}NO_4)_2]$	$F(000) = 402$
$M_r = 383.26$	$D_x = 1.609$ Mg m^{-3}
Monoclinic, $P2_1/c$	Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å
$a = 9.932$ (2) Å	Cell parameters from 7077 reflections
$b = 11.388$ (2) Å	$\theta = 3.4$–$27.6°$
$c = 7.4477$ (15) Å	$\mu = 1.13$ mm^{-1}
$\beta = 110.12$ (3)°	$T = 293$ K
$V = 791.0$ (3) Å^3	Block, red
$Z = 2$	0.2 × 0.18 × 0.18 mm

Data collection

Rigaku SCXmini diffractometer	1819 independent reflections
Radiation source: fine-focus sealed tube	1357 reflections with $I > 2\sigma(I)$
graphite	$R_{int} = 0.072$
ω scans	$\theta_{max} = 27.5°$, $\theta_{min} = 3.4°$
Absorption correction: multi-scan (*ABSCOR*; Higashi, 1995)	$h = -12 \rightarrow 12$
$T_{min} = 0.736$, $T_{max} = 1.000$	$k = -14 \rightarrow 14$
8129 measured reflections	$l = -9 \rightarrow 9$

Refinement

Refinement on F^2	Primary atom site location: structure-invariant direct methods
Least-squares matrix: full	Secondary atom site location: difference Fourier map
$R[F^2 > 2\sigma(F^2)] = 0.057$	Hydrogen site location: inferred from neighbouring sites
$wR(F^2) = 0.159$	H-atom parameters constrained
$S = 1.00$	$w = 1/[\sigma^2(F_o^2) + (0.1P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
1819 reflections	$(\Delta/\sigma)_{max} < 0.001$
106 parameters	$\Delta\rho_{max} = 0.48$ e Å^{-3}

0 restraints $\Delta\rho_{min} = -0.36$ e Å^{-3}

Special details

Geometry. All esds (except the esd in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell esds are taken into account individually in the estimation of esds in distances, angles and torsion angles; correlations between esds in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell esds is used for estimating esds involving l.s. planes.

Refinement. Refinement of F^2 against ALL reflections. The weighted *R*-factor *wR* and goodness of fit *S* are based on F^2, conventional *R*-factors *R* are based on *F*, with *F* set to zero for negative F^2. The threshold expression of $F^2 > \sigma(F^2)$ is used only for calculating *R*-factors(gt) *etc*. and is not relevant to the choice of reflections for refinement. *R*-factors based on F^2 are statistically about twice as large as those based on *F*, and *R*- factors based on ALL data will be even larger.

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å^2)

	x	*y*	*z*	U_{iso}*/U_{eq}
Co1	0.5000	0.5000	0.5000	0.0244 (3)
O1	0.0043 (3)	0.3365 (3)	0.0259 (4)	0.0552 (9)
H11	−0.0846	0.3211	−0.0073	0.066*
O2	0.5173 (3)	0.4447 (3)	0.7743 (4)	0.0347 (7)
H12	0.5746	0.3883	0.8218	0.042*
O3	0.2823 (3)	0.7874 (2)	0.5700 (4)	0.0449 (8)
O4	0.4555 (3)	0.6656 (2)	0.5703 (4)	0.0333 (6)
N1	0.2727 (3)	0.4762 (2)	0.4479 (5)	0.0270 (7)
C1	0.0483 (4)	0.3862 (4)	0.2103 (6)	0.0431 (10)
H1A	0.0377	0.3299	0.3022	0.052*
H1B	−0.0090	0.4550	0.2118	0.052*
C2	0.2040 (4)	0.4198 (3)	0.2589 (5)	0.0329 (9)
H2A	0.2579	0.3496	0.2538	0.040*
H2B	0.2115	0.4730	0.1610	0.040*
C3	0.2708 (4)	0.3967 (4)	0.6042 (6)	0.0363 (9)
H3A	0.2918	0.3173	0.5750	0.044*
H3B	0.1758	0.3970	0.6137	0.044*
C4	0.3792 (4)	0.4339 (4)	0.7929 (6)	0.0401 (10)
H4A	0.3510	0.5086	0.8317	0.048*
H4B	0.3830	0.3762	0.8902	0.048*
C5	0.2141 (4)	0.5937 (3)	0.4614 (6)	0.0309 (8)
H5A	0.1554	0.5882	0.5416	0.037*
H5B	0.1521	0.6172	0.3347	0.037*
C6	0.3256 (4)	0.6887 (3)	0.5411 (5)	0.0310 (9)

Atomic displacement parameters (Å^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Co1	0.0203 (4)	0.0227 (4)	0.0279 (4)	0.0026 (3)	0.0055 (3)	−0.0003 (3)
O1	0.0397 (18)	0.066 (2)	0.053 (2)	−0.0136 (15)	0.0076 (15)	−0.0177 (16)
O2	0.0302 (14)	0.0401 (16)	0.0306 (15)	0.0078 (13)	0.0065 (11)	0.0075 (12)

O3	0.0249 (15)	0.0323 (15)	0.068 (2)	0.0053 (12)	0.0029 (14)	−0.0206 (14)
O4	0.0227 (13)	0.0269 (13)	0.0468 (17)	0.0006 (11)	0.0076 (12)	−0.0064 (11)
N1	0.0241 (16)	0.0217 (15)	0.0329 (17)	−0.0002 (12)	0.0067 (13)	−0.0023 (11)
C1	0.037 (2)	0.047 (2)	0.039 (2)	−0.013 (2)	0.0060 (18)	−0.0058 (19)
C2	0.0244 (19)	0.037 (2)	0.036 (2)	−0.0001 (16)	0.0081 (16)	−0.0030 (17)
C3	0.034 (2)	0.035 (2)	0.041 (2)	−0.0042 (18)	0.0142 (18)	0.0034 (17)
C4	0.034 (2)	0.050 (3)	0.036 (2)	0.003 (2)	0.0119 (18)	0.0074 (19)
C5	0.0216 (18)	0.034 (2)	0.035 (2)	0.0020 (16)	0.0072 (15)	−0.0028 (16)
C6	0.0258 (19)	0.032 (2)	0.031 (2)	0.0047 (16)	0.0048 (15)	−0.0049 (15)

Geometric parameters (Å, °)

Co1—O4	2.046 (2)	N1—C2	1.483 (5)
Co1—O4^{i}	2.046 (2)	C1—C2	1.512 (5)
Co1—O2	2.088 (3)	C1—H1A	0.9700
Co1—O2^{i}	2.088 (3)	C1—H1B	0.9700
Co1—N1^{i}	2.172 (3)	C2—H2A	0.9700
Co1—N1	2.172 (3)	C2—H2B	0.9700
O1—C1	1.409 (5)	C3—C4	1.507 (5)
O1—H11	0.8499	C3—H3A	0.9700
O2—C4	1.430 (5)	C3—H3B	0.9700
O2—H12	0.8500	C4—H4A	0.9700
O3—C6	1.249 (4)	C4—H4B	0.9700
O4—C6	1.260 (4)	C5—C6	1.515 (5)
N1—C5	1.476 (4)	C5—H5A	0.9700
N1—C3	1.480 (5)	C5—H5B	0.9700
O4—Co1—O4^{i}	180.0	C2—C1—H1B	110.4
O4—Co1—O2	88.86 (11)	H1A—C1—H1B	108.6
O4^{i}—Co1—O2	91.14 (11)	N1—C2—C1	115.8 (3)
O4—Co1—O2^{i}	91.14 (11)	N1—C2—H2A	108.3
O4^{i}—Co1—O2^{i}	88.86 (11)	C1—C2—H2A	108.3
O2—Co1—O2^{i}	180.0	N1—C2—H2B	108.3
O4—Co1—N1^{i}	98.17 (10)	C1—C2—H2B	108.3
O4^{i}—Co1—N1^{i}	81.83 (10)	H2A—C2—H2B	107.4
O2—Co1—N1^{i}	97.61 (11)	N1—C3—C4	111.3 (3)
O2^{i}—Co1—N1^{i}	82.39 (11)	N1—C3—H3A	109.4
O4—Co1—N1	81.83 (10)	C4—C3—H3A	109.4
O4^{i}—Co1—N1	98.17 (10)	N1—C3—H3B	109.4
O2—Co1—N1	82.39 (11)	C4—C3—H3B	109.4
O2^{i}—Co1—N1	97.61 (11)	H3A—C3—H3B	108.0
N1^{i}—Co1—N1	180.0	O2—C4—C3	109.6 (3)
C1—O1—H11	108.0	O2—C4—H4A	109.8
C4—O2—Co1	111.2 (2)	C3—C4—H4A	109.8
C4—O2—H12	115.0	O2—C4—H4B	109.8
Co1—O2—H12	116.9	C3—C4—H4B	109.8
C6—O4—Co1	116.5 (2)	H4A—C4—H4B	108.2

C5—N1—C3	112.9 (3)	N1—C5—C6	114.9 (3)
C5—N1—C2	113.2 (3)	N1—C5—H5A	108.5
C3—N1—C2	110.9 (3)	C6—C5—H5A	108.5
C5—N1—Co1	106.5 (2)	N1—C5—H5B	108.5
C3—N1—Co1	103.3 (2)	C6—C5—H5B	108.5
C2—N1—Co1	109.5 (2)	H5A—C5—H5B	107.5
O1—C1—C2	106.5 (3)	O3—C6—O4	123.4 (3)
O1—C1—H1A	110.4	O3—C6—C5	117.5 (3)
C2—C1—H1A	110.4	O4—C6—C5	119.1 (3)
O1—C1—H1B	110.4		
O4—Co1—O2—C4	75.2 (3)	$O4^{i}$—Co1—N1—C2	−48.4 (2)
$O4^{i}$—Co1—O2—C4	−104.8 (3)	O2—Co1—N1—C2	−138.4 (2)
$O2^{i}$—Co1—O2—C4	−9(84)	$O2^{i}$—Co1—N1—C2	41.6 (2)
$N1^{i}$—Co1—O2—C4	173.3 (3)	$N1^{i}$—Co1—N1—C2	35 (100)
N1—Co1—O2—C4	−6.7 (3)	C5—N1—C2—C1	−67.2 (4)
$O4^{i}$—Co1—O4—C6	37 (100)	C3—N1—C2—C1	60.8 (4)
O2—Co1—O4—C6	−88.4 (3)	Co1—N1—C2—C1	174.1 (3)
$O2^{i}$—Co1—O4—C6	91.6 (3)	O1—C1—C2—N1	179.1 (3)
$N1^{i}$—Co1—O4—C6	174.1 (3)	C5—N1—C3—C4	−70.5 (4)
N1—Co1—O4—C6	−5.9 (3)	C2—N1—C3—C4	161.4 (3)
O4—Co1—N1—C5	8.9 (2)	Co1—N1—C3—C4	44.2 (3)
$O4^{i}$—Co1—N1—C5	−171.1 (2)	Co1—O2—C4—C3	32.5 (4)
O2—Co1—N1—C5	98.9 (2)	N1—C3—C4—O2	−53.5 (4)
$O2^{i}$—Co1—N1—C5	−81.1 (2)	C3—N1—C5—C6	101.7 (4)
$N1^{i}$—Co1—N1—C5	−88 (100)	C2—N1—C5—C6	−131.4 (3)
O4—Co1—N1—C3	−110.2 (2)	Co1—N1—C5—C6	−11.0 (4)
$O4^{i}$—Co1—N1—C3	69.8 (2)	Co1—O4—C6—O3	−177.0 (3)
O2—Co1—N1—C3	−20.3 (2)	Co1—O4—C6—C5	1.1 (5)
$O2^{i}$—Co1—N1—C3	159.7 (2)	N1—C5—C6—O3	−174.3 (3)
$N1^{i}$—Co1—N1—C3	153 (100)	N1—C5—C6—O4	7.4 (5)
O4—Co1—N1—C2	131.6 (2)		

Symmetry codes: (i) −*x*+1, −*y*+1, −*z*+1.

Hydrogen-bond geometry (Å, °)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
O2—H12···$O3^{ii}$	0.85	1.79	2.632 (4)	171
O1—H11···$O3^{iii}$	0.85	1.89	2.744 (4)	178

Symmetry codes: (ii) −*x*+1, *y*−1/2, −*z*+3/2; (iii) −*x*, *y*−1/2, −*z*+1/2.

Fig. 1

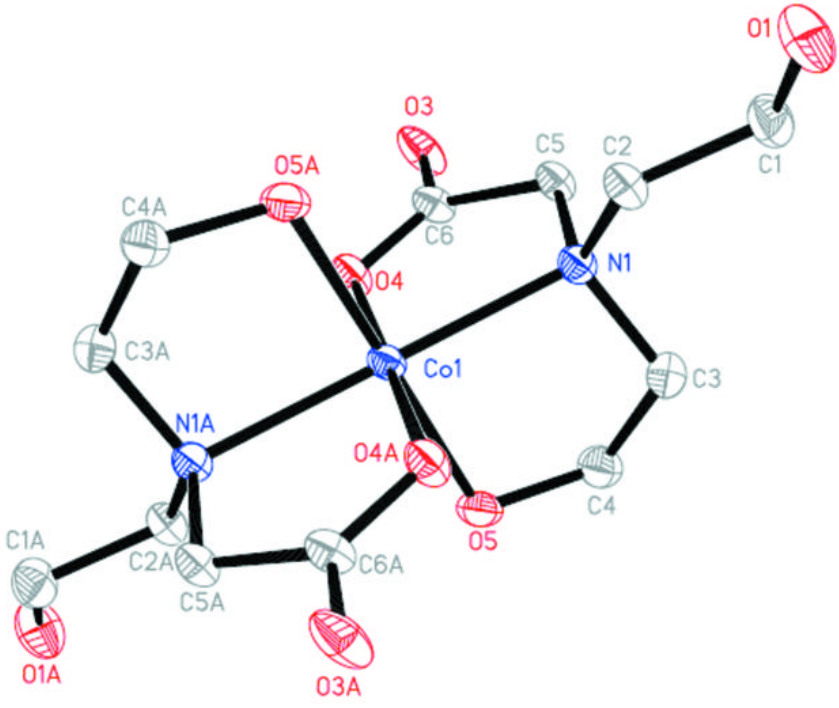
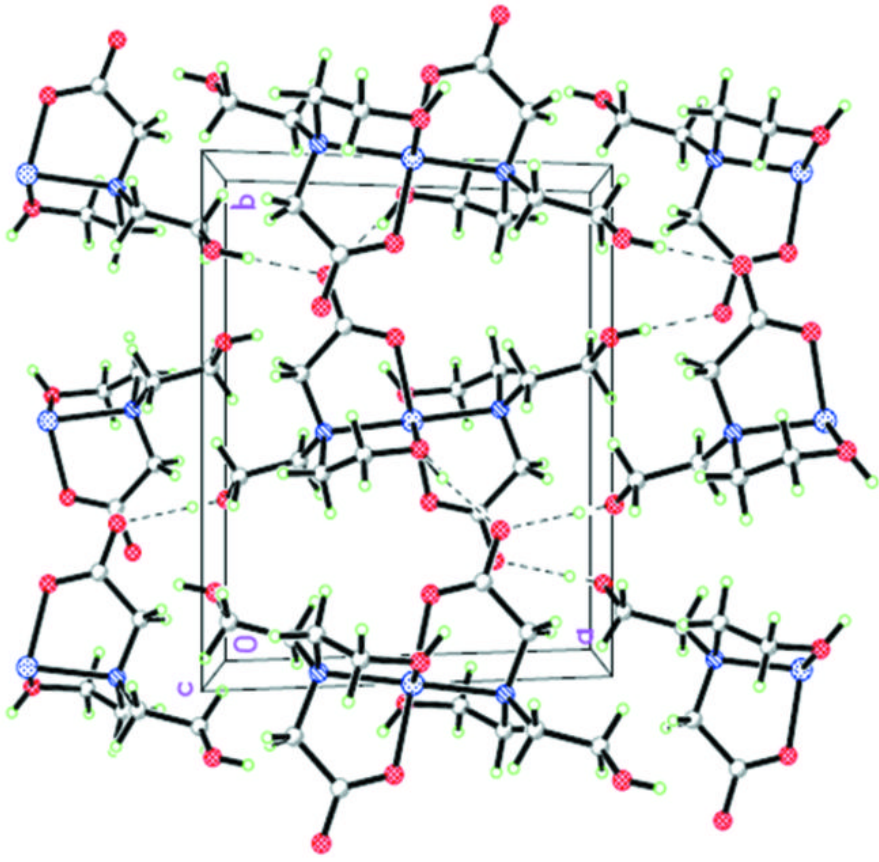

O1
O3
C5
C2
C1
O5A
C4A
C6
O4
N1
C3A
Co1
C3
N1A
O4A
C4
O5
C1A
C2A
C6A
C5A
O1A
O3A

Fig. 2



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N-[3-Chloro-4-(3-fluorobenzyloxy)-phenyl]-6-iodoquinazolin-4-amine

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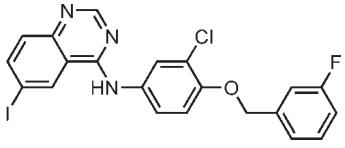
Key indicators: single-crystal X-ray study; T = 113 K; mean σ(C–C) = 0.007 Å; R factor = 0.030; wR factor = 0.067; data-to-parameter ratio = 12.3.

In the title molecule, $C_{21}H_{14}ClFIN_3O$, the bicyclic ring system has a twisted conformation; the two fused rings form a dihedral angle of 4.5 (1)°. The dihedral angles between the fused ring system and the benzene rings are 27.3 (6) and 5.3 (5)° while the dihedral angle between the benzene rings is 22.0 (5)°. In the crystal structure, weak intermolecular N—H···N hydrogen bonds link the molecules into chains propagating in [100]. A short intermolecular distance of 3.806 (3) Å between the centroids of the fluorobenzene and iodobenzene rings suggests the existence of π–π stacking interactions.

Related literature

For a related structure, see: Calestani *et al.* (2001). The title compound is an important intermediate in the synthesis of the anticancer agent lapatinib, see: Kimberly *et al.* (2006).



Experimental

Crystal data

$C_{21}H_{14}ClFIN_3O$
M_r = 505.70
Orthorhombic, $Pca2_1$
a = 13.128 (3) Å
b = 7.6293 (15) Å
c = 18.898 (4) Å
V = 1892.8 (7) Å^3
Z = 4
Mo $K\alpha$ radiation
μ = 1.86 mm^{-1}
T = 113 K
0.20 × 0.18 × 0.06 mm

Data collection

Rigaku Saturn CCD area-detector diffractometer
Absorption correction: multi-scan (*ABSCOR*; Higashi, 1995)
T_{min} = 0.707, T_{max} = 0.897
11905 measured reflections
3183 independent reflections
2510 reflections with $I > 2\sigma(I)$
R_{int} = 0.045

Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.030
$wR(F^2)$ = 0.067
S = 1.01
3183 reflections
258 parameters
1 restraint
H atoms treated by a mixture of independent and constrained refinement
$\Delta\rho_{max}$ = 1.24 e Å^{-3}
$\Delta\rho_{min}$ = −0.70 e Å^{-3}
Absolute structure: Flack (1983), 1433 Friedel pairs
Flack parameter: −0.039 (19)

Table 1
Hydrogen-bond geometry (Å, °).

D—H···A	D—H	H···A	D···A	D—H···A
N1—H21···N3^{i}	0.81 (6)	2.39 (6)	3.128 (6)	151 (6)

Symmetry code: (i) $x-\frac{1}{2}, -y+1, z$.

Data collection: *RAPID-AUTO* (Rigaku, 1998); cell refinement: *RAPID-AUTO*; data reduction: *CrystalStructure* (Rigaku/MSC, 2002); program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *SHELXTL* (Sheldrick, 2008); software used to prepare material for publication: *SHELXTL*.

The authors thank the State Key Laboratory of Elemento-organic Chemistry, Nankai University, for the X-ray data collection.

Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: CV2724).

References

Calestani, G., Capella, L., Leardini, R., Minozzi, M., Nanni, D., Papa, R. & Zanardi, G. (2001). *Tetrahedron*, **57**, 7221–7223.
Flack, H. D. (1983). *Acta Cryst.* A**39**, 876–881.
Higashi, T. (1995). *ABSCOR*. Rigaku Corporation, Tokyo, Japan.
Kimberly, G. P., Zhang, Y. M., Malcolm, C., Cockerill, G. S., Dickerson, S., Cassandra, A. G., Guo, Y., Robert, A. M., David, W. R., Ann, L. W., Edgar, R. W. & Karen, E. L. (2006). *Bioorg. Med. Chem. Lett.* **16**, 4686–4691.
Rigaku (1998). *RAPID-AUTO*. Rigaku Corporation, Tokyo, Japan.
Rigaku/MSC (2002). *CrystalStructure*. Rigaku/MSC, The Woodlands, Texas, USA.
Sheldrick, G. M. (2008). *Acta Cryst.* A**64**, 112–122.

supplementary materials

Acta Cryst. (2010). E**66**, o1810 [**doi:10.1107/S1600536810021847**]

N-[3-Chloro-4-(3-fluorobenzyloxy)phenyl]-6-iodoquinazolin-4-amine

Z.-Q. Cai, J.-G. Liu, W.-W. Zhou and Y.-L. Li

Comment

The title compound (I) is an important intermediate in the preparation of anticancer agent lapatinib (Kimberly *et al.*, 2006). Herein, the synthesis and the crystal structure of (I) are reported.

In (I) (Fig. 1), all bond lengths and angles are normal and comparable with those observed in the related compound (Calestani *et al.*, 2001). The bicycle quinazoline system has a twisted conformation - two fused rings form a dihedral angle of 4.5 (1)°. In the crystal structure, weak intermolecular N—H···N hydrogen bonds (Table 1) link molecules into chains propagated in direction [100]. Short intermolecular distance of 3.806 (3) Å between the centroids of aromatic rings suggests an existence of π-π interactions.

Experimental

2-Chloro-4-(6-iodo-quinazolin-4-ylamino)-phenol (10 mmol) in acetone (5 ml) was added to a stirred mixture of anhydrous potassium carbonate (20 mmol) and 1-Chloromethyl-3-fluoro-benzene (10 mmol) in dry acetone (25 ml). It was stirred at room temperature for 6 h. Upon completion reaction mixture was diluted with water, extracted with dichloromethane and concentrated. Recrystallization from ethyl acetate afforded title compound in 89% yield as yellow crystal: 1H NMR (DMSO-d6): 9.82 (1*H*, s, NH), 8.94(1*H*, s, ArH), 8.60(1*H*, s, ArH), 8.08(1*H*, dd, ArH), 8.01(1*H*, d ArH), 7.72 (1*H*, dd ArH), 7.49(1*H*, d ArH), 7.43 (1*H*, dd ArH), 7.19 (3*H*, m ArH), 7.14 (1*H*, t ArH), 5.24(2*H*, s CH2).

Refinement

All H atoms were initially located in a difference Fourier map. C-bound H atoms were then constrained to an ideal geometry (C—H 0.93 Å), N-bound H atom was refined with N—H bond restraint of 0.83 (5) Å. All H-atoms were refined with U_{iso}(H) = 1.2U_{eq}(C,*N*).

Figures

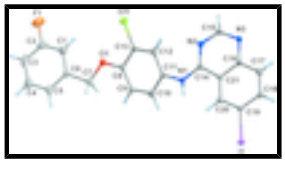


Fig. 1. The structure of $C_{21}H_{14}ClFIN_3O$ with atom-labelling scheme and ellipsoids drawn at the 50% probability level.

N-[3-Chloro-4-(3-fluorobenzyloxy)phenyl]-6-iodoquinazolin-4-amine

Crystal data

$C_{21}H_{14}ClFIN_3O$ $F(000) = 992$

M_r = 505.70	D_x = 1.775 Mg m^{-3}
Orthorhombic, $Pca2_1$	Mo $K\alpha$ radiation, λ = 0.71073 Å
Hall symbol: P 2c -2ac	Cell parameters from 7022 reflections
a = 13.128 (3) Å	θ = 1.1–27.9°
b = 7.6293 (15) Å	μ = 1.86 mm^{-1}
c = 18.898 (4) Å	T = 113 K
V = 1892.8 (7) Å^3	Prism, colourless
Z = 4	0.20 × 0.18 × 0.06 mm

Data collection

Rigaku Saturn CCD area-detector diffractometer	3183 independent reflections
Radiation source: fine-focus sealed tube	2510 reflections with $I > 2\sigma(I)$
graphite	R_{int} = 0.045
Detector resolution: 14.63 pixels mm^{-1}	θ_{max} = 25.0°, θ_{min} = 3.1°
ω scan	h = −15→15
Absorption correction: multi-scan (*ABSCOR*; Higashi, 1995)	k = −8→9
T_{min} = 0.707, T_{max} = 0.897	l = −21→22
11905 measured reflections	

Refinement

Refinement on F^2	Hydrogen site location: inferred from neighbouring sites
Least-squares matrix: full	H atoms treated by a mixture of independent and constrained refinement
$R[F^2 > 2\sigma(F^2)]$ = 0.030	$w = 1/[\sigma^2(F_o^2) + (0.0292P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
$wR(F^2)$ = 0.067	$(\Delta/\sigma)_{max}$ = 0.001
S = 1.00	$\Delta\rho_{max}$ = 1.24 e Å^{-3}
3183 reflections	$\Delta\rho_{min}$ = −0.70 e Å^{-3}
258 parameters	Extinction correction: *SHELXL97* (Sheldrick, 2008), $Fc^*=kFc[1+0.001xFc^2\lambda^3/\sin(2\theta)]^{-1/4}$
1 restraint	Extinction coefficient: 0.0309 (8)
Primary atom site location: structure-invariant direct methods	Absolute structure: Flack (1983), 1433 Friedel pairs
Secondary atom site location: difference Fourier map	Flack parameter: −0.039 (19)

Special details

Geometry. All e.s.d.'s (except the e.s.d. in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell e.s.d.'s are taken into account individually in the estimation of e.s.d.'s in distances, angles and torsion angles; correlations between e.s.d.'s in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell e.s.d.'s is used for estimating e.s.d.'s involving l.s. planes.

Refinement. Refinement of F^2 against ALL reflections. The weighted *R*-factor *wR* and goodness of fit *S* are based on F^2, conventional *R*-factors *R* are based on *F*, with *F* set to zero for negative F^2. The threshold expression of $F^2 > \sigma(F^2)$ is used only for calculating *R*-factors(gt) *etc*. and is not relevant to the choice of reflections for refinement. *R*-factors based on F^2 are statistically about twice as large as those based on *F*, and *R*- factors based on ALL data will be even larger.

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å^2)

	x	*y*	*z*	U_{iso}*/U_{eq}
I1	0.299873 (18)	−0.00631 (3)	0.50844 (4)	0.01983 (11)
Cl1	0.28694 (8)	1.26802 (14)	0.25075 (8)	0.0248 (3)
F1	0.0085 (3)	1.7039 (4)	0.0746 (2)	0.0538 (10)
O1	0.0946 (2)	1.1497 (4)	0.19493 (17)	0.0220 (8)
N1	0.2954 (3)	0.6395 (5)	0.3538 (2)	0.0165 (9)
N2	0.4616 (3)	0.7425 (5)	0.3551 (2)	0.0185 (10)
N3	0.6006 (3)	0.5682 (5)	0.3991 (2)	0.0173 (9)
C1	0.0028 (5)	1.4220 (8)	0.1242 (3)	0.0289 (14)
H1	0.0727	1.4259	0.1319	0.035*
C2	−0.0476 (4)	1.5583 (9)	0.0935 (3)	0.0288 (16)
C3	−0.1501 (5)	1.5661 (7)	0.0807 (3)	0.0336 (14)
H3	−0.1804	1.6640	0.0603	0.040*
C4	−0.2058 (4)	1.4207 (7)	0.0999 (3)	0.0290 (13)
H4	−0.2756	1.4188	0.0914	0.035*
C5	−0.1602 (3)	1.2779 (6)	0.1315 (3)	0.0225 (12)
H5	−0.1995	1.1821	0.1449	0.027*
C6	−0.0549 (4)	1.2766 (6)	0.1433 (3)	0.0171 (12)
C7	−0.0070 (3)	1.1135 (6)	0.1729 (3)	0.0201 (11)
H7A	−0.0466	1.0720	0.2129	0.024*
H7B	−0.0066	1.0223	0.1371	0.024*
C8	0.1419 (4)	1.0178 (5)	0.2308 (3)	0.0177 (11)
C9	0.1065 (4)	0.8496 (6)	0.2378 (3)	0.0193 (11)
H9	0.0455	0.8177	0.2163	0.023*
C10	0.1605 (4)	0.7262 (6)	0.2767 (2)	0.0210 (12)
H10	0.1359	0.6121	0.2797	0.025*
C11	0.2503 (3)	0.7694 (6)	0.3110 (2)	0.0138 (10)
C12	0.2883 (4)	0.9387 (7)	0.3038 (3)	0.0175 (11)
H12	0.3480	0.9709	0.3268	0.021*
C13	0.2365 (4)	1.0605 (5)	0.2618 (3)	0.0168 (11)
C14	0.3949 (3)	0.6194 (6)	0.3725 (2)	0.0158 (10)
C15	0.5600 (4)	0.7107 (7)	0.3715 (3)	0.0202 (13)
H15	0.6052	0.8015	0.3620	0.024*
C16	0.5303 (4)	0.4390 (8)	0.4183 (3)	0.0164 (13)
C17	0.5680 (4)	0.2842 (6)	0.4475 (3)	0.0209 (12)
H17	0.6380	0.2679	0.4516	0.025*
C18	0.5028 (3)	0.1559 (6)	0.4703 (2)	0.0179 (10)
H18	0.5282	0.0517	0.4887	0.022*
C19	0.3977 (3)	0.1828 (5)	0.4656 (2)	0.0156 (10)
C20	0.3593 (3)	0.3317 (5)	0.4348 (3)	0.0170 (11)
H20	0.2893	0.3468	0.4307	0.020*

C21	0.4254 (4)	0.4606 (6)	0.4094 (3)	0.0158 (11)
H21	0.260 (5)	0.555 (7)	0.363 (4)	0.05 (2)*

Atomic displacement parameters (Å^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
I1	0.01930 (17)	0.01590 (15)	0.02429 (18)	−0.00277 (13)	0.0006 (2)	0.00282 (15)
Cl1	0.0276 (6)	0.0170 (6)	0.0299 (8)	−0.0025 (5)	−0.0030 (7)	0.0048 (5)
F1	0.065 (2)	0.034 (2)	0.062 (3)	−0.0141 (18)	−0.011 (2)	0.0118 (17)
O1	0.0168 (18)	0.0207 (18)	0.029 (2)	0.0031 (15)	−0.0055 (17)	0.0074 (15)
N1	0.013 (2)	0.014 (2)	0.022 (3)	−0.0002 (18)	0.0021 (18)	0.0039 (17)
N2	0.013 (2)	0.021 (2)	0.021 (3)	0.0003 (17)	0.0004 (17)	0.0033 (18)
N3	0.014 (2)	0.017 (2)	0.021 (3)	0.002 (2)	0.002 (2)	0.0030 (18)
C1	0.028 (3)	0.025 (3)	0.034 (4)	0.002 (3)	0.000 (3)	0.001 (3)
C2	0.046 (5)	0.022 (3)	0.019 (4)	−0.009 (3)	−0.007 (3)	0.001 (3)
C3	0.052 (4)	0.027 (3)	0.022 (3)	0.024 (3)	−0.013 (3)	−0.006 (2)
C4	0.035 (3)	0.033 (3)	0.019 (3)	0.010 (3)	−0.004 (2)	−0.005 (2)
C5	0.021 (3)	0.027 (3)	0.018 (3)	0.004 (2)	−0.005 (2)	0.001 (2)
C6	0.024 (3)	0.017 (3)	0.010 (3)	0.003 (2)	−0.003 (2)	0.004 (2)
C7	0.018 (3)	0.021 (3)	0.022 (3)	−0.001 (2)	−0.001 (2)	0.003 (2)
C8	0.015 (3)	0.022 (3)	0.016 (3)	0.008 (2)	0.002 (2)	0.005 (2)
C9	0.015 (2)	0.022 (3)	0.021 (3)	−0.003 (2)	−0.003 (2)	−0.002 (2)
C10	0.030 (3)	0.013 (2)	0.021 (3)	0.001 (2)	0.002 (2)	0.0024 (19)
C11	0.014 (2)	0.016 (2)	0.012 (3)	0.004 (2)	0.000 (2)	0.0000 (18)
C12	0.012 (3)	0.028 (3)	0.013 (3)	0.005 (2)	0.001 (2)	−0.002 (2)
C13	0.017 (3)	0.0134 (19)	0.020 (3)	−0.004 (2)	0.004 (2)	0.001 (3)
C14	0.013 (2)	0.017 (2)	0.017 (3)	0.002 (2)	0.001 (2)	−0.0035 (19)
C15	0.015 (3)	0.019 (3)	0.027 (4)	−0.003 (2)	0.005 (2)	0.004 (2)
C16	0.018 (3)	0.012 (3)	0.019 (4)	0.002 (2)	0.007 (2)	0.002 (2)
C17	0.019 (3)	0.021 (3)	0.022 (3)	0.003 (2)	0.000 (2)	−0.001 (2)
C18	0.020 (3)	0.015 (2)	0.019 (3)	0.005 (2)	−0.001 (2)	0.003 (2)
C19	0.017 (3)	0.014 (2)	0.016 (3)	−0.004 (2)	0.001 (2)	0.0003 (19)
C20	0.015 (3)	0.022 (3)	0.015 (3)	0.000 (2)	−0.003 (2)	−0.003 (2)
C21	0.013 (3)	0.019 (3)	0.016 (3)	−0.003 (2)	−0.001 (2)	0.0007 (19)

Geometric parameters (Å, °)

I1—C19	2.094 (4)	C7—H7A	0.9700
Cl1—C13	1.729 (4)	C7—H7B	0.9700
F1—C2	1.380 (7)	C8—C9	1.372 (6)
O1—C8	1.363 (5)	C8—C13	1.411 (8)
O1—C7	1.425 (5)	C9—C10	1.389 (6)
N1—C14	1.362 (5)	C9—H9	0.9300
N1—C11	1.408 (6)	C10—C11	1.386 (6)
N1—H21	0.81 (6)	C10—H10	0.9300
N2—C14	1.326 (6)	C11—C12	1.392 (7)
N2—C15	1.350 (6)	C12—C13	1.398 (8)
N3—C15	1.318 (6)	C12—H12	0.9300
N3—C16	1.399 (7)	C14—C21	1.454 (7)

C1—C2	1.363 (9)	C15—H15	0.9300
C1—C6	1.391 (7)	C16—C17	1.395 (7)
C1—H1	0.9300	C16—C21	1.397 (7)
C2—C3	1.368 (8)	C17—C18	1.370 (6)
C3—C4	1.377 (9)	C17—H17	0.9300
C3—H3	0.9300	C18—C19	1.398 (6)
C4—C5	1.380 (7)	C18—H18	0.9300
C4—H4	0.9300	C19—C20	1.373 (6)
C5—C6	1.400 (6)	C20—C21	1.396 (7)
C5—H5	0.9300	C20—H20	0.9300
C6—C7	1.502 (6)		
C8—O1—C7	115.4 (4)	C11—C10—C9	121.4 (4)
C14—N1—C11	129.1 (4)	C11—C10—H10	119.3
C14—N1—H21	114 (5)	C9—C10—H10	119.3
C11—N1—H21	116 (5)	C10—C11—C12	118.6 (4)
C14—N2—C15	116.6 (4)	C10—C11—N1	117.3 (4)
C15—N3—C16	114.6 (4)	C12—C11—N1	124.0 (4)
C2—C1—C6	117.0 (6)	C11—C12—C13	119.9 (5)
C2—C1—H1	121.5	C11—C12—H12	120.0
C6—C1—H1	121.5	C13—C12—H12	120.0
C1—C2—C3	125.9 (6)	C12—C13—C8	120.7 (4)
C1—C2—F1	117.7 (5)	C12—C13—Cl1	119.4 (4)
C3—C2—F1	116.4 (6)	C8—C13—Cl1	119.9 (4)
C2—C3—C4	116.2 (6)	N2—C14—N1	119.3 (4)
C2—C3—H3	121.9	N2—C14—C21	121.8 (4)
C4—C3—H3	121.9	N1—C14—C21	118.9 (4)
C3—C4—C5	121.3 (5)	N3—C15—N2	128.8 (5)
C3—C4—H4	119.4	N3—C15—H15	115.6
C5—C4—H4	119.4	N2—C15—H15	115.6
C4—C5—C6	120.2 (5)	C17—C16—C21	119.8 (5)
C4—C5—H5	119.9	C17—C16—N3	117.7 (5)
C6—C5—H5	119.9	C21—C16—N3	122.4 (5)
C1—C6—C5	119.4 (5)	C18—C17—C16	120.5 (5)
C1—C6—C7	122.0 (5)	C18—C17—H17	119.8
C5—C6—C7	118.5 (4)	C16—C17—H17	119.8
O1—C7—C6	109.9 (4)	C17—C18—C19	119.5 (4)
O1—C7—H7A	109.7	C17—C18—H18	120.2
C6—C7—H7A	109.7	C19—C18—H18	120.2
O1—C7—H7B	109.7	C20—C19—C18	120.7 (4)
C6—C7—H7B	109.7	C20—C19—I1	120.6 (3)
H7A—C7—H7B	108.2	C18—C19—I1	118.7 (3)
O1—C8—C9	125.8 (5)	C19—C20—C21	120.1 (4)
O1—C8—C13	115.9 (4)	C19—C20—H20	120.0
C9—C8—C13	118.3 (4)	C21—C20—H20	120.0
C8—C9—C10	120.8 (5)	C20—C21—C16	119.2 (5)
C8—C9—H9	119.6	C20—C21—C14	125.4 (4)
C10—C9—H9	119.6	C16—C21—C14	115.3 (5)
C6—C1—C2—C3	1.0 (10)	O1—C8—C13—Cl1	−1.9 (7)

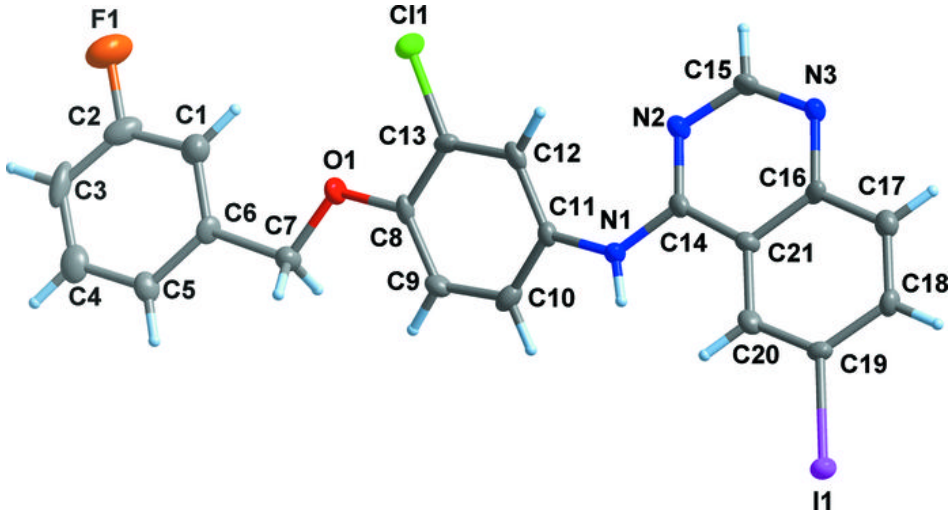
C6—C1—C2—F1	179.6 (5)	C9—C8—C13—Cl1	177.0 (4)
C1—C2—C3—C4	−1.1 (10)	C15—N2—C14—N1	−176.3 (5)
F1—C2—C3—C4	−179.8 (5)	C15—N2—C14—C21	1.9 (7)
C2—C3—C4—C5	1.3 (8)	C11—N1—C14—N2	6.6 (7)
C3—C4—C5—C6	−1.4 (8)	C11—N1—C14—C21	−171.6 (5)
C2—C1—C6—C5	−1.0 (8)	C16—N3—C15—N2	−5.0 (8)
C2—C1—C6—C7	175.8 (5)	C14—N2—C15—N3	4.3 (8)
C4—C5—C6—C1	1.2 (8)	C15—N3—C16—C17	179.7 (5)
C4—C5—C6—C7	−175.6 (5)	C15—N3—C16—C21	−0.6 (8)
C8—O1—C7—C6	172.2 (4)	C21—C16—C17—C18	−2.7 (8)
C1—C6—C7—O1	15.5 (7)	N3—C16—C17—C18	177.1 (5)
C5—C6—C7—O1	−167.8 (4)	C16—C17—C18—C19	−1.6 (7)
C7—O1—C8—C9	10.2 (7)	C17—C18—C19—C20	3.9 (7)
C7—O1—C8—C13	−171.0 (4)	C17—C18—C19—I1	−175.0 (4)
O1—C8—C9—C10	−178.9 (4)	C18—C19—C20—C21	−1.8 (7)
C13—C8—C9—C10	2.3 (8)	I1—C19—C20—C21	177.0 (4)
C8—C9—C10—C11	1.7 (7)	C19—C20—C21—C16	−2.5 (8)
C9—C10—C11—C12	−2.5 (7)	C19—C20—C21—C14	176.7 (5)
C9—C10—C11—N1	175.0 (4)	C17—C16—C21—C20	4.7 (8)
C14—N1—C11—C10	154.4 (5)	N3—C16—C21—C20	−175.1 (5)
C14—N1—C11—C12	−28.3 (8)	C17—C16—C21—C14	−174.5 (5)
C10—C11—C12—C13	−0.7 (7)	N3—C16—C21—C14	5.7 (8)
N1—C11—C12—C13	−178.0 (5)	N2—C14—C21—C20	174.4 (5)
C11—C12—C13—C8	4.7 (8)	N1—C14—C21—C20	−7.4 (8)
C11—C12—C13—Cl1	−177.7 (4)	N2—C14—C21—C16	−6.4 (7)
O1—C8—C13—C12	175.6 (5)	N1—C14—C21—C16	171.8 (5)
C9—C8—C13—C12	−5.5 (8)		

Hydrogen-bond geometry (Å, °)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
N1—H21···N3^{i}	0.81 (6)	2.39 (6)	3.128 (6)	151 (6)

Symmetry codes: (i) *x*−1/2, −*y*+1, *z*.

Fig. 1


F1
Cl1
C15
N3
C2
C1
N2
C13
C12
O1
C16
C17
C3
C6
C7
C11
N1
C8
C14
C21
C18
C4
C5
C9
C10
C20
C19
I1

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3,5-Diamino-1-phenyl-1,2,4-triazolium bromide

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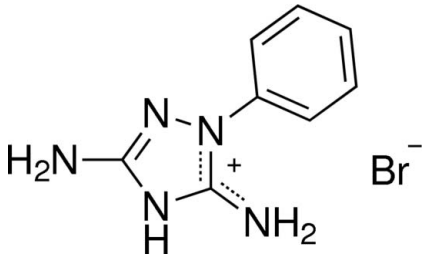
Key indicators: single-crystal X-ray study; T = 100 K; mean σ(C–C) = 0.003 Å; R factor = 0.027; wR factor = 0.071; data-to-parameter ratio = 17.1.

The title salt, $C_8H_{10}N_5^+\cdot Br^-$, crystallizes with two independent structural units in the asymmetric unit. The two independent cations have different conformations, the triazole and phenyl rings forming dihedral angles of 32.57 (6) and 52.27 (7)°. In both cations, the amino groups are planar (the sum of the angles at the N atom of each amino group is 360°) and conjugated with the triazole ring. Intermolecular N—H···N and N—H···Br hydrogen bonds consolidate the crystal packing.

Related literature

For the crystal structures of protonated *C*-amino-1,2,4-triazoles, see: Reck *et al.* (1982); Lynch *et al.* (1998, 1999); Baouab *et al.* (2000); Bichay *et al.* (2006); Guerfel *et al.* (2007); Matulková *et al.* (2007). For the crystal structure of 3,5-diamino-1,2,4-triazole, see: Starova *et al.* (1980). For the theoretical investigation of the protonation of *C*-amino-1,2,4-triazoles, see: Anders *et al.* (1997). For the reactions of 1-substituted 3,5-diamino-1,2,4-triazoles with electrophilic reagents, see: Steck *et al.* (1958); Chernyshev *et al.* (2005, 2008). For the use of 1-substituted 3,5-diamino-1,2,4-triazoles as building blocks in the synthesis of various derivatives of 1,2,4-triazole and fused heterocyclic systems, see: Dunstan *et al.* (1998); Chernyshev *et al.* (2006, 2009, 2010). For a description of the Cambridge Structural Database, see: Allen (2002).



Experimental

Crystal data

$C_8H_{10}N_5^+\cdot Br^-$
M_r = 256.12
Monoclinic, $P2_1/n$
a = 13.752 (2) Å
b = 7.1172 (13) Å
c = 20.394 (4) Å
β = 95.519 (3)°
V = 1986.7 (6) Å^3
Z = 8
Mo $K\alpha$ radiation
μ = 4.11 mm^{-1}
T = 100 K
0.55 × 0.40 × 0.30 mm

Data collection

Bruker APEXII CCD area-detector diffractometer
Absorption correction: multi-scan (*SADABS*; Bruker, 2004)
T_{min} = 0.211, T_{max} = 0.372
19484 measured reflections
4314 independent reflections
3808 reflections with $I > 2\sigma(I)$
R_{int} = 0.033

Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.027
$wR(F^2)$ = 0.071
S = 1.00
4314 reflections
253 parameters
H-atom parameters constrained
$\Delta\rho_{max}$ = 0.63 e Å^{-3}
$\Delta\rho_{min}$ = −0.52 e Å^{-3}

Table 1
Hydrogen-bond geometry (Å, °).

D—H···A	D—H	H···A	D···A	D—H···A
N3—H3A···N2$'^{i}$	0.86	2.20	3.037 (3)	164
N3—H3B···Br1	0.86	2.56	3.387 (2)	163
N3$'$—H3$'A$···N2^{ii}	0.86	2.34	3.046 (3)	140
N3$'$—H3$'B$···Br2	0.86	2.65	3.404 (3)	147
N4—H4···Br2	0.86	2.74	3.417 (3)	137
N4$'$—H4$'$···Br2	0.86	2.51	3.254 (3)	145
N5—H5A···Br1^{iii}	0.86	2.69	3.369 (3)	137
N5—H5B···Br2	0.86	2.49	3.281 (3)	153
N5$'$—H5$'A$···Br1^{iv}	0.86	2.84	3.489 (3)	133
N5$'$—H5$'B$···Br1	0.86	2.43	3.278 (3)	167

Symmetry codes: (i) $x+\frac{1}{2}, -y+\frac{1}{2}, z+\frac{1}{2}$; (ii) $x-\frac{1}{2}, -y+\frac{1}{2}, z-\frac{1}{2}$; (iii) $-x+\frac{1}{2}, y+\frac{1}{2}, -z+\frac{3}{2}$; (iv) $-x+1, -y, -z+1$.

Data collection: *APEX2* (Bruker, 2004); cell refinement: *SAINT* (Bruker, 2004); data reduction: *SAINT* and *XPREP* (Bruker, 2005); program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *Mercury* (Macrae *et al.*, 2006); software used to prepare material for publication: *SHELXTL* (Sheldrick, 2008), *publCIF* (Westrip, 2010) and *PLATON* (Spek, 2009).

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Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: CV2726).

References

Allen, F. H. (2002). *Acta Cryst.* B**58**, 380–388.
Anders, E., Wermann, K., Wiedel, B. & Vanden Eynde, J.-J. (1997). *Lieb. Ann. Recueil*, 745–752.
Baouab, L., Guerfel, T., Soussi, M. & Jouini, A. (2000). *J. Chem. Crystallogr.* **30**, 805–809.

Bichay, M., Fronabarger, J. W., Gilardi, R., Butcher, R. J., Sanborn, W. B., Sitzmann, M. E. & Williams, M. D. (2006). *Tetrahedron Lett.* **47**, 6663–6666.
Bruker (2004). *APEX2*, *SADABS* and *SAINT*. Bruker AXS Inc., Madison, Wisconsin, USA.
Bruker (2005). *XPREP*. Bruker AXS Inc., Madison, Wisconsin, USA.
Chernyshev, V. M., Astakhov, A. V. & Starikova, Z. A. (2010). *Tetrahedron*, **66**, 3301–3313.
Chernyshev, V. M., Rakitov, V. A., Astakhov, A. V., Sokolov, A. N., Zemlyakov, N. D. & Taranushich, V. A. (2006). *Russ. J. Appl. Chem.* **79**, 624–630.
Chernyshev, V. M., Rakitov, V. A., Blinov, V. V., Taranushich, V. A. & Starikova, Z. A. (2009). *Chem. Heterocycl. Compd*, **45**, 436–444.
Chernyshev, V. M., Rakitov, V. A., Taranushich, V. A. & Blinov, V. V. (2005). *Chem. Heterocycl. Compd*, **41**, 1139–1146.
Chernyshev, V. M., Sokolov, A. N., Khoroshkin, D. A. & Taranushich, V. A. (2008). *Russ. J. Org. Chem.* **44**, 715–722.
Dunstan, A. R., Weber, H.-P., Rihs, G., Widmer, H. & Dziadulewicz, E. K. (1998). *Tetrahedron. Lett.* **39**, 7983–7986.
Guerfel, T., Guelmami, L. & Jouini, A. (2007). *J. Soc. Alger. Chim.* **17**, 27–35.
Lynch, D. E., Dougall, T., Smith, G., Byriel, K. A. & Kennard, C. H. L. (1999). *J. Chem. Crystallogr.* **29**, 67–73.
Lynch, D. E., Latif, T., Smith, G., Byriel, K. A., Kennard, C. H. L. & Parsons, S. (1998). *Aust. J. Chem.* **51**, 403–408.
Macrae, C. F., Edgington, P. R., McCabe, P., Pidcock, E., Shields, G. P., Taylor, R., Towler, M. & van de Streek, J. (2006). *J. Appl. Cryst.* **39**, 453–457.
Matulková, I., Němec, I., Císařová, I., Němec, P. & Mička, Z. (2007). *J. Mol. Struct.* **834**, 328–335.
Reck, G. & Just, M. (1982). *Cryst. Struct. Commun.* **11**, 1857–1861.
Sheldrick, G. M. (2008). *Acta Cryst.* A**64**, 112–122.
Spek, A. L. (2009). *Acta Cryst.* D**65**, 148–155.
Starova, G. L., Frank-Kamenetskaya, O. V., Makarskii, V. V. & Lopirev, V. A. (1980). *Kristallografiya*, **25**, 1292–1295.
Steck, E. A., Brundage, R. P. & Fletcher, L. T. (1958). *J. Am. Chem. Soc.* **80**, 3929–3931.
Westrip, S. P. (2010). *J. Appl. Cryst.* **43**. Submitted.

supplementary materials

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3,5-Diamino-1-phenyl-1,2,4-triazolium bromide

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Comment

1-Substituted 3,5-diamino-1,2,4-triazoles are employed as convenient models for investigating the reactions of *C*-amino-1,2,4-triazoles with electrophiles so far as their molecules contain two amino groups having greatly varied nucleophilicity in positions 3 and 5 of triazole cycle (Chernyshev *et al.*, 2005, 2008, 2010). Relatively high reactivity toward electrophiles allows to use 1-substituted 3,5-diamino-1,2,4-triazoles as starting materials for the selective synthesis of 1,2,4-triazole derivatives and annulated heterocycles (Dunstan *et al.*, 1998; Chernyshev *et al.*, 2006, 2009, 2010). Some contradictions concerning the direction of several reactions of these compounds with electrophiles are present in the literature. For example, it was reported that quaternization of 1-substituted 3,5-diamino-1,2,4-triazoles by alkyl halides (Steck *et al.*, 1958) resulted in formation of 1,2-disubstituted 3,5-diamino-1,2,4-triazolium salts (Fig. 1). However these data are in contrast with quantum chemical calculations and synthetic experiments according to which the quaternization of 1-substituted 3-amino-1,2,4-triazoles as well as 1-substituted 5-amino-1,2,4-triazoles occurs at the atom N4 of triazole cycle (Anders *et al.*; 1997). While studying the quaternization of 2-amino-4,5,6,7-tetrahydro-[1,2,4]triazolo[1,5-*a*]pyrimidines (Chernyshev *et al.*, 2008), which are analogous to 1-substituted 3,5-diamino-1,2,4-triazoles in most of reactions with electrophiles, we found that alkylation takes place at the atom N4 of triazole cycle (a prevailing product) and at the C3-amino group (a minor product). The quantum chemical calculations predict that the direction of protonation and quaternization of 1-substituted *C*-amino-1,2,4-triazoles should be identical (Anders *et al.*, 1997). Therefore protonation can be used as model reaction for investigation of quaternization of 1-substituted 3,5-diamino-1,2,4-triazoles by alkyl halides. It should be noted that the data concerning the crystal structure of salts of 1-substituted *C*-amino-1,2,4-triazoles with proton acids were absent in the Cambridge Structural Database so far (Allen, 2002). Here we report the crystal structure of the title compound, 1-phenyl-1*H*-1,2,4-triazole-3,5-diamine hydrobromide (Fig. 2). The crystals of this compound were surprisingly obtained in attempting to grow the crystal of 3-amino-5,7-dimethyl-2-phenyl-[1,2,4]triazolo[4,3-*a*]pyrimidin-2-ium bromide, suitable for X-ray investigation, from water-acetonitrile. Obviously, the starting triazolopyrimidine gradually hydrolyzed to the 1-phenyl-1*H*-1,2,4-triazole-3,5-diamine hydrobromide and 2,4-pentanedion. It indicates that 1-substituted [1,2,4]triazolo[4,3-*a*]pyrimidin-2-ium salts are inclined to hydrolyze even at room temperature (Fig. 3).

According to our X-ray investigation, the asymmetric unit of the crystal structure consists of two crystallographically independent cations further denoted as the cation A (N1N2C3··· *etc*.) and the cation B (N1'N2'C3'··· *etc*.), and two bromide anions (Br1 and Br2). The cations A and B somewhat differ in bond lengths and mutual orientation of benzene and triazole rings. The dihedral angle between the benzene and triazole cycles is 32.57 (6)° in the cation A whereas that is 52.27 (7)° in the cation B. The triazole cycle is planar in both cations (the deviation of atoms from the mean-square planes does not exceed 0.008 (2) Å). As with the other salts of *C*-amino-1,2,4-triazoles (Reck *et al.*, 1982; Lynch *et al.*, 1998, 1999; Baouab *et al.*, 2000; Bichay *et al.*, 2006; Guerfel *et al.*, 2007; Matulková *et al.*, 2007), the acid proton is attached to the atom N4, amino groups are planar and conjugated with the π-system of triazole cycle. In contrast to the unprotonated 3,5-diamino-1,2,4-triazole (Starova *et al.*, 1980) and alkyl derivatives of 3,5-diamino-1-phenyl-1,2,4-triazole (Dunstan *et al.*, 1998), in the cations A and B the C5—N1 and C3—N2 bonds are shorter than the C3—N4 and C5—N4 bonds. An analogous regularity is observed for the majority of other salts of *C*-amino-1,2,4-triazoles (Reck *et al.*, 1982; Lynch *et al.*, 1998, 1999;

Baouab *et al.*, 2000; Bichay *et al.*, 2006; Guerfel *et al.*, 2007; Matulková *et al.*, 2007). Thus, the majority of protonated *C*-amino-1,2,4-triazoles should be considered as derivatives of 4*H*-1,2,4-triazol-1-ium rather than 1*H*-1,2,4-triazol-4-ium cation, except of 5-amino-3-azido-1*H*-1,2,4-triazol-4-ium nitrate (Bichay *et al.*, 2006). It is remarkable that the bond C5—N5 (1.325 (3) Å) in the cation A is shorter than the bonds C5—N1 (1.335 (3) Å) and C5—N4 (1.358 (3) Å). The analysis of bond lengths indicates that molecules forming by cation A can be described in the best way by the resonance structure of 5-amino-2-phenyl-2,4-dihydro-3*H*-1,2,4-triazol-3-iminium bromide (Fig. 4). A similar distributions of bond lengths are observed in many other salts of *C*-amino-1,2,4-triazoles (for example, see: Reck *et al.*, 1982; Lynch *et al.*, 1998, 1999; Bichay *et al.*, 2006; Matulková *et al.*, 2007; Guerfel *et al.*, 2007). Therefore, it can be concluded that the C5—NH_2 group plays an important role in the redistribution of positive charge in the *C*-amino-1,2,4-triazolium cations. Molecules including cation B are properly described by the resonance structure of 3,5-diamino-1-phenyl-4*H*-1,2,4-triazol-1-ium bromide (Fig. 4).

In the crystal the identical and parallel cations of type A or B form stacks along the *b* axis of the monoclinic cell (Fig. 5). In the direction [$\bar{1}$01] the adjacent stacks of the different-type cations form pairs in which they are displaced from each other on 0.5 cell parameter *b*. One-type cations from the nearest stacks are related in the same direction by a glide plane n perpendicular to [0, 1, 0] with glide component [1/2, 0, 1/2]. In the direction *c* the cations are turned from each other by 180° and displaced on 0.5 of cell parameter, *i.e.* are space related by 2-fold screw axis with direction [0, 1, 0] at 1/4, *y*, 1/4 with screw component [0, 1/2, 0]. Along the *c* axis one can see parallel linear chains which "links" consist of pairs of cations A and B connected with bromide anions Br1 and Br2 by means of the hydrogen bonds N3—H3B···Br1, N5'—H5'B···Br1, N4—H4···Br2, N4'—H4'···Br2, N5—H5B···Br2, N3'—H3'B···Br2 (Table 1). The nearest chains in the plane perpendicular to *b* axis are connected with each other by continuous net of hydrogen bonds N3—H3A···N2^{i} and N3'—H3'A···N2^{ii}, forming parallel molecular layers with identity period equal to the unit-cell parameter *b* (Fig. 6). The layers are connected with one another by hydrogen bonds N5—H5A···Br1^{iii} and N5'—H5'A···Br1^{iv}. In the parallel layers one-type cations are turned from each other by 180°, *i.e.* they are space related by inversion centre with coordinates [0, 0, 0]. Thereby, the $C_8H_{10}N_5^+$ cations and bromide anions form a three-dimensional framework in the crystal.

In conclusion, the present study and previously reported theoretical (Anders *et al.*, 1997) and experimental (Chernyshev *et al.*, 2008) results indicate that the structures attributed to the products of quaternization of 1-substituted 3,5-diamino-1,2,4-triazoles (Steck *et al.*, 1958), apparently, are erroneous and need correction by means of modern analytical methods. Also it would be interesting to investigate the structure of salts of another 1-substituted 3-amino-1,2,4-triazoles with a view to evaluate the role of C3—NH_2 group in the delocalization of positive charge in 3-amino-1,2,4-triazolium cations.

Experimental

The crystals of 1-phenyl-1*H*-1,2,4-triazole-3,5-diamine hydrobromide suitable for X-ray analysis were obtained from a solution of 3-amino-5,7-dimethyl-2-phenyl-[1,2,4]triazolo[4,3-*a*]pyrimidin-2-ium bromide (TPB) in 1:9 water: acetonitrile mixture as a result of hydrolysis in the course of slow evaporation at room temperature during one week. The TPB was prepared by the following procedure.

A mixture of 1-phenyl-1*H*-1,2,4-triazole-3,5-diamine hydrobromide (0.73 g, 2.85 mmol), 2,4-pentanedion (0.371 g, 3.71 mmol) and ethanol (5 ml) was refluxed for 15 min and then cooled to room temperature. The precipitate formed was filtered off and recrystallized from ethanol to give 0.757 g (83% yield) of TPB, mp 221–223 °C. ^{1}H NMR (300 MHz) δ: 1.95 (s, 3H, CH_3), 2.95 (s, 3H, CH_3), 7.22 (s, 1H, CH), 7.67–7.83 (m, 5H, Ph), 8.37 (s, 2H, NH_2). ^{13}C NMR (150 MHz) δ: 17.66,

24.37, 113.62, 130.13, 130.30, 132.16, 132.63, 147.86, 153.85, 159.74, 170.43. LCMS: 240.29 [$C_{13}H_{14}N_5^+$]. Anal. Calcd for $C_{13}H_{14}BrN_5$: C, 48.76; H, 4.41; N, 21.87. Found: C, 48.81; H, 4.21; N, 21.98.

Starting 1-phenyl-1*H*-1,2,4-triazole-3,5-diamine hydrobromide used for the preparation of TPB was obtained by addition of equimolar amount of 48% hydrobromic acid to an ethanol solution of 3,5-diamino-1-phenyl-1,2,4-triazole. The latter compound was synthesized by known method (Steck *et al.*, 1958).

Refinement

C-bound H atoms were positioned geometrically (C—H 0.93 Å), while the rest H atoms were located on difference map and further placed in idealized positions (N—H 0.86 Å). All H atoms were refined as riding on their parent atoms, with U_{iso}(H) = 1.2 U_{eq}(parent atom).

Figures

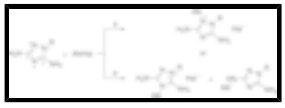


Fig. 1. The supposed directions of quaternization of 1-substituted 3,5-diamino-1,2,4-triazoles by halogen alkanes according to the literature data: *a* - Steck *et al.* (1958), *b* - Chernyshev *et al.* (2008).

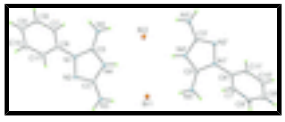


Fig. 2. The molecular structure of 1-phenyl-1*H*-1,2,4-triazole-3,5-diamine hydrobromide with the atomic numbering scheme. Displacement ellipsoids are drawn at the 50% probability level.

Fig. 3. Hydrolysis of 3-amino-5,7-dimethyl-2-phenyl-[1,2,4]triazolo[4,3-*a*]pyrimidin-2-ium bromide.

Fig. 4. The resonance structures, corresponding to the 5-amino-2-phenyl-2,4-dihydro-3*H*-1,2,4-triazol-3-iminium bromide (A) and 3,5-diamino-1-phenyl-4*H*-1,2,4-triazol-1-ium bromide (B).

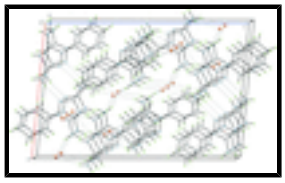


Fig. 5. Molecular packing in the crystal, viewed down the *b* axis. Hydrogen bonds are shown as dashed lines.

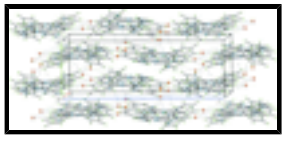


Fig. 6. The crystal packing of the title compound, viewed down the *a* axis showing molecular layers in the planes perpendicular to the *b* axis. Hydrogen bonds are shown as dashed lines.

3,5-Diamino-1-phenyl-1,2,4-triazolium bromide

Crystal data

$C_8H_{10}N_5^+ \cdot Br^-$	$F(000) = 1024$
$M_r = 256.12$	$D_x = 1.713$ Mg m^{-3}
Monoclinic, $P2_1/n$	Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å
Hall symbol: -P 2yn	Cell parameters from 568 reflections

a = 13.752 (2) Å	θ = 3–26°
b = 7.1172 (13) Å	μ = 4.11 mm^{-1}
c = 20.394 (4) Å	T = 100 K
β = 95.519 (3)°	Plate, colourless
V = 1986.7 (6) Å^3	0.55 × 0.40 × 0.30 mm
Z = 8	

Data collection

Bruker APEXII CCD area-detector diffractometer	4314 independent reflections
Radiation source: fine-focus sealed tube	3808 reflections with $I > 2\sigma(I)$
graphite	R_{int} = 0.033
ω scans	θ_{max} = 27.0°, θ_{min} = 1.7°
Absorption correction: multi-scan (*SADABS*; Bruker, 2004)	h = −17→17
T_{min} = 0.211, T_{max} = 0.372	k = −9→9
19484 measured reflections	l = −26→26

Refinement

Refinement on F^2	Primary atom site location: structure-invariant direct methods
Least-squares matrix: full	Secondary atom site location: difference Fourier map
$R[F^2 > 2\sigma(F^2)]$ = 0.027	Hydrogen site location: difference Fourier map
$wR(F^2)$ = 0.071	H-atom parameters constrained
S = 1.00	$w = 1/[\sigma^2(F_o^2) + (0.0375P)^2 + 2.843P]$ where $P = (F_o^2 + 2F_c^2)/3$
4314 reflections	$(\Delta/\sigma)_{max}$ = 0.001
253 parameters	$\Delta\rho_{max}$ = 0.63 e Å^{-3}
0 restraints	$\Delta\rho_{min}$ = −0.52 e Å^{-3}

Special details

Geometry. All e.s.d.'s (except the e.s.d. in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell e.s.d.'s are taken into account individually in the estimation of e.s.d.'s in distances, angles and torsion angles; correlations between e.s.d.'s in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell e.s.d.'s is used for estimating e.s.d.'s involving l.s. planes.

Refinement. Refinement of F^2 against ALL reflections. The weighted R-factor wR and goodness of fit S are based on F^2, conventional R-factors R are based on F, with F set to zero for negative F^2. The threshold expression of $F^2 > \sigma(F^2)$ is used only for calculating R-factors(gt) *etc*. and is not relevant to the choice of reflections for refinement. R-factors based on F^2 are statistically about twice as large as those based on F, and R- factors based on ALL data will be even larger.

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å^2)

	x	y	z	U_{iso}*/U_{eq}
Br1	0.469797 (17)	0.08357 (3)	0.629576 (11)	0.01647 (7)

Br2	0.183938 (18)	0.24667 (3)	0.647848 (11)	0.01826 (8)
N1'	0.28802 (13)	0.3108 (3)	0.40098 (9)	0.0106 (4)
N1	0.33201 (14)	0.2566 (3)	0.88547 (9)	0.0105 (4)
C5	0.28387 (16)	0.2595 (3)	0.82544 (11)	0.0109 (4)
C3'	0.17571 (16)	0.3375 (3)	0.46553 (11)	0.0109 (4)
N2	0.43255 (13)	0.2227 (3)	0.88259 (9)	0.0110 (4)
N2'	0.18826 (13)	0.3526 (3)	0.40275 (9)	0.0110 (4)
C3	0.44019 (16)	0.2009 (3)	0.81952 (11)	0.0112 (4)
C5'	0.33040 (16)	0.2696 (3)	0.46079 (11)	0.0108 (4)
N3	0.52349 (14)	0.1671 (3)	0.79256 (10)	0.0155 (4)
H3A	0.5776	0.1581	0.8172	0.019*
H3B	0.5228	0.1544	0.7506	0.019*
C6	0.29678 (17)	0.2856 (3)	0.94788 (11)	0.0112 (4)
C6'	0.33268 (16)	0.3120 (3)	0.34068 (11)	0.0108 (4)
N3'	0.09158 (14)	0.3663 (3)	0.49263 (10)	0.0139 (4)
H3'A	0.0397	0.3978	0.4682	0.017*
H3'B	0.0897	0.3533	0.5344	0.017*
C7'	0.41759 (17)	0.4159 (3)	0.33736 (12)	0.0141 (4)
H7'	0.4425	0.4895	0.3727	0.017*
N4'	0.26139 (14)	0.2888 (3)	0.50273 (9)	0.0106 (4)
H4'	0.2691	0.2737	0.5447	0.013*
N4	0.35127 (14)	0.2222 (3)	0.78272 (9)	0.0110 (4)
H4	0.3406	0.2134	0.7406	0.013*
C7	0.20341 (17)	0.2241 (3)	0.95945 (12)	0.0144 (5)
H7	0.1630	0.1663	0.9262	0.017*
C8'	0.46478 (17)	0.4074 (3)	0.27991 (12)	0.0168 (5)
H8'	0.5225	0.4738	0.2771	0.020*
N5	0.18967 (14)	0.2885 (3)	0.80841 (10)	0.0139 (4)
H5A	0.1508	0.3091	0.8382	0.017*
H5B	0.1674	0.2869	0.7675	0.017*
N5'	0.42386 (14)	0.2226 (3)	0.47651 (10)	0.0140 (4)
H5'A	0.4634	0.2166	0.4464	0.017*
H5'B	0.4445	0.1983	0.5168	0.017*
C8	0.17218 (18)	0.2512 (4)	1.02182 (12)	0.0189 (5)
H8	0.1098	0.2134	1.0300	0.023*
C9'	0.42605 (18)	0.3005 (4)	0.22696 (12)	0.0184 (5)
H9'	0.4585	0.2932	0.1891	0.022*
C9	0.2331 (2)	0.3340 (4)	1.07174 (12)	0.0203 (5)
H9	0.2116	0.3514	1.1132	0.024*
C10'	0.33847 (19)	0.2038 (3)	0.23038 (12)	0.0177 (5)
H10'	0.3116	0.1362	0.1940	0.021*
C10	0.32641 (19)	0.3909 (3)	1.05977 (12)	0.0184 (5)
H10	0.3677	0.4445	1.0935	0.022*
C11	0.35831 (17)	0.3681 (3)	0.99777 (11)	0.0142 (5)
H11	0.4205	0.4078	0.9897	0.017*
C11'	0.29117 (17)	0.2074 (3)	0.28729 (11)	0.0135 (4)
H11'	0.2332	0.1418	0.2899	0.016*

Atomic displacement parameters (Å^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Br1	0.01631 (12)	0.02134 (13)	0.01186 (12)	−0.00248 (9)	0.00199 (8)	0.00081 (9)
Br2	0.02081 (13)	0.02303 (14)	0.01122 (12)	0.00564 (10)	0.00289 (9)	−0.00001 (9)
N1'	0.0066 (9)	0.0153 (9)	0.0099 (9)	−0.0003 (7)	0.0012 (7)	0.0007 (7)
N1	0.0081 (9)	0.0145 (9)	0.0089 (9)	0.0022 (7)	0.0008 (7)	−0.0006 (7)
C5	0.0112 (10)	0.0094 (10)	0.0122 (10)	−0.0009 (8)	0.0013 (8)	−0.0006 (8)
C3'	0.0107 (10)	0.0097 (10)	0.0123 (10)	−0.0016 (8)	0.0008 (8)	−0.0007 (8)
N2	0.0074 (9)	0.0150 (9)	0.0108 (9)	0.0020 (7)	0.0020 (7)	−0.0005 (7)
N2'	0.0064 (9)	0.0146 (9)	0.0122 (9)	0.0006 (7)	0.0016 (7)	0.0012 (7)
C3	0.0129 (11)	0.0092 (10)	0.0115 (10)	0.0011 (8)	0.0014 (8)	0.0000 (8)
C5'	0.0110 (10)	0.0106 (10)	0.0109 (10)	−0.0014 (8)	0.0017 (8)	−0.0001 (8)
N3	0.0117 (9)	0.0250 (11)	0.0100 (9)	0.0050 (8)	0.0028 (7)	−0.0012 (8)
C6	0.0143 (11)	0.0106 (10)	0.0090 (10)	0.0053 (8)	0.0027 (8)	0.0015 (8)
C6'	0.0117 (10)	0.0117 (10)	0.0092 (10)	0.0030 (8)	0.0023 (8)	0.0026 (8)
N3'	0.0105 (9)	0.0209 (10)	0.0106 (9)	0.0019 (8)	0.0027 (7)	−0.0005 (8)
C7'	0.0134 (11)	0.0144 (11)	0.0146 (11)	0.0005 (9)	0.0014 (8)	0.0017 (9)
N4'	0.0111 (9)	0.0139 (9)	0.0069 (9)	−0.0009 (7)	0.0012 (7)	−0.0004 (7)
N4	0.0114 (9)	0.0141 (9)	0.0076 (9)	0.0014 (7)	0.0008 (7)	−0.0005 (7)
C7	0.0120 (11)	0.0169 (11)	0.0141 (11)	0.0040 (9)	0.0008 (9)	0.0038 (9)
C8'	0.0119 (11)	0.0193 (12)	0.0197 (12)	0.0013 (9)	0.0045 (9)	0.0094 (10)
N5	0.0102 (9)	0.0214 (10)	0.0097 (9)	0.0024 (8)	−0.0009 (7)	−0.0026 (8)
N5'	0.0099 (9)	0.0212 (10)	0.0108 (9)	0.0015 (8)	−0.0002 (7)	0.0021 (8)
C8	0.0160 (12)	0.0233 (13)	0.0187 (12)	0.0094 (10)	0.0079 (9)	0.0094 (10)
C9'	0.0202 (12)	0.0225 (12)	0.0137 (11)	0.0086 (10)	0.0084 (9)	0.0073 (10)
C9	0.0297 (14)	0.0207 (12)	0.0112 (11)	0.0139 (11)	0.0065 (10)	0.0030 (9)
C10'	0.0222 (12)	0.0182 (12)	0.0126 (11)	0.0070 (10)	0.0004 (9)	−0.0006 (9)
C10	0.0268 (13)	0.0161 (12)	0.0118 (11)	0.0074 (10)	−0.0010 (9)	−0.0016 (9)
C11	0.0158 (11)	0.0121 (10)	0.0143 (11)	0.0039 (9)	−0.0003 (9)	0.0000 (9)
C11'	0.0138 (11)	0.0137 (11)	0.0130 (11)	0.0009 (9)	0.0002 (9)	0.0011 (9)

Geometric parameters (Å, °)

N1'—C5'	1.333 (3)	C7'—C8'	1.394 (3)
N1'—N2'	1.408 (2)	C7'—H7'	0.9300
N1'—C6'	1.426 (3)	N4'—H4'	0.8600
N1—C5	1.335 (3)	N4—H4	0.8600
N1—N2	1.410 (3)	C7—C8	1.395 (3)
N1—C6	1.420 (3)	C7—H7	0.9300
C5—N5	1.325 (3)	C8'—C9'	1.385 (4)
C5—N4	1.358 (3)	C8'—H8'	0.9300
C3'—N2'	1.313 (3)	N5—H5A	0.8600
C3'—N3'	1.345 (3)	N5—H5B	0.8600
C3'—N4'	1.383 (3)	N5'—H5'A	0.8600
N2—C3	1.310 (3)	N5'—H5'B	0.8600
C3—N3	1.339 (3)	C8—C9	1.386 (4)
C3—N4	1.380 (3)	C8—H8	0.9300

C5'—N5'	1.337 (3)	C9'—C10'	1.395 (4)
C5'—N4'	1.344 (3)	C9'—H9'	0.9300
N3—H3A	0.8600	C9—C10	1.389 (4)
N3—H3B	0.8600	C9—H9	0.9300
C6—C11	1.389 (3)	C10'—C11'	1.384 (3)
C6—C7	1.398 (3)	C10'—H10'	0.9300
C6'—C7'	1.389 (3)	C10—C11	1.387 (3)
C6'—C11'	1.395 (3)	C10—H10	0.9300
N3'—H3'A	0.8600	C11—H11	0.9300
N3'—H3'B	0.8600	C11'—H11'	0.9300
C5'—N1'—N2'	111.37 (18)	C3'—N4'—H4'	126.5
C5'—N1'—C6'	127.14 (19)	C5—N4—C3	107.23 (18)
N2'—N1'—C6'	121.48 (17)	C5—N4—H4	126.4
C5—N1—N2	111.48 (18)	C3—N4—H4	126.4
C5—N1—C6	129.6 (2)	C8—C7—C6	118.6 (2)
N2—N1—C6	118.86 (18)	C8—C7—H7	120.7
N5—C5—N1	129.0 (2)	C6—C7—H7	120.7
N5—C5—N4	125.0 (2)	C9'—C8'—C7'	120.2 (2)
N1—C5—N4	106.04 (19)	C9'—C8'—H8'	119.9
N2'—C3'—N3'	126.0 (2)	C7'—C8'—H8'	119.9
N2'—C3'—N4'	111.76 (19)	C5—N5—H5A	120.0
N3'—C3'—N4'	122.3 (2)	C5—N5—H5B	120.0
C3—N2—N1	103.46 (17)	H5A—N5—H5B	120.0
C3'—N2'—N1'	103.15 (17)	C5'—N5'—H5'A	120.0
N2—C3—N3	125.2 (2)	C5'—N5'—H5'B	120.0
N2—C3—N4	111.75 (19)	H5'A—N5'—H5'B	120.0
N3—C3—N4	123.0 (2)	C9—C8—C7	120.8 (2)
N1'—C5'—N5'	126.9 (2)	C9—C8—H8	119.6
N1'—C5'—N4'	106.66 (19)	C7—C8—H8	119.6
N5'—C5'—N4'	126.5 (2)	C8'—C9'—C10'	120.1 (2)
C3—N3—H3A	120.0	C8'—C9'—H9'	120.0
C3—N3—H3B	120.0	C10'—C9'—H9'	120.0
H3A—N3—H3B	120.0	C8—C9—C10	119.9 (2)
C11—C6—C7	120.9 (2)	C8—C9—H9	120.1
C11—C6—N1	118.8 (2)	C10—C9—H9	120.1
C7—C6—N1	120.3 (2)	C11'—C10'—C9'	120.7 (2)
C7'—C6'—C11'	121.9 (2)	C11'—C10'—H10'	119.7
C7'—C6'—N1'	118.6 (2)	C9'—C10'—H10'	119.7
C11'—C6'—N1'	119.5 (2)	C11—C10—C9	120.3 (2)
C3'—N3'—H3'A	120.0	C11—C10—H10	119.8
C3'—N3'—H3'B	120.0	C9—C10—H10	119.8
H3'A—N3'—H3'B	120.0	C10—C11—C6	119.6 (2)
C6'—C7'—C8'	118.7 (2)	C10—C11—H11	120.2
C6'—C7'—H7'	120.7	C6—C11—H11	120.2
C8'—C7'—H7'	120.7	C10'—C11'—C6'	118.3 (2)
C5'—N4'—C3'	107.03 (18)	C10'—C11'—H11'	120.8
C5'—N4'—H4'	126.5	C6'—C11'—H11'	120.8
N2—N1—C5—N5	−179.4 (2)	C11'—C6'—C7'—C8'	−3.1 (3)

C6—N1—C5—N5	−0.8 (4)	N1'—C6'—C7'—C8'	175.9 (2)
N2—N1—C5—N4	1.8 (2)	N1'—C5'—N4'—C3'	1.7 (2)
C6—N1—C5—N4	−179.6 (2)	N5'—C5'—N4'—C3'	−179.7 (2)
C5—N1—N2—C3	−1.7 (2)	N2'—C3'—N4'—C5'	−1.1 (3)
C6—N1—N2—C3	179.49 (19)	N3'—C3'—N4'—C5'	179.6 (2)
N3'—C3'—N2'—N1'	179.3 (2)	N5—C5—N4—C3	−180.0 (2)
N4'—C3'—N2'—N1'	0.0 (2)	N1—C5—N4—C3	−1.1 (2)
C5'—N1'—N2'—C3'	1.2 (2)	N2—C3—N4—C5	0.0 (3)
C6'—N1'—N2'—C3'	−179.8 (2)	N3—C3—N4—C5	−178.4 (2)
N1—N2—C3—N3	179.3 (2)	C11—C6—C7—C8	1.5 (3)
N1—N2—C3—N4	1.0 (2)	N1—C6—C7—C8	178.6 (2)
N2'—N1'—C5'—N5'	179.6 (2)	C6'—C7'—C8'—C9'	1.4 (3)
C6'—N1'—C5'—N5'	0.7 (4)	C6—C7—C8—C9	−1.3 (3)
N2'—N1'—C5'—N4'	−1.8 (2)	C7'—C8'—C9'—C10'	1.3 (4)
C6'—N1'—C5'—N4'	179.2 (2)	C7—C8—C9—C10	0.0 (4)
C5—N1—C6—C11	−147.8 (2)	C8'—C9'—C10'—C11'	−2.4 (4)
N2—N1—C6—C11	30.7 (3)	C8—C9—C10—C11	1.1 (4)
C5—N1—C6—C7	35.1 (3)	C9—C10—C11—C6	−0.9 (3)
N2—N1—C6—C7	−146.4 (2)	C7—C6—C11—C10	−0.4 (3)
C5'—N1'—C6'—C7'	−52.8 (3)	N1—C6—C11—C10	−177.5 (2)
N2'—N1'—C6'—C7'	128.4 (2)	C9'—C10'—C11'—C6'	0.8 (3)
C5'—N1'—C6'—C11'	126.2 (2)	C7'—C6'—C11'—C10'	2.0 (3)
N2'—N1'—C6'—C11'	−52.6 (3)	N1'—C6'—C11'—C10'	−177.0 (2)

Hydrogen-bond geometry (Å, °)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
N3—H3A···N2'^{i}	0.86	2.20	3.037 (3)	164
N3—H3B···Br1	0.86	2.56	3.387 (2)	163
N3'—H3'A···N2^{ii}	0.86	2.34	3.046 (3)	140
N3'—H3'B···Br2	0.86	2.65	3.404 (3)	147
N4—H4···Br2	0.86	2.74	3.417 (3)	137
N4'—H4'···Br2	0.86	2.51	3.254 (3)	145
N5—H5A···Br1^{iii}	0.86	2.69	3.369 (3)	137
N5—H5B···Br2	0.86	2.49	3.281 (3)	153
N5'—H5'A···Br1^{iv}	0.86	2.84	3.489 (3)	133
N5'—H5'B···Br1	0.86	2.43	3.278 (3)	167

Symmetry codes: (i) *x*+1/2, −*y*+1/2, *z*+1/2; (ii) *x*−1/2, −*y*+1/2, *z*−1/2; (iii) −*x*+1/2, *y*+1/2, −*z*+3/2; (iv) −*x*+1, −*y*, −*z*+1.

Fig. 1

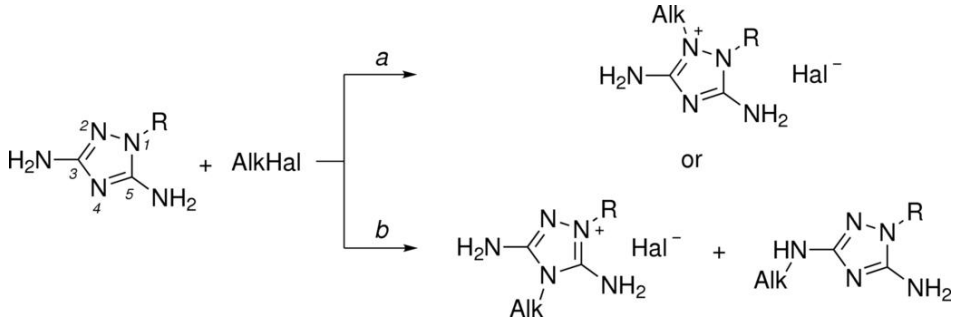


Fig. 2

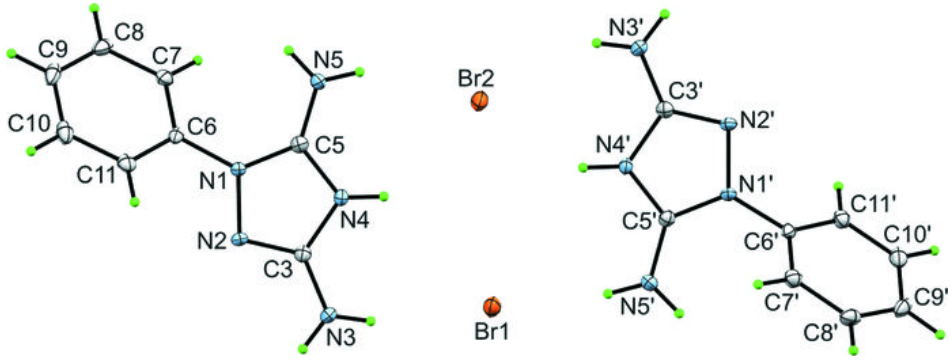

C8
C9
C7
N5
C10
C6
C5
C11
N1
N4
N2
C3
N3
Br2
Br1
N3'
C3'
N2'
N4'
N1'
C11'
C5'
C6'
C10'
N5'
C7'
C9'
C8'

Fig. 3

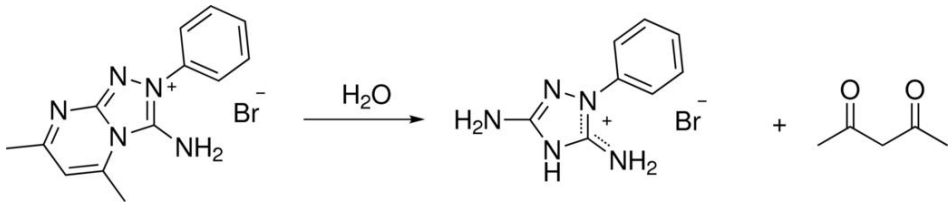
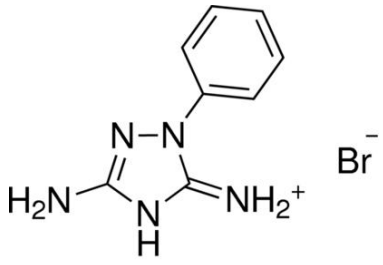
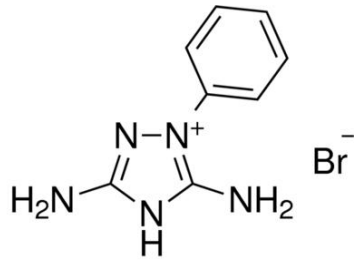


Fig. 4



A



B

Fig. 5

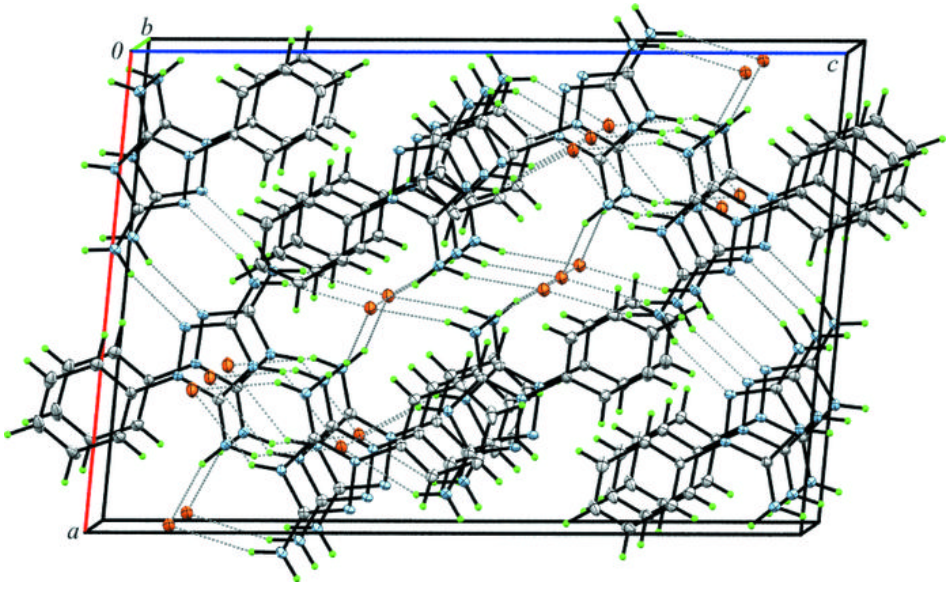
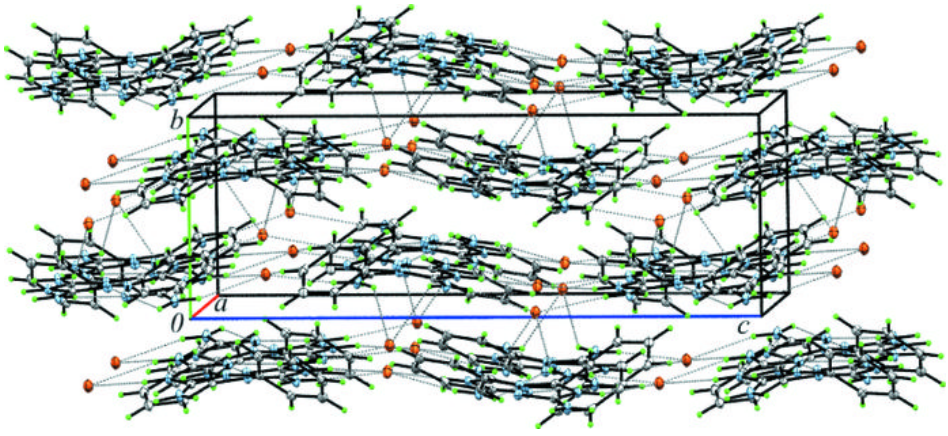


Fig. 6



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Diaqua(isonicotinamide-κN^1)-(4-methoxybenzoato-$\kappa^2 O,O'$)-(4-methoxybenzoato-κO)cobalt(II)

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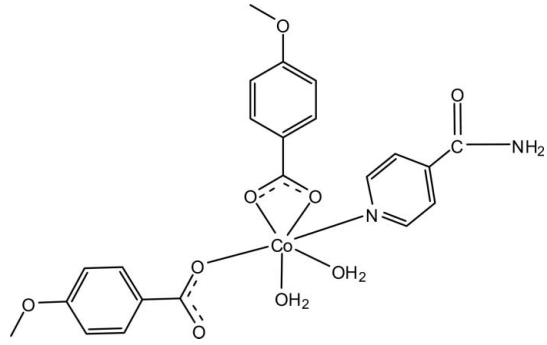
Key indicators: single-crystal X-ray study; T = 100 K; mean σ(C–C) = 0.002 Å; R factor = 0.022; wR factor = 0.050; data-to-parameter ratio = 14.5.

In the title complex, $[Co(C_8H_7O_3)_2(C_6H_6N_2O)(H_2O)_2]$, the Co^{II} atom is coordinated by three O atoms from two 4-methoxybenzoate ligands, which act in different modes, *viz.* monodentate and bidentate, two water molecules and one N atom of the isonicotinamide ligand in a distorted octahedral geometry. The monodentate-coordinated carboxylate group is involved in an intramolecular O—H···O hydrogen bond with the coordinated water molecule. In the crystal structure, intermolecular O—H···O and N—H···O hydrogen bonds link the molecules into layers parallel to the *ab* plane. The crystal packing is further stabilized by weak C—H···O hydrogen bonds and π–π interactions indicated by the short distance of 3.6181 (8) Å between the centroids of the benzene and pyridine rings of neighbouring molecules.

Related literature

For general background to niacin and the nicotinic acid derivative *N*,*N*-diethylnicotinamide, see: Krishnamachari (1974) and Bigoli *et al.* (1972), respectively. For related structures, see: Greenaway *et al.* (1984); Hökelek *et al.* (2009*a*,*b*,*c*,*d*); Necefoğlu *et al.* (2010).



Experimental

Crystal data

$[Co(C_8H_7O_3)_2(C_6H_6N_2O)(H_2O)_2]$
M_r = 519.36
Monoclinic, $P2_1$
a = 8.2666 (2) Å
b = 6.8055 (2) Å
c = 20.5415 (4) Å
β = 99.808 (2)°
V = 1138.74 (5) Å^3
Z = 2
Mo $K\alpha$ radiation
μ = 0.81 mm^{-1}
T = 100 K
0.39 × 0.32 × 0.28 mm

Data collection

Bruker Kappa APEXII CCD area-detector diffractometer
Absorption correction: multi-scan (*SADABS*; Bruker, 2005)
T_{min} = 0.739, T_{max} = 0.791
11263 measured reflections
4838 independent reflections
4597 reflections with $I > 2\sigma(I)$
R_{int} = 0.020

Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.022
$wR(F^2)$ = 0.050
S = 1.01
4838 reflections
333 parameters
H atoms treated by a mixture of independent and constrained refinement
$\Delta\rho_{max}$ = 0.29 e Å^{-3}
$\Delta\rho_{min}$ = −0.24 e Å^{-3}
Absolute structure: Flack (1983), 1761 Friedel pairs
Flack parameter: 0.015 (7)

Table 1
Hydrogen-bond geometry (Å, °).

D—H···A	D—H	H···A	D···A	D—H···A
N2—H2A···O2^{i}	0.79 (3)	2.11 (3)	2.877 (2)	164.0 (17)
N2—H2B···O1^{ii}	0.91 (3)	2.16 (3)	3.050 (2)	167 (2)
O8—H81···O4	0.83 (3)	1.84 (3)	2.6577 (17)	167 (3)
O8—H82···O7^{iii}	0.89 (2)	1.86 (3)	2.7427 (16)	172 (2)
O9—H91···O6^{iv}	0.786 (19)	2.078 (19)	2.8384 (16)	163 (2)
O9—H92···O4^{v}	0.91 (3)	1.72 (3)	2.6307 (18)	174.1 (15)
C8—H8A···O7^{vi}	0.96	2.53	3.466 (2)	166
C16—H16B···O4^{vii}	0.96	2.52	3.4752 (18)	171

Symmetry codes: (i) $x+1, y, z$; (ii) $x+1, y+1, z$; (iii) $x-1, y-1, z$; (iv) $x-1, y+1, z$; (v) $x, y+1, z$; (vi) $-x+2, y-\frac{3}{2}, -z+2$; (vii) $-x+2, y-\frac{1}{2}, -z+1$.

Data collection: *APEX2* (Bruker, 2007); cell refinement: *SAINT* (Bruker, 2007); data reduction: *SAINT*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *ORTEP-3 for Windows* (Farrugia, 1997); software used to prepare material for publication: *WinGX* (Farrugia, 1999) and *PLATON* (Spek, 2009).

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Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: CV2727).

References

Bigoli, F., Braibanti, A., Pellinghelli, M. A. & Tiripicchio, A. (1972). *Acta Cryst.* B**28**, 962–966.
Bruker (2005). *SADABS*. Bruker AXS Inc., Madison, Wisconsin, USA.
Bruker (2007). *APEX2* and *SAINT*. Bruker AXS Inc., Madison, Wisconsin, USA.
Farrugia, L. J. (1997). *J. Appl. Cryst.* **30**, 565.
Farrugia, L. J. (1999). *J. Appl. Cryst.* **32**, 837–838.
Flack, H. D. (1983). *Acta Cryst.* A**39**, 876–881.
Greenaway, F. T., Pazeshk, A., Cordes, A. W., Noble, M. C. & Sorenson, J. R. J. (1984). *Inorg. Chim. Acta*, **93**, 67–71.
Hökelek, T., Dal, H., Tercan, B., Aybirdi, Ö. & Necefoğlu, H. (2009*a*). *Acta Cryst.* E**65**, m1037–m1038.
Hökelek, T., Dal, H., Tercan, B., Aybirdi, Ö. & Necefoğlu, H. (2009*b*). *Acta Cryst.* E**65**, m627–m628.
Hökelek, T., Dal, H., Tercan, B., Aybirdi, Ö. & Necefoğlu, H. (2009*c*). *Acta Cryst.* E**65**, m651–m652.
Hökelek, T., Dal, H., Tercan, B., Aybirdi, Ö. & Necefoğlu, H. (2009*d*). *Acta Cryst.* E**65**, m1365–m1366.
Krishnamachari, K. A. V. R. (1974). *Am. J. Clin. Nutr.* **27**, 108–111.
Necefoğlu, H., Çimen, E., Tercan, B., Süzen, Y. & Hökelek, T. (2010). *Acta Cryst.* E**66**, m392–m393.
Sheldrick, G. M. (2008). *Acta Cryst.* A**64**, 112–122.
Spek, A. L. (2009). *Acta Cryst.* D**65**, 148–155.

supplementary materials

Acta Cryst. (2010). E**66**, m784-m785 [**doi:10.1107/S160053681002194X**]

Diaqua(isonicotinamide-κN^1)(4-methoxybenzoato-$\kappa^2 O,O'$)(4-methoxybenzoato-κO)cobalt(II)

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Comment

As a part of our ongoing investigation on transition metal complexes of nicotinamide (NA), one form of niacin (Krishnamachari, 1974), and/or the nicotinic acid derivative *N*,*N*-diethylnicotinamide (DENA), an important respiratory stimulant (Bigoli *et al.*, 1972), the title compound has been synthesized. Herein we report its crystal structure.

The title compound, (I), is a monomeric complex, where the Co^{II} ion is surrounded by two methoxybenzoate (MB) anions, one isonicotinamide (INA) ligand and two coordinated water molecules. One of the MB anions acts as a bidentate ligand, while the other is monodentate. The structures of similar complexes , $[Mn(C_9H_{10}NO_2)_2(C_6H_6N_2O)(H_2O)_2]$ (II) (Hökelek *et al.*, 2009*a*), $[Co(C_9H_{10}NO_2)_2(C_6H_6N_2O)(H_2O)_2]$ (III) (Hökelek *et al.*, 2009*b*), $[Cd(C_8H_7O_2)_2(C_6H_6N_2O)_2(H_2O)].H_2O$ (IV) (Necefoğlu *et al.*, 2010), $[Zn(C_9H_{10}NO_2)_2(C_6H_6N_2O)(H_2O)_2]$ (V) (Hökelek *et al.*, 2009*c*) and $[Zn(C_8H_8NO_2)_2(C_6H_6N_2O)_2].H_2O$ (VI) (Hökelek *et al.*, 2009d) have also been determined.

In (I) (Fig. 1), the four O atoms (O1, O2, O5 and O9) in the equatorial plane around the Co1 form a highly distorted square-planar arrangement, while the distorted octahedral coordination geometry is completed by the N atom (N1) of INA ligand and the O atom (O8) of the second water molecule in the axial positions. The average Co—O bond length is 2.1171 (12) Å and the Co atom is displaced out of the least-squares planes of the carboxylate groups (O1/C1/O2) and (O4/C9/O5) by -0.0061 (2) Å and -0.5367 (2) Å, respectively. The dihedral angle between the planar carboxylate groups and the adjacent benzene rings A (C2—C7) and B (C9—C14) are 12.12 (12)° and 9.26 (13)°, respectively, while those between rings A, B and C (N1/C17—C21) are A/B = 78.18 (4), A/C = 74.20 (5) and B/C = 6.23 (5) °. The intramolecular O—H···O hydrogen bond (Table 1) between the monodentate-coordinated carboxyl group and a coordinated water molecule results in a six-membered ring D (Co1/O4/O5/O8/C9/H81) adopting envelope conformation, with atom Co1 displaced by -0.5481 (2) Å from the plane of the other ring atoms. In (I), the O1—Co1—O2 angle is 60.32 (4)°. The corresponding O—M—O (where *M* is a metal) angles are 54.71 (4)° in (IV), 60.03 (6)° in (V), 59.02 (8)° in (VI) and 55.2 (1)° in $[Cu(Asp)_2(py)_2]$ (where Asp is acetylsalicylate and py is pyridine) [(VII); Greenaway *et al.*, 1984].

In the crystal structure, intermolecular O—H···O and N—H···O hydrogen bonds (Table 1) link the molecules into layers parallel to *ab* plane. The crystal packing is further stabilized by the weak C—H···O hydrogen bonds (Table 1). The π–π contact between the benzene and pyridine rings, *Cg*2—*Cg*3^{i} [symmetry code: (i) *x*, *y* + 1, *z*, where *Cg*2 and *Cg*3 are the centroids of the rings B (C9—C14) and C (N1/C17—C21), respectively] may also stabilize the structure, with centroid-centroid distance of 3.6181 (8) Å.

Experimental

The title compound was prepared by the reaction of $CoSO_4.7H_2O$ (2.81 g, 10 mmol) in H_2O (50 ml) and INA (2.44 g, 20 mmol) in H_2O (50 ml) with sodium 4-methoxybenzoate (3.48 g, 20 mmol) in H_2O (100 ml). The mixture was filtered and set aside to crystallize at ambient temperature for one week, giving brown single crystals.

Refinement

Atoms H81, H82, H91, H92 (for water molecules) and H2A, H2B (for NH_2) were located in difference Fourier maps and refined isotropically. The remaining H atoms were positioned geometrically with C—H = 0.93 and 0.96 Å for aromatic and methyl H atoms, respectively, and constrained to ride on their parent atoms, with U_{iso}(H) = 1.2-1.5U_{eq}(C).

Figures

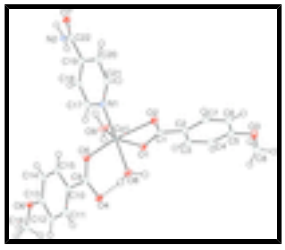


Fig. 1. The molecular structure of (I) with the atom-numbering scheme. Displacement ellipsoids are drawn at the 50% probability level. Dashed line indicates the hydrogen-bonding.

Diaqua(isonicotinamide-κN^1)(4-methoxybenzoato- κ$^2O,O'$)(4-methoxybenzoato-κO)cobalt(II)

Crystal data

$[Co(C_8H_7O_3)_2(C_6H_6N_2O)(H_2O)_2]$	$F(000)$ = 538
M_r = 519.36	D_x = 1.515 Mg m^{-3}
Monoclinic, $P2_1$	Mo $K\alpha$ radiation, λ = 0.71073 Å
Hall symbol: P 2yb	Cell parameters from 6882 reflections
a = 8.2666 (2) Å	θ = 2.5–28.4°
b = 6.8055 (2) Å	μ = 0.81 mm^{-1}
c = 20.5415 (4) Å	T = 100 K
β = 99.808 (2)°	Block, brown
V = 1138.74 (5) Å^3	0.39 × 0.32 × 0.28 mm
Z = 2	

Data collection

Bruker Kappa APEXII CCD area-detector diffractometer	4838 independent reflections
Radiation source: fine-focus sealed tube	4597 reflections with $I > 2\sigma(I)$
graphite	R_{int} = 0.020
φ and ω scans	θ_{max} = 28.4°, θ_{min} = 1.0°
Absorption correction: multi-scan (*SADABS*; Bruker, 2005)	h = −11→9
T_{min} = 0.739, T_{max} = 0.791	k = −8→9
11263 measured reflections	l = −27→27

Refinement

Refinement on F^2	Hydrogen site location: inferred from neighbouring sites
Least-squares matrix: full	H atoms treated by a mixture of independent and constrained refinement
$R[F^2 > 2\sigma(F^2)] = 0.022$	$w = 1/[\sigma^2(F_o^2) + (0.0215P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
$wR(F^2) = 0.050$	$(\Delta/\sigma)_{max} = 0.003$
$S = 1.01$	$\Delta\rho_{max} = 0.29$ e Å^{-3}
4838 reflections	$\Delta\rho_{min} = -0.24$ e Å^{-3}
333 parameters	Absolute structure: Flack (1983), 1761 Friedel pairs
Primary atom site location: structure-invariant direct methods	Flack parameter: 0.015 (7)
Secondary atom site location: difference Fourier map	

Special details

Geometry. All e.s.d.'s (except the e.s.d. in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell e.s.d.'s are taken into account individually in the estimation of e.s.d.'s in distances, angles and torsion angles; correlations between e.s.d.'s in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell e.s.d.'s is used for estimating e.s.d.'s involving l.s. planes.

Refinement. Refinement of F^2 against ALL reflections. The weighted *R*-factor *wR* and goodness of fit *S* are based on F^2, conventional *R*-factors *R* are based on *F*, with *F* set to zero for negative F^2. The threshold expression of $F^2 > \sigma(F^2)$ is used only for calculating *R*-factors(gt) *etc*. and is not relevant to the choice of reflections for refinement. *R*-factors based on F^2 are statistically about twice as large as those based on *F*, and *R*- factors based on ALL data will be even larger.

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å^2)

	x	*y*	*z*	U_{iso}*/U_{eq}
Co1	0.83963 (2)	0.92738 (3)	0.717117 (8)	0.01106 (5)
O1	0.87439 (13)	0.72789 (18)	0.79844 (5)	0.0132 (2)
O2	0.75818 (13)	1.01182 (18)	0.81134 (5)	0.0145 (2)
O3	0.68768 (15)	0.5746 (2)	1.08004 (5)	0.0212 (3)
O4	0.78237 (13)	0.51498 (18)	0.63163 (5)	0.0156 (2)
O5	0.95880 (13)	0.76378 (18)	0.65605 (5)	0.0146 (2)
O6	1.43741 (13)	0.13627 (18)	0.56391 (5)	0.0160 (2)
O7	1.44482 (14)	1.65456 (18)	0.77779 (5)	0.0160 (2)
O8	0.60930 (14)	0.78883 (19)	0.68139 (6)	0.0147 (2)
H81	0.652 (3)	0.692 (4)	0.6668 (10)	0.024 (6)*
H82	0.564 (3)	0.750 (4)	0.7153 (12)	0.052 (7)*
O9	0.72143 (15)	1.1511 (2)	0.66328 (6)	0.0177 (3)
H91	0.639 (2)	1.126 (4)	0.6396 (10)	0.024 (6)*
H92	0.749 (2)	1.277 (4)	0.6543 (9)	0.021 (5)*
N1	1.05301 (16)	1.0966 (2)	0.74674 (6)	0.0127 (3)
N2	1.62169 (17)	1.4016 (3)	0.79899 (7)	0.0175 (3)

H2A	1.643 (2)	1.290 (4)	0.8055 (9)	0.015 (5)*
H2B	1.708 (3)	1.486 (4)	0.8026 (10)	0.033 (6)*
C1	0.80942 (19)	0.8473 (3)	0.83434 (7)	0.0130 (3)
C2	0.79173 (19)	0.7843 (3)	0.90221 (7)	0.0140 (3)
C3	0.86387 (19)	0.6109 (3)	0.92813 (7)	0.0172 (3)
H3	0.9323	0.5420	0.9046	0.021*
C4	0.8362 (2)	0.5378 (3)	0.98853 (7)	0.0190 (4)
H4	0.8862	0.4220	1.0056	0.023*
C5	0.7328 (2)	0.6403 (3)	1.02288 (7)	0.0172 (4)
C6	0.6650 (2)	0.8189 (3)	0.99909 (8)	0.0200 (4)
H6	0.6001	0.8901	1.0235	0.024*
C7	0.69427 (19)	0.8905 (3)	0.93914 (7)	0.0172 (4)
H7	0.6489	1.0099	0.9233	0.021*
C8	0.7330 (2)	0.3780 (3)	1.10016 (8)	0.0238 (4)
H8A	0.6763	0.3397	1.1352	0.036*
H8B	0.8493	0.3718	1.1154	0.036*
H8C	0.7038	0.2906	1.0633	0.036*
C9	0.92278 (19)	0.5941 (2)	0.63394 (7)	0.0125 (3)
C10	1.05374 (18)	0.4757 (2)	0.60954 (7)	0.0122 (4)
C11	1.0197 (2)	0.2936 (3)	0.57978 (7)	0.0160 (3)
H11	0.9117	0.2493	0.5716	0.019*
C12	1.14209 (19)	0.1759 (3)	0.56200 (7)	0.0160 (3)
H12	1.1168	0.0551	0.5416	0.019*
C13	1.30388 (19)	0.2427 (3)	0.57528 (7)	0.0135 (3)
C14	1.33919 (17)	0.4281 (3)	0.60267 (6)	0.0160 (3)
H14	1.4464	0.4749	0.6093	0.019*
C15	1.2158 (2)	0.5421 (3)	0.61986 (7)	0.0148 (3)
H15	1.2406	0.6651	0.6386	0.018*
C16	1.4086 (2)	−0.0503 (3)	0.53119 (7)	0.0191 (4)
H16A	1.5118	−0.1095	0.5271	0.029*
H16B	1.3448	−0.0312	0.4880	0.029*
H16C	1.3501	−0.1347	0.5566	0.029*
C17	1.20276 (19)	1.0299 (3)	0.74076 (7)	0.0156 (3)
H17	1.2125	0.9018	0.7261	0.019*
C18	1.34326 (19)	1.1433 (3)	0.75550 (7)	0.0143 (3)
H18	1.4452	1.0910	0.7518	0.017*
C19	1.32986 (18)	1.3358 (2)	0.77577 (7)	0.0119 (3)
C20	1.17472 (17)	1.4047 (3)	0.78314 (6)	0.0132 (3)
H20	1.1614	1.5323	0.7975	0.016*
C21	1.04258 (19)	1.2809 (3)	0.76878 (7)	0.0145 (3)
H21	0.9402	1.3273	0.7746	0.017*
C22	1.47067 (19)	1.4762 (2)	0.78517 (7)	0.0135 (3)

Atomic displacement parameters (Å^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Co1	0.00979 (9)	0.00942 (10)	0.01397 (8)	−0.00058 (10)	0.00201 (6)	−0.00009 (9)
O1	0.0127 (5)	0.0116 (6)	0.0158 (5)	0.0014 (5)	0.0036 (4)	−0.0003 (4)

O2	0.0120 (6)	0.0131 (6)	0.0190 (5)	0.0013 (5)	0.0042 (4)	0.0016 (5)
O3	0.0236 (7)	0.0243 (8)	0.0170 (5)	0.0001 (6)	0.0068 (5)	0.0039 (5)
O4	0.0115 (5)	0.0136 (6)	0.0223 (5)	−0.0021 (5)	0.0046 (4)	−0.0018 (5)
O5	0.0133 (5)	0.0123 (6)	0.0191 (5)	−0.0025 (5)	0.0051 (4)	−0.0027 (5)
O6	0.0133 (5)	0.0146 (7)	0.0201 (5)	0.0021 (5)	0.0033 (4)	−0.0031 (5)
O7	0.0144 (6)	0.0106 (6)	0.0237 (5)	0.0000 (5)	0.0057 (4)	−0.0008 (5)
O8	0.0124 (6)	0.0125 (7)	0.0192 (5)	−0.0017 (5)	0.0029 (4)	−0.0006 (5)
O9	0.0139 (6)	0.0125 (7)	0.0246 (6)	−0.0031 (5)	−0.0029 (5)	0.0033 (5)
N1	0.0124 (6)	0.0120 (7)	0.0137 (5)	−0.0005 (6)	0.0024 (5)	0.0007 (5)
N2	0.0111 (6)	0.0087 (9)	0.0324 (7)	−0.0007 (6)	0.0029 (5)	−0.0019 (7)
C1	0.0066 (7)	0.0138 (8)	0.0178 (7)	−0.0038 (6)	0.0000 (6)	−0.0006 (6)
C2	0.0121 (7)	0.0141 (9)	0.0153 (6)	−0.0031 (7)	0.0010 (5)	0.0003 (6)
C3	0.0148 (8)	0.0194 (10)	0.0174 (7)	0.0026 (7)	0.0031 (6)	−0.0007 (7)
C4	0.0178 (8)	0.0183 (10)	0.0202 (7)	0.0026 (7)	0.0015 (6)	0.0033 (7)
C5	0.0148 (8)	0.0226 (10)	0.0139 (6)	−0.0037 (7)	0.0019 (6)	0.0004 (6)
C6	0.0211 (9)	0.0204 (10)	0.0201 (7)	0.0019 (7)	0.0076 (6)	−0.0029 (7)
C7	0.0174 (7)	0.0140 (11)	0.0206 (7)	−0.0004 (7)	0.0042 (6)	−0.0006 (6)
C8	0.0236 (9)	0.0289 (13)	0.0188 (7)	−0.0002 (8)	0.0030 (6)	0.0080 (7)
C9	0.0140 (8)	0.0123 (9)	0.0112 (6)	0.0002 (6)	0.0017 (6)	0.0016 (6)
C10	0.0117 (7)	0.0137 (10)	0.0115 (6)	0.0007 (6)	0.0025 (5)	0.0023 (5)
C11	0.0116 (8)	0.0175 (9)	0.0189 (7)	−0.0026 (7)	0.0025 (6)	−0.0010 (7)
C12	0.0167 (8)	0.0138 (9)	0.0174 (7)	−0.0025 (7)	0.0029 (6)	−0.0037 (6)
C13	0.0150 (8)	0.0143 (9)	0.0116 (6)	0.0008 (7)	0.0031 (5)	0.0004 (6)
C14	0.0126 (6)	0.0170 (8)	0.0187 (6)	−0.0038 (9)	0.0034 (5)	−0.0018 (8)
C15	0.0175 (8)	0.0120 (9)	0.0151 (6)	−0.0023 (7)	0.0031 (6)	−0.0033 (6)
C16	0.0222 (8)	0.0158 (10)	0.0191 (6)	0.0021 (8)	0.0035 (6)	−0.0044 (7)
C17	0.0151 (8)	0.0119 (9)	0.0198 (7)	0.0013 (7)	0.0030 (6)	−0.0024 (6)
C18	0.0101 (7)	0.0135 (9)	0.0200 (7)	0.0021 (7)	0.0047 (6)	−0.0011 (6)
C19	0.0121 (7)	0.0126 (8)	0.0116 (6)	−0.0016 (6)	0.0031 (5)	0.0008 (6)
C20	0.0139 (7)	0.0089 (10)	0.0175 (6)	0.0032 (7)	0.0048 (5)	−0.0019 (6)
C21	0.0122 (8)	0.0142 (9)	0.0178 (7)	0.0008 (7)	0.0047 (6)	−0.0010 (6)
C22	0.0136 (7)	0.0136 (10)	0.0145 (6)	−0.0018 (6)	0.0052 (5)	−0.0022 (5)

Geometric parameters (Å, °)

Co1—O1	2.1338 (11)	C6—C5	1.392 (3)
Co1—O2	2.2301 (11)	C6—H6	0.9300
Co1—O5	2.0506 (11)	C7—C6	1.383 (2)
Co1—O8	2.1394 (12)	C7—H7	0.9300
Co1—O9	2.0317 (13)	C8—H8A	0.9600
Co1—N1	2.1077 (13)	C8—H8B	0.9600
O1—C1	1.276 (2)	C8—H8C	0.9600
O2—C1	1.260 (2)	C10—C9	1.502 (2)
O3—C5	1.3662 (19)	C10—C11	1.389 (2)
O3—C8	1.431 (2)	C10—C15	1.395 (2)
O4—C9	1.2729 (19)	C11—H11	0.9300
O5—C9	1.258 (2)	C12—C11	1.387 (2)
O6—C13	1.3730 (19)	C12—C13	1.395 (2)
O6—C16	1.437 (2)	C12—H12	0.9300

O7—C22	1.237 (2)	C14—C13	1.392 (3)
O8—H81	0.83 (2)	C14—C15	1.375 (2)
O8—H82	0.89 (3)	C14—H14	0.9300
O9—H91	0.79 (2)	C15—H15	0.9300
O9—H92	0.91 (2)	C16—H16A	0.9600
N1—C17	1.344 (2)	C16—H16B	0.9600
N1—C21	1.342 (2)	C16—H16C	0.9600
N2—C22	1.333 (2)	C17—C18	1.385 (2)
N2—H2A	0.79 (2)	C17—H17	0.9300
N2—H2B	0.91 (2)	C18—H18	0.9300
C2—C1	1.489 (2)	C19—C18	1.385 (2)
C2—C3	1.387 (2)	C19—C20	1.398 (2)
C2—C7	1.398 (2)	C20—H20	0.9300
C3—C4	1.392 (2)	C21—C20	1.371 (2)
C3—H3	0.9300	C21—H21	0.9300
C4—H4	0.9300	C22—C19	1.493 (2)
C5—C4	1.386 (2)		
O1—Co1—O2	60.32 (4)	C6—C7—H7	119.8
O1—Co1—O8	88.94 (4)	O3—C8—H8A	109.5
O5—Co1—O1	96.83 (4)	O3—C8—H8B	109.5
O5—Co1—O2	156.69 (4)	O3—C8—H8C	109.5
O5—Co1—O8	92.47 (5)	H8A—C8—H8B	109.5
O5—Co1—N1	90.44 (5)	H8A—C8—H8C	109.5
O8—Co1—O2	91.64 (5)	H8B—C8—H8C	109.5
O9—Co1—O1	153.01 (5)	O4—C9—C10	117.72 (14)
O9—Co1—O2	95.22 (5)	O5—C9—O4	124.05 (14)
O9—Co1—O5	108.09 (5)	O5—C9—C10	118.23 (13)
O9—Co1—O8	79.99 (5)	C11—C10—C9	121.43 (14)
O9—Co1—N1	92.80 (5)	C11—C10—C15	118.24 (15)
N1—Co1—O1	97.30 (5)	C15—C10—C9	120.23 (14)
N1—Co1—O2	88.29 (5)	C10—C11—H11	119.1
N1—Co1—O8	172.76 (5)	C12—C11—C10	121.90 (15)
C1—O1—Co1	91.92 (10)	C12—C11—H11	119.1
C1—O2—Co1	87.97 (10)	C11—C12—C13	118.61 (16)
C5—O3—C8	117.25 (14)	C11—C12—H12	120.7
C9—O5—Co1	127.62 (10)	C13—C12—H12	120.7
C13—O6—C16	118.14 (12)	O6—C13—C14	115.31 (13)
Co1—O8—H81	93.8 (15)	O6—C13—C12	124.54 (15)
Co1—O8—H82	109.5 (15)	C14—C13—C12	120.15 (15)
H81—O8—H82	108 (2)	C13—C14—H14	119.9
Co1—O9—H91	117.3 (17)	C15—C14—C13	120.10 (14)
Co1—O9—H92	134.2 (12)	C15—C14—H14	119.9
H91—O9—H92	108 (2)	C10—C15—H15	119.6
C17—N1—Co1	121.84 (11)	C14—C15—C10	120.90 (16)
C21—N1—Co1	120.64 (11)	C14—C15—H15	119.6
C21—N1—C17	117.40 (14)	O6—C16—H16A	109.5
C22—N2—H2A	125.4 (14)	O6—C16—H16B	109.5
C22—N2—H2B	118.0 (14)	O6—C16—H16C	109.5
H2A—N2—H2B	117 (2)	H16A—C16—H16B	109.5

O1—C1—C2	118.41 (15)	H16A—C16—H16C	109.5
O2—C1—O1	119.79 (14)	H16B—C16—H16C	109.5
O2—C1—C2	121.77 (15)	N1—C17—C18	122.89 (16)
C3—C2—C7	118.77 (14)	N1—C17—H17	118.6
C3—C2—C1	120.01 (15)	C18—C17—H17	118.6
C7—C2—C1	121.09 (15)	C17—C18—H18	120.5
C2—C3—C4	121.42 (16)	C19—C18—C17	119.09 (15)
C2—C3—H3	119.3	C19—C18—H18	120.5
C4—C3—H3	119.3	C18—C19—C20	118.15 (15)
C3—C4—H4	120.6	C18—C19—C22	122.94 (15)
C5—C4—C3	118.90 (17)	C20—C19—C22	118.75 (15)
C5—C4—H4	120.6	C19—C20—H20	120.6
O3—C5—C4	123.71 (17)	C21—C20—C19	118.87 (17)
O3—C5—C6	115.79 (15)	C21—C20—H20	120.6
C4—C5—C6	120.49 (15)	N1—C21—C20	123.53 (15)
C7—C6—C5	119.92 (16)	N1—C21—H21	118.2
C7—C6—H6	120.0	C20—C21—H21	118.2
C5—C6—H6	120.0	O7—C22—N2	122.40 (15)
C2—C7—H7	119.8	O7—C22—C19	119.83 (14)
C6—C7—C2	120.36 (16)	N2—C22—C19	117.72 (15)
O2—Co1—O1—C1	0.09 (8)	C7—C2—C1—O2	10.6 (2)
O5—Co1—O1—C1	175.24 (9)	C3—C2—C1—O1	8.3 (2)
O8—Co1—O1—C1	−92.40 (9)	C7—C2—C1—O1	−167.51 (14)
O9—Co1—O1—C1	−27.20 (15)	C1—C2—C3—C4	−173.46 (15)
N1—Co1—O1—C1	83.91 (9)	C7—C2—C3—C4	2.4 (2)
O1—Co1—O2—C1	−0.10 (8)	C1—C2—C7—C6	173.09 (15)
O5—Co1—O2—C1	−12.36 (15)	C3—C2—C7—C6	−2.8 (2)
O8—Co1—O2—C1	87.75 (9)	C2—C3—C4—C5	0.7 (3)
O9—Co1—O2—C1	167.84 (9)	O3—C5—C4—C3	175.05 (15)
N1—Co1—O2—C1	−99.50 (9)	C6—C5—C4—C3	−3.5 (2)
O1—Co1—O5—C9	60.93 (12)	C7—C6—C5—O3	−175.47 (15)
O2—Co1—O5—C9	71.64 (17)	C7—C6—C5—C4	3.2 (2)
O8—Co1—O5—C9	−28.29 (12)	C2—C7—C6—C5	0.0 (2)
O9—Co1—O5—C9	−108.57 (12)	C11—C10—C9—O4	5.9 (2)
N1—Co1—O5—C9	158.34 (12)	C11—C10—C9—O5	−174.93 (13)
O1—Co1—N1—C17	75.29 (12)	C15—C10—C9—O4	−170.39 (13)
O1—Co1—N1—C21	−108.72 (11)	C15—C10—C9—O5	8.8 (2)
O2—Co1—N1—C17	135.07 (12)	C9—C10—C11—C12	−174.61 (14)
O2—Co1—N1—C21	−48.93 (11)	C15—C10—C11—C12	1.7 (2)
O5—Co1—N1—C17	−21.65 (12)	C9—C10—C15—C14	174.66 (14)
O5—Co1—N1—C21	154.35 (11)	C11—C10—C15—C14	−1.7 (2)
O9—Co1—N1—C17	−129.79 (12)	C13—C12—C11—C10	0.8 (2)
O9—Co1—N1—C21	46.21 (12)	C11—C12—C13—O6	175.92 (14)
Co1—O1—C1—O2	−0.17 (14)	C11—C12—C13—C14	−3.3 (2)
Co1—O1—C1—C2	177.95 (12)	C15—C14—C13—O6	−175.95 (13)
Co1—O2—C1—O1	0.16 (14)	C15—C14—C13—C12	3.3 (2)
Co1—O2—C1—C2	−177.89 (13)	C13—C14—C15—C10	−0.8 (2)
C8—O3—C5—C4	−8.5 (2)	N1—C17—C18—C19	−1.6 (2)
C8—O3—C5—C6	170.10 (14)	C20—C19—C18—C17	2.6 (2)

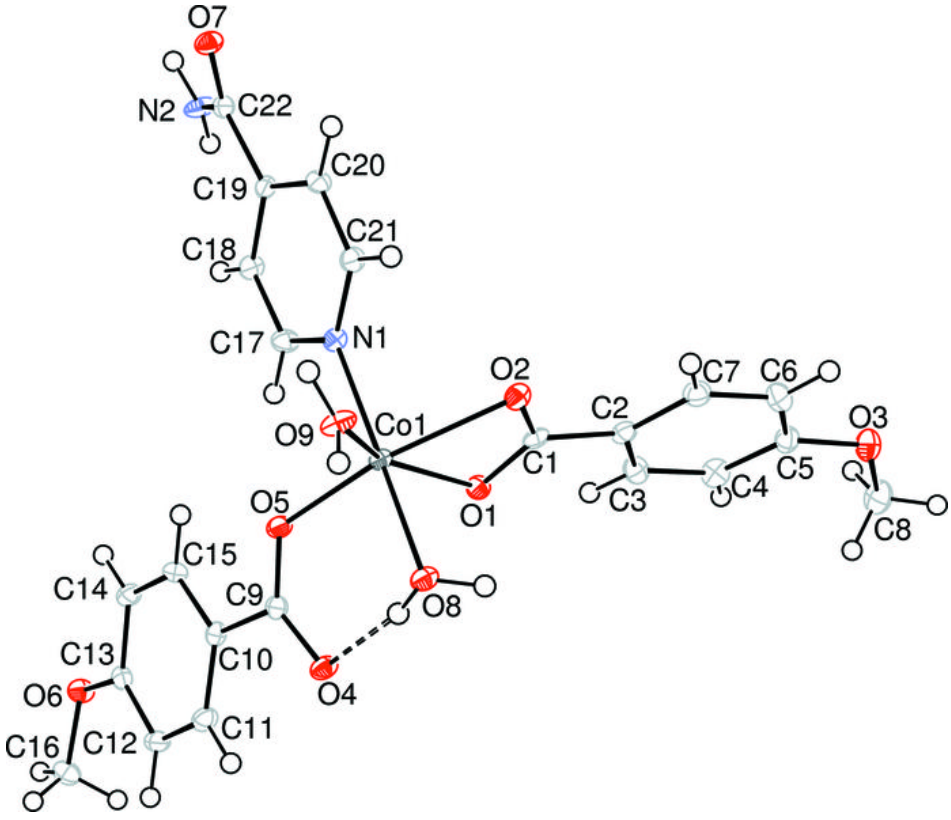
Co1—O5—C9—O4	19.3 (2)	C22—C19—C18—C17	−172.69 (13)
Co1—O5—C9—C10	−159.84 (9)	C18—C19—C20—C21	−1.3 (2)
C16—O6—C13—C12	5.3 (2)	C22—C19—C20—C21	174.22 (13)
C16—O6—C13—C14	−175.44 (13)	N1—C21—C20—C19	−1.2 (2)
Co1—N1—C17—C18	175.31 (11)	O7—C22—C19—C18	151.80 (15)
C21—N1—C17—C18	−0.8 (2)	N2—C22—C19—C18	−25.7 (2)
Co1—N1—C21—C20	−173.91 (11)	O7—C22—C19—C20	−23.5 (2)
C17—N1—C21—C20	2.3 (2)	N2—C22—C19—C20	158.99 (13)
C3—C2—C1—O2	−173.63 (14)		

Hydrogen-bond geometry (Å, °)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
N2—H2A···O2^{i}	0.79 (3)	2.11 (3)	2.877 (2)	164.0 (17)
N2—H2B···O1^{ii}	0.91 (3)	2.16 (3)	3.050 (2)	167 (2)
O8—H81···O4	0.83 (3)	1.84 (3)	2.6577 (17)	167 (3)
O8—H82···O7^{iii}	0.89 (2)	1.86 (3)	2.7427 (16)	172 (2)
O9—H91···O6^{iv}	0.786 (19)	2.078 (19)	2.8384 (16)	163 (2)
O9—H92···O4^{v}	0.91 (3)	1.72 (3)	2.6307 (18)	174.1 (15)
C8—H8A···O7^{vi}	0.96	2.53	3.466 (2)	166
C16—H16B···O4^{vii}	0.96	2.52	3.4752 (18)	171

Symmetry codes: (i) *x*+1, *y*, *z*; (ii) *x*+1, *y*+1, *z*; (iii) *x*−1, *y*−1, *z*; (iv) *x*−1, *y*+1, *z*; (v) *x*, *y*+1, *z*; (vi) −*x*+2, *y*−3/2, −*z*+2; (vii) −*x*+2, *y*−1/2, −*z*+1.

Fig. 1


O7
N2
C22
C20
C19
C21
C18
C17
N1
O2
C7
C6
O9
Co1
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O3
C1
C5
O5
O1
C3
C4
C8
C15
C14
C9
O8
C13
C10
O4
O6
C11
C16
C12

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(2*E*)-1-(2-Bromophenyl)-3-(4-methoxyphenyl)prop-2-en-1-one

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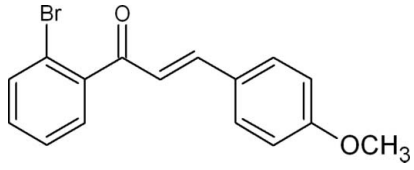
Key indicators: single-crystal X-ray study; T = 110 K; mean σ(C–C) = 0.006 Å; R factor = 0.034; wR factor = 0.091; data-to-parameter ratio = 9.5.

In the title compound, $C_{16}H_{13}BrO_2$, two benzene rings form a dihedral angle of 44.3 (9)°. In the crystal, weak intermolecular C—H···O hydrogen bonds link the molecules into chains propagating in [010]. The crystal packing also exhibits short Br···Br contacts of 3.4787 (8) Å. A comparison of the DFT-optimized gas-phase molecular geometry with that in the crystal structure revealed only small differences.

Related literature

For the radical quenching properties of included phenol groups, see: Dhar (1981). For related structures, see: Arai *et al.* (1994); Li *et al.* (1992); Patil *et al.* (2007); Shettigar *et al.* (2006). For standard bond lengths, see Allen *et al.* (1987). For density functional theory, see: Schmidt & Polik (2007); Hehre *et al.* (1986).



Experimental

Crystal data

$C_{16}H_{13}BrO_2$
M_r = 317.17
Monoclinic, $P2_1$
a = 12.7300 (8) Å
b = 4.0061 (3) Å
c = 13.0035 (6) Å
β = 100.671 (5)°
V = 651.68 (7) Å^3
Z = 2
Cu $K\alpha$ radiation
μ = 4.25 mm^{-1}
T = 110 K
0.48 × 0.41 × 0.28 mm

Data collection

Oxford Diffraction Xcalibur diffractometer with Ruby (Gemini Cu) detector
Absorption correction: multi-scan (*CrysAlis RED*; Oxford Diffraction, 2007)
T_{min} = 0.423, T_{max} = 1.000
2117 measured reflections
1641 independent reflections
1621 reflections with $I > 2\sigma(I)$
R_{int} = 0.018

Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.034
$wR(F^2)$ = 0.091
S = 1.07
1641 reflections
173 parameters
1 restraint
H-atom parameters constrained
$\Delta\rho_{max}$ = 0.71 e Å^{-3}
$\Delta\rho_{min}$ = −0.65 e Å^{-3}
Absolute structure: Flack (1983), 133 Friedel pairs
Flack parameter: 0.00 (3)

Table 1
Hydrogen-bond geometry (Å, °).

D—H···A	D—H	H···A	D···A	D—H···A
C12—H12A···O1^{i}	0.95	2.59	3.541 (5)	174

Symmetry code: (i) $-x+1, y-\frac{1}{2}, -z$.

Data collection: *CrysAlis PRO* (Oxford Diffraction, 2007); cell refinement: *CrysAlis PRO*; data reduction: *CrysAlis PRO*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *SHELXTL* (Sheldrick, 2008); software used to prepare material for publication: *SHELXTL*.

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Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: CV2728).

References

Allen, F. H., Kennard, O., Watson, D. G., Brammer, L., Orpen, A. G. & Taylor, R. (1987). *J. Chem. Soc. Perkin Trans. 2*, pp. S1–19.
Arai, H., Higashigaki, Y., Goto, M. & Yano, S. (1994). *Jpn. J. Appl. Phys.* **33**, 5755–5758.
Dhar, D. N. (1981). *The Chemistry of Chalcones and Related Compounds*. New York: John Wiley.
Flack, H. D. (1983). *Acta Cryst.* A**39**, 876–881.
Hehre, W. J., Random, L., Schleyer, P. R. & Pople, J. A. (1986). *Ab Initio Molecular Orbital Theory*. New York: John Wiley.
Li, Z.-D., Huang, L.-R., Su, G.-B. & Wang, H.-J. (1992). *Jiegou Huaxue*, **11**, 1–4.
Oxford Diffraction (2007). *CrysAlis PRO* and *CrysAlis RED*. Oxford Diffraction Ltd, Abingdon, England.
Patil, P. S., Chantrapromma, S., Fun, H.-K., Dharmaprakash, S. M. & Babu, H. B. R. (2007). *Acta Cryst.* E**63**, o2612.
Schmidt, J. R. & Polik, W. F. (2007). *WebMO Pro*. WebMO, LLC, Holland, MI, USA, available from http://www.webmo.net.
Sheldrick, G. M. (2008). *Acta Cryst.* A**64**, 112–122.
Shettigar, V., Rosli, M. M., Fun, H.-K., Razak, I. A., Patil, P. S. & Dharmaprakash, S. M. (2006). *Acta Cryst.* E**62**, o4128–o4129.

supplementary materials

Acta Cryst. (2010). E**66**, o1661 [**doi:10.1107/S160053681002218X**]

(2*E*)-1-(2-Bromophenyl)-3-(4-methoxyphenyl)prop-2-en-1-one

J. P. Jasinski, R. J. Butcher, K. Veena, B. Narayana and H. S. Yathirajan

Comment

Chalcones, or 1,3-diaryl-2-propen-1-ones, belong to the flavonoid family. Chemically they consist of open-chain flavonoids in which the two aromatic rings are joined by a three-carbon α,β-unsaturated carbonyl system. A vast number of naturally occurring chalcones are polyhydroxylated in the aryl rings. The radical quenching properties of the phenolic groups present in many chalcones have raised interest in using the compounds or chalcone rich plant extracts as drugs or food preservatives (Dhar, 1981). The crystal structures of some closely related chalcones, *viz*., 1-(4-bromophenyl)-3-(3-methoxy-phenyl)prop-2-en-1-one (Patil *et al.*, 2007); 4-bromo-4'-methoxy-chalcone (Li *et al.*, 1992), 4-bromo-4'-methoxychalcone (Arai *et al.*, 1994) and 1-(4-bromophenyl)-3-(4-methoxyphenyl)prop-2-en-1-one (Shettigar *et al.*, 2006) have been reported. Hence in continuation with the synthesis and crystal structure determination and also owing to the importance of these flavonoid analogs, this new bromo chalcone, (I), $C_{16}H_{13}BrO_2$, is synthesized and its crystal structure is reported.

The title compound, (I), $C_{16}H_{13}BrO_2$, is a chalcone with 4-methoxyphenyl and 2-bromophenyl rings bonded at opposite rings of a propene group (Fig. 1). The dihedral angle between mean planes of the *para*-methoxy and *ortho*-bromo substituted benzene rings is 44.3 (9)°. The angles between the mean plane of the prop-2-ene-1-one group and the mean planes of the 4-meyhoxyphenyl and 2-bromophenyl rings are 6.3 (1)° and 44.6(36°, respectively. Bond distances and angles are in normal ranges (Allen *et al.*, 1987). While no classical hydrogen bonds are present, a weak intermolecular C12—H12A···O1 interaction (Table 1) is observed which contributes to the stability of crystal packing.

A density functional theory (DFT) geometry optimization molecular orbital calculation (Schmidt & Polik, 2007) was performed on (I) with the B3LYP 6–31-G(*d*) basis set (Hehre *et al.*, 1986). The dihedral angle between mean planes of the *para*-methoxy and *ortho*-bromo substituted benzene rings becomes 45.98°, an increase of 1.59°. The angles between the mean plane of the prop-2-ene-1-one group and the mean planes of the 4-meyhoxyphenyl and 2-bromophenyl rings become 3.65° and 42.40°, changes of -2.65° and +0.74°, respectively. These observations suggest that the weak intermolecular C12—H12A···O1 interaction produces a small effect on crystal stability.

Experimental

A 50% KOH solution was added to a mixture of 2-bromo acetophenone (0.01 mol, 1.99 g) and 4-methoxy benzaldehyde (0.01 mol, 1.36 g) in 25 ml of ethanol (Fig. 2). The mixture was stirred for an hour at room temperature and the precipitate was collected by filtration and purified by recrystallization from ethanol. The single-crystal was grown from ethyl acetate by slow evaporation method and yield of the compound was 50% (m.p.336–338 K). Analytical data, composition (%): found (calculated): C: 60.52 (60.59%); H: 4.10 (4.13%).

Refinement

The H atoms were placed in geometrically idealized positions and constrained to ride on their parent atoms, with C–H distances = 0.95–0.98Å and with U_{iso}(H) = 1.17–1.47 U_{eq}(C).

Figures

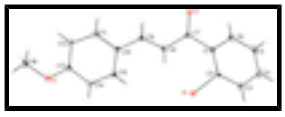


Fig. 1. Molecular structure of (I) showing the atom labeling scheme and 50% probability displacement ellipsoids.

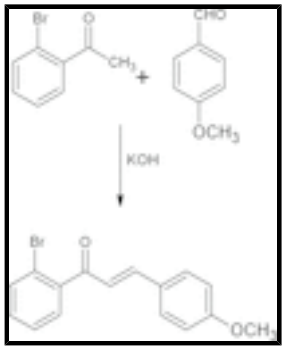


Fig. 2. Scheme for the synthesis of (I).

(2E)-1-(2-Bromophenyl)-3-(4-methoxyphenyl)prop-2-en-1-one

Crystal data

$C_{16}H_{13}BrO_2$	$F(000) = 320$
$M_r = 317.17$	$D_x = 1.616$ Mg m^{-3}
Monoclinic, $P2_1$	Cu $K\alpha$ radiation, $\lambda = 1.54184$ Å
Hall symbol: P 2yb	Cell parameters from 1981 reflections
$a = 12.7300$ (8) Å	$\theta = 4.5$–$74.1°$
$b = 4.0061$ (3) Å	$\mu = 4.25$ mm^{-1}
$c = 13.0035$ (6) Å	$T = 110$ K
$\beta = 100.671$ (5)°	Chunk, colourless
$V = 651.68$ (7) Å^3	0.48 × 0.41 × 0.28 mm
$Z = 2$	

Data collection

Oxford Diffraction Xcalibur diffractometer with Ruby (Gemini Cu) detector	1641 independent reflections
Radiation source: Enhance (Cu) X-ray Source	1621 reflections with $I > 2\sigma(I)$
graphite	$R_{int} = 0.018$
Detector resolution: 10.5081 pixels mm^{-1}	$\theta_{max} = 74.1°$, $\theta_{min} = 4.5°$
ω scans	$h = -9 \rightarrow 15$
Absorption correction: multi-scan (*CrysAlis RED*; Oxford Diffraction, 2007)	$k = -2 \rightarrow 4$
$T_{min} = 0.423$, $T_{max} = 1.000$	$l = -15 \rightarrow 16$
2117 measured reflections	

Refinement

Refinement on F^2	Secondary atom site location: difference Fourier map

Least-squares matrix: full	Hydrogen site location: inferred from neighbouring sites
$R[F^2 > 2\sigma(F^2)] = 0.034$	H-atom parameters constrained
$wR(F^2) = 0.091$	$w = 1/[\sigma^2(F_o^2) + (0.0718P)^2 + 0.5775P]$ where $P = (F_o^2 + 2F_c^2)/3$
$S = 1.07$	$(\Delta/\sigma)_{max} = 0.001$
1641 reflections	$\Delta\rho_{max} = 0.71$ e Å^{-3}
173 parameters	$\Delta\rho_{min} = -0.65$ e Å^{-3}
1 restraint	Absolute structure: Flack (1983), 133 Friedel pairs
Primary atom site location: structure-invariant direct methods	Flack parameter: 0.00 (3)

Special details

Experimental. IR data (KBr) ν cm^{-1}: 2998 cm^{-1}, 2937 cm^{-1}, 2839 cm^{-1} (C—H al.str), 3058 cm^{-1} (C—H ar. str) 1646 cm^{-1} (C=O), 1580 cm^{-1} (C=C); 1245 cm^{-1} (C—O—C).

Geometry. All e.s.d.'s (except the e.s.d. in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell e.s.d.'s are taken into account individually in the estimation of e.s.d.'s in distances, angles and torsion angles; correlations between e.s.d.'s in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell e.s.d.'s is used for estimating e.s.d.'s involving l.s. planes.

Refinement. Refinement of F^2 against ALL reflections. The weighted *R*-factor *wR* and goodness of fit *S* are based on F^2, conventional *R*-factors *R* are based on *F*, with *F* set to zero for negative F^2. The threshold expression of $F^2 > \sigma(F^2)$ is used only for calculating *R*-factors(gt) *etc*. and is not relevant to the choice of reflections for refinement. *R*-factors based on F^2 are statistically about twice as large as those based on *F*, and *R*- factors based on ALL data will be even larger.

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å^2)

	x	*y*	*z*	U_{iso}*/U_{eq}
Br	0.38764 (3)	0.18817 (18)	0.46303 (2)	0.01538 (15)
O1	0.2178 (2)	0.2427 (10)	0.1406 (2)	0.0211 (8)
O2	0.8860 (2)	0.2977 (9)	0.1659 (2)	0.0209 (7)
C1	0.2190 (3)	0.4727 (13)	0.3077 (3)	0.0149 (9)
C2	0.2577 (3)	0.4233 (12)	0.4142 (3)	0.0119 (8)
C3	0.2022 (3)	0.5312 (12)	0.4896 (3)	0.0166 (9)
H3A	0.2299	0.4917	0.5616	0.020*
C4	0.1060 (3)	0.6971 (19)	0.4599 (3)	0.0223 (8)
H4A	0.0679	0.7740	0.5116	0.027*
C5	0.0651 (3)	0.7513 (12)	0.3545 (3)	0.0211 (11)
H5A	−0.0008	0.8660	0.3342	0.025*
C6	0.1203 (3)	0.6385 (14)	0.2797 (3)	0.0187 (10)
H6A	0.0913	0.6732	0.2078	0.022*
C7	0.2730 (3)	0.3590 (12)	0.2195 (3)	0.0173 (9)
C8	0.3891 (3)	0.4058 (13)	0.2303 (3)	0.0160 (9)
H8A	0.4255	0.5526	0.2824	0.019*
C9	0.4441 (3)	0.2431 (12)	0.1673 (3)	0.0161 (10)
H9A	0.4037	0.1037	0.1154	0.019*

C10	0.5595 (3)	0.2564 (10)	0.1697 (3)	0.0145 (11)
C11	0.5999 (3)	0.1064 (11)	0.0878 (3)	0.0164 (10)
H11A	0.5519	−0.0064	0.0344	0.020*
C12	0.7083 (3)	0.1171 (11)	0.0822 (3)	0.0155 (10)
H12A	0.7334	0.0191	0.0248	0.019*
C13	0.7787 (3)	0.2733 (11)	0.1619 (3)	0.0156 (10)
C14	0.7411 (4)	0.4183 (13)	0.2470 (3)	0.0186 (9)
H14A	0.7897	0.5209	0.3022	0.022*
C15	0.6327 (3)	0.4102 (13)	0.2495 (3)	0.0175 (9)
H15A	0.6075	0.5107	0.3065	0.021*
C16	0.9272 (3)	0.1512 (18)	0.0810 (3)	0.0223 (11)
H16A	0.9121	−0.0888	0.0783	0.033*
H16B	1.0046	0.1870	0.0916	0.033*
H16C	0.8930	0.2553	0.0151	0.033*

Atomic displacement parameters (Å^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Br	0.0159 (2)	0.0153 (2)	0.0148 (2)	−0.0005 (2)	0.00224 (13)	0.00195 (19)
O1	0.0204 (13)	0.028 (2)	0.0151 (11)	−0.0044 (15)	0.0031 (10)	−0.0034 (14)
O2	0.0169 (14)	0.027 (2)	0.0207 (14)	−0.0012 (13)	0.0070 (12)	−0.0027 (13)
C1	0.0154 (18)	0.016 (2)	0.0154 (17)	−0.0033 (18)	0.0081 (15)	−0.0001 (17)
C2	0.0083 (16)	0.008 (2)	0.0179 (17)	0.0027 (16)	−0.0026 (13)	0.0032 (17)
C3	0.021 (2)	0.014 (2)	0.0160 (18)	−0.0060 (18)	0.0067 (15)	−0.0023 (16)
C4	0.0242 (18)	0.018 (2)	0.0292 (19)	−0.004 (3)	0.0173 (15)	−0.006 (3)
C5	0.0136 (17)	0.016 (3)	0.034 (2)	0.0014 (18)	0.0047 (16)	0.0002 (19)
C6	0.0165 (17)	0.016 (3)	0.0228 (17)	−0.003 (2)	0.0023 (14)	0.0024 (19)
C7	0.023 (2)	0.015 (2)	0.0152 (18)	−0.0028 (19)	0.0061 (16)	0.0040 (17)
C8	0.0176 (19)	0.015 (3)	0.0155 (17)	−0.0006 (18)	0.0036 (14)	0.0011 (17)
C9	0.0189 (17)	0.016 (3)	0.0131 (15)	−0.0011 (18)	0.0025 (13)	0.0027 (18)
C10	0.0197 (18)	0.014 (3)	0.0113 (15)	0.0016 (17)	0.0058 (14)	0.0018 (15)
C11	0.0208 (19)	0.015 (3)	0.0135 (16)	0.0001 (17)	0.0037 (14)	0.0000 (15)
C12	0.0200 (18)	0.015 (3)	0.0124 (15)	0.0016 (17)	0.0062 (14)	−0.0020 (15)
C13	0.0179 (18)	0.014 (3)	0.0159 (17)	0.0019 (16)	0.0068 (14)	0.0034 (16)
C14	0.024 (2)	0.019 (2)	0.0122 (16)	−0.001 (2)	0.0024 (15)	−0.0014 (18)
C15	0.022 (2)	0.020 (3)	0.0116 (16)	0.002 (2)	0.0071 (15)	0.0001 (18)
C16	0.0181 (17)	0.025 (3)	0.0261 (18)	0.000 (2)	0.0101 (14)	−0.004 (2)

Geometric parameters (Å, °)

Br—C2	1.907 (4)	C8—H8A	0.9500
O1—C7	1.224 (5)	C9—C10	1.464 (5)
O2—C13	1.361 (5)	C9—H9A	0.9500
O2—C16	1.433 (5)	C10—C11	1.401 (6)
C1—C2	1.396 (5)	C10—C15	1.403 (6)
C1—C6	1.408 (6)	C11—C12	1.396 (6)
C1—C7	1.512 (5)	C11—H11A	0.9500
C2—C3	1.380 (6)	C12—C13	1.387 (6)
C3—C4	1.384 (7)	C12—H12A	0.9500

C3—H3A	0.9500	C13—C14	1.410 (6)
C4—C5	1.390 (6)	C14—C15	1.387 (6)
C4—H4A	0.9500	C14—H14A	0.9500
C5—C6	1.379 (6)	C15—H15A	0.9500
C5—H5A	0.9500	C16—H16A	0.9800
C6—H6A	0.9500	C16—H16B	0.9800
C7—C8	1.471 (6)	C16—H16C	0.9800
C8—C9	1.341 (6)		
C13—O2—C16	116.7 (3)	C8—C9—H9A	116.4
C2—C1—C6	117.3 (4)	C10—C9—H9A	116.4
C2—C1—C7	125.7 (4)	C11—C10—C15	117.6 (4)
C6—C1—C7	117.1 (4)	C11—C10—C9	118.5 (4)
C3—C2—C1	121.9 (4)	C15—C10—C9	123.9 (4)
C3—C2—Br	116.4 (3)	C12—C11—C10	122.2 (4)
C1—C2—Br	121.7 (3)	C12—C11—H11A	118.9
C2—C3—C4	119.7 (4)	C10—C11—H11A	118.9
C2—C3—H3A	120.2	C13—C12—C11	118.9 (4)
C4—C3—H3A	120.2	C13—C12—H12A	120.6
C3—C4—C5	120.1 (4)	C11—C12—H12A	120.6
C3—C4—H4A	120.0	O2—C13—C12	124.5 (4)
C5—C4—H4A	120.0	O2—C13—C14	115.1 (4)
C6—C5—C4	119.9 (4)	C12—C13—C14	120.4 (4)
C6—C5—H5A	120.1	C15—C14—C13	119.5 (4)
C4—C5—H5A	120.1	C15—C14—H14A	120.2
C5—C6—C1	121.3 (4)	C13—C14—H14A	120.2
C5—C6—H6A	119.4	C14—C15—C10	121.3 (4)
C1—C6—H6A	119.4	C14—C15—H15A	119.3
O1—C7—C8	122.6 (4)	C10—C15—H15A	119.3
O1—C7—C1	118.7 (4)	O2—C16—H16A	109.5
C8—C7—C1	118.6 (4)	O2—C16—H16B	109.5
C9—C8—C7	120.5 (4)	H16A—C16—H16B	109.5
C9—C8—H8A	119.7	O2—C16—H16C	109.5
C7—C8—H8A	119.7	H16A—C16—H16C	109.5
C8—C9—C10	127.2 (4)	H16B—C16—H16C	109.5
C6—C1—C2—C3	0.1 (7)	C1—C7—C8—C9	164.4 (4)
C7—C1—C2—C3	−179.0 (4)	C7—C8—C9—C10	−178.4 (4)
C6—C1—C2—Br	177.7 (4)	C8—C9—C10—C11	−170.9 (4)
C7—C1—C2—Br	−1.3 (7)	C8—C9—C10—C15	9.4 (7)
C1—C2—C3—C4	−0.8 (7)	C15—C10—C11—C12	−2.4 (6)
Br—C2—C3—C4	−178.6 (4)	C9—C10—C11—C12	177.9 (4)
C2—C3—C4—C5	0.7 (8)	C10—C11—C12—C13	1.9 (6)
C3—C4—C5—C6	0.2 (9)	C16—O2—C13—C12	0.2 (7)
C4—C5—C6—C1	−1.1 (8)	C16—O2—C13—C14	179.6 (5)
C2—C1—C6—C5	0.9 (7)	C11—C12—C13—O2	179.4 (4)
C7—C1—C6—C5	180.0 (4)	C11—C12—C13—C14	0.0 (6)
C2—C1—C7—O1	139.4 (5)	O2—C13—C14—C15	179.2 (4)
C6—C1—C7—O1	−39.6 (7)	C12—C13—C14—C15	−1.4 (7)
C2—C1—C7—C8	−43.2 (7)	C13—C14—C15—C10	0.8 (7)

C6—C1—C7—C8	137.8 (5)	C11—C10—C15—C14	1.0 (7)
O1—C7—C8—C9	−18.2 (7)	C9—C10—C15—C14	−179.3 (4)

Hydrogen-bond geometry (Å, °)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
C12—H12A···O1^{i}	0.95	2.59	3.541 (5)	174.

Symmetry codes: (i) −*x*+1, *y*−1/2, −*z*.

Fig. 1

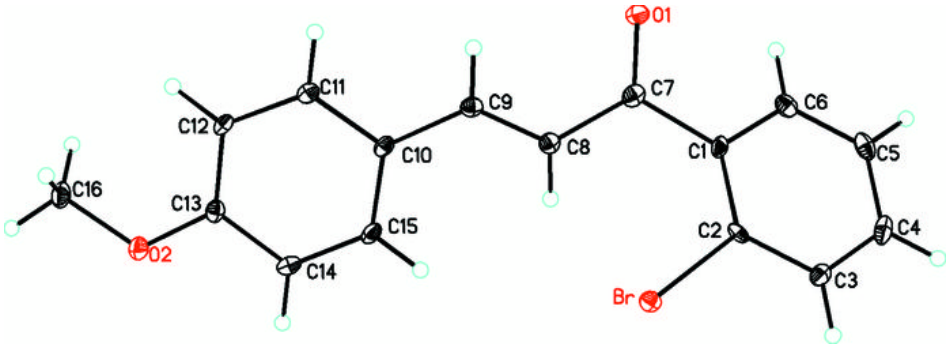
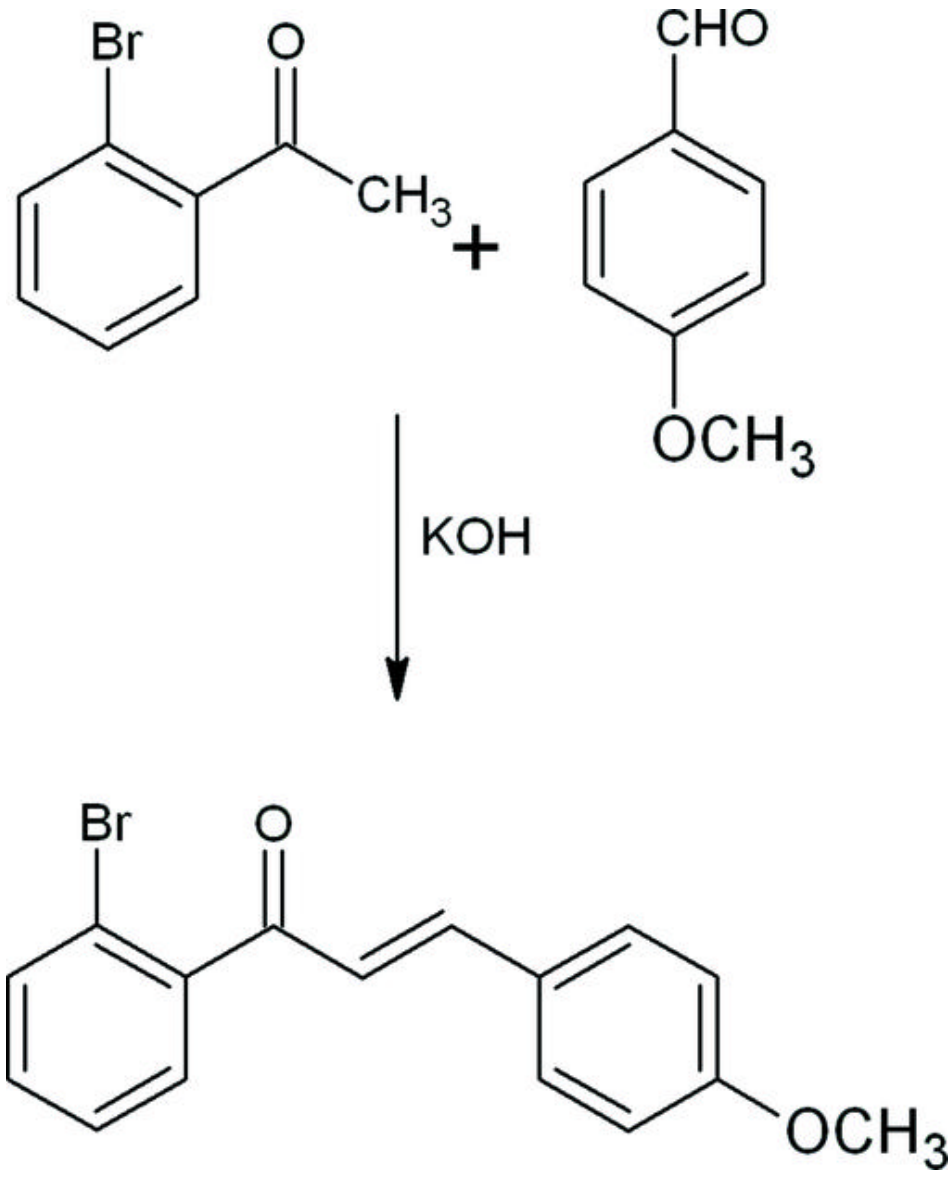


Fig. 2



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Di-μ-nicotinamide-κ^2O:N^1;κ^2N^1:O-bis[aquabis(4-methoxybenzoato-κO)-copper(II)]

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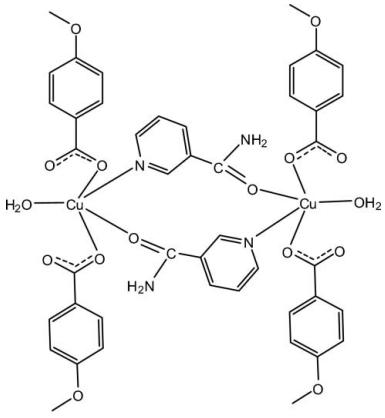
Key indicators: single-crystal X-ray study; T = 100 K; mean σ(C–C) = 0.002 Å; R factor = 0.026; wR factor = 0.072; data-to-parameter ratio = 17.1.

The asymmetric unit of the centrosymmetric dinuclear title compound, $[Cu_2(C_8H_7O_3)_4(C_6H_6N_2O)_2(H_2O)_2]$, contains one half of the complex molecule. Each Cu^{II} atom is five-coordinated by one N atom from one bridging nicotinamide ligand and one O atom from another symmetry-related bridging nicotinamide ligand, two O atoms from two 4-methoxybenzoate ligands, and one water molecule, forming a distorted square-pyramidal geometry. Intermolecular O—H···O and N—H···O hydrogen bonds link the molecules into layers parallel to $(\bar{1}01)$. π–π interactions, indicated by short intermolecular distances of 3.801 (1) Å between the centroids of the benzene rings and 3.653 (1) Å between the centroids of the pyridine rings, further stabilize the structure.

Related literature

For related structures, see: Hökelek & Necefoğlu (1996); Hökelek *et al.* (2009*a*,*b*,*c*,*d*).



Experimental

Crystal data

$[Cu_2(C_8H_7O_3)_4(C_6H_6N_2O)_2(H_2O)_2]$
M_r = 1011.93
Monoclinic, $P2_1/n$
a = 14.1707 (3) Å
b = 8.4319 (2) Å
c = 18.0225 (3) Å
β = 95.847 (2)°
V = 2142.23 (8) Å^3
Z = 2
Mo $K\alpha$ radiation
μ = 1.07 mm^{-1}
T = 100 K
0.37 × 0.37 × 0.23 mm

Data collection

Bruker Kappa APEXII CCD area-detector diffractometer
Absorption correction: multi-scan (*SADABS*; Bruker, 2005)
T_{min} = 0.678, T_{max} = 0.781
20329 measured reflections
5403 independent reflections
4813 reflections with $I > 2\sigma(I)$
R_{int} = 0.021

Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.026
$wR(F^2)$ = 0.072
S = 1.05
5403 reflections
316 parameters
H atoms treated by a mixture of independent and constrained refinement
$\Delta\rho_{max}$ = 0.47 e Å^{-3}
$\Delta\rho_{min}$ = −0.29 e Å^{-3}

Table 1
Hydrogen-bond geometry (Å, °).

D—H···A	D—H	H···A	D···A	D—H···A
N2—H2A···O1^{i}	0.86 (2)	2.03 (2)	2.8407 (18)	158 (2)
N2—H2B···O4^{ii}	0.83 (2)	2.29 (2)	2.9897 (17)	141.4 (18)
O8—H81···O1^{iii}	0.79 (3)	1.97 (3)	2.7236 (15)	159 (3)
O8—H82···O4^{iii}	0.825 (18)	1.803 (18)	2.6052 (16)	163.9 (18)

Symmetry codes: (i) $-x+2, -y+1, -z+1$; (ii) $x+\frac{1}{2}, -y+\frac{1}{2}, z+\frac{1}{2}$; (iii) $-x+\frac{3}{2}, y-\frac{1}{2}, -z+\frac{1}{2}$.

Data collection: *APEX2* (Bruker, 2007); cell refinement: *SAINT* (Bruker, 2007); data reduction: *SAINT*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *Mercury* (Macrae *et al.*, 2006); software used to prepare material for publication: *WinGX* (Farrugia, 1999) and *PLATON* (Spek, 2009).

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Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: CV2731).

References

Bruker (2005). *SADABS*. Bruker AXS Inc., Madison, Wisconsin, USA.
Bruker (2007). *APEX2* and *SAINT*. Bruker AXS Inc., Madison, Wisconsin, USA.
Farrugia, L. J. (1999). *J. Appl. Cryst.* **32**, 837–838.
Hökelek, T., Dal, H., Tercan, B., Aybirdi, Ö. & Necefoğlu, H. (2009*a*). *Acta Cryst.* E**65**, m627–m628.
Hökelek, T., Dal, H., Tercan, B., Aybirdi, Ö. & Necefoğlu, H. (2009*b*). *Acta Cryst.* E**65**, m1037–m1038.
Hökelek, T., Dal, H., Tercan, B., Aybirdi, Ö. & Necefoğlu, H. (2009*c*). *Acta Cryst.* E**65**, m1365–m1366.
Hökelek, T. & Necefoğlu, H. (1996). *Acta Cryst.* C**52**, 1128–1131.

Hökelek, T., Yılmaz, F., Tercan, B., Gürgen, F. & Necefoğlu, H. (2009*d*). *Acta Cryst.* E**65**, m1416–m1417.
Macrae, C. F., Edgington, P. R., McCabe, P., Pidcock, E., Shields, G. P., Taylor, R., Towler, M. & van de Streek, J. (2006). *J. Appl. Cryst.* **39**, 453–457.
Sheldrick, G. M. (2008). *Acta Cryst.* A**64**, 112–122.
Spek, A. L. (2009). *Acta Cryst.* D**65**, 148–155.

supplementary materials

Acta Cryst. (2010). E**66**, m807-m808 [**doi:10.1107/S1600536810022415**]

Di-μ-nicotinamide-κ^2O:N^1;κ^2N^1:O-bis[aquabis(4-methoxybenzoato-κO)copper(II)]

T. Hökelek, Y. Süzen, B. Tercan, E. Tenlik and H. Necefoglu

Comment

As a part of our ongoing study of transition metal complexes of nicotinamide (Hökelek & Necefoğlu, 1996; Hökelek *et al.*, 2009*a, b, c, d*), herein we report the crystal structure of the title dinuclear complex.

The title compound, (I), consists of dimeric units located around a crystallographic symmetry centre and made up of two Cu cations, four 4-methoxybenzoate (MB) anions, two nicotinamide (NA) ligands and two water molecules (Fig. 1). Both of the Cu^{II} centres are five-coordinated with distorted square-pyramidal environments, and the two monomeric units are bridged through the two nicotinamide (NA) ligands about an inversion center. The Cu1···Cu1^{i} (symmetry code: (i) 2 - *x*, -*y*, 1 - *z*) distance is 7.1368 (3) Å. The average Cu—O bond length is 2.0626 (10) Å, and the Cu atom is displaced out of the least-squares planes of the carboxylate groups (O1/C1/O2) and (O4/C9/O5) by 0.0015 (2) and -0.2589 (2) Å, respectively.

The dihedral angles between the planar carboxylate groups and the adjacent benzene rings A (C2—C7) and B (C10—C15) are 1.85 (5) and 10.16 (7) °, respectively, while those between rings A, B and C (N1/C17—C21) are A/B = 28.50 (4), A/C = 81.64 (4), B/C = 58.50 (4) °.

In the crystal structure, intermolecular O—H···O and N—H···O hydrogen bonds (Table 1) link the molecules into layers. The π–π contacts between the benzene rings and between the pyridine rings, *Cg*2—*Cg*2^{i} and *Cg*3—*Cg*3^{ii} [symmetry codes: (i) 2 - *x*, 2 - *y*, -*z*; (ii) 1 - *x*, 2 - *y*, -*z*, where *Cg*2 and *Cg*3 are the centroids of the rings B (C10—C15) and C (N1/C17—C21)] may further stabilize the structure, with centroid-centroid distances of 3.801 (1) and 3.653 (1) Å, respectively.

Experimental

The title compound was prepared by the reaction of $CuSO_4.5H_2O$ (2.50 g, 10 mmol) in H_2O (50 ml) and NA (2.44 g, 20 mmol) in H_2O (50 ml) with sodium 4-methoxybenzoate (3.48 g, 20 mmol) in H_2O (100 ml). The mixture was filtered and set aside to crystallize at ambient temperature for one week, giving blue single crystals.

Refinement

Atoms H81, H82 (for H_2O) and H2A, H2B (for NH_2) were located in difference Fourier maps and refined isotropically. The remaining H atoms were positioned geometrically with C—H = 0.93 and 0.96 Å for aromatic and methyl H atoms, respectively, and constrained to ride on their parent atoms, with U_{iso}(H) = xU_{eq}(C), where x = 1.5 for methyl H and x = 1.2 for aromatic H atoms.

Figures

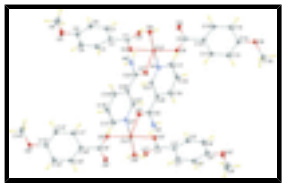


Fig. 1. The molecular structure of the title molecule with the atom-numbering scheme. Displacement ellipsoids are drawn at the 50% probability level [symmetry code: (') 2 - *x*, -*y*, 1 - *z*].

Di-μ-nicotinamide-κ^2*O*:*N*^{1};κ^2*N*^{1}:*O*- bis[aquabis(4-methoxybenzoato-κ*O*)copper(II)]

Crystal data

$[Cu_2(C_8H_7O_3)_4(C_6H_6N_2O)_2(H_2O)_2]$	$F(000) = 1044$
$M_r = 1011.93$	$D_x = 1.569$ Mg m^{-3}
Monoclinic, $P2_1/n$	Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å
Hall symbol: -P 2yn	Cell parameters from 9977 reflections
$a = 14.1707$ (3) Å	$\theta = 2.7–28.5°$
$b = 8.4319$ (2) Å	$\mu = 1.07$ mm^{-1}
$c = 18.0225$ (3) Å	$T = 100$ K
$\beta = 95.847$ (2)°	Block, blue
$V = 2142.23$ (8) Å^3	0.37 × 0.37 × 0.23 mm
$Z = 2$	

Data collection

Bruker Kappa APEXII CCD area-detector diffractometer	5403 independent reflections
Radiation source: fine-focus sealed tube	4813 reflections with $I > 2\sigma(I)$
graphite	$R_{int} = 0.021$
φ and ω scans	$\theta_{max} = 28.5°$, $\theta_{min} = 1.7°$
Absorption correction: multi-scan (*SADABS*; Bruker, 2005)	$h = -18\rightarrow18$
$T_{min} = 0.678$, $T_{max} = 0.781$	$k = -10\rightarrow11$
20329 measured reflections	$l = -24\rightarrow24$

Refinement

Refinement on F^2	Primary atom site location: structure-invariant direct methods
Least-squares matrix: full	Secondary atom site location: difference Fourier map
$R[F^2 > 2\sigma(F^2)] = 0.026$	Hydrogen site location: inferred from neighbouring sites
$wR(F^2) = 0.072$	H atoms treated by a mixture of independent and constrained refinement
$S = 1.05$	$w = 1/[\sigma^2(F_o^2) + (0.0384P)^2 + 1.1134P]$ where $P = (F_o^2 + 2F_c^2)/3$
5403 reflections	$(\Delta/\sigma)_{max} = 0.001$

316 parameters

0 restraints

$\Delta\rho_{max} = 0.47$ e Å^{-3}

$\Delta\rho_{min} = -0.29$ e Å^{-3}

Special details

Geometry. All e.s.d.'s (except the e.s.d. in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell e.s.d.'s are taken into account individually in the estimation of e.s.d.'s in distances, angles and torsion angles; correlations between e.s.d.'s in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell e.s.d.'s is used for estimating e.s.d.'s involving l.s. planes.

Refinement. Refinement of F^2 against ALL reflections. The weighted *R*-factor *wR* and goodness of fit *S* are based on F^2, conventional *R*-factors *R* are based on *F*, with *F* set to zero for negative F^2. The threshold expression of $F^2 > \sigma(F^2)$ is used only for calculating *R*-factors(gt) *etc*. and is not relevant to the choice of reflections for refinement. *R*-factors based on F^2 are statistically about twice as large as those based on *F*, and *R*- factors based on ALL data will be even larger.

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å^2)

	x	*y*	*z*	U_{iso}*/U_{eq}
Cu1	0.832076 (11)	0.152692 (19)	0.356751 (8)	0.00986 (6)
O1	0.89942 (7)	0.40998 (13)	0.27780 (5)	0.0155 (2)
O2	0.94951 (7)	0.16598 (12)	0.30792 (5)	0.01368 (19)
O3	1.28693 (8)	0.39532 (15)	0.12796 (7)	0.0251 (2)
O4	0.66614 (8)	0.34649 (13)	0.32513 (6)	0.0181 (2)
O5	0.71138 (7)	0.14541 (12)	0.40038 (5)	0.01317 (19)
O6	0.32798 (7)	0.34252 (13)	0.52920 (6)	0.0170 (2)
O7	1.10015 (7)	0.07805 (12)	0.58526 (5)	0.0153 (2)
O8	0.77027 (8)	0.04960 (14)	0.26669 (6)	0.0167 (2)
H81	0.7200 (18)	0.008 (3)	0.2652 (13)	0.047 (7)*
H82	0.7977 (13)	−0.001 (2)	0.2360 (10)	0.017 (4)*
N1	0.88593 (8)	0.27822 (14)	0.44653 (6)	0.0118 (2)
N2	1.09767 (9)	0.27022 (17)	0.67244 (7)	0.0171 (3)
H2A	1.0823 (15)	0.365 (3)	0.6840 (12)	0.029 (5)*
H2B	1.1375 (14)	0.224 (2)	0.7019 (11)	0.022 (5)*
C1	0.95896 (9)	0.30016 (17)	0.27686 (7)	0.0125 (3)
C2	1.04648 (9)	0.32640 (17)	0.23831 (7)	0.0125 (3)
C3	1.11660 (10)	0.20966 (18)	0.23693 (8)	0.0152 (3)
H3	1.1096	0.1132	0.2608	0.018*
C4	1.19625 (10)	0.23685 (19)	0.20030 (8)	0.0187 (3)
H4	1.2429	0.1594	0.2003	0.022*
C5	1.20666 (10)	0.38071 (19)	0.16333 (8)	0.0173 (3)
C6	1.13758 (10)	0.49779 (18)	0.16412 (8)	0.0166 (3)
H6	1.1442	0.5936	0.1396	0.020*
C7	1.05849 (10)	0.46977 (18)	0.20197 (7)	0.0153 (3)
H7	1.0126	0.5484	0.2031	0.018*
C8	1.29541 (12)	0.5321 (2)	0.08255 (9)	0.0254 (3)
H8A	1.3544	0.5279	0.0607	0.038*
H8B	1.2938	0.6258	0.1126	0.038*
H8C	1.2437	0.5346	0.0437	0.038*

C9	0.65288 (9)	0.25480 (17)	0.37733 (7)	0.0123 (3)
C10	0.56660 (9)	0.27358 (16)	0.41748 (7)	0.0121 (2)
C11	0.55839 (10)	0.19292 (18)	0.48349 (8)	0.0148 (3)
H11	0.6064	0.1240	0.5019	0.018*
C12	0.47980 (10)	0.21312 (18)	0.52268 (8)	0.0159 (3)
H12	0.4753	0.1586	0.5670	0.019*
C13	0.40798 (10)	0.31546 (17)	0.49503 (8)	0.0134 (3)
C14	0.41505 (10)	0.39815 (18)	0.42856 (8)	0.0156 (3)
H14	0.3669	0.4669	0.4102	0.019*
C15	0.49373 (10)	0.37730 (17)	0.39027 (8)	0.0142 (3)
H15	0.4985	0.4324	0.3461	0.017*
C16	0.32415 (10)	0.26991 (19)	0.60087 (8)	0.0190 (3)
H16A	0.2661	0.2992	0.6205	0.028*
H16B	0.3771	0.3052	0.6343	0.028*
H16C	0.3267	0.1567	0.5958	0.028*
C17	0.83872 (10)	0.40389 (17)	0.47003 (8)	0.0152 (3)
H17	0.7874	0.4437	0.4394	0.018*
C18	0.86367 (10)	0.47614 (18)	0.53812 (8)	0.0169 (3)
H18	0.8306	0.5645	0.5524	0.020*
C19	0.93883 (10)	0.41469 (17)	0.58490 (8)	0.0153 (3)
H19	0.9555	0.4591	0.6316	0.018*
C20	0.98863 (9)	0.28598 (16)	0.56074 (7)	0.0114 (2)
C21	0.96065 (9)	0.22322 (16)	0.49060 (7)	0.0117 (2)
H21	0.9953	0.1395	0.4735	0.014*
C22	1.06782 (9)	0.20324 (17)	0.60760 (7)	0.0120 (2)

Atomic displacement parameters (Å^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Cu1	0.00880 (8)	0.01102 (9)	0.00963 (8)	0.00027 (6)	0.00037 (6)	−0.00144 (6)
O1	0.0127 (4)	0.0164 (5)	0.0175 (5)	0.0029 (4)	0.0014 (4)	−0.0019 (4)
O2	0.0120 (4)	0.0141 (5)	0.0153 (4)	−0.0002 (4)	0.0033 (4)	−0.0005 (4)
O3	0.0202 (5)	0.0259 (6)	0.0315 (6)	−0.0008 (5)	0.0141 (5)	0.0034 (5)
O4	0.0195 (5)	0.0198 (6)	0.0158 (5)	−0.0003 (4)	0.0055 (4)	0.0042 (4)
O5	0.0114 (4)	0.0150 (5)	0.0133 (4)	0.0011 (4)	0.0024 (3)	−0.0006 (4)
O6	0.0133 (5)	0.0200 (5)	0.0183 (5)	0.0049 (4)	0.0049 (4)	0.0030 (4)
O7	0.0165 (5)	0.0120 (5)	0.0168 (5)	0.0028 (4)	−0.0017 (4)	−0.0015 (4)
O8	0.0116 (5)	0.0229 (6)	0.0154 (5)	−0.0010 (4)	0.0013 (4)	−0.0084 (4)
N1	0.0112 (5)	0.0113 (6)	0.0128 (5)	0.0002 (4)	0.0002 (4)	−0.0008 (4)
N2	0.0184 (6)	0.0162 (7)	0.0155 (6)	0.0042 (5)	−0.0048 (5)	−0.0034 (5)
C1	0.0118 (6)	0.0150 (6)	0.0102 (5)	−0.0009 (5)	−0.0017 (5)	−0.0029 (5)
C2	0.0113 (6)	0.0147 (7)	0.0113 (6)	−0.0004 (5)	0.0001 (5)	−0.0018 (5)
C3	0.0154 (6)	0.0133 (7)	0.0171 (6)	0.0007 (5)	0.0025 (5)	0.0006 (5)
C4	0.0154 (6)	0.0186 (7)	0.0224 (7)	0.0039 (6)	0.0042 (5)	0.0005 (6)
C5	0.0139 (6)	0.0213 (7)	0.0172 (6)	−0.0031 (6)	0.0046 (5)	−0.0014 (6)
C6	0.0191 (7)	0.0153 (7)	0.0155 (6)	−0.0014 (5)	0.0025 (5)	0.0012 (5)
C7	0.0156 (6)	0.0156 (7)	0.0147 (6)	0.0013 (5)	0.0010 (5)	−0.0008 (5)
C8	0.0256 (8)	0.0279 (9)	0.0243 (7)	−0.0082 (7)	0.0101 (6)	0.0011 (7)

C9	0.0124 (6)	0.0130 (6)	0.0112 (6)	−0.0021 (5)	0.0001 (5)	−0.0027 (5)
C10	0.0117 (6)	0.0118 (6)	0.0128 (6)	−0.0004 (5)	0.0009 (5)	−0.0007 (5)
C11	0.0139 (6)	0.0156 (7)	0.0149 (6)	0.0048 (5)	0.0021 (5)	0.0026 (5)
C12	0.0175 (7)	0.0165 (7)	0.0141 (6)	0.0036 (5)	0.0037 (5)	0.0038 (5)
C13	0.0117 (6)	0.0136 (7)	0.0153 (6)	0.0005 (5)	0.0028 (5)	−0.0015 (5)
C14	0.0140 (6)	0.0141 (7)	0.0184 (6)	0.0033 (5)	−0.0005 (5)	0.0024 (5)
C15	0.0149 (6)	0.0137 (7)	0.0138 (6)	0.0005 (5)	0.0002 (5)	0.0031 (5)
C16	0.0178 (7)	0.0209 (8)	0.0194 (7)	0.0025 (6)	0.0079 (5)	0.0020 (6)
C17	0.0131 (6)	0.0132 (7)	0.0186 (6)	0.0019 (5)	−0.0024 (5)	−0.0015 (5)
C18	0.0151 (6)	0.0146 (7)	0.0205 (7)	0.0045 (5)	−0.0013 (5)	−0.0051 (5)
C19	0.0146 (6)	0.0155 (7)	0.0153 (6)	0.0000 (5)	−0.0011 (5)	−0.0053 (5)
C20	0.0100 (6)	0.0110 (6)	0.0132 (6)	−0.0010 (5)	0.0006 (5)	0.0001 (5)
C21	0.0106 (6)	0.0111 (6)	0.0136 (6)	−0.0005 (5)	0.0019 (5)	−0.0002 (5)
C22	0.0108 (6)	0.0121 (6)	0.0131 (6)	−0.0005 (5)	0.0006 (5)	0.0018 (5)

Geometric parameters (Å, °)

Cu1—O2	1.9634 (10)	C6—H6	0.9300
Cu1—O5	1.9548 (10)	C7—H7	0.9300
Cu1—O7^{i}	2.3655 (10)	C8—H8A	0.9600
Cu1—O8	1.9667 (10)	C8—H8B	0.9600
Cu1—N1	2.0171 (11)	C8—H8C	0.9600
O1—C1	1.2540 (17)	C9—C10	1.4912 (18)
O2—C1	1.2754 (17)	C10—C15	1.4030 (19)
O3—C8	1.426 (2)	C11—C10	1.3856 (19)
O4—C9	1.2466 (17)	C11—C12	1.3886 (19)
O5—C9	1.2808 (17)	C11—H11	0.9300
O6—C13	1.3634 (17)	C12—C13	1.3876 (19)
O6—C16	1.4355 (17)	C12—H12	0.9300
O7—Cu1^{i}	2.3655 (10)	C13—C14	1.399 (2)
O8—H81	0.79 (3)	C14—C15	1.381 (2)
O8—H82	0.83 (2)	C14—H14	0.9300
N1—C17	1.3444 (18)	C15—H15	0.9300
N1—C21	1.3401 (17)	C16—H16A	0.9600
N2—C22	1.3278 (18)	C16—H16B	0.9600
N2—H2A	0.86 (2)	C16—H16C	0.9600
N2—H2B	0.83 (2)	C17—H17	0.9300
C1—C2	1.4985 (19)	C18—C17	1.3833 (19)
C2—C7	1.394 (2)	C18—C19	1.3895 (19)
C3—C2	1.4007 (19)	C18—H18	0.9300
C3—C4	1.383 (2)	C19—H19	0.9300
C3—H3	0.9300	C20—C19	1.3886 (19)
C4—H4	0.9300	C20—C21	1.3903 (18)
C5—O3	1.3650 (17)	C21—H21	0.9300
C5—C4	1.399 (2)	C22—O7	1.2345 (17)
C5—C6	1.391 (2)	C22—C20	1.5053 (18)
C6—C7	1.390 (2)		
O2—Cu1—O7^{i}	85.44 (4)	H8A—C8—H8B	109.5

O2—Cu1—O8	88.96 (4)	H8A—C8—H8C	109.5
O2—Cu1—N1	93.49 (4)	H8B—C8—H8C	109.5
O5—Cu1—O2	176.73 (4)	O4—C9—O5	123.30 (13)
O5—Cu1—O7^{i}	97.41 (4)	O4—C9—C10	119.63 (12)
O5—Cu1—O8	89.07 (4)	O5—C9—C10	117.05 (12)
O5—Cu1—N1	88.22 (4)	C11—C10—C9	120.61 (12)
O8—Cu1—O7^{i}	97.34 (4)	C11—C10—C15	118.88 (13)
O8—Cu1—N1	173.84 (5)	C15—C10—C9	120.48 (12)
N1—Cu1—O7^{i}	88.50 (4)	C10—C11—C12	121.22 (13)
C1—O2—Cu1	112.27 (9)	C10—C11—H11	119.4
C5—O3—C8	117.64 (13)	C12—C11—H11	119.4
C9—O5—Cu1	114.26 (9)	C11—C12—H12	120.3
C13—O6—C16	116.39 (11)	C13—C12—C11	119.38 (13)
C22—O7—Cu1^{i}	134.96 (9)	C13—C12—H12	120.3
Cu1—O8—H82	125.4 (12)	O6—C13—C12	123.72 (13)
Cu1—O8—H81	123.2 (18)	O6—C13—C14	116.04 (12)
H82—O8—H81	103 (2)	C12—C13—C14	120.24 (13)
C17—N1—Cu1	120.44 (9)	C13—C14—H14	120.1
C21—N1—Cu1	120.36 (9)	C15—C14—C13	119.77 (13)
C21—N1—C17	118.32 (12)	C15—C14—H14	120.1
C22—N2—H2A	122.8 (14)	C10—C15—H15	119.7
C22—N2—H2B	120.0 (14)	C14—C15—C10	120.51 (13)
H2B—N2—H2A	116.8 (19)	C14—C15—H15	119.7
O1—C1—O2	123.25 (13)	O6—C16—H16A	109.5
O1—C1—C2	119.15 (13)	O6—C16—H16B	109.5
O2—C1—C2	117.60 (12)	O6—C16—H16C	109.5
C3—C2—C1	121.78 (13)	H16A—C16—H16B	109.5
C7—C2—C1	119.50 (12)	H16A—C16—H16C	109.5
C7—C2—C3	118.72 (13)	H16B—C16—H16C	109.5
C2—C3—H3	119.8	N1—C17—C18	122.43 (12)
C4—C3—C2	120.44 (14)	N1—C17—H17	118.8
C4—C3—H3	119.8	C18—C17—H17	118.8
C3—C4—C5	120.11 (14)	C17—C18—C19	119.00 (13)
C3—C4—H4	119.9	C17—C18—H18	120.5
C5—C4—H4	119.9	C19—C18—H18	120.5
O3—C5—C4	115.72 (14)	C18—C19—H19	120.5
O3—C5—C6	124.15 (14)	C20—C19—C18	118.94 (12)
C6—C5—C4	120.13 (13)	C20—C19—H19	120.5
C5—C6—H6	120.4	C19—C20—C21	118.40 (12)
C7—C6—C5	119.18 (14)	C19—C20—C22	124.05 (12)
C7—C6—H6	120.4	C21—C20—C22	117.45 (12)
C2—C7—H7	119.3	N1—C21—C20	122.83 (13)
C6—C7—C2	121.41 (13)	N1—C21—H21	118.6
C6—C7—H7	119.3	C20—C21—H21	118.6
O3—C8—H8A	109.5	O7—C22—N2	123.72 (13)
O3—C8—H8B	109.5	O7—C22—C20	119.57 (12)
O3—C8—H8C	109.5	N2—C22—C20	116.69 (12)
O7^{i}—Cu1—O2—C1	−166.69 (9)	C6—C5—O3—C8	−6.9 (2)

O8—Cu1—O2—C1	95.87 (9)	O3—C5—C4—C3	−179.07 (13)
N1—Cu1—O2—C1	−78.48 (9)	C6—C5—C4—C3	0.9 (2)
O7^{i}—Cu1—O5—C9	−177.06 (9)	O3—C5—C6—C7	179.92 (13)
O8—Cu1—O5—C9	−79.78 (9)	C4—C5—C6—C7	0.0 (2)
N1—Cu1—O5—C9	94.69 (9)	C5—C6—C7—C2	−0.8 (2)
O2—Cu1—N1—C17	128.61 (11)	O4—C9—C10—C11	−168.45 (13)
O2—Cu1—N1—C21	−62.33 (11)	O4—C9—C10—C15	9.4 (2)
O5—Cu1—N1—C17	−48.59 (11)	O5—C9—C10—C11	9.80 (19)
O5—Cu1—N1—C21	120.47 (11)	O5—C9—C10—C15	−172.30 (12)
O7^{i}—Cu1—N1—C17	−146.05 (11)	C9—C10—C15—C14	−178.15 (13)
O7^{i}—Cu1—N1—C21	23.01 (10)	C11—C10—C15—C14	−0.2 (2)
Cu1—O2—C1—O1	−0.05 (16)	C12—C11—C10—C9	177.95 (13)
Cu1—O2—C1—C2	179.28 (9)	C12—C11—C10—C15	0.0 (2)
Cu1—O5—C9—O4	8.36 (17)	C10—C11—C12—C13	0.3 (2)
Cu1—O5—C9—C10	−169.82 (9)	C11—C12—C13—O6	179.65 (13)
C16—O6—C13—C12	5.6 (2)	C11—C12—C13—C14	−0.4 (2)
C16—O6—C13—C14	−174.33 (13)	O6—C13—C14—C15	−179.84 (13)
Cu1—N1—C17—C18	168.29 (11)	C12—C13—C14—C15	0.2 (2)
C21—N1—C17—C18	−1.0 (2)	C13—C14—C15—C10	0.1 (2)
Cu1—N1—C21—C20	−166.33 (10)	C19—C18—C17—N1	−1.6 (2)
C17—N1—C21—C20	3.0 (2)	C17—C18—C19—C20	2.2 (2)
O1—C1—C2—C3	178.44 (12)	C21—C20—C19—C18	−0.4 (2)
O1—C1—C2—C7	−2.31 (19)	C22—C20—C19—C18	−176.58 (13)
O2—C1—C2—C3	−0.91 (19)	C19—C20—C21—N1	−2.3 (2)
O2—C1—C2—C7	178.33 (12)	C22—C20—C21—N1	174.18 (12)
C1—C2—C7—C6	−178.58 (12)	O7—C22—C20—C19	170.96 (14)
C3—C2—C7—C6	0.7 (2)	O7—C22—C20—C21	−5.28 (19)
C4—C3—C2—C1	179.42 (13)	N2—C22—O7—Cu1^{i}	29.9 (2)
C4—C3—C2—C7	0.2 (2)	N2—C22—C20—C19	−7.8 (2)
C2—C3—C4—C5	−0.9 (2)	N2—C22—C20—C21	175.94 (13)
C4—C5—O3—C8	173.01 (14)	C20—C22—O7—Cu1^{i}	−148.77 (10)

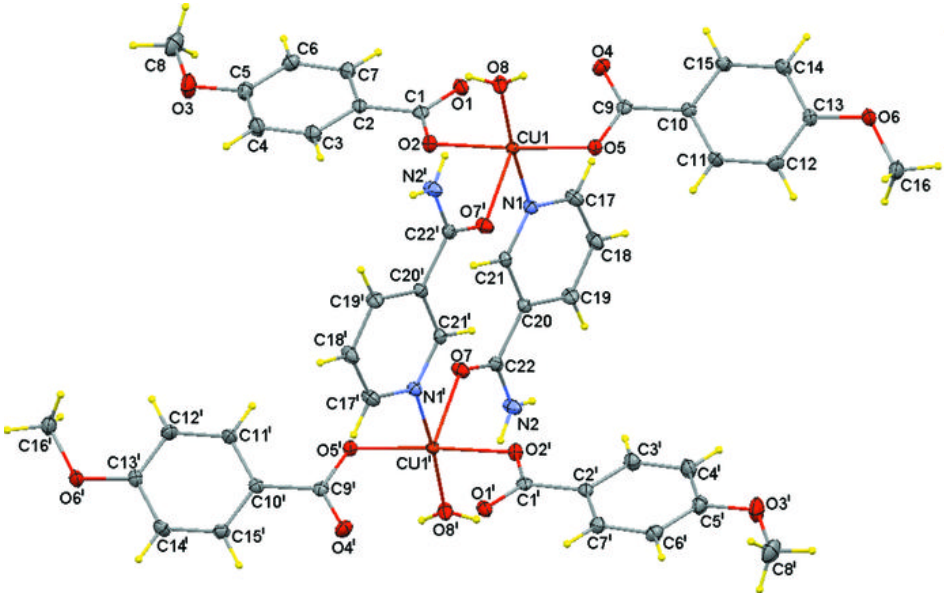
Symmetry codes: (i) −*x*+2, −*y*, −*z*+1.

Hydrogen-bond geometry (Å, °)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
N2—H2A···O1^{ii}	0.86 (2)	2.03 (2)	2.8407 (18)	158 (2)
N2—H2B···O4^{iii}	0.83 (2)	2.29 (2)	2.9897 (17)	141.4 (18)
O8—H81···O1^{iv}	0.79 (3)	1.97 (3)	2.7236 (15)	159 (3)
O8—H82···O4^{iv}	0.825 (18)	1.803 (18)	2.6052 (16)	163.9 (18)

Symmetry codes: (ii) −*x*+2, −*y*+1, −*z*+1; (iii) *x*+1/2, −*y*+1/2, *z*+1/2; (iv) −*x*+3/2, *y*−1/2, −*z*+1/2.

Fig. 1


C8
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C6
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C3
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C10
C15
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Bis(μ-4-phenylpyridine *N*-oxide-κ^2O:*O*)-bis[bis(1,1,1,5,5,5-hexafluoropentane-2,4-dionato)copper(II)]

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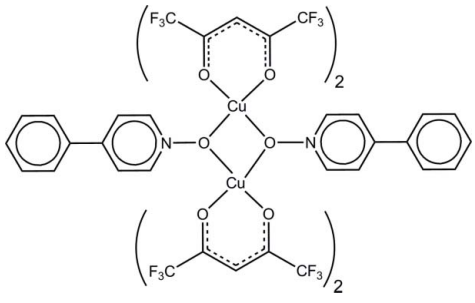
Key indicators: single-crystal X-ray study; T = 150 K; mean σ(C–C) = 0.004 Å; disorder in main residue; R factor = 0.048; wR factor = 0.139; data-to-parameter ratio = 16.2.

The asymmetric unit of the title compound, $[Cu_2(C_5HF_6O_2)_4(C_{11}H_9NO)_2]$, contains one half of the centrosymmetric dinuclear complex. The coordination geometry of the Cu^{II} atom is octahedral, exhibiting a typical Jahn–Teller distortion. One trifluoromethyl group is rotationally disordered between two orientations in a 1:1 ratio.

Related literature

For the use of copper complexes in optical devices, see: Akkılıç *et al.* (2010); Armaroli *et al.* (2007); Bessho *et al.* (2008); Chan *et al.* (2010); Daniel *et al.* (2009); Jeon *et al.* (2008); Kambayashi *et al.* (2005); Peranantham *et al.* (2007); Si *et al.* (2008); Vogler & Kunkely (2001); Walsh *et al.* (2009). For related complexes with 4-phenylpyridine-*N*-oxide, see: Papadaki *et al.* (1999); Watson & Johnson (1971). For general background to studies on copper complexes from our research group, see: Fernandes *et al.* (2010); Shi *et al.* (2006); Paz *et al.* (2005); Girginova *et al.* (2005); Brandão *et al.* (2005). For a description of the Cambridge Structural Database, see: Allen (2002).



Experimental

Crystal data

$[Cu_2(C_5HF_6O_2)_4(C_{11}H_9NO)_2]$
M_r = 1297.70
Triclinic, $P\overline{1}$
a = 10.3830 (4) Å
b = 10.7870 (4) Å
c = 11.2498 (4) Å
α = 99.055 (2)°
β = 99.036 (2)°
γ = 98.258 (2)°
V = 1210.40 (8) Å^3
Z = 1
Mo $K\alpha$ radiation
μ = 1.03 mm^{-1}
T = 150 K
0.18 × 0.10 × 0.09 mm

Data collection

Bruker X8 Kappa CCD APEXII diffractometer
Absorption correction: multi-scan (*SADABS*; Sheldrick, 1997)
T_{min} = 0.836, T_{max} = 0.913
47759 measured reflections
6427 independent reflections
5461 reflections with $I > 2\sigma(I)$
R_{int} = 0.029

Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.048
$wR(F^2)$ = 0.139
S = 1.04
6427 reflections
397 parameters
24 restraints
H-atom parameters constrained
$\Delta\rho_{max}$ = 1.21 e Å^{-3}
$\Delta\rho_{min}$ = −1.40 e Å^{-3}

Data collection: *APEX2* (Bruker, 2006); cell refinement: *SAINT-Plus* (Bruker, 2005); data reduction: *SAINT-Plus*; program(s) used to solve structure: *SHELXTL* (Sheldrick, 2008); program(s) used to refine structure: *SHELXTL*; molecular graphics: *DIAMOND* (Brandenburg, 2009); software used to prepare material for publication: *SHELXTL*.

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Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: CV2732).

References

Akkılıç, K., Ocak, Y. S., Kılıçoğlu, T., İlhan, S. & Temel, H. (2010). *Curr. Appl. Phys.* **10**, 337–341.
Allen, F. H. (2002). *Acta Cryst.* B**58**, 380–388.
Armaroli, N., Accorsi, G., Cardinali, F. & Listorti, A. (2007). *Top. Curr. Chem.* **280**, 69–115.
Bessho, T., Constable, E. C., Graetzel, M., Redondo, A. H., Housecroft, C. E., Kylberg, W., Nazeeruddin, M. K., Neuburger, M. & Schaffner, S. (2008). *Chem. Commun.* pp. 3717–3719.
Brandão, P., Paz, F. A. A. & Rocha, J. (2005). *Chem. Commun.* pp. 171–173.
Brandenburg, K. (2009). *DIAMOND*. Crystal Impact GbR, Bonn, Germany.
Bruker (2005). *SAINT-Plus*. Bruker AXS Inc., Madison, Wisconsin, USA.
Bruker (2006). *APEX2*. Bruker AXS, Delft, The Netherlands.
Chan, C. P., Lam, H. & Surya, C. (2010). *Sol. Energ. Mater.* **94**, 207–211.
Daniel, A., Le Pen, C., Archambeau, C. & Reniers, F. (2009). *Appl. Surf. Sci.* **256**, S82–S85.
Fernandes, J. A., Ramos, A. I., Silva, P., Braga, S. S., Ribeiro-Claro, P., Rocha, J. & Paz, F. A. A. (2010). *Acta Cryst.* E**66**, m626–m627.
Girginova, P. I., Paz, F. A. A., Nogueira, H. I. S., Silva, N. J. O., Amaral, V. S., Klinowski, J. & Trindade, T. (2005). *J. Mol. Struct.* **737**, 221–229.

Jeon, B. P., Lee, S. & Lee, J. K. (2008). *Surf. Coat. Technol.* **202**, 1839–1846.
Kambayashi, T., Ohta, H., Hoshi, H., Hirano, M., Hosono, H., Takezoe, H. & Ishikawa, K. (2005). *Cryst. Growth Des.* **5**, 143–146.
Papadaki, H., Christofides, A., Jeffery, J. C. & Bakas, T. (1999). *J. Coord. Chem.* **47**, 559–572.
Paz, F. A. A., Shi, F. N., Trindade, T., Klinowski, J. & Rocha, J. (2005). *Acta Cryst.* E**61**, m2247–m2250.
Peranantham, P., Jeyachandran, Y. L., Viswanathan, C., Praveena, N. N., Chitra, P. C., Mangalaraj, D. & Narayandass, S. K. (2007). *Mater. Charact.* **58**, 756–764.
Sheldrick, G. M. (1997). *SADABS*. Bruker AXS Inc., Madison, Wisconsin, USA.
Sheldrick, G. M. (2008). *Acta Cryst.* A**64**, 112–122.
Shi, F. N., Paz, F. A. A., Trindade, T. & Rocha, J. (2006). *Acta Cryst.* E**62**, m335–m338.
Si, Z., Li, J., Li, B., Lui, S. & Li, W. (2008). *J. Lumin.* **129**, 181–186.
Vogler, A. & Kunkely, H. (2001). *Topics in Current Chemistry*, 1st ed. Berlin: Springer-Verlag.
Walsh, P. J., Lundin, N. J., Gordon, K. C., Kim, J.-Y. & Lee, C.-H. (2009). *Opt. Mat.* **31**, 1525–1531.
Watson, W. H. & Johnson, D. R. (1971). *J. Coord. Chem.* **1**, 145–153.

supplementary materials

Acta Cryst. (2010). E**66**, m824-m825 [**doi:10.1107/S1600536810022567**]

Bis(μ-4-phenylpyridine *N*-oxide-κ^2O:*O*)bis[bis(1,1,1,5,5,5-hexafluoropentane-2,4-dionato)copper(II)]

A. I. Ramos, J. A. Fernandes, P. Silva, P. J. A. Ribeiro-Claro, S. S. Braga and F. A. Almeida Paz

Comment

The coordination chemistry of 4-phenylpyridine-*N*-oxide (PPNO; $C_{11}H_9NO$) is rather unknown. Surveying the Cambridge Structural Database (Allen, 2002) only two coordination compounds were found, namely a copper (Watson & Johnson, 1971) and a tin compound (Papadaki *et al.*, 1999).

The title compound, $[Cu(C_5HF_6O_2)_2(C_{11}H_9NO)_2]$ (**I**) (where $C_5HF_6O_2^-$ is hexafluoroacetylacetonate and $C_{11}H_9NO$ corresponds to 4-phenylpyridine-*N*-oxide), has a bright green colour which is of interest for the potential use as a dye in several applications, such as in organic electronics. Coloured materials, including metal coordination compounds, have been explored in the last decades because pigmentation is a strong indicative of promising physical and optical properties (Vogler & Kunkely, 2001). Recent applications of copper coordination complexes include a Schottky diode based on a macrocyclic binuclear Cu^{2+} complex (Akkılıç *et al.*, 2010) and a series of Graetzel solar cells using 6,6'-dimethyl-dicarboxylated-bipyridine complexes (Bessho *et al.*, 2008). The use of Cu^{2+} complexes in OLEDs is still limited (Armaroli *et al.*, 2007), and emission still relies mostly on Cu^+ complexes, such as [Cu(I)*bis*(triphenylphosphine)dipyridophenazine] (Walsh *et al.*, 2009) and three Cu(I)pyridylbenzimidazole complexes (Si *et al.*, 2008). In addition, copper complexes are advantageous from the technological processing perspective, adaptable to various film deposition techniques: molecular beam epitaxy (Kambayashi *et al.*, 2005), vacuum evaporation (Peranantham *et al.*, 2007), electrodeposition (Chan *et al.*, 2010) and chemical vapour deposition (CVD), either plasma-enhanced (Daniel *et al.*, 2009) or the widespread metal organic CVD (Jeon *et al.*, 2008).

Following our interest in the preparation and study of the properties of copper compounds (Fernandes *et al.*, 2010; Shi *et al.*, 2006; Paz *et al.*, 2005; Girginova *et al.*, 2005; Brandão *et al.*, 2005) we have reacted $[Cu(hfac)_2]$ (where $hfac^-$ stands for hexafluoroacetylacetonate) with PPNO, affording the title compound as a vivid green crystalline material, whose crystal structure we report herein.

The structure is dimeric having a point of inversion in the geometrical centre of the quadrangle defined by $Cu1\cdots O5\cdots Cu1^{(i)}\cdots O5^{(i)}$ (Figure 1) [symmetry code: (i) 2 - *x*, -*y*, -*z*]. The asymmetric unit contains one PPNO ligand and one $[Cu(hfac)_2]$ moiety. The atoms Cu1, O2, O4 and O5, and their symmetry-related counterparts [symmetry code (i)], form a plane (longest distance to the average plane of about 0.041 Å). Likewise, atoms Cu1, O1 and O3, and their symmetry-related counterparts [symmetry code (i)], define a second plane (longest distance to this average plane of about 0.048 Å), which is perpendicular to the previous one. The Cu^{2+} centre exhibits a typical octahedral coordination environment with a strong Jahn-Teller distortion: the Cu—O bonds (equatorial plane) range from 1.9500 (19) to 1.9751 (18) Å, while the Cu—O bonds (at apical positions) are either 2.251 (2) or 2.4427 (18) Å. With the exception of the angles O5—Cu1—$O5^{(i)}$ [76.90 (7)°] and O2—Cu1—O4 [101.08 (8)°], the *cis* octahedral angles fall within a rather short range around the ideal value: 84.55 (7)–97.37 (8)° (Table 1). The *trans* octahedral angles are between 161.06 (8)° and 174.96 (8)°. The two average

planes containing the aromatic rings of PPNO are mutually rotated by *ca* 37°. The structure exhibits crystallographic disorder associated with the fluorine atoms F4, F5 and F6 (rates of occupancy 50% for each location). Noteworthy, symmetry-related copper complexes are located at the vertex of the unit cell (Figure 2), with the inner space being essentially occupied by the coordinated organic ligands, leading to a hydrophobic empty space of about 36 $Å^3$.

Experimental

Chemicals were purchased from commercial sources and were used as received without purification.

4-Phenylpyridine-*N*-oxide (PPNO, 71.7 mg, 0.419 mmol, Aldrich) was slowly added to a previously-prepared $[Cu(hfac)_2]$ (100.0 mg, 0.209 mmol; $hfac^-$ stands for hexafluoroacetylacetonate) solution in 10 ml of acetone. The resulting solution was magnetically stirred at 30 °C for 30 minutes. By slow evaporation to dryness, a green solid was obtained, which was dissolved in ethanol, gravity filtered and deposited above a water layer. Green crystals of the title compound formed after two days.

Refinement

Hydrogen atoms bound to carbon were located at their idealized positions and were included in the final structural model in riding-motion approximation with C—H = 0.95 Å. The isotropic displacement parameters for these atoms were fixed at 1.2 times U_{eq} of the respective carbon atom.

The substituent —CF_3 groups were found to be severely affected by thermal disorder. Attempts to model this disorder were only successful for one moiety which was included in the final structure with two crystallographic positions (fixed rate of occupancy of 50% for each). In order to ensure a chemically reasonable geometry for this disorder moiety all C—F and F···F distances in the structure were restrained to common refineable values.

Figures

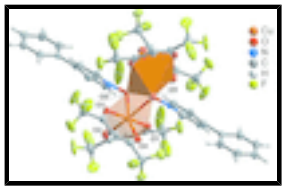


Fig. 1. Schematic representation, in ball-and-stick and polyhedral fashions, of the molecular structure of the title compound. The crystallographic disorder associated with the —CF_3 group was omitted for simplicity. Symmetry code: (i) 2 - *x*, -*y*, -*z*.

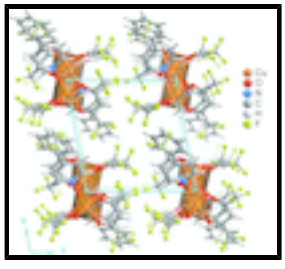


Fig. 2. Perspective view along the *c* axis of the unit cell of the crystal packing of the title compound.

Bis(μ-4-phenylpyridine *N*-oxide-κ^2*O*:*O*)bis[bis(1,1,1,5,5,5- hexafluoropentane-2,4-dionato)copper(II)]

Crystal data

$[Cu_2(C_5HF_6O_2)_4(C_{11}H_9NO)_2]$	$Z = 1$
$M_r = 1297.70$	$F(000) = 642$
Triclinic, $P\overline{1}$	$D_x = 1.780$ Mg m^{-3}
Hall symbol: -P 1	Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å
$a = 10.3830$ (4) Å	Cell parameters from 9842 reflections
$b = 10.7870$ (4) Å	$\theta = 2.9$–$28.6°$
$c = 11.2498$ (4) Å	$\mu = 1.03$ mm^{-1}
$\alpha = 99.055$ (2)°	$T = 150$ K
$\beta = 99.036$ (2)°	Block, green
$\gamma = 98.258$ (2)°	0.18 × 0.10 × 0.09 mm
$V = 1210.40$ (8) Å^3	

Data collection

Bruker X8 Kappa CCD APEXII diffractometer	6427 independent reflections
Radiation source: fine-focus sealed tube	5461 reflections with $I > 2\sigma(I)$
graphite	$R_{int} = 0.029$
ω/phi scans	$\theta_{max} = 29.1°$, $\theta_{min} = 3.7°$
Absorption correction: multi-scan (*SADABS*; Sheldrick, 1997)	$h = -14 \rightarrow 14$
$T_{min} = 0.836$, $T_{max} = 0.913$	$k = -14 \rightarrow 14$
47759 measured reflections	$l = -15 \rightarrow 15$

Refinement

Refinement on F^2	Primary atom site location: structure-invariant direct methods
Least-squares matrix: full	Secondary atom site location: difference Fourier map
$R[F^2 > 2\sigma(F^2)] = 0.048$	Hydrogen site location: inferred from neighbouring sites
$wR(F^2) = 0.139$	H-atom parameters constrained
$S = 1.04$	$w = 1/[\sigma^2(F_o^2) + (0.0712P)^2 + 2.0571P]$ where $P = (F_o^2 + 2F_c^2)/3$
6427 reflections	$(\Delta/\sigma)_{max} = 0.003$
397 parameters	$\Delta\rho_{max} = 1.21$ e Å^{-3}
24 restraints	$\Delta\rho_{min} = -1.40$ e Å^{-3}

Special details

Geometry. All e.s.d.'s (except the e.s.d. in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell e.s.d.'s are taken into account individually in the estimation of e.s.d.'s in distances, angles and torsion angles; correlations

between e.s.d.'s in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell e.s.d.'s is used for estimating e.s.d.'s involving l.s. planes.

Refinement. Refinement of F^2 against ALL reflections. The weighted *R*-factor *wR* and goodness of fit *S* are based on F^2, conventional *R*-factors *R* are based on *F*, with *F* set to zero for negative F^2. The threshold expression of $F^2 > \sigma(F^2)$ is used only for calculating *R*-factors(gt) *etc*. and is not relevant to the choice of reflections for refinement. *R*-factors based on F^2 are statistically about twice as large as those based on *F*, and *R*- factors based on ALL data will be even larger.

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters ($Å^2$)

	x	*y*	*z*	U_{iso}*/U_{eq}	Occ. (<1)
Cu1	1.01536 (3)	0.13209 (3)	−0.07044 (3)	0.02205 (10)	
O1	1.17596 (17)	0.20733 (17)	0.05247 (16)	0.0235 (4)	
O2	1.12021 (19)	0.2109 (2)	−0.21003 (18)	0.0312 (4)	
O3	0.86603 (19)	0.05900 (18)	−0.20302 (18)	0.0284 (4)	
O4	0.93026 (17)	0.27435 (17)	−0.01281 (18)	0.0255 (4)	
O5	0.91578 (18)	0.02993 (17)	0.08021 (16)	0.0238 (4)	
N1	0.8997 (2)	0.0995 (2)	0.18579 (19)	0.0217 (4)	
C1	1.4020 (2)	0.2518 (2)	0.14122 (18)	0.0382 (7)	
C2	1.2903 (2)	0.2335 (2)	0.0291 (2)	0.0227 (5)	
C3	1.3311 (3)	0.2502 (3)	−0.0794 (2)	0.0273 (5)	
H3	1.4233	0.2686	−0.0795	0.033*	
C4	1.2419 (3)	0.2411 (3)	−0.1900 (2)	0.0261 (5)	
C5	1.3046 (2)	0.2749 (3)	−0.2985 (2)	0.0426 (7)	
C6	0.6641 (2)	0.03964 (18)	−0.3416 (2)	0.0404 (7)	
C7	0.7645 (3)	0.1076 (3)	−0.2257 (2)	0.0272 (5)	
C8	0.7299 (3)	0.2135 (3)	−0.1602 (3)	0.0329 (6)	
H8	0.6459	0.2359	−0.1852	0.039*	
C9	0.8158 (2)	0.2876 (2)	−0.0585 (2)	0.0247 (5)	
C10	0.7717 (3)	0.4038 (3)	0.0107 (3)	0.0303 (6)	
C11	1.0036 (3)	0.1754 (3)	0.2619 (2)	0.0272 (5)	
H11	1.0903	0.1761	0.2446	0.033*	
C12	0.9841 (3)	0.2522 (3)	0.3650 (2)	0.0261 (5)	
H12	1.0580	0.3048	0.4192	0.031*	
C13	0.8573 (2)	0.2537 (2)	0.3912 (2)	0.0214 (4)	
C14	0.7527 (2)	0.1713 (3)	0.3101 (2)	0.0256 (5)	
H14	0.6651	0.1677	0.3258	0.031*	
C15	0.7754 (2)	0.0959 (2)	0.2086 (2)	0.0249 (5)	
H15	0.7035	0.0408	0.1539	0.030*	
C16	0.8344 (2)	0.3403 (2)	0.4986 (2)	0.0228 (5)	
C17	0.9250 (3)	0.3653 (3)	0.6087 (2)	0.0299 (5)	
H17	1.0018	0.3265	0.6148	0.036*	
C18	0.9035 (3)	0.4465 (3)	0.7091 (3)	0.0356 (6)	
H18	0.9657	0.4631	0.7837	0.043*	
C19	0.7924 (3)	0.5035 (3)	0.7018 (3)	0.0365 (6)	
H19	0.7783	0.5591	0.7711	0.044*	
C20	0.7019 (3)	0.4793 (3)	0.5936 (3)	0.0398 (7)	
H20	0.6254	0.5185	0.5884	0.048*	
C21	0.7225 (3)	0.3976 (3)	0.4916 (3)	0.0325 (6)	

H21	0.6598	0.3811	0.4173	0.039*	
F1	1.36023 (19)	0.2437 (2)	0.24323 (16)	0.0546 (6)	
F2	1.4801 (3)	0.3614 (3)	0.1595 (2)	0.1153 (16)	
F3	1.4749 (3)	0.1648 (3)	0.1247 (2)	0.150 (2)	
F4	1.3541 (8)	0.3951 (3)	−0.2833 (5)	0.122 (4)	0.50
F5	1.4012 (5)	0.2125 (7)	−0.3118 (5)	0.084 (3)	0.50
F6	1.2224 (4)	0.2467 (7)	−0.4024 (3)	0.0588 (17)	0.50
F4'	1.2595 (7)	0.3725 (7)	−0.3328 (9)	0.109 (4)	0.50
F5'	1.4329 (2)	0.3025 (8)	−0.2815 (7)	0.098 (4)	0.50
F6'	1.2680 (10)	0.1810 (7)	−0.3909 (6)	0.199 (8)	0.50
F7	0.7002 (2)	−0.0620 (2)	−0.3950 (2)	0.0803 (9)	
F8	0.6504 (3)	0.1140 (2)	−0.4212 (2)	0.0945 (12)	
F9	0.54684 (19)	0.0040 (2)	−0.3187 (2)	0.0723 (8)	
F10	0.85443 (17)	0.51032 (16)	0.01099 (18)	0.0366 (4)	
F11	0.7719 (2)	0.3931 (2)	0.12708 (19)	0.0483 (5)	
F12	0.65074 (17)	0.41987 (19)	−0.0375 (2)	0.0465 (5)	

Atomic displacement parameters (Å^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Cu1	0.01770 (15)	0.02152 (16)	0.02440 (17)	0.00386 (11)	−0.00051 (11)	0.00057 (11)
O1	0.0194 (8)	0.0263 (9)	0.0232 (8)	0.0029 (7)	0.0011 (6)	0.0031 (7)
O2	0.0260 (9)	0.0402 (11)	0.0265 (9)	0.0039 (8)	−0.0006 (7)	0.0109 (8)
O3	0.0249 (9)	0.0284 (9)	0.0276 (9)	0.0032 (7)	−0.0020 (7)	0.0005 (7)
O4	0.0194 (8)	0.0235 (8)	0.0314 (9)	0.0055 (7)	−0.0009 (7)	0.0023 (7)
O5	0.0282 (9)	0.0230 (8)	0.0208 (8)	0.0081 (7)	0.0062 (7)	0.0007 (6)
N1	0.0212 (9)	0.0218 (9)	0.0222 (10)	0.0047 (8)	0.0049 (8)	0.0026 (8)
C1	0.0215 (12)	0.060 (2)	0.0305 (14)	0.0032 (13)	−0.0010 (11)	0.0098 (13)
C2	0.0196 (10)	0.0218 (11)	0.0250 (12)	0.0052 (9)	−0.0009 (9)	0.0031 (9)
C3	0.0187 (11)	0.0348 (14)	0.0291 (13)	0.0053 (10)	0.0032 (9)	0.0088 (10)
C4	0.0272 (12)	0.0279 (12)	0.0260 (12)	0.0100 (10)	0.0061 (10)	0.0074 (10)
C5	0.0358 (16)	0.065 (2)	0.0313 (15)	0.0122 (15)	0.0082 (12)	0.0154 (15)
C6	0.0387 (16)	0.0369 (16)	0.0368 (16)	−0.0026 (13)	−0.0103 (13)	0.0061 (13)
C7	0.0217 (11)	0.0285 (12)	0.0276 (13)	−0.0030 (10)	−0.0033 (9)	0.0077 (10)
C8	0.0198 (12)	0.0331 (14)	0.0421 (16)	0.0046 (10)	−0.0038 (11)	0.0054 (12)
C9	0.0197 (11)	0.0221 (11)	0.0330 (13)	0.0031 (9)	0.0046 (9)	0.0081 (10)
C10	0.0209 (12)	0.0301 (13)	0.0405 (15)	0.0068 (10)	0.0048 (10)	0.0062 (11)
C11	0.0189 (11)	0.0329 (13)	0.0283 (13)	0.0016 (10)	0.0064 (9)	0.0013 (10)
C12	0.0217 (11)	0.0303 (13)	0.0236 (12)	−0.0002 (10)	0.0041 (9)	0.0008 (10)
C13	0.0215 (11)	0.0227 (11)	0.0208 (11)	0.0045 (9)	0.0043 (9)	0.0049 (9)
C14	0.0180 (11)	0.0312 (13)	0.0268 (12)	0.0053 (9)	0.0039 (9)	0.0022 (10)
C15	0.0185 (11)	0.0270 (12)	0.0267 (12)	0.0034 (9)	0.0011 (9)	0.0008 (10)
C16	0.0240 (11)	0.0237 (11)	0.0202 (11)	0.0025 (9)	0.0047 (9)	0.0036 (9)
C17	0.0266 (13)	0.0378 (14)	0.0242 (12)	0.0063 (11)	0.0033 (10)	0.0033 (11)
C18	0.0371 (15)	0.0429 (16)	0.0214 (13)	0.0002 (13)	0.0017 (11)	−0.0002 (11)
C19	0.0498 (18)	0.0337 (15)	0.0253 (13)	0.0071 (13)	0.0126 (12)	−0.0019 (11)
C20	0.0433 (17)	0.0414 (17)	0.0357 (16)	0.0191 (14)	0.0085 (13)	−0.0012 (13)
C21	0.0330 (14)	0.0362 (14)	0.0270 (13)	0.0135 (12)	0.0007 (11)	0.0003 (11)

F1	0.0415 (11)	0.0933 (18)	0.0272 (9)	0.0156 (11)	−0.0025 (8)	0.0110 (10)
F2	0.084 (2)	0.159 (3)	0.0636 (18)	−0.081 (2)	−0.0360 (15)	0.046 (2)
F3	0.147 (3)	0.261 (5)	0.0483 (15)	0.177 (4)	−0.0346 (18)	−0.029 (2)
F4	0.228 (11)	0.058 (4)	0.073 (5)	−0.050 (5)	0.081 (7)	0.007 (3)
F5	0.048 (3)	0.180 (9)	0.061 (4)	0.065 (4)	0.038 (3)	0.063 (5)
F6	0.035 (2)	0.128 (6)	0.0152 (19)	0.018 (3)	0.0034 (15)	0.016 (3)
F4'	0.070 (4)	0.180 (10)	0.137 (8)	0.059 (5)	0.055 (5)	0.135 (8)
F5'	0.029 (2)	0.201 (10)	0.090 (5)	0.011 (4)	0.018 (3)	0.101 (7)
F6'	0.313 (19)	0.144 (9)	0.111 (8)	−0.082 (10)	0.155 (11)	−0.072 (7)
F7	0.0761 (18)	0.0833 (19)	0.0559 (15)	0.0243 (15)	−0.0267 (13)	−0.0345 (14)
F8	0.128 (3)	0.0745 (18)	0.0489 (14)	−0.0453 (18)	−0.0450 (15)	0.0346 (13)
F9	0.0367 (12)	0.0837 (18)	0.0747 (17)	−0.0197 (12)	−0.0092 (11)	−0.0045 (14)
F10	0.0320 (9)	0.0236 (8)	0.0516 (11)	0.0037 (7)	0.0063 (8)	0.0015 (7)
F11	0.0546 (12)	0.0560 (12)	0.0441 (11)	0.0220 (10)	0.0241 (10)	0.0124 (9)
F12	0.0235 (8)	0.0407 (10)	0.0724 (14)	0.0138 (7)	0.0003 (9)	0.0024 (9)

Geometric parameters (Å, °)

Cu1—O1	1.9711 (17)	C7—C8	1.383 (4)
Cu1—O2	2.251 (2)	C8—C9	1.390 (4)
Cu1—O3	1.9500 (19)	C8—H8	0.9500
Cu1—O4	1.9524 (18)	C9—C10	1.535 (4)
Cu1—O5	2.4427 (18)	C10—F10	1.331 (3)
Cu1—O5^{i}	1.9751 (18)	C10—F11	1.332 (4)
O1—C2	1.258 (3)	C10—F12	1.334 (3)
O2—C4	1.234 (3)	C11—C12	1.375 (4)
O3—C7	1.252 (3)	C11—H11	0.9500
O4—C9	1.256 (3)	C12—C13	1.395 (3)
O5—N1	1.349 (3)	C12—H12	0.9500
O5—Cu1^{i}	1.9751 (18)	C13—C14	1.399 (4)
N1—C11	1.343 (3)	C13—C16	1.479 (3)
N1—C15	1.351 (3)	C14—C15	1.367 (4)
N1—Cu1^{i}	2.945 (2)	C14—H14	0.9500
C1—F3	1.297 (4)	C15—H15	0.9500
C1—F1	1.300 (3)	C16—C21	1.390 (4)
C1—F2	1.301 (4)	C16—C17	1.396 (4)
C1—C2	1.540 (3)	C17—C18	1.384 (4)
C2—C3	1.383 (4)	C17—H17	0.9500
C3—C4	1.410 (4)	C18—C19	1.381 (5)
C3—H3	0.9500	C18—H18	0.9500
C4—C5	1.540 (3)	C19—C20	1.380 (5)
C5—F6'	1.2982 (15)	C19—H19	0.9500
C5—F4	1.2985 (15)	C20—C21	1.397 (4)
C5—F6	1.2987 (15)	C20—H20	0.9500
C5—F5'	1.2989 (15)	C21—H21	0.9500
C5—F4'	1.2998 (15)	F4—F4'	1.025 (7)
C5—F5	1.3003 (15)	F4—F5'	1.379 (6)
C6—F7	1.298 (3)	F5—F5'	0.968 (7)

C6—F8	1.298 (3)	F5—F6'	1.485 (7)
C6—F9	1.301 (3)	F6—F6'	0.921 (9)
C6—C7	1.542 (3)	F6—F4'	1.423 (7)
O1—Cu1—O2	87.50 (7)	O3—C7—C6	115.7 (2)
O1—Cu1—O5	91.03 (7)	C8—C7—C6	115.7 (2)
O1—Cu1—O5^{i}	86.68 (8)	C8—C7—Cu1	94.49 (17)
O2—Cu1—O5	174.17 (7)	C6—C7—Cu1	149.74 (18)
O3—Cu1—O1	174.96 (8)	C7—C8—C9	121.1 (2)
O3—Cu1—O2	87.73 (8)	C7—C8—Cu1	60.54 (14)
O3—Cu1—O4	92.62 (8)	C9—C8—Cu1	60.60 (15)
O3—Cu1—O5	93.57 (7)	C7—C8—H8	119.4
O3—Cu1—O5^{i}	92.35 (8)	C9—C8—H8	119.4
O4—Cu1—O1	89.86 (8)	Cu1—C8—H8	178.7
O4—Cu1—O2	101.08 (8)	O4—C9—C8	128.7 (3)
O4—Cu1—O5	84.55 (7)	O4—C9—C10	112.6 (2)
O4—Cu1—O5^{i}	161.06 (8)	C8—C9—C10	118.7 (2)
O5^{i}—Cu1—O2	97.37 (8)	C8—C9—Cu1	94.28 (17)
O5^{i}—Cu1—O5	76.90 (7)	C10—C9—Cu1	146.95 (18)
C2—O1—Cu1	125.00 (16)	F10—C10—F11	107.2 (2)
C4—O2—Cu1	120.66 (17)	F10—C10—F12	107.2 (2)
C7—O3—Cu1	124.47 (18)	F11—C10—F12	107.7 (2)
C9—O4—Cu1	124.12 (18)	F10—C10—C9	110.8 (2)
N1—O5—Cu1^{i}	123.68 (14)	F11—C10—C9	110.5 (2)
N1—O5—Cu1	120.78 (14)	F12—C10—C9	113.3 (2)
Cu1^{i}—O5—Cu1	103.10 (7)	N1—C11—C12	119.8 (2)
C11—N1—O5	120.6 (2)	N1—C11—H11	120.1
C11—N1—C15	121.3 (2)	C12—C11—H11	120.1
O5—N1—C15	117.9 (2)	C11—C12—C13	120.9 (2)
C11—N1—Cu1^{i}	109.45 (16)	C11—C12—H12	119.5
C15—N1—Cu1^{i}	120.81 (16)	C13—C12—H12	119.5
F3—C1—F1	106.88 (13)	C12—C13—C14	117.0 (2)
F3—C1—F2	106.82 (13)	C12—C13—C16	121.4 (2)
F1—C1—F2	106.45 (13)	C14—C13—C16	121.6 (2)
F3—C1—C2	109.60 (18)	C15—C14—C13	120.6 (2)
F1—C1—C2	113.95 (18)	C15—C14—H14	119.7
F2—C1—C2	112.73 (19)	C13—C14—H14	119.7
O1—C2—C3	130.7 (2)	N1—C15—C14	120.2 (2)
O1—C2—C1	113.9 (2)	N1—C15—H15	119.9
C3—C2—C1	115.4 (2)	C14—C15—H15	119.9
C3—C2—Cu1	97.93 (16)	C21—C16—C17	119.1 (2)
C1—C2—Cu1	145.40 (16)	C21—C16—C13	120.6 (2)
C2—C3—C4	122.9 (2)	C17—C16—C13	120.3 (2)
C2—C3—H3	118.5	C18—C17—C16	120.3 (3)
C4—C3—H3	118.5	C18—C17—H17	119.9
O2—C4—C3	128.2 (2)	C16—C17—H17	119.9
O2—C4—C5	116.2 (2)	C19—C18—C17	120.6 (3)
C3—C4—C5	115.6 (2)	C19—C18—H18	119.7

C3—C4—Cu1	89.46 (16)	C17—C18—H18	119.7
C5—C4—Cu1	154.41 (17)	C20—C19—C18	119.7 (3)
F6'—C5—F4	135.8 (5)	C20—C19—H19	120.1
F4—C5—F6	106.84 (14)	C18—C19—H19	120.1
F6'—C5—F5'	106.86 (14)	C19—C20—C21	120.3 (3)
F4—C5—F5'	64.2 (3)	C19—C20—H20	119.9
F6—C5—F5'	127.3 (4)	C21—C20—H20	119.9
F6'—C5—F4'	106.77 (15)	C16—C21—C20	120.1 (3)
F4—C5—F4'	46.5 (3)	C16—C21—H21	119.9
F6—C5—F4'	66.4 (4)	C20—C21—H21	119.9
F5'—C5—F4'	106.66 (14)	F4'—F4—C5	66.82 (18)
F6'—C5—F5	69.7 (4)	F4'—F4—F5'	119.4 (3)
F4—C5—F5	106.75 (14)	C5—F4—F5'	57.93 (16)
F6—C5—F5	106.59 (14)	F5'—F5—C5	68.07 (17)
F4'—C5—F5	139.5 (4)	F5'—F5—F6'	114.9 (4)
F6'—C5—C4	109.4 (4)	C5—F5—F6'	55.1 (2)
F4—C5—C4	112.7 (3)	F6'—F6—C5	69.2 (2)
F6—C5—C4	113.5 (3)	F6'—F6—F4'	124.3 (2)
F5'—C5—C4	117.6 (3)	C5—F6—F4'	56.8 (2)
F4'—C5—C4	109.0 (3)	F4—F4'—C5	66.69 (17)
F5—C5—C4	110.1 (3)	F4—F4'—F6	115.9 (4)
F7—C6—F8	107.26 (13)	C5—F4'—F6	56.8 (2)
F7—C6—F9	106.60 (13)	F5—F5'—C5	68.22 (18)
F8—C6—F9	106.74 (13)	F5—F5'—F4	124.5 (2)
F7—C6—C7	112.20 (19)	C5—F5'—F4	57.91 (16)
F8—C6—C7	111.06 (18)	F6—F6'—C5	69.3 (2)
F9—C6—C7	112.64 (19)	F6—F6'—F5	118.1 (4)
O3—C7—C8	128.7 (2)	C5—F6'—F5	55.2 (2)
O4—Cu1—O1—C2	−124.4 (2)	O4—Cu1—C8—C9	−1.75 (16)
$O5^{i}$—Cu1—O1—C2	74.2 (2)	O1—Cu1—C8—C9	−7.0 (2)
O2—Cu1—O1—C2	−23.3 (2)	$O5^{i}$—Cu1—C8—C9	151.74 (16)
O5—Cu1—O1—C2	151.0 (2)	O2—Cu1—C8—C9	−100.53 (17)
O3—Cu1—O2—C4	−158.9 (2)	O5—Cu1—C8—C9	82.53 (17)
O4—Cu1—O2—C4	108.8 (2)	Cu1—O4—C9—C8	−4.4 (4)
O1—Cu1—O2—C4	19.5 (2)	Cu1—O4—C9—C10	176.38 (17)
$O5^{i}$—Cu1—O2—C4	−66.9 (2)	C7—C8—C9—O4	1.0 (5)
O4—Cu1—O3—C7	1.8 (2)	Cu1—C8—C9—O4	2.5 (2)
$O5^{i}$—Cu1—O3—C7	163.5 (2)	C7—C8—C9—C10	−179.8 (3)
O2—Cu1—O3—C7	−99.2 (2)	Cu1—C8—C9—C10	−178.3 (3)
O5—Cu1—O3—C7	86.5 (2)	C7—C8—C9—Cu1	−1.5 (3)
O3—Cu1—O4—C9	2.8 (2)	O3—Cu1—C9—O4	−177.1 (2)
O1—Cu1—O4—C9	178.4 (2)	O1—Cu1—C9—O4	−1.7 (2)
$O5^{i}$—Cu1—O4—C9	−102.3 (3)	$O5^{i}$—Cu1—C9—O4	131.5 (2)
O2—Cu1—O4—C9	91.0 (2)	O2—Cu1—C9—O4	−93.2 (2)
O5—Cu1—O4—C9	−90.5 (2)	O5—Cu1—C9—O4	87.5 (2)
O3—Cu1—O5—N1	−125.16 (16)	O3—Cu1—C9—C8	−0.53 (17)
O4—Cu1—O5—N1	−32.87 (16)	O4—Cu1—C9—C8	176.5 (3)
O1—Cu1—O5—N1	56.90 (16)	O1—Cu1—C9—C8	174.81 (16)

O5^{i}—Cu1—O5—N1	143.3 (2)	O5^{i}—Cu1—C9—C8	−52.0 (3)
O3—Cu1—O5—Cu1^{i}	91.59 (9)	O2—Cu1—C9—C8	83.36 (18)
O4—Cu1—O5—Cu1^{i}	−176.12 (9)	O5—Cu1—C9—C8	−95.98 (17)
O1—Cu1—O5—Cu1^{i}	−86.35 (8)	O3—Cu1—C9—C10	176.8 (3)
O5^{i}—Cu1—O5—Cu1^{i}	0.0	O4—Cu1—C9—C10	−6.1 (3)
Cu1^{i}—O5—N1—C11	79.3 (3)	O1—Cu1—C9—C10	−7.9 (3)
Cu1—O5—N1—C11	−56.3 (3)	O5^{i}—Cu1—C9—C10	125.3 (3)
Cu1^{i}—O5—N1—C15	−104.5 (2)	O2—Cu1—C9—C10	−99.3 (3)
Cu1—O5—N1—C15	119.9 (2)	O5—Cu1—C9—C10	81.4 (3)
Cu1—O5—N1—Cu1^{i}	−135.6 (2)	O4—C9—C10—F10	59.0 (3)
Cu1—O1—C2—C3	18.9 (4)	C8—C9—C10—F10	−120.3 (3)
Cu1—O1—C2—C1	−162.19 (14)	Cu1—C9—C10—F10	62.7 (4)
F3—C1—C2—O1	116.4 (2)	O4—C9—C10—F11	−59.7 (3)
F1—C1—C2—O1	−3.3 (3)	C8—C9—C10—F11	121.0 (3)
F2—C1—C2—O1	−124.8 (2)	Cu1—C9—C10—F11	−55.9 (4)
F3—C1—C2—C3	−64.5 (3)	O4—C9—C10—F12	179.4 (2)
F1—C1—C2—C3	175.8 (2)	C8—C9—C10—F12	0.1 (4)
F2—C1—C2—C3	54.3 (3)	Cu1—C9—C10—F12	−176.8 (2)
F3—C1—C2—Cu1	98.8 (3)	O5—N1—C11—C12	175.6 (2)
F1—C1—C2—Cu1	−20.9 (3)	C15—N1—C11—C12	−0.5 (4)
F2—C1—C2—Cu1	−142.3 (3)	Cu1^{i}—N1—C11—C12	−148.8 (2)
O3—Cu1—C2—O1	179.0 (2)	N1—C11—C12—C13	−0.8 (4)
O4—Cu1—C2—O1	57.4 (2)	C11—C12—C13—C14	1.9 (4)
O5^{i}—Cu1—C2—O1	−103.6 (2)	C11—C12—C13—C16	−177.1 (2)
O2—Cu1—C2—O1	154.8 (2)	C12—C13—C14—C15	−1.7 (4)
O5—Cu1—C2—O1	−30.8 (2)	C16—C13—C14—C15	177.3 (2)
O3—Cu1—C2—C3	13.4 (3)	C11—N1—C15—C14	0.7 (4)
O4—Cu1—C2—C3	−108.30 (17)	O5—N1—C15—C14	−175.5 (2)
O1—Cu1—C2—C3	−165.7 (3)	Cu1^{i}—N1—C15—C14	145.5 (2)
O5^{i}—Cu1—C2—C3	90.73 (17)	C13—C14—C15—N1	0.5 (4)
O2—Cu1—C2—C3	−10.82 (16)	C12—C13—C16—C21	142.6 (3)
O5—Cu1—C2—C3	163.51 (16)	C14—C13—C16—C21	−36.3 (4)
O3—Cu1—C2—C1	−151.5 (2)	C12—C13—C16—C17	−37.6 (4)
O4—Cu1—C2—C1	86.9 (3)	C14—C13—C16—C17	143.5 (3)
O1—Cu1—C2—C1	29.5 (2)	C21—C16—C17—C18	−0.2 (4)
O5^{i}—Cu1—C2—C1	−74.1 (3)	C13—C16—C17—C18	179.9 (3)
O2—Cu1—C2—C1	−175.7 (3)	C16—C17—C18—C19	0.1 (5)
O5—Cu1—C2—C1	−1.3 (3)	C17—C18—C19—C20	0.0 (5)
O1—C2—C3—C4	1.0 (5)	C18—C19—C20—C21	0.0 (5)
C1—C2—C3—C4	−177.9 (2)	C17—C16—C21—C20	0.3 (4)
Cu1—C2—C3—C4	11.5 (3)	C13—C16—C21—C20	−179.9 (3)
Cu1—O2—C4—C3	−9.7 (4)	C19—C20—C21—C16	−0.2 (5)
Cu1—O2—C4—C5	171.25 (17)	F6'—C5—F4—F4'	66.1 (6)
C2—C3—C4—O2	−4.6 (5)	F6—C5—F4—F4'	30.2 (6)
C2—C3—C4—C5	174.4 (2)	F5'—C5—F4—F4'	154.1 (6)
C2—C3—C4—Cu1	−10.7 (3)	F5—C5—F4—F4'	144.0 (6)

O3—Cu1—C4—O2	22.0 (2)	C4—C5—F4—F4'	−95.1 (6)
O4—Cu1—C4—O2	−76.0 (2)	F6'—C5—F4—F5'	−88.0 (4)
O1—Cu1—C4—O2	−159.0 (2)	F6—C5—F4—F5'	−123.8 (5)
O5^{i}—Cu1—C4—O2	114.2 (2)	F4'—C5—F4—F5'	−154.1 (6)
O5—Cu1—C4—O2	168.04 (19)	F5—C5—F4—F5'	−10.1 (5)
O3—Cu1—C4—C3	−165.59 (16)	C4—C5—F4—F5'	110.8 (4)
O4—Cu1—C4—C3	96.36 (16)	F6'—C5—F5—F5'	146.6 (6)
O1—Cu1—C4—C3	13.38 (16)	F4—C5—F5—F5'	13.2 (6)
O5^{i}—Cu1—C4—C3	−73.38 (16)	F6—C5—F5—F5'	127.1 (6)
O2—Cu1—C4—C3	172.4 (3)	F4'—C5—F5—F5'	54.2 (9)
O5—Cu1—C4—C3	−19.6 (3)	C4—C5—F5—F5'	−109.4 (6)
O3—Cu1—C4—C5	3.6 (4)	F4—C5—F5—F6'	−133.4 (5)
O4—Cu1—C4—C5	−94.5 (4)	F6—C5—F5—F6'	−19.4 (5)
O1—Cu1—C4—C5	−177.4 (4)	F5'—C5—F5—F6'	−146.6 (6)
O5^{i}—Cu1—C4—C5	95.8 (4)	F4'—C5—F5—F6'	−92.3 (5)
O2—Cu1—C4—C5	−18.4 (3)	C4—C5—F5—F6'	104.0 (4)
O5—Cu1—C4—C5	149.6 (3)	F4—C5—F6—F6'	141.9 (6)
O2—C4—C5—F6'	−55.4 (6)	F5'—C5—F6—F6'	71.9 (6)
C3—C4—C5—F6'	125.4 (6)	F4'—C5—F6—F6'	165.4 (7)
Cu1—C4—C5—F6'	−42.6 (7)	F5—C5—F6—F6'	28.1 (6)
O2—C4—C5—F4	110.8 (5)	C4—C5—F6—F6'	−93.2 (7)
C3—C4—C5—F4	−68.4 (5)	F6'—C5—F6—F4'	−165.4 (7)
Cu1—C4—C5—F4	123.6 (5)	F4—C5—F6—F4'	−23.5 (4)
O2—C4—C5—F6	−10.8 (4)	F5'—C5—F6—F4'	−93.5 (4)
C3—C4—C5—F6	170.0 (4)	F5—C5—F6—F4'	−137.3 (4)
Cu1—C4—C5—F6	2.0 (6)	C4—C5—F6—F4'	101.3 (3)
O2—C4—C5—F5'	−177.5 (5)	F5'—F4—F4'—C5	25.2 (5)
C3—C4—C5—F5'	3.3 (5)	C5—F4—F4'—F6	−29.3 (4)
Cu1—C4—C5—F5'	−164.7 (5)	F5'—F4—F4'—F6	−4.1 (8)
O2—C4—C5—F4'	61.0 (5)	F6'—C5—F4'—F4	−138.2 (6)
C3—C4—C5—F4'	−118.2 (5)	F6—C5—F4'—F4	−148.3 (6)
Cu1—C4—C5—F4'	73.8 (6)	F5'—C5—F4'—F4	−24.3 (6)
O2—C4—C5—F5	−130.2 (4)	F5—C5—F4'—F4	−60.1 (8)
C3—C4—C5—F5	50.6 (4)	C4—C5—F4'—F4	103.7 (5)
Cu1—C4—C5—F5	−117.3 (5)	F6'—C5—F4'—F6	10.0 (5)
Cu1—O3—C7—C8	−5.6 (4)	F4—C5—F4'—F6	148.3 (6)
Cu1—O3—C7—C6	174.94 (14)	F5'—C5—F4'—F6	124.0 (5)
F7—C6—C7—O3	2.6 (3)	F5—C5—F4'—F6	88.2 (5)
F8—C6—C7—O3	−117.5 (2)	C4—C5—F4'—F6	−108.1 (3)
F9—C6—C7—O3	122.9 (2)	F6'—F6—F4'—F4	15.9 (10)
F7—C6—C7—C8	−177.0 (2)	C5—F6—F4'—F4	32.5 (5)
F8—C6—C7—C8	63.0 (3)	F6'—F6—F4'—C5	−16.5 (7)
F9—C6—C7—C8	−56.7 (3)	F6'—F5—F5'—C5	29.9 (4)
F7—C6—C7—Cu1	8.2 (4)	C5—F5—F5'—F4	−14.5 (6)
F8—C6—C7—Cu1	−111.8 (3)	F6'—F5—F5'—F4	15.4 (9)
F9—C6—C7—Cu1	128.5 (3)	F6'—C5—F5'—F5	−32.7 (7)
O4—Cu1—C7—O3	−178.1 (2)	F4—C5—F5'—F5	−165.9 (7)
O1—Cu1—C7—O3	166.4 (2)	F6—C5—F5'—F5	−73.9 (5)

O5^{i}—Cu1—C7—O3	−17.9 (2)	F4'—C5—F5'—F5	−146.6 (6)
O2—Cu1—C7—O3	80.6 (2)	C4—C5—F5'—F5	90.8 (6)
O5—Cu1—C7—O3	−94.6 (2)	F6'—C5—F5'—F4	133.3 (5)
O3—Cu1—C7—C8	175.6 (3)	F6—C5—F5'—F4	92.1 (3)
O4—Cu1—C7—C8	−2.47 (17)	F4'—C5—F5'—F4	19.3 (5)
O1—Cu1—C7—C8	−17.9 (3)	F5—C5—F5'—F4	165.9 (7)
O5^{i}—Cu1—C7—C8	157.75 (17)	C4—C5—F5'—F4	−103.3 (3)
O2—Cu1—C7—C8	−103.75 (18)	F4'—F4—F5'—F5	−11.6 (11)
O5—Cu1—C7—C8	81.09 (18)	C5—F4—F5'—F5	15.9 (7)
O3—Cu1—C7—C6	−9.1 (3)	F4'—F4—F5'—C5	−27.5 (6)
O4—Cu1—C7—C6	172.8 (3)	F4'—F6—F6'—C5	14.8 (7)
O1—Cu1—C7—C6	157.4 (3)	C5—F6—F6'—F5	−26.6 (5)
O5^{i}—Cu1—C7—C6	−27.0 (3)	F4'—F6—F6'—F5	−11.8 (10)
O2—Cu1—C7—C6	71.5 (3)	F4—C5—F6'—F6	−57.8 (7)
O5—Cu1—C7—C6	−103.6 (3)	F5'—C5—F6'—F6	−127.8 (6)
O3—C7—C8—C9	4.6 (5)	F4'—C5—F6'—F6	−13.9 (6)
C6—C7—C8—C9	−175.9 (2)	F5—C5—F6'—F6	−151.2 (6)
Cu1—C7—C8—C9	1.5 (3)	C4—C5—F6'—F6	103.9 (6)
O3—C7—C8—Cu1	3.1 (2)	F4—C5—F6'—F5	93.5 (5)
C6—C7—C8—Cu1	−177.4 (2)	F6—C5—F6'—F5	151.2 (6)
O3—Cu1—C8—C7	−2.18 (16)	F5'—C5—F6'—F5	23.4 (4)
O4—Cu1—C8—C7	176.8 (2)	F4'—C5—F6'—F5	137.3 (4)
O1—Cu1—C8—C7	171.52 (16)	C4—C5—F6'—F5	−104.9 (3)
O5^{i}—Cu1—C8—C7	−29.7 (2)	F5'—F5—F6'—F6	−3.6 (8)
O2—Cu1—C8—C7	77.99 (18)	C5—F5—F6'—F6	30.7 (6)
O5—Cu1—C8—C7	−98.95 (18)	F5'—F5—F6'—C5	−34.3 (5)
O3—Cu1—C8—C9	179.3 (2)		

Symmetry codes: (i) −*x*+2, −*y*, −*z*.

Fig. 1

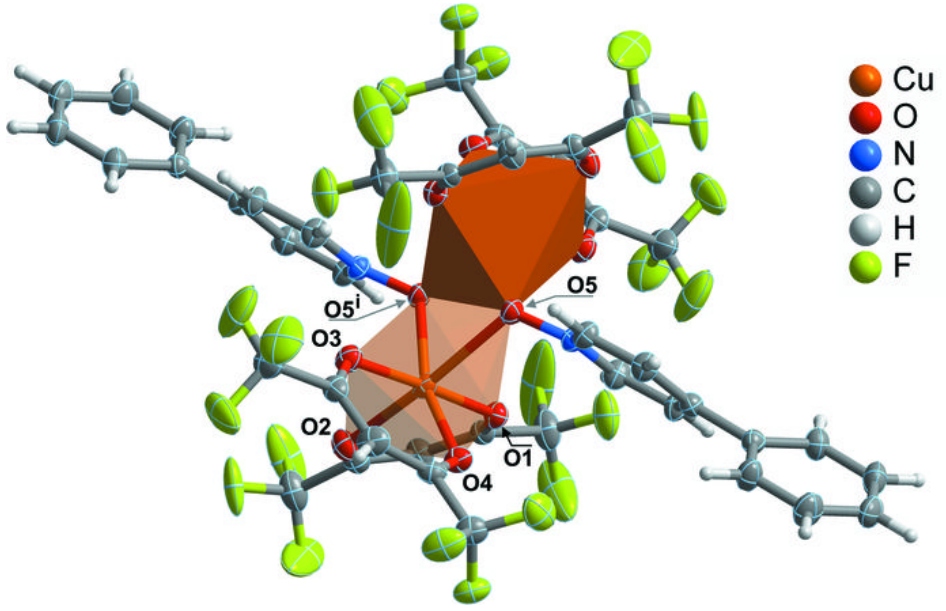
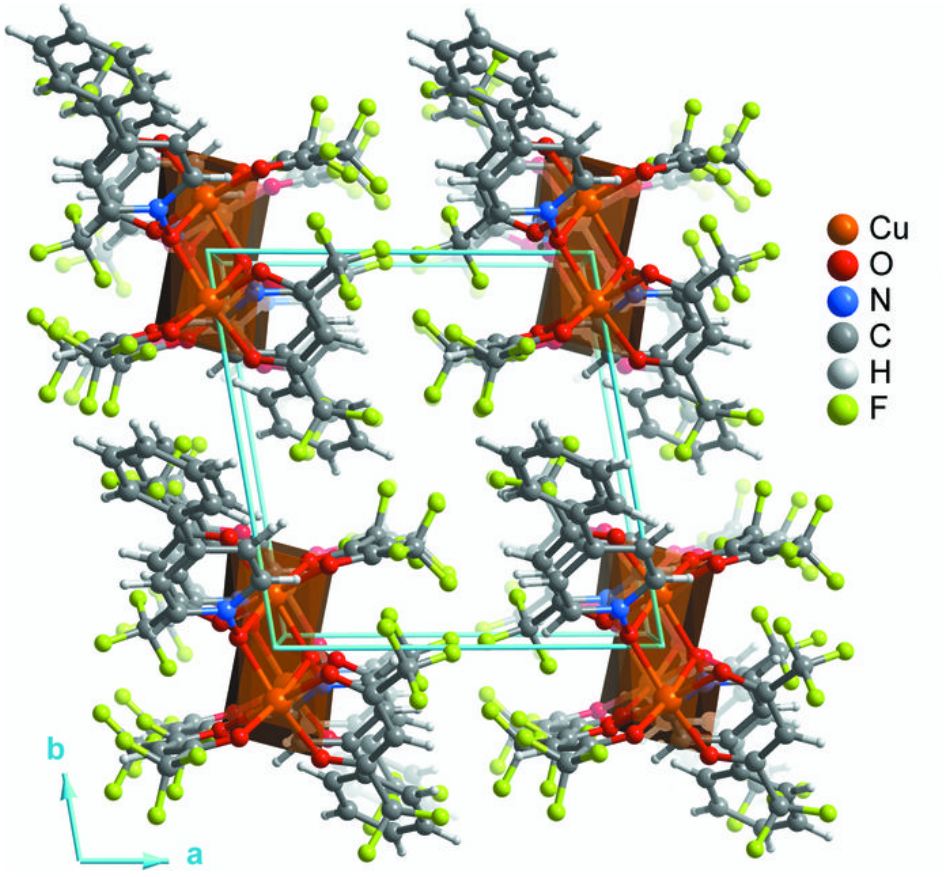


Fig. 2



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4-[(3,4-Dimethoxybenzylidene)amino]-1,5-dimethyl-2-phenyl-1*H*-pyrazol-3(2*H*)-one

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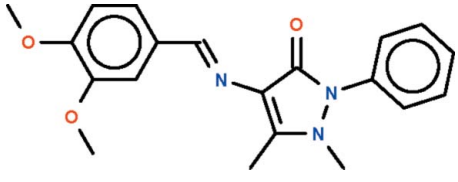
Key indicators: single-crystal X-ray study; T = 100 K; mean σ(C–C) = 0.002 Å; R factor = 0.037; wR factor = 0.103; data-to-parameter ratio = 17.4.

The imino–carbon double-bond in the title Schiff base, $C_{20}H_{21}N_3O_3$, has an E configuration; the six-membered aromatic substituent (r.m.s. deviation = 0.012 Å) is nearly coplanar with five-membered pyrazole substituent (r.m.s. deviation = 0.031 Å), the dihedral angle between the two systems being 11.4 (1)°]. The phenyl ring connected to the pyrazole ring is aligned at 45.5 (1)° with respect to this five-membered ring. The N atoms in the ring show pyramidal coordinations.

Related literature

For background literature on Schiff bases derived from 4-aminoantipyridine, see: Montalvo-González & Ariza-Castolo (2003).



Experimental

Crystal data

$C_{20}H_{21}N_3O_3$
M_r = 351.40
Monoclinic, $P2_1/c$
a = 12.5584 (8) Å
b = 10.4752 (7) Å
c = 14.6002 (9) Å
β = 109.039 (1)°
V = 1815.6 (2) Å^3
Z = 4
Mo $K\alpha$ radiation
μ = 0.09 mm^{-1}
T = 100 K
0.35 × 0.25 × 0.15 mm

Data collection

Bruker SMART APEX diffractometer
16900 measured reflections
4164 independent reflections
3442 reflections with $I > 2\sigma(I)$
R_{int} = 0.031

Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.037
$wR(F^2)$ = 0.103
S = 1.00
4164 reflections
239 parameters
H-atom parameters constrained
$\Delta\rho_{max}$ = 0.23 e Å^{-3}
$\Delta\rho_{min}$ = −0.24 e Å^{-3}

Data collection: *APEX2* (Bruker, 2009); cell refinement: *SAINT* (Bruker, 2009); data reduction: *SAINT*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *X-SEED* (Barbour, 2001); software used to prepare material for publication: *publCIF* (Westrip, 2010).

We thank King Abdul Aziz University and the University of Malaya for supporting this study.

Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: CV2733).

References

Barbour, L. J. (2001). *J. Supramol. Chem.* **1**, 189–191.
Bruker (2009). *APEX2* and *SAINT*. Bruker AXS Inc., Madison, Wisconsin, USA.
Montalvo-González, R. & Ariza-Castolo, A. (2003). *J. Mol. Struct.* **655**, 375–389.
Sheldrick, G. M. (2008). *Acta Cryst.* A**64**, 112–122.
Westrip, S. P. (2010). *J. Appl. Cryst.* **43**. Submitted.

supplementary materials

Acta Cryst. (2010). E**66**, o1732 [**doi:10.1107/S1600536810023238**]

4-[(3,4-Dimethoxybenzylidene)amino]-1,5-dimethyl-2-phenyl-1*H*-pyrazol-3(2*H*)-one

A. M. Asiri, S. A. Khan, K. W. Tan and S. W. Ng

Comment

4-Aminoantipyrine (4-amino-1,2-dihydro-1,5-dimethyl-2-phenyl-3*H*-pyrazol-3-one) possesses an aminopyrazolone unit, a feature that allows the compound to condense with aromatic aldehydes to yield Schiff bases. The Schiff base derived from the benzaldehyde homolog has nearly coplanar phenyl and pyrazoly rings (Montalvo-González & Ariza-Castolo, 2003). In the title benzaldehyde analog (Scheme I, Fig. 1), the 6-membered ring is nearly coplanar with 5-membered pyrazolyl ring [dihedral angle between the two systems 11.4 (1) °]. The phenyl ring connected to the pyrazolyl ring is aligned at 45.5 (1)°.

Experimental

3,4-Dimethoxybenzaldehyde (0.36 g, 2.2 mmol) and 4-aminoantipyrine (0.45 g, 2.2 mmol) here heated in methanol (15 ml) for 5 h to afford a colorless precipitate. The solid material was collected and recrystallized from methanol.

Refinement

Carbon-bound H-atoms were placed in calculated positions [C–H 0.95 to 0.98 Å, U(H) 1.2 to 1.5U_{eq}(C)] and were included in the refinement in the riding model approximation.

Figures

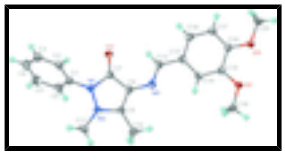


Fig. 1. Displacement ellipsoid plot (Barbour, 2001) of $C_{20}H_{21}N_3O_3$ at the 70% probability level; hydrogen atoms are drawn as spheres of arbitrary radius.

4-[(3,4-Dimethoxybenzylidene)amino]-1,5-dimethyl-2-phenyl- 1*H*-pyrazol-3(2*H*)-one

Crystal data

$C_{20}H_{21}N_3O_3$	F(000) = 744
M_r = 351.40	D_x = 1.286 Mg m^{-3}
Monoclinic, $P2_1/c$	Mo $K\alpha$ radiation, λ = 0.71073 Å
Hall symbol: -P 2ybc	Cell parameters from 6153 reflections
a = 12.5584 (8) Å	θ = 2.4–28.2°
b = 10.4752 (7) Å	μ = 0.09 mm^{-1}
c = 14.6002 (9) Å	T = 100 K
β = 109.039 (1)°	Prism, colourless
V = 1815.6 (2) Å^3	0.35 × 0.25 × 0.15 mm

$Z = 4$

Data collection

Bruker SMART APEX diffractometer	3442 reflections with $I > 2\sigma(I)$
Radiation source: fine-focus sealed tube	$R_{int} = 0.031$
graphite	$\theta_{max} = 27.5°$, $\theta_{min} = 1.7°$
ω scans	$h = -16 \rightarrow 16$
16900 measured reflections	$k = -13 \rightarrow 12$
4164 independent reflections	$l = -18 \rightarrow 17$

Refinement

Refinement on F^2	Primary atom site location: structure-invariant direct methods
Least-squares matrix: full	Secondary atom site location: difference Fourier map
$R[F^2 > 2\sigma(F^2)] = 0.037$	Hydrogen site location: inferred from neighbouring sites
$wR(F^2) = 0.103$	H-atom parameters constrained
$S = 1.00$	$w = 1/[\sigma^2(F_o^2) + (0.0548P)^2 + 0.5659P]$ where $P = (F_o^2 + 2F_c^2)/3$
4164 reflections	$(\Delta/\sigma)_{max} = 0.001$
239 parameters	$\Delta\rho_{max} = 0.23$ e Å^{-3}
0 restraints	$\Delta\rho_{min} = -0.24$ e Å^{-3}

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å^2)

	x	*y*	*z*	U_{iso}*/U_{eq}
O1	0.28425 (6)	0.77513 (8)	0.59527 (6)	0.01980 (19)
O2	0.86240 (7)	0.62990 (8)	0.50221 (6)	0.02147 (19)
O3	0.86452 (8)	0.84966 (8)	0.42541 (7)	0.0292 (2)
N1	0.26678 (8)	0.60441 (9)	0.69085 (7)	0.0185 (2)
N2	0.33485 (8)	0.50111 (9)	0.73701 (7)	0.0190 (2)
N3	0.50498 (8)	0.62594 (9)	0.60372 (7)	0.0187 (2)
C1	0.18777 (9)	0.65675 (11)	0.73138 (8)	0.0189 (2)
C2	0.09077 (9)	0.71284 (11)	0.66951 (9)	0.0204 (2)
H2	0.0778	0.7155	0.6017	0.025*
C3	0.01286 (10)	0.76508 (12)	0.70792 (9)	0.0235 (3)
H3	−0.0530	0.8052	0.6662	0.028*
C4	0.03033 (10)	0.75915 (12)	0.80662 (9)	0.0252 (3)
H4	−0.0240	0.7936	0.8323	0.030*
C5	0.12751 (11)	0.70267 (13)	0.86781 (9)	0.0258 (3)
H5	0.1394	0.6982	0.9354	0.031*
C6	0.20713 (10)	0.65278 (12)	0.83089 (9)	0.0230 (3)
H6	0.2745	0.6161	0.8731	0.028*
C7	0.31965 (9)	0.67280 (11)	0.63587 (8)	0.0171 (2)
C8	0.41934 (9)	0.59911 (11)	0.64197 (8)	0.0173 (2)

C9	0.42229 (9)	0.49573 (11)	0.70009 (8)	0.0179 (2)
C10	0.50361 (10)	0.38826 (12)	0.72347 (9)	0.0231 (3)
H10A	0.5663	0.4077	0.6996	0.035*
H10B	0.4657	0.3102	0.6924	0.035*
H10C	0.5326	0.3759	0.7938	0.035*
C11	0.27490 (10)	0.38645 (11)	0.75111 (9)	0.0225 (3)
H11A	0.2343	0.4054	0.7965	0.034*
H11B	0.3292	0.3177	0.7774	0.034*
H11C	0.2212	0.3597	0.6888	0.034*
C12	0.49724 (9)	0.72136 (11)	0.54678 (8)	0.0191 (2)
H12	0.4304	0.7713	0.5274	0.023*
C13	0.59014 (9)	0.75419 (11)	0.51128 (8)	0.0187 (2)
C14	0.68242 (9)	0.67130 (11)	0.52633 (8)	0.0182 (2)
H14	0.6838	0.5919	0.5582	0.022*
C15	0.77102 (9)	0.70504 (11)	0.49495 (8)	0.0186 (2)
C16	0.77122 (10)	0.82494 (11)	0.45064 (9)	0.0213 (2)
C17	0.68007 (11)	0.90626 (12)	0.43516 (9)	0.0241 (3)
H17	0.6794	0.9867	0.4049	0.029*
C18	0.58924 (10)	0.86946 (11)	0.46420 (9)	0.0222 (3)
H18	0.5257	0.9242	0.4515	0.027*
C19	0.87115 (10)	0.51317 (11)	0.55464 (9)	0.0229 (3)
H19A	0.9404	0.4687	0.5564	0.034*
H19B	0.8060	0.4590	0.5226	0.034*
H19C	0.8730	0.5316	0.6209	0.034*
C20	0.86692 (15)	0.96944 (14)	0.37878 (14)	0.0452 (4)
H20A	0.9381	0.9775	0.3652	0.068*
H20B	0.8605	1.0393	0.4213	0.068*
H20C	0.8038	0.9735	0.3179	0.068*

Atomic displacement parameters (Å^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
O1	0.0190 (4)	0.0167 (4)	0.0230 (4)	0.0009 (3)	0.0060 (3)	0.0034 (3)
O2	0.0217 (4)	0.0182 (4)	0.0269 (4)	0.0041 (3)	0.0112 (3)	0.0044 (3)
O3	0.0333 (5)	0.0184 (4)	0.0463 (6)	0.0023 (4)	0.0273 (4)	0.0066 (4)
N1	0.0171 (4)	0.0173 (5)	0.0208 (5)	0.0008 (4)	0.0060 (4)	0.0036 (4)
N2	0.0183 (4)	0.0165 (5)	0.0216 (5)	0.0006 (4)	0.0057 (4)	0.0036 (4)
N3	0.0178 (4)	0.0192 (5)	0.0192 (5)	−0.0019 (4)	0.0062 (4)	−0.0020 (4)
C1	0.0170 (5)	0.0173 (5)	0.0228 (6)	−0.0038 (4)	0.0071 (4)	−0.0013 (5)
C2	0.0188 (5)	0.0214 (6)	0.0208 (6)	−0.0040 (4)	0.0060 (4)	−0.0001 (5)
C3	0.0176 (5)	0.0232 (6)	0.0293 (6)	−0.0018 (5)	0.0071 (5)	−0.0010 (5)
C4	0.0241 (6)	0.0237 (6)	0.0319 (7)	−0.0058 (5)	0.0147 (5)	−0.0083 (5)
C5	0.0302 (6)	0.0271 (7)	0.0212 (6)	−0.0061 (5)	0.0097 (5)	−0.0051 (5)
C6	0.0220 (6)	0.0236 (6)	0.0211 (6)	−0.0021 (5)	0.0039 (5)	−0.0013 (5)
C7	0.0164 (5)	0.0169 (5)	0.0167 (5)	−0.0032 (4)	0.0038 (4)	−0.0016 (4)
C8	0.0163 (5)	0.0172 (5)	0.0174 (5)	−0.0008 (4)	0.0042 (4)	−0.0013 (4)
C9	0.0169 (5)	0.0179 (5)	0.0170 (5)	−0.0012 (4)	0.0030 (4)	−0.0019 (4)
C10	0.0232 (6)	0.0190 (6)	0.0258 (6)	0.0036 (5)	0.0064 (5)	0.0027 (5)

C11	0.0249 (6)	0.0185 (6)	0.0251 (6)	−0.0033 (5)	0.0096 (5)	0.0031 (5)
C12	0.0184 (5)	0.0198 (6)	0.0189 (5)	0.0007 (4)	0.0060 (4)	−0.0012 (4)
C13	0.0207 (5)	0.0190 (6)	0.0171 (5)	−0.0008 (4)	0.0070 (4)	−0.0022 (4)
C14	0.0219 (5)	0.0160 (5)	0.0170 (5)	−0.0006 (4)	0.0069 (4)	0.0001 (4)
C15	0.0206 (5)	0.0161 (5)	0.0192 (5)	0.0017 (4)	0.0069 (4)	−0.0019 (4)
C16	0.0250 (6)	0.0184 (6)	0.0253 (6)	−0.0005 (5)	0.0149 (5)	−0.0008 (5)
C17	0.0325 (6)	0.0166 (6)	0.0284 (6)	0.0030 (5)	0.0169 (5)	0.0034 (5)
C18	0.0256 (6)	0.0191 (6)	0.0241 (6)	0.0046 (5)	0.0113 (5)	0.0006 (5)
C19	0.0246 (6)	0.0176 (6)	0.0273 (6)	0.0028 (5)	0.0095 (5)	0.0041 (5)
C20	0.0552 (9)	0.0222 (7)	0.0797 (12)	0.0092 (7)	0.0513 (9)	0.0175 (7)

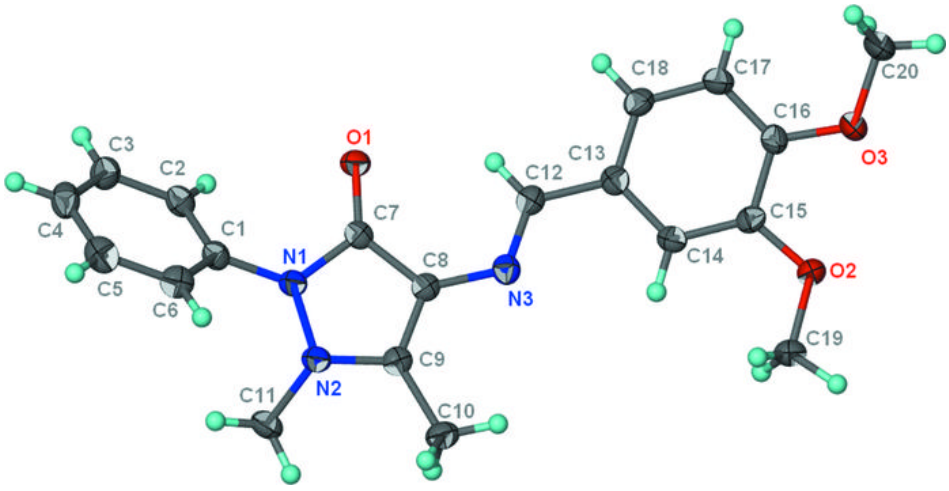
Geometric parameters (Å, °)

O1—C7	1.2354 (14)	C9—C10	1.4830 (16)
O2—C15	1.3669 (14)	C10—H10A	0.9800
O2—C19	1.4277 (14)	C10—H10B	0.9800
O3—C16	1.3627 (14)	C10—H10C	0.9800
O3—C20	1.4326 (16)	C11—H11A	0.9800
N1—C7	1.3950 (14)	C11—H11B	0.9800
N1—N2	1.4072 (13)	C11—H11C	0.9800
N1—C1	1.4206 (15)	C12—C13	1.4638 (16)
N2—C9	1.3731 (15)	C12—H12	0.9500
N2—C11	1.4673 (14)	C13—C18	1.3876 (17)
N3—C12	1.2833 (15)	C13—C14	1.4067 (16)
N3—C8	1.3926 (14)	C14—C15	1.3804 (16)
C1—C2	1.3883 (16)	C14—H14	0.9500
C1—C6	1.3933 (17)	C15—C16	1.4132 (16)
C2—C3	1.3890 (17)	C16—C17	1.3851 (17)
C2—H2	0.9500	C17—C18	1.3946 (17)
C3—C4	1.3865 (18)	C17—H17	0.9500
C3—H3	0.9500	C18—H18	0.9500
C4—C5	1.3879 (19)	C19—H19A	0.9800
C4—H4	0.9500	C19—H19B	0.9800
C5—C6	1.3839 (18)	C19—H19C	0.9800
C5—H5	0.9500	C20—H20A	0.9800
C6—H6	0.9500	C20—H20B	0.9800
C7—C8	1.4486 (15)	C20—H20C	0.9800
C8—C9	1.3688 (16)		
C15—O2—C19	116.78 (9)	H10B—C10—H10C	109.5
C16—O3—C20	116.62 (10)	N2—C11—H11A	109.5
C7—N1—N2	109.98 (9)	N2—C11—H11B	109.5
C7—N1—C1	124.72 (10)	H11A—C11—H11B	109.5
N2—N1—C1	119.67 (9)	N2—C11—H11C	109.5
C9—N2—N1	106.39 (9)	H11A—C11—H11C	109.5
C9—N2—C11	122.28 (10)	H11B—C11—H11C	109.5
N1—N2—C11	115.93 (9)	N3—C12—C13	120.78 (10)
C12—N3—C8	120.78 (10)	N3—C12—H12	119.6
C2—C1—C6	120.57 (11)	C13—C12—H12	119.6
C2—C1—N1	118.44 (10)	C18—C13—C14	119.19 (11)

C6—C1—N1	120.99 (10)	C18—C13—C12	120.08 (10)
C1—C2—C3	119.23 (11)	C14—C13—C12	120.71 (10)
C1—C2—H2	120.4	C15—C14—C13	120.15 (11)
C3—C2—H2	120.4	C15—C14—H14	119.9
C4—C3—C2	120.56 (11)	C13—C14—H14	119.9
C4—C3—H3	119.7	O2—C15—C14	125.03 (10)
C2—C3—H3	119.7	O2—C15—C16	114.87 (10)
C3—C4—C5	119.73 (11)	C14—C15—C16	120.10 (10)
C3—C4—H4	120.1	O3—C16—C17	125.23 (11)
C5—C4—H4	120.1	O3—C16—C15	115.00 (10)
C6—C5—C4	120.37 (12)	C17—C16—C15	119.77 (11)
C6—C5—H5	119.8	C16—C17—C18	119.66 (11)
C4—C5—H5	119.8	C16—C17—H17	120.2
C5—C6—C1	119.50 (11)	C18—C17—H17	120.2
C5—C6—H6	120.2	C13—C18—C17	121.05 (11)
C1—C6—H6	120.2	C13—C18—H18	119.5
O1—C7—N1	123.87 (10)	C17—C18—H18	119.5
O1—C7—C8	131.33 (10)	O2—C19—H19A	109.5
N1—C7—C8	104.77 (9)	O2—C19—H19B	109.5
C9—C8—N3	122.68 (10)	H19A—C19—H19B	109.5
C9—C8—C7	107.92 (10)	O2—C19—H19C	109.5
N3—C8—C7	129.26 (10)	H19A—C19—H19C	109.5
C8—C9—N2	110.34 (10)	H19B—C19—H19C	109.5
C8—C9—C10	128.36 (11)	O3—C20—H20A	109.5
N2—C9—C10	121.31 (10)	O3—C20—H20B	109.5
C9—C10—H10A	109.5	H20A—C20—H20B	109.5
C9—C10—H10B	109.5	O3—C20—H20C	109.5
H10A—C10—H10B	109.5	H20A—C20—H20C	109.5
C9—C10—H10C	109.5	H20B—C20—H20C	109.5
H10A—C10—H10C	109.5		
C7—N1—N2—C9	−8.00 (12)	C7—C8—C9—N2	−3.61 (13)
C1—N1—N2—C9	−162.78 (10)	N3—C8—C9—C10	−8.03 (19)
C7—N1—N2—C11	−147.65 (10)	C7—C8—C9—C10	175.83 (11)
C1—N1—N2—C11	57.57 (13)	N1—N2—C9—C8	7.08 (12)
C7—N1—C1—C2	58.12 (15)	C11—N2—C9—C8	143.54 (11)
N2—N1—C1—C2	−151.03 (10)	N1—N2—C9—C10	−172.41 (10)
C7—N1—C1—C6	−121.50 (12)	C11—N2—C9—C10	−35.94 (16)
N2—N1—C1—C6	29.34 (16)	C8—N3—C12—C13	176.26 (10)
C6—C1—C2—C3	−0.05 (17)	N3—C12—C13—C18	−168.62 (11)
N1—C1—C2—C3	−179.68 (10)	N3—C12—C13—C14	9.85 (17)
C1—C2—C3—C4	−1.31 (18)	C18—C13—C14—C15	0.35 (17)
C2—C3—C4—C5	1.22 (18)	C12—C13—C14—C15	−178.13 (10)
C3—C4—C5—C6	0.25 (19)	C19—O2—C15—C14	−6.31 (16)
C4—C5—C6—C1	−1.59 (19)	C19—O2—C15—C16	174.22 (10)
C2—C1—C6—C5	1.50 (18)	C13—C14—C15—O2	−177.20 (10)
N1—C1—C6—C5	−178.89 (11)	C13—C14—C15—C16	2.23 (17)
N2—N1—C7—O1	−172.69 (10)	C20—O3—C16—C17	−0.3 (2)
C1—N1—C7—O1	−19.46 (17)	C20—O3—C16—C15	178.96 (13)
N2—N1—C7—C8	5.75 (12)	O2—C15—C16—O3	−2.53 (15)

C1—N1—C7—C8	158.98 (10)	C14—C15—C16—O3	177.98 (11)
C12—N3—C8—C9	177.56 (11)	O2—C15—C16—C17	176.81 (11)
C12—N3—C8—C7	−7.18 (18)	C14—C15—C16—C17	−2.68 (18)
O1—C7—C8—C9	176.90 (12)	O3—C16—C17—C18	179.80 (12)
N1—C7—C8—C9	−1.37 (12)	C15—C16—C17—C18	0.52 (19)
O1—C7—C8—N3	1.1 (2)	C14—C13—C18—C17	−2.54 (18)
N1—C7—C8—N3	−177.18 (11)	C12—C13—C18—C17	175.95 (11)
N3—C8—C9—N2	172.54 (10)	C16—C17—C18—C13	2.10 (19)

Fig. 1


C18
C17
C20
C16
O3
O1
C3
C2
C12
C13
C7
C15
C4
C1
N1
C8
C14
O2
C5
C6
N3
C19
C9
N2
C11
C10

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N-Ethyl-*N*-(2-methoxyphenyl)benzenesulfonamide

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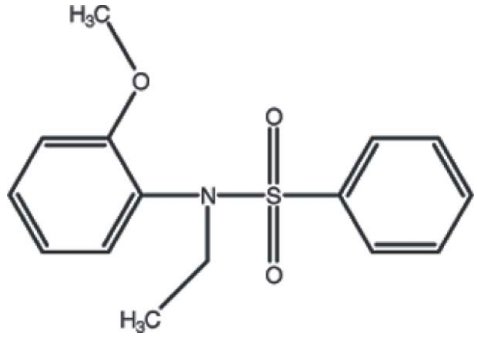
Key indicators: single-crystal X-ray study; T = 296 K; mean σ(C–C) = 0.004 Å; R factor = 0.051; wR factor = 0.157; data-to-parameter ratio = 20.1.

In the title molecule, $C_{15}H_{17}NO_3S$, the C—S—N—$C_{benzene}$ torsion angle is 81.45 (16)°, and the two aromatic rings form a dihedral angle of 45.83 (12)°. In the crystal structure, weak intermolecular C—H···O hydrogen bonds link the molecules into chains parallel to the b axis.

Related literature

For the biological activity of sulfonamides, see: Ozbek *et al.* (2007); Parari *et al.* (2008). For related structures, see: Mariam *et al.* (2009); Arshad *et al.* (2009); Asiri *et al.* (2009); Khan *et al.* (2010); Akkurt *et al.* (2010*a*,*b*).



Experimental

Crystal data

$C_{15}H_{17}NO_3S$
M_r = 291.37
Monoclinic, $P2_1/c$
a = 9.3098 (5) Å
b = 9.5664 (6) Å
c = 17.1949 (10) Å
β = 104.040 (2)°
V = 1485.65 (15) Å^3
Z = 4
Mo $K\alpha$ radiation
μ = 0.22 mm^{-1}
T = 296 K
0.15 × 0.10 × 0.06 mm

Data collection

Bruker APEXII CCD diffractometer
13197 measured reflections
3670 independent reflections
1963 reflections with $I > 2\sigma(I)$
R_{int} = 0.045

Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.051
$wR(F^2)$ = 0.157
S = 0.99
3670 reflections
183 parameters
H-atom parameters constrained
$\Delta\rho_{max}$ = 0.30 e Å^{-3}
$\Delta\rho_{min}$ = −0.27 e Å^{-3}

Table 1
Hydrogen-bond geometry (Å, °).

D—H···A	D—H	H···A	D···A	D—H···A
C6—H6···O2^{i}	0.93	2.53	3.300 (3)	140

Symmetry code: (i) $-x+2, y-\frac{1}{2}, -z+\frac{1}{2}$.

Data collection: *APEX2* (Bruker, 2007); cell refinement: *SAINT* (Bruker, 2007); data reduction: *SAINT*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *ORTEP-3 for Windows* (Farrugia, 1997); software used to prepare material for publication: *WinGX* (Farrugia, 1999) and *PLATON* (Spek, 2009).

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Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: CV2735).

References

Akkurt, M., Yalçın, Ş. P., Türkmen, H. & Büyükgüngör, O. (2010*a*). *Acta Cryst.* E**66**, o1596.
Akkurt, M., Yalçın, Ş. P., Türkmen, H. & Büyükgüngör, O. (2010*b*). *Acta Cryst.* E**66**, o1559–o1560.
Arshad, M. N., Khan, I. U., Akkurt, M. & Shafiq, M. (2009). *Acta Cryst.* E**65**, o1953–o1954.
Asiri, A. M., Akkurt, M., Khan, S. A., Arshad, M. N., Khan, I. U. & Sharif, H. M. A. (2009). *Acta Cryst.* E**65**, o1246–o1247.
Bruker (2007). *APEX2* and *SAINT*. Bruker AXS Inc., Madison, Wisconsin, USA.
Farrugia, L. J. (1997). *J. Appl. Cryst.* **30**, 565.
Farrugia, L. J. (1999). *J. Appl. Cryst.* **32**, 837–838.
Khan, I. U., Sharif, S., Akkurt, M., Sajjad, A. & Ahmad, J. (2010). *Acta Cryst.* E**66**, o786.
Mariam, I., Akkurt, M., Sharif, S., Akhtar, N. & Khan, I. U. (2009). *Acta Cryst.* E**65**, o2797.
Ozbek, N., Katircioglu, H., Karacan, N. & Baykal, T. (2007). *Bioorg. Med. Chem.* **15**, 5105–5109.
Parari, M. K., Panda, G., Srivastava, K. & Puri, S. K. (2008). *Bioorg. Med. Chem. Lett.* **18**, 776–781.
Sheldrick, G. M. (2008). *Acta Cryst.* A**64**, 112–122.
Spek, A. L. (2009). *Acta Cryst.* D**65**, 148–155.

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supplementary materials

Acta Cryst. (2010). E**66**, o1728 [**doi:10.1107/S1600536810023287**]

N-Ethyl-*N*-(2-methoxyphenyl)benzenesulfonamide

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Comment

Sulfonamides are known as biologically active compounds (Ozbek *et al.*, 2007; Parari *et al.*, 2008). As a contribution to a structural study of sulfonamide derivatives (Mariam *et al.*, 2009; Arshad *et al.*, 2009; Asiri *et al.*, 2009; Khan *et al.*, 2010; Akkurt *et al.*, 2010*a*,b) we present here the title compound, (I).

The title molecule (Fig. 1) is bent at the S atoms with the C1—S1—N1—C9 torsion angle of 81.45 (16)°. The dihedral angle between the phenyl (C1–C6) and benzene (C9–C14) rings is 45.83 (12)°.

In the crystal structure of (I), weak intermolecular C—H···O hydrogen bonds (Table 1) link the molecules into chains parallel to *b* axis.

Experimental

A mixture of *N*-(2-methoxyphenyl)benzenesulfonamide (1.24 g, 5.0 mmol), sodium hydride (0.24 g, 10 mmol) and *N*,*N*-dimethylformamide (10 ml) was stirred at room temperature for 30 min and then ethyl iodide (0.4 ml, 5.0 mmol) was added. The stirring was continued further for a period of 3 h and the contents were poured over crushed ice. The precipitated product was isolated, washed and re-crystallized from methanolic solution. It was crystallized by slow evaporation of the solvent. Yield 72%.

Refinement

All H atoms bonded to C atoms were positioned geometrically and refined using a riding model, with C—H = 0.93Å (aromatic), 0.96 Å (methyl) and 0.97 Å (methylene) with U_{iso}(H) = 1.2U_{eq}(aromatic, methylene) and U_{iso}(H) = 1.5U_{eq}(methyl).

Figures

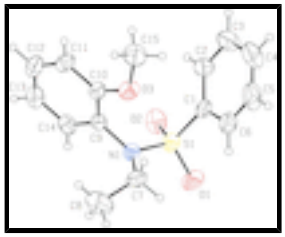


Fig. 1. Molecular structure of (I) showing the atom labelling scheme, Displacement ellipsoids are drawn at the 30% probability level.

N-Ethyl-*N*-(2-methoxyphenyl)benzenesulfonamide

Crystal data

$C_{15}H_{17}NO_3S$	$F(000) = 616$
$M_r = 291.37$	$D_x = 1.303$ Mg m^{-3}
Monoclinic, $P2_1/c$	Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å
Hall symbol: -P 2ybc	Cell parameters from 3431 reflections
$a = 9.3098$ (5) Å	$\theta = 2.3$–$24.5°$
$b = 9.5664$ (6) Å	$\mu = 0.22$ mm^{-1}
$c = 17.1949$ (10) Å	$T = 296$ K
$\beta = 104.040$ (2)°	Block, colourless
$V = 1485.65$ (15) Å^3	0.15 × 0.10 × 0.06 mm
$Z = 4$	

Data collection

Bruker APEXII CCD diffractometer	1963 reflections with $I > 2\sigma(I)$
Radiation source: sealed tube	$R_{int} = 0.045$
graphite	$\theta_{max} = 28.3°$, $\theta_{min} = 3.1°$
φ and ω scans	$h = -12\rightarrow10$
13197 measured reflections	$k = -11\rightarrow12$
3670 independent reflections	$l = -20\rightarrow22$

Refinement

Refinement on F^2	Primary atom site location: structure-invariant direct methods
Least-squares matrix: full	Secondary atom site location: difference Fourier map
$R[F^2 > 2\sigma(F^2)] = 0.051$	Hydrogen site location: inferred from neighbouring sites
$wR(F^2) = 0.157$	H-atom parameters constrained
$S = 0.99$	$w = 1/[\sigma^2(F_o^2) + (0.0842P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
3670 reflections	$(\Delta/\sigma)_{max} < 0.001$
183 parameters	$\Delta\rho_{max} = 0.30$ e Å^{-3}
0 restraints	$\Delta\rho_{min} = -0.27$ e Å^{-3}

Special details

Geometry. Bond distances, angles *etc*. have been calculated using the rounded fractional coordinates. All su's are estimated from the variances of the (full) variance-covariance matrix. The cell e.s.d.'s are taken into account in the estimation of distances, angles and torsion angles

Refinement. Refinement on F^2 for ALL reflections except those flagged by the user for potential systematic errors. Weighted *R*-factors *wR* and all goodnesses of fit *S* are based on F^2, conventional *R*-factors *R* are based on *F*, with *F* set to zero for negative F^2. The

observed criterion of $F^2 > \sigma(F^2)$ is used only for calculating -*R*-factor-obs *etc*. and is not relevant to the choice of reflections for refinement. *R*-factors based on F^2 are statistically about twice as large as those based on *F*, and *R*-factors based on ALL data will be even larger.

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å^2)

	x	*y*	*z*	U_{iso}*/U_{eq}
S1	0.86267 (6)	0.81474 (6)	0.18075 (4)	0.0619 (2)
O1	0.99631 (18)	0.7591 (2)	0.16733 (12)	0.0964 (8)
O2	0.81194 (19)	0.94809 (17)	0.14864 (9)	0.0771 (7)
O3	0.57342 (18)	0.66902 (16)	0.25621 (9)	0.0675 (6)
N1	0.73281 (18)	0.70249 (17)	0.14324 (10)	0.0532 (6)
C1	0.8828 (2)	0.8200 (2)	0.28471 (13)	0.0557 (7)
C2	0.8216 (3)	0.9285 (2)	0.31844 (14)	0.0687 (9)
C3	0.8335 (3)	0.9308 (3)	0.39875 (16)	0.0899 (11)
C4	0.9055 (4)	0.8251 (4)	0.44612 (18)	0.1036 (15)
C5	0.9646 (4)	0.7163 (4)	0.4127 (2)	0.1047 (14)
C6	0.9558 (3)	0.7136 (3)	0.33214 (17)	0.0809 (10)
C7	0.7640 (3)	0.5514 (2)	0.15704 (15)	0.0723 (9)
C8	0.6825 (4)	0.4652 (3)	0.09012 (17)	0.1080 (13)
C9	0.5821 (2)	0.7500 (2)	0.12968 (11)	0.0476 (7)
C10	0.5011 (2)	0.7321 (2)	0.18716 (12)	0.0498 (7)
C11	0.3558 (2)	0.7784 (2)	0.17143 (14)	0.0633 (9)
C12	0.2933 (3)	0.8395 (2)	0.09883 (17)	0.0740 (10)
C13	0.3707 (3)	0.8566 (2)	0.04225 (15)	0.0722 (9)
C14	0.5157 (3)	0.8111 (2)	0.05732 (13)	0.0605 (8)
C15	0.5112 (3)	0.6721 (3)	0.32343 (15)	0.0878 (11)
H2	0.77210	1.00010	0.28620	0.0820*
H3	0.79260	1.00430	0.42150	0.1080*
H4	0.91440	0.82730	0.50120	0.1240*
H5	1.01110	0.64350	0.44500	0.1260*
H6	0.99860	0.64090	0.30970	0.0970*
H7A	0.86930	0.53530	0.16450	0.0870*
H7B	0.73710	0.52310	0.20580	0.0870*
H8A	0.57950	0.46310	0.09050	0.1620*
H8B	0.72140	0.37180	0.09570	0.1620*
H8C	0.69320	0.50430	0.04040	0.1620*
H11	0.30120	0.76820	0.20970	0.0760*
H12	0.19550	0.86980	0.08830	0.0890*
H13	0.32660	0.89860	−0.00640	0.0870*
H14	0.56880	0.82170	0.01840	0.0730*
H15A	0.47490	0.76430	0.32950	0.1320*
H15B	0.58550	0.64750	0.37070	0.1320*
H15C	0.43090	0.60650	0.31570	0.1320*

Atomic displacement parameters (Å^2)

U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}

S1	0.0444 (4)	0.0686 (4)	0.0765 (4)	−0.0128 (3)	0.0219 (3)	−0.0093 (3)
O1	0.0473 (10)	0.1239 (15)	0.1290 (16)	−0.0121 (10)	0.0426 (10)	−0.0311 (12)
O2	0.0798 (12)	0.0655 (11)	0.0836 (11)	−0.0281 (9)	0.0152 (8)	0.0088 (8)
O3	0.0664 (10)	0.0780 (11)	0.0630 (10)	0.0078 (8)	0.0252 (8)	0.0158 (7)
N1	0.0449 (10)	0.0534 (11)	0.0631 (11)	−0.0040 (8)	0.0167 (8)	−0.0081 (8)
C1	0.0362 (11)	0.0496 (12)	0.0761 (15)	−0.0024 (9)	0.0033 (10)	−0.0073 (10)
C2	0.0755 (17)	0.0528 (14)	0.0751 (16)	0.0057 (12)	0.0132 (12)	−0.0031 (11)
C3	0.111 (2)	0.0808 (19)	0.0776 (19)	0.0022 (17)	0.0224 (16)	−0.0168 (15)
C4	0.127 (3)	0.106 (3)	0.0640 (17)	−0.010 (2)	−0.0037 (17)	−0.0083 (16)
C5	0.110 (3)	0.089 (2)	0.087 (2)	0.0113 (18)	−0.0303 (18)	0.0097 (17)
C6	0.0691 (17)	0.0680 (16)	0.089 (2)	0.0152 (13)	−0.0131 (14)	−0.0081 (13)
C7	0.0600 (15)	0.0580 (15)	0.1008 (18)	0.0077 (11)	0.0233 (13)	−0.0162 (12)
C8	0.143 (3)	0.0672 (18)	0.122 (2)	−0.0313 (18)	0.048 (2)	−0.0282 (16)
C9	0.0446 (12)	0.0434 (11)	0.0553 (12)	−0.0076 (9)	0.0130 (9)	−0.0070 (9)
C10	0.0464 (12)	0.0459 (11)	0.0576 (12)	−0.0058 (9)	0.0135 (9)	−0.0012 (9)
C11	0.0455 (13)	0.0638 (14)	0.0839 (17)	−0.0052 (10)	0.0224 (11)	−0.0003 (12)
C12	0.0492 (14)	0.0662 (16)	0.099 (2)	0.0021 (11)	0.0035 (13)	0.0004 (13)
C13	0.0691 (18)	0.0655 (15)	0.0701 (16)	−0.0038 (12)	−0.0059 (13)	0.0066 (12)
C14	0.0645 (15)	0.0628 (14)	0.0537 (13)	−0.0128 (11)	0.0132 (11)	−0.0029 (10)
C15	0.093 (2)	0.110 (2)	0.0686 (17)	−0.0052 (17)	0.0353 (14)	0.0107 (14)

Geometric parameters (Å, °)

S1—O1	1.4226 (19)	C12—C13	1.354 (4)
S1—O2	1.4243 (17)	C13—C14	1.382 (4)
S1—N1	1.6286 (18)	C2—H2	0.9300
S1—C1	1.752 (2)	C3—H3	0.9300
O3—C10	1.356 (2)	C4—H4	0.9300
O3—C15	1.413 (3)	C5—H5	0.9300
N1—C7	1.482 (3)	C6—H6	0.9300
N1—C9	1.439 (3)	C7—H7A	0.9700
C1—C2	1.378 (3)	C7—H7B	0.9700
C1—C6	1.376 (3)	C8—H8A	0.9600
C2—C3	1.359 (4)	C8—H8B	0.9600
C3—C4	1.368 (5)	C8—H8C	0.9600
C4—C5	1.367 (5)	C11—H11	0.9300
C5—C6	1.368 (4)	C12—H12	0.9300
C7—C8	1.468 (4)	C13—H13	0.9300
C9—C10	1.392 (3)	C14—H14	0.9300
C9—C14	1.378 (3)	C15—H15A	0.9600
C10—C11	1.386 (3)	C15—H15B	0.9600
C11—C12	1.373 (4)	C15—H15C	0.9600
O1···C11^{i}	3.336 (3)	C11···H15A	2.6800
O1···C12^{i}	3.347 (3)	C11···H15C	2.9200
O2···C6^{ii}	3.300 (3)	C15···H11	2.5800
O2···C14	3.113 (3)	H2···O2	2.5300
O3···N1	2.734 (2)	H2···C11^{v}	3.0800
O3···C2	3.383 (3)	H2···H15C^{v}	2.4600

O3···C7	2.965 (3)	H3···H8C^{viii}	2.4400
O3···C1	3.152 (3)	H4···O1^{viii}	2.8900
O1···H11^{i}	2.7600	H6···O1	2.6900
O1···H7A	2.4400	H6···O2^{vi}	2.5300
O1···H4^{iii}	2.8900	H7A···O1	2.4400
O1···H12^{i}	2.7600	H7A···C1^{vi}	3.0600
O1···H6	2.6900	H7A···C2^{vi}	3.0000
O2···H13^{iv}	2.8800	H7B···O3	2.3800
O2···H15C^{v}	2.9100	H7B···C10	2.9300
O2···H2	2.5300	H8A···C9	2.8200
O2···H6^{ii}	2.5300	H8A···H15A^{ix}	2.4700
O3···H7B	2.3800	H8C···C3^{iii}	3.0900
N1···O3	2.734 (2)	H8C···H3^{iii}	2.4400
C1···O3	3.152 (3)	H11···O1^{vii}	2.7600
C2···O3	3.383 (3)	H11···C15	2.5800
C6···O2^{vi}	3.300 (3)	H11···H15A	2.2900
C6···C7	3.472 (4)	H11···H15C	2.4700
C7···C6	3.472 (4)	H12···O1^{vii}	2.7600
C7···O3	2.965 (3)	H13···O2^{iv}	2.8800
C11···O1^{vii}	3.336 (3)	H14···H15B^{iii}	2.6000
C12···O1^{vii}	3.347 (3)	H15A···C11	2.6800
C14···O2	3.113 (3)	H15A···H11	2.2900
C1···H7A^{ii}	3.0600	H15A···C8^{v}	2.9600
C2···H7A^{ii}	3.0000	H15A···H8A^{v}	2.4700
C3···H8C^{viii}	3.0900	H15B···H14^{viii}	2.6000
C8···H15A^{ix}	2.9600	H15C···C11	2.9200
C9···H8A	2.8200	H15C···H11	2.4700
C10···H7B	2.9300	H15C···O2^{ix}	2.9100
C11···H2^{ix}	3.0800	H15C···H2^{ix}	2.4600
O1—S1—O2	119.54 (11)	C4—C3—H3	120.00
O1—S1—N1	106.47 (10)	C3—C4—H4	120.00
O1—S1—C1	107.15 (11)	C5—C4—H4	120.00
O2—S1—N1	107.01 (10)	C4—C5—H5	120.00
O2—S1—C1	108.24 (10)	C6—C5—H5	120.00
N1—S1—C1	107.96 (9)	C1—C6—H6	120.00
C10—O3—C15	119.46 (18)	C5—C6—H6	120.00
S1—N1—C7	118.81 (15)	N1—C7—H7A	109.00
S1—N1—C9	117.18 (13)	N1—C7—H7B	109.00
C7—N1—C9	118.65 (18)	C8—C7—H7A	109.00
S1—C1—C2	119.88 (16)	C8—C7—H7B	109.00
S1—C1—C6	119.90 (18)	H7A—C7—H7B	108.00
C2—C1—C6	120.2 (2)	C7—C8—H8A	109.00
C1—C2—C3	120.0 (2)	C7—C8—H8B	109.00
C2—C3—C4	120.1 (3)	C7—C8—H8C	109.00

C3—C4—C5	120.1 (3)	H8A—C8—H8B	109.00
C4—C5—C6	120.6 (3)	H8A—C8—H8C	109.00
C1—C6—C5	119.1 (3)	H8B—C8—H8C	109.00
N1—C7—C8	112.2 (2)	C10—C11—H11	120.00
N1—C9—C10	121.41 (17)	C12—C11—H11	120.00
N1—C9—C14	119.11 (19)	C11—C12—H12	119.00
C10—C9—C14	119.5 (2)	C13—C12—H12	119.00
O3—C10—C9	115.92 (17)	C12—C13—H13	120.00
O3—C10—C11	124.52 (19)	C14—C13—H13	120.00
C9—C10—C11	119.56 (19)	C9—C14—H14	120.00
C10—C11—C12	119.4 (2)	C13—C14—H14	120.00
C11—C12—C13	121.5 (2)	O3—C15—H15A	109.00
C12—C13—C14	119.6 (2)	O3—C15—H15B	109.00
C9—C14—C13	120.5 (2)	O3—C15—H15C	109.00
C1—C2—H2	120.00	H15A—C15—H15B	109.00
C3—C2—H2	120.00	H15A—C15—H15C	109.00
C2—C3—H3	120.00	H15B—C15—H15C	109.00
O1—S1—N1—C7	42.39 (19)	S1—C1—C2—C3	178.2 (2)
O1—S1—N1—C9	−163.78 (15)	C6—C1—C2—C3	0.1 (4)
O2—S1—N1—C7	171.30 (16)	S1—C1—C6—C5	−177.1 (2)
O2—S1—N1—C9	−34.87 (17)	C2—C1—C6—C5	1.0 (4)
C1—S1—N1—C7	−72.39 (18)	C1—C2—C3—C4	−0.4 (4)
C1—S1—N1—C9	81.45 (16)	C2—C3—C4—C5	−0.5 (5)
O1—S1—C1—C2	144.01 (19)	C3—C4—C5—C6	1.7 (6)
O1—S1—C1—C6	−38.0 (2)	C4—C5—C6—C1	−1.9 (5)
O2—S1—C1—C2	13.9 (2)	N1—C9—C10—O3	0.7 (3)
O2—S1—C1—C6	−168.12 (19)	N1—C9—C10—C11	−179.48 (18)
N1—S1—C1—C2	−101.66 (19)	C14—C9—C10—O3	178.90 (18)
N1—S1—C1—C6	76.4 (2)	C14—C9—C10—C11	−1.2 (3)
C15—O3—C10—C9	167.2 (2)	N1—C9—C14—C13	179.41 (18)
C15—O3—C10—C11	−12.7 (3)	C10—C9—C14—C13	1.1 (3)
S1—N1—C7—C8	−148.4 (2)	O3—C10—C11—C12	−179.24 (19)
C9—N1—C7—C8	58.1 (3)	C9—C10—C11—C12	0.9 (3)
S1—N1—C9—C10	−93.0 (2)	C10—C11—C12—C13	−0.5 (3)
S1—N1—C9—C14	88.8 (2)	C11—C12—C13—C14	0.4 (3)
C7—N1—C9—C10	60.9 (3)	C12—C13—C14—C9	−0.7 (3)
C7—N1—C9—C14	−117.4 (2)		

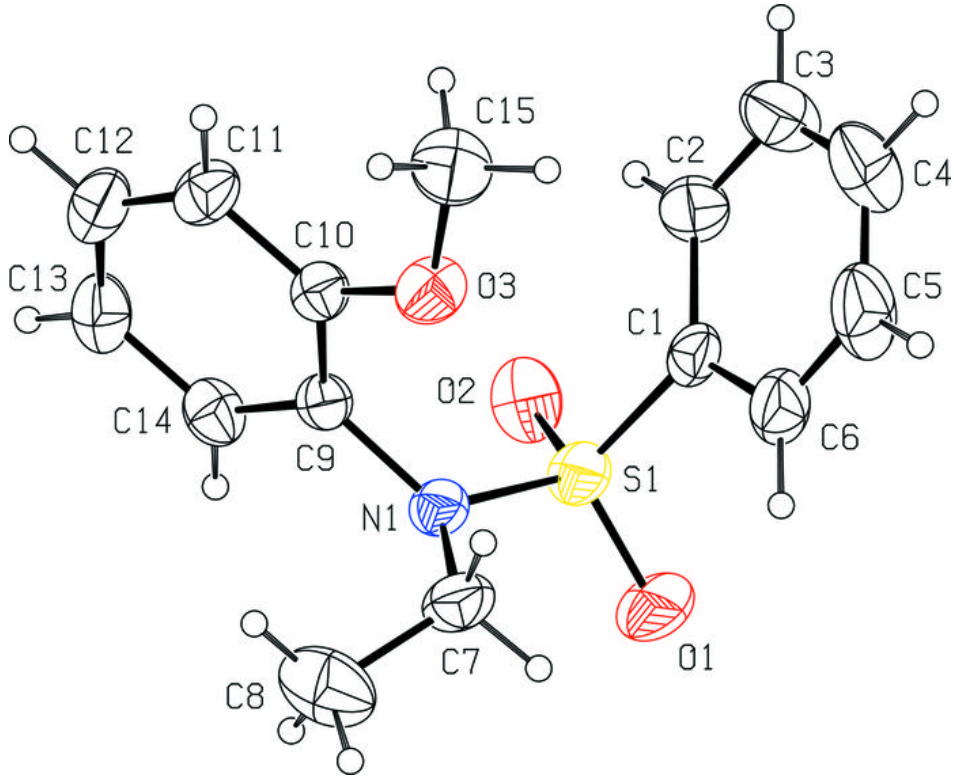
Symmetry codes: (i) *x*+1, *y*, *z*; (ii) −*x*+2, *y*+1/2, −*z*+1/2; (iii) *x*, −*y*+3/2, *z*−1/2; (iv) −*x*+1, −*y*+2, −*z*; (v) −*x*+1, *y*+1/2, −*z*+1/2; (vi) −*x*+2, *y*−1/2, −*z*+1/2; (vii) *x*−1, *y*, *z*; (viii) *x*, −*y*+3/2, *z*+1/2; (ix) −*x*+1, *y*−1/2, −*z*+1/2.

Hydrogen-bond geometry (Å, °)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
C2—H2···O2	0.93	2.53	2.905 (3)	104
C6—H6···O2^{vi}	0.93	2.53	3.300 (3)	140
C7—H7A···O1	0.97	2.44	2.911 (3)	109
C7—H7B···O3	0.97	2.38	2.965 (3)	118

Symmetry codes: (vi) −*x*+2, *y*−1/2, −*z*+1/2.

Fig. 1



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(*E*)-2-[(4-Iodophenyl)iminomethyl]-6-methylphenol

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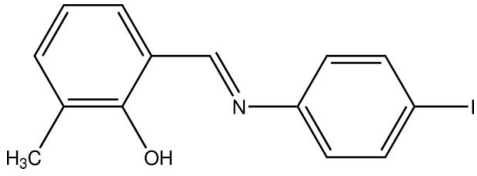
Key indicators: single-crystal X-ray study; T = 293 K; mean σ(C–C) = 0.010 Å; R factor = 0.037; wR factor = 0.078; data-to-parameter ratio = 14.5.

The title compound, $C_{14}H_{12}INO$, adopts the phenol–imine tautomeric form. The dihedral angle between the aromatic rings is 20.6 (3)°. The molecular conformation is stabilized by an intramolecular O—H···N hydrogen bond while in the crystal, weak intermolecular C—H···O hydrogen bonds link the molecules into a zigzag chain parallel to the *b* axis.

Related literature

For background to the properties and uses of Schiff bases, see: Barton & Ollis (1979); Layer (1963); Ingold (1969); Cohen *et al.* (1964); Taggi *et al.* (2002). For hydrogen-bond motifs, see: Bernstein *et al.* (1995). For comparative bond lengths, see: Şahin *et al.* (2009). For related structures, see: Özdemir *et al.* (2010); Tanak *et al.* (2009).



Experimental

Crystal data

$C_{14}H_{12}INO$
M_r = 337.15
Orthorhombic, $P2_12_12_1$
a = 4.6773 (4) Å
b = 11.6092 (12) Å
c = 23.6751 (4) Å
V = 1285.55 (17) Å^3
Z = 4
Mo $K\alpha$ radiation
μ = 2.47 mm^{-1}
T = 293 K
0.48 × 0.24 × 0.09 mm

Data collection

Stoe IPDS II diffractometer
Absorption correction: numerical (*X-AREA*; Stoe & Cie, 2002)
T_{min} = 0.520, T_{max} = 0.769
7548 measured reflections
2267 independent reflections
1541 reflections with $I > 2\sigma(I)$
R_{int} = 0.086

Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.037
$wR(F^2)$ = 0.078
S = 0.86
2267 reflections
156 parameters
H-atom parameters constrained
$\Delta\rho_{max}$ = 0.65 e Å^{-3}
$\Delta\rho_{min}$ = −0.29 e Å^{-3}
Absolute structure: Flack (1983), 901 Friedel pairs
Flack parameter: 0.10 (5)

Table 1
Hydrogen-bond geometry (Å, °).

D—H···A	D—H	H···A	D···A	D—H···A
O1—H1···N1	0.82	1.86	2.591 (8)	147
C13—H13···O1^{i}	0.93	2.51	3.348 (8)	150

Symmetry code: (i) $-x, y-\frac{1}{2}, -z+\frac{3}{2}$.

Data collection: *X-AREA* (Stoe & Cie, 2002); cell refinement: *X-AREA*; data reduction: *X-AREA*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *ORTEPIII* (Burnett & Johnson, 1996), *ORTEP-3 for Windows* (Farrugia, 1997) and *PLATON* (Spek, 2009); software used to prepare material for publication: *SHELXL97*.

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Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: DN2563).

References

Barton, D. & Ollis, W. D. (1979). *Comprehensive Organic Chemistry*, Vol 2. Oxford: Pergamon.
Bernstein, J., Davies, R. E., Shimoni, L. & Chang, N.-L. (1995). *Angew. Chem. Int. Ed. Engl.* **34**, 1555–1573.
Burnett, M. N. & Johnson, C. K. (1996). *ORTEPIII*. Report ORNL-6895. Oak Ridge National Laboratory, Tennessee, USA.
Cohen, M. D., Schmidt, G. M. J. & Flavian, S. (1964). *J. Chem. Soc.* pp. 1041–2051.
Farrugia, L. J. (1997). *J. Appl. Cryst.* **30**, 565.
Flack, H. D. (1983). *Acta Cryst.* A**39**, 876–881.
Ingold, C. K. (1969). Structure and Mechanism in Organic Chemistry, 2nd ed. Ithaca, USA: Cornell University.
Layer, R. W. (1963). *Chem. Rev.* **63**, 489–510.
Özdemir Tarı, G., Tanak, H., Macit, M., Erşahin, F. & Isık, Ş. (2010). *Acta Cryst.* E**66**, o85.
Şahin, Z. S., Işık, Ş., Erşahin, F. & Ağar, E. (2009). *Acta Cryst.* E**65**, o811.
Sheldrick, G. M. (2008). *Acta Cryst.* A**64**, 112–122.
Spek, A. L. (2009). *Acta Cryst.* D**65**, 148–155.
Stoe & Cie (2002). *X-AREA*. Stoe & Cie, Darmstadt, Germany.
Taggi, A. E., Hafez, A. M., Wack, H., Young, B., Ferraris, D. & Lectka, T. (2002). *J. Am. Chem. Soc.* **124**, 6626–6635.
Tanak, H., Erşahin, F., Köysal, Y., Agar, E., Işık, Ş. & Yavuz, M. (2009). *J. Mol. Model.* **15**, 1281–1290.

supplementary materials

Acta Cryst. (2010). E**66**, o1568 [**doi:10.1107/S160053681001826X**]

(*E*)-2-[(4-Iodophenyl)iminomethyl]-6-methylphenol

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Comment

Schiff bases are used as starting materials in the synthesis of important drugs, such as antibiotics and antiallergic, antiphlogistic, and antitumor substances (Barton *et al.*, 1979; Layer, 1963; Ingold 1969). On the industrial scale, they have a wide range of applications, such as dyes and pigments (Taggi *et al.*, 2002). There are two characteristic properties of Schiff bases, viz. Photochromism and thermochromism (Cohen *et al.*, 1964). In general, Schiff bases display two possible tautomeric forms, the phenol-imine (OH) and the keto-amine (NH) forms. Depending on the tautomers, two types of intramolecular hydrogen bonds are observed in Schiff bases: O—H···N in phenol-imine (Şahin *et al.*, 2009) and N—H···O in keto-amine tautomers (Tanak *et al.*, 2009). Another form of the Schiff base compounds is also known as zwitterion having an ionic intramolecular hydrogen bond (N^+—H···O^-) and this form is rarely seen in the solid state (Özdemir *et al.*, 2010).

The molecular structure of the title compound, $C_{14}H_{17}O_1N_1I_1$, shows that the molecule exists in the phenol-imine form (Fig. 1). The C1=N1 [1.269 (8) Å] and C9=N1 [1.397 (7) Å] bond distances are of double-bond character, whereas, C7—O1 [1.332 (8) Å] distance is single bond. These distances are similar to that reported in the literature [1.277 (3) Å] and [1.402 (3) Å] for C=N and [1.347 (3) Å] for C—O respectively (Şahin *et al.*, 2009).

The molecule of title compound is non-planar (Fig. 1), the two phenyl rings are twisted by a dihedral angle of 20.6 (3)°. This conformation is stabilized by intramolecular N-H···O hydrogen bond (Table 1, Fig. 1) forming S(6) ring (Bernstein *et al.*, 1995). weak intermolecular C-H···O hydrogen bonds link the molecules forming a zig-zag chain parallel to the b axis (Table 1, Fig. 2). The I atom is slightly out of the C9-C14 ring by 0.18 (1)Å.

Experimental

The compound (*E*)-2-[(4-Iodophenylimino)methyl]-6-methylphenol was prepared by reflux a mixture of a solution containing 3-methylsalicylaldehyde (0.1 ml 0.82 mmol) in 20 ml e thanol and solution containing 4-Iodoaniline (0.179 g 0.82 mmol) in 20 ml e thanol.The reaction mixture was stirred for 1 hunder reflux. The crystals of (*E*)-2-[(4-Iodophenylimino)methyl]-6-methylphenol suitable for x-ray analysis were obtained from ethylalcohol by slow evaporation (yield 51%; m.p.350-353 K).

Refinement

The position of the H1 atom was obtained from a difference map of the electron density in the unit-cell and was refined freely. Other H atoms were positioned geometrically and treated using a riding model, fixing the bond lengths at 0.93 Å for aromatic CH and at 0.96 Å for CH_3. The displacement parameters of the H atoms were constrained as $U_{iso}(H)= 1.2U_{eq}$($1.5U_{eq}$ for methyl) of the parent atom.

Figures

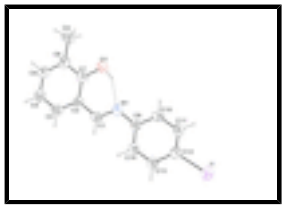


Fig. 1. The molecular structure of the title compound, showing the atom-numbering scheme and 30% probability displacement ellipsoids. H atoms are represented as small spheres of arbitrary radii. H bond is shown as dashed lines.

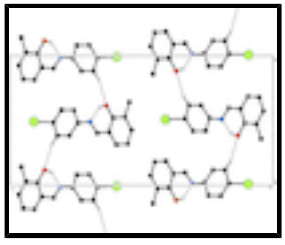


Fig. 2. Partial packing view showing the formation of zig-zag chain parallel to the b axis. H atoms not involved in hydrogen bondings have been omitted for clarity. C-H···O hydrogen bonds are represented as dashed lines

(*E*)-2-[(4-Iodophenyl)iminomethyl]-6-methylphenol

Crystal data

$C_{14}H_{12}INO$	$F(000) = 656$
$M_r = 337.15$	$D_x = 1.742$ Mg m^{-3}
Orthorhombic, $P2_12_12_1$	Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å
Hall symbol: P 2ac 2ab	Cell parameters from 7912 reflections
$a = 4.6773$ (4) Å	$\theta = 1.7$–$27.8°$
$b = 11.6092$ (12) Å	$\mu = 2.47$ mm^{-1}
$c = 23.6751$ (4) Å	$T = 293$ K
$V = 1285.55$ (17) Å^3	Prism, yellow
$Z = 4$	0.48 × 0.24 × 0.09 mm

Data collection

Stoe IPDS II diffractometer	2267 independent reflections
Radiation source: fine-focus sealed tube	1541 reflections with $I > 2\sigma(I)$
graphite	$R_{int} = 0.086$
Detector resolution: 6.67 pixels mm^{-1}	$\theta_{max} = 25.0°$, $\theta_{min} = 1.7°$
rotation method scans	$h = -5 \rightarrow 5$
Absorption correction: numerical (*X-AREA*; Stoe & Cie, 2002)	$k = -13 \rightarrow 13$
$T_{min} = 0.520$, $T_{max} = 0.769$	$l = -28 \rightarrow 28$
7548 measured reflections	

Refinement

Refinement on F^2	Secondary atom site location: difference Fourier map

Least-squares matrix: full	Hydrogen site location: inferred from neighbouring sites
$R[F^2 > 2\sigma(F^2)] = 0.037$	H-atom parameters constrained
$wR(F^2) = 0.078$	$w = 1/[\sigma^2(F_o^2) + (0.0321P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
$S = 0.86$	$(\Delta/\sigma)_{max} = 0.001$
2267 reflections	$\Delta\rho_{max} = 0.65$ e Å^{-3}
156 parameters	$\Delta\rho_{min} = -0.29$ e Å^{-3}
0 restraints	Absolute structure: Flack (1983), 901 Friedel pairs
Primary atom site location: structure-invariant direct methods	Flack parameter: 0.10 (5)

Special details

Geometry. All esds (except the esd in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell esds are taken into account individually in the estimation of esds in distances, angles and torsion angles; correlations between esds in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell esds is used for estimating esds involving l.s. planes.

Refinement. Refinement of F^2 against ALL reflections. The weighted *R*-factor wR and goodness of fit *S* are based on F^2, conventional *R*-factors *R* are based on *F*, with *F* set to zero for negative F^2. The threshold expression of $F^2 > \sigma(F^2)$ is used only for calculating *R*-factors(gt) etc. and is not relevant to the choice of reflections for refinement. *R*-factors based on F^2 are statistically about twice as large as those based on *F*, and *R*- factors based on ALL data will be even larger.

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å^2)

	x	*y*	*z*	U_{iso}*/U_{eq}
I1	0.81565 (9)	0.49212 (4)	0.907466 (15)	0.07878 (18)
O1	−0.3098 (17)	0.6170 (3)	0.6324 (2)	0.0759 (15)
H1	−0.2028	0.6014	0.6588	0.114*
N1	0.0187 (10)	0.4895 (5)	0.69451 (16)	0.0621 (12)
C1	−0.0685 (14)	0.4026 (6)	0.6669 (2)	0.0596 (16)
H15	0.0064	0.3306	0.6757	0.071*
C2	−0.2788 (18)	0.4106 (5)	0.6224 (3)	0.0553 (19)
C3	−0.3704 (13)	0.3134 (5)	0.5941 (3)	0.0639 (16)
H3	−0.2933	0.2423	0.6037	0.077*
C4	−0.5711 (17)	0.3190 (6)	0.5522 (3)	0.071 (2)
H4	−0.6369	0.2523	0.5348	0.085*
C5	−0.6755 (18)	0.4266 (6)	0.5361 (3)	0.0680 (18)
H5	−0.8058	0.4307	0.5065	0.082*
C6	−0.5925 (14)	0.5272 (6)	0.5624 (3)	0.0660 (19)
C7	−0.3895 (13)	0.5201 (5)	0.6065 (2)	0.0568 (15)
C8	−0.699 (2)	0.6422 (6)	0.5449 (3)	0.091 (3)
H8A	−0.8417	0.6332	0.5161	0.137*
H8B	−0.5434	0.6872	0.5305	0.137*
H8C	−0.7818	0.6806	0.5769	0.137*
C9	0.2092 (13)	0.4822 (5)	0.7398 (2)	0.0582 (13)
C10	0.3469 (18)	0.5806 (5)	0.7557 (3)	0.068 (2)

H10	0.3162	0.6479	0.7353	0.082*
C11	0.5354 (18)	0.5827 (6)	0.8024 (3)	0.069 (2)
H11	0.6340	0.6496	0.8118	0.083*
C12	0.5693 (13)	0.4850 (7)	0.8333 (2)	0.0636 (15)
C13	0.4354 (17)	0.3826 (6)	0.8184 (3)	0.0658 (19)
H13	0.4652	0.3158	0.8392	0.079*
C14	0.2599 (16)	0.3824 (5)	0.7726 (3)	0.068 (2)
H14	0.1697	0.3141	0.7625	0.081*

Atomic displacement parameters (Å^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
I1	0.0755 (3)	0.0930 (3)	0.0679 (2)	−0.0021 (4)	−0.0059 (2)	−0.0085 (3)
O1	0.099 (5)	0.053 (2)	0.076 (3)	−0.001 (3)	0.001 (3)	−0.001 (2)
N1	0.060 (3)	0.068 (3)	0.058 (2)	−0.011 (4)	0.002 (2)	−0.007 (3)
C1	0.058 (4)	0.056 (4)	0.064 (4)	0.008 (3)	0.009 (3)	0.002 (3)
C2	0.050 (5)	0.060 (4)	0.057 (3)	0.004 (3)	0.001 (3)	−0.001 (3)
C3	0.068 (5)	0.060 (3)	0.064 (3)	0.012 (3)	0.003 (4)	−0.003 (3)
C4	0.071 (5)	0.076 (5)	0.067 (4)	−0.004 (4)	0.000 (4)	−0.010 (3)
C5	0.060 (4)	0.086 (5)	0.058 (4)	0.005 (5)	0.006 (4)	0.010 (3)
C6	0.066 (4)	0.072 (5)	0.060 (3)	−0.007 (4)	0.011 (3)	0.012 (3)
C7	0.059 (4)	0.061 (4)	0.051 (3)	0.002 (4)	0.012 (2)	0.007 (3)
C8	0.109 (9)	0.080 (5)	0.085 (5)	0.012 (6)	−0.006 (5)	0.016 (4)
C9	0.058 (3)	0.052 (3)	0.066 (3)	0.003 (4)	0.003 (3)	−0.006 (3)
C10	0.078 (6)	0.054 (4)	0.073 (4)	0.005 (4)	0.007 (4)	0.014 (3)
C11	0.078 (5)	0.064 (4)	0.067 (4)	−0.017 (4)	0.001 (4)	−0.005 (3)
C12	0.063 (3)	0.076 (5)	0.052 (3)	0.000 (4)	0.004 (2)	0.001 (4)
C13	0.075 (5)	0.060 (4)	0.063 (4)	−0.001 (4)	−0.004 (4)	−0.002 (3)
C14	0.074 (7)	0.058 (4)	0.071 (4)	−0.006 (4)	−0.010 (4)	−0.007 (3)

Geometric parameters (Å, °)

I1—C12	2.102 (5)	C6—C7	1.415 (8)
O1—C7	1.334 (7)	C6—C8	1.484 (9)
O1—H1	0.8200	C8—H8A	0.9600
N1—C1	1.269 (8)	C8—H8B	0.9600
N1—C9	1.397 (7)	C8—H8C	0.9600
C1—C2	1.444 (10)	C9—C10	1.364 (9)
C1—H15	0.9300	C9—C14	1.414 (9)
C2—C3	1.381 (8)	C10—C11	1.415 (10)
C2—C7	1.423 (9)	C10—H10	0.9300
C3—C4	1.367 (9)	C11—C12	1.358 (9)
C3—H3	0.9300	C11—H11	0.9300
C4—C5	1.394 (10)	C12—C13	1.389 (10)
C4—H4	0.9300	C13—C14	1.359 (9)
C5—C6	1.379 (9)	C13—H13	0.9300
C5—H5	0.9300	C14—H14	0.9300
C7—O1—H1	109.5	C6—C8—H8B	109.5

C1—N1—C9	123.5 (6)	H8A—C8—H8B	109.5
N1—C1—C2	122.9 (6)	C6—C8—H8C	109.5
N1—C1—H15	118.5	H8A—C8—H8C	109.5
C2—C1—H15	118.5	H8B—C8—H8C	109.5
C3—C2—C7	119.2 (6)	C10—C9—N1	117.5 (6)
C3—C2—C1	120.9 (6)	C10—C9—C14	117.1 (5)
C7—C2—C1	119.9 (6)	N1—C9—C14	125.3 (6)
C4—C3—C2	121.8 (6)	C9—C10—C11	121.6 (6)
C4—C3—H3	119.1	C9—C10—H10	119.2
C2—C3—H3	119.1	C11—C10—H10	119.2
C3—C4—C5	118.8 (6)	C12—C11—C10	118.6 (6)
C3—C4—H4	120.6	C12—C11—H11	120.7
C5—C4—H4	120.6	C10—C11—H11	120.7
C6—C5—C4	122.4 (6)	C11—C12—C13	121.7 (5)
C6—C5—H5	118.8	C11—C12—I1	118.7 (5)
C4—C5—H5	118.8	C13—C12—I1	119.5 (5)
C5—C6—C7	118.3 (6)	C14—C13—C12	118.4 (6)
C5—C6—C8	122.8 (6)	C14—C13—H13	120.8
C7—C6—C8	118.9 (7)	C12—C13—H13	120.8
O1—C7—C6	118.6 (6)	C13—C14—C9	122.5 (6)
O1—C7—C2	122.0 (5)	C13—C14—H14	118.7
C6—C7—C2	119.4 (6)	C9—C14—H14	118.7
C6—C8—H8A	109.5		
C9—N1—C1—C2	176.1 (5)	C3—C2—C7—C6	0.5 (9)
N1—C1—C2—C3	−179.1 (6)	C1—C2—C7—C6	179.1 (5)
N1—C1—C2—C7	2.3 (9)	C1—N1—C9—C10	162.2 (6)
C7—C2—C3—C4	−2.0 (10)	C1—N1—C9—C14	−21.4 (9)
C1—C2—C3—C4	179.4 (6)	N1—C9—C10—C11	177.6 (6)
C2—C3—C4—C5	3.1 (10)	C14—C9—C10—C11	0.8 (10)
C3—C4—C5—C6	−2.8 (11)	C9—C10—C11—C12	−2.7 (11)
C4—C5—C6—C7	1.3 (10)	C10—C11—C12—C13	3.3 (11)
C4—C5—C6—C8	179.1 (7)	C10—C11—C12—I1	−173.8 (5)
C5—C6—C7—O1	−179.6 (6)	C11—C12—C13—C14	−2.0 (11)
C8—C6—C7—O1	2.6 (9)	I1—C12—C13—C14	175.1 (5)
C5—C6—C7—C2	−0.2 (9)	C12—C13—C14—C9	0.1 (11)
C8—C6—C7—C2	−178.0 (6)	C10—C9—C14—C13	0.5 (10)
C3—C2—C7—O1	179.9 (7)	N1—C9—C14—C13	−176.0 (6)
C1—C2—C7—O1	−1.5 (9)	C2—C1—N1—C9	176.1 (5)

Hydrogen-bond geometry (Å, °)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
O1—H1···N1	0.82	1.86	2.591 (8)	147.
C13—H13···O1^{i}	0.93	2.51	3.348 (8)	150.

Symmetry codes: (i) −*x*, *y*−1/2, −*z*+3/2.

Fig. 1

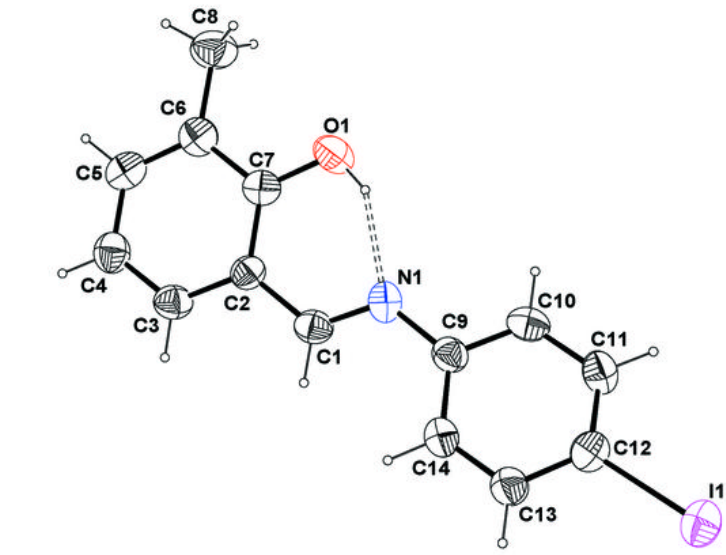
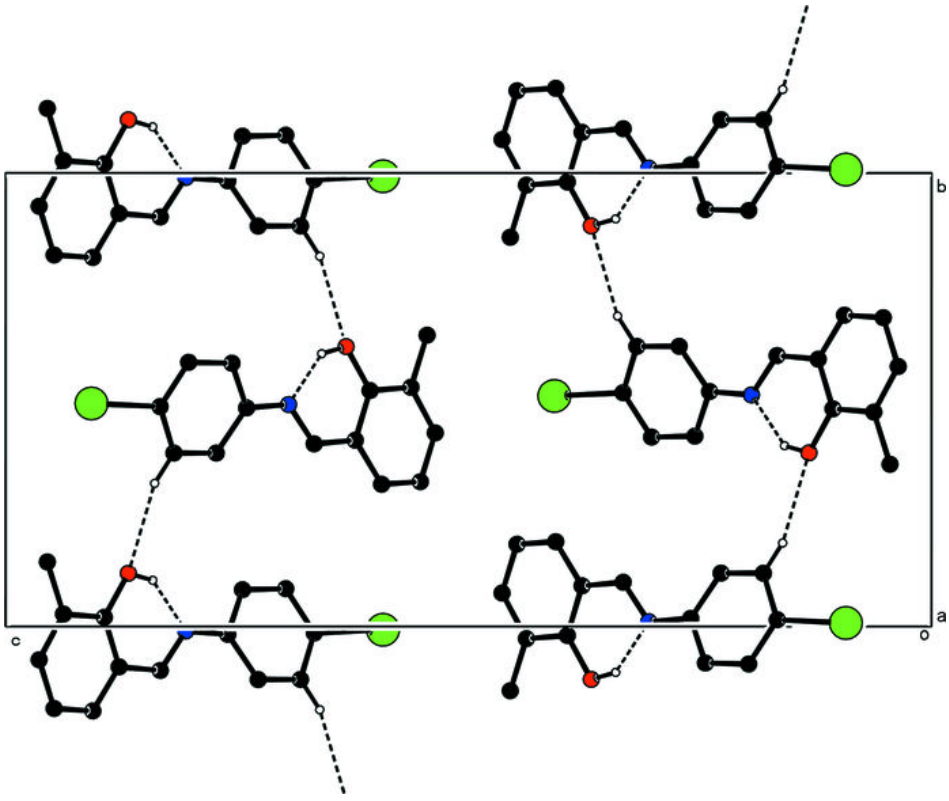


Fig. 2



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(*RS*)-1-(1-Acetylindolin-5-yl)-2-chloropropan-1-one

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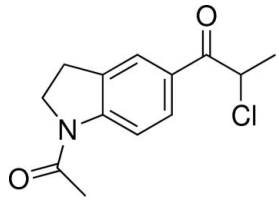
Key indicators: single-crystal X-ray study; T = 173 K; mean σ(C–C) = 0.003 Å; disorder in main residue; R factor = 0.043; wR factor = 0.111; data-to-parameter ratio = 14.6.

The molecule of the title compound, $C_{13}H_{14}ClNO_2$, is roughly planar [maximum deviation = 0.060 (2) Å] with the disordered Cl/CH_3 group asymetrically distributed on both sides of the mean plane. Indeed, the Cl and CH_3 located on the stereogenic carbon exchange each other with occupancy factors in the ratio 0.60:0.40. The whole crystal is a racemate. Non-classical C—H···O hydrogen bonds and π–π interactions [centroid–centroid distance = 3.6959 (9) Å] between symmetry-related phenyl rings stabilize the crystal structure.

Related literature

The title compound was synthesised as an intermediate in a search for a new synthetic route for silodosin, an adrenoceptor antagonist, see: Asselin *et al.* (2000); Bremner *et al.* (2000); Elworthy *et al.* (1997); Sorbera *et al.* (2001). For related structures, see: Moreno *et al.* (1998); Wang *et al.* (2007).



Experimental

Crystal data

$C_{13}H_{14}ClNO_2$
M_r = 251.70
Triclinic, $P\overline{1}$
a = 8.4748 (5) Å
b = 9.0928 (5) Å
c = 9.4952 (5) Å
α = 112.071 (1)°
β = 110.345 (1)°
γ = 99.913 (1)°
V = 595.92 (6) Å^3
Z = 2
Mo $K\alpha$ radiation
μ = 0.31 mm^{-1}
T = 173 K
0.46 × 0.36 × 0.15 mm

Data collection

Bruker SMART 1000 CCD diffractometer
Absorption correction: multi-scan (*SADABS*; Sheldrick, 2008*a*)
T_{min} = 0.871, T_{max} = 0.955
6682 measured reflections
2594 independent reflections
2242 reflections with $I > 2\sigma(I)$
R_{int} = 0.018

Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.043
$wR(F^2)$ = 0.111
S = 1.18
2594 reflections
178 parameters
3 restraints
H-atom parameters constrained
$\Delta\rho_{max}$ = 0.27 e Å^{-3}
$\Delta\rho_{min}$ = −0.21 e Å^{-3}

Table 1
Hydrogen-bond geometry (Å, °).

D—H···A	D—H	H···A	D···A	D—H···A
C1—H1B···O2^{i}	0.99	2.44	3.252 (3)	139
C4—H4···O1^{ii}	0.95	2.48	3.430 (2)	177
C12—H12···O1^{ii}	1.00	2.41	3.318 (2)	151

Symmetry codes: (i) $x, y-1, z$; (ii) $x-1, y, z$.

Data collection: *SMART* (Bruker, 2001); cell refinement: *SAINT-Plus* (Bruker, 2003); data reduction: *SAINT-Plus*; program(s) used to solve structure: *SHELXTL* (Sheldrick, 2008*b*); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *ORTEPIII* (Burnett & Johnson, 1996), *ORTEP-3 for Windows* (Farrugia, 1997) and *PLATON* (Spek, 2009); software used to prepare material for publication: *SHELXL97*.

The author thanks Mr Feng for helpful discussions.

Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: DN2565).

References

Asselin, A. A., Humber, L. G., Crocilla, D., Oshiro, G., Wojdan, A., Grimes, D., Heaslip, R. J., Rimele, T. J. & Shaw, C. C. (2000). *J. Med. Chem.* **29**, 1009–1015.
Bremner, J. B., Coban, B., Griffith, G., Groenewoud, K. M. & Yates, B. F. (2000). *Bioorg. Med. Chem.* **8**, 201–214.
Bruker (2001). *SMART*. Bruker AXS Inc., Madison, Wisconsin, USA.
Bruker (2003). *SAINT-Plus*. Bruker AXS Inc., Madison, Wisconsin, USA.
Burnett, M. N. & Johnson, C. K. (1996). *ORTEPIII*. Report ORNL-6895. Oak Ridge National Laboratory, Tennessee, USA.
Elworthy, T. R., Ford, A. P., Bantle, G. W. & Morgans, D. J. (1997). *J. Med. Chem.* **40**, 2674–2687.
Farrugia, L. J. (1997). *J. Appl. Cryst.* **30**, 565.
Moreno, M. M. T., Santos, R. H. A., Gambardella, M. T. P., Camargo, A. J., da Silva, A. B. F. & Trsic, M. (1998). *Struct. Chem.* **9**, 365–373.
Sheldrick, G. M. (2008*a*). *SADABS*. University of Göttingen, Germany.
Sheldrick, G. M. (2008*b*). *Acta Cryst.* A**64**, 112–122.
Sorbera, L. A., Caster, J. & Silvestre, J. S. (2001). *Drugs Future*, **26**, 553–555.
Spek, A. L. (2009). *Acta Cryst.* D**65**, 148–155.
Wang, Z., Wan, W., Jiang, H. & Hao, J. (2007). *J. Org. Chem.* **72**, 9364–9367.

supplementary materials

Acta Cryst. (2010). E**66**, o1617 [**doi:10.1107/S1600536810020969**]

(*RS*)-1-(1-Acetylindolin-5-yl)-2-chloropropan-1-one

X.-M. Yang

Comment

In searching for new synthetic route of silodosin, a adrenoceptor antagonist (Sorbera *et al.* 2001; Elworthy *et al.* 1997; Asselin *et al.* 2000; Bremner *et al.* 2000), we synthesized the racemic intermediate,(*R*/*S*)-1-(1-acetylindolin-5-yl)-2-chloropropan-1-one.

The single-crystal structure analysis shows that the Cl and CH_3 located on the stereogenic carbon exchange each other with occupancy factor in the ration 60/40. Except for these disordered atoms, the molecule is roughly planar with the largest deviation from the mean plane (all heavy atoms except Cl and C13) being 0.060 (2)Å at C7 (Fig. 1). The two disordered atoms are dissymetrically distributed on both side of the mean plane. The geometry within the 1-acetylindoline fragment compares well with related structures as 1-acetylindoline (Moreno *et al.*, 1998) or 1-(trifluoro)acetylindoline (Wang *et al.*, 2007).

Non-classical C—H···O hydrogen bonds (Table 1, Fig. 2) link the molecules forming layers parallel to the (0 0 1) plane. These layers are further connected throught π-π interactions between symmetry related phenyl rings (Table 2).

Experimental

3.3 g aluminium trichloride was added to 20 ml dichloromethane, and stirred for 10 min. Then 2 g chloropropionyl-chloride was added, controling the temperature below 5¯C. A dichloromethane solution of 1-acetyl-indoline was added dropwise to the reaction solution, and stirred overnight to get 1.3 g crystalline solid (yield 72%). Crystals suitable for X-ray diffraction were obtained by slow evaporation of an ethyl acetate solution. Spectroscopic analysis: ^{1}H NMR (CD-Cl_3,δ, p.p.m.): 1.723–1.760(d, 3H), 2.259–2.269(s, 3H), 3.232–3.289(t, 2H), 4.109–4.166(t, 2H), 5.197–5.263(m, 1H), 7.864(s,1*H*), 7.864–7.895(d, 1H), 8.245–8.273(d, 1H).

Refinement

All H atoms attached to C atoms and N atom were fixed geometrically and treated as riding with C—H = 0.98 Å (methyl), 0.99 Å (methylene) and 1.0 Å (methine) with U_{iso}(H) = 1.2U_{eq}(Cmethine, Cmethylene) or U_{iso}(H) = 1.5U_{eq}(Cmethyl).

The Cl and CH3 substituents on the stereogenic carbon are exchanging each other and such disorder induces two configurations. Two sets of positions were defined for the atoms of this group and the site occupation factor of each conformation were refined while restraining their sum to unity and using restraints on C—C and C—Cl distances with the help of SAME and PART instructions within *SHELXL97* (Sheldrick, 2008). In the last stage of refinement, the disordered Cl and C atoms were anisotropically refined but the anistropic thermal parameters of the C atoms were restrained to have similar atomic displacement parameters within a tolerance s.u. of 0.01 Å^2.

Figures

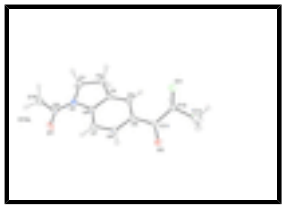


Fig. 1. The asymmetric unit of (I) with the atom-labelling scheme. Displacement ellipsoids are drawn at the 30% probability level. H atoms are represented as small spheres of arbitrary radii. For clarity, only the major component of the disorder is represented.

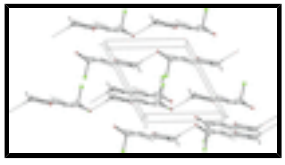


Fig. 2. Packing view showing the layers formed by C—H···O interaction. Hydrogen bonds are shown as dashed lines. H atoms not involved in hydrogen bondings have been omitted for clarity.

(*RS*)-1-(1-Acetylindolin-5-yl)-2-chloropropan-1-one

Crystal data

$C_{13}H_{14}ClNO_2$	$Z = 2$
$M_r = 251.70$	$F(000) = 264$
Triclinic, $P\overline{1}$	$D_x = 1.403$ Mg m^{-3}
Hall symbol: -P 1	Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å
$a = 8.4748$ (5) Å	Cell parameters from 4108 reflections
$b = 9.0928$ (5) Å	$\theta = 2.6$–$27.0°$
$c = 9.4952$ (5) Å	$\mu = 0.31$ mm^{-1}
$\alpha = 112.071$ (1)°	$T = 173$ K
$\beta = 110.345$ (1)°	Block, colorless
$\gamma = 99.913$ (1)°	0.46 × 0.36 × 0.15 mm
$V = 595.92$ (6) Å^3	

Data collection

Bruker SMART 1000 CCD diffractometer	2594 independent reflections
Radiation source: fine-focus sealed tube	2242 reflections with $I > 2\sigma(I)$
graphite	$R_{int} = 0.018$
ω scans	$\theta_{max} = 27.1°$, $\theta_{min} = 2.6°$
Absorption correction: multi-scan (*SADABS*; Sheldrick, 2008a)	$h = -10 \rightarrow 10$
$T_{min} = 0.871$, $T_{max} = 0.955$	$k = -11 \rightarrow 11$
6682 measured reflections	$l = -12 \rightarrow 12$

Refinement

Refinement on F^2	Primary atom site location: structure-invariant direct methods
Least-squares matrix: full	Secondary atom site location: difference Fourier map

$R[F^2 > 2\sigma(F^2)] = 0.043$	Hydrogen site location: inferred from neighbouring sites
$wR(F^2) = 0.111$	H-atom parameters constrained
$S = 1.18$	$w = 1/[\sigma^2(F_o^2) + (0.0322P)^2 + 0.3925P]$ where $P = (F_o^2 + 2F_c^2)/3$
2594 reflections	$(\Delta/\sigma)_{max} = 0.001$
178 parameters	$\Delta\rho_{max} = 0.27$ e Å^{-3}
3 restraints	$\Delta\rho_{min} = -0.20$ e Å^{-3}

Special details

Geometry. All e.s.d.'s (except the e.s.d. in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell e.s.d.'s are taken into account individually in the estimation of e.s.d.'s in distances, angles and torsion angles; correlations between e.s.d.'s in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell e.s.d.'s is used for estimating e.s.d.'s involving l.s. planes.

Refinement. Refinement of F^2 against ALL reflections. The weighted *R*-factor *wR* and goodness of fit *S* are based on F^2, conventional *R*-factors *R* are based on *F*, with *F* set to zero for negative F^2. The threshold expression of $F^2 > \sigma(F^2)$ is used only for calculating *R*-factors(gt) *etc*. and is not relevant to the choice of reflections for refinement. *R*-factors based on F^2 are statistically about twice as large as those based on *F*, and *R*- factors based on ALL data will be even larger.

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å^2)

	x	*y*	*z*	U_{iso}*/U_{eq}	Occ. (<1)
O1	0.9779 (2)	−0.01243 (19)	0.2587 (2)	0.0410 (4)	
O2	0.35372 (18)	0.39091 (17)	0.09272 (18)	0.0348 (3)	
N1	0.7298 (2)	−0.10127 (19)	0.28713 (19)	0.0271 (3)	
C1	0.6190 (3)	−0.2154 (3)	0.3214 (3)	0.0394 (5)	
H1A	0.6802	−0.1916	0.4415	0.047*	
H1B	0.5956	−0.3354	0.2463	0.047*	
C2	0.4441 (3)	−0.1788 (2)	0.2847 (3)	0.0323 (4)	
H2A	0.3427	−0.2765	0.1824	0.039*	
H2B	0.4166	−0.1526	0.3827	0.039*	
C3	0.4790 (2)	−0.0270 (2)	0.2553 (2)	0.0252 (4)	
C4	0.3712 (2)	0.0667 (2)	0.2265 (2)	0.0253 (4)	
H4	0.2594	0.0427	0.2300	0.030*	
C5	0.4281 (2)	0.1977 (2)	0.1918 (2)	0.0249 (4)	
C6	0.5941 (2)	0.2322 (2)	0.1900 (2)	0.0279 (4)	
H6	0.6319	0.3208	0.1661	0.033*	
C7	0.7055 (2)	0.1416 (2)	0.2219 (2)	0.0292 (4)	
H7	0.8188	0.1677	0.2217	0.035*	
C8	0.6455 (2)	0.0109 (2)	0.2544 (2)	0.0245 (4)	
C9	0.8883 (2)	−0.1095 (2)	0.2860 (2)	0.0296 (4)	
C10	0.9462 (3)	−0.2455 (3)	0.3189 (3)	0.0358 (4)	
H10A	0.8635	−0.3568	0.2239	0.054*	
H10B	0.9452	−0.2369	0.4246	0.054*	
H10C	1.0679	−0.2313	0.3298	0.054*	
C11	0.3175 (2)	0.3004 (2)	0.1525 (2)	0.0264 (4)	

C12	0.1597 (3)	0.2956 (2)	0.1952 (2)	0.0306 (4)	
H12	0.1025	0.1787	0.1740	0.037*	
C13	0.0115 (16)	0.3460 (17)	0.0833 (16)	0.058 (4)	0.60
H13A	−0.0826	0.3497	0.1206	0.087*	0.60
H13B	−0.0414	0.2617	−0.0370	0.087*	0.60
H13C	0.0678	0.4576	0.0975	0.087*	0.60
Cl1	0.2419 (3)	0.4356 (3)	0.40972 (18)	0.0464 (6)	0.60
C13B	0.244 (2)	0.4216 (19)	0.4003 (16)	0.072 (6)	0.40
H13D	0.3329	0.3851	0.4631	0.108*	0.40
H13E	0.1470	0.4173	0.4347	0.108*	0.40
H13F	0.3008	0.5379	0.4258	0.108*	0.40
Cl1B	0.0086 (5)	0.3588 (5)	0.0840 (4)	0.0361 (9)	0.40

Atomic displacement parameters (Å^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
O1	0.0371 (8)	0.0425 (8)	0.0621 (10)	0.0207 (7)	0.0328 (7)	0.0302 (8)
O2	0.0361 (8)	0.0331 (7)	0.0443 (8)	0.0126 (6)	0.0193 (6)	0.0256 (7)
N1	0.0263 (8)	0.0247 (7)	0.0326 (8)	0.0101 (6)	0.0141 (6)	0.0145 (6)
C1	0.0302 (10)	0.0397 (11)	0.0618 (14)	0.0153 (9)	0.0227 (10)	0.0337 (11)
C2	0.0300 (10)	0.0315 (10)	0.0448 (11)	0.0132 (8)	0.0193 (9)	0.0236 (9)
C3	0.0254 (9)	0.0245 (8)	0.0262 (9)	0.0074 (7)	0.0123 (7)	0.0123 (7)
C4	0.0241 (8)	0.0263 (9)	0.0282 (9)	0.0089 (7)	0.0139 (7)	0.0134 (7)
C5	0.0261 (9)	0.0228 (8)	0.0234 (8)	0.0082 (7)	0.0106 (7)	0.0092 (7)
C6	0.0298 (9)	0.0242 (9)	0.0324 (9)	0.0073 (7)	0.0160 (8)	0.0150 (8)
C7	0.0269 (9)	0.0290 (9)	0.0350 (10)	0.0095 (7)	0.0174 (8)	0.0152 (8)
C8	0.0247 (9)	0.0234 (8)	0.0240 (8)	0.0091 (7)	0.0112 (7)	0.0094 (7)
C9	0.0280 (9)	0.0282 (9)	0.0300 (9)	0.0120 (7)	0.0137 (8)	0.0097 (8)
C10	0.0338 (10)	0.0345 (10)	0.0415 (11)	0.0183 (8)	0.0179 (9)	0.0168 (9)
C11	0.0277 (9)	0.0208 (8)	0.0253 (9)	0.0056 (7)	0.0091 (7)	0.0094 (7)
C12	0.0346 (10)	0.0273 (9)	0.0390 (10)	0.0151 (8)	0.0197 (8)	0.0195 (8)
C13	0.058 (7)	0.049 (6)	0.073 (7)	0.007 (4)	0.035 (5)	0.034 (5)
Cl1	0.0466 (10)	0.0642 (12)	0.0263 (6)	0.0269 (8)	0.0168 (6)	0.0158 (6)
C13B	0.091 (12)	0.052 (7)	0.118 (12)	0.036 (7)	0.066 (9)	0.060 (8)
Cl1B	0.0366 (17)	0.0457 (16)	0.0344 (14)	0.0273 (14)	0.0139 (11)	0.0231 (12)

Geometric parameters (Å, °)

O1—C9	1.225 (2)	C7—C8	1.393 (3)
O2—C11	1.216 (2)	C7—H7	0.9500
N1—C9	1.362 (2)	C9—C10	1.504 (3)
N1—C8	1.408 (2)	C10—H10A	0.9800
N1—C1	1.482 (2)	C10—H10B	0.9800
C1—C2	1.525 (3)	C10—H10C	0.9800
C1—H1A	0.9900	C11—C12	1.525 (3)
C1—H1B	0.9900	C12—C13	1.598 (10)
C2—C3	1.509 (2)	C12—C13B	1.641 (13)
C2—H2A	0.9900	C12—Cl1B	1.689 (3)
C2—H2B	0.9900	C12—Cl1	1.736 (3)

C3—C4	1.380 (2)	C12—H12	0.9997
C3—C8	1.398 (2)	C13—H13A	0.9800
C4—C5	1.402 (2)	C13—H13B	0.9800
C4—H4	0.9500	C13—H13C	0.9800
C5—C6	1.395 (3)	C13B—H13D	0.9800
C5—C11	1.487 (2)	C13B—H13E	0.9800
C6—C7	1.385 (3)	C13B—H13F	0.9800
C6—H6	0.9500		
C9—N1—C8	126.44 (15)	N1—C9—C10	116.09 (17)
C9—N1—C1	123.37 (15)	C9—C10—H10A	109.5
C8—N1—C1	110.18 (14)	C9—C10—H10B	109.5
N1—C1—C2	105.33 (15)	H10A—C10—H10B	109.5
N1—C1—H1A	110.7	C9—C10—H10C	109.5
C2—C1—H1A	110.7	H10A—C10—H10C	109.5
N1—C1—H1B	110.7	H10B—C10—H10C	109.5
C2—C1—H1B	110.7	O2—C11—C5	121.51 (17)
H1A—C1—H1B	108.8	O2—C11—C12	119.99 (16)
C3—C2—C1	104.15 (15)	C5—C11—C12	118.47 (15)
C3—C2—H2A	110.9	C11—C12—C13	112.2 (5)
C1—C2—H2A	110.9	C11—C12—C13B	106.7 (7)
C3—C2—H2B	110.9	C13—C12—C13B	112.7 (8)
C1—C2—H2B	110.9	C11—C12—Cl1B	112.0 (2)
H2A—C2—H2B	108.9	C13—C12—Cl1B	2.8 (6)
C4—C3—C8	120.43 (16)	C13B—C12—Cl1B	110.3 (6)
C4—C3—C2	129.55 (16)	C11—C12—Cl1	108.14 (15)
C8—C3—C2	109.99 (15)	C13—C12—Cl1	109.6 (5)
C3—C4—C5	119.36 (16)	C13B—C12—Cl1	3.1 (7)
C3—C4—H4	120.3	Cl1B—C12—Cl1	107.28 (18)
C5—C4—H4	120.3	C11—C12—H12	109.1
C6—C5—C4	119.17 (16)	C13—C12—H12	108.7
C6—C5—C11	117.85 (16)	C13B—C12—H12	107.3
C4—C5—C11	122.97 (16)	Cl1B—C12—H12	111.2
C7—C6—C5	122.22 (16)	Cl1—C12—H12	109.0
C7—C6—H6	118.9	C12—C13—H13A	109.5
C5—C6—H6	118.9	C12—C13—H13B	109.5
C6—C7—C8	117.69 (17)	C12—C13—H13C	109.5
C6—C7—H7	121.2	C12—C13B—H13D	109.5
C8—C7—H7	121.2	C12—C13B—H13E	109.5
C7—C8—C3	121.11 (16)	H13D—C13B—H13E	109.5
C7—C8—N1	129.13 (16)	C12—C13B—H13F	109.5
C3—C8—N1	109.75 (15)	H13D—C13B—H13F	109.5
O1—C9—N1	121.97 (17)	H13E—C13B—H13F	109.5
O1—C9—C10	121.94 (17)		
C9—N1—C1—C2	−172.04 (17)	C9—N1—C8—C3	175.76 (17)
C8—N1—C1—C2	7.0 (2)	C1—N1—C8—C3	−3.2 (2)
N1—C1—C2—C3	−7.7 (2)	C8—N1—C9—O1	1.8 (3)
C1—C2—C3—C4	−175.90 (19)	C1—N1—C9—O1	−179.33 (19)
C1—C2—C3—C8	6.2 (2)	C8—N1—C9—C10	−177.82 (17)

C8—C3—C4—C5	1.6 (3)	C1—N1—C9—C10	1.1 (3)
C2—C3—C4—C5	−176.09 (18)	C6—C5—C11—O2	12.3 (3)
C3—C4—C5—C6	−1.0 (3)	C4—C5—C11—O2	−166.21 (17)
C3—C4—C5—C11	177.50 (16)	C6—C5—C11—C12	−165.37 (16)
C4—C5—C6—C7	−0.2 (3)	C4—C5—C11—C12	16.1 (3)
C11—C5—C6—C7	−178.82 (17)	O2—C11—C12—C13	25.4 (6)
C5—C6—C7—C8	0.8 (3)	C5—C11—C12—C13	−156.9 (5)
C6—C7—C8—C3	−0.2 (3)	O2—C11—C12—C13B	−98.5 (6)
C6—C7—C8—N1	178.75 (17)	C5—C11—C12—C13B	79.3 (6)
C4—C3—C8—C7	−1.0 (3)	O2—C11—C12—Cl1B	22.4 (3)
C2—C3—C8—C7	177.12 (17)	C5—C11—C12—Cl1B	−159.9 (2)
C4—C3—C8—N1	179.83 (16)	O2—C11—C12—Cl1	−95.6 (2)
C2—C3—C8—N1	−2.0 (2)	C5—C11—C12—Cl1	82.12 (19)
C9—N1—C8—C7	−3.3 (3)	C5—C11—C12—Cl1	82.12 (19)
C1—N1—C8—C7	177.69 (19)	C5—C11—C12—Cl1B	−159.9 (2)

Hydrogen-bond geometry (Å, °)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
C1—H1B···O2^{i}	0.99	2.44	3.252 (3)	139
C4—H4···O1^{ii}	0.95	2.48	3.430 (2)	177
C12—H12···O1^{ii}	1.00	2.41	3.318 (2)	151

Symmetry codes: (i) *x*, *y*−1, *z*; (ii) *x*−1, *y*, *z*.

Table 2

π-π stacking between symmetry-related phenyl rings. [Symmetry code: (iii) 1-x, -y, -z]

	Centroid–Centroid (Å)	Centroid-to-plane (Å)	Slippage (Å)
Cg1···Cg1^{iii}	3.6959 (9)	3.4713 (6)	1.269

Fig. 1

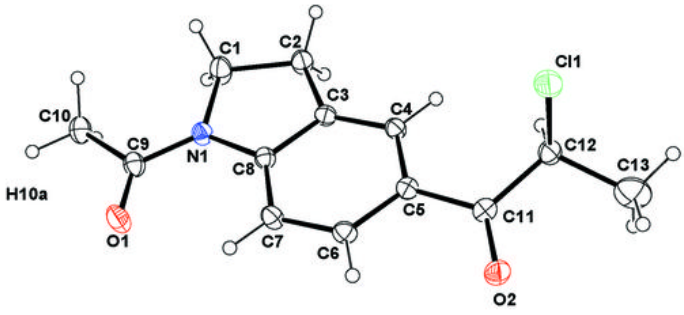
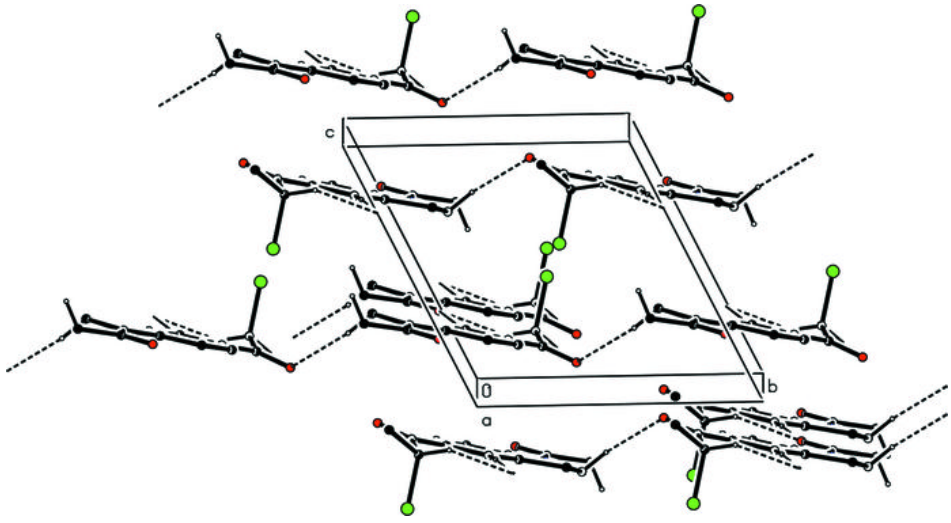


Fig. 2



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catena-Poly[di-$\mu_{1,1}$-azido-(1,10-phenanthroline)cadmium(II)]

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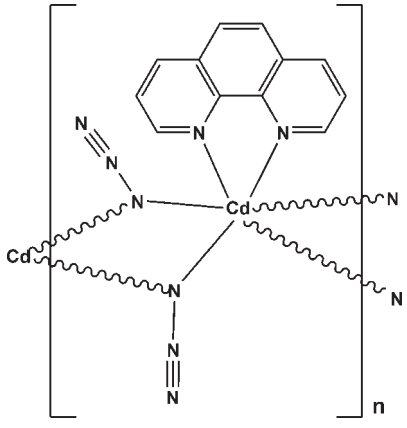
Key indicators: single-crystal X-ray study; T = 293 K; mean σ(C–C) = 0.004 Å; R factor = 0.020; wR factor = 0.056; data-to-parameter ratio = 12.7.

The asymmetric unit of the title Cd^{II} compound, $[Cd(N_3)_2(C_{12}H_8N_2)]_n$, contains a Cd^{II} atom, located on a twofold axis passing through the middle of the phenanthroline molecule, one azide ion and half of a 1,10-phenanthroline molecule. The Cd^{II} atom exhibits a distorted octahedral coordination including one chelating 1,10-phenanthroline ligand and four azide ligands. The crystal structure features chains along the c direction in which azide groups doubly bridge two adjacent Cd^{II} atoms in an end-on (EO) mode. Interchain π–π stacking interactions, with centroid–centroid separations of 3.408 (2) Å between the central aromatic rings of 1,10-phenanthroline molecules, lead to a supramolecular sheet parallel to the bc plane.

Related literature

For the structures of related metal-azido compounds, see: Goher *et al.* (2008); Ribas *et al.* (1999); Liu *et al.* (2007); Cano *et al.* (2005); Abu-Youssef *et al.* (2000); Bose *et al.* (2004); Mautner *et al.* (2010); Meyer *et al.* (2005); Gao *et al.* (2004).



Experimental

Crystal data

$[Cd(N_3)_2(C_{12}H_8N_2)]$
M_r = 376.67
Monoclinic, $C2/c$
a = 19.4591 (17) Å
b = 10.2988 (6) Å
c = 6.8151 (6) Å
β = 106.033 (4)°
V = 1312.66 (18) Å^3
Z = 4
Mo $K\alpha$ radiation
μ = 1.67 mm^{-1}
T = 293 K
0.30 × 0.20 × 0.18 mm

Data collection

Rigaku Mercury CCD diffractometer
Absorption correction: multi-scan (*CrystalClear*; Rigaku, 2002)
T_{min} = 0.774, T_{max} = 1.000
4185 measured reflections
1217 independent reflections
1133 reflections with $I > 2\sigma(I)$
R_{int} = 0.023

Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.020
$wR(F^2)$ = 0.056
S = 1.05
1217 reflections
96 parameters
H-atom parameters constrained
$\Delta\rho_{max}$ = 0.78 e Å^{-3}
$\Delta\rho_{min}$ = −0.48 e Å^{-3}

Data collection: *CrystalClear* (Rigaku, 2002); cell refinement: *CrystalClear*; data reduction: *CrystalClear*; program(s) used to solve structure: *SHELXTL* (Sheldrick, 2008); program(s) used to refine structure: *SHELXTL*; molecular graphics: *SHELXTL*; software used to prepare material for publication: *SHELXTL*.

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Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: DN2567).

References

Abu-Youssef, M. A. M., Escuer, A., Goher, M. A. S., Mautner, F. A., Reiss, G. J. & Vicente, R. (2000). *Angew. Chem. Int. Ed.* **39**, 1624–1626.
Bose, D., Rahaman, S. H., Mostafa, G., Walsh, R. D. B., Zaworotko, M. J. & Ghosh, B. K. (2004). *Polyhedron*, **23**, 545–552.
Cano, J., Journaux, Y., Goher, M. A. S., Abu-Youssef, M. A. M., Mautner, F. A., Reiss, G. J., Escuer, A. & Vicente, R. (2005). *New J. Chem.* **29**, 306–314.
Gao, E.-Q., Yue, Y.-F., Bai, S.-Q., He, Z., Zhang, S.-W. & Yan, C.-H. (2004). *Chem. Mater.* **16**, 1590–1596.
Goher, M. A. S., Mautner, F. A., Gatterer, K., Abu-Youssef, M. A. M., Badr, A. M. A., Sodin, B. & Gspan, C. (2008). *J. Mol. Struct.* **876**, 199–205.
Liu, F.-C., Zeng, Y.-F., Zhao, J.-P., Hu, B.-W., Bu, X.-H., Ribas, J. & Cano, J. (2007). *Inorg. Chem.* **46**, 1520–1522.
Mautner, F. A., Egger, A., Sodin, B., Goher, M. A. S., Abu-Youssef, M. A. M., Massoud, A., Escuer, A. & Vicente, R. (2010). *J. Mol. Struct.* **969**, 192–196.
Meyer, F., Demeshko, S., Leibeling, G., Kersting, B., Kaifer, E. & Pritzkow, H. (2005). *Chem. Eur. J.* **11**, 1518–1526.
Ribas, J., Escuer, A., Monfort, M., Vicente, R., Cortés, R., Lezama, L. & Rojo, T. (1999). *Coord. Chem. Rev.* **193–195**, 1027–1068.
Rigaku (2002). *CrystalClear*. Rigaku Corporation, Tokyo, Japan.
Sheldrick, G. M. (2008). *Acta Cryst.* A**64**, 112–122.

supplementary materials

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catena-Poly[di-$\mu_{1,1}$-azido-(1,10-phenanthroline)cadmium(II)]

F. Chen, F.-K. Zheng, G.-N. Liu, M.-F. Wu and G.-C. Guo

Comment

Many compounds with uncommon magnetic properties have been widely investigated by using azido ligand, resulting from its rich coordination fashions (Ribas *et al.*, 1999; Gao *et al.*, 2004). The azido ligand exhibits a variety of bridging modes such as bi-dentate end-on (EO) and end-to-end (EE) bridging fashions (Liu *et al.*, 2007; Cano *et al.*, 2005; Goher *et al.*, 2008; Mautner *et al.*, 2010). A number of compounds with various structures have been obtained by introducing auxiliary ligands to the metal-azido system (Abu-Youssef *et al.*, 2000; Bose *et al.*, 2004; Meyer *et al.*, 2005). The present example shows an infinite wavelike chain compound with 1,10-phenanthroline as an auxiliary ligand, $[Cd(N_3)_2(C_{12}H_8N_2)]$, in which azido ligand adopts the EO mode.

The asymmetric unit of the title compound contains half a Cd^{II} ion, one azido ion and half a 1,10-phenanthroline molecule (Fig. 1). The Cd^{II} ion exhibits a distorted octahedral geometry, coordinated by one chelating 1,10-phenanthroline ligand and four azido ligands with the end-on (EO) mode. The distances of Cd—N vary from 2.306 (2) to 2.411 (3) Å . The azido ligands doubly bridge neighbouring Cd^{II} centers in the EO fashion, yielding an infinite wave-like Cd^{II}-azido chain along the *c* direction with the shortest Cd···Cd separation being 3.764 (3) Å.

The adjacent Cd^{II}-azido chains are mediated by interchained π-π stacking interactions between the aromatic rings of 1,10-phenanthroline molecules, which arrange in the opposite direction alternatively. The centroid-to-centroid distance between the central rings of the phenanthroline is 3.408 (2)Å and the centroid-to-plane distance is 3.28 Å leading to a slippage of 0.936Å. This π-π stacking builts up a 2-D supramolecular layer parallel to the *bc* plane (Fig. 2).

Experimental

A mixture of $Cd(NO_3)_2.4H_2O$ (0.308 g, 1.00 mmol), NaN_3 (0.065 g, 1.00 mmol), Na(3-cba) (0.085 g, 0.50 mmol 3-Hcba = 3-cyanobenzoate acid), 1,10-phenanthroline (0.099 g, 0.50 mmol) and H_2O (8 ml) was placed in a Teflon-lined stainless container, and then heated at 453 K for 2 days, after cooled to room temperature for 2 days. Pale-yellow prism-shaped crystals of the title compound were obtained. IR peaks (KBr, cm^{-1}): 2053 s, 2037 s h, 1589 w, 1515 w, 1425 w, 1333 w, 1284 w, 846 m, 772 w, 727 m, 656 w. A strong band around 2053 cm^{-1} indicates the presence of the azido group.

Refinement

Hydrogen atoms were allowed to ride on their respective parent atoms with C—H distances of 0.93 Å, and were included in the refinement with isotropic displacement parameters $U_{iso}(H) = 1.2U_{eq}(C)$.

Figures

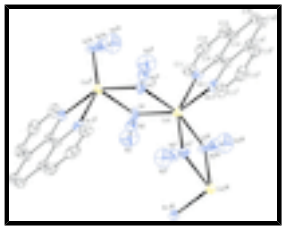


Fig. 1. View of the title compound with the atom labeling scheme. Ellipsoids are drawn at the 30% probability level. H atoms have been omitted for clarity.[Symmetry codes: (i) -*x*+1, *y*, -*z*+1/2; (ii) -*x*+1, -*y*+2, -*z*; (iii) *x*, -*y*+2, *z*+1/2; (iv) x, -y+2, z-1/2].

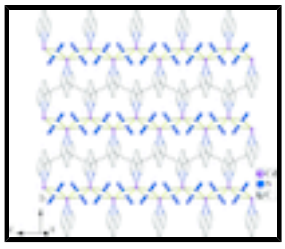


Fig. 2. View of the 2-D layer structure of the title compound formed by 1-D Cd^{II}-azido chains linked through π-π stacking interactions (black dotted lines) between symetry related 1,10-phenanthroline molecules. Hydrogen atoms have been omitted for clarity.

catena-Poly[di-μ$_{1,1}$-azido-(1,10-phenanthroline)cadmium(II)]

Crystal data

$[Cd(N_3)_2(C_{12}H_8N_2)]$	$F(000) = 736$
$M_r = 376.67$	$D_x = 1.906$ Mg m^{-3}
Monoclinic, *C*2/*c*	Mo *K*α radiation, λ = 0.71073 Å
Hall symbol: -C 2yc	Cell parameters from 1622 reflections
a = 19.4591 (17) Å	θ = 2.3–27.5°
b = 10.2988 (6) Å	μ = 1.67 mm^{-1}
c = 6.8151 (6) Å	*T* = 293 K
β = 106.033 (4)°	Prism, pale-yellow
V = 1312.66 (18) Å^3	0.30 × 0.20 × 0.18 mm
Z = 4	

Data collection

Rigaku Mercury CCD diffractometer	1217 independent reflections
Radiation source: fine-focus sealed tube	1133 reflections with $I > 2\sigma(I)$
graphite	$R_{int} = 0.023$
Detector resolution: 13.6612 pixels mm^{-1}	$\theta_{max} = 25.5°$, $\theta_{min} = 3.6°$
CCD_Profile_fitting scans	*h* = −23→22
Absorption correction: multi-scan (*CrystalClear*; Rigaku, 2002)	*k* = −12→12
$T_{min} = 0.774$, $T_{max} = 1.000$	*l* = −8→8
4185 measured reflections	

Refinement

Refinement on F^2	Primary atom site location: structure-invariant direct methods
Least-squares matrix: full	Secondary atom site location: difference Fourier map
$R[F^2 > 2\sigma(F^2)] = 0.020$	Hydrogen site location: inferred from neighbouring sites
$wR(F^2) = 0.056$	H-atom parameters constrained
$S = 1.05$	$w = 1/[\sigma^2(F_o^2) + (0.0373P)^2 + 0.2202P]$ where $P = (F_o^2 + 2F_c^2)/3$
1217 reflections	$(\Delta/\sigma)_{max} = 0.001$
96 parameters	$\Delta\rho_{max} = 0.78$ e Å^{-3}
0 restraints	$\Delta\rho_{min} = -0.48$ e Å^{-3}

Special details

Geometry. All esds (except the esd in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell esds are taken into account individually in the estimation of esds in distances, angles and torsion angles; correlations between esds in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell esds is used for estimating esds involving l.s. planes.

Refinement. Refinement of F^2 against ALL reflections. The weighted *R*-factor wR and goodness of fit *S* are based on F^2, conventional *R*-factors *R* are based on *F*, with *F* set to zero for negative F^2. The threshold expression of $F^2 > \sigma(F^2)$ is used only for calculating *R*-factors(gt) etc. and is not relevant to the choice of reflections for refinement. *R*-factors based on F^2 are statistically about twice as large as those based on *F*, and *R*- factors based on ALL data will be even larger.

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å^2)

	x	*y*	*z*	U_{iso}*/U_{eq}
Cd1	0.5000	0.922344 (19)	0.2500	0.03485 (12)
N1	0.43055 (13)	1.0473 (2)	−0.0103 (3)	0.0446 (5)
N2	0.37375 (13)	1.0889 (2)	−0.0144 (4)	0.0459 (6)
N3	0.31894 (16)	1.1315 (4)	−0.0167 (6)	0.0898 (10)
N11	0.43063 (10)	0.73525 (19)	0.1345 (3)	0.0367 (4)
C11	0.36250 (14)	0.7349 (3)	0.0214 (4)	0.0488 (6)
H11A	0.3404	0.8140	−0.0213	0.059*
C12	0.32340 (16)	0.6220 (4)	−0.0352 (5)	0.0587 (8)
H12A	0.2758	0.6260	−0.1114	0.070*
C13	0.35523 (17)	0.5055 (3)	0.0218 (4)	0.0551 (8)
H13A	0.3293	0.4291	−0.0144	0.066*
C14	0.42742 (16)	0.5003 (2)	0.1357 (4)	0.0447 (6)
C15	0.46270 (13)	0.6200 (2)	0.1908 (3)	0.0344 (5)
C16	0.46560 (18)	0.3819 (3)	0.1969 (4)	0.0552 (8)
H16A	0.4420	0.3032	0.1619	0.066*

Atomic displacement parameters (Å^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Cd1	0.03961 (17)	0.03359 (16)	0.02969 (16)	0.000	0.00680 (11)	0.000
N1	0.0461 (13)	0.0517 (11)	0.0384 (12)	0.0101 (11)	0.0156 (10)	0.0139 (10)
N2	0.0417 (14)	0.0477 (13)	0.0439 (13)	0.0009 (10)	0.0047 (10)	−0.0005 (9)
N3	0.0428 (16)	0.116 (3)	0.105 (3)	0.0208 (18)	0.0108 (16)	−0.008 (2)
N11	0.0368 (10)	0.0410 (11)	0.0332 (10)	0.0009 (9)	0.0109 (8)	−0.0043 (8)
C11	0.0405 (13)	0.0601 (17)	0.0449 (14)	0.0015 (13)	0.0099 (11)	−0.0113 (13)
C12	0.0430 (15)	0.084 (2)	0.0481 (16)	−0.0126 (16)	0.0112 (13)	−0.0179 (16)
C13	0.0651 (19)	0.0630 (18)	0.0434 (15)	−0.0282 (16)	0.0257 (14)	−0.0187 (13)
C14	0.0678 (18)	0.0436 (14)	0.0314 (12)	−0.0137 (12)	0.0282 (13)	−0.0088 (10)
C15	0.0436 (13)	0.0385 (11)	0.0241 (11)	−0.0021 (11)	0.0146 (10)	−0.0024 (9)
C16	0.099 (2)	0.0354 (11)	0.0409 (16)	−0.0135 (14)	0.0363 (15)	−0.0077 (11)

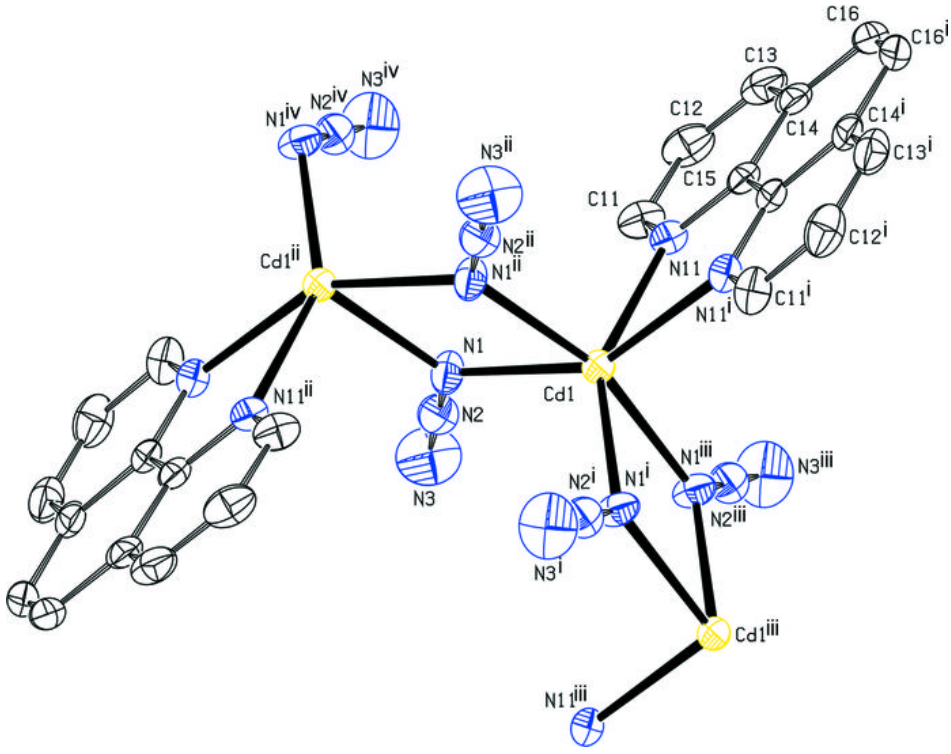
Geometric parameters (Å, °)

Cd1—N1^{i}	2.303 (2)	C11—C12	1.385 (5)
Cd1—N1	2.303 (2)	C11—H11A	0.9300
Cd1—N11	2.3596 (19)	C12—C13	1.357 (5)
Cd1—N11^{i}	2.3596 (19)	C12—H12A	0.9300
Cd1—N1^{ii}	2.411 (2)	C13—C14	1.406 (4)
Cd1—N1^{iii}	2.411 (2)	C13—H13A	0.9300
N1—N2	1.179 (3)	C14—C15	1.410 (4)
N1—Cd1^{ii}	2.411 (2)	C14—C16	1.429 (4)
N2—N3	1.149 (4)	C15—C15^{i}	1.453 (5)
N11—C11	1.337 (3)	C16—C16^{i}	1.335 (7)
N11—C15	1.347 (3)	C16—H16A	0.9300
N1^{i}—Cd1—N1	112.07 (12)	C11—N11—Cd1	125.41 (18)
N1^{i}—Cd1—N11	150.83 (8)	C15—N11—Cd1	116.58 (15)
N1—Cd1—N11	92.25 (8)	N11—C11—C12	122.9 (3)
N1^{i}—Cd1—N11^{i}	92.25 (8)	N11—C11—H11A	118.5
N1—Cd1—N11^{i}	150.83 (8)	C12—C11—H11A	118.5
N11—Cd1—N11^{i}	70.51 (9)	C13—C12—C11	119.4 (3)
N1^{i}—Cd1—N1^{ii}	97.46 (8)	C13—C12—H12A	120.3
N1—Cd1—N1^{ii}	74.05 (9)	C11—C12—H12A	120.3
N11—Cd1—N1^{ii}	104.83 (8)	C12—C13—C14	119.9 (3)
N11^{i}—Cd1—N1^{ii}	87.47 (7)	C12—C13—H13A	120.0
N1^{i}—Cd1—N1^{iii}	74.05 (9)	C14—C13—H13A	120.0
N1—Cd1—N1^{iii}	97.46 (8)	C13—C14—C15	116.9 (3)
N11—Cd1—N1^{iii}	87.47 (7)	C13—C14—C16	123.6 (3)
N11^{i}—Cd1—N1^{iii}	104.83 (8)	C15—C14—C16	119.5 (3)
N1^{ii}—Cd1—N1^{iii}	165.09 (11)	N11—C15—C14	122.8 (2)

N2—N1—Cd1	124.66 (19)	N11—C15—C15^{i}	118.13 (13)
N2—N1—Cd1^{ii}	129.35 (18)	C14—C15—C15^{i}	119.09 (16)
Cd1—N1—Cd1^{ii}	105.95 (9)	C16^{i}—C16—C14	121.41 (17)
N3—N2—N1	178.8 (3)	C16^{i}—C16—H16A	119.3
C11—N11—C15	118.0 (2)	C14—C16—H16A	119.3

Symmetry codes: (i) −*x*+1, *y*, −*z*+1/2; (ii) −*x*+1, −*y*+2, −*z*; (iii) *x*, −*y*+2, *z*+1/2.

Fig. 1


C16
C16i
C13
C12
C14
C14i
C13i
C15
C11
N3ii
N2ii
N1ii
Cd1ii
N11
C12i
C11i
N11i
N3iv
N2iv
N1iv
N1
Cd1
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N3
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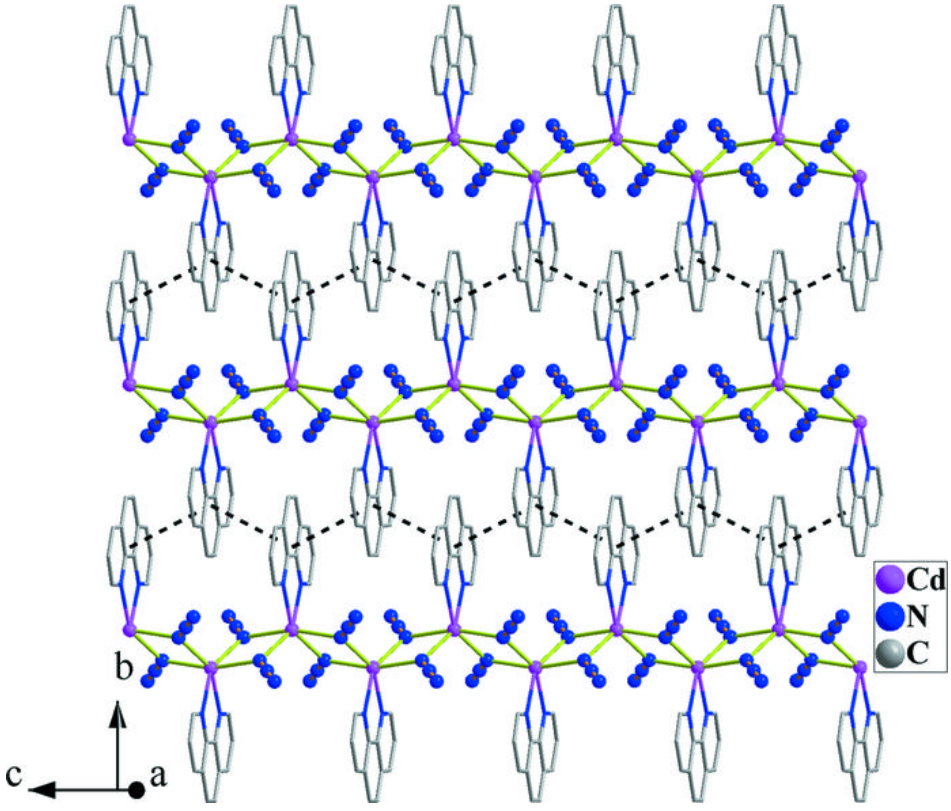
N3iii
N2i
N1i
N2iii
N3i
Cd1iii
N11iii

Fig. 2



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N-(2-Methylphenyl)maleamic acid

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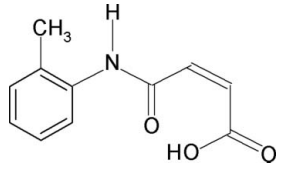
Key indicators: single-crystal X-ray study; T = 295 K; mean σ(C–C) = 0.002 Å; R factor = 0.034; wR factor = 0.098; data-to-parameter ratio = 13.0.

In the title compound, $C_{11}H_{11}NO_3$, the conformation of the N—H bond is *anti* to the C=O bond in the amide segment, while it is *syn* to the *ortho*-methyl group in the phenyl ring. In the maleamic acid unit, the amide C=O bond is *anti* to the adjacent C—H bond, while the carboxyl C=O bond is *syn* to the adjacent C—H bond. The C=O and O—H bonds of the acid group are in the relatively rare *anti* position to each other. This is an obvious consequence of the intramolecular O—H···O hydrogen bond donated to the amide carbonyl group. The *ortho*-substituted phenyl ring makes a dihedral angle of 12.7 (1)° with the mean plane of the maleamic acid unit. In the crystal structure, intermolecular N—H···O hydrogen bonds link the molecules into zigzag chains parallel to [001]. These chains are further linked into sheet by weak π–π interactions [centroid–centroid distance = 3.425 (2) Å].

Related literature

For studies on the effect of ring- and side-chain substitutions on the crystal structures of amides, see: Gowda *et al.* (2009*a*,*b*,*c*); Prasad *et al.* (2002). For the modes of interlinking carboxylic acids by hydrogen bonds, see: Jagannathan *et al.* (1994); Leiserowitz (1976).



Experimental

Crystal data

$C_{11}H_{11}NO_3$
M_r = 205.21
Monoclinic, $P2_1/c$
a = 7.3942 (3) Å
b = 11.5898 (4) Å
c = 12.9903 (3) Å
β = 114.534 (2)°
V = 1012.72 (5) Å^3
Z = 4
Mo $K\alpha$ radiation
μ = 0.10 mm^{-1}
T = 295 K
0.58 × 0.42 × 0.42 mm

Data collection

Oxford Diffraction Gemini R CCD diffractometer
Absorption correction: analytical (*CrysAlis PRO*; Oxford Diffraction, 2009)
T_{min} = 0.922, T_{max} = 0.962
15644 measured reflections
1776 independent reflections
1453 reflections with $I > 2\sigma(I)$
R_{int} = 0.027

Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.034
$wR(F^2)$ = 0.098
S = 1.07
1776 reflections
137 parameters
H-atom parameters constrained
$\Delta\rho_{max}$ = 0.17 e Å^{-3}
$\Delta\rho_{min}$ = −0.13 e Å^{-3}

Table 1
Hydrogen-bond geometry (Å, °).

D—H···A	D—H	H···A	D···A	D—H···A
N1—H1*N*···O3^{i}	0.86	2.22	3.0665 (14)	167
O2—H2*A*···O1	0.92	1.56	2.4822 (13)	178

Symmetry code: (i) $x, -y+\frac{3}{2}, z-\frac{1}{2}$.

Data collection: *CrysAlis PRO* (Oxford Diffraction, 2009); cell refinement: *CrysAlis PRO*; data reduction: *CrysAlis PRO*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *ORTEP-3* (Farrugia, 1997) and *DIAMOND* (Brandenburg, 2002); software used to prepare material for publication: *SHELXL97*, *PLATON* (Spek, 2009) and *WinGX* (Farrugia, 1999).

MT and JK thank the Grant Agency of the Slovak Republic (VEGA 1/0817/08) and the Structural Funds, Interreg IIIA, for financial support in purchasing the diffractometer. K. thanks the University Grants Commission, Government of India, New Delhi, for the award of a research fellowship under its faculty improvement program.

Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: DN2569).

References

Brandenburg, K. (2002). *DIAMOND*. Crystal Impact GbR, Bonn, Germany.
Farrugia, L. J. (1997). *J. Appl. Cryst.* **30**, 565.
Farrugia, L. J. (1999). *J. Appl. Cryst.* **32**, 837–838.
Gowda, B. T., Tokarčík, M., Kožíšek, J., Shakunthala, K. & Fuess, H. (2009*a*). *Acta Cryst.* E**65**, o2807.
Gowda, B. T., Tokarčík, M., Kožíšek, J., Shakunthala, K. & Fuess, H. (2009*b*). *Acta Cryst.* E**65**, o2874.
Gowda, B. T., Tokarčík, M., Kožíšek, J., Shakunthala, K. & Fuess, H. (2009*c*). *Acta Cryst.* E**65**, o2945.
Jagannathan, N. R., Rajan, S. S. & Subramanian, E. (1994). *J. Chem. Crystallogr.* **24**, 75–78.
Leiserowitz, L. (1976). *Acta Cryst.* B**32**, 775–802.
Oxford Diffraction (2009). *CrysAlis PRO*. Oxford Diffraction Ltd, Yarnton, England.
Prasad, S. M., Sinha, R. B. P., Mandal, D. K. & Rani, A. (2002). *Acta Cryst.* E**58**, o891–o892.
Sheldrick, G. M. (2008). *Acta Cryst.* A**64**, 112–122.
Spek, A. L. (2009). *Acta Cryst.* D**65**, 148–155.

supplementary materials

Acta Cryst. (2010). E**66**, o1554 [**doi:10.1107/S160053681002012X**]

N-(2-Methylphenyl)maleamic acid

B. T. Gowda, M. Tokarcík, K. Shakuntala, J. Kozísek and H. Fuess

Comment

The amide moiety is an important constituent of many biologically significant compounds. As a part of studying the effect of ring and side chain substitutions on the crystal structures of this class of compounds (Gowda *et al.*, 2009*a,b,c*; Prasad *et al.*, 2002), the crystal structure of *N*-(2-methylphenyl)-maleamic acid (I) has been determined (Fig. 1). The conformations of the N—H and the C=O bonds in the amide segment are *anti* to each other. But the conformation of the N—H bond is *syn* to the *ortho*-methyl group in the phenyl ring. In the maleamic acid moiety, the amide C=O bond is *anti* to the adjacent C—H bond, while the carboxyl C=O bond is *syn* to the adjacent C—H bond. The observed rare *anti* conformation of the C=O and O—H bonds of the acid group is similar to that obsrved in *N*-(2,6-dimethylphenyl)-maleamic acid (Gowda *et al.*, 2009*a*), *N*-(3,4-dimethylphenyl)-maleamic acid (Gowda *et al.*, 2009*b*) and *N*-(2,4,6-trimethylphenyl)- maleamic acid (Gowda *et al.*, 2009*c*).

The *ortho*-substituted phenyl ring makes a dihedral angle of 12.7 (1)° with the mean plane of the maleamic acid moiety (atoms C1, C2, C3, C4, N1, O1, O2 and O3). The orientation of the central amide group –NHOC– with respect to the phenyl ring is partially affected by the intramolecular hydrogen bond C10—H10···O1(amide) and is given by the torsion angle C10—C5—N1—C1 = -17.3 (2)°. Short intramolecular hydrogen bond O—H···O (Table 1) is important characteristic of the maleamic acid moiety. The C2–C3 bond length of 1.330 (2)Å clearly indicates the double bond character. In the crystal structure, the intermolecular N–H···O hydrogen bonds, having the amide N1 atom as donor and carbonyl O3 atom of the carboxyl group as acceptor, link the molecules into zigzag chains running along the [0 0 1] direction. Due to weak π-π interaction between the phenyl and maleamic acid moieties the chains are assembled to form sheets parallel to the *bc*-plane. One mode of the chain coupling is shown in Fig. 2 as a short contact between the phenyl ring centroid *Cg* and the C4 atom of the carboxylic group at (-*x*,-*y* + 1,-*z* + 1).

The various modes of interlinking carboxylic acids by hydrogen bonds is described elsewhere (Leiserowitz, 1976). The packing of molecules involving dimeric hydrogen bonded association of each carboxyl group with a centrosymmetrically related neighbor has also been observed (Jagannathan *et al.*, 1994).

Experimental

The solution of maleic anhydride (0.025 mol) in toluene (25 ml) was treated dropwise with the solution of 2-methylaniline (0.025 mol) also in toluene (20 ml) with constant stirring. The resulting mixture was stirred for about 30 min and set aside for an additional 30 min at room temperature for the completion of reaction. The mixture was then treated with dilute hydrochloric acid to remove the unreacted 2-methylaniline. The resultant solid *N*-(2-methylphenyl)maleamic acid was filtered under suction and washed thoroughly with water to remove the unreacted maleic anhydride and maleic acid. It was recrystallized to constant melting point from ethanol. The purity of the compound was checked by elemental analysis and characterized by its infrared spectra. The single crystals used in X-ray diffraction studies were grown in an ethanol solution by slow evaporation at room temperature.

Refinement

All H atoms attached to C atoms, N atom and O atom were fixed geometrically and treated as riding with C—H = 0.96 Å (methyl) or 0.93 Å (aromatic), N—H = 0.86 Å and O—H= 0.92Å with U_{iso}(H) = 1.2U_{eq}($C_{aromatic}$, N) or U_{iso}(H) = 1.5U_{eq}(C_{methyl}, O).

Figures

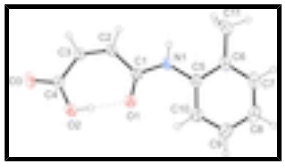


Fig. 1. Molecular structure of (I) showing the atom labelling scheme. Displacement ellipsoids are drawn at the 30% probability level and H atoms are represented as small spheres of arbitrary radii.

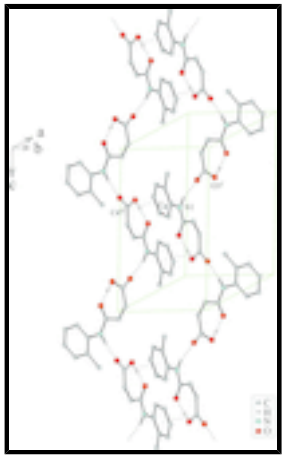


Fig. 2. Part of the crystal structure of (I) showing the zigzag chains generated by N—H···O hydrogen bonds and extending parallel to the *c* axis. The chains are weakly coupled by π-π interaction between the phenyl rings and maleamic acid groups. The dashed lines depict the hydrogen bonds, the dotted line depicts the short contact *Cg*···C4^{ii}. H atoms not involved in hydrogen bonding have been omitted. [Symmetry codes (i): *x*, -*y* + 3/2, *z* - 1/2; (ii) -*x*,-*y* + 1,-*z* + 1].

N-(2-Methylphenyl)maleamic acid

Crystal data

$C_{11}H_{11}NO_3$	$F(000)$ = 432
M_r = 205.21	D_x = 1.346 Mg m^{-3}
Monoclinic, $P2_1/c$	Mo $K\alpha$ radiation, λ = 0.71073 Å
Hall symbol: -P 2ybc	Cell parameters from 8927 reflections
a = 7.3942 (3) Å	θ = 2.5–29.5°
b = 11.5898 (4) Å	μ = 0.10 mm^{-1}
c = 12.9903 (3) Å	*T* = 295 K
β = 114.534 (2)°	Prism, colourless
V = 1012.72 (5) Å^3	0.58 × 0.42 × 0.42 mm
Z = 4	

Data collection

Oxford Diffraction Gemini R CCD diffractometer	1776 independent reflections

graphite

Detector resolution: 10.434 pixels mm^{-1}

ω scans

Absorption correction: analytical (*CrysAlis PRO*; Oxford Diffraction, 2009)

T_{min} = 0.922, T_{max} = 0.962

15644 measured reflections

1453 reflections with $I > 2\sigma(I)$

R_{int} = 0.027

θ_{max} = 25°, θ_{min} = 2.5°

$h = -8 \rightarrow 8$

$k = -13 \rightarrow 13$

$l = -15 \rightarrow 15$

Refinement

Refinement on F^2

Least-squares matrix: full

$R[F^2 > 2\sigma(F^2)]$ = 0.034

$wR(F^2)$ = 0.098

S = 1.07

1776 reflections

137 parameters

0 restraints

Primary atom site location: structure-invariant direct methods

Secondary atom site location: difference Fourier map

Hydrogen site location: inferred from neighbouring sites

H-atom parameters constrained

$w = 1/[\sigma^2(F_o^2) + (0.056P)^2 + 0.0996P]$ where $P = (F_o^2 + 2F_c^2)/3$

$(\Delta/\sigma)_{max} < 0.001$

$\Delta\rho_{max}$ = 0.17 e $Å^{-3}$

$\Delta\rho_{min}$ = −0.13 e $Å^{-3}$

Special details

Geometry. All e.s.d.'s (except the e.s.d. in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell e.s.d.'s are taken into account individually in the estimation of e.s.d.'s in distances, angles and torsion angles; correlations between e.s.d.'s in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell e.s.d.'s is used for estimating e.s.d.'s involving l.s. planes.

Refinement. Refinement of F^2 against ALL reflections. The weighted *R*-factor *wR* and goodness of fit *S* are based on F^2, conventional *R*-factors *R* are based on *F*, with *F* set to zero for negative F^2. The threshold expression of $F^2 > \sigma(F^2)$ is used only for calculating *R*-factors(gt) *etc*. and is not relevant to the choice of reflections for refinement. *R*-factors based on F^2 are statistically about twice as large as those based on *F*, and *R*- factors based on ALL data will be even larger.

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters ($Å^2$)

	x	*y*	*z*	U_{iso}*/U_{eq}
O1	0.24625 (18)	0.49123 (8)	0.59119 (8)	0.0661 (3)
O2	0.26421 (19)	0.62958 (9)	0.74100 (8)	0.0701 (4)
H2A	0.2600	0.5770	0.6870	0.105*
O3	0.24623 (18)	0.81655 (10)	0.75227 (8)	0.0711 (4)
N1	0.24594 (15)	0.49437 (9)	0.41733 (8)	0.0432 (3)
H1N	0.2368	0.5389	0.3624	0.052*
C1	0.23624 (18)	0.54568 (11)	0.50723 (9)	0.0416 (3)
C2	0.2115 (2)	0.67235 (11)	0.49860 (10)	0.0444 (3)
H2	0.1931	0.7044	0.4293	0.053*
C3	0.2122 (2)	0.74646 (11)	0.57694 (11)	0.0463 (3)
H3	0.1892	0.8224	0.5517	0.056*

C4	0.2424 (2)	0.73222 (12)	0.69681 (11)	0.0488 (4)
C5	0.26967 (19)	0.37432 (11)	0.40204 (11)	0.0432 (3)
C6	0.2264 (2)	0.33549 (12)	0.29220 (11)	0.0502 (4)
C7	0.2520 (2)	0.21851 (13)	0.27818 (14)	0.0614 (4)
H7	0.2247	0.1910	0.2060	0.074*
C8	0.3162 (3)	0.14215 (13)	0.36698 (15)	0.0680 (5)
H8	0.3303	0.0643	0.3547	0.082*
C9	0.3591 (3)	0.18185 (13)	0.47378 (14)	0.0648 (4)
H9	0.4031	0.1307	0.5345	0.078*
C10	0.3376 (2)	0.29766 (12)	0.49199 (12)	0.0550 (4)
H10	0.3688	0.3242	0.5650	0.066*
C11	0.1553 (3)	0.41495 (15)	0.19286 (12)	0.0711 (5)
H11A	0.1342	0.3721	0.1256	0.107*
H11B	0.2532	0.4737	0.2041	0.107*
H11C	0.0326	0.4502	0.1849	0.107*

Atomic displacement parameters (Å^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
O1	0.1258 (10)	0.0400 (6)	0.0506 (6)	0.0030 (6)	0.0547 (6)	0.0022 (5)
O2	0.1294 (10)	0.0507 (6)	0.0420 (5)	0.0101 (6)	0.0472 (6)	0.0033 (4)
O3	0.1142 (10)	0.0573 (7)	0.0486 (6)	0.0083 (6)	0.0406 (6)	−0.0134 (5)
N1	0.0616 (7)	0.0386 (6)	0.0353 (5)	−0.0011 (5)	0.0261 (5)	−0.0029 (5)
C1	0.0547 (8)	0.0400 (7)	0.0348 (6)	−0.0020 (6)	0.0233 (6)	−0.0022 (5)
C2	0.0620 (8)	0.0418 (7)	0.0327 (6)	0.0025 (6)	0.0231 (6)	0.0018 (5)
C3	0.0650 (9)	0.0367 (6)	0.0397 (7)	0.0057 (6)	0.0243 (6)	0.0008 (5)
C4	0.0642 (9)	0.0468 (8)	0.0397 (7)	0.0051 (6)	0.0260 (6)	−0.0044 (6)
C5	0.0500 (8)	0.0392 (7)	0.0474 (7)	−0.0045 (5)	0.0272 (6)	−0.0079 (6)
C6	0.0567 (8)	0.0491 (8)	0.0485 (7)	−0.0072 (6)	0.0254 (6)	−0.0151 (6)
C7	0.0701 (10)	0.0541 (9)	0.0626 (9)	−0.0079 (7)	0.0301 (8)	−0.0254 (8)
C8	0.0793 (11)	0.0406 (8)	0.0926 (13)	−0.0042 (7)	0.0441 (10)	−0.0151 (8)
C9	0.0849 (12)	0.0444 (8)	0.0776 (11)	0.0072 (7)	0.0461 (9)	0.0057 (8)
C10	0.0737 (10)	0.0482 (8)	0.0532 (8)	0.0046 (7)	0.0364 (7)	−0.0016 (6)
C11	0.1050 (13)	0.0666 (10)	0.0427 (8)	0.0016 (9)	0.0316 (9)	−0.0134 (7)

Geometric parameters (Å, °)

O1—C1	1.2355 (14)	C5—C6	1.4005 (17)
O2—C4	1.3015 (17)	C6—C7	1.391 (2)
O2—H2A	0.9200	C6—C11	1.492 (2)
O3—C4	1.2076 (16)	C7—C8	1.373 (2)
N1—C1	1.3387 (14)	C7—H7	0.9300
N1—C5	1.4265 (16)	C8—C9	1.368 (2)
N1—H1N	0.8602	C8—H8	0.9300
C1—C2	1.4779 (18)	C9—C10	1.384 (2)
C2—C3	1.3301 (18)	C9—H9	0.9300
C2—H2	0.9300	C10—H10	0.9300
C3—C4	1.4876 (18)	C11—H11A	0.9600
C3—H3	0.9300	C11—H11B	0.9600

C5—C10	1.3856 (19)	C11—H11C	0.9600
C4—O2—H2A	108.1	C7—C6—C11	120.42 (12)
C1—N1—C5	127.52 (10)	C5—C6—C11	122.15 (12)
C1—N1—H1N	116.3	C8—C7—C6	122.44 (14)
C5—N1—H1N	116.2	C8—C7—H7	118.8
O1—C1—N1	122.54 (11)	C6—C7—H7	118.8
O1—C1—C2	122.32 (10)	C9—C8—C7	119.28 (14)
N1—C1—C2	115.14 (10)	C9—C8—H8	120.4
C3—C2—C1	128.49 (11)	C7—C8—H8	120.4
C3—C2—H2	115.8	C8—C9—C10	120.33 (15)
C1—C2—H2	115.8	C8—C9—H9	119.8
C2—C3—C4	132.88 (12)	C10—C9—H9	119.8
C2—C3—H3	113.6	C9—C10—C5	120.33 (13)
C4—C3—H3	113.6	C9—C10—H10	119.8
O3—C4—O2	120.58 (12)	C5—C10—H10	119.8
O3—C4—C3	119.39 (13)	C6—C11—H11A	109.5
O2—C4—C3	120.03 (11)	C6—C11—H11B	109.5
C10—C5—C6	120.17 (12)	H11A—C11—H11B	109.5
C10—C5—N1	122.04 (11)	C6—C11—H11C	109.5
C6—C5—N1	117.77 (11)	H11A—C11—H11C	109.5
C7—C6—C5	117.43 (13)	H11B—C11—H11C	109.5
C5—N1—C1—O1	−0.5 (2)	N1—C5—C6—C7	179.30 (12)
C5—N1—C1—C2	179.87 (12)	C10—C5—C6—C11	−179.25 (14)
O1—C1—C2—C3	5.8 (2)	N1—C5—C6—C11	−0.7 (2)
N1—C1—C2—C3	−174.52 (14)	C5—C6—C7—C8	0.3 (2)
C1—C2—C3—C4	2.1 (3)	C11—C6—C7—C8	−179.68 (15)
C2—C3—C4—O3	175.97 (16)	C6—C7—C8—C9	−0.8 (2)
C2—C3—C4—O2	−4.1 (3)	C7—C8—C9—C10	0.2 (2)
C1—N1—C5—C10	−17.3 (2)	C8—C9—C10—C5	0.9 (2)
C1—N1—C5—C6	164.21 (12)	C6—C5—C10—C9	−1.4 (2)
C10—C5—C6—C7	0.8 (2)	N1—C5—C10—C9	−179.82 (13)

Hydrogen-bond geometry (Å, °)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
N1—H1N···O3^{i}	0.86	2.22	3.0665 (14)	167.
O2—H2A···O1	0.92	1.56	2.4822 (13)	178.

Symmetry codes: (i) *x*, −*y*+3/2, *z*−1/2.

Fig. 1

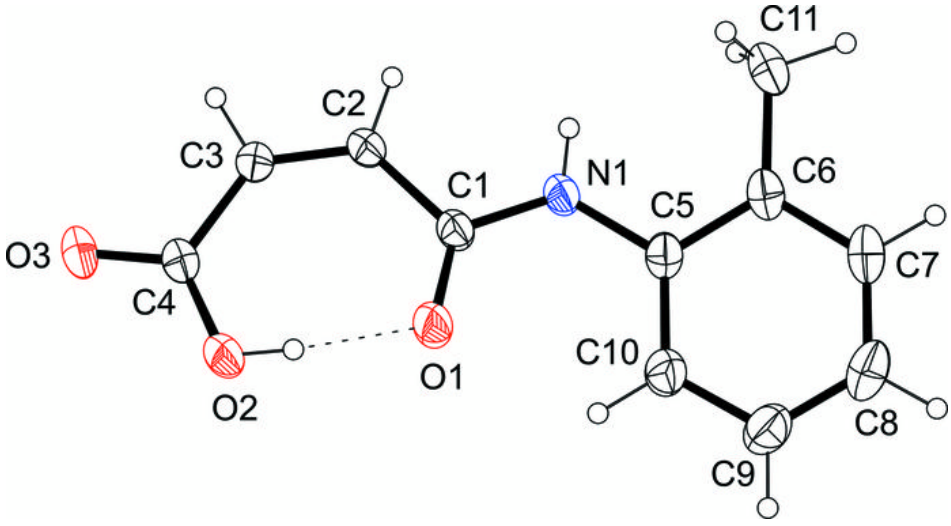
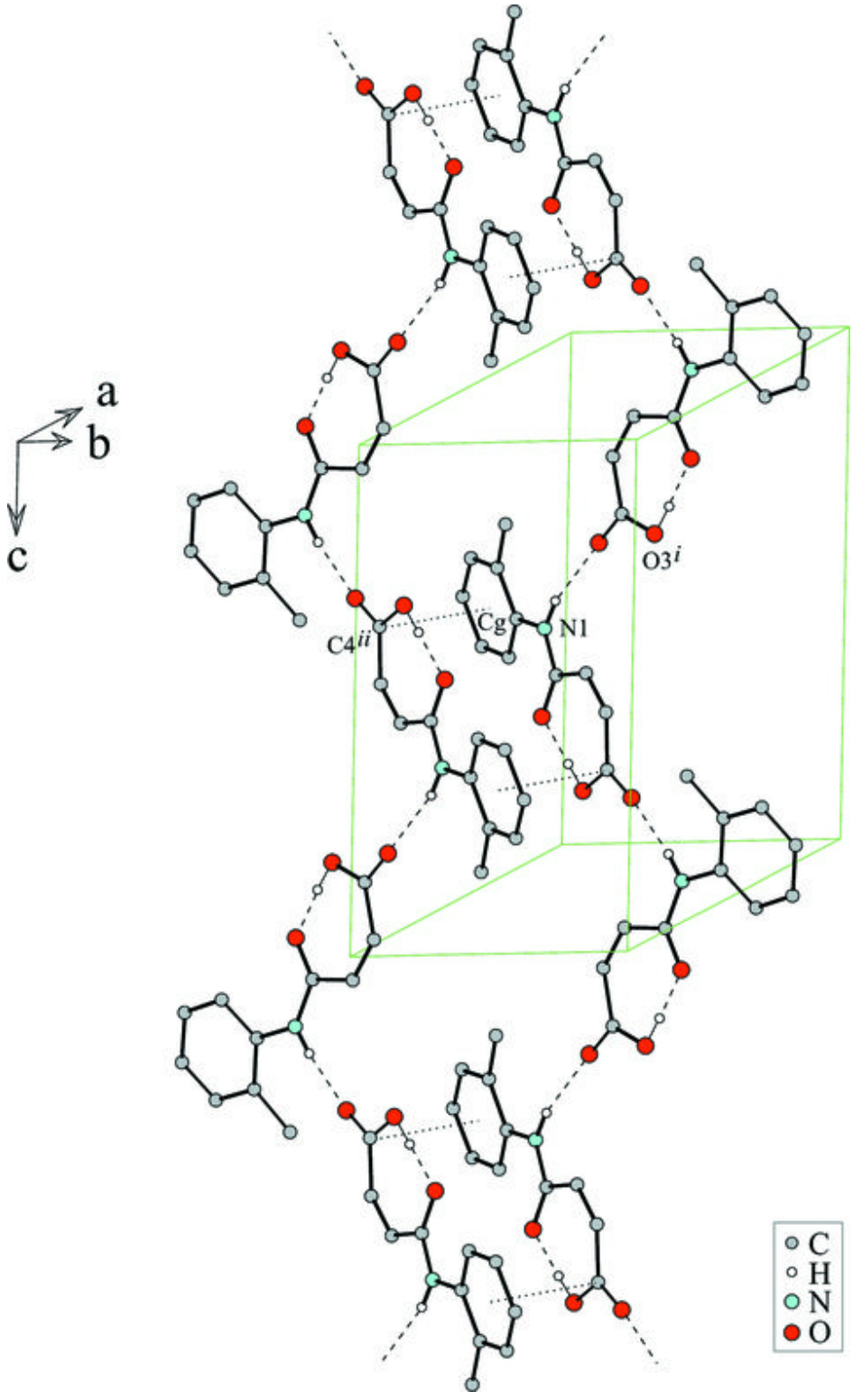


Fig. 2



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Benzyl(methyl)phosphinic acid

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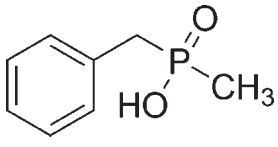
Key indicators: single-crystal X-ray study; T = 293 K; mean σ(C–C) = 0.003 Å; R factor = 0.038; wR factor = 0.096; data-to-parameter ratio = 17.7.

The title compound, $C_8H_{11}O_2P$, is a phosphinic compound with a tetracoordinate pentavalent P atom. The phosphinic function plays a predominant role in the cohesion of the crystal structure, both by forming chains along the b axis *via* strong intermolecular O—H···O hydrogen bonds and by cross-linking these chains perpendicularly *via* weak intermolecular C—H···O hydrogen bonds, generating a two-dimensional network parallel to (001).

Related literature

For general background to phosphinic compounds and their biological applications, see: Ye *et al.* (2007); Abrunhosa-Thomas *et al.* (2007); Wang *et al.* (2009). For their inhibitor properties and use as antibacterial agents, see: Boyd *et al.* (1994); Matziari *et al.* (2004); Ryglowski & Kafarski (1996). For the preparation of phosphinic acid, see: Montchamp (2005); Dingwall *et al.* (1989); Fougère *et al.* (2009). For related structures, see: Frantz *et al.* (2003); Langley *et al.* (1996); Cai *et al.* (2003); Meyer *et al.* (2003).



Experimental

Crystal data

$C_8H_{11}O_2P$
M_r = 170.14
Monoclinic, $P2_1/c$
a = 9.3075 (4) Å
b = 8.2526 (4) Å
c = 11.8890 (4) Å
β = 108.657 (3)°
V = 865.22 (6) Å^3
Z = 4
Mo $K\alpha$ radiation
μ = 0.27 mm^{-1}
T = 293 K
0.60 × 0.25 × 0.06 mm

Data collection

Nonius KappaCCD diffractometer
10548 measured reflections
1767 independent reflections
1320 reflections with $I > 2\sigma(I)$
R_{int} = 0.050

Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.038
$wR(F^2)$ = 0.096
S = 1.05
1767 reflections
100 parameters
H-atom parameters constrained
$\Delta\rho_{max}$ = 0.18 e Å^{-3}
$\Delta\rho_{min}$ = −0.29 e Å^{-3}

Table 1
Hydrogen-bond geometry (Å, °).

D—H···A	D—H	H···A	D···A	D—H···A
O1—H1···O2^{i}	0.82	1.70	2.493 (2)	162
C7—H7···O2^{ii}	0.93	2.54	3.377 (3)	151

Symmetry codes: (i) $-x+1, y+\frac{1}{2}, -z+\frac{1}{2}$; (ii) $x-1, y, z$.

Data collection: *COLLECT* (Hooft, 1998); cell refinement: *HKL* (Otwinowski & Minor, 1997); data reduction: *COLLECT*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *ORTEP-3 for Windows* (Farrugia, 1997) and *PLATON* (Spek, 2009); software used to prepare material for publication: *WinGX* (Farrugia, 1999) and *CrystalBuilder* (Welter, 2006).

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Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: DN2573).

References

Abrunhosa-Thomas, I., Sellers, C. E. & Montchamp, J.-L. (2007). *J. Org. Chem.* **72**, 2851–2856.
Boyd, E. A., Regan, A. C. & James, K. (1994). *Tetrahedron Lett.* **35**, 4223–4226.
Cai, J., Zhou, Z., Zhao, G. & Tang, C. (2003). *Heteroat. Chem.* **14**, 312–315.
Dingwall, J. G., Ehrenfreund, J. & Hall, R. G. (1989). *Tetrahedron*, **45**, 3787–3808.
Farrugia, L. J. (1997). *J. Appl. Cryst.* **30**, 565.
Farrugia, L. J. (1999). *J. Appl. Cryst.* **32**, 837–838.
Fougère, C., Guénin, E., Hardouin, J. & Lecouvey, M. (2009). *Eur. J. Org. Chem.* **34**, 6048–6054.
Frantz, R., Durand, J. O., Carré, F., Lanneau, G., Le Bideau, J., Alonso, B. & Massiot, D. (2003). *Chem. Eur. J.* **9**, 770–775.
Hooft, R. W. W. (1998). *COLLECT*. Nonius BV, Delft, The Netherlands.
Langley, K. J., Squattrito, P., Adani, F. & Montoneri, E. (1996). *Inorg. Chim. Acta*, **253**, 77–85.
Matziari, M., Beau, F., Cuniasse, P., Dive, V. & Yiotakis, A. (2004). *J. Med. Chem.* **47**, 325–336.
Meyer, E. A., Castellano, R. K. & Diederich, F. (2003). *Angew. Chem. Int. Ed.* **42**, 1210–1250.
Montchamp, J. L. (2005). *J. Organomet. Chem.* **690**, 2388–2406.
Otwinowski, Z. & Minor, W. (1997). *Methods in Enzymology*, Vol. 276, *Macromolecular Crystallography*, Part A, edited by C. W. Carter Jr & R. M. Sweet, pp. 307–326. New York: Academic Press.
Ryglowski, A. & Kafarski, P. (1996). *Tetrahedron*, **52**, 10685–10692.
Sheldrick, G. M. (2008). *Acta Cryst.* A**64**, 112–122.
Spek, A. L. (2009). *Acta Cryst.* D**65**, 148–155.
Wang, Y., Wang, Y., Yu, J., Miao, Z. & Chen, R. (2009). *Chem. Eur. J.* **15**, 9290–9293.
Welter, R. (2006). *Acta Cryst.* A**62**, s252.
Ye, Y., Liu, M., Kao, J. L.-F. & Marshall, G. R. (2007). *Biopolymers*, **89**, 72–85.

supplementary materials

Acta Cryst. (2010). E**66**, o1786 [**doi:10.1107/S1600536810024116**]

Benzyl(methyl)phosphinic acid

C. Fougère, E. Guénin, P. Retailleau and C. Barbey

Comment

The title compound, $C_8H_{11}O_2P$, belongs to the phosphinic acid family (*R*'P(O)OHR"). These compounds are important substrates in the study of biochemical processes, and those comprising tetracoordinate pentavalent phosphorus are widely used as biologically active compounds. Mimics of amino acids in which the carboxylic function is replaced by phosphorus analogues have attracted particular interest. Among these phosphorus functions, phosphinic acid moiety is an excellent mimic of the tetrahedral transition state of amid bond hydrolysis and is more stable than phosphonic or phosphonamidic isosters. Thus, phosphinic compounds occupy an important place and reveal diverse and interesting biological and biochemical properties (Ye *et al.*, 2007; Abrunhosa-Thomas *et al.*, 2007; Wang *et al.*, 2009): phosphinic peptides have been reported to be potent inhibitors of several matrixins (MMPs) (Matziari *et al.*, 2004) and are widely studied as antibacterial agents, enzyme inhibitors, haptens for catalytic antibodies, or anti HIV agents (Boyd *et al.*, 1994; Ryglowski & Kafarski, 1996).

The development of methods for the preparation of phosphinic acids is so important and currently attracting growing interest (Montchamp, 2005; Dingwall *et al.*, 1989). The most commonly employed methods to prepare phosphinic acids suffer from several limitations: large excess of reagents, difficulties to avoid formation of symmetrically disubstituted phosphinic acids, handling difficulties of some starting materials. A new synthesis of unsymmetrical phosphinic acids *R*'P(O)OHR" was performed. The first P—C bond formation was achieved using a base-promoted H-phosphinate alkylation from a protected H-phosphinate, easier and safer to handle. A one pot methodology was developed for the second P–C bond formation involving sila-Arbuzov reaction (Fougère *et al.*, 2009).

An *ORTEP* plot of the molecule is given in Fig. 1. Geometric parameters are in the usual ranges, *e.g.*; typical P = O, P—O and P—C bonds as it was found earlier in phosphonic acid crystal structures (Langley *et al.*, 1996; Frantz *et al.*, 2003; Meyer *et al.*, 2003; Cai *et al.*, 2003).

In the crystal packing, one molecule is linked to two adjacent symmetric molecules *via* strong intermolecular O–H···O==P hydrogen bonds (Table 1). These hydrogen bonds between phosphinic groups built an infinite intermolecular hydrogen-bond network along the *b* direction (Fig. 2), forming chains of molecules. These chains are perpendicularly cross-linked *via* weak hydrogen bonds between C-H from the aromatic ring and O from the phosphinic group (Table 1, Fig 2), that give rise to a bidimensionnal organization parallel to the (001) plane. The packing of the structure can also be described as a bidimensionnal organization piled up to the third direction with hydrophobic functions face to face.

Experimental

To benzyl phosphinate (20 mmol) in acetonitrile (20 ml), bromotrimethylsilane (7 equiv) was added under argon bubbling. The triethylamine (2 equiv) was added, followed 5 minutes later by the bromide derivatives (1 equiv). The mixture was cooled to 0°C and absolute ethanol was added to quench the reaction. After 30 min., the solvent was removed and the residue was taken up in distilled water and extracted with ethyl acetate. The organic layer was dried under $MgSO_4$; filtrated and evaporated under reduced pressure to give the crude product. This product was taken up in water (20 ml) and washed with

ether (3 *x* 20 ml), followed by a reversed phase column chromatography (water/methanol 1:1) to give a white solid with high yield (76%). Single crystals suitable for X-ray structure analysis could be obtained by slow evaporation of a concentrated water/methanol (1/1) solution at room temperature.

Refinement

All Hydrogen atoms attached to C atoms were fixed geometrically and treated as riding with C—H = 0.93 Å (aromatic), 0.96 Å (methylene) or 0.97 Å (secondary CH2 group) with U_{iso}(H) = 1.2 U_{eq}(C) (aromatic) or 1.5 U_{eq}(C) for others. H atom of the hydroxyl was located in difference Fourier syntheses and was treated in the last stage of refinement as riding on it parent O atom with O—H = 0.82 Å and U_{iso}(H) = 1.2 U_{eq}(O).

Figures

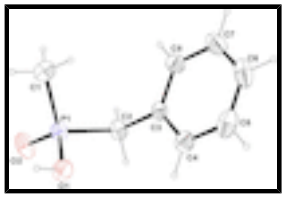


Fig. 1. Molecular View of the title compound. Displacement ellipsoids are drawn at the 30% probability level.

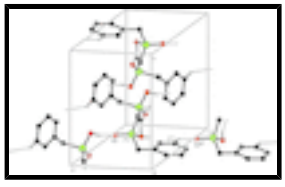


Fig. 2. Molecular packing view with intermolecular hydrogen bonds drawn as dashed lines. H atoms not involved in hydrogen bondings have been omitted for clarity. [Symmetry codes: (i) -*x*+1, *y*+1/2, -*z*+1/2; (ii) *x*-1, *y*, *z*]

Benzyl(methyl)phosphinic acid

Crystal data

$C_8H_{11}O_2P$	$F(000)$ = 360
M_r = 170.14	D_x = 1.306 Mg m^{-3}
Monoclinic, $P2_1/c$	Mo $K\alpha$ radiation, λ = 0.71070 Å
Hall symbol: -P 2ybc	Cell parameters from 1896 reflections
a = 9.3075 (4) Å	θ = 0.4–26.4°
b = 8.2526 (4) Å	μ = 0.27 mm^{-1}
c = 11.8890 (4) Å	*T* = 293 K
β = 108.657 (3)°	Parallelepipedic, colourless
V = 865.22 (6) Å^3	0.60 × 0.25 × 0.06 mm
Z = 4	

Data collection

Nonius KappaCCD diffractometer	1320 reflections with $I > 2\sigma(I)$
Radiation source: fine-focus sealed tube	R_{int} = 0.050
graphite	θ_{max} = 26.3°, θ_{min} = 2.3°

Detector resolution: 9 pixels mm^{-1}	$h = -11 \rightarrow 11$
φ and ω scans	$k = -10 \rightarrow 10$
10548 measured reflections	$l = -14 \rightarrow 14$
1767 independent reflections	

Refinement

Refinement on F^2	Primary atom site location: structure-invariant direct methods
Least-squares matrix: full	Secondary atom site location: difference Fourier map
$R[F^2 > 2\sigma(F^2)] = 0.038$	Hydrogen site location: inferred from neighbouring sites
$wR(F^2) = 0.096$	H-atom parameters constrained
$S = 1.05$	$w = 1/[\sigma^2(F_o^2) + (0.0381P)^2 + 0.2898P]$ where $P = (F_o^2 + 2F_c^2)/3$
1767 reflections	$(\Delta/\sigma)_{max} < 0.001$
100 parameters	$\Delta\rho_{max} = 0.18$ e Å^{-3}
0 restraints	$\Delta\rho_{min} = -0.29$ e Å^{-3}

Special details

Geometry. All e.s.d.'s (except the e.s.d. in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell e.s.d.'s are taken into account individually in the estimation of e.s.d.'s in distances, angles and torsion angles; correlations between e.s.d.'s in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell e.s.d.'s is used for estimating e.s.d.'s involving l.s. planes.

Refinement. Refinement of F^2 against ALL reflections. The weighted *R*-factor *wR* and goodness of fit *S* are based on F^2, conventional *R*-factors *R* are based on *F*, with *F* set to zero for negative F^2. The threshold expression of $F^2 > \sigma(F^2)$ is used only for calculating *R*-factors(gt) *etc*. and is not relevant to the choice of reflections for refinement. *R*-factors based on F^2 are statistically about twice as large as those based on *F*, and *R*- factors based on ALL data will be even larger.

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å^2)

	x	*y*	*z*	U_{iso}*/U_{eq}
P1	0.37056 (5)	0.18896 (6)	0.22698 (4)	0.03697 (18)
C1	0.3422 (3)	0.2500 (3)	0.36151 (18)	0.0574 (6)
H11	0.3450	0.1566	0.4103	0.086*
H12	0.2454	0.3023	0.3441	0.086*
H13	0.4209	0.3241	0.4029	0.086*
O1	0.36315 (16)	0.34293 (17)	0.15063 (12)	0.0487 (4)
H1	0.4189	0.4128	0.1909	0.058*
O2	0.51352 (16)	0.09571 (18)	0.24906 (16)	0.0606 (4)
C2	0.2113 (2)	0.0707 (2)	0.14174 (19)	0.0440 (5)
H21	0.2228	0.0488	0.0649	0.066*
H22	0.2144	−0.0326	0.1814	0.066*
C3	0.0567 (2)	0.1455 (2)	0.12169 (17)	0.0376 (5)
C4	−0.0016 (3)	0.2590 (3)	0.03332 (17)	0.0485 (5)
H4	0.0557	0.2914	−0.0140	0.058*

C5	−0.1435 (3)	0.3248 (3)	0.0144 (2)	0.0618 (7)
H5	−0.1812	0.4011	−0.0454	0.074*
C6	−0.2295 (3)	0.2779 (3)	0.0838 (2)	0.0640 (7)
H6	−0.3255	0.3218	0.0709	0.077*
C7	−0.1734 (3)	0.1669 (3)	0.1716 (2)	0.0613 (7)
H7	−0.2312	0.1352	0.2187	0.074*
C8	−0.0310 (2)	0.1011 (3)	0.19124 (19)	0.0509 (6)
H8	0.0064	0.0260	0.2519	0.061*

Atomic displacement parameters (Å^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
P1	0.0327 (3)	0.0317 (3)	0.0455 (3)	0.0038 (2)	0.0113 (2)	0.0036 (2)
C1	0.0587 (14)	0.0668 (16)	0.0453 (12)	−0.0012 (12)	0.0147 (10)	0.0005 (12)
O1	0.0563 (9)	0.0378 (9)	0.0471 (8)	−0.0077 (7)	0.0097 (6)	0.0053 (6)
O2	0.0367 (8)	0.0452 (9)	0.0993 (12)	0.0114 (7)	0.0209 (8)	0.0051 (9)
C2	0.0418 (11)	0.0336 (11)	0.0557 (12)	−0.0018 (9)	0.0143 (9)	−0.0032 (9)
C3	0.0343 (10)	0.0351 (11)	0.0406 (10)	−0.0066 (8)	0.0081 (8)	−0.0062 (8)
C4	0.0508 (12)	0.0475 (13)	0.0442 (11)	−0.0013 (11)	0.0111 (10)	0.0027 (10)
C5	0.0581 (15)	0.0499 (15)	0.0602 (14)	0.0081 (12)	−0.0050 (11)	−0.0017 (12)
C6	0.0364 (12)	0.0625 (17)	0.0836 (17)	0.0008 (12)	0.0061 (12)	−0.0282 (15)
C7	0.0463 (13)	0.0689 (17)	0.0751 (16)	−0.0124 (13)	0.0284 (12)	−0.0164 (14)
C8	0.0471 (13)	0.0531 (14)	0.0525 (12)	−0.0080 (11)	0.0159 (10)	0.0034 (11)

Geometric parameters (Å, °)

P1—O2	1.4859 (14)	C3—C4	1.382 (3)
P1—O1	1.5502 (14)	C3—C8	1.384 (3)
P1—C1	1.775 (2)	C4—C5	1.378 (3)
P1—C2	1.793 (2)	C4—H4	0.9300
C1—H11	0.9600	C5—C6	1.377 (4)
C1—H12	0.9600	C5—H5	0.9300
C1—H13	0.9600	C6—C7	1.361 (4)
O1—H1	0.8200	C6—H6	0.9300
C2—C3	1.514 (3)	C7—C8	1.381 (3)
C2—H21	0.9700	C7—H7	0.9300
C2—H22	0.9700	C8—H8	0.9300
O2—P1—O1	113.42 (9)	C4—C3—C8	118.07 (19)
O2—P1—C1	111.74 (11)	C4—C3—C2	121.23 (18)
O1—P1—C1	107.66 (10)	C8—C3—C2	120.70 (18)
O2—P1—C2	110.46 (9)	C5—C4—C3	120.9 (2)
O1—P1—C2	103.96 (9)	C5—C4—H4	119.5
C1—P1—C2	109.24 (10)	C3—C4—H4	119.5
P1—C1—H11	109.5	C6—C5—C4	120.1 (2)
P1—C1—H12	109.5	C6—C5—H5	119.9
H11—C1—H12	109.5	C4—C5—H5	119.9
P1—C1—H13	109.5	C7—C6—C5	119.6 (2)
H11—C1—H13	109.5	C7—C6—H6	120.2

H12—C1—H13	109.5	C5—C6—H6	120.2
P1—O1—H1	109.5	C6—C7—C8	120.5 (2)
C3—C2—P1	116.08 (14)	C6—C7—H7	119.8
C3—C2—H21	108.3	C8—C7—H7	119.8
P1—C2—H21	108.3	C7—C8—C3	120.8 (2)
C3—C2—H22	108.3	C7—C8—H8	119.6
P1—C2—H22	108.3	C3—C8—H8	119.6
H21—C2—H22	107.4		
O2—P1—C2—C3	174.91 (15)	C3—C4—C5—C6	0.0 (3)
O1—P1—C2—C3	−63.09 (17)	C4—C5—C6—C7	0.3 (4)
C1—P1—C2—C3	51.61 (18)	C5—C6—C7—C8	−0.1 (4)
P1—C2—C3—C4	81.4 (2)	C6—C7—C8—C3	−0.5 (4)
P1—C2—C3—C8	−99.0 (2)	C4—C3—C8—C7	0.8 (3)
C8—C3—C4—C5	−0.6 (3)	C2—C3—C8—C7	−178.8 (2)
C2—C3—C4—C5	179.01 (19)		

Hydrogen-bond geometry (Å, °)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
O1—H1···O2^{i}	0.82	1.70	2.493 (2)	162
C7—H7···O2^{ii}	0.93	2.54	3.377 (3)	151

Symmetry codes: (i) −*x*+1, *y*+1/2, −*z*+1/2; (ii) *x*−1, *y*, *z*.

Fig. 1

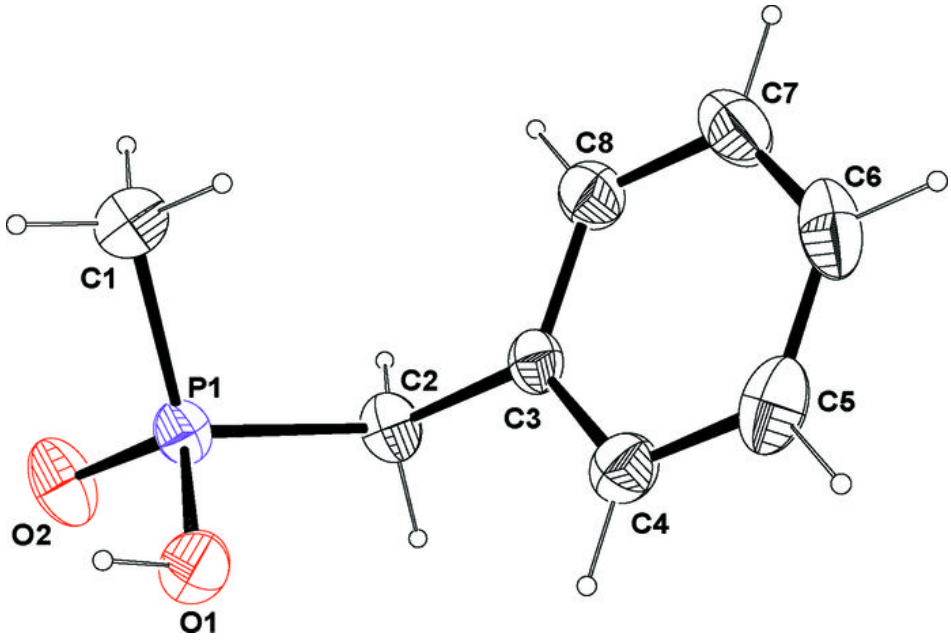
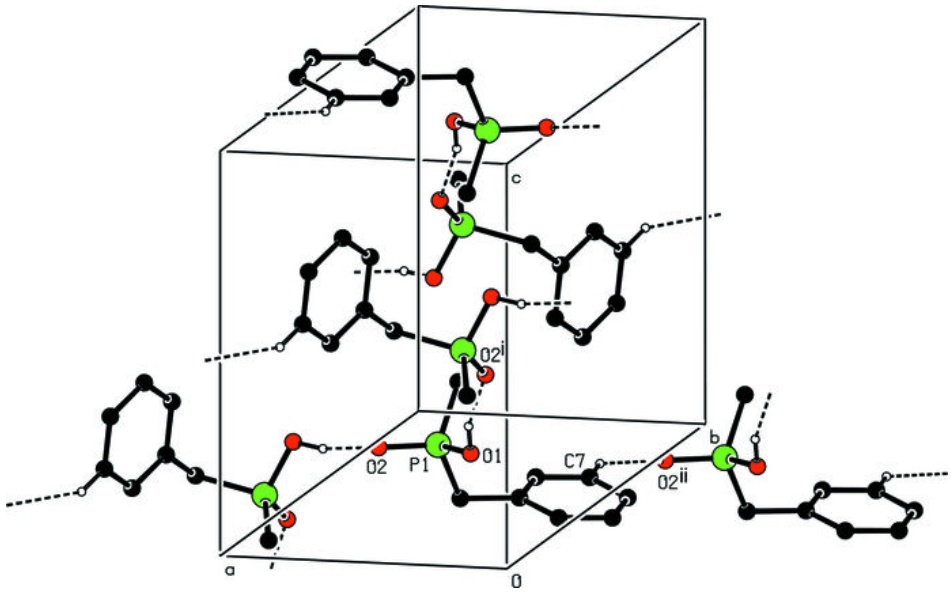


Fig. 2



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Hydrogen bis[2-(4-ammoniophenoxy)-acetate] triiodide

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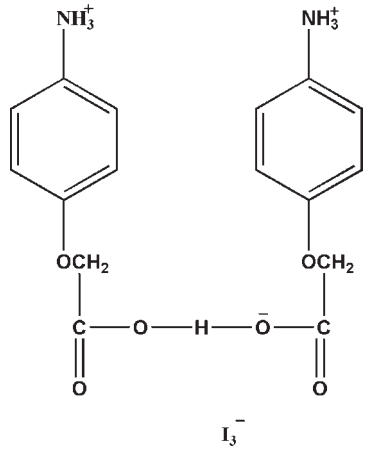
Key indicators: single-crystal X-ray study; T = 293 K; mean σ(C–C) = 0.004 Å; R factor = 0.028; wR factor = 0.062; data-to-parameter ratio = 19.4.

In the title compound, $C_{16}H_{19}N_2O_6^+\cdot I_3^-$, the carboxylate groups of a pair of (4-aminophenoxy) acetate ligands are bridged by an H atom in a rather classical configuration. The H atom is located on an inversion center and the pair of carboxylate groups are centrosymmetrically related with an O···O distance of 2.494 (5) Å. The I_3^- anion is also located on an inversion center. In the crystal, N—H···O and N—H···I hydrogen-bond interactions build up a three-dimensionnal network.

Related literature

For dielectric–ferroelectric materials, see: Hang *et al.* (2009); Li *et al.* (2008). For related structures, see: Antolic *et al.* (1999); Bacon *et al.* (1977); Chen & Mak (1994); Godzisz *et al.* (2003); Kay (1977); Li *et al.* (1998); McAdam *et al.* (1971); Pogorzelec & Garbarczyk (2002); Sridhar *et al.* (2001); Videnova-Adrabinska *et al.* (2007); Zhu *et al.* (2002).



Experimental

Crystal data

$C_{16}H_{19}N_2O_6^+\cdot I_3^-$
M_r = 716.03
Monoclinic, $P2_1/n$
a = 5.065 (1) Å
b = 13.780 (3) Å
c = 14.982 (3) Å
β = 91.45 (3)°
V = 1045.4 (4) Å^3
Z = 2
Mo $K\alpha$ radiation
μ = 4.52 mm^{-1}
T = 293 K
0.40 × 0.30 × 0.20 mm

Data collection

Rigaku SCXmini diffractometer
Absorption correction: multi-scan (*CrystalClear*; Rigaku, 2005)
T_{min} = 0.52, T_{max} = 0.58
10680 measured reflections
2408 independent reflections
2182 reflections with $I > 2\sigma(I)$
R_{int} = 0.034

Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.028
$wR(F^2)$ = 0.062
S = 1.14
2408 reflections
124 parameters
H-atom parameters constrained
$\Delta\rho_{max}$ = 0.85 e Å^{-3}
$\Delta\rho_{min}$ = −0.75 e Å^{-3}

Table 1
Hydrogen-bond geometry (Å, °).

D—H···A	D—H	H···A	D···A	D—H···A
O3—H3···O3^{i}	1.25	1.25	2.495 (5)	180
N1—H1A···I1^{ii}	0.89	2.85	3.665 (3)	152
N1—H1B···O2^{iii}	0.89	2.13	2.907 (4)	146
N1—H1C···O2^{iv}	0.89	2.05	2.935 (4)	172

Symmetry codes: (i) $-x+1, -y+1, -z+1$; (ii) $x+1, y+1, z$; (iii) $-x+\frac{5}{2}, y+\frac{1}{2}, -z+\frac{3}{2}$; (iv) $-x+\frac{3}{2}, y+\frac{1}{2}, -z+\frac{3}{2}$.

Data collection: *CrystalClear* (Rigaku, 2005); cell refinement: *CrystalClear*; data reduction: *CrystalClear*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *ORTEPIII* (Burnett & Johnson, 1996), *ORTEP-3 for Windows* (Farrugia, 1997) and *PLATON* (Spek, 2009); software used to prepare material for publication: *SHELXL97*.

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Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: DN2575).

References

Antolic, S., Salopek, B., Kojic-Prodic, B., Magnus, V. & Cohen, J. D. (1999). *Plant. Growth Regul.* **27**, 21–31.
Bacon, G. E., Walker, C. R. & Speakman, J. C. (1977). *J. Chem. Soc. Perkin Trans. 2*, pp. 979–983.
Burnett, M. N. & Johnson, C. K. (1996). *ORTEPIII*. Report ORNL-6895. Oak Ridge National Laboratory, Tennessee, USA.
Chen, X.-M. & Mak, T. C. W. (1994). *Acta Cryst.* C**50**, 1807–1809.
Farrugia, L. J. (1997). *J. Appl. Cryst.* **30**, 565.
Godzisz, D., Llczyszyn, M. & Ciunik, Z. (2003). *Spectrochim. Acta Part A*, **59**, 235–244.
Hang, T., Fu, D. W., Ye, Q. & Xiong, R. G. (2009). *Cryst. Growth Des.* **5**, 2026–2029.
Kay, M. I. (1977). *Ferroelectrics*, **17**, 415–418.
Li, X. Z., Qu, Z. R. & Xiong, R. G. (2008). *Chin. J. Chem.* **11**, 1959–1962.
Li, P., Wang, T., Emge, T. & Zhao, K. (1998). *J. Am. Chem. Soc.* **120**, 7391–7392.

McAdam, A., Currie, M. & Speakman, J. C. (1971). *J. Chem. Soc. A*, pp. 1994–1997.
Pogorzelec, K. & Garbarczyk, J. (2002). *Mol. Phys. Rep.* **35**, 132–141.
Rigaku (2005). *CrystalClear*. Rigaku Corporation, Tokyo, Japan.
Sheldrick, G. M. (2008). *Acta Cryst.* A**64**, 112–122.
Spek, A. L. (2009). *Acta Cryst.* D**65**, 148–155.
Sridhar, B., Srinivasan, N. & Rajaram, R. K. (2001). *Acta Cryst.* E**57**, o1004–o1006.
Videnova-Adrabinska, V., Obara, E. & Lis, T. (2007). *New J. Chem.* **31**, 287–295.
Zhu, H.-F., Fan, J., Okamura, T., Sun, W.-Y. & Ueyama, N. (2002). *Chem. Lett.* pp. 898–899.

supplementary materials

Acta Cryst. (2010). E**66**, o1872-o1873 [**doi:10.1107/S1600536810024852**]

Hydrogen bis[2-(4-ammoniophenoxy)acetate] triiodide

W.-X. Wang

Comment

We are interested in the dielectric-ferroelectric materials, including organic ligands (Li *et al.*,2008), metal-organic coordination compounds (Hang *et al.*, 2009) and organic-inorganic hybrids. Recent studies have revealed that in amino acid-inorganic acid complexes, when the number of H atoms liberated from the inorganic acid is less than the number of amino acids, the H atom is shared by two amino acids, resulting in short symmetric O—H···O hydrogen bonds, as evidenced in triglycine sulfate (Kay *et al.*, 1977), leading to phase transitions. Thus, we want to find aromatic compounds containing amidogens having dielectric-ferroelectric properties. As part of our ongoing studies, we report here the crystal structure of the title compound.

In the title compound, $C_{16}H_{19}N_2O_6^+.I_3^-$, the carboxylate groups of a pair of (4-aminophenoxy) acetate are bridged by a proton (Fig. 1) as already observed in many carboxylate derivative (Antolic *et al.*, 1999; Bacon *et al.*,1977; Chen & Mak, 1994; Godzisz *et al.*, 2003; Kay, 1977; Li *et al.*, 1998; McAdam *et al.*,1971; Pogorzelec & Garbarczyk, 2002; Sridhar *et al.*, 2001; Videnova-Adrabinska *et al.*, 2007; Zhu *et al.*, 2002). The proton is located on an inversion center and the pair of carboxylate groups are centrosymmetrically related with an O···O distance of ca 2.494 (5) Å. The two carboxylate frameworks are in the same plane with the largest deviation from the plane being 0.013 (3) Å. This plane is making a dihedral angle of 84.1 (1)° with the phenyl ring.

The anion I_3^- is also located around inversion center. The occurence of N-H···O and N-H···I hydrogen interactions build up a three dimensionnal network (Fig. 2).

Experimental

ethyl 2-(4-aminophenoxy)acetate (1.95 g) and methanol(30 ml) were added to a round-bottomed flask with a magnetic stirrer bar, then hydrofluoric acid(52%) 2.4 g was added into the mixture. Yellow plate-like crystals of (I) were grown from an ethanol solution of the title compound by slow evaporation at room temperature.

Refinement

All H atoms attached to C atoms and N atom were fixed geometrically and treated as riding with C—H = 0.93 Å (aromatic) or 0.97 Å (methylene) and N—H = 0.89 Å with $U_{iso}(H) = 1.2U_{eq}(C,N,O)$.

Figures

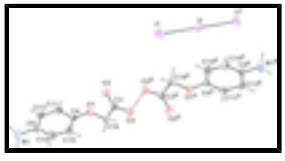


Fig. 1. The molecular structure of the title compound, with the atomic numbering scheme. Displacement ellipsoids are drawn at the 30% probability level. H atoms are represented as small spheres of arbitrary radii. [Symmetry codes : (i) -x+1, -y, -z+1; (ii) 1-x, 1-y, 1-z]

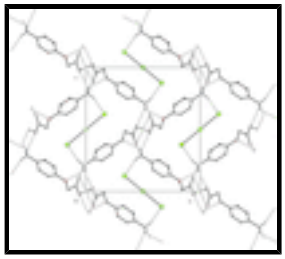


Fig. 2. Packing view of the title compound, the *a* axis. Dashed lines indicate hydrogen bonds. H atoms not involved in hydrogen bondings have been omitted for clarity.

Hydrogen bis[2-(4-ammoniophenoxy)acetate] triiodide

Crystal data

$C_{16}H_{19}N_2O_6^+ \cdot I_3^-$	$F(000) = 672$
$M_r = 716.03$	$D_x = 2.275$ Mg m^{-3}
Monoclinic, $P2_1/n$	Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å
Hall symbol: -P 2yn	Cell parameters from 10680 reflections
$a = 5.065$ (1) Å	$\theta = 3.1–27.5°$
$b = 13.780$ (3) Å	$\mu = 4.52$ mm^{-1}
$c = 14.982$ (3) Å	$T = 293$ K
$\beta = 91.45$ (3)°	Prism, yellow
$V = 1045.4$ (4) Å^3	0.40 × 0.30 × 0.20 mm
$Z = 2$	

Data collection

Rigaku SCXmini diffractometer	2408 independent reflections
Radiation source: fine-focus sealed tube	2182 reflections with $I > 2\sigma(I)$
graphite	$R_{int} = 0.034$
Detector resolution: 13.6612 pixels mm^{-1}	$\theta_{max} = 27.5°$, $\theta_{min} = 3.1°$
ω scans	$h = -6 \rightarrow 6$
Absorption correction: multi-scan (*CrystalClear*; Rigaku, 2005)	$k = -17 \rightarrow 17$
$T_{min} = 0.52$, $T_{max} = 0.58$	$l = -19 \rightarrow 19$
10680 measured reflections	

Refinement

Refinement on F^2	Primary atom site location: structure-invariant direct methods
Least-squares matrix: full	Secondary atom site location: difference Fourier map
$R[F^2 > 2\sigma(F^2)] = 0.028$	Hydrogen site location: inferred from neighbouring sites
$wR(F^2) = 0.062$	H-atom parameters constrained
$S = 1.14$	$w = 1/[\sigma^2(F_o^2) + (0.0183P)^2 + 1.2671P]$ where $P = (F_o^2 + 2F_c^2)/3$
2408 reflections	$(\Delta/\sigma)_{max} = 0.002$

124 parameters	$\Delta\rho_{max}$ = 0.85 e Å^{-3}
0 restraints	$\Delta\rho_{min}$ = −0.74 e Å^{-3}

Special details

Geometry. All esds (except the esd in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell esds are taken into account individually in the estimation of esds in distances, angles and torsion angles; correlations between esds in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell esds is used for estimating esds involving l.s. planes.

Refinement. Refinement of F^2 against ALL reflections. The weighted *R*-factor *wR* and goodness of fit *S* are based on F^2, conventional *R*-factors *R* are based on *F*, with *F* set to zero for negative F^2. The threshold expression of $F^2 > \sigma(F^2)$ is used only for calculating *R*-factors(gt) *etc*. and is not relevant to the choice of reflections for refinement. *R*-factors based on F^2 are statistically about twice as large as those based on *F*, and *R*- factors based on ALL data will be even larger.

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å^2)

	x	*y*	*z*	U_{iso}*/U_{eq}
O1	1.2218 (4)	0.67887 (15)	0.58467 (15)	0.0326 (5)
O2	0.8079 (4)	0.56039 (18)	0.62140 (14)	0.0365 (5)
O3	0.6743 (4)	0.55858 (17)	0.47780 (15)	0.0367 (5)
H3	0.5000	0.5000	0.5000	0.044*
N1	1.1886 (6)	1.0177 (2)	0.7898 (2)	0.0412 (7)
H1A	1.2238	1.0675	0.7542	0.049*
H1B	1.3108	1.0144	0.8334	0.049*
H1C	1.0304	1.0259	0.8132	0.049*
C3	0.8242 (6)	0.5871 (2)	0.5433 (2)	0.0266 (6)
C4	1.1951 (6)	0.7628 (2)	0.63381 (19)	0.0253 (6)
C9	1.1900 (6)	0.9274 (2)	0.73775 (19)	0.0295 (6)
C11	1.3912 (6)	0.7776 (2)	0.6988 (2)	0.0335 (7)
H11A	1.5251	0.7321	0.7070	0.040*
C13	1.3875 (6)	0.8600 (2)	0.7513 (2)	0.0332 (7)
H13A	1.5172	0.8698	0.7955	0.040*
C14	0.9956 (6)	0.9123 (3)	0.6741 (2)	0.0369 (7)
H14A	0.8617	0.9579	0.6662	0.044*
C15	0.9965 (6)	0.8299 (3)	0.6217 (2)	0.0361 (7)
H15A	0.8640	0.8199	0.5785	0.043*
C16	1.0386 (6)	0.6569 (2)	0.5143 (2)	0.0311 (7)
H16A	1.1324	0.6284	0.4651	0.037*
H16B	0.9570	0.7166	0.4931	0.037*
I1	0.53672 (6)	0.162582 (19)	0.624725 (17)	0.05293 (10)
I2	0.5000	0.0000	0.5000	0.03753 (10)

Atomic displacement parameters (Å^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
O1	0.0381 (12)	0.0215 (10)	0.0377 (12)	−0.0003 (9)	−0.0087 (9)	−0.0031 (9)
O2	0.0356 (12)	0.0465 (14)	0.0272 (11)	−0.0053 (10)	−0.0027 (9)	0.0036 (10)

O3	0.0373 (12)	0.0434 (13)	0.0290 (11)	−0.0057 (10)	−0.0059 (9)	−0.0062 (10)
N1	0.0396 (16)	0.0464 (17)	0.0376 (16)	−0.0077 (13)	0.0043 (12)	−0.0193 (13)
C3	0.0285 (15)	0.0233 (14)	0.0280 (15)	0.0060 (11)	−0.0017 (11)	−0.0031 (12)
C4	0.0283 (14)	0.0212 (14)	0.0264 (14)	−0.0055 (11)	0.0002 (11)	0.0026 (11)
C9	0.0344 (16)	0.0309 (16)	0.0234 (14)	−0.0087 (13)	0.0041 (12)	−0.0055 (12)
C11	0.0330 (16)	0.0298 (16)	0.0372 (17)	−0.0007 (13)	−0.0100 (13)	0.0042 (14)
C13	0.0341 (16)	0.0382 (17)	0.0269 (15)	−0.0050 (14)	−0.0084 (12)	0.0009 (13)
C14	0.0332 (17)	0.0375 (18)	0.0398 (18)	0.0090 (14)	−0.0057 (13)	−0.0088 (15)
C15	0.0295 (16)	0.0404 (19)	0.0379 (18)	0.0040 (13)	−0.0117 (13)	−0.0102 (15)
C16	0.0413 (18)	0.0228 (15)	0.0290 (15)	−0.0011 (12)	−0.0050 (13)	−0.0014 (12)
I1	0.0714 (2)	0.04395 (16)	0.04379 (15)	−0.00423 (12)	0.00786 (12)	−0.00539 (11)
I2	0.04291 (18)	0.04059 (18)	0.02891 (16)	0.00398 (13)	−0.00235 (12)	0.00590 (12)

Geometric parameters (Å, °)

O1—C4	1.380 (4)	C4—C11	1.388 (4)
O1—C16	1.419 (4)	C9—C14	1.369 (4)
O2—C3	1.232 (4)	C9—C13	1.376 (5)
O3—C3	1.287 (4)	C11—C13	1.382 (5)
O3—O3^{i}	2.495 (5)	C11—H11A	0.9300
O3—H3	1.2476	C13—H13A	0.9300
N1—C9	1.467 (4)	C14—C15	1.381 (5)
N1—H1A	0.8899	C14—H14A	0.9300
N1—H1B	0.8896	C15—H15A	0.9300
N1—H1C	0.8899	C16—H16A	0.9700
C3—C16	1.522 (4)	C16—H16B	0.9700
C4—C15	1.375 (4)	I1—I2	2.9203 (5)
C4—O1—C16	120.3 (2)	C13—C11—C4	120.0 (3)
C3—O3—O3^{i}	113.7 (2)	C13—C11—H11A	120.0
C3—O3—H3	113.7	C4—C11—H11A	120.0
C9—N1—H1A	109.4	C9—C13—C11	119.4 (3)
C9—N1—H1B	109.5	C9—C13—H13A	120.3
H1A—N1—H1B	109.5	C11—C13—H13A	120.3
C9—N1—H1C	109.5	C9—C14—C15	120.6 (3)
H1A—N1—H1C	109.5	C9—C14—H14A	119.7
H1B—N1—H1C	109.5	C15—C14—H14A	119.7
O2—C3—O3	125.5 (3)	C4—C15—C14	119.3 (3)
O2—C3—C16	121.7 (3)	C4—C15—H15A	120.3
O3—C3—C16	112.8 (3)	C14—C15—H15A	120.3
C15—C4—O1	125.1 (3)	O1—C16—C3	112.4 (2)
C15—C4—C11	120.2 (3)	O1—C16—H16A	109.1
O1—C4—C11	114.8 (3)	C3—C16—H16A	109.1
C14—C9—C13	120.5 (3)	O1—C16—H16B	109.1
C14—C9—N1	119.1 (3)	C3—C16—H16B	109.1
C13—C9—N1	120.4 (3)	H16A—C16—H16B	107.9

Symmetry codes: (i) −*x*+1, −*y*+1, −*z*+1.

Hydrogen-bond geometry (Å, °)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
O3—H3···O3^{i}	1.25	1.25	2.495 (5)	180
N1—H1A···I1^{ii}	0.89	2.85	3.665 (3)	152
N1—H1B···O2^{iii}	0.89	2.13	2.907 (4)	146
N1—H1C···O2^{iv}	0.89	2.05	2.935 (4)	172

Symmetry codes: (i) −*x*+1, −*y*+1, −*z*+1; (ii) *x*+1, *y*+1, *z*; (iii) −*x*+5/2, *y*+1/2, −*z*+3/2; (iv) −*x*+3/2, *y*+1/2, −*z*+3/2.

Fig. 1

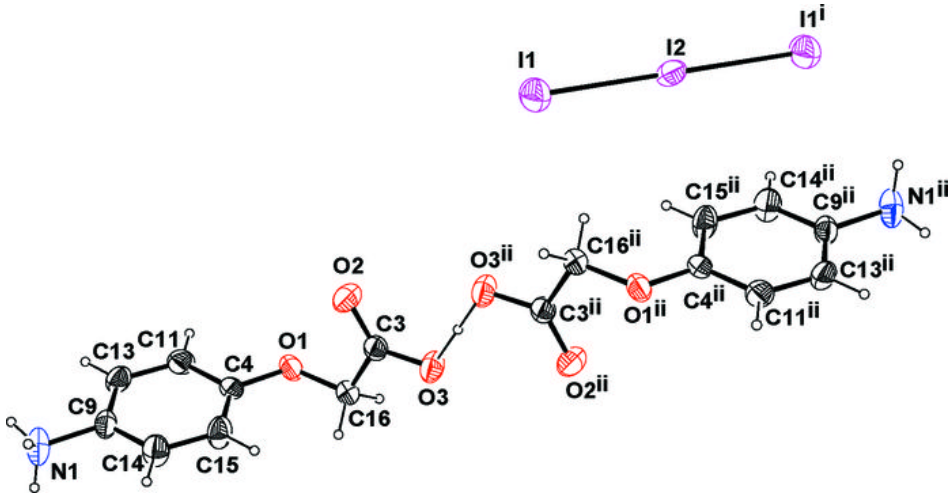
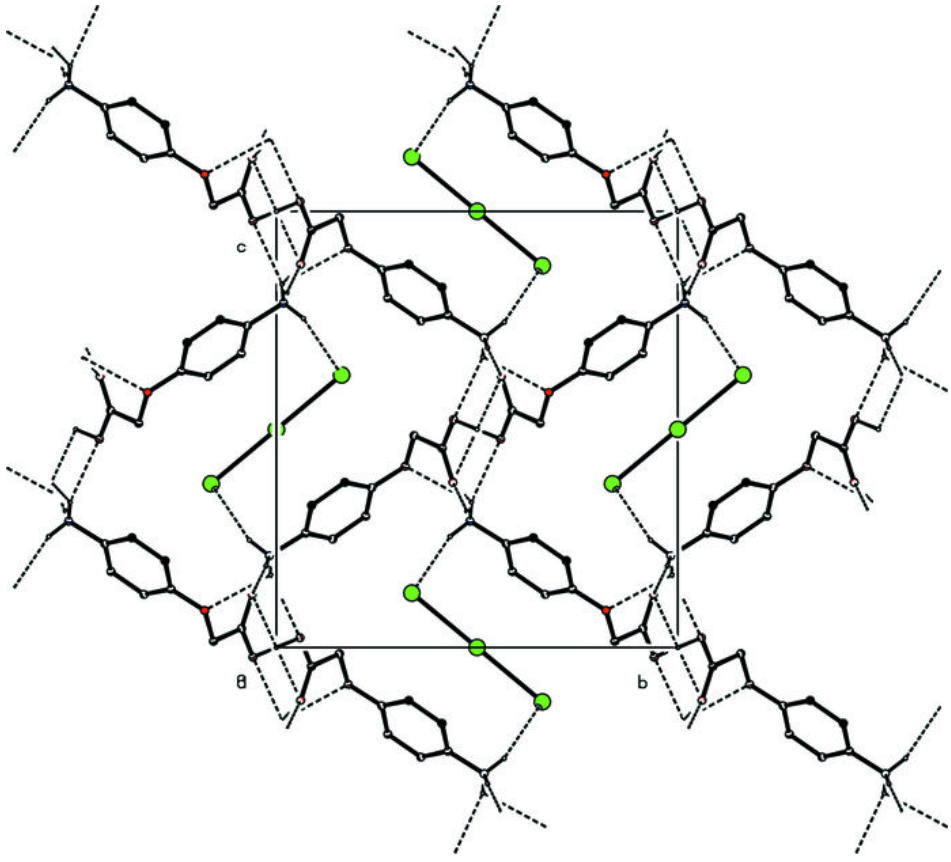

I1
I2
I1i
C15ii
C14ii
C9ii
N1ii
C16ii
O3ii
O2
C3
C13ii
C4ii
O1ii
C3ii
C11ii
C13
C11
O1
C4
C9
O3
C16
O2ii
N1
C14
C15

Fig. 2



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2-(2,3,4,9-Tetrahydro-1*H*-carbazol-1-ylidene)propanedinitrile

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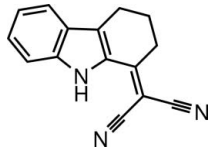
Key indicators: single-crystal X-ray study; T = 110 K; mean σ(C–C) = 0.001 Å; R factor = 0.043; wR factor = 0.115; data-to-parameter ratio = 22.9.

In the title molecule, $C_{15}H_{11}N_3$, the dihedral angle between the benzene ring and the fused pyrrole ring is 1.07 (5)°. The cyclohexene ring adopts an envelope conformation: the dicyanomethylene group at position 1 has a coplanar orientation. An intramolecular N—H···N hydrogen bond generates an S(7) ring motif. Intermolecular N—H···N hydrogen bonds form an R_2^2(14) ring in the crystal. A C—H···π interaction involving the benzene ring is also found in the structure.

Related literature

For naturally occurring carbazole alkaloids see: Scott *et al.* (2006). For the biological activity of carbazole alkaloids see: Ramsewak *et al.*(1999); Tachibana *et al.* (2001); Nakahara *et al.* (2002). For the crystal structures of substituted carbazole derivatives see: Gunaseelan *et al.* (2007*a*,*b*, 2009); Thiruvalluvar *et al.* (2007); Sridharan *et al.* (2008). For ring conformations, see: Cremer & Pople (1975). For hydrogen-bond motifs, see: Bernstein *et al.* (1995).



Experimental

Crystal data

$C_{15}H_{11}N_3$
M_r = 233.27
Monoclinic, $P2_1/n$
a = 8.4794 (3) Å
b = 10.5542 (4) Å
c = 13.0575 (5) Å
β = 97.366 (3)°
V = 1158.92 (8) Å^3
Z = 4
Mo $K\alpha$ radiation
μ = 0.08 mm^{-1}
T = 110 K
0.53 × 0.38 × 0.31 mm

Data collection

Oxford Diffraction Xcalibur Ruby Gemini diffractometer
Absorption correction: multi-scan (*CrysAlis PRO*; Oxford Diffraction, 2009)
T_{min} = 0.939, T_{max} = 1.000
8311 measured reflections
3822 independent reflections
2854 reflections with $I > 2\sigma(I)$
R_{int} = 0.021

Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.043
$wR(F^2)$ = 0.115
S = 0.98
3822 reflections
167 parameters
H atoms treated by a mixture of independent and constrained refinement
$\Delta\rho_{max}$ = 0.40 e Å^{-3}
$\Delta\rho_{min}$ = −0.24 e Å^{-3}

Table 1
Hydrogen-bond geometry (Å, °).

*Cg*1 is the centroid of the C4*B*,C5–C8,C8*A* ring.

D—H···A	D—H	H···A	D···A	D—H···A
N9—H9···N13	0.913 (14)	2.508 (14)	3.2626 (12)	140.3 (11)
N9—H9···N13^{i}	0.913 (14)	2.553 (14)	3.2267 (12)	131.1 (11)
C2—H2*A*···*Cg*1^{ii}	0.99	2.79	3.6244 (10)	142

Symmetry codes: (i) $-x+1, -y+1, -z$; (ii) $-x+\frac{1}{2}, y-\frac{1}{2}, -z+\frac{1}{2}$.

Data collection: *CrysAlis PRO* (Oxford Diffraction, 2009); cell refinement: *CrysAlis PRO*; data reduction: *CrysAlis PRO*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *ORTEP-3* (Farrugia, 1997); software used to prepare material for publication: *PLATON* (Spek, 2009).

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Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: DN2576).

References

Bernstein, J., Davis, R. E., Shimoni, L. & Chang, N.-L. (1995). *Angew. Chem. Int. Ed. Engl.* **34**, 1555–1573.
Cremer, D. & Pople, J. A. (1975). *J. Am. Chem. Soc.* **97**, 1354–1358.
Farrugia, L. J. (1997). *J. Appl. Cryst.* **30**, 565.
Gunaseelan, A. T., Prabakaran, K., Prasad, K. J. R., Thiruvalluvar, A. & Butcher, R. J. (2009). *Acta Cryst.* E**65**, o1946–o1947.
Gunaseelan, A. T., Thiruvalluvar, A., Martin, A. E. & Prasad, K. J. R. (2007*a*). *Acta Cryst.* E**63**, o2413–o2414.
Gunaseelan, A. T., Thiruvalluvar, A., Martin, A. E. & Prasad, K. J. R. (2007*b*). *Acta Cryst.* E**63**, o2729–o2730.
Nakahara, K., Trakoontivakorn, G., Alzoreky, N. S., Ono, H., Onishi-Kameyama, M. & Yoshida, M. (2002). *J. Agric. Food Chem.* **50**, 4796–4802.
Oxford Diffraction (2009). *CrysAlis PRO*. Oxford Diffraction Ltd, Yarnton, England.
Ramsewak, R. S., Nair, M. G., Strasburg, G. M., DeWitt, D. L. & Nitiss, J. L. (1999). *J. Agric. Food Chem.* **47**, 444–447.
Scott, T. L., Yu, X., Gorugantula, S. P., Carrero-Martinez, G. & Söderberg, B. C. G. (2006). *Tetrahedron*, **62**, 10835–10842.
Sheldrick, G. M. (2008). *Acta Cryst.* A**64**, 112–122.
Spek, A. L. (2009). *Acta Cryst.* D**65**, 148–155.
Sridharan, M., Prasad, K. J. R., Gunaseelan, A. T., Thiruvalluvar, A. & Linden, A. (2008). *Acta Cryst.* E**64**, o763–o764.
Tachibana, Y., Kikuzaki, H., Lajis, N. H. & Nakatani, N. (2001). *J. Agric. Food Chem.* **49**, 5589–5594.
Thiruvalluvar, A., Gunaseelan, A. T., Martin, A. E., Prasad, K. J. R. & Butcher, R. J. (2007). *Acta Cryst.* E**63**, o3524.

supplementary materials

Acta Cryst. (2010). E**66**, o1713 [**doi:10.1107/S1600536810022671**]

2-(2,3,4,9-Tetrahydro-1*H*-carbazol-1-ylidene)propanedinitrile

R. Archana, K. Prabakaran, K. J. Rajendra Prasad, A. Thiruvalluvar and R. J. Butcher

Comment

Tetrahydrocarbazolones have been used extensively as advanced intermediates in synthetic efforts toward a number of naturally occurring carbazole alkaloids (Scott *et al.*, 2006). Carbazole alkaloids possess various biological activities such as anti-tumor, anti-oxidative, anti-mutagenic, and anti-inflammatory activities (Ramsewak *et al.*, 1999; Tachibana *et al.*, 2001; Nakahara *et al.*, 2002). Since it is known that carbazole alkaloids possess anti-tumor activity, the identification of alkaloids that are cytotoxic against tumor cells could lead to the development of a chemopreventive agent for tumor treatment.

Gunaseelan *et al.* (2007*a*,b), Gunaseelan *et al.* (2009), Thiruvalluvar *et al.* (2007) and Sridharan *et al.* (2008) have reported the crystal structures of substituted carbazole derivatives, in which the carbazole units are not planar. In the title molecule (Scheme I, Fig. 1), $C_{15}H_{11}N_3$, the carbazole unit is not planar. The dihedral angle between the benzene ring and the fused pyrrole ring is 1.07 (5)°. The r.m.s. deviation of a mean plane fitted through all non hydrogen atoms excluding C3 of the carbazole unit is 0.0263 Å; C3 deviates from this plane by 0.576 (1) Å. The cyclohexene ring adopts an envelope conformation. The puckering parameters (Cremer & Pople, 1975) are q2=0.3482 (10) Å, q3=-0.2564 (10) Å, Q=0.4324 (10) Å, θ=126.37 (13)° and φ=293.46 (16)°. The dicyanomethylene group at position 1 has a coplanar orientation. An intramolecular hydrogen contact N9—H9···N13 generates a ring of graph-set motif S(7) (Bernstein *et al.*, 1995)(Table 1, Fig. 1). Intermolecular N9—H9···N13 hydrogen bonds form a $R^2_2(14)$(Bernstein *et al.*, 1995) ring in the crystal structure (Table 1, Fig. 2). A C2—H2A···π interaction involving the benzene (C4B,C5—C8,C8A) ring is also found in the structure(Table 1).

Experimental

A mixture of 2,3,4,9-tetrahydro-1*H*-carbazol-1-one (0.199 g, 0.001 mol), malononitrile (0.066 g, 0.001 mol), ammonium acetate (0.092 g, 0.0012 mol) and few drops of acetic acid in 5 ml of toluene was refluxed at 383 K for 6 h. On cooling, the precipitate that formed was filtered off, washed with petroleum ether and dried. The crude product thus obtained was purified by column chromatography over silica gel using petroleum ether: ethyl acetate (99:1, *v*/*v*) to yield the titled product (0.173 g, 74%). This was recrystallized from ethyl acetate.

Refinement

The H atom bonded to N9 was located in a difference Fourier map and refined freely. Other H atoms were positioned geometrically and allowed to ride on their parent atoms, with C—H = 0.95–0.99 Å and U_{iso}(H) = 1.2U_{eq}(parent atom).

Figures

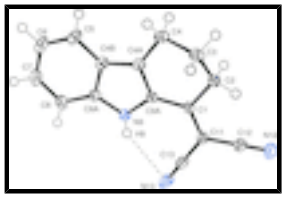


Fig. 1. The molecular structure of the title compound, showing the atom-numbering scheme and displacement ellipsoids drawn at the 50% probability level. H atoms are shown as small spheres of arbitrary radius.

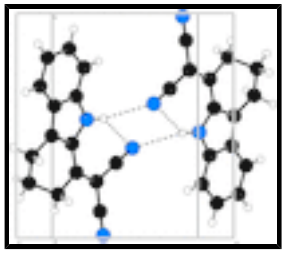


Fig. 2. A part of the crystal structure of (I), viewed along *c* axis, showing the formation of a $R^2_2(14)$ ring.

2-(2,3,4,9-Tetrahydro-1*H*-carbazol-1-ylidene)propanedinitrile

Crystal data

$C_{15}H_{11}N_3$	$F(000) = 488$
$M_r = 233.27$	$D_x = 1.337$ Mg m^{-3}
Monoclinic, $P2_1/n$	Melting point: 470 K
Hall symbol: -P 2yn	Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å
$a = 8.4794$ (3) Å	Cell parameters from 4130 reflections
$b = 10.5542$ (4) Å	$\theta = 4.7$–$32.6°$
$c = 13.0575$ (5) Å	$\mu = 0.08$ mm^{-1}
$\beta = 97.366$ (3)°	$T = 110$ K
$V = 1158.92$ (8) Å^3	Prism, pale-yellow
$Z = 4$	0.53 × 0.38 × 0.31 mm

Data collection

Oxford Diffraction Xcalibur Ruby Gemini diffractometer	3822 independent reflections
Radiation source: Enhance (Mo) X-ray Source	2854 reflections with $I > 2\sigma(I)$
graphite	$R_{int} = 0.021$
Detector resolution: 10.5081 pixels mm^{-1}	$\theta_{max} = 32.6°$, $\theta_{min} = 4.7°$
ω scans	$h = -12 \rightarrow 12$
Absorption correction: multi-scan (*CrysAlis PRO*; Oxford Diffraction, 2009)	$k = -15 \rightarrow 15$
$T_{min} = 0.939$, $T_{max} = 1.000$	$l = -19 \rightarrow 16$
8311 measured reflections	

Refinement

Refinement on F^2	Primary atom site location: structure-invariant direct methods

Least-squares matrix: full	Secondary atom site location: difference Fourier map
$R[F^2 > 2\sigma(F^2)] = 0.043$	Hydrogen site location: inferred from neighbouring sites
$wR(F^2) = 0.115$	H atoms treated by a mixture of independent and constrained refinement
$S = 0.98$	$w = 1/[\sigma^2(F_o^2) + (0.0736P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
3822 reflections	$(\Delta/\sigma)_{max} = 0.001$
167 parameters	$\Delta\rho_{max} = 0.40$ e Å^{-3}
0 restraints	$\Delta\rho_{min} = -0.24$ e Å^{-3}

Special details

Geometry. Bond distances, angles *etc*. have been calculated using the rounded fractional coordinates. All su's are estimated from the variances of the (full) variance-covariance matrix. The cell e.s.d.'s are taken into account in the estimation of distances, angles and torsion angles

Refinement. Refinement of F^2 against ALL reflections. The weighted *R*-factor *wR* and goodness of fit *S* are based on F^2, conventional *R*-factors *R* are based on *F*, with *F* set to zero for negative F^2. The threshold expression of $F^2 > 2\sigma(F^2)$ is used only for calculating *R*-factors(gt) *etc*. and is not relevant to the choice of reflections for refinement. *R*-factors based on F^2 are statistically about twice as large as those based on *F*, and *R*- factors based on ALL data will be even larger.

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å^2)

	x	*y*	*z*	U_{iso}*/U_{eq}
N9	0.20402 (9)	0.52842 (7)	0.07142 (6)	0.0170 (2)
N12	0.27359 (12)	0.01410 (9)	−0.03875 (8)	0.0333 (3)
N13	0.42310 (11)	0.40137 (9)	−0.08917 (7)	0.0351 (3)
C1	0.14687 (10)	0.29269 (9)	0.07178 (6)	0.0152 (2)
C2	0.05668 (11)	0.19571 (9)	0.12634 (7)	0.0194 (2)
C3	−0.09527 (10)	0.24541 (10)	0.16360 (7)	0.0219 (3)
C4	−0.06619 (11)	0.36476 (10)	0.22890 (7)	0.0212 (3)
C4A	0.03186 (10)	0.45589 (9)	0.17735 (6)	0.0166 (2)
C4B	0.04943 (10)	0.58875 (9)	0.19177 (7)	0.0179 (2)
C5	−0.01638 (11)	0.67652 (10)	0.25578 (8)	0.0238 (3)
C6	0.02314 (12)	0.80254 (10)	0.24880 (8)	0.0275 (3)
C7	0.12868 (12)	0.84267 (10)	0.18004 (8)	0.0264 (3)
C8	0.19716 (11)	0.75911 (9)	0.11745 (7)	0.0221 (2)
C8A	0.15696 (10)	0.63122 (9)	0.12427 (7)	0.0173 (2)
C9A	0.12894 (10)	0.42084 (8)	0.10364 (6)	0.0151 (2)
C11	0.24383 (10)	0.25207 (9)	0.00157 (7)	0.0178 (2)
C12	0.25910 (11)	0.12004 (10)	−0.02084 (7)	0.0222 (3)
C13	0.34255 (11)	0.33496 (10)	−0.04916 (7)	0.0226 (2)
H2A	0.12768	0.16285	0.18658	0.0232*
H2B	0.02872	0.12377	0.07880	0.0232*
H3A	−0.17457	0.26402	0.10301	0.0262*
H3B	−0.14007	0.17888	0.20485	0.0262*
H4A	−0.16918	0.40435	0.23835	0.0255*

H4B	−0.01056	0.34246	0.29787	0.0255*
H5	−0.08640	0.64936	0.30266	0.0286*
H6	−0.02115	0.86313	0.29074	0.0330*
H7	0.15343	0.93025	0.17673	0.0317*
H8	0.26848	0.78727	0.07176	0.0265*
H9	0.2890 (16)	0.5317 (13)	0.0351 (11)	0.043 (4)*

Atomic displacement parameters (Å^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
N9	0.0188 (3)	0.0158 (4)	0.0172 (3)	−0.0019 (3)	0.0052 (3)	−0.0004 (3)
N12	0.0414 (5)	0.0225 (4)	0.0389 (5)	−0.0017 (4)	0.0158 (4)	−0.0055 (4)
N13	0.0396 (5)	0.0323 (5)	0.0383 (5)	−0.0131 (4)	0.0240 (4)	−0.0134 (4)
C1	0.0148 (4)	0.0166 (4)	0.0140 (4)	−0.0015 (3)	0.0007 (3)	0.0009 (3)
C2	0.0228 (4)	0.0177 (4)	0.0181 (4)	−0.0047 (3)	0.0046 (3)	0.0012 (4)
C3	0.0198 (4)	0.0262 (5)	0.0205 (4)	−0.0062 (4)	0.0057 (3)	0.0006 (4)
C4	0.0185 (4)	0.0271 (5)	0.0194 (4)	−0.0021 (4)	0.0074 (3)	−0.0002 (4)
C4A	0.0144 (4)	0.0204 (4)	0.0149 (4)	0.0006 (3)	0.0018 (3)	0.0004 (3)
C4B	0.0149 (4)	0.0208 (4)	0.0176 (4)	0.0022 (3)	0.0002 (3)	−0.0015 (4)
C5	0.0179 (4)	0.0290 (5)	0.0240 (4)	0.0059 (4)	0.0007 (3)	−0.0076 (4)
C6	0.0250 (5)	0.0263 (5)	0.0293 (5)	0.0096 (4)	−0.0040 (4)	−0.0107 (4)
C7	0.0292 (5)	0.0179 (4)	0.0290 (5)	0.0037 (4)	−0.0081 (4)	−0.0037 (4)
C8	0.0255 (4)	0.0175 (4)	0.0218 (4)	−0.0003 (4)	−0.0028 (3)	0.0007 (4)
C8A	0.0181 (4)	0.0169 (4)	0.0160 (4)	0.0014 (3)	−0.0013 (3)	−0.0009 (3)
C9A	0.0153 (4)	0.0157 (4)	0.0143 (4)	−0.0015 (3)	0.0023 (3)	0.0013 (3)
C11	0.0189 (4)	0.0166 (4)	0.0183 (4)	−0.0025 (3)	0.0044 (3)	−0.0026 (3)
C12	0.0238 (4)	0.0220 (5)	0.0219 (4)	−0.0014 (4)	0.0067 (3)	−0.0026 (4)
C13	0.0236 (4)	0.0221 (4)	0.0238 (4)	−0.0037 (4)	0.0097 (4)	−0.0081 (4)

Geometric parameters (Å, °)

N9—C8A	1.3723 (12)	C6—C7	1.4115 (15)
N9—C9A	1.3929 (11)	C7—C8	1.3801 (14)
N12—C12	1.1521 (14)	C8—C8A	1.3978 (13)
N13—C13	1.1499 (14)	C11—C12	1.4331 (14)
N9—H9	0.913 (14)	C11—C13	1.4307 (13)
C1—C2	1.5099 (13)	C2—H2A	0.9900
C1—C11	1.3760 (12)	C2—H2B	0.9900
C1—C9A	1.4289 (13)	C3—H3A	0.9900
C2—C3	1.5273 (13)	C3—H3B	0.9900
C3—C4	1.5234 (14)	C4—H4A	0.9900
C4—C4A	1.4876 (13)	C4—H4B	0.9900
C4A—C9A	1.3943 (12)	C5—H5	0.9500
C4A—C4B	1.4201 (13)	C6—H6	0.9500
C4B—C5	1.4099 (14)	C7—H7	0.9500
C4B—C8A	1.4196 (13)	C8—H8	0.9500
C5—C6	1.3775 (15)		
N9···N13	3.2626 (12)	C8A···H2A^{vii}	2.9000

N9···C13	2.9158 (13)	C9A···H3A	3.0600
N9···N13^{i}	3.2267 (12)	C11···H9	3.001 (14)
N9···C9A^{ii}	3.4392 (11)	C12···H2A	3.0900
N12···C3^{iii}	3.4371 (14)	C12···H2B	2.4800
N13···N9	3.2626 (12)	C13···H9	2.420 (14)
N13···N9^{i}	3.2267 (12)	H2A···C12	3.0900
N13···N13^{i}	3.2679 (13)	H2A···H7^{iv}	2.4700
N12···H2B^{iii}	2.9400	H2A···C4B^{vi}	3.0800
N12···H8^{iv}	2.8000	H2A···C8^{vi}	2.9700
N13···H9	2.508 (14)	H2A···C8A^{vi}	2.9000
N13···H9^{i}	2.553 (14)	H2B···C12	2.4800
N13···H3B^{v}	2.8100	H2B···H7^{iv}	2.5600
C1···C6^{vi}	3.4129 (13)	H2B···N12^{iii}	2.9400
C1···C7^{vi}	3.5806 (13)	H3A···C9A	3.0600
C1···C8A^{ii}	3.4849 (12)	H3A···C8^{ii}	2.8700
C3···N12^{iii}	3.4371 (14)	H3A···H8^{ii}	2.3800
C4A···C7^{vi}	3.4360 (13)	H3B···C5^{viii}	3.0200
C6···C9A^{vii}	3.5380 (13)	H3B···H5^{viii}	2.3300
C6···C1^{vii}	3.4129 (13)	H3B···N13^{x}	2.8100
C7···C9A^{vii}	3.3756 (13)	H4B···C8^{vi}	2.8800
C7···C1^{vii}	3.5806 (13)	H4B···H8^{vi}	2.5600
C7···C4A^{vii}	3.4360 (13)	H5···C3^{ix}	2.9700
C8A···C1^{ii}	3.4849 (12)	H5···H3B^{ix}	2.3300
C9A···N9^{ii}	3.4392 (11)	H7···C2^{xi}	2.9700
C9A···C6^{vi}	3.5380 (13)	H7···H2A^{xi}	2.4700
C9A···C7^{vi}	3.3756 (13)	H7···H2B^{xi}	2.5600
C13···N9	2.9158 (13)	H7···C4A^{vii}	3.0900
C2···H7^{iv}	2.9700	H8···N12^{xi}	2.8000
C3···H5^{viii}	2.9700	H8···H4B^{vii}	2.5600
C4A···H7^{vi}	3.0900	H8···H3A^{ii}	2.3800
C4B···H2A^{vii}	3.0800	H9···N13	2.508 (14)
C5···H3B^{ix}	3.0200	H9···C11	3.001 (14)
C8···H3A^{ii}	2.8700	H9···C13	2.420 (14)
C8···H2A^{vii}	2.9700	H9···N13^{i}	2.553 (14)
C8···H4B^{vii}	2.8800		
C8A—N9—C9A	108.60 (7)	C12—C11—C13	115.24 (8)
C9A—N9—H9	127.6 (9)	N12—C12—C11	179.07 (10)
C8A—N9—H9	122.1 (9)	N13—C13—C11	179.33 (10)
C2—C1—C11	119.03 (8)	C1—C2—H2A	109.00
C2—C1—C9A	115.16 (7)	C1—C2—H2B	109.00
C9A—C1—C11	125.72 (8)	C3—C2—H2A	109.00
C1—C2—C3	114.61 (8)	C3—C2—H2B	109.00

C2—C3—C4	112.31 (8)	H2A—C2—H2B	108.00
C3—C4—C4A	109.95 (7)	C2—C3—H3A	109.00
C4—C4A—C9A	123.68 (8)	C2—C3—H3B	109.00
C4B—C4A—C9A	107.00 (8)	C4—C3—H3A	109.00
C4—C4A—C4B	129.32 (8)	C4—C3—H3B	109.00
C5—C4B—C8A	119.68 (9)	H3A—C3—H3B	108.00
C4A—C4B—C5	133.21 (8)	C3—C4—H4A	110.00
C4A—C4B—C8A	107.11 (8)	C3—C4—H4B	110.00
C4B—C5—C6	118.49 (9)	C4A—C4—H4A	110.00
C5—C6—C7	120.75 (10)	C4A—C4—H4B	110.00
C6—C7—C8	122.29 (10)	H4A—C4—H4B	108.00
C7—C8—C8A	117.05 (9)	C4B—C5—H5	121.00
N9—C8A—C4B	108.30 (8)	C6—C5—H5	121.00
N9—C8A—C8	129.97 (8)	C5—C6—H6	120.00
C4B—C8A—C8	121.72 (8)	C7—C6—H6	120.00
N9—C9A—C1	127.87 (8)	C6—C7—H7	119.00
C1—C9A—C4A	123.12 (8)	C8—C7—H7	119.00
N9—C9A—C4A	108.99 (8)	C7—C8—H8	121.00
C1—C11—C13	123.57 (9)	C8A—C8—H8	121.00
C1—C11—C12	121.09 (8)		

C9A—N9—C8A—C4B	−0.03 (12)	C4—C4A—C4B—C8A	179.76 (8)
C9A—N9—C8A—C8	−178.67 (9)	C9A—C4A—C4B—C5	−179.41 (10)
C8A—N9—C9A—C1	−177.78 (8)	C9A—C4A—C4B—C8A	0.72 (10)
C8A—N9—C9A—C4A	0.48 (10)	C4—C4A—C9A—N9	−179.85 (8)
C9A—C1—C2—C3	28.90 (11)	C4—C4A—C9A—C1	−1.49 (13)
C11—C1—C2—C3	−154.52 (8)	C4B—C4A—C9A—N9	−0.75 (9)
C2—C1—C9A—N9	176.14 (8)	C4B—C4A—C9A—C1	177.62 (8)
C2—C1—C9A—C4A	−1.90 (12)	C4A—C4B—C5—C6	−178.23 (10)
C11—C1—C9A—N9	−0.17 (14)	C8A—C4B—C5—C6	1.62 (14)
C11—C1—C9A—C4A	−178.21 (8)	C4A—C4B—C8A—N9	−0.44 (10)
C2—C1—C11—C12	0.52 (13)	C4A—C4B—C8A—C8	178.34 (8)
C2—C1—C11—C13	−175.65 (8)	C5—C4B—C8A—N9	179.67 (8)
C9A—C1—C11—C12	176.71 (8)	C5—C4B—C8A—C8	−1.55 (14)
C9A—C1—C11—C13	0.54 (14)	C4B—C5—C6—C7	−0.78 (15)
C1—C2—C3—C4	−52.67 (10)	C5—C6—C7—C8	−0.22 (16)
C2—C3—C4—C4A	46.84 (10)	C6—C7—C8—C8A	0.34 (15)
C3—C4—C4A—C4B	159.52 (9)	C7—C8—C8A—N9	179.04 (9)
C3—C4—C4A—C9A	−21.59 (12)	C7—C8—C8A—C4B	0.55 (14)
C4—C4A—C4B—C5	−0.37 (17)		

Symmetry codes: (i) −*x*+1, −*y*+1, −*z*; (ii) −*x*, −*y*+1, −*z*; (iii) −*x*, −*y*, −*z*; (iv) *x*, *y*−1, *z*; (v) *x*+1/2, −*y*+1/2, *z*−1/2; (vi) −*x*+1/2, *y*−1/2, −*z*+1/2; (vii) −*x*+1/2, *y*+1/2, −*z*+1/2; (viii) −*x*−1/2, *y*−1/2, −*z*+1/2; (ix) −*x*−1/2, *y*+1/2, −*z*+1/2; (x) *x*−1/2, −*y*+1/2, *z*+1/2; (xi) *x*, *y*+1, *z*.

Hydrogen-bond geometry (Å, °)

Cg1 is the centroid of the C4B,C5–C8,C8A ring.

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
N9—H9···N13	0.913 (14)	2.508 (14)	3.2626 (12)	140.3 (11)
N9—H9···N13^{i}	0.913 (14)	2.553 (14)	3.2267 (12)	131.1 (11)

C2—H2A···Cg1^{vi}	0.99	2.79	3.6244 (10)	142

Symmetry codes: (i) −*x*+1, −*y*+1, −*z*; (vi) −*x*+1/2, *y*−1/2, −*z*+1/2.

Fig. 1

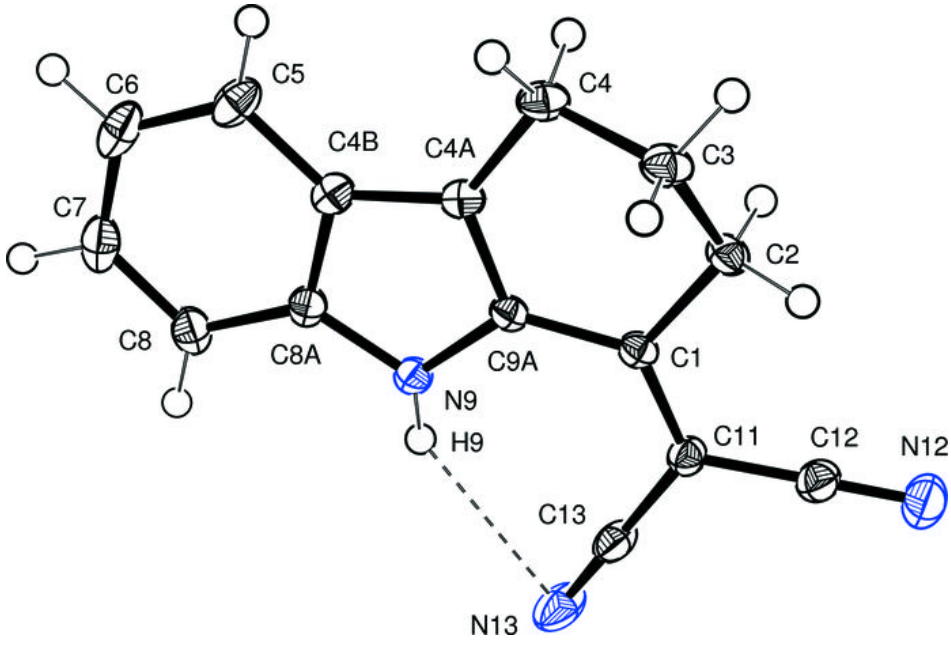
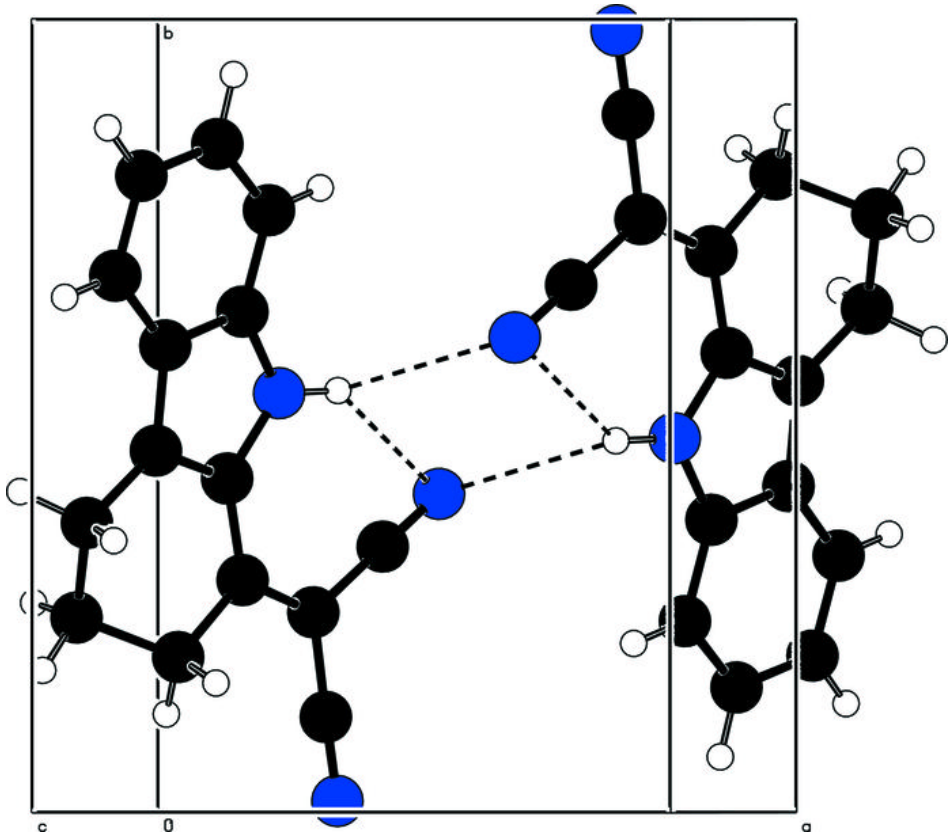


Fig. 2



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(2*E*)-1-(2-Bromophenyl)-3-(4-bromophenyl)prop-2-en-1-one

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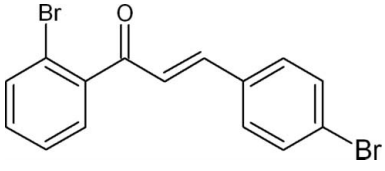
Key indicators: single-crystal X-ray study; T = 110 K; mean σ(C–C) = 0.008 Å; R factor = 0.045; wR factor = 0.152; data-to-parameter ratio = 15.4.

The title compound, $C_{15}H_{10}Br_2O$, is a chalcone with 2-bromophenyl and 4-bromophenyl rings bonded to opposite sides of a propenone group. The dihedral angle between mean planes of the benzene rings is 71.3 (1)°. The angle between the mean plane of the prop-2-ene-1-one group and the mean planes of the 2-bromophenyl and 4-bromophenyl rings are 64.2 (9) and 71.3 (1)°, respectively. A weak intermolecular C—H···O interaction and two weak C—Br···π interactions are observed, which contribute to the stability of the crystal packing.

Related literature

For the radical quenching properties of included phenol groups, see: Dhar (1981). For the biological activity of chalcones, see: Dimmock *et al.* (1999). For related structures, see: Ng *et al.* (2006); Teh *et al.* (2006). For bond-length data, see: Allen *et al.* (1987)



Experimental

Crystal data

$C_{15}H_{10}Br_2O$
M_r = 366.05
Monoclinic, $P2_1/c$
a = 5.6988 (5) Å
b = 9.5462 (9) Å
c = 23.8532 (15) Å
β = 91.021 (8)°
V = 1297.46 (18) Å^3
Z = 4
Cu $K\alpha$ radiation
μ = 7.79 mm^{-1}
T = 110 K
0.62 × 0.47 × 0.26 mm

Data collection

Oxford Diffraction Xcalibur Ruby Gemini diffractometer
Absorption correction: analytical (*CrysAlis RED*; Oxford Diffraction, 2007)
T_{min} = 0.078, T_{max} = 0.315
4592 measured reflections
2532 independent reflections
2454 reflections with $I > 2\sigma(I)$
R_{int} = 0.027

Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.045
$wR(F^2)$ = 0.152
S = 1.32
2532 reflections
164 parameters
H-atom parameters constrained
$\Delta\rho_{max}$ = 1.27 e Å^{-3}
$\Delta\rho_{min}$ = −1.00 e Å^{-3}

Table 1
Hydrogen-bond geometry (Å, °).

D—H···A	D—H	H···A	D···A	D—H···A
C12—H12A···O1^{i}	0.95	2.46	3.368 (7)	159

Symmetry code: (i) $-x+2, -y, -z+1$.

Table 2
C—Br···π interactions (Å, °).

*Cg*1 and *Cg*2 are the centroids of the C1–C6 and C10–C15 rings, respectively.

	Br1···*Cg*2	Br1–Perp	C2—Br1···*Cg*2
C2—Br1···*Cg*2^{i}	3.522 (2)	3.488	154.82 (17)
C13—-Br2···*Cg*1^{ii}	3.827 (2)	3.377	165.44 (17)

Symmetry codes: (i) $2-x, 1-y, 1-z$; (ii) $1+x, \frac{1}{2}-y, \frac{1}{2}+z$.

Data collection: *CrysAlis PRO* (Oxford Diffraction, 2007); cell refinement: *CrysAlis PRO*; data reduction: *CrysAlis PRO*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *SHELXTL* (Sheldrick, 2008); software used to prepare material for publication: *SHELXTL*.

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Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: DN2577).

References

Allen, F. H., Kennard, O., Watson, D. G., Brammer, L., Orpen, A. G. & Taylor, R. (1987). *J. Chem. Soc. Perkin Trans. 2*, pp. S1–19.
Dhar, D. N. (1981). *The Chemistry of Chalcones and Related Compounds*. New York: John Wiley.
Dimmock, J. R., Elias, D. W., Beazely, M. A. & Kandepu, N. M. (1999). *Curr. Med. Chem.* **6**, 1125–1149.
Ng, S.-L., Shettigar, V., Razak, I. A., Fun, H.-K., Patil, P. S. & Dharmaprakash, S. M. (2006). *Acta Cryst.* E**62**, o1421–o1423.
Oxford Diffraction (2007). *CrysAlis PRO* and *CrysAlis RED*. Oxford Diffraction Ltd, Abingdon, England.
Sheldrick, G. M. (2008). *Acta Cryst.* A**64**, 112–122.
Teh, J. B.-J., Patil, P. S., Fun, H.-K., Razak, I. A. & Dharmaprakash, S. M. (2006). *Acta Cryst.* E**62**, o2399–o2400.

supplementary materials

Acta Cryst. (2010). E**66**, o1701 [**doi:10.1107/S1600536810022956**]

(2*E*)-1-(2-Bromophenyl)-3-(4-bromophenyl)prop-2-en-1-one

J. P. Jasinski, R. J. Butcher, K. Veena, B. Narayana and H. S. Yathirajan

Comment

Chalcones, or 1,3-diaryl-2-propen-1-ones, belong to the flavonoid family. Chemically they consist of open-chain flavonoids in which the two aromatic rings are joined by a three-carbon α,β-unsaturated carbonyl system. A vast number of naturally occurring chalcones are polyhydroxylated in the aryl rings. The radical quenching properties of the phenol groups present in many chalcones have raised interest in using the compounds or chalcone rich plant extracts as drugs or food preservatives (Dhar, 1981). Chalcones have been reported to possess many useful properties, including anti-inflammatory, antimicrobial, antifungal, antioxidant, cytotoxic, anticancer activities (Dimmock *et al.*, 1999). The crystal structures of closely related chalcones, *viz*., 1,3-bis(4-bromophenyl)prop-2-en-1-one (Ng *et al.*, 2006) and 3-(3-bromophenyl)-1-(4-bromophenyl)prop-2-en-1-one (Teh *et al.*, 2006) have been reported. Hence in continuation with the synthesis and crystal structure determination and also owing to the importance of these flavanoid analogs, this bromo chalcone, $C_{15}H_{10}Br_2O$, is synthesized and its crystal structure is reported.

The title compound, $C_{15}H_{10}Br_2O$, is a chalcone with 2-bromophenyl and 4-bromophenyl rings bonded to opposite sides of a propenone group (Fig. 2). The dihedral angle between mean planes of the benzene rings in the *ortho*-bromo and *para*-bromo substituted rings is 71.3 (1)°. The angle between the mean plane of the prop-2-ene-1-one group (C1/C7/O1/C8) and the mean planes of the benzene rings in the 2-bromophenyl (C1–C6) and 4-bromophenyl rings (C10–C15) are 64.2 (9)° and 71.3 (1)°, respectively. Bond distances and angles are in normal ranges (Allen *et al.*, 1987). While no classical hydrogen bonds are present, a weak intermolecular C12—H12A···O1 interaction (Table 1) and two weak π-ring intermolecular interactions (Table 2) are observed which contribute to the stability of crystal packing.

Experimental

A 50% KOH solution was added to a mixture of 2-bromo acetophenone (0.01 mol, 1.99 g) and 4-bromo benzaldehyde (0.01 mol, 1.85 g) in 25 ml of ethanol (Fig. 1). The mixture was stirred for an hour at room temperature and the precipitate was collected by filtration and purified by recrystallization from ethanol. The single-crystal was grown from ethyl acetate by slow evaporation method and yield of the compound was 68% (m.p.373–375 K). Analytical data: Found (Calculated): C %: 49.19 (49.22%); H%: 2.73 (2.75%).

Refinement

The H atoms were placed in geometrically idealized positions and constrained to ride on their parent atoms with C–H distances = 0.95Å and with U_{iso}(H) = 1.17–1.22 U_{eq}(C).

Figures

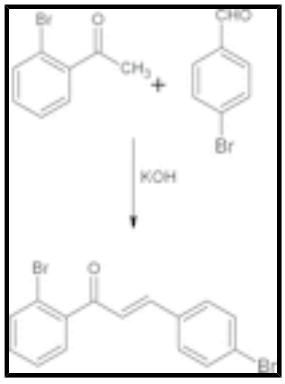


Fig. 1. Reaction Scheme for the title compound.

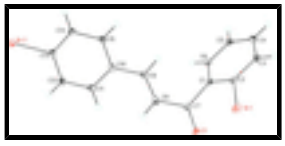


Fig. 2. Molecular structure of the title compound, $C_{15}H_{10}Br_2O$, showing the atom labeling scheme and 50% probability displacement ellipsoids.

(2*E*)-1-(2-Bromophenyl)-3-(4-bromophenyl)prop-2-en-1-one

Crystal data

$C_{15}H_{10}Br_2O$	$F(000) = 712$
$M_r = 366.05$	$D_x = 1.874$ Mg m^{-3}
Monoclinic, $P2_1/c$	Cu $K\alpha$ radiation, $\lambda = 1.54178$ Å
Hall symbol: -P 2ybc	Cell parameters from 3417 reflections
$a = 5.6988$ (5) Å	$\theta = 4.6$–$74.1°$
$b = 9.5462$ (9) Å	$\mu = 7.79$ mm^{-1}
$c = 23.8532$ (15) Å	$T = 110$ K
$\beta = 91.021$ (8)°	Prism, colorless
$V = 1297.46$ (18) Å^3	0.62 × 0.47 × 0.26 mm
$Z = 4$	

Data collection

Oxford Diffraction Xcalibur Ruby Gemini diffractometer	2532 independent reflections
Radiation source: Enhance (Cu) X-ray Source	2454 reflections with $I > 2\sigma(I)$
graphite	$R_{int} = 0.027$
Detector resolution: 10.5081 pixels mm^{-1}	$\theta_{max} = 74.1°$, $\theta_{min} = 5.0°$
ω scans	$h = -6 \rightarrow 6$
Absorption correction: analytical (*CrysAlis RED*; Oxford Diffraction, 2007)	$k = -6 \rightarrow 11$
$T_{min} = 0.078$, $T_{max} = 0.315$	$l = -29 \rightarrow 25$
4592 measured reflections	

Refinement

Refinement on F^2	Secondary atom site location: difference Fourier map
Least-squares matrix: full	Hydrogen site location: inferred from neighbouring sites
$R[F^2 > 2\sigma(F^2)] = 0.045$	H-atom parameters constrained
$wR(F^2) = 0.152$	$w = 1/[\sigma^2(F_o^2) + (0.0631P)^2 + 9.323P]$ where $P = (F_o^2 + 2F_c^2)/3$
$S = 1.32$	$(\Delta/\sigma)_{max} < 0.001$
2532 reflections	$\Delta\rho_{max} = 1.27$ e Å^{-3}
164 parameters	$\Delta\rho_{min} = -1.00$ e Å^{-3}
0 restraints	Extinction correction: *SHELXL97* (Sheldrick, 2008), $Fc^*=kFc[1+0.001xFc^2\lambda^3/\sin(2\theta)]^{-1/4}$
Primary atom site location: structure-invariant direct methods	Extinction coefficient: 0.0029 (4)

Special details

Experimental. IR data (KBr) ν cm^{-1}: 3048 cm^{-1} (C—H str) 1671 cm^{-1} (C=O), 1685 cm^{-1} (C=C).

Geometry. All e.s.d.'s (except the e.s.d. in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell e.s.d.'s are taken into account individually in the estimation of e.s.d.'s in distances, angles and torsion angles; correlations between e.s.d.'s in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell e.s.d.'s is used for estimating e.s.d.'s involving l.s. planes.

Refinement. Refinement of F^2 against ALL reflections. The weighted *R*-factor *wR* and goodness of fit *S* are based on F^2, conventional *R*-factors *R* are based on *F*, with *F* set to zero for negative F^2. The threshold expression of $F^2 > \sigma(F^2)$ is used only for calculating *R*-factors(gt) *etc*. and is not relevant to the choice of reflections for refinement. *R*-factors based on F^2 are statistically about twice as large as those based on *F*, and *R*- factors based on ALL data will be even larger.

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å^2)

	x	*y*	*z*	U_{iso}*/U_{eq}
Br1	1.27853 (11)	0.55820 (6)	0.36129 (3)	0.0217 (3)
Br2	0.14170 (10)	0.10866 (6)	0.65074 (2)	0.0182 (2)
O1	1.2468 (7)	0.2116 (5)	0.37198 (18)	0.0211 (9)
C1	0.9316 (10)	0.3480 (6)	0.3361 (2)	0.0144 (11)
C2	1.0220 (10)	0.4768 (6)	0.3200 (2)	0.0157 (11)
C3	0.9269 (12)	0.5525 (7)	0.2759 (3)	0.0223 (13)
H3A	0.9912	0.6406	0.2658	0.027*
C4	0.7337 (12)	0.4969 (7)	0.2462 (2)	0.0239 (14)
H4A	0.6670	0.5468	0.2154	0.029*
C5	0.6406 (11)	0.3698 (7)	0.2619 (3)	0.0219 (13)
H5A	0.5103	0.3320	0.2416	0.026*
C6	0.7359 (10)	0.2973 (6)	0.3069 (2)	0.0180 (12)
H6A	0.6669	0.2114	0.3180	0.022*
C7	1.0493 (10)	0.2574 (6)	0.3798 (2)	0.0149 (11)

C8	0.9223 (11)	0.2193 (6)	0.4304 (2)	0.0181 (12)
H8A	0.9888	0.1485	0.4537	0.022*
C9	0.7192 (10)	0.2767 (6)	0.4462 (2)	0.0162 (11)
H9A	0.6527	0.3466	0.4225	0.019*
C10	0.5903 (10)	0.2408 (6)	0.4972 (2)	0.0162 (11)
C11	0.6596 (11)	0.1294 (7)	0.5320 (3)	0.0201 (12)
H11A	0.7986	0.0790	0.5238	0.024*
C12	0.5304 (11)	0.0913 (6)	0.5780 (3)	0.0190 (12)
H12A	0.5788	0.0155	0.6013	0.023*
C13	0.3279 (10)	0.1664 (6)	0.5895 (2)	0.0151 (11)
C14	0.2554 (10)	0.2787 (6)	0.5566 (2)	0.0180 (12)
H14A	0.1178	0.3299	0.5654	0.022*
C15	0.3891 (10)	0.3146 (6)	0.5105 (2)	0.0173 (12)
H15A	0.3415	0.3914	0.4877	0.021*

Atomic displacement parameters (Å^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Br1	0.0195 (4)	0.0157 (4)	0.0300 (4)	−0.0029 (2)	0.0034 (3)	−0.0038 (2)
Br2	0.0190 (4)	0.0196 (4)	0.0161 (3)	−0.0020 (2)	0.0042 (2)	0.0011 (2)
O1	0.015 (2)	0.021 (2)	0.027 (2)	0.0034 (17)	0.0043 (16)	0.0015 (18)
C1	0.015 (3)	0.016 (3)	0.012 (2)	0.004 (2)	0.007 (2)	−0.001 (2)
C2	0.013 (3)	0.017 (3)	0.017 (3)	−0.001 (2)	0.005 (2)	−0.003 (2)
C3	0.028 (3)	0.020 (3)	0.019 (3)	0.006 (2)	0.012 (2)	0.002 (2)
C4	0.027 (3)	0.030 (4)	0.015 (3)	0.014 (3)	0.004 (2)	0.003 (2)
C5	0.018 (3)	0.029 (3)	0.019 (3)	0.007 (2)	0.001 (2)	−0.005 (2)
C6	0.013 (3)	0.019 (3)	0.022 (3)	−0.001 (2)	0.004 (2)	−0.001 (2)
C7	0.015 (3)	0.009 (2)	0.020 (3)	−0.001 (2)	−0.001 (2)	−0.004 (2)
C8	0.023 (3)	0.014 (3)	0.017 (3)	−0.002 (2)	0.000 (2)	0.000 (2)
C9	0.017 (3)	0.013 (3)	0.018 (3)	−0.001 (2)	−0.002 (2)	0.000 (2)
C10	0.018 (3)	0.014 (3)	0.017 (3)	−0.002 (2)	−0.001 (2)	−0.001 (2)
C11	0.020 (3)	0.018 (3)	0.022 (3)	0.005 (2)	0.001 (2)	0.002 (2)
C12	0.022 (3)	0.016 (3)	0.019 (3)	0.003 (2)	0.000 (2)	0.003 (2)
C13	0.018 (3)	0.016 (3)	0.011 (2)	−0.003 (2)	0.002 (2)	−0.001 (2)
C14	0.014 (3)	0.020 (3)	0.020 (3)	0.003 (2)	0.002 (2)	−0.001 (2)
C15	0.017 (3)	0.016 (3)	0.020 (3)	0.000 (2)	−0.001 (2)	0.003 (2)

Geometric parameters (Å, °)

Br1—C2	1.913 (6)	C8—C9	1.341 (9)
Br2—C13	1.903 (6)	C8—H8A	0.9500
O1—C7	1.225 (7)	C9—C10	1.471 (8)
C1—C2	1.389 (8)	C9—H9A	0.9500
C1—C6	1.391 (8)	C10—C15	1.388 (8)
C1—C7	1.504 (8)	C10—C11	1.402 (8)
C2—C3	1.380 (9)	C11—C12	1.381 (9)
C3—C4	1.403 (10)	C11—H11A	0.9500
C3—H3A	0.9500	C12—C13	1.390 (9)
C4—C5	1.378 (10)	C12—H12A	0.9500

C4—H4A	0.9500	C13—C14	1.386 (8)
C5—C6	1.380 (9)	C14—C15	1.392 (8)
C5—H5A	0.9500	C14—H14A	0.9500
C6—H6A	0.9500	C15—H15A	0.9500
C7—C8	1.463 (8)		
C2—C1—C6	117.9 (5)	C7—C8—H8A	117.5
C2—C1—C7	122.5 (5)	C8—C9—C10	125.7 (5)
C6—C1—C7	119.4 (5)	C8—C9—H9A	117.1
C3—C2—C1	122.1 (6)	C10—C9—H9A	117.1
C3—C2—Br1	117.8 (5)	C15—C10—C11	118.3 (5)
C1—C2—Br1	120.1 (4)	C15—C10—C9	119.9 (5)
C2—C3—C4	118.7 (6)	C11—C10—C9	121.8 (5)
C2—C3—H3A	120.6	C12—C11—C10	121.5 (6)
C4—C3—H3A	120.6	C12—C11—H11A	119.3
C5—C4—C3	119.9 (6)	C10—C11—H11A	119.3
C5—C4—H4A	120.0	C11—C12—C13	118.4 (5)
C3—C4—H4A	120.0	C11—C12—H12A	120.8
C4—C5—C6	120.3 (6)	C13—C12—H12A	120.8
C4—C5—H5A	119.9	C14—C13—C12	121.9 (5)
C6—C5—H5A	119.9	C14—C13—Br2	119.6 (4)
C5—C6—C1	121.1 (6)	C12—C13—Br2	118.5 (4)
C5—C6—H6A	119.5	C13—C14—C15	118.4 (5)
C1—C6—H6A	119.5	C13—C14—H14A	120.8
O1—C7—C8	120.4 (5)	C15—C14—H14A	120.8
O1—C7—C1	120.0 (5)	C10—C15—C14	121.5 (5)
C8—C7—C1	119.6 (5)	C10—C15—H15A	119.3
C9—C8—C7	124.9 (5)	C14—C15—H15A	119.3
C9—C8—H8A	117.5		
C6—C1—C2—C3	−1.4 (8)	O1—C7—C8—C9	171.3 (6)
C7—C1—C2—C3	173.0 (5)	C1—C7—C8—C9	−11.4 (9)
C6—C1—C2—Br1	176.2 (4)	C7—C8—C9—C10	−179.3 (5)
C7—C1—C2—Br1	−9.4 (7)	C8—C9—C10—C15	175.9 (6)
C1—C2—C3—C4	−0.3 (9)	C8—C9—C10—C11	−6.7 (9)
Br1—C2—C3—C4	−177.9 (4)	C15—C10—C11—C12	1.2 (9)
C2—C3—C4—C5	0.8 (9)	C9—C10—C11—C12	−176.3 (6)
C3—C4—C5—C6	0.4 (9)	C10—C11—C12—C13	−0.2 (9)
C4—C5—C6—C1	−2.1 (9)	C11—C12—C13—C14	−0.9 (9)
C2—C1—C6—C5	2.6 (8)	C11—C12—C13—Br2	177.1 (5)
C7—C1—C6—C5	−172.0 (5)	C12—C13—C14—C15	1.0 (9)
C2—C1—C7—O1	−62.2 (7)	Br2—C13—C14—C15	−177.1 (4)
C6—C1—C7—O1	112.2 (6)	C11—C10—C15—C14	−1.1 (9)
C2—C1—C7—C8	120.6 (6)	C9—C10—C15—C14	176.4 (5)
C6—C1—C7—C8	−65.1 (7)	C13—C14—C15—C10	0.1 (9)

Hydrogen-bond geometry (Å, °)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
C12—H12A···O1^{i}	0.95	2.46	3.368 (7)	159.

Symmetry codes: (i) −*x*+2, −*y*, −*z*+1.

Table 2
C—Br···π interactions (Å, °)

Cg1 and Cg2 are the centroids of the C1–C6 and C10–C15 rings, respectively.

	Br1···Cg2	Br1–Perp	C2—Br1···Cg2
C2—Br1···Cg2^{i}	3.522 (2)	3.488	154.82 (17)
C13—-Br2···Cg1^{ii}	3.827 (2)	3.377	165.44 (17)

Symmetry codes: (i) 2-x, 1-y, 1-z; (ii) 1+x, 1/2-y, 1/2+z.

Fig. 1

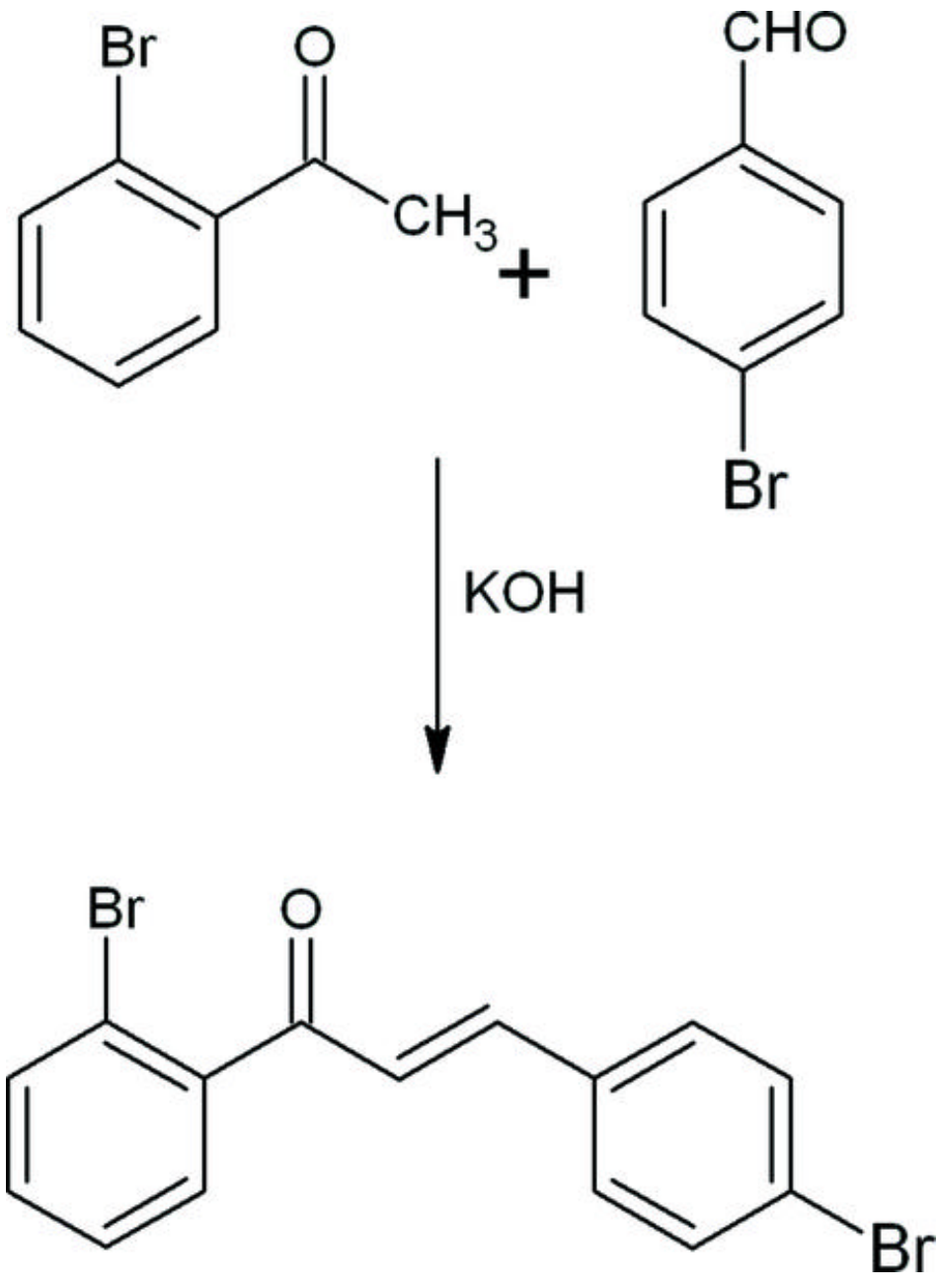
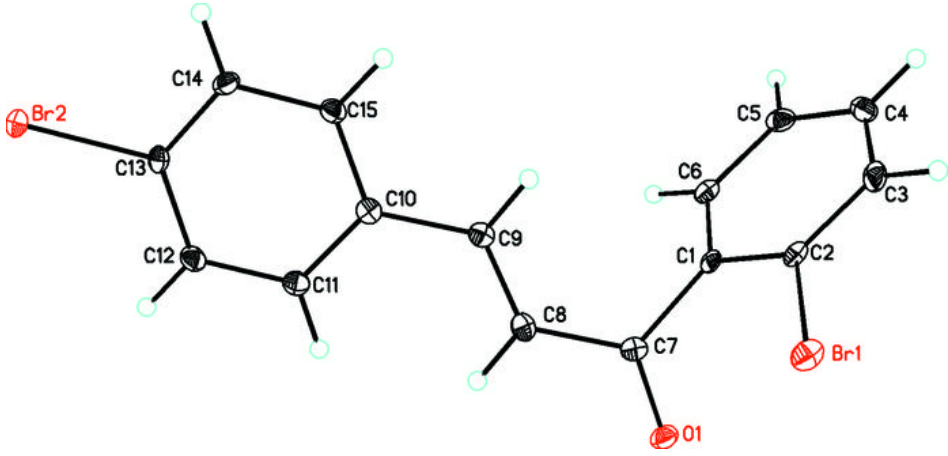


Fig. 2



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(1*R*,6*R*,13*R*,18*R*)-(*Z*,*Z*)-1,18-Bis[(4*R*)-2,2-dimethyl-1,3-dioxolan-4-yl]-3,16-dimethylene-8,20-diazadispiro[5.6.5.6]-tetracosa-7,19-diene

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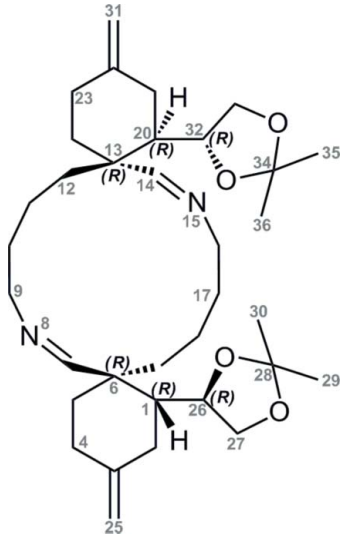
Key indicators: single-crystal X-ray study; T = 93 K; mean σ(C–C) = 0.003 Å; R factor = 0.035; wR factor = 0.091; data-to-parameter ratio = 10.5.

The crystal structure of the title compound, $C_{34}H_{54}N_2O_4$, has been solved in order to prove the relative and absolute chirality of the newly-formed stereocentres which were established using an asymmetric Diels–Alder reaction at an earlier stage in the synthesis. This unprecedented stable dialdimine contains a 14-membered ring and was obtained as the minor diastereoisomer in the Diels–Alder reaction. The absolute stereochemistry of the stereocentres of the acetal functionality was known to be *R* based on the use of a chiral (*R*)-trisubstituted dienophile derived from enantiopure (*S*)-glyceraldehyde. The assignment of the configuration in the dienophile and the title di-aldimine differs from (*S*)-glyceraldehyde due to a change in the priority order of the substituents. The crystal structure establishes the presence of six stereocentres all attributed to be *R*. The 14-membered ring contains two aldimine bonds [C—N = 1.258 (2) and 1.259 (2) Å]. It adopts a similar conformation to that proposed for *trans–trans*-cyclotetradeca-1,8-dienes.

Related literature

For related structures, see: Allmann (1974); Dale (1966). For background to the spirolide family, see: Gill *et al.* (2003); Guéret & Brimble (2010); Hu *et al.* (1995, 2001). For the applications of Danishefsky's diene, see: Asano *et al.* (2006); Danishefsky *et al.* (1990); Petrzilka & Grayson (1981).



Experimental

Crystal data

$C_{34}H_{54}N_2O_4$
M_r = 554.80
Triclinic, $P\overline{1}$
a = 6.8710 (1) Å
b = 10.1701 (2) Å
c = 11.7947 (2) Å
α = 79.143 (1)°
β = 88.043 (1)°
γ = 83.855 (1)°
V = 804.71 (2) Å^3
Z = 1
Mo $K\alpha$ radiation
μ = 0.07 mm^{-1}
T = 93 K
0.36 × 0.19 × 0.1 mm

Data collection

Siemens SMART CCD diffractometer
19146 measured reflections
3824 independent reflections
3555 reflections with $I > 2\sigma(I)$
R_{int} = 0.042

Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.035
$wR(F^2)$ = 0.091
S = 0.92
3824 reflections
365 parameters
3 restraints
H-atom parameters constrained
$\Delta\rho_{max}$ = 0.28 e Å^{-3}
$\Delta\rho_{min}$ = −0.18 e Å^{-3}

Data collection: *SMART* (Siemens, 1995); cell refinement: *SAINT* (Siemens, 1995); data reduction: *SAINT*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *ORTEPIII* (Burnett & Johnson, 1996), *ORTEP-3 for Windows* (Farrugia, 1997) and *Mercury* (Macrae *et al.*, 2006); software used to prepare material for publication: *WinGX* (Farrugia, 1999) and *publCIF* (Westrip, 2010).

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Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: DN2578).

References

Allmann, R. (1974). *Cryst. Struct. Commun.* **3**, 83–86.
Asano, M., Inoue, M., Watanabe, K., Abe, H. & Katoh, T. (2006). *J. Org. Chem.* **71**, 6942–6951.
Burnett, M. N. & Johnson, C. K. (1996). *ORTEPIII*. Report ORNL-6895. Oak Ridge National Laboratory, Tennessee, USA.
Dale, J. (1966). *Angew. Chem. Int. Ed.* **5**, 1000–1021.
Danishefsky, S., Kitahara, T. & Schuda, P. F. (1990). *Org. Synth. Coll.* **7**, 312–315.
Farrugia, L. J. (1997). *J. Appl. Cryst.* **30**, 565.
Farrugia, L. J. (1999). *J. Appl. Cryst.* **32**, 837–838.
Gill, S., Murphy, M., Clausen, J., Richard, D., Quilliam, M., MacKinnon, S., LaBlanc, P., Mueller, R. & Pulido, O. (2003). *Neurotoxicology*, **24**, 593–604.
Guéret, S. M. & Brimble, M. A. (2010). *Nat. Prod. Rep.* In the press.
Hu, T. M., Burton, I. W., Cembella, A. D., Curtis, J. M., Quilliam, M. A., Walter, J. A. & Wright, J. L. C. (2001). *J. Nat. Prod.* **64**, 308–312.
Hu, T., Curtis, J. M., Oshima, Y., Quilliam, M. A., Walter, J. A., Watson-Wright, W. M. & Wright, J. L. C. (1995). *J. Chem. Soc. Chem. Commun.* pp. 2159–2161.
Macrae, C. F., Edgington, P. R., McCabe, P., Pidcock, E., Shields, G. P., Taylor, R., Towler, M. & van de Streek, J. (2006). *J. Appl. Cryst.* **39**, 453–457.
Petrzilka, M. & Grayson, J. I. (1981). *Synthesis*, pp. 753–786.
Sheldrick, G. M. (2008). *Acta Cryst.* A**64**, 112–122.
Siemens (1995). *SMART* and *SAINT* . Siemens Analytical X-ray Instruments Inc., Madison, Wisconsin, USA.
Westrip, S. P. (2010). *J. Appl. Cryst.* **43**. Submitted.

supplementary materials

Acta Cryst. (2010). E**66**, o1778-o1779 [**doi:10.1107/S1600536810023998**]

(1*R*,6*R*,13*R*,18*R*)-(*Z*,*Z*)-1,18-Bis[(4*R*)-2,2-dimethyl-1,3-dioxolan-4-yl]-3,16-dimethylene-8,20-diazadispiro[5.6.5.6]tetracosa-7,19-diene

S. M. Guéret, P. D. W. Boyd and M. A. Brimble

Comment

The title spiro-di-aldimine was obtained as part of a synthetic program directed towards the synthesis of the spiroimine unit of the spirolides AD. This family of marine toxins were isolated from the digestive glands of contaminated mussels, scallops and toxic plankton from the East coast of Nova Scotia in Canada and are considered as fast-acting toxins (Hu *et al.*, 1995; Hu *et al.*, 2001; Gill *et al.*, 2003; Guéret & Brimble, 2010). The work demonstrates a new method to access an enantiopure spiro-di-aldimine and an enantiopure bicyclic ketimine in good overall yield. The synthesis of the spiroimine is a synthetic challenge and to date the synthesis of the 7,6-spiroimine moiety of the spirolides has not been achieved. By reaction of a chiral (*R*)-trisubstituted dienophile derived from (*S*)-glyceraldehyde with Danishefsky's diene (Asano *et al.*, 2006; Danishefsky *et al.*, 1990; Petrzilka & Grayson, 1981), the resultant Diels-Alder adducts were afforded as a mixture of 3 diastereoisomers in a 5:2:1 ratio. The undesired minor diastereoisomer was used to develop the synthetic route to the desired spiroaldimine. The Diels-Alder adduct was converted to the spiroimine precursor in several steps. Reaction of this advanced azido-aldehyde intermediate with triphenylphosphine surprisingly afforded the stable title dimer instead of the expected 7,6-bicyclic aldimine. The stability of the title dimer is unexpected compared to the known instability of aldimines in general. Given that the stereochemistry at C26 and C32 is known to be *R* (based on using enantiopure (*S*)-glyceraldehyde as the starting material), the absolute configuration at C1, C6, C13 and C20 has therefore also been assigned as *R*. The assignment of configuration of the trisubstituted dienophile and the title di-aldimine differs from the starting (*S*)-glyceraldehyde due to a change in the priority order of substituents.

The molecular structure, Fig. 1, indicates that the acetal unit and the imine part adopt an axial position in both cyclohexane rings. The 14-membered ring contains two aldimine bonds(C14—N15 1.258 (2),C7—N8 1.259 (2)). It adopts a similar conformation to that proposed for *trans-trans* cyclotetradeca-1,8-dienes (Dale, 1966) except for an alternate conformation for C17, C18 and C19. A 14-membered *tetra*-azacyclotetradeca-1,8-diene which has *R* and *S* centres shows similar conformational characteristics (Allmann, 1974). The diazaspirocyclotetradecan-7,14-ene molecules assemble in the crystal in linear arrays. Each ring is offset with the six membered rings from a neighbouring molecule aligned over the ring centre, Fig. 2.

Experimental

To 2-(2",2"-dimethyl-1",3"-dioxolan-4"-yl)-4-methylene-1-(4'-azidobutyl)cyclohexane carbaldehyde (7.8 mg, 24 µmol) in toluene-d8 (0.6 ml) was added triphenylphosphine (6.3 mg, 24 µmol). The resulting mixture was stirred for 1 h at room temperature then warmed to 55 °C and stirred at this temperature for 17 h. After cooling to room temperature, the mixture was concentrated in vacuo. The crude imine was purified by column chromatography (20: 80 EtOAc–hexanes) to give the *title compound* (4.6 mg, 71%) as a white crystalline solid. Dilution in CH_2Cl_2/hexanes (1: 1, 2 ml) and slow evaporation of the solvent afforded white prisms.

M. P. 171.8–172.3 °C.

HRMS (ESI) calculated for $C_{34}H_{55}N_2O_4$ $[M + H]^+$: 555.4156, found 555.4143.

IR (neat) ν_{max} 3060, 2985, 2935, 1675, 1635, 1610, 1455, 1380, 1195, 1065, 895 cm^{-1}.

^1H NMR (400 MHz, $CDCl_3$) δ 7.49 (2*H*, s, 7 and 14-C*H*=N), 4.60 (4 H, d,*J* = 28 Hz, 25 and 31-CH_2=C), 4.10 (4 H, m, 26 and 32-C*H* and 27 and 33-CH_aH$_b$), 3.60 (2 H, m, 27 and 33-CH$_a$$H_b$), 3.47 (2 H, m, 9 and 16-CH_aH$_b$), 3.38 (2 H, m, 9 and 16-CH$_a$$H_b$), 2.23 (2 H, dd, *J* = 4 and 12 Hz, 2 and 21-CH_aH$_b$), 2.11 (6 H, t, *J* = 4 Hz, 1 and 20-C*H* and 4 and 23-CH_2), 1.94 (2 H, dd, *J* = 8 and 12 Hz, 2 and 21-CH$_a$$H_b$), 1.71 (6 H, m, 5 and 24-CH_2 and 12 and 19-CH_aH$_b$), 1.61 (4 H, m, 12 and 19-CH$_a$$H_b$ and 10 and 17-CH_aH$_b$), 1.45 (2 H, td, *J* = 4 and 12 Hz, 10 and 17-CH$_a$$H_b$), 1.34 (6 H, s, 29 or 30-CH_3 and 35 or 36-CH_3), 1.34 (6 H, s, 29 or 30-CH_3 and 35 or 36-CH_3), 1.22 (2 H, m, 11 and 18-CH_aH$_b$), 1.09 (11 and 18-CH$_a$$H_b$).

^{13}C NMR (100 MHz, $CDCl_3$) δ 171.8 (7 and 14-*C*H=N), 146.7 (3 and 22-*C*), 108.4 (28 and 34-*C*), 108.1 (25 and 31-*C*H_2), 76.1 (26 and 32-*C*HO), 68.6 (27 and 33-*C*H_2O), 60.9 (9 and 16-*C*H_2N), 45.5 (6 and 25-*C*), 44.6 (1 and 20-*C*H), 33.4 (12 and 19-*C*H_2), 33.2 (5 and 24-*C*H_2), 33.1 (2 and 21-*C*H_2), 30.9 (4 and 23-*C*H_2), 29.9 (10 and 17-*C*H_2), 26.7 (29 or 30-*C*H_3 and 35 or 36-*C*H_3), 26,3 (29 or 30-*C*H_3 and 35 or 36-*C*H_3), 21.5 (11 and 18-*C*H_2).

m/z (ESI-MS) 195 ($[M]^+$, 100), 278 (40), 220 (12%).

$[\alpha]_D^{20}$ -25.5 (c 1/5, CH_2Cl_2).

Refinement

In the absence of significant anomalous scattering, the absolute configuration could not be reliably determined from the X-ray analyses and then the Friedel pairs were merged and any references to the Flack parameter were removed.

Atoms were placed in calculated positions and a riding model (C–H = 0.93 or 0.97 Å), with U_{iso}(H) = 1.2 or 1.5 times U_{eq}(C) was used during refinement.

Figures

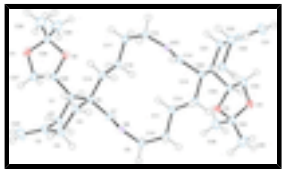


Fig. 1. The molecular view of the title compound with the atom-labelling scheme. Displacement ellipsoids are drawn at the 50% probability level. H atoms are represented as small spheres of arbitrary radii.

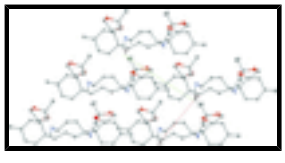


Fig. 2. The molecular packing diagram of the title compound, viewed along *c* axis. The hydrogen atoms have been omitted for clarity.

(1*R*,6*R*,13*R*,18*R*)-(*Z*,*Z*)- 1,18-Bis[(4*R*)-2,2-dimethyl-1,3-dioxolan-4-yl]-3,16-dimethylene- 8,20-diazadispiro[5.6.5.6]tetracosa-7,19-diene

Crystal data

$C_{34}H_{54}N_2O_4$	$Z = 1$
$M_r = 554.80$	$F(000) = 304$
Triclinic, $P\overline{1}$	$D_x = 1.145$ Mg m^{-3}
Hall symbol: P -1	Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å
$a = 6.8710$ (1) Å	Cell parameters from 6455 reflections
$b = 10.1701$ (2) Å	$\theta = 1.8$–$27.9°$
$c = 11.7947$ (2) Å	$\mu = 0.07$ mm^{-1}
$\alpha = 79.143$ (1)°	$T = 93$ K
$\beta = 88.043$ (1)°	Needle, colourless
$\gamma = 83.855$ (1)°	0.36 × 0.19 × 0.1 mm
$V = 804.71$ (2) Å^3	

Data collection

Siemens SMART CCD diffractometer	3555 reflections with $I > 2\sigma(I)$
Radiation source: fine-focus sealed tube	$R_{int} = 0.042$
graphite	$\theta_{max} = 27.9°$, $\theta_{min} = 1.8°$
ω scans	$h = -9 \rightarrow 9$
19146 measured reflections	$k = -13 \rightarrow 13$
3824 independent reflections	$l = -15 \rightarrow 15$

Refinement

Refinement on F^2	Primary atom site location: structure-invariant direct methods
Least-squares matrix: full	Secondary atom site location: difference Fourier map
$R[F^2 > 2\sigma(F^2)] = 0.035$	Hydrogen site location: inferred from neighbouring sites
$wR(F^2) = 0.091$	H-atom parameters constrained
$S = 0.92$	$w = 1/[\sigma^2(F_o^2) + (0.0645P)^2 + 0.1019P]$ where $P = (F_o^2 + 2F_c^2)/3$
3824 reflections	$(\Delta/\sigma)_{max} < 0.001$
365 parameters	$\Delta\rho_{max} = 0.28$ e Å^{-3}
3 restraints	$\Delta\rho_{min} = -0.18$ e Å^{-3}

Special details

Geometry. All e.s.d.'s (except the e.s.d. in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell e.s.d.'s are taken into account individually in the estimation of e.s.d.'s in distances, angles and torsion angles; correlations

between e.s.d.'s in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell e.s.d.'s is used for estimating e.s.d.'s involving l.s. planes.

Refinement. Refinement of F^2 against ALL reflections. The weighted *R*-factor *wR* and goodness of fit *S* are based on F^2, conventional *R*-factors *R* are based on *F*, with *F* set to zero for negative F^2. The threshold expression of $F^2 > \sigma(F^2)$ is used only for calculating *R*-factors(gt) *etc*. and is not relevant to the choice of reflections for refinement. *R*-factors based on F^2 are statistically about twice as large as those based on *F*, and *R*- factors based on ALL data will be even larger. Three restraints for a floating origins were used.

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å^2)

	x	*y*	*z*	U_{iso}*/U_{eq}
C5	0.4859 (3)	−0.46661 (18)	0.09602 (16)	0.0179 (3)
H1A	0.6114	−0.4649	0.0558	0.021*
H1B	0.5112	−0.4882	0.1782	0.021*
C4	0.3776 (3)	−0.57809 (18)	0.06285 (17)	0.0213 (4)
H2A	0.3781	−0.5684	−0.0206	0.026*
H2B	0.4463	−0.6650	0.0942	0.026*
C3	0.1690 (3)	−0.57332 (19)	0.10718 (17)	0.0220 (4)
C2	0.0573 (3)	−0.43578 (19)	0.07628 (17)	0.0203 (4)
H4A	−0.0731	−0.4383	0.1103	0.024*
H4B	0.0441	−0.4122	−0.0069	0.024*
C1	0.1606 (3)	−0.32679 (18)	0.11917 (16)	0.0157 (3)
H5	0.0887	−0.2394	0.0889	0.019*
C6	0.3720 (3)	−0.32518 (17)	0.06741 (15)	0.0154 (3)
C19	0.4921 (3)	−0.22460 (17)	0.11200 (15)	0.0168 (3)
H7A	0.5030	−0.2515	0.1951	0.020*
H7B	0.6233	−0.2327	0.0793	0.020*
C18	0.4100 (3)	−0.07590 (18)	0.08484 (16)	0.0181 (4)
H8A	0.4276	−0.0419	0.0030	0.022*
H8B	0.2705	−0.0689	0.1019	0.022*
C17	0.5083 (3)	0.01164 (19)	0.15356 (16)	0.0217 (4)
H9A	0.4320	0.0988	0.1453	0.026*
H9B	0.5053	−0.0297	0.2346	0.026*
C16	0.7199 (3)	0.03345 (19)	0.11786 (16)	0.0204 (4)
H10A	0.7725	0.0862	0.1679	0.024*
H10B	0.7985	−0.0529	0.1267	0.024*
C14	0.8639 (3)	0.05893 (18)	−0.06562 (16)	0.0172 (3)
H11	0.9483	−0.0144	−0.0314	0.021*
C13	0.8986 (3)	0.11417 (17)	−0.19270 (15)	0.0158 (3)
C12	0.8646 (3)	−0.00132 (17)	−0.25696 (15)	0.0166 (3)
H13A	0.8760	0.0318	−0.3393	0.020*
H13B	0.9680	−0.0739	−0.2363	0.020*
C11	0.6682 (3)	−0.05878 (18)	−0.23246 (16)	0.0185 (4)
H14A	0.5636	0.0120	−0.2564	0.022*
H14B	0.6535	−0.0900	−0.1500	0.022*
C10	0.6486 (3)	−0.17543 (19)	−0.29504 (16)	0.0211 (4)
H15A	0.6386	−0.1407	−0.3773	0.025*
H15B	0.7658	−0.2383	−0.2827	0.025*
C9	0.4705 (3)	−0.25019 (19)	−0.25415 (16)	0.0200 (4)

H16A	0.3527	−0.1878	−0.2649	0.024*
H16B	0.4596	−0.3191	−0.2997	0.024*
C7	0.3587 (3)	−0.27786 (17)	−0.06275 (15)	0.0168 (3)
H17	0.2497	−0.2210	−0.0922	0.020*
C24	1.1175 (3)	0.13759 (19)	−0.20847 (16)	0.0186 (4)
H24A	1.1966	0.0552	−0.1758	0.022*
H24B	1.1485	0.1584	−0.2903	0.022*
C23	1.1716 (3)	0.2520 (2)	−0.15120 (18)	0.0228 (4)
H19A	1.1577	0.2268	−0.0680	0.027*
H19B	1.3070	0.2674	−0.1692	0.027*
C22	1.0408 (3)	0.37918 (19)	−0.19363 (17)	0.0215 (4)
C21	0.8255 (3)	0.36185 (18)	−0.17768 (16)	0.0192 (4)
H21A	0.7500	0.4456	−0.2108	0.023*
H21B	0.7945	0.3424	−0.0958	0.023*
C20	0.7648 (3)	0.24717 (17)	−0.23484 (15)	0.0161 (3)
H22	0.6311	0.2313	−0.2085	0.019*
C25	0.0869 (4)	−0.6775 (2)	0.1672 (2)	0.0326 (5)
H23A	0.1591	−0.7612	0.1848	0.039*
H23B	−0.0430	−0.6667	0.1917	0.039*
C26	0.1524 (3)	−0.34631 (18)	0.25092 (15)	0.0177 (3)
H24	0.2561	−0.4151	0.2841	0.021*
C27	−0.0430 (3)	−0.3762 (2)	0.30981 (17)	0.0253 (4)
H25A	−0.1517	−0.3269	0.2644	0.030*
H25B	−0.0578	−0.4716	0.3225	0.030*
C28	0.0987 (3)	−0.2278 (2)	0.39969 (16)	0.0252 (4)
C29	−0.0117 (5)	−0.0934 (3)	0.4064 (2)	0.0448 (7)
H27A	−0.0607	−0.0939	0.4837	0.067*
H27B	−0.1193	−0.0765	0.3540	0.067*
H27C	0.0743	−0.0240	0.3858	0.067*
C30	0.2597 (4)	−0.2692 (3)	0.4873 (2)	0.0409 (6)
H28A	0.3296	−0.3527	0.4758	0.061*
H28B	0.2036	−0.2803	0.5637	0.061*
H28C	0.3482	−0.2009	0.4780	0.061*
C31	1.1091 (3)	0.4943 (2)	−0.2410 (2)	0.0293 (4)
H29A	1.2434	0.4991	−0.2492	0.035*
H29B	1.0228	0.5704	−0.2660	0.035*
C32	0.7610 (3)	0.28862 (18)	−0.36663 (16)	0.0186 (4)
H30	0.8924	0.2709	−0.3990	0.022*
C33	0.6765 (3)	0.4318 (2)	−0.41643 (17)	0.0232 (4)
H31A	0.5655	0.4606	−0.3708	0.028*
H31B	0.7745	0.4945	−0.4207	0.028*
C34	0.5546 (3)	0.28908 (19)	−0.52033 (16)	0.0232 (4)
C36	0.3332 (3)	0.2966 (2)	−0.5167 (2)	0.0309 (5)
H33A	0.2833	0.3430	−0.4564	0.046*
H33B	0.2935	0.2072	−0.5020	0.046*
H33C	0.2825	0.3443	−0.5895	0.046*
C35	0.6449 (4)	0.2274 (2)	−0.61933 (19)	0.0352 (5)
H34A	0.6040	0.1391	−0.6145	0.053*
H34B	0.7850	0.2209	−0.6152	0.053*

H34C	0.6031	0.2829	−0.6912	0.053*
N15	0.7312 (2)	0.10360 (16)	−0.00257 (14)	0.0188 (3)
N8	0.4889 (2)	−0.31236 (15)	−0.13220 (13)	0.0183 (3)
O1	−0.0310 (2)	−0.33110 (17)	0.41672 (13)	0.0323 (4)
O2	0.1763 (2)	−0.22053 (14)	0.28513 (11)	0.0225 (3)
O3	0.6256 (2)	0.21281 (14)	−0.41259 (12)	0.0250 (3)
O4	0.6178 (2)	0.42036 (14)	−0.52929 (12)	0.0261 (3)

Atomic displacement parameters (Å^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
C5	0.0147 (8)	0.0156 (8)	0.0226 (9)	−0.0016 (7)	−0.0016 (7)	−0.0012 (7)
C4	0.0204 (9)	0.0150 (8)	0.0286 (10)	−0.0041 (7)	0.0015 (7)	−0.0036 (7)
C3	0.0213 (10)	0.0216 (9)	0.0257 (10)	−0.0065 (7)	−0.0005 (8)	−0.0081 (7)
C2	0.0145 (8)	0.0245 (9)	0.0235 (9)	−0.0059 (7)	−0.0016 (7)	−0.0066 (7)
C1	0.0120 (8)	0.0160 (7)	0.0190 (8)	−0.0015 (6)	−0.0016 (6)	−0.0026 (6)
C6	0.0138 (8)	0.0144 (8)	0.0181 (8)	−0.0028 (6)	−0.0007 (6)	−0.0023 (6)
C19	0.0152 (8)	0.0162 (8)	0.0191 (8)	−0.0026 (7)	−0.0017 (7)	−0.0029 (7)
C18	0.0173 (9)	0.0176 (8)	0.0189 (8)	−0.0023 (7)	0.0006 (7)	−0.0022 (7)
C17	0.0286 (10)	0.0175 (9)	0.0202 (9)	−0.0065 (7)	0.0057 (8)	−0.0050 (7)
C16	0.0259 (10)	0.0197 (8)	0.0172 (8)	−0.0076 (7)	0.0013 (7)	−0.0048 (7)
C14	0.0165 (9)	0.0162 (8)	0.0196 (8)	−0.0024 (7)	−0.0028 (7)	−0.0044 (7)
C13	0.0152 (9)	0.0155 (8)	0.0177 (8)	−0.0030 (6)	0.0009 (7)	−0.0049 (6)
C12	0.0167 (8)	0.0153 (8)	0.0179 (8)	−0.0023 (7)	0.0021 (7)	−0.0036 (6)
C11	0.0191 (9)	0.0166 (8)	0.0206 (8)	−0.0039 (7)	0.0023 (7)	−0.0046 (7)
C10	0.0237 (9)	0.0220 (9)	0.0198 (8)	−0.0078 (7)	0.0043 (7)	−0.0075 (7)
C9	0.0239 (9)	0.0202 (8)	0.0182 (8)	−0.0075 (7)	0.0004 (7)	−0.0064 (7)
C7	0.0163 (9)	0.0141 (8)	0.0199 (8)	−0.0021 (7)	−0.0027 (7)	−0.0020 (6)
C24	0.0131 (8)	0.0202 (9)	0.0230 (9)	−0.0020 (7)	0.0022 (7)	−0.0052 (7)
C23	0.0162 (9)	0.0232 (9)	0.0301 (10)	−0.0050 (7)	0.0022 (8)	−0.0068 (8)
C22	0.0226 (10)	0.0216 (9)	0.0226 (9)	−0.0061 (8)	0.0028 (7)	−0.0087 (7)
C21	0.0209 (9)	0.0147 (8)	0.0223 (9)	−0.0023 (7)	0.0024 (7)	−0.0046 (7)
C20	0.0145 (8)	0.0156 (8)	0.0180 (8)	−0.0030 (6)	0.0024 (6)	−0.0022 (6)
C25	0.0293 (11)	0.0237 (10)	0.0451 (13)	−0.0077 (8)	0.0085 (10)	−0.0061 (9)
C26	0.0191 (9)	0.0159 (8)	0.0176 (8)	−0.0039 (7)	−0.0003 (7)	−0.0008 (6)
C27	0.0243 (10)	0.0339 (11)	0.0185 (9)	−0.0090 (8)	0.0015 (8)	−0.0040 (8)
C28	0.0303 (11)	0.0298 (10)	0.0159 (8)	−0.0079 (8)	0.0021 (8)	−0.0032 (7)
C29	0.0646 (18)	0.0409 (13)	0.0276 (11)	0.0057 (12)	0.0111 (11)	−0.0115 (10)
C30	0.0420 (14)	0.0545 (15)	0.0261 (11)	−0.0148 (12)	−0.0092 (10)	0.0001 (10)
C31	0.0250 (10)	0.0236 (10)	0.0409 (12)	−0.0096 (8)	0.0057 (9)	−0.0073 (9)
C32	0.0189 (9)	0.0162 (8)	0.0205 (8)	−0.0044 (7)	0.0006 (7)	−0.0015 (6)
C33	0.0249 (10)	0.0201 (9)	0.0234 (9)	−0.0025 (8)	−0.0019 (8)	−0.0008 (7)
C34	0.0277 (10)	0.0212 (9)	0.0186 (9)	−0.0031 (8)	−0.0005 (8)	0.0025 (7)
C36	0.0266 (11)	0.0340 (11)	0.0306 (11)	−0.0048 (9)	−0.0026 (9)	−0.0005 (9)
C35	0.0470 (14)	0.0316 (11)	0.0243 (10)	0.0027 (10)	0.0038 (10)	−0.0028 (9)
N15	0.0205 (8)	0.0176 (7)	0.0186 (7)	−0.0051 (6)	0.0020 (6)	−0.0026 (6)
N8	0.0202 (8)	0.0151 (7)	0.0209 (7)	−0.0064 (6)	0.0011 (6)	−0.0044 (6)
O1	0.0334 (9)	0.0466 (10)	0.0200 (7)	−0.0171 (7)	0.0064 (6)	−0.0085 (7)

O2	0.0295 (8)	0.0223 (6)	0.0174 (6)	−0.0072 (6)	0.0051 (5)	−0.0067 (5)
O3	0.0331 (8)	0.0200 (6)	0.0213 (7)	−0.0086 (6)	−0.0082 (6)	0.0024 (5)
O4	0.0322 (8)	0.0218 (7)	0.0220 (7)	−0.0065 (6)	−0.0028 (6)	0.0039 (5)

Geometric parameters (Å, °)

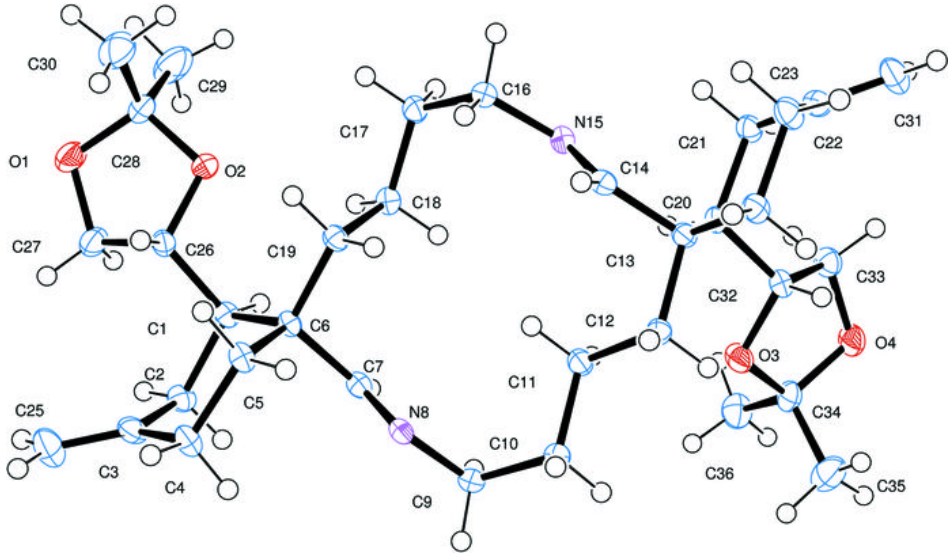
C5—C4	1.536 (3)	C24—C23	1.535 (3)
C5—C6	1.546 (2)	C24—H24A	0.9700
C5—H1A	0.9700	C24—H24B	0.9700
C5—H1B	0.9700	C23—C22	1.506 (3)
C4—C3	1.507 (3)	C23—H19A	0.9700
C4—H2A	0.9700	C23—H19B	0.9700
C4—H2B	0.9700	C22—C31	1.326 (3)
C3—C25	1.327 (3)	C22—C21	1.509 (3)
C3—C2	1.509 (3)	C21—C20	1.552 (2)
C2—C1	1.547 (2)	C21—H21A	0.9700
C2—H4A	0.9700	C21—H21B	0.9700
C2—H4B	0.9700	C20—C32	1.532 (3)
C1—C26	1.529 (2)	C20—H22	0.9800
C1—C6	1.557 (2)	C25—H23A	0.9300
C1—H5	0.9800	C25—H23B	0.9300
C6—C7	1.523 (2)	C26—O2	1.439 (2)
C6—C19	1.554 (2)	C26—C27	1.523 (3)
C19—C18	1.535 (2)	C26—H24	0.9800
C19—H7A	0.9700	C27—O1	1.428 (2)
C19—H7B	0.9700	C27—H25A	0.9700
C18—C17	1.531 (3)	C27—H25B	0.9700
C18—H8A	0.9700	C28—O2	1.427 (2)
C18—H8B	0.9700	C28—O1	1.430 (3)
C17—C16	1.527 (3)	C28—C29	1.505 (3)
C17—H9A	0.9700	C28—C30	1.511 (3)
C17—H9B	0.9700	C29—H27A	0.9600
C16—N15	1.468 (2)	C29—H27B	0.9600
C16—H10A	0.9700	C29—H27C	0.9600
C16—H10B	0.9700	C30—H28A	0.9600
C14—N15	1.258 (2)	C30—H28B	0.9600
C14—C13	1.518 (2)	C30—H28C	0.9600
C14—H11	0.9300	C31—H29A	0.9300
C13—C24	1.547 (3)	C31—H29B	0.9300
C13—C12	1.554 (2)	C32—O3	1.449 (2)
C13—C20	1.560 (2)	C32—C33	1.524 (3)
C12—C11	1.525 (3)	C32—H30	0.9800
C12—H13A	0.9700	C33—O4	1.433 (2)
C12—H13B	0.9700	C33—H31A	0.9700
C11—C10	1.530 (2)	C33—H31B	0.9700
C11—H14A	0.9700	C34—O4	1.432 (2)
C11—H14B	0.9700	C34—O3	1.430 (2)
C10—C9	1.526 (3)	C34—C36	1.514 (3)
C10—H15A	0.9700	C34—C35	1.512 (3)

C10—H15B	0.9700	C36—H33A	0.9600
C9—N8	1.462 (2)	C36—H33B	0.9600
C9—H16A	0.9700	C36—H33C	0.9600
C9—H16B	0.9700	C35—H34A	0.9600
C7—N8	1.259 (2)	C35—H34B	0.9600
C7—H17	0.9300	C35—H34C	0.9600
C4—C5—C6	113.61 (15)	C23—C24—H24B	109.0
C4—C5—H1A	108.8	C13—C24—H24B	109.0
C6—C5—H1A	108.8	H24A—C24—H24B	107.8
C4—C5—H1B	108.8	C22—C23—C24	110.26 (16)
C6—C5—H1B	108.8	C22—C23—H19A	109.6
H1A—C5—H1B	107.7	C24—C23—H19A	109.6
C3—C4—C5	112.00 (16)	C22—C23—H19B	109.6
C3—C4—H2A	109.2	C24—C23—H19B	109.6
C5—C4—H2A	109.2	H19A—C23—H19B	108.1
C3—C4—H2B	109.2	C31—C22—C23	122.99 (19)
C5—C4—H2B	109.2	C31—C22—C21	123.65 (19)
H2A—C4—H2B	107.9	C23—C22—C21	113.35 (16)
C25—C3—C4	124.92 (19)	C22—C21—C20	112.61 (15)
C25—C3—C2	121.83 (19)	C22—C21—H21A	109.1
C4—C3—C2	113.25 (16)	C20—C21—H21A	109.1
C3—C2—C1	111.92 (15)	C22—C21—H21B	109.1
C3—C2—H4A	109.2	C20—C21—H21B	109.1
C1—C2—H4A	109.2	H21A—C21—H21B	107.8
C3—C2—H4B	109.2	C32—C20—C21	111.26 (15)
C1—C2—H4B	109.2	C32—C20—C13	113.04 (14)
H4A—C2—H4B	107.9	C21—C20—C13	110.28 (14)
C26—C1—C2	110.97 (15)	C32—C20—H22	107.3
C26—C1—C6	113.77 (14)	C21—C20—H22	107.3
C2—C1—C6	109.36 (14)	C13—C20—H22	107.3
C26—C1—H5	107.5	C3—C25—H23A	120.0
C2—C1—H5	107.5	C3—C25—H23B	120.0
C6—C1—H5	107.5	H23A—C25—H23B	120.0
C7—C6—C5	110.47 (14)	O2—C26—C27	100.21 (15)
C7—C6—C19	105.98 (14)	O2—C26—C1	109.10 (14)
C5—C6—C19	108.03 (14)	C27—C26—C1	117.03 (15)
C7—C6—C1	108.50 (14)	O2—C26—H24	110.0
C5—C6—C1	110.72 (14)	C27—C26—H24	110.0
C19—C6—C1	113.04 (14)	C1—C26—H24	110.0
C18—C19—C6	116.21 (14)	O1—C27—C26	102.98 (16)
C18—C19—H7A	108.2	O1—C27—H25A	111.2
C6—C19—H7A	108.2	C26—C27—H25A	111.2
C18—C19—H7B	108.2	O1—C27—H25B	111.2
C6—C19—H7B	108.2	C26—C27—H25B	111.2
H7A—C19—H7B	107.4	H25A—C27—H25B	109.1
C17—C18—C19	112.92 (15)	O2—C28—O1	106.40 (15)
C17—C18—H8A	109.0	O2—C28—C29	107.56 (17)
C19—C18—H8A	109.0	O1—C28—C29	110.7 (2)
C17—C18—H8B	109.0	O2—C28—C30	110.74 (19)

C19—C18—H8B	109.0	O1—C28—C30	107.89 (18)
H8A—C18—H8B	107.8	C29—C28—C30	113.4 (2)
C16—C17—C18	114.97 (15)	C28—C29—H27A	109.5
C16—C17—H9A	108.5	C28—C29—H27B	109.5
C18—C17—H9A	108.5	H27A—C29—H27B	109.5
C16—C17—H9B	108.5	C28—C29—H27C	109.5
C18—C17—H9B	108.5	H27A—C29—H27C	109.5
H9A—C17—H9B	107.5	H27B—C29—H27C	109.5
N15—C16—C17	110.75 (16)	C28—C30—H28A	109.5
N15—C16—H10A	109.5	C28—C30—H28B	109.5
C17—C16—H10A	109.5	H28A—C30—H28B	109.5
N15—C16—H10B	109.5	C28—C30—H28C	109.5
C17—C16—H10B	109.5	H28A—C30—H28C	109.5
H10A—C16—H10B	108.1	H28B—C30—H28C	109.5
N15—C14—C13	125.76 (16)	C22—C31—H29A	120.0
N15—C14—H11	117.1	C22—C31—H29B	120.0
C13—C14—H11	117.1	H29A—C31—H29B	120.0
C14—C13—C24	107.37 (14)	O3—C32—C33	100.30 (15)
C14—C13—C12	105.58 (14)	O3—C32—C20	109.32 (15)
C24—C13—C12	107.31 (14)	C33—C32—C20	117.28 (15)
C14—C13—C20	111.65 (14)	O3—C32—H30	109.8
C24—C13—C20	110.94 (14)	C33—C32—H30	109.8
C12—C13—C20	113.61 (14)	C20—C32—H30	109.8
C11—C12—C13	115.48 (15)	O4—C33—C32	102.53 (15)
C11—C12—H13A	108.4	O4—C33—H31A	111.3
C13—C12—H13A	108.4	C32—C33—H31A	111.3
C11—C12—H13B	108.4	O4—C33—H31B	111.3
C13—C12—H13B	108.4	C32—C33—H31B	111.3
H13A—C12—H13B	107.5	H31A—C33—H31B	109.2
C12—C11—C10	112.45 (15)	O4—C34—O3	106.23 (15)
C12—C11—H14A	109.1	O4—C34—C36	110.57 (17)
C10—C11—H14A	109.1	O3—C34—C36	108.03 (16)
C12—C11—H14B	109.1	O4—C34—C35	108.48 (17)
C10—C11—H14B	109.1	O3—C34—C35	110.33 (17)
H14A—C11—H14B	107.8	C36—C34—C35	112.99 (19)
C9—C10—C11	112.78 (16)	C34—C36—H33A	109.5
C9—C10—H15A	109.0	C34—C36—H33B	109.5
C11—C10—H15A	109.0	H33A—C36—H33B	109.5
C9—C10—H15B	109.0	C34—C36—H33C	109.5
C11—C10—H15B	109.0	H33A—C36—H33C	109.5
H15A—C10—H15B	107.8	H33B—C36—H33C	109.5
N8—C9—C10	110.21 (15)	C34—C35—H34A	109.5
N8—C9—H16A	109.6	C34—C35—H34B	109.5
C10—C9—H16A	109.6	H34A—C35—H34B	109.5
N8—C9—H16B	109.6	C34—C35—H34C	109.5
C10—C9—H16B	109.6	H34A—C35—H34C	109.5
H16A—C9—H16B	108.1	H34B—C35—H34C	109.5
N8—C7—C6	122.82 (16)	C14—N15—C16	117.19 (16)
N8—C7—H17	118.6	C7—N8—C9	118.06 (16)

C6—C7—H17	118.6	C27—O1—C28	107.81 (15)
C23—C24—C13	113.04 (15)	C28—O2—C26	107.24 (14)
C23—C24—H24A	109.0	C34—O3—C32	108.65 (14)
C13—C24—H24A	109.0	C34—O4—C33	107.11 (14)

Fig. 1


C30
C29
O1
C28
O2
C27
C26
C1
C2
C25
C3
C4
C5
C6
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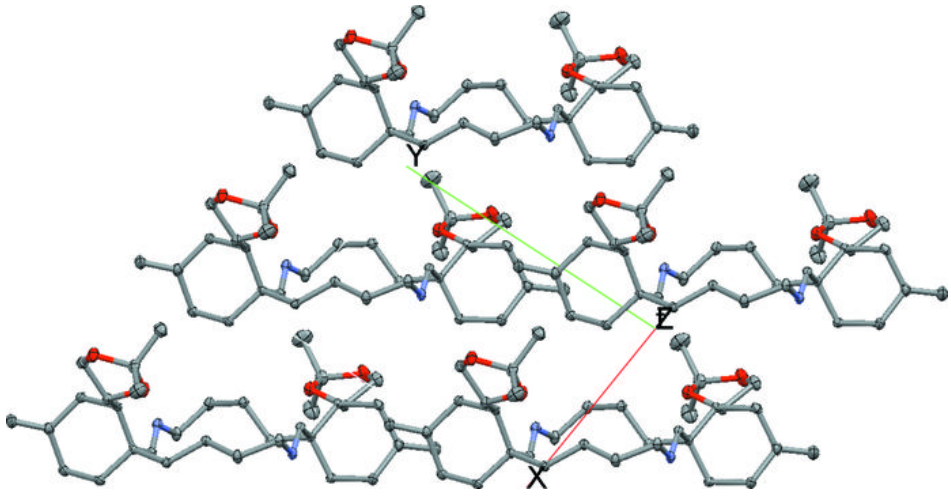
C16
N15
C18
C14
C20
C13
C12
C7
N8
C11
C10
C9
C21
C23
C22
C31
C32
C33
O3
O4
C34
C36
C35

Fig. 2



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3-Methyl-1-(prop-2-en-1-yl)quinoxalin-2(1*H*)-one

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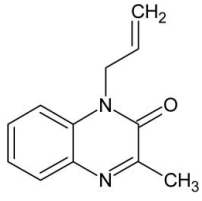
Key indicators: single-crystal X-ray study; T = 296 K, P = 0.0 kPa; mean σ(C–C) = 0.002 Å; R factor = 0.051; wR factor = 0.151; data-to-parameter ratio = 18.5.

In the molecule of the title compound, $C_{12}H_{12}N_2O$, the quinoxaline ring is planar with an r.m.s. deviation of 0.007 (15) Å. The dihedral angle between the quinoxaline and propenyl planes is 82.1 (2)°. The crystal packing is stabilized by offset π–π stacking between the quinoxaline rings [centroid–centroid distance = 3.8832 (9) Å].

Related literature

For biological activity of quinoxaline derivatives, see: Kleim *et al.* (1995). For their antitumor, and antituberculous properties, see: Abasolo *et al.* (1987); Rodrigo *et al.* (2002). For the antifungal, herbicidal, antidyslipidemic and anti-oxidative activities of quinoxaline derivatives, see: Jampilek *et al.* (2005); Sashidhara *et al.* (2009); Watkins *et al.* (2009). For bond-length data, see: Allen *et al.* (1987).



Experimental

Crystal data

$C_{12}H_{12}N_2O$
M_r = 200.24
Monoclinic, $P2_1/c$
a = 5.0722 (5) Å
b = 13.4707 (13) Å
c = 15.0507 (13) Å
β = 95.082 (5)°
V = 1024.31 (17) Å^3
Z = 4
Mo $K\alpha$ radiation
μ = 0.09 mm^{-1}
T = 296 K
0.32 × 0.31 × 0.13 mm

Data collection

Bruker X8 APEXII CCD area-detector diffractometer
11850 measured reflections
2546 independent reflections
1726 reflections with $I > 2\sigma(I)$
R_{int} = 0.049

Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.051
$wR(F^2)$ = 0.151
S = 1.08
2546 reflections
137 parameters
H-atom parameters constrained
$\Delta\rho_{max}$ = 0.23 e Å^{-3}
$\Delta\rho_{min}$ = −0.17 e Å^{-3}

Data collection: *APEX2* (Bruker, 2005); cell refinement: *SAINT* (Bruker, 2005); data reduction: *SAINT*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *ORTEPIII* (Burnett & Johnson, 1996), *ORTEP-3 for Windows* (Farrugia, 1997) and *PLATON* (Spek, 2009); software used to prepare material for publication: *WinGX* (Farrugia, 1999) and *publCIF* (Westrip, 2010).

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Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: DN2579).

References

Abasolo, M. I., Gaozza, C. H. & Fernandez, B. M. J. (1987). *Heterocycl. Chem.* **24**, 1771–1775.
Allen, F. H., Kennard, O., Watson, D. G., Brammer, L., Orpen, A. G. & Taylor, R. (1987). *J. Chem. Soc. Perkin Trans. 2*, pp. S1–19.
Bruker (2005). *APEX2* and *SAINT*. Bruker AXS Inc., Madison, Wisconsin, USA.
Burnett, M. N. & Johnson, C. K. (1996). *ORTEPIII*. Report ORNL-6895. Oak Ridge National Laboratory, Tennessee, USA.
Farrugia, L. J. (1997). *J. Appl. Cryst.* **30**, 565.
Farrugia, L. J. (1999). *J. Appl. Cryst.* **32**, 837–838.
Jampilek, J., Dolezal, M., Kunes, J., Buchta, V. & Kralova, K. (2005). *Med. Chem.* **1**, 591–599.
Kleim, J. P., Bender, R., Kirsch, R., Meichsner, C., Paessens, A., Rosner, M., Rubsamen Waigmann, H., Kaiser, R., Wichers, M., Schneweis, K. E., Winkler, I. & Riess, G. (1995). *Antimicrob. Agents Chemother.* **39**, 2253–2257.
Rodrigo, G. A., Robinshon, A. E., Hedrera, M. E., Kogan, M., Sicardi, S. M. & Fernaandez, B. M. (2002). *Trends Heterocycl. Chem.* **8**, 137–143.
Sashidhara, K. V., Kumar, A., Bhatia, G., Khan, M. M., Khanna, A. K. & Saxena, J. K. (2009). *Eur. J. Med. Chem.* **44**, 1813–1818.
Sheldrick, G. M. (2008). *Acta Cryst.* A**64**, 112–122.
Spek, A. L. (2009). *Acta Cryst.* D**65**, 148–155.
Watkins, A. J., Nicol, G. W. & Shawa, L. J. (2009). *Soil Biol. Biochem.* **41**, 580–585.
Westrip, S. P. (2010). *J. Appl. Cryst.* **43**. Submitted.

supplementary materials

Acta Cryst. (2010). E**66**, o1767 [**doi:10.1107/S1600536810023640**]

3-Methyl-1-(prop-2-en-1-yl)quinoxalin-2(1*H*)-one

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Comment

Quinoxaline derivatives are a very important class of nitrogen-containing compounds and have been widely used in dyes, pharmaceuticals and electrical/photochemical materials. Quinoxaline ring moiety constitute part of the chemical structures of various antibiotics such as Echinomycin, Levomycin and Actinoleutin that are known to inhibit growth of gram positive bacteria and are active against various transplantable tumors.

Quinoxaline derivatives were found to exhibit antimicrobial [Kleim *et al.* 1995], antitumor [Abasolo *et al.* 1987], and antituberculous activity [Rodrigo *et al.*2002]. They, also, exhibit interesting antifungal, herbicidal, Antidyslipidemic and antioxidative activities of quinoxaline derivatives, see: (Jampilek *et al.* 2005, Sashidhara *et al.* 2009, Watkins *et al.* 2009).

The dihedral angle between the quinoxaline and propenyl planes is 82.1 (2) (Fig. 1). Bond lengths and angles in title molecule are normal (Allen *et al.*, 1987). The crystal packing is stabilized by offset π-π stacking between the quinoxalin rings.

Experimental

To a solution of 3-methylquinoxali-2(1*H*)-one (1 g) in 20 ml of dimethylformamide was added allylchloride (0.85 ml),K2CO3 (0.95 g) and catalytic amont of tetrabutylammonium bromide.The mixture was stirred at room temperature for 24 h.Then the solvent was remdove under reduce pressure,the residue was cristallized in ethanol to afford the product.

Refinement

Although found in a difference map, H atoms were introduced in calculated positions and treated as riding with C—H = 0.96 Å for methyl groups, C—H = 0.93 Å for aromatic and C—H = 0.97 Å for methine with U iso (H) = 1.2U_{eq} (aromatic, methine) or U iso (H) = 1.5U_{eq} (methyl).

Figures

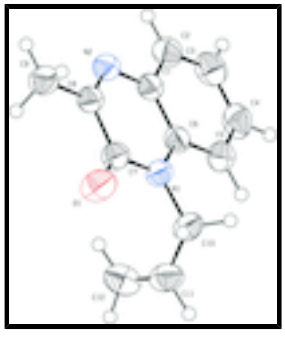


Fig. 1. : Molecular structure of the title compound with the atom-labelling scheme. Displacement ellipsoids are drawn at the 50% probability level. H atoms are represented as small spheres of arbitrary radii.

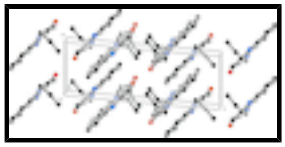


Fig. 2. : Packing view of the crystal structure of the title compound.

3-Methyl-1-(prop-2-en-1-yl)quinoxalin-2(1*H*)-one

Crystal data

$C_{12}H_{12}N_2O$	$F(000) = 424$
$M_r = 200.24$	$D_x = 1.298$ Mg m^{-3}
Monoclinic, $P2_1/c$	Melting point: 1486 K
Hall symbol: -P 2ybc	Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å
$a = 5.0722$ (5) Å	Cell parameters from 2764 reflections
$b = 13.4707$ (13) Å	$\theta = 2.4$–$27.4°$
$c = 15.0507$ (13) Å	$\mu = 0.09$ mm^{-1}
$\beta = 95.082$ (5)°	$T = 296$ K
$V = 1024.31$ (17) Å^3	Block, colourless
$Z = 4$	0.32 × 0.31 × 0.13 mm

Data collection

Bruker X8 APEXII CCD area-detector diffractometer	1726 reflections with $I > 2\sigma(I)$
Radiation source: fine-focus sealed tube	$R_{int} = 0.049$
graphite	$\theta_{max} = 28.3°$, $\theta_{min} = 2.7°$
φ and ω scans	$h = -6\rightarrow6$
11850 measured reflections	$k = 0\rightarrow17$
2546 independent reflections	$l = 0\rightarrow20$

Refinement

Refinement on F^2	Primary atom site location: structure-invariant direct methods
Least-squares matrix: full	Secondary atom site location: difference Fourier map
$R[F^2 > 2\sigma(F^2)] = 0.051$	Hydrogen site location: inferred from neighbouring sites
$wR(F^2) = 0.151$	H-atom parameters constrained
$S = 1.08$	$w = 1/[\sigma^2(F_o^2) + (0.0723P)^2 + 0.0888P]$ where $P = (F_o^2 + 2F_c^2)/3$
2546 reflections	$(\Delta/\sigma)_{max} = 0.001$
137 parameters	$\Delta\rho_{max} = 0.23$ e Å^{-3}
0 restraints	$\Delta\rho_{min} = -0.17$ e Å^{-3}

Special details

Experimental. The data collection nominally covered a sphere of reciprocal space, by a combination of seven sets of exposures; each set had a different φ angle for the crystal and each exposure covered 0.5° in ω and 30 s in time. The crystal-to-detector distance was 37.5 mm.

Geometry. All esds (except the esd in the dihedral angle between two l.s. planes) are estimatedusing the full covariance matrix. The cell esds are taken into account individually in the estimation of esds in distances, angles and torsion angles; correlations between esds in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell esds is used for estimating esds involving l.s. planes.

Refinement. Refinement of F^2 against ALL reflections. The weighted *R*-factor *wR* and goodness of fit *S* are based on F^2, conventional *R*-factors *R* are based on *F*, with *F* set to zero for negative F^2. The threshold expression of $F^2 > \sigma(F^2)$ is used only for calculating *R*-factors(gt) *etc*. and is not relevant to the choice of reflections for refinement. *R*-factors based on F^2 are statistically about twice as large as those based on *F*, and *R*- factors based on ALL datawill be even larger.

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å^2)

	x	*y*	*z*	U_{iso}*/U_{eq}
O1	−0.3390 (2)	0.34712 (9)	0.06022 (9)	0.0657 (4)
N1	−0.0193 (2)	0.29591 (9)	0.16502 (8)	0.0408 (3)
N2	0.1311 (2)	0.49458 (9)	0.18738 (8)	0.0445 (3)
C1	0.2649 (3)	0.41959 (11)	0.23590 (9)	0.0408 (3)
C2	0.4769 (3)	0.44552 (13)	0.29645 (10)	0.0514 (4)
H2	0.5253	0.5119	0.3030	0.062*
C3	0.6150 (3)	0.37488 (15)	0.34638 (11)	0.0589 (5)
H3	0.7560	0.3931	0.3868	0.071*
C4	0.5434 (3)	0.27599 (15)	0.33625 (11)	0.0579 (5)
H4	0.6364	0.2278	0.3704	0.069*
C5	0.3375 (3)	0.24845 (13)	0.27651 (11)	0.0503 (4)
H5	0.2932	0.1817	0.2698	0.060*
C6	0.1937 (3)	0.31975 (11)	0.22568 (9)	0.0395 (3)
C7	−0.1541 (3)	0.36731 (11)	0.11482 (10)	0.0441 (4)
C8	−0.0643 (3)	0.47053 (11)	0.13088 (9)	0.0424 (4)
C9	−0.2158 (3)	0.54800 (12)	0.07845 (11)	0.0543 (4)
H9A	−0.3878	0.5548	0.0997	0.081*
H9B	−0.2343	0.5293	0.0167	0.081*
H9C	−0.1233	0.6101	0.0850	0.081*
C10	−0.1160 (3)	0.19385 (11)	0.15522 (11)	0.0483 (4)
H10A	−0.3032	0.1956	0.1355	0.058*
H10B	−0.0975	0.1621	0.2133	0.058*
C11	0.0207 (3)	0.13211 (13)	0.09201 (12)	0.0578 (5)
H11	−0.0243	0.0652	0.0896	0.069*
C12	0.1942 (4)	0.16040 (15)	0.04015 (13)	0.0669 (5)
H12A	0.2467	0.2265	0.0398	0.080*
H12B	0.2672	0.1147	0.0030	0.080*

Atomic displacement parameters (Å^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
O1	0.0682 (8)	0.0524 (8)	0.0700 (8)	−0.0060 (6)	−0.0296 (7)	0.0027 (6)
N1	0.0443 (6)	0.0358 (7)	0.0413 (6)	−0.0016 (5)	−0.0024 (5)	0.0006 (5)
N2	0.0518 (7)	0.0402 (7)	0.0407 (6)	−0.0005 (5)	−0.0013 (5)	−0.0018 (5)
C1	0.0435 (7)	0.0433 (9)	0.0353 (7)	0.0004 (6)	0.0020 (6)	−0.0008 (6)
C2	0.0527 (9)	0.0550 (10)	0.0452 (8)	−0.0061 (7)	−0.0038 (7)	−0.0033 (7)
C3	0.0527 (9)	0.0755 (13)	0.0458 (9)	−0.0016 (8)	−0.0107 (7)	−0.0006 (8)
C4	0.0592 (10)	0.0648 (12)	0.0474 (9)	0.0098 (8)	−0.0080 (7)	0.0103 (8)
C5	0.0568 (9)	0.0471 (9)	0.0460 (8)	0.0046 (7)	−0.0014 (7)	0.0053 (7)
C6	0.0416 (7)	0.0415 (9)	0.0352 (7)	0.0006 (6)	0.0026 (6)	−0.0005 (6)
C7	0.0464 (8)	0.0423 (9)	0.0420 (8)	0.0003 (6)	−0.0045 (6)	−0.0002 (6)
C8	0.0487 (8)	0.0398 (8)	0.0380 (7)	0.0027 (6)	0.0003 (6)	−0.0005 (6)
C9	0.0653 (10)	0.0439 (9)	0.0518 (9)	0.0069 (7)	−0.0059 (8)	0.0015 (7)
C10	0.0488 (8)	0.0387 (9)	0.0560 (9)	−0.0052 (6)	−0.0032 (7)	0.0022 (7)
C11	0.0625 (10)	0.0455 (10)	0.0633 (10)	−0.0042 (8)	−0.0060 (9)	−0.0077 (8)
C12	0.0696 (11)	0.0701 (13)	0.0602 (11)	−0.0030 (9)	0.0008 (9)	−0.0162 (9)

Geometric parameters (Å, °)

O1—C7	1.2215 (18)	C5—C6	1.393 (2)
N1—C7	1.3683 (19)	C5—H5	0.9300
N1—C6	1.3889 (18)	C7—C8	1.476 (2)
N1—C10	1.4629 (19)	C8—C9	1.482 (2)
N2—C8	1.2887 (18)	C9—H9A	0.9600
N2—C1	1.3881 (19)	C9—H9B	0.9600
C1—C2	1.391 (2)	C9—H9C	0.9600
C1—C6	1.397 (2)	C10—C11	1.481 (2)
C2—C3	1.367 (2)	C10—H10A	0.9700
C2—H2	0.9300	C10—H10B	0.9700
C3—C4	1.386 (3)	C11—C12	1.285 (3)
C3—H3	0.9300	C11—H11	0.9300
C4—C5	1.368 (2)	C12—H12A	0.9300
C4—H4	0.9300	C12—H12B	0.9300
C7—N1—C6	121.48 (13)	O1—C7—C8	121.81 (14)
C7—N1—C10	117.26 (12)	N1—C7—C8	116.08 (13)
C6—N1—C10	121.20 (12)	N2—C8—C7	123.57 (13)
C8—N2—C1	118.41 (13)	N2—C8—C9	120.44 (14)
N2—C1—C2	118.39 (14)	C7—C8—C9	115.99 (13)
N2—C1—C6	122.20 (13)	C8—C9—H9A	109.5
C2—C1—C6	119.41 (14)	C8—C9—H9B	109.5
C3—C2—C1	120.95 (16)	H9A—C9—H9B	109.5
C3—C2—H2	119.5	C8—C9—H9C	109.5
C1—C2—H2	119.5	H9A—C9—H9C	109.5
C2—C3—C4	119.49 (15)	H9B—C9—H9C	109.5
C2—C3—H3	120.3	N1—C10—C11	114.87 (13)

C4—C3—H3	120.3	N1—C10—H10A	108.6
C5—C4—C3	120.70 (16)	C11—C10—H10A	108.6
C5—C4—H4	119.7	N1—C10—H10B	108.6
C3—C4—H4	119.7	C11—C10—H10B	108.6
C4—C5—C6	120.41 (16)	H10A—C10—H10B	107.5
C4—C5—H5	119.8	C12—C11—C10	127.48 (17)
C6—C5—H5	119.8	C12—C11—H11	116.3
N1—C6—C5	122.71 (14)	C10—C11—H11	116.3
N1—C6—C1	118.25 (13)	C11—C12—H12A	120.0
C5—C6—C1	119.04 (14)	C11—C12—H12B	120.0
O1—C7—N1	122.11 (14)	H12A—C12—H12B	120.0
C12—C11—C10—N1	−6.7 (3)		

Table 1

Offset π–π stacking between the quinoxaline rings.

Cg1 is the centroid of ring N1,C6,C1,N2,C8,C7 and Cg2 the centroid of ring C1–C6.

	Centroid-to-centroid(Å)	plane-to-plane(Å)	offset(°)
Cg1–Cg2^{i}	3.8832 (9)	3.509	25.4

Symmetry code: (i) -1+x, y, z.

Fig. 1

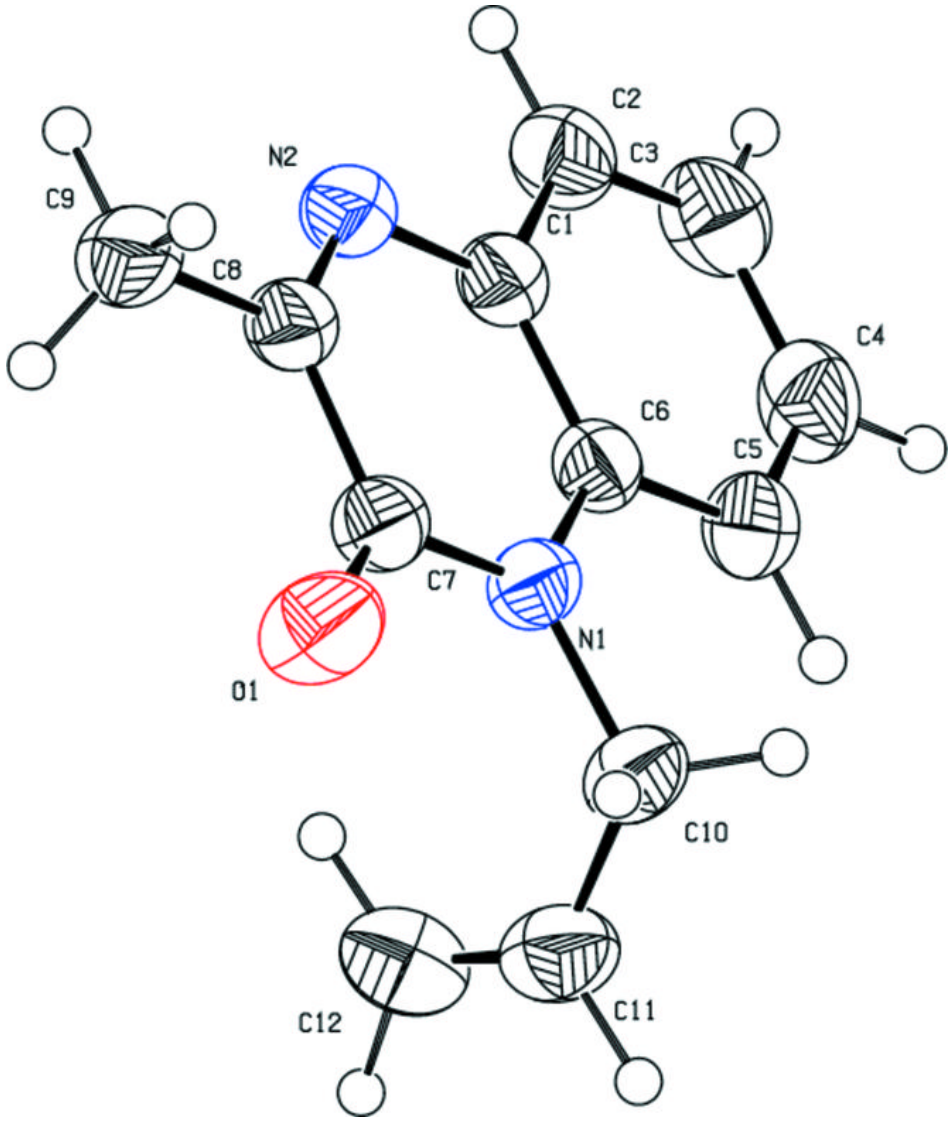
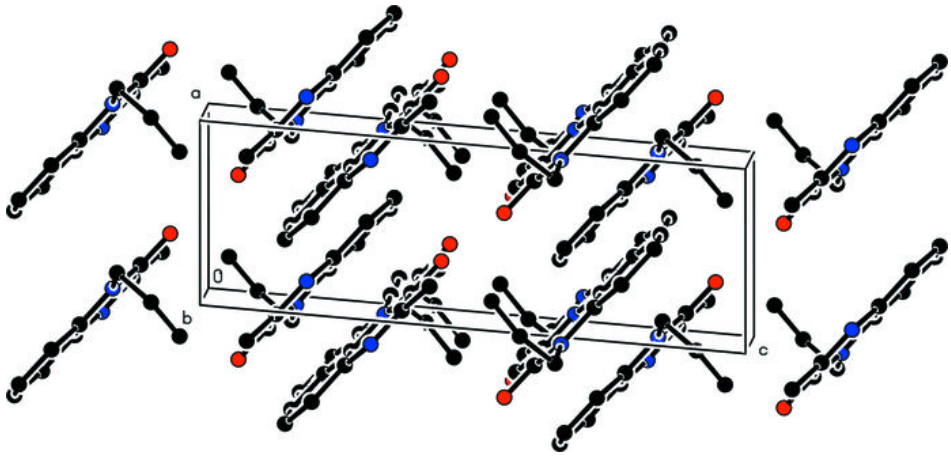


Fig. 2



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1-Benzyl-3-[(trimethylsilyl)methyl]-benzimidazolium chloride monohydrate

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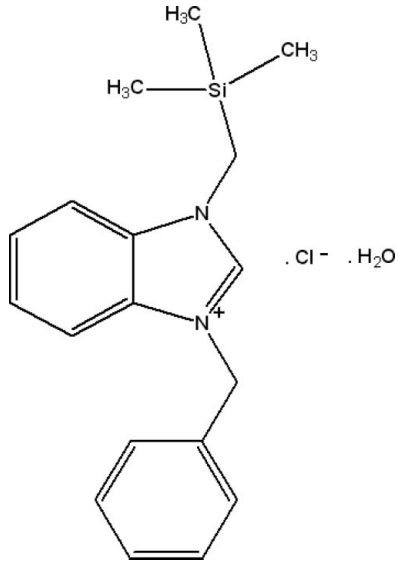
Key indicators: single-crystal X-ray study; T = 296 K; mean σ(C–C) = 0.004 Å; R factor = 0.049; wR factor = 0.135; data-to-parameter ratio = 18.9.

The title compound, $C_{18}H_{23}N_2Si^+\cdot Cl^-\cdot H_2O$, was synthesized from 1-[(trimethylsilyl)methyl]benzimidazole and benzyl chloride in dimethylformamide. The benzimidazole ring system is approximately planar, with a maximum deviation of 0.022 (2) Å, and makes an angle of 74.80 (12)° with the phenyl ring. The crystal packing is stabilized by O—H···Cl, C—H···Cl, C—H···O and C—H···π interactions between symmetry-related molecules together with π–π stacking interactions between the imidazolium and benzene rings [centroid–centroid distance = 3.5690 (15) Å] and between the benzene rings [centroid–centroid distance = 3.7223 (14) Å].

Related literature

For general background to benzimidazole compounds and for the biological activity of related structures, see: Galal *et al.* (2009); Huang *et al.* (2006); Küçükbay & Durmaz (1997); Küçükbay *et al.* (1995, 2003, 2004, 2010); Lukevics *et al.* (2001); Singh & Lown (2000); Tavman *et al.* (2005); Turner & Denny (1996); Williams *et al.* (2002); Yılmaz & Küçükbay (2009); Çetinkaya *et al.* (1996). For similar structures, see: Akkurt *et al.* (2008, 2010).



Experimental

Crystal data

$C_{18}H_{23}N_2Si^+\cdot Cl^-\cdot H_2O$
M_r = 348.94
Triclinic, $P\overline{1}$
a = 9.3592 (7) Å
b = 10.9500 (9) Å
c = 11.0522 (8) Å
α = 117.594 (6)°
β = 103.295 (6)°
γ = 92.094 (6)°
V = 963.39 (15) Å^3
Z = 2
Mo $K\alpha$ radiation
μ = 0.27 mm^{-1}
T = 296 K
0.57 × 0.50 × 0.36 mm

Data collection

Stoe IPDS 2 diffractometer
Absorption correction: integration (*X-RED32*; Stoe & Cie, 2002)
T_{min} = 0.859, T_{max} = 0.909
12149 measured reflections
3987 independent reflections
3241 reflections with $I > 2\sigma(I)$
R_{int} = 0.029

Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.049
$wR(F^2)$ = 0.135
S = 1.07
3987 reflections
211 parameters
H-atom parameters constrained
$\Delta\rho_{max}$ = 0.32 e Å^{-3}
$\Delta\rho_{min}$ = −0.32 e Å^{-3}

Table 1
Hydrogen-bond geometry (Å, °).

*Cg*3 is the centroid of the C9–C14 ring.

D—H···A	D—H	H···A	D···A	D—H···A
O1—H1*A*···Cl1	0.86	2.45	3.257 (2)	157
O1—H1*B*···Cl1^{i}	0.85	2.45	3.250 (3)	158
C7—H7···O1	0.93	2.51	3.170 (3)	128
C8—H8*A*···Cl1	0.97	2.81	3.703 (2)	153
C3—H3···*Cg*3^{ii}	0.93	2.69	3.526 (2)	151

Symmetry codes: (i) $-x+2, -y+1, -z+2$; (ii) $x-1, y, z$.

Data collection: *X-AREA* (Stoe & Cie, 2002); cell refinement: *X-AREA*; data reduction: *X-RED32* (Stoe & Cie, 2002); program(s) used to solve structure: *SIR97* (Altomare *et al.*, 1999); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *ORTEPIII* (Burnett & Johnson, 1996), *ORTEP-3 for Windows* (Farrugia, 1997) and *PLATON* (Spek, 2009); software used to prepare material for publication: *WinGX* (Farrugia, 1999).

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Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: DN2582).

References

Akkurt, M., Karaca, S., Küçükbay, H., Şireci, N. & Büyükgüngör, O. (2008). *Acta Cryst.* E**64**, o809.

Akkurt, M., Yalçın, Ş. P., Şireci, N., Küçükbay, H. & Tahir, M. N. (2010). *Acta Cryst.* E**66**, m253–m254.

Altomare, A., Burla, M. C., Camalli, M., Cascarano, G. L., Giacovazzo, C., Guagliardi, A., Moliterni, A. G. G., Polidori, G. & Spagna, R. (1999). *J. Appl. Cryst.* **32**, 115–119.

Burnett, M. N. & Johnson, C. K. (1996). *ORTEPIII.* Report ORNL-6895. Oak Ridge National Laboratory, Tennessee, USA.

Çetinkaya, B., Çetinkaya, E., Küçükbay, H. & Durmaz, R. (1996). *Arzneim. Forsch. Drug Res.* **46**, 1154–1158.

Farrugia, L. J. (1997). *J. Appl. Cryst.* **30**, 565.

Farrugia, L. J. (1999). *J. Appl. Cryst.* **32**, 837–838.

Galal, S. A., Hegab, K. H., Kassab, A. S., Rodriguez, M. L., Kerwin, S. M., El-Khamry, A. M. A. & El-Diwani, H. I. (2009). *Eur. J. Med. Chem.* **44**, 1500–1508.

Huang, S. T., Hsei, I. J. & Chen, C. (2006). *Bioorg. Med. Chem.* **14**, 6106–6119.

Küçükbay, H., Çetinkaya, E. & Durmaz, R. (1995). *Arzneim. Forsch. Drug Res.* **45**, 1331–1334.

Küçükbay, H. & Durmaz, B. (1997). *Arzneim. Forsch. Drug Res.* **47**, 667–670.

Küçükbay, H., Durmaz, R., Okuyucu, N. & Günal, S. (2003). *Fol. Microbiol.* **48**, 679–681.

Küçükbay, H., Durmaz, R., Okuyucu, N., Günal, S. & Kazaz, C. (2004). *Arzneim. Forsch./Drug Res.* **54**, 64–68.

Küçükbay, H., Durmaz, R., Şireci, N. & Günal, S. (2010). *Asian J. Chem.* **22**, 2816–2824.

Lukevics, E., Arsenyan, P., Shestakova, I., Domracheva, I., Nesterova, A. & Pudova, O. (2001). *Eur. J. Med. Chem.* **36**, 507–515.

Sheldrick, G. M. (2008). *Acta Cryst.* A**64**, 112–122.

Singh, A. K. & Lown, J. W. (2000). *Anticancer Drug Des.* **15**, 265–275.

Spek, A. L. (2009). *Acta Cryst.* D**65**, 148–155.

Stoe & Cie (2002). *X-AREA* and *X-RED32*. Stoe & Cie, Darmstadt, Germany.

Tavman, A., Birteksöz, S. & Ötük, G. (2005). *Folia Mirobiol.*, **50**, 467–472.

Turner, P. R. & Denny, W. A. (1996). *Mutat. Res.* **355**, 141–169.

Williams, D. A., Lemke, T. L. & Foye, O. (2002). *Foye's Principles of Medicinal Chemistry*, 5th ed. Philadelphia, USA: Lippincott Williams and Wilkins.

Yılmaz, Ü. & Küçükbay, H. (2009). *Asian J. Chem.* **21**, 6149–6155.

supplementary materials

Acta Cryst. (2010). E**66**, o1770-o1771 [**doi:10.1107/S1600536810024128**]

1-Benzyl-3-[(trimethylsilyl)methyl]benzimidazolium chloride monohydrate

M. Akkurt, Í. Çelik, H. Küçükbay, N. Sireci and O. Büyükgüngör

Comment

Although there are different antibacterial and antifungal drugs used in the treatment of bacterial and fungal infections, some of them have undesirable side effects. In addition, some of them become less effective due to the development of resistance to these drugs (Williams *et al.*, 2002). Therefore, many clinically effective antibacterial and antifungal drugs have become less effective due to the development of resistance to these drugs. Since, benzimidazole compounds have been found to have a broad range of pharmacological activity, many research groups as well as our group have been interested in these type of heterocyclic compounds (Singh *et al.*, 2000; Huang *et al.* 2006; Turner & Denny, 1996; Lukevics *et al.*, 2001; Galal *et al.* 2009; Çetinkaya *et al.*, 1996; Küçükbay *et al.*, 1995, 1997, 2003, 2004, 2010; Yılmaz & Küçükbay, 2009; Tavman *et al.*, 2005). In recent years, considerable attention has been given to the synthesis of alkylsilyl substituted benzimidazole derivatives because of their properties in cancer therapy. For example, 1-(3-trimethylsilylpropyl)benzimidazole inhibits carcinoma S-180 tumour growth in dose 1 mg.kg^{-1} by 62% (on ICR mice) (Lukevics *et al.*, 2001). These properties of silylsubstituted benzimidazole compounds, triggered us to synthesis novel trimethylsilyl substituted benzimidazole compounds. The objectives of this study were to synthesize and elucidate the crystal structure of the title compound, 1-benzyl-3-trimethylsilylmethylbenzimidazolium chloride monohydrate, (I).

In the title molecule, (Fig. 1), the benzimidazole ring system (N1/N2/C1–C7) is approximately planar, with maximum deviations of -0.022 (2) Å for C6, -0.018 (2) for C1 and 0.015 (2) for C7. The benzimidazole (N1/N2/C1–C7) and phenyl (C9–C14) systems make an angle of 74.80 (12)°. The values of the geometric parameters in (I) are comparable with those observed for other similar compounds (Akkurt *et al.*, 2008, 2010). The average value of the Si—C bond length is 1.854 (4) Å. The angles around the Si atoms with a distorted tetrahedral geometry rang from 105.86 (16)° to 111.81 (16)°.

The crystal packing of (I) is stabilized by O—H···Cl, C—H···Cl and C—H···π interactions between symmetry-related molecules (Fig. 2 and Table 1), together with π-π stacking interactions between imidazolium and benzene (Table 2).

Experimental

A mixture of 1-trimethylsilylmethylbenzimidazole (1.02 g, 5 mmol) and benzyl chloride (0.60 cm^3, 5 mmol) in dimethylformamide (5 ml) was refluxed for 3 h. The mixture was then cooled and the volatiles were removed *in vacuo*. The residue was crystallized from a dimethylformamide/ethanol (1:1). White crystals of the title compound (1.36 g, 82%) were obtained, m.p. 425–426 K; $\nu_{(CN)}$ = 1553 cm^{-1}. Anal. Found: C 61.64, H 7.19, N 7.93%. Calculated for $C_{18}H_{25}ClN_2OSi$: C 61.96, H 7.22, N 8.03%. ^{1}H NMR (δ, DMSO-d$_6$): 10.21 (s, 1H, NCHN), 8.11 - 7.59 (m, 4H, C_6H_4), 7.56–7.33 (m, 5H, C_6H_5), 5.86 (s, 2H, CH_2 benzyl), 4.30 (s, 2H, CH_2Si) and 0.14 [s, 9H, $(CH_3)_3Si$]. ^{13}C NMR (δ, DMSO-d$_6$): 141.6 (NCHN), 134.6, 132.1, 130.8, 129.1, 128.8 and 128.3 (C_6H_4), 126.8, 126.5, 114.3 and 113.9 (C_6H_5), 49.8 (CH_2 benzyl), 38.1(CH_2Si) and -2.5 [$(CH_3)_3Si$].

Refinement

All H atoms attached to C atoms were fixed geometrically and treated as riding with C—H = 0.93 Å (aromatic), 0.96 Å (methyl) and 0.97 Å (methylene) with U_{iso}(H) = 1.2U_{eq}(C) or 1.5U_{eq}(methyl). H atoms of water molecule were located in difference Fourier maps and included in the subsequent refinement using restraints (O-H= 0.83 (1)Å and H···H= 1.40 (2)Å) with U_{iso}(H) = 1.5U_{eq}(O).In the last cycles of refinement, they were treated as riding on the O atoms.

Figures

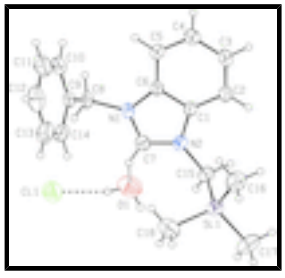


Fig. 1. View of the title molecule in the asymmetric unit, with the atom numbering scheme. Displacement ellipsoids for non-H atoms are drawn at the 30% probability level. H atoms are represented as small spheres of arbitrary radii and H bonds are shown as dashed lines.

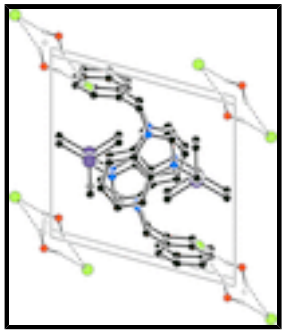


Fig. 2. View of the packing and hydrogen bonding interactions of (I) down the *b* axis. All hydrogen atoms not involved in hydrogen bonding have been omitted for clarity.

1-Benzyl-3-[(trimethylsilyl)methyl]benzimidazolium chloride monohydrate

Crystal data

$C_{18}H_{23}N_2Si^+·Cl^-·H_2O$	Z = 2
M_r = 348.94	F(000) = 372
Triclinic, $P\overline{1}$	D_x = 1.203 Mg m^{-3}
Hall symbol: -P 1	Mo $K\alpha$ radiation, λ = 0.71073 Å
a = 9.3592 (7) Å	Cell parameters from 28124 reflections
b = 10.9500 (9) Å	θ = 2.1–28.0°
c = 11.0522 (8) Å	μ = 0.27 mm^{-1}
α = 117.594 (6)°	T = 296 K
β = 103.295 (6)°	Prism, colourless
γ = 92.094 (6)°	0.57 × 0.50 × 0.36 mm
V = 963.39 (15) Å^3	

Data collection

Stoe IPDS 2 diffractometer	3987 independent reflections
Radiation source: sealed X-ray tube, 12 x 0.4 mm long-fine focus	3241 reflections with $I > 2\sigma(I)$
plane graphite	$R_{int} = 0.029$
Detector resolution: 6.67 pixels mm^{-1}	$\theta_{max} = 26.5°$, $\theta_{min} = 2.1°$
ω scans	$h = -11 \rightarrow 11$
Absorption correction: integration (*X-RED32*; Stoe & Cie, 2002)	$k = -13 \rightarrow 12$
$T_{min} = 0.859$, $T_{max} = 0.909$	$l = -13 \rightarrow 13$
12149 measured reflections	

Refinement

Refinement on F^2	Primary atom site location: structure-invariant direct methods
Least-squares matrix: full	Secondary atom site location: difference Fourier map
$R[F^2 > 2\sigma(F^2)] = 0.049$	Hydrogen site location: inferred from neighbouring sites
$wR(F^2) = 0.135$	H-atom parameters constrained
$S = 1.07$	$w = 1/[\sigma^2(F_o^2) + (0.0637P)^2 + 0.2683P]$ where $P = (F_o^2 + 2F_c^2)/3$
3987 reflections	$(\Delta/\sigma)_{max} < 0.001$
211 parameters	$\Delta\rho_{max} = 0.32$ e Å^{-3}
0 restraints	$\Delta\rho_{min} = -0.32$ e Å^{-3}

Special details

Geometry. All esds (except the esd in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell esds are taken into account individually in the estimation of esds in distances, angles and torsion angles; correlations between esds in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell esds is used for estimating esds involving l.s. planes.

Refinement. Refinement on F^2 for ALL reflections except those flagged by the user for potential systematic errors. Weighted *R*-factors *wR* and all goodnesses of fit *S* are based on F^2, conventional *R*-factors *R* are based on *F*, with *F* set to zero for negative F^2. The observed criterion of $F^2 > \sigma(F^2)$ is used only for calculating -*R*-factor-obs *etc*. and is not relevant to the choice of reflections for refinement. *R*-factors based on F^2 are statistically about twice as large as those based on *F*, and *R*-factors based on ALL data will be even larger.

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å^2)

	x	*y*	*z*	U_{iso}*/U_{eq}
Si1	0.53328 (7)	0.20172 (7)	0.79168 (6)	0.05705 (19)
N1	0.72385 (17)	0.36741 (17)	0.52896 (17)	0.0466 (4)
N2	0.59349 (17)	0.36730 (17)	0.66907 (17)	0.0466 (4)

C1	0.4923 (2)	0.33506 (19)	0.54087 (19)	0.0428 (4)
C2	0.3377 (2)	0.3101 (2)	0.4971 (2)	0.0521 (5)
H2	0.2816	0.3104	0.5566	0.063*
C3	0.2721 (2)	0.2847 (2)	0.3611 (2)	0.0587 (5)
H3	0.1688	0.2667	0.3276	0.070*
C4	0.3560 (2)	0.2853 (3)	0.2717 (2)	0.0592 (5)
H4	0.3071	0.2682	0.1806	0.071*
C5	0.5084 (2)	0.3104 (2)	0.3150 (2)	0.0532 (5)
H5	0.5641	0.3111	0.2555	0.064*
C6	0.57570 (19)	0.33479 (19)	0.4512 (2)	0.0432 (4)
C7	0.7293 (2)	0.3855 (2)	0.6574 (2)	0.0505 (5)
H7	0.8165	0.4079	0.7293	0.061*
C8	0.8534 (2)	0.3833 (2)	0.4794 (2)	0.0547 (5)
H8A	0.9413	0.4273	0.5602	0.066*
H8B	0.8371	0.4442	0.4377	0.066*
C9	0.8803 (2)	0.2461 (2)	0.3720 (2)	0.0510 (5)
C10	0.8520 (3)	0.2111 (3)	0.2308 (3)	0.0717 (7)
H10	0.8171	0.2741	0.2014	0.086*
C11	0.8748 (3)	0.0831 (4)	0.1329 (3)	0.0935 (10)
H11	0.8546	0.0600	0.0377	0.112*
C12	0.9272 (3)	−0.0100 (3)	0.1753 (4)	0.0947 (10)
H12	0.9404	−0.0970	0.1089	0.114*
C13	0.9600 (3)	0.0255 (3)	0.3158 (4)	0.0909 (10)
H13	0.9980	−0.0367	0.3451	0.109*
C14	0.9372 (3)	0.1527 (3)	0.4141 (3)	0.0700 (7)
H14	0.9602	0.1760	0.5095	0.084*
C15	0.5549 (3)	0.3754 (2)	0.7947 (2)	0.0549 (5)
H15A	0.4625	0.4122	0.8003	0.066*
H15B	0.6320	0.4406	0.8796	0.066*
C16	0.3837 (3)	0.0757 (3)	0.6328 (3)	0.0812 (8)
H16A	0.4063	0.0662	0.5487	0.122*
H16B	0.2907	0.1090	0.6377	0.122*
H16C	0.3767	−0.0135	0.6297	0.122*
C17	0.4849 (4)	0.2374 (4)	0.9569 (3)	0.1001 (10)
H17A	0.4744	0.1524	0.9619	0.150*
H17B	0.3928	0.2732	0.9569	0.150*
H17C	0.5624	0.3050	1.0376	0.150*
C18	0.7121 (3)	0.1391 (3)	0.7877 (3)	0.0899 (9)
H18A	0.7028	0.0478	0.7796	0.135*
H18B	0.7869	0.2023	0.8737	0.135*
H18C	0.7403	0.1344	0.7076	0.135*
O1	0.9113 (3)	0.6314 (2)	0.9603 (2)	0.1024 (7)
H1A	0.9910	0.6000	0.9420	0.154*
H1B	0.9090	0.6350	1.0380	0.154*
Cl1	1.14370 (9)	0.44812 (10)	0.80296 (8)	0.0961 (3)

Atomic displacement parameters (Å^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Si1	0.0616 (4)	0.0668 (4)	0.0477 (3)	0.0106 (3)	0.0191 (3)	0.0301 (3)
N1	0.0349 (8)	0.0565 (9)	0.0533 (9)	0.0048 (7)	0.0145 (7)	0.0295 (8)
N2	0.0448 (9)	0.0524 (9)	0.0460 (8)	0.0074 (7)	0.0162 (7)	0.0251 (7)
C1	0.0401 (9)	0.0458 (9)	0.0466 (9)	0.0086 (7)	0.0162 (8)	0.0238 (8)
C2	0.0404 (10)	0.0611 (12)	0.0632 (12)	0.0110 (9)	0.0240 (9)	0.0324 (10)
C3	0.0358 (10)	0.0717 (14)	0.0673 (13)	0.0081 (9)	0.0120 (9)	0.0339 (11)
C4	0.0471 (12)	0.0770 (14)	0.0527 (11)	0.0088 (10)	0.0087 (9)	0.0333 (11)
C5	0.0486 (11)	0.0686 (13)	0.0516 (11)	0.0106 (9)	0.0193 (9)	0.0340 (10)
C6	0.0343 (9)	0.0484 (10)	0.0507 (10)	0.0068 (7)	0.0145 (8)	0.0260 (8)
C7	0.0418 (10)	0.0554 (11)	0.0511 (11)	0.0031 (8)	0.0079 (8)	0.0260 (9)
C8	0.0360 (10)	0.0667 (13)	0.0736 (13)	0.0050 (9)	0.0216 (9)	0.0412 (11)
C9	0.0311 (9)	0.0671 (12)	0.0673 (12)	0.0090 (8)	0.0197 (9)	0.0400 (10)
C10	0.0529 (13)	0.1023 (19)	0.0737 (15)	0.0312 (13)	0.0236 (12)	0.0498 (15)
C11	0.0647 (17)	0.126 (3)	0.0702 (17)	0.0308 (17)	0.0212 (14)	0.0299 (17)
C12	0.0684 (18)	0.0793 (19)	0.120 (3)	0.0195 (15)	0.0432 (18)	0.0266 (18)
C13	0.087 (2)	0.088 (2)	0.146 (3)	0.0402 (16)	0.069 (2)	0.077 (2)
C14	0.0671 (15)	0.0864 (17)	0.0943 (18)	0.0279 (13)	0.0444 (14)	0.0631 (15)
C15	0.0599 (12)	0.0622 (12)	0.0420 (10)	0.0129 (10)	0.0203 (9)	0.0217 (9)
C16	0.0781 (18)	0.0771 (17)	0.0790 (17)	−0.0077 (13)	0.0151 (14)	0.0347 (14)
C17	0.142 (3)	0.111 (2)	0.0703 (17)	0.022 (2)	0.0513 (19)	0.0526 (17)
C18	0.0818 (19)	0.093 (2)	0.088 (2)	0.0247 (16)	0.0135 (16)	0.0423 (17)
O1	0.1114 (17)	0.0974 (15)	0.0822 (13)	0.0288 (13)	0.0144 (12)	0.0355 (12)
Cl1	0.0818 (5)	0.1278 (7)	0.0780 (5)	0.0348 (4)	0.0259 (4)	0.0465 (4)

Geometric parameters (Å, °)

Si1—C18	1.834 (3)	C9—C10	1.378 (3)
Si1—C17	1.850 (3)	C9—C14	1.383 (3)
Si1—C16	1.852 (3)	C10—C11	1.380 (4)
Si1—C15	1.890 (2)	C10—H10	0.9300
N1—C7	1.328 (3)	C11—C12	1.368 (5)
N1—C6	1.386 (2)	C11—H11	0.9300
N1—C8	1.476 (2)	C12—C13	1.367 (5)
N2—C7	1.324 (2)	C12—H12	0.9300
N2—C1	1.387 (2)	C13—C14	1.376 (4)
N2—C15	1.478 (2)	C13—H13	0.9300
C1—C2	1.389 (3)	C14—H14	0.9300
C1—C6	1.394 (2)	C15—H15A	0.9700
C2—C3	1.374 (3)	C15—H15B	0.9700
C2—H2	0.9300	C16—H16A	0.9600
C3—C4	1.398 (3)	C16—H16B	0.9600
C3—H3	0.9300	C16—H16C	0.9600
C4—C5	1.369 (3)	C17—H17A	0.9600
C4—H4	0.9300	C17—H17B	0.9600
C5—C6	1.384 (3)	C17—H17C	0.9600

C5—H5	0.9300	C18—H18A	0.9600
C7—H7	0.9300	C18—H18B	0.9600
C8—C9	1.497 (3)	C18—H18C	0.9600
C8—H8A	0.9700	O1—H1A	0.8598
C8—H8B	0.9700	O1—H1B	0.8466
C18—Si1—C17	111.82 (16)	C14—C9—C8	120.0 (2)
C18—Si1—C16	110.58 (15)	C9—C10—C11	120.5 (3)
C17—Si1—C16	110.93 (16)	C9—C10—H10	119.8
C18—Si1—C15	107.44 (14)	C11—C10—H10	119.8
C17—Si1—C15	105.86 (13)	C12—C11—C10	120.2 (3)
C16—Si1—C15	110.04 (12)	C12—C11—H11	119.9
C7—N1—C6	108.20 (15)	C10—C11—H11	119.9
C7—N1—C8	125.70 (17)	C13—C12—C11	119.7 (3)
C6—N1—C8	126.08 (16)	C13—C12—H12	120.1
C7—N2—C1	108.16 (15)	C11—C12—H12	120.1
C7—N2—C15	126.39 (17)	C12—C13—C14	120.4 (3)
C1—N2—C15	125.43 (16)	C12—C13—H13	119.8
N2—C1—C2	131.97 (17)	C14—C13—H13	119.8
N2—C1—C6	106.56 (16)	C13—C14—C9	120.4 (3)
C2—C1—C6	121.45 (18)	C13—C14—H14	119.8
C3—C2—C1	116.40 (18)	C9—C14—H14	119.8
C3—C2—H2	121.8	N2—C15—Si1	113.64 (13)
C1—C2—H2	121.8	N2—C15—H15A	108.8
C2—C3—C4	122.03 (19)	Si1—C15—H15A	108.8
C2—C3—H3	119.0	N2—C15—H15B	108.8
C4—C3—H3	119.0	Si1—C15—H15B	108.8
C5—C4—C3	121.6 (2)	H15A—C15—H15B	107.7
C5—C4—H4	119.2	Si1—C16—H16A	109.5
C3—C4—H4	119.2	Si1—C16—H16B	109.5
C4—C5—C6	116.92 (18)	H16A—C16—H16B	109.5
C4—C5—H5	121.5	Si1—C16—H16C	109.5
C6—C5—H5	121.5	H16A—C16—H16C	109.5
C5—C6—N1	131.92 (17)	H16B—C16—H16C	109.5
C5—C6—C1	121.62 (17)	Si1—C17—H17A	109.5
N1—C6—C1	106.41 (16)	Si1—C17—H17B	109.5
N2—C7—N1	110.68 (17)	H17A—C17—H17B	109.5
N2—C7—H7	124.7	Si1—C17—H17C	109.5
N1—C7—H7	124.7	H17A—C17—H17C	109.5
N1—C8—C9	112.22 (16)	H17B—C17—H17C	109.5
N1—C8—H8A	109.2	Si1—C18—H18A	109.5
C9—C8—H8A	109.2	Si1—C18—H18B	109.5
N1—C8—H8B	109.2	H18A—C18—H18B	109.5
C9—C8—H8B	109.2	Si1—C18—H18C	109.5
H8A—C8—H8B	107.9	H18A—C18—H18C	109.5
C10—C9—C14	118.7 (2)	H18B—C18—H18C	109.5
C10—C9—C8	121.3 (2)	H1A—O1—H1B	107.0
C7—N2—C1—C2	−178.0 (2)	C15—N2—C7—N1	178.44 (17)
C15—N2—C1—C2	3.6 (3)	C6—N1—C7—N2	−0.3 (2)

C7—N2—C1—C6	0.1 (2)	C8—N1—C7—N2	178.18 (18)
C15—N2—C1—C6	−178.27 (17)	C7—N1—C8—C9	109.6 (2)
N2—C1—C2—C3	178.1 (2)	C6—N1—C8—C9	−72.2 (2)
C6—C1—C2—C3	0.2 (3)	N1—C8—C9—C10	108.7 (2)
C1—C2—C3—C4	−0.6 (3)	N1—C8—C9—C14	−72.5 (2)
C2—C3—C4—C5	0.4 (4)	C14—C9—C10—C11	2.3 (4)
C3—C4—C5—C6	0.2 (3)	C8—C9—C10—C11	−178.8 (2)
C4—C5—C6—N1	−177.7 (2)	C9—C10—C11—C12	−0.5 (4)
C4—C5—C6—C1	−0.6 (3)	C10—C11—C12—C13	−1.5 (5)
C7—N1—C6—C5	177.7 (2)	C11—C12—C13—C14	1.7 (5)
C8—N1—C6—C5	−0.7 (3)	C12—C13—C14—C9	0.2 (4)
C7—N1—C6—C1	0.3 (2)	C10—C9—C14—C13	−2.2 (3)
C8—N1—C6—C1	−178.13 (17)	C8—C9—C14—C13	179.0 (2)
N2—C1—C6—C5	−177.97 (18)	C7—N2—C15—Si1	−91.7 (2)
C2—C1—C6—C5	0.4 (3)	C1—N2—C15—Si1	86.4 (2)
N2—C1—C6—N1	−0.2 (2)	C18—Si1—C15—N2	60.61 (19)
C2—C1—C6—N1	178.10 (18)	C17—Si1—C15—N2	−179.77 (18)
C1—N2—C7—N1	0.1 (2)	C16—Si1—C15—N2	−59.84 (19)

Hydrogen-bond geometry (Å, °)

Cg3 is the centroid of the C9–C14 ring.

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
O1—H1A···Cl1	0.86	2.45	3.257 (2)	157
O1—H1B···Cl1^{i}	0.85	2.45	3.250 (3)	158
C7—H7···O1	0.93	2.51	3.170 (3)	128
C8—H8A···Cl1	0.97	2.81	3.703 (2)	153
C3—H3···Cg3^{ii}	0.93	2.69	3.526 (2)	151

Symmetry codes: (i) −*x*+2, −*y*+1, −*z*+2; (ii) *x*−1, *y*, *z*.

Table 2

π–π stacking in the title compound (Å, °).

Cg1 is the centroid of the N1, C6, C1, N2, C7 ring and Cg2 is the centroid of C1 to C6 ring. Offset is the angle between the centroid-to-centroid and plane-to-plane vectors.

	Centroid–centroid	plane–plane	offset
Cg1···Cg2^{i}	3.5690 (15)	3.430 (1)	16.0
Cg2···Cg2^{i}	3.7223 (14)	3.446 (1)	22.2

Symmetry code: (i) 1-x, 1-y, 1-z.

Fig. 1

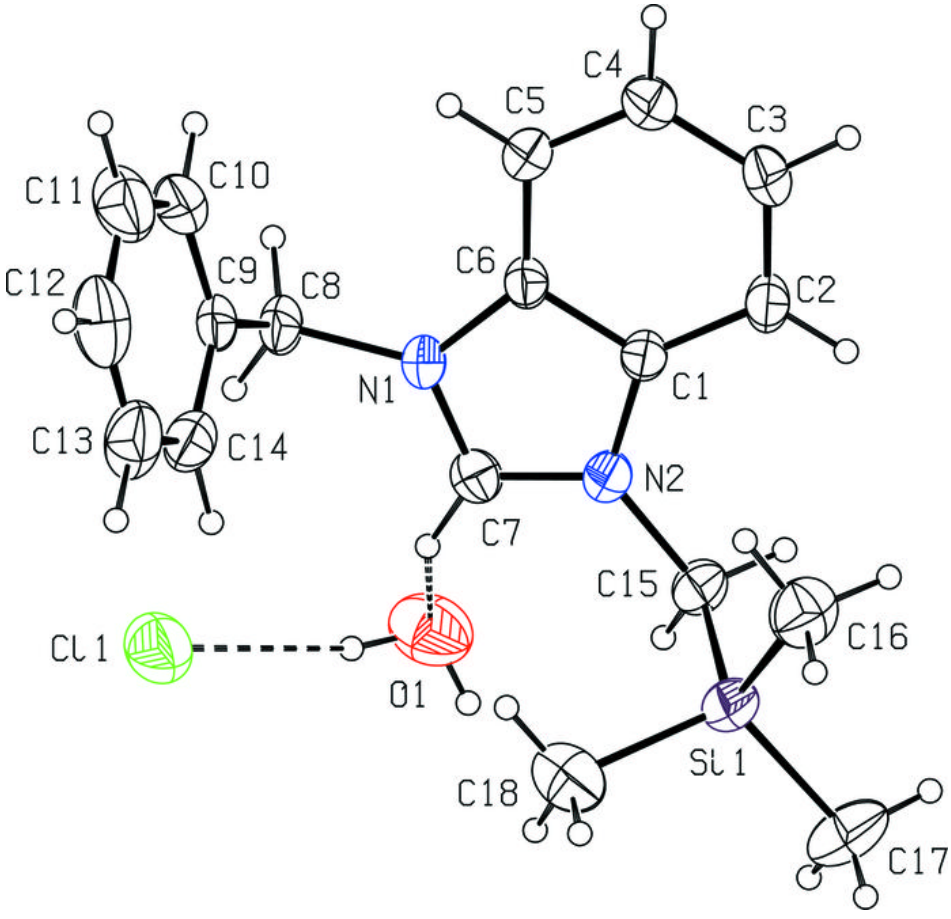
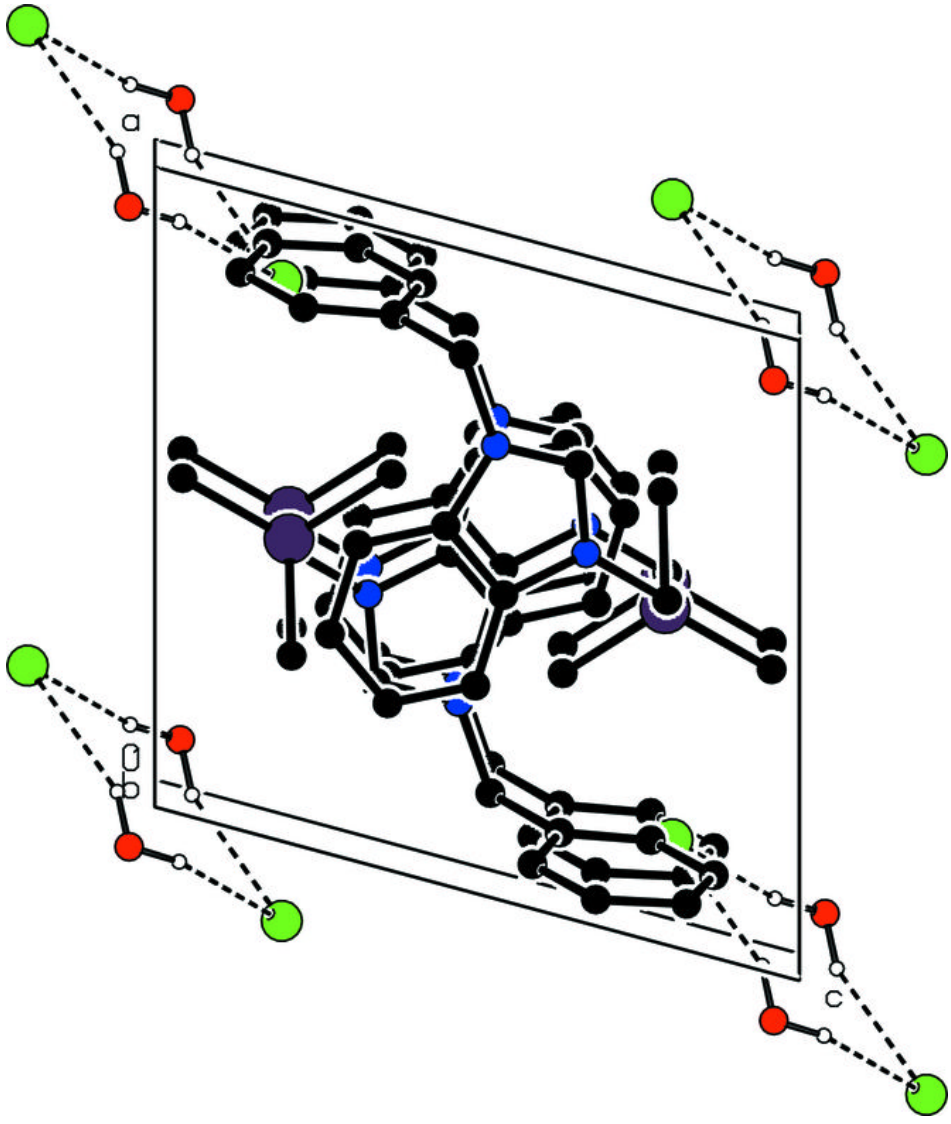

C4
C5
C3
C11
C10
C6
C12
C9
C8
C2
N1
C1
C13
C14
N2
C7
C15
C16
Cl1
O1
Si1
C18
C17

Fig. 2



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(2-Decanamidoethyl)dimethylamine *N*-oxide

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Key indicators: single-crystal X-ray study; T = 100 K; mean σ(C–C) = 0.002 Å; R factor = 0.033; wR factor = 0.094; data-to-parameter ratio = 18.6.

In the title compound, $C_{14}H_{30}N_2O_2$, the almost planar nonyl chains are fully extended: the N—C—C—N torsion angle of −161.95 (8)° indicates an *anti* conformation. The crystal structure features N—H···O hydrogen bonds and C—H···O interactions.

Related literature

For the bond lengths and angles of nonyl chains, see: Low *et al.* (1999); Kato & Ikemori (2003); Ulrich *et al.* (1990). For related structures containing the amide group, see: Belicchi-Ferrari *et al.* (2007); Jeffrey & Maluszynska (1989). For N—O bond lengths, see: Katrusiak *et al.* (1987); Kemmitt *et al.* (2002); Maia *et al.* (1984); Boese *et al.* (1999); Palatinus & Damay (2009). For a related structure, see: Sauer *et al.* (2003). For the synthesis, see: Piłakowska-Pietras *et al.* (2008). For hydrogen-bond motifs, see: Bernstein *et al.* (1995); Rospenk *et al.* (1989).

Experimental

Crystal data

$C_{14}H_{30}N_2O_2$
M_r = 258.40
Triclinic, $P\overline{1}$
a = 5.378 (2) Å
b = 8.113 (4) Å
c = 17.801 (5) Å
α = 79.55 (4)°
β = 86.38 (3)°
γ = 86.36 (4)°
V = 761.2 (5) Å^3
Z = 2
Mo $K\alpha$ radiation
μ = 0.08 mm^{-1}
T = 100 K
0.23 × 0.19 × 0.08 mm

Data collection

Oxford Diffraction Xcalibur Sapphire2 diffractometer
10305 measured reflections
3149 independent reflections
2746 reflections with $I > 2\sigma(I)$
R_{int} = 0.018

Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.033
$wR(F^2)$ = 0.094
S = 1.06
3149 reflections
169 parameters
H atoms treated by a mixture of independent and constrained refinement
$\Delta\rho_{max}$ = 0.33 e Å^{-3}
$\Delta\rho_{min}$ = −0.16 e Å^{-3}

Table 1
Hydrogen-bond geometry (Å, °).

D—H···A	D—H	H···A	D···A	D—H···A
N2—H2···O1^{i}	0.87 (2)	1.89 (2)	2.753 (2)	168.9 (2)
C1—H1A···O2^{ii}	0.99	2.48	3.453 (2)	166
C1—H1B···O2^{iii}	0.99	2.47	3.363 (2)	150
C4—H4A···O1^{i}	0.99	2.32	3.204 (2)	148
C13—H13C···O2^{iii}	0.98	2.58	3.438 (2)	146
C14—H14B···O2^{iii}	0.98	2.60	3.449 (2)	145

Symmetry codes: (i) $-x, -y+1, -z+1$; (ii) $x-1, y, z$; (iii) $-x+1, -y, -z+1$.

Data collection: *CrysAlis CCD* (Oxford Diffraction, 2007); cell refinement: *CrysAlis RED* (Oxford Diffraction, 2007); data reduction: *CrysAlis RED*; program(s) used to solve structure: *SHELXTL* (Sheldrick, 2008); program(s) used to refine structure: *SHELXTL*; molecular graphics: *SHELXTL*; software used to prepare material for publication: *SHELXTL*.

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Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: DS2034).

References

Belicchi-Ferrari, M., Bisceglie, F., Pelosi, G., Pinelli, S. & Tarasconi, P. (2007). *Polyhedron*, **26**, 5150–5161.
Bernstein, J., Davis, R. E., Shimoni, L. & Chang, N.-L. (1995). *Angew. Chem. Int. Ed. Engl.* **34**, 1555–1573.
Boese, R., Blaeser, D. & Weiss, H.-C. (1999). *Angew. Chem. Int. Ed.* **38**, 988–992.
Jeffrey, G. A. & Maluszynska, H. (1989). *Acta Cryst.* B**45**, 447–452.
Kato, M. & Ikemori, M. (2003). *Acta Cryst.* C**59**, m25–m26.
Katrusiak, A., Ratajczak-Sitarz, M. & Kałuski, Z. (1987). *Acta Cryst.* C**43**, 2386–2389.
Kemmitt, T., Gainsford, G. J., Steel, P. J. & Wikaira, J. (2002). *Acta Cryst.* E**58**, o851–o852.
Low, J. N., Cook, A., Imrie, C. T. & Wardell, J. L. (1999). *Acta Cryst.* C**55**, IUC9900123,1999
Maia, E. R., Peguy, A. & Perez, S. (1984). *Can. J. Chem.* **62**, 6–10.
Oxford Diffraction (2007). *CrysAlis CCD* and *CrysAlis RED*. Oxford Diffraction Ltd, Abingdon, Oxfordshire, England.
Palatinus, L. & Damay, F. (2009). *Acta Cryst.* B**65**, 784–786.
Piłakowska-Pietras, A., Baran, D., Krasowska, A. & Piasecki, A. (2008). *J. Surfact. Deterg.* **11** 187–194
Rospenk, M., Koll, A., Glowiak, T. & Sobczyk, L. (1989). *J. Mol. Struct.* **195**, 33–38.
Sauer, J. D., Elnagar, H. Y. & Fronczek, F. R. (2003). *Acta Cryst.* C**59**, o62–o64.
Sheldrick, G. M. (2008). *Acta Cryst.* A**64**, 112–122.
Ulrich, G., Klaska, K. H., Jarchow, O. H., Schmalle, H. W., König, W. A., Heitsch, H., Rathmann, R., Hausen, B. M. & Schulz, K.-H. (1990). *Acta Cryst.* C**46**, 1715–1718.

supplementary materials

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(2-Decanamidoethyl)dimethylamine *N*-oxide

A. Lewinska

Comment

Surfactants are amphiphilic molecules composed by at least two parts, one of them is polar or hydrophilic and the other one nonpolar or hydrophobic. A special group of surface active amine oxides are amidoamine oxides based on fatty monocarboxylic acids and diamines, particularly *N*,*N*-dimethylethylenediamine and *N*,*N*-dimethyl-1,3-propanediamine. These surfactants are typically employed in hair and body care, cleaning and shampoo formulations as foaming agents, wetting agents, thickeners and conditioners They are low or nontoxic to humans and higherorganisms but at the same time exhibit an antimicrobial activity.

The crystal and molecular structure of typical N-oxide derivatives were previously determined for 17-oxosparteine N(*l*)-oxide hydrochloride (A. Katrusiak, *et al.*) and 4-methylpyridine-N-oxide (L.Palatinus *et al*.). The crystal and molecular structure recognized for N-oxide surfactant, *N*,*N*-dimethyl-n-tetradecylamine oxide (Fronczek *et al.*), in some degree is similar to the structure of our compound**.** In general, N-oxide derivatives and especially N-oxide surfactants are known as very difficult for crystallization, so the crystal structure solution for 2-(decanoylamino)ethyldimethylamine-N-oxide presented in this report is a very rare case.

The title compound consists of a hydrophobic alkyl chain and a lipophilic moiety represented by amide and N-oxide groups bridged by ethyl group (Figure 1). The planar nine carbon side adopt fully extended conformations and is twisted 45.6 (1)° from the plane of adjacent amide moiety. The torsion angle N1—C1—C2—N2 of -161.95 (8)° shows that this part takes an antiperiplanar conformation. The bond lengths and angles of nonyl chain Low *et al.* (1999) and amide group Belicchi-Ferrari *et al.* (2007) are within the normal ranges and comparable to the previously reported structures. The N—O bond length of is slightly shorter than the corresponding distances in tertiary acyclic amine oxides Boese *et al.* (1999).

The crystal structures is composed of the alternated hydrophilic and hydrophobic layers (Figure 1). The components in the hydrophilic parts are linked to each other *via* N—H···O bonds of R2,2(10) ring motifs Ulrich *et al.* (1990) and the weak C—H···O interactions (Table 2), whereas in the hydrophobic regions they interact through van der Waals contacts.

Experimental

A title compound was synthesized according to method given by Piłakowska-Pietras *et al.* (2008) The surfactant was carefully purificated several times. Suitable single crystalwere obtained by slow evaporation of thecompoundsolutionin a chloroform–hexane mixture and kept cold at -5^{-}C. The crystals of 2-(decanoylamino)ethyldimethylamine-N-oxides appeared unexpectedly taking into account well known problems with the surfactants crystallization.

Refinement

All the H atoms were positioned geometrically and refined using a riding model with C—H = 0.98–0.99 Å. The U_{iso} values were constrained to be -1.5U_{equ} (methyl H atoms) and -1.2U_{equ} (other H atoms). The rotating model group was

considered for the methyl group. In the case of N1, the hydrogen atom was located from a difference Fourier map and refined isotropically.

Figures

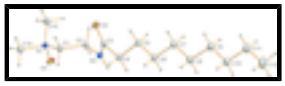


Fig. 1. Table 1. Selected geometric parameters (Å, °).

Fig. 2. Table 2. Hydrogen bond parameters (Å, °).

(2-Decanamidoethyl)dimethylamine *N*-oxide

Crystal data

$C_{14}H_{30}N_2O_2$	$Z = 2$
$M_r = 258.40$	$F(000) = 288$
Triclinic, $P\overline{1}$	$D_x = 1.127$ Mg m^{-3}
Hall symbol: -P 1	Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å
$a = 5.378$ (2) Å	Cell parameters from 9030 reflections
$b = 8.113$ (4) Å	$\theta = 3$–$36°$
$c = 17.801$ (5) Å	$\mu = 0.08$ mm^{-1}
$\alpha = 79.55$ (4)°	$T = 100$ K
$\beta = 86.38$ (3)°	Block, colorless
$\gamma = 86.36$ (4)°	0.23 × 0.19 × 0.08 mm
$V = 761.2$ (5) Å^3	

Data collection

Oxford Diffraction Xcalibur Sapphire2 (large Be window) diffractometer	2746 reflections with $I > 2\sigma(I)$
Radiation source: fine-focus sealed tube	$R_{int} = 0.018$
graphite	$\theta_{max} = 26.5°$, $\theta_{min} = 3.0°$
ω scans	$h = -6\rightarrow6$
10305 measured reflections	$k = -8\rightarrow10$
3149 independent reflections	$l = -22\rightarrow22$

Refinement

Refinement on F^2	Primary atom site location: structure-invariant direct methods
Least-squares matrix: full	Secondary atom site location: difference Fourier map
$R[F^2 > 2\sigma(F^2)] = 0.033$	Hydrogen site location: inferred from neighbouring sites

$wR(F^2) = 0.094$	H atoms treated by a mixture of independent and constrained refinement
$S = 1.06$	$w = 1/[\sigma^2(F_o^2) + (0.0535P)^2 + 0.1328P]$ where $P = (F_o^2 + 2F_c^2)/3$
3149 reflections	$(\Delta/\sigma)_{max} = 0.001$
169 parameters	$\Delta\rho_{max} = 0.33$ e Å^{-3}
0 restraints	$\Delta\rho_{min} = -0.15$ e Å^{-3}

Special details

Geometry. All e.s.d.'s (except the e.s.d. in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell e.s.d.'s are taken into account individually in the estimation of e.s.d.'s in distances, angles and torsion angles; correlations between e.s.d.'s in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell e.s.d.'s is used for estimating e.s.d.'s involving l.s. planes.

Refinement. Refinement of F^2 against ALL reflections. The weighted *R*-factor *wR* and goodness of fit *S* are based on F^2, conventional *R*-factors *R* are based on *F*, with *F* set to zero for negative F^2. The threshold expression of $F^2 > \sigma(F^2)$ is used only for calculating *R*-factors(gt) *etc*. and is not relevant to the choice of reflections for refinement. *R*-factors based on F^2 are statistically about twice as large as those based on *F*, and *R*- factors based on ALL data will be even larger.

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å^2)

	x	*y*	*z*	U_{iso}*/U_{eq}
O1	−0.14655 (12)	0.29531 (8)	0.63607 (4)	0.01841 (17)
O2	0.61547 (12)	0.19768 (8)	0.42458 (4)	0.01908 (17)
N1	−0.00050 (14)	0.15787 (9)	0.61997 (4)	0.01399 (18)
N2	0.31670 (14)	0.39834 (10)	0.44253 (4)	0.01548 (18)
C1	0.11161 (17)	0.19110 (11)	0.53929 (5)	0.0149 (2)
H1A	−0.0245	0.2133	0.5033	0.018*
H1B	0.2102	0.0895	0.5291	0.018*
C2	0.27914 (17)	0.33925 (11)	0.52434 (5)	0.01533 (19)
H2A	0.2015	0.4313	0.5490	0.018*
H2B	0.4422	0.3047	0.5468	0.018*
C3	0.48478 (16)	0.32380 (11)	0.39906 (5)	0.01460 (19)
C4	0.49927 (17)	0.40400 (12)	0.31534 (5)	0.0169 (2)
H4A	0.4090	0.5154	0.3094	0.020*
H4B	0.4129	0.3340	0.2861	0.020*
C5	0.76504 (17)	0.42604 (12)	0.28085 (5)	0.0175 (2)
H5A	0.8587	0.4857	0.3128	0.021*
H5B	0.8504	0.3144	0.2805	0.021*
C6	0.76453 (18)	0.52507 (12)	0.19949 (5)	0.0187 (2)
H6A	0.6695	0.6335	0.2000	0.022*
H6B	0.6765	0.4620	0.1675	0.022*
C7	1.02383 (18)	0.55974 (13)	0.16275 (6)	0.0210 (2)
H7A	1.1189	0.4515	0.1617	0.025*
H7B	1.1125	0.6227	0.1946	0.025*
C8	1.01841 (18)	0.65973 (13)	0.08150 (5)	0.0217 (2)
H8A	0.9321	0.5957	0.0496	0.026*

H8B	0.9202	0.7668	0.0825	0.026*
C9	1.27600 (19)	0.69820 (13)	0.04450 (6)	0.0218 (2)
H9A	1.3607	0.7643	0.0759	0.026*
H9B	1.3753	0.5911	0.0446	0.026*
C10	1.27329 (19)	0.79467 (13)	−0.03721 (6)	0.0218 (2)
H10A	1.1736	0.9017	−0.0377	0.026*
H10B	1.1907	0.7284	−0.0690	0.026*
C11	1.5337 (2)	0.83259 (13)	−0.07251 (6)	0.0246 (2)
H11A	1.6154	0.8998	−0.0409	0.030*
H11B	1.6338	0.7256	−0.0714	0.030*
C12	1.5335 (2)	0.92734 (15)	−0.15446 (6)	0.0327 (3)
H12A	1.7055	0.9478	−0.1738	0.049*
H12B	1.4383	1.0348	−0.1559	0.049*
H12C	1.4566	0.8605	−0.1865	0.049*
C13	0.19656 (17)	0.11555 (12)	0.67652 (5)	0.0181 (2)
H13A	0.1186	0.0964	0.7284	0.027*
H13B	0.3077	0.2087	0.6709	0.027*
H13C	0.2931	0.0138	0.6675	0.027*
C14	−0.15989 (17)	0.01185 (11)	0.62702 (5)	0.0180 (2)
H14A	−0.2401	−0.0103	0.6786	0.027*
H14B	−0.0565	−0.0872	0.6179	0.027*
H14C	−0.2881	0.0369	0.5892	0.027*
H2	0.246 (2)	0.4950 (17)	0.4221 (7)	0.027 (3)*

Atomic displacement parameters (Å^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
O1	0.0201 (3)	0.0152 (3)	0.0181 (3)	0.0071 (3)	0.0033 (3)	−0.0022 (3)
O2	0.0176 (3)	0.0169 (3)	0.0207 (4)	0.0037 (3)	0.0009 (3)	−0.0003 (3)
N1	0.0136 (4)	0.0137 (4)	0.0135 (4)	0.0021 (3)	0.0010 (3)	−0.0008 (3)
N2	0.0151 (4)	0.0140 (4)	0.0154 (4)	0.0010 (3)	0.0015 (3)	0.0013 (3)
C1	0.0156 (4)	0.0163 (4)	0.0119 (4)	−0.0004 (3)	0.0012 (3)	−0.0013 (3)
C2	0.0149 (4)	0.0163 (4)	0.0139 (4)	−0.0006 (3)	0.0010 (3)	−0.0007 (3)
C3	0.0124 (4)	0.0136 (4)	0.0174 (4)	−0.0024 (3)	0.0002 (3)	−0.0017 (3)
C4	0.0153 (4)	0.0182 (5)	0.0160 (5)	0.0009 (3)	0.0010 (3)	−0.0015 (3)
C5	0.0158 (4)	0.0186 (5)	0.0163 (5)	0.0011 (3)	0.0026 (3)	−0.0002 (4)
C6	0.0180 (5)	0.0206 (5)	0.0159 (5)	−0.0002 (4)	0.0019 (4)	−0.0005 (4)
C7	0.0189 (5)	0.0248 (5)	0.0170 (5)	−0.0003 (4)	0.0024 (4)	0.0012 (4)
C8	0.0209 (5)	0.0260 (5)	0.0161 (5)	−0.0018 (4)	0.0018 (4)	0.0013 (4)
C9	0.0217 (5)	0.0244 (5)	0.0171 (5)	−0.0020 (4)	0.0021 (4)	0.0012 (4)
C10	0.0239 (5)	0.0236 (5)	0.0165 (5)	−0.0029 (4)	0.0015 (4)	0.0001 (4)
C11	0.0267 (5)	0.0266 (5)	0.0183 (5)	−0.0032 (4)	0.0038 (4)	0.0007 (4)
C12	0.0408 (7)	0.0354 (6)	0.0193 (5)	−0.0086 (5)	0.0057 (5)	0.0016 (4)
C13	0.0177 (4)	0.0208 (5)	0.0145 (4)	0.0018 (4)	−0.0030 (3)	0.0001 (4)
C14	0.0157 (4)	0.0168 (5)	0.0201 (5)	−0.0021 (3)	0.0027 (4)	−0.0008 (4)

Geometric parameters (Å, °)

O1—N1	1.385 (2)	C5—H5A	0.9900

O2—C3	1.237 (2)	C5—H5B	0.9900
N1—C1	1.506 (2)	C6—H6A	0.9900
N1—C13	1.489 (2)	C6—H6B	0.9900
N1—C14	1.489 (2)	C7—H7A	0.9900
N2—C2	1.454 (2)	C7—H7B	0.9900
N2—C3	1.340 (2)	C8—H8A	0.9900
N2—H2	0.87 (2)	C8—H8B	0.9900
C1—C2	1.523 (2)	C9—H9A	0.9900
C3—C4	1.514 (2)	C9—H9B	0.9900
C4—C5	1.528 (2)	C10—H10A	0.9900
C5—C6	1.523 (2)	C10—H10B	0.9900
C6—C7	1.524 (2)	C11—H11A	0.9900
C7—C8	1.525 (2)	C11—H11B	0.9900
C8—C9	1.522 (2)	C12—H12A	0.9800
C9—C10	1.522 (2)	C12—H12B	0.9800
C10—C11	1.524 (2)	C12—H12C	0.9800
C11—C12	1.520 (2)	C13—H13A	0.9800
C1—H1A	0.9900	C13—H13B	0.9800
C1—H1B	0.9900	C13—H13C	0.9800
C2—H2A	0.9900	C14—H14A	0.9800
C2—H2B	0.9900	C14—H14B	0.9800
C4—H4A	0.9900	C14—H14C	0.9800
C4—H4B	0.9900		
O1—N1—C1	111.04 (7)	C7—C6—H6B	109.00
O1—N1—C13	109.25 (7)	H6A—C6—H6B	108.00
O1—N1—C14	108.99 (7)	C6—C7—H7A	109.00
C1—N1—C13	111.29 (7)	C6—C7—H7B	109.00
C1—N1—C14	107.63 (7)	C8—C7—H7A	109.00
C13—N1—C14	108.58 (8)	C8—C7—H7B	109.00
C2—N2—C3	122.22 (8)	H7A—C7—H7B	108.00
C3—N2—H2	117.9 (8)	C7—C8—H8A	109.00
C2—N2—H2	119.1 (8)	C7—C8—H8B	109.00
N1—C1—C2	112.89 (8)	C9—C8—H8A	109.00
N2—C2—C1	110.07 (8)	C9—C8—H8B	109.00
O2—C3—N2	123.01 (9)	H8A—C8—H8B	108.00
O2—C3—C4	122.25 (9)	C8—C9—H9A	109.00
N2—C3—C4	114.73 (8)	C8—C9—H9B	109.00
C3—C4—C5	114.08 (8)	C10—C9—H9A	109.00
C4—C5—C6	110.99 (8)	C10—C9—H9B	109.00
C5—C6—C7	113.98 (8)	H9A—C9—H9B	108.00
C6—C7—C8	112.97 (8)	C9—C10—H10A	109.00
C7—C8—C9	113.64 (8)	C9—C10—H10B	109.00
C8—C9—C10	114.14 (9)	C11—C10—H10A	109.00
C9—C10—C11	112.91 (8)	C11—C10—H10B	109.00
C10—C11—C12	113.41 (9)	H10A—C10—H10B	108.00
N1—C1—H1A	109.00	C10—C11—H11A	109.00
N1—C1—H1B	109.00	C10—C11—H11B	109.00
C2—C1—H1A	109.00	C12—C11—H11A	109.00
C2—C1—H1B	109.00	C12—C11—H11B	109.00

H1A—C1—H1B	108.00	H11A—C11—H11B	108.00
N2—C2—H2A	110.00	C11—C12—H12A	109.00
N2—C2—H2B	110.00	C11—C12—H12B	109.00
C1—C2—H2A	110.00	C11—C12—H12C	109.00
C1—C2—H2B	110.00	H12A—C12—H12B	110.00
H2A—C2—H2B	108.00	H12A—C12—H12C	109.00
C3—C4—H4A	109.00	H12B—C12—H12C	109.00
C3—C4—H4B	109.00	N1—C13—H13A	109.00
C5—C4—H4A	109.00	N1—C13—H13B	109.00
C5—C4—H4B	109.00	N1—C13—H13C	110.00
H4A—C4—H4B	108.00	H13A—C13—H13B	109.00
C4—C5—H5A	109.00	H13A—C13—H13C	109.00
C4—C5—H5B	109.00	H13B—C13—H13C	109.00
C6—C5—H5A	109.00	N1—C14—H14A	109.00
C6—C5—H5B	109.00	N1—C14—H14B	109.00
H5A—C5—H5B	108.00	N1—C14—H14C	109.00
C5—C6—H6A	109.00	H14A—C14—H14B	110.00
C5—C6—H6B	109.00	H14A—C14—H14C	109.00
C7—C6—H6A	109.00	H14B—C14—H14C	109.00
O1—N1—C1—C2	60.52 (9)	N2—C3—C4—C5	135.19 (9)
C13—N1—C1—C2	−61.41 (9)	C3—C4—C5—C6	−173.49 (8)
C14—N1—C1—C2	179.74 (8)	C4—C5—C6—C7	177.04 (8)
C3—N2—C2—C1	−81.38 (10)	C5—C6—C7—C8	−179.74 (9)
C2—N2—C3—O2	1.92 (13)	C6—C7—C8—C9	178.94 (9)
C2—N2—C3—C4	−179.36 (8)	C7—C8—C9—C10	178.76 (9)
N1—C1—C2—N2	−161.95 (8)	C8—C9—C10—C11	179.52 (9)
O2—C3—C4—C5	−46.08 (12)	C9—C10—C11—C12	179.38 (9)

Hydrogen-bond geometry (Å, °)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
N2—H2···O1^{i}	0.87 (2)	1.89 (2)	2.753 (2)	168.9 (2)
C1—H1A···O2^{ii}	0.99	2.48	3.453 (2)	166
C1—H1B···O2^{iii}	0.99	2.47	3.363 (2)	150
C4—H4A···O1^{i}	0.99	2.32	3.204 (2)	148
C13—H13C···O2^{iii}	0.98	2.58	3.438 (2)	146
C14—H14B···O2^{iii}	0.98	2.60	3.449 (2)	145

Symmetry codes: (i) −*x*, −*y*+1, −*z*+1; (ii) *x*−1, *y*, *z*; (iii) −*x*+1, −*y*, −*z*+1.

Fig. 1

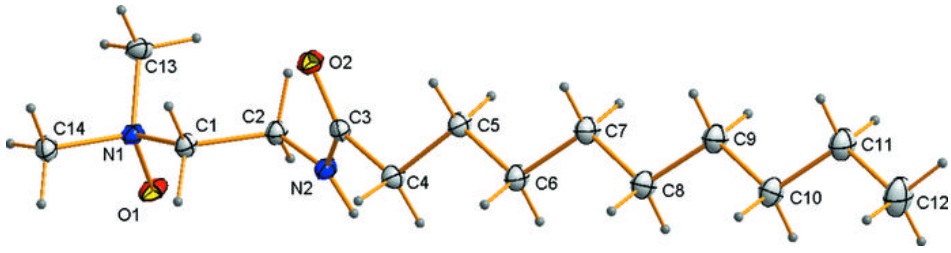
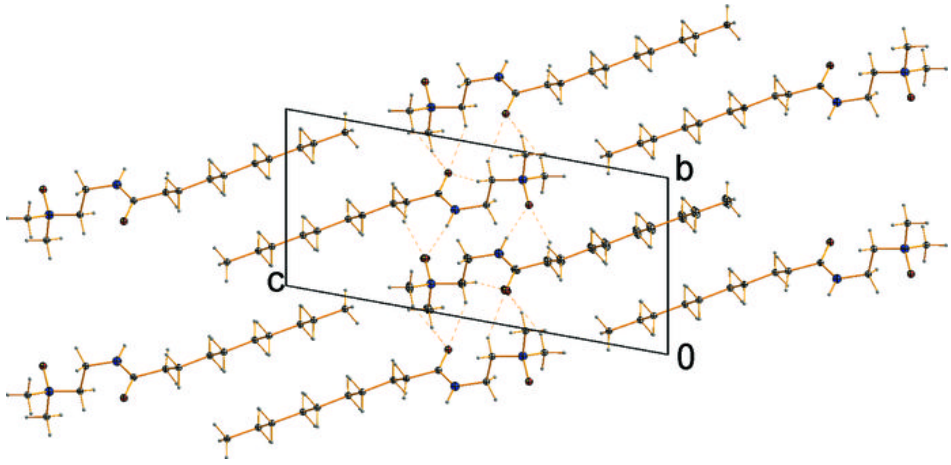


Fig. 2



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N-(3-Nitrophenyl)maleamic acid

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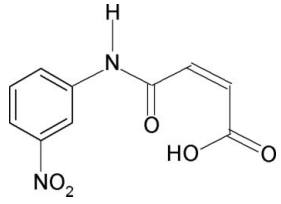
Key indicators: single-crystal X-ray study; T = 295 K; mean σ(C–C) = 0.002 Å; R factor = 0.034; wR factor = 0.097; data-to-parameter ratio = 11.6.

In the title compound, $C_{10}H_8N_2O_5$, the molecule is slightly distorted from planarity. The molecular structure is stabilized by two intramolecular hydrogen bonds. The first is a short O—H···O hydrogen bond (H···O distance = 1.57 Å) within the maleamic acid unit and the second is a C—H···O hydrogen bond (H···O distance = 2.24 Å) which connects the amide group with the benzene ring. The nitro group is twisted by 6.2 (2)° out of the plane of the benzene ring. The crystal structure manifests a variety of hydrogen bonding. The packing is dominated by a strong intermolecular N—H···O interaction which links the molecules into chains running along the *b* axis. The chains within a plane are further assembled by three additional types of intermolecular C—H···O hydrogen bonds to form a sheet parallel to the ($\bar{1}$01) plane.

Related literature

For studies on the effect of ring- and side-chain substitutions on the crystal structures of amides, see: Gowda, Tokarčík, Kožíšek *et al.* (2010); Gowda *et al.* (2010*a*,*b*); Prasad *et al.* (2002). For hydrogen-bond motifs, see: Bernstein *et al.* (1995).



Experimental

Crystal data

$C_{10}H_8N_2O_5$
M_r = 236.18
Monoclinic, $P2_1/c$
a = 7.9965 (2) Å
b = 14.0253 (3) Å
c = 9.1026 (2) Å
β = 100.147 (3)°
V = 1004.92 (4) Å^3
Z = 4
Mo $K\alpha$ radiation
μ = 0.13 mm^{-1}
T = 295 K
0.57 × 0.33 × 0.28 mm

Data collection

Oxford Diffraction Gemini R CCD diffractometer
Absorption correction: analytical (*CrysAlis PRO*; Oxford Diffraction, 2009)
T_{min} = 0.926, T_{max} = 0.971
17136 measured reflections
1793 independent reflections
1544 reflections with $I > 2\sigma(I)$
R_{int} = 0.023

Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.034
$wR(F^2)$ = 0.097
S = 1.08
1793 reflections
154 parameters
H-atom parameters constrained
$\Delta\rho_{max}$ = 0.15 e Å^{-3}
$\Delta\rho_{min}$ = −0.19 e Å^{-3}

Table 1
Hydrogen-bond geometry (Å, °).

D—H···A	D—H	H···A	D···A	D—H···A
O2—H2*A*···O1	0.93	1.57	2.4978 (13)	176
C6—H6···O1	0.93	2.24	2.8302 (15)	121
N1—H1*N*···O3^{i}	0.86	2.05	2.8929 (14)	167
C10—H10···O3^{i}	0.93	2.51	3.2781 (17)	140
C3—H3···O5^{ii}	0.93	2.57	3.2959 (17)	135
C9—H9···O4^{iii}	0.93	2.51	3.1793 (17)	129
C8—H8···O2^{iii}	0.93	2.57	3.4877 (17)	170

Symmetry codes: (i) $-x+1, y-\frac{1}{2}, -z+\frac{3}{2}$; (ii) $x+1, y, z+1$; (iii) $-x, y-\frac{1}{2}, -z+\frac{1}{2}$.

Data collection: *CrysAlis PRO* (Oxford Diffraction, 2009); cell refinement: *CrysAlis PRO*; data reduction: *CrysAlis PRO*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *ORTEP-3* (Farrugia, 1997) and *DIAMOND* (Brandenburg, 2002); software used to prepare material for publication: *SHELXL97*, *PLATON* (Spek, 2009) and *WinGX* (Farrugia, 1999).

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Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: DS2039).

References

Bernstein, J., Davis, R. E., Shimoni, L. & Chang, N.-L. (1995). *Angew. Chem. Int. Ed. Engl.* **34**, 1555–1573.
Brandenburg, K. (2002). *DIAMOND*. Crystal Impact GbR, Bonn, Germany.
Farrugia, L. J. (1997). *J. Appl. Cryst.* **30**, 565.
Farrugia, L. J. (1999). *J. Appl. Cryst.* **32**, 837–838.
Gowda, B. T., Tokarčík, M., Kožíšek, J., Shakuntala, K. & Fuess, H. (2010). *Acta Cryst.* E**66**, o51.
Gowda, B. T., Tokarčík, M., Shakuntala, K., Kožíšek, J. & Fuess, H. (2010*a*). *Acta Cryst.* E**66**, o1554.
Gowda, B. T., Tokarčík, M., Shakuntala, K., Kožíšek, J. & Fuess, H. (2010*b*). *Acta Cryst.* E**66**, o1643.

Oxford Diffraction (2009). *CrysAlis PRO*. Oxford Diffraction Ltd, Abingdon, Oxfordshire, England.
Prasad, S. M., Sinha, R. B. P., Mandal, D. K. & Rani, A. (2002). *Acta Cryst.* E**58**, o1296–o1297.
Sheldrick, G. M. (2008). *Acta Cryst.* A**64**, 112–122.
Spek, A. L. (2009). *Acta Cryst.* D**65**, 148–155.

supplementary materials

Acta Cryst. (2010). E**66**, o1671-o1672 [**doi:10.1107/S1600536810022245**]

N-(3-Nitrophenyl)maleamic acid

B. T. Gowda, M. Tokarcík, K. Shakuntala, J. Kozísek and H. Fuess

Comment

In the present study, as a part of studying the effect of ring and side chain substitutions on the crystal structures of biologically significant amides (Gowda *et al.*, 2010*a,b,c*; Prasad *et al.*, 2002), the crystal structure of *N*-(3-nitrophenyl)maleamic acid (I) has been determined (Fig. 1). The conformation of the N—H in the amide segment is *anti* to the C=O bond and is also *anti* to the *meta*-nitro group in the phenyl ring.

In the maleamic acid moiety, the amide C=O bond is *anti* to the adjacent C—H bond, while the carboxyl C=O bond is *syn* to the adjacent C—H bond. The observed rare *anti* conformation of the C=O and O—H bonds of the acid group is similar to that obsrved in *N*-(2-methylphenyl)-maleamic acid (Gowda *et al.*, 2010*b*), *N*-(3-chlorophenyl)-maleamic acid (Gowda *et al.*, 2010*c*) and *N*-(3,5-dichlorophenyl)- maleamic acid (Gowda *et al.*, 2010*a*).

The molecule in (I) is slightly distorted from planarity as indicated by the dihedral angle of 4.5 (1)° between the least squares planes of the maleamic acid unit (r.m.s. deviation of 0.050 Å) and the phenyl ring. The molecular structure (Fig. 1) is stabilized by two intramolecular hydrogen bonds (Table 1). The first is a short O–H···O hydrogen bond ((H···O distance of 1.57 Å) within the maleamic acid unit; the second one is a C–H···O hydrogen bond (H···O distance of 2.24 Å) which connects the amide group with the phenyl ring. The nitro group - known to be a strong electron- withdrawing substituent - opens up the *ipso* C–C–C angle and narrows the two adjacent intracyclic angles. This fact is evident from the intracyclic bond angles C6–C7–C8, C5–C6–C7 and C7–C8–C9 of 123.99 (12)°, 117.49 (12)° and 117.64 (12)° respectively. The nitro group is twisted 6.2 (2)° out of the plane of the phenyl ring.

The crystal structure (Fig. 2) manifests a variety of hydrogen bonding. The packing is dominated by a strong intermolecular N–H···O interaction (H···O distance of 2.05 Å) which links the molecules into the chains running along the *b* axis. The chains within a plane are further assembled by additional three types of intermolecular C–H···O hydrogen bonds to form a sheet parallel to the (-1 0 1) plane (Bernstein *et al.*, 1995).

Experimental

The solution of maleic anhydride (0.025 mol) in toluene (25 ml) was treated dropwise with the solution of 3-nitroaniline (0.025 mol) also in toluene (20 ml) with constant stirring. The resulting mixture was warmed with stirring for over 30 min and set aside for an additional 30 min at room temperature for completion of the reaction. The mixture was then treated with dilute hydrochloric acid to remove the unreacted 3-nitroaniline. The resultant solid *N*-(3-nitrophenyl)maleamic acid was filtered under suction and washed thoroughly with water to remove the unreacted maleic anhydride and maleic acid. It was recrystallized to constant melting point from ethanol. The purity of the compound was checked by elemental analysis and characterized by its infrared spectra.

Prism like light brown single crystals used in X-ray diffraction studies were grown in an ethanol solution by slow evaporation at room temperature.

Refinement

All H atoms were visible in difference maps. The positions of carboxyl and amide H atoms were tested in preliminary refinement using a soft restraints on the O–H and N–H distances. Finally, all H atoms were positioned with idealized geometry using a riding model with the distances C–H = 0.93 Å, N–H = 0.86 Å and O–H = 0.93 Å. The U_{iso}(H) values were set at $1.2U_{eq}$(C aromatic, N) and $1.5U_{eq}$(O).

Figures

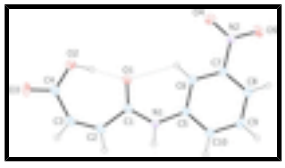

Fig. 1. Molecular structure of (I) showing the atom labelling scheme. Displacement ellipsoids are drawn at the 30% probability level. Two short intramolecular bonds are indicated by dashed lines. H atoms are represented as small spheres of arbitrary radii.

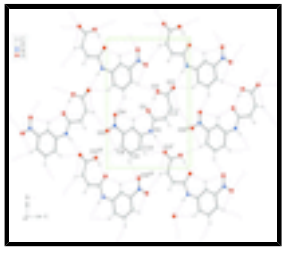

Fig. 2. Part of crystal structure of (I) viewed down the *a* axis and showing a two-dimensional network of molecules linked by several types of intermolecular N–H···O and C–H···O hydrogen bonds (dashed lines). Symmetry codes (i): -*x* + 1, *y* - 1/2, -*z* + 3/2; (ii): *x* + 1, *y*, *z* + 1; (iii): -*x*, *y* - 1/2, -*z* + 1/2.

N-(3-Nitrophenyl)maleamic acid

Crystal data

$C_{10}H_8N_2O_5$	$F(000)$ = 488
M_r = 236.18	D_x = 1.561 Mg m^{-3}
Monoclinic, $P2_1/c$	Mo $K\alpha$ radiation, λ = 0.71073 Å
Hall symbol: -P 2ybc	Cell parameters from 10218 reflections
a = 7.9965 (2) Å	θ = 2.3–29.4°
b = 14.0253 (3) Å	μ = 0.13 mm^{-1}
c = 9.1026 (2) Å	*T* = 295 K
β = 100.147 (3)°	Prism, light brown
V = 1004.92 (4) Å^3	0.57 × 0.33 × 0.28 mm
Z = 4	

Data collection

Oxford Diffraction Gemini R CCD diffractometer	1793 independent reflections
graphite	1544 reflections with $I > 2\sigma(I)$
Detector resolution: 10.434 pixels mm^{-1}	R_{int} = 0.023
ω scans	θ_{max} = 25.1°, θ_{min} = 2.6°
Absorption correction: analytical (*CrysAlis PRO*; Oxford Diffraction, 2009)	*h* = −9→9

T_{min} = 0.926, T_{max} = 0.971	k = −16→16
17136 measured reflections	l = −10→10

Refinement

Refinement on F^2	Primary atom site location: structure-invariant direct methods
Least-squares matrix: full	Secondary atom site location: difference Fourier map
$R[F^2 > 2\sigma(F^2)]$ = 0.034	Hydrogen site location: inferred from neighbouring sites
$wR(F^2)$ = 0.097	H-atom parameters constrained
S = 1.08	$w = 1/[\sigma^2(F_o^2) + (0.0618P)^2 + 0.1002P]$ where $P = (F_o^2 + 2F_c^2)/3$
1793 reflections	$(\Delta/\sigma)_{max} < 0.001$
154 parameters	$\Delta\rho_{max}$ = 0.15 e Å^{-3}
0 restraints	$\Delta\rho_{min}$ = −0.19 e Å^{-3}

Special details

Geometry. All e.s.d.'s (except the e.s.d. in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell e.s.d.'s are taken into account individually in the estimation of e.s.d.'s in distances, angles and torsion angles; correlations between e.s.d.'s in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell e.s.d.'s is used for estimating e.s.d.'s involving l.s. planes.

Refinement. Refinement of F^2 against ALL reflections. The weighted R-factor wR and goodness of fit S are based on F^2, conventional R-factors R are based on F, with F set to zero for negative F^2. The threshold expression of $F^2 > \sigma(F^2)$ is used only for calculating R-factors(gt) *etc*. and is not relevant to the choice of reflections for refinement. R-factors based on F^2 are statistically about twice as large as those based on F, and R- factors based on ALL data will be even larger.

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å^2)

	x	y	z	U_{iso}*/U_{eq}
C1	0.30465 (16)	0.37499 (8)	0.57539 (15)	0.0361 (3)
C2	0.44044 (17)	0.38197 (9)	0.70806 (15)	0.0406 (3)
H2	0.4755	0.3245	0.7543	0.049*
C3	0.51952 (16)	0.45956 (10)	0.77048 (15)	0.0418 (3)
H3	0.5991	0.4471	0.8559	0.05*
C4	0.50454 (17)	0.56183 (10)	0.72945 (15)	0.0421 (3)
C5	0.13141 (15)	0.25342 (9)	0.41799 (14)	0.0342 (3)
C6	0.02666 (15)	0.31456 (9)	0.32224 (14)	0.0365 (3)
H6	0.0378	0.3804	0.3312	0.044*
C7	−0.09413 (16)	0.27380 (9)	0.21369 (13)	0.0357 (3)
C8	−0.11652 (17)	0.17731 (9)	0.19464 (16)	0.0422 (3)
H8	−0.1995	0.1528	0.1196	0.051*
C9	−0.01165 (19)	0.11799 (9)	0.29057 (17)	0.0476 (4)
H9	−0.0236	0.0522	0.2806	0.057*
C10	0.11119 (17)	0.15542 (9)	0.40145 (15)	0.0417 (3)
H10	0.181	0.1146	0.4656	0.05*

N1	0.25906 (14)	0.28534 (7)	0.53544 (12)	0.0389 (3)
H1N	0.3151	0.2413	0.5885	0.047*
N2	−0.20553 (14)	0.33698 (8)	0.11149 (12)	0.0442 (3)
O1	0.23643 (13)	0.44532 (6)	0.50694 (11)	0.0487 (3)
O2	0.38964 (13)	0.59058 (7)	0.61814 (12)	0.0547 (3)
H2A	0.3292	0.5383	0.5739	0.082*
O3	0.60038 (15)	0.61868 (8)	0.80038 (13)	0.0649 (3)
O4	−0.17942 (14)	0.42253 (7)	0.11665 (12)	0.0596 (3)
O5	−0.32118 (15)	0.30062 (8)	0.02350 (14)	0.0752 (4)

Atomic displacement parameters (Å^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
C1	0.0377 (7)	0.0306 (7)	0.0363 (7)	0.0005 (5)	−0.0039 (6)	0.0012 (5)
C2	0.0439 (7)	0.0332 (7)	0.0393 (7)	0.0036 (5)	−0.0078 (6)	0.0031 (5)
C3	0.0418 (7)	0.0415 (8)	0.0355 (7)	0.0014 (5)	−0.0115 (6)	−0.0003 (6)
C4	0.0467 (8)	0.0376 (7)	0.0381 (7)	−0.0022 (6)	−0.0034 (6)	−0.0044 (6)
C5	0.0359 (7)	0.0313 (7)	0.0326 (7)	−0.0003 (5)	−0.0018 (5)	−0.0013 (5)
C6	0.0406 (7)	0.0278 (6)	0.0373 (7)	−0.0016 (5)	−0.0035 (6)	−0.0011 (5)
C7	0.0372 (7)	0.0336 (7)	0.0334 (7)	0.0013 (5)	−0.0014 (5)	0.0014 (5)
C8	0.0431 (7)	0.0354 (7)	0.0429 (7)	−0.0039 (5)	−0.0069 (6)	−0.0052 (5)
C9	0.0559 (9)	0.0260 (7)	0.0547 (9)	−0.0017 (6)	−0.0071 (7)	−0.0031 (6)
C10	0.0452 (7)	0.0310 (7)	0.0441 (7)	0.0027 (5)	−0.0050 (6)	0.0023 (6)
N1	0.0424 (6)	0.0290 (5)	0.0388 (6)	0.0021 (4)	−0.0106 (5)	0.0024 (4)
N2	0.0475 (7)	0.0373 (7)	0.0413 (6)	0.0004 (5)	−0.0100 (5)	0.0006 (5)
O1	0.0556 (6)	0.0307 (5)	0.0493 (6)	0.0003 (4)	−0.0201 (5)	0.0031 (4)
O2	0.0659 (7)	0.0326 (6)	0.0549 (6)	−0.0029 (4)	−0.0190 (5)	0.0035 (4)
O3	0.0759 (8)	0.0444 (6)	0.0630 (7)	−0.0147 (5)	−0.0195 (6)	−0.0104 (5)
O4	0.0713 (7)	0.0326 (6)	0.0637 (7)	−0.0011 (5)	−0.0194 (5)	0.0051 (5)
O5	0.0769 (8)	0.0490 (7)	0.0778 (8)	−0.0031 (6)	−0.0463 (7)	0.0003 (6)

Geometric parameters (Å, °)

C1—O1	1.2406 (15)	C6—H6	0.93
C1—N1	1.3414 (16)	C7—C8	1.3721 (18)
C1—C2	1.4782 (19)	C7—N2	1.4670 (16)
C2—C3	1.3343 (19)	C8—C9	1.378 (2)
C2—H2	0.93	C8—H8	0.93
C3—C4	1.4817 (19)	C9—C10	1.3820 (19)
C3—H3	0.93	C9—H9	0.93
C4—O3	1.2106 (17)	C10—H10	0.93
C4—O2	1.3059 (17)	N1—H1N	0.86
C5—C10	1.3890 (18)	N2—O4	1.2174 (15)
C5—C6	1.3925 (17)	N2—O5	1.2231 (15)
C5—N1	1.4145 (16)	O2—H2A	0.93
C6—C7	1.3784 (17)		
O1—C1—N1	122.32 (12)	C8—C7—N2	117.68 (11)
O1—C1—C2	123.53 (11)	C6—C7—N2	118.33 (11)

N1—C1—C2	114.14 (10)	C7—C8—C9	117.64 (12)
C3—C2—C1	128.80 (12)	C7—C8—H8	121.2
C3—C2—H2	115.6	C9—C8—H8	121.2
C1—C2—H2	115.6	C8—C9—C10	120.55 (12)
C2—C3—C4	132.14 (13)	C8—C9—H9	119.7
C2—C3—H3	113.9	C10—C9—H9	119.7
C4—C3—H3	113.9	C9—C10—C5	120.61 (12)
O3—C4—O2	120.21 (13)	C9—C10—H10	119.7
O3—C4—C3	119.18 (13)	C5—C10—H10	119.7
O2—C4—C3	120.60 (12)	C1—N1—C5	128.83 (11)
C10—C5—C6	119.72 (12)	C1—N1—H1N	115.6
C10—C5—N1	116.73 (11)	C5—N1—H1N	115.6
C6—C5—N1	123.54 (11)	O4—N2—O5	122.75 (11)
C7—C6—C5	117.49 (12)	O4—N2—C7	119.35 (10)
C7—C6—H6	121.3	O5—N2—C7	117.90 (11)
C5—C6—H6	121.3	C4—O2—H2A	109.5
C8—C7—C6	123.99 (12)		
O1—C1—C2—C3	−4.7 (2)	C8—C9—C10—C5	−0.1 (2)
N1—C1—C2—C3	176.01 (13)	C6—C5—C10—C9	0.2 (2)
C1—C2—C3—C4	−1.9 (3)	N1—C5—C10—C9	179.35 (12)
C2—C3—C4—O3	−175.18 (15)	O1—C1—N1—C5	−1.3 (2)
C2—C3—C4—O2	4.8 (2)	C2—C1—N1—C5	177.97 (11)
C10—C5—C6—C7	−0.04 (18)	C10—C5—N1—C1	179.91 (12)
N1—C5—C6—C7	−179.15 (11)	C6—C5—N1—C1	−1.0 (2)
C5—C6—C7—C8	−0.15 (19)	C8—C7—N2—O4	−173.53 (12)
C5—C6—C7—N2	−179.87 (11)	C6—C7—N2—O4	6.21 (18)
C6—C7—C8—C9	0.2 (2)	C8—C7—N2—O5	6.09 (18)
N2—C7—C8—C9	179.91 (12)	C6—C7—N2—O5	−174.17 (12)
C7—C8—C9—C10	0.0 (2)		

Hydrogen-bond geometry (Å, °)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
O2—H2A···O1	0.93	1.57	2.4978 (13)	176
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C3—H3···O5^{ii}	0.93	2.57	3.2959 (17)	135
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C8—H8···O2^{iii}	0.93	2.57	3.4877 (17)	170

Symmetry codes: (i) −*x*+1, *y*−1/2, −*z*+3/2; (ii) *x*+1, *y*, *z*+1; (iii) −*x*, *y*−1/2, −*z*+1/2.

Fig. 1

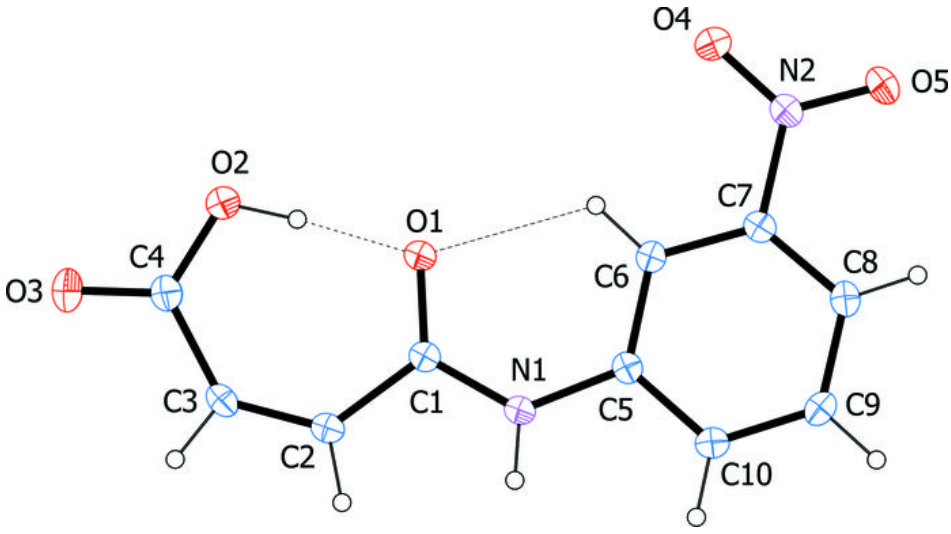
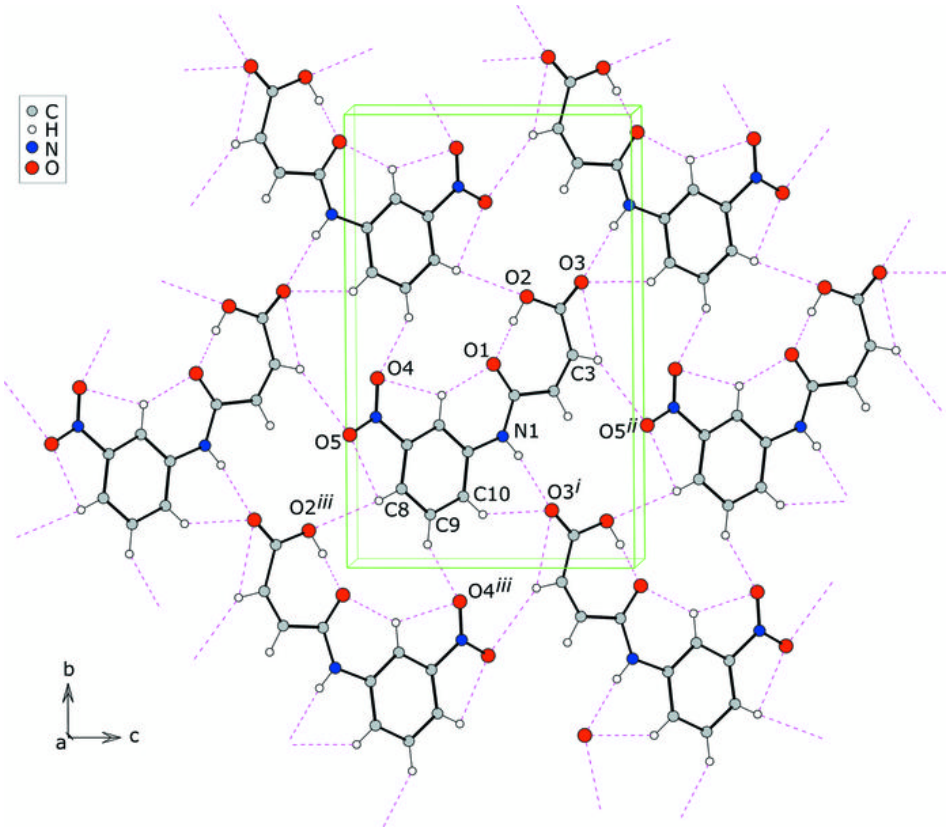


Fig. 2



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3-(4-Fluorophenylsulfonyl)-2,5,7-trimethyl-1-benzofuran

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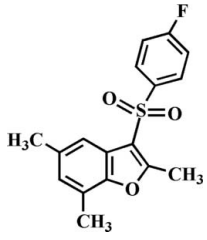
Key indicators: single-crystal X-ray study; T = 173 K; mean σ(C–C) = 0.002 Å; R factor = 0.038; wR factor = 0.105; data-to-parameter ratio = 17.1.

In the title compound, $C_{17}H_{15}FO_3S$, the 4-fluorophenyl ring makes a dihedral angle of 72.67 (5)° with the benzofuran plane. In the crystal, molecules are linked by weak intermolecular C—H···O hydrogen bonds.

Related literature

For the pharmacological activity of benzofuran compounds, see: Aslam *et al.* (2006); Galal *et al.* (2009); Khan *et al.* (2005). For natural products with benzofuran rings, see: Akgul & Anil (2003); Soekamto *et al.* (2003). For the crystal structures of related 2,5-dimethyl-3-phenylsulfonyl-1-benzofuran derivatives, see: Choi *et al.* (2008*a*,*b*).



Experimental

Crystal data

$C_{17}H_{15}FO_3S$
M_r = 318.35
Triclinic, $P\overline{1}$
a = 8.2851 (2) Å
b = 9.3762 (2) Å
c = 11.2241 (3) Å
α = 70.441 (1)°
β = 71.177 (1)°
γ = 69.407 (1)°
V = 748.07 (3) Å^3
Z = 2
Mo $K\alpha$ radiation
μ = 0.24 mm^{-1}
T = 173 K
0.23 × 0.21 × 0.19 mm

Data collection

Bruker SMART APEXII CCD diffractometer
Absorption correction: multi-scan (*SADABS*; Bruker, 2009)
T_{min} = 0.948, T_{max} = 0.957
13476 measured reflections
3449 independent reflections
3097 reflections with $I > 2\sigma(I)$
R_{int} = 0.026

Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.038
$wR(F^2)$ = 0.105
S = 1.04
3449 reflections
202 parameters
H-atom parameters constrained
$\Delta\rho_{max}$ = 0.28 e Å^{-3}
$\Delta\rho_{min}$ = −0.38 e Å^{-3}

Table 1
Hydrogen-bond geometry (Å, °).

D—H···A	D—H	H···A	D···A	D—H···A
C10—H10B···O2^{i}	0.98	2.56	3.363 (2)	139
C13—H13···O2^{ii}	0.95	2.45	3.365 (2)	160
C17—H17···O3^{iii}	0.95	2.50	3.198 (2)	130

Symmetry codes: (i) $-x+1, -y+1, -z+1$; (ii) $-x+1, -y+2, -z+1$; (iii) $-x+1, -y+2, -z$.

Data collection: *APEX2* (Bruker, 2009); cell refinement: *SAINT* (Bruker, 2009); data reduction: *SAINT*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *ORTEP-3* (Farrugia, 1997) and *DIAMOND* (Brandenburg, 1998); software used to prepare material for publication: *SHELXL97*.

Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: DS2040).

References

Akgul, Y. Y. & Anil, H. (2003). *Phytochemistry*, **63**, 939–943.
Aslam, S. N., Stevenson, P. C., Phythian, S. J., Veitch, N. C. & Hall, D. R. (2006). *Tetrahedron*, **62**, 4214–4226.
Brandenburg, K. (1998). *DIAMOND*. Crystal Impact GbR, Bonn, Germany.
Bruker (2009). *APEX2*. *SADABS* and *SAINT*. Bruker AXS Inc., Madison, Wisconsin, USA.
Choi, H. D., Seo, P. J., Son, B. W. & Lee, U. (2008*a*). *Acta Cryst.* E**64**, o794.
Choi, H. D., Seo, P. J., Son, B. W. & Lee, U. (2008*b*). *Acta Cryst.* E**64**, o850.
Farrugia, L. J. (1997). *J. Appl. Cryst.* **30**, 565.
Galal, S. A., Abd El-All, A. S., Abdallah, M. M. & El-Diwani, H. I. (2009). *Bioorg. Med. Chem. Lett.* **19**, 2420–2428.
Khan, M. W., Alam, M. J., Rashid, M. A. & Chowdhury, R. (2005). *Bioorg. Med. Chem.* **13**, 4796–4805.
Sheldrick, G. M. (2008). *Acta Cryst.* A**64**, 112–122.
Soekamto, N. H., Achmad, S. A., Ghisalberti, E. L., Hakim, E. H. & Syah, Y. M. (2003). *Phytochemistry*, **64**, 831–834.

supplementary materials

Acta Cryst. (2010). E**66**, o1813 [**doi:10.1107/S1600536810023834**]

3-(4-Fluorophenylsulfonyl)-2,5,7-trimethyl-1-benzofuran

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Comment

Compounds containing a benzofuran moiety show potent pharmacological properties such as antifungal (Aslam *et al.*., 2006), antitumor and antiviral (Galal *et al.*., 2009), antimicrobial (Khan *et al.*., 2005) activities. These compounds widely occur in nature (Akgul & Anil, 2003; Soekamto *et al.*. 2003). As a part of our ongoing studies of the effect of side chain substituents on the solid state structures of 2,5-dimethyl-3-phenylsulfonyl-1-benzofuran analogues (Choi *et al.*., 2008*a, b*), we report the crystal structure of the title compound (Fig. 1).

The benzofuran unit is essentially planar, with a mean deviation of 0.009 (1) Å from the least-squares plane defined by the nine constituent atoms. The 4-fluorophenyl ring makes a dihedral angle of 72.67 (5)° with the benzofuran plane. The crystal packing (Fig. 2) is stabilized by three intermolecular C—H···O hydrogen bonds; the first one between the methyl H atom and the oxygen of the O═S═O unit, with a C10—H10B···O2^{i}, the second one between the 4-fluorophenyl H atom and the oxygen of the O═S═O unit, with a C13—H13···O2^{ii}, and the third one between the 4-fluorophenyl H atom and the oxygen of the O═S═O unit, with a C17—H17···O3^{iii}, respectively (Table 1).

Experimental

77% 3-Chloroperoxybenzoic acid (538 mg, 2.4 mmol) was added in small portions to a stirred solution of 3-(4-fluorophenyl-sulfanyl)-2,5,7-trimethy-1-benzofuran (343 mg, 1.2 mmol) in dichloromethane (50 mL) at 273 K. After being stirred at room temperature for 8h, the mixture was washed with saturated sodium bicarbonate solution and the organic layer was separated, dried over magnesium sulfate, filtered and concentrated at reduced pressure. The residue was purified by column chromatography (silica gel, hexane-ethyl acetate, 2:1 v/v) to afford the title compound as a colorless solid [yield 79%, m.p. 414-415 K; R_f = 0.41 (benzene)]. Single crystals suitable for X-ray diffraction were prepared by slow evaporation of a solution of the title compound in diisopropyl ether at room temperature.

Refinement

All H atoms were positioned geometrically and refined using a riding model, with C—H = 0.95 Å for aryl and 0.98 Å for methyl H atoms, U_{iso}(H) = 1.2 U_{eq}(C) for aryl and 1.5U_{eq}(C) for methyl H atoms.

Figures

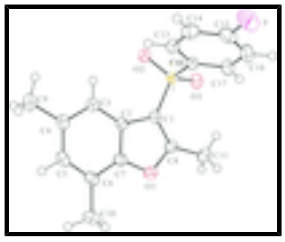


Fig. 1. The molecular structure of the title compound with the atom numbering scheme. Displacement ellipsoids are drawn at the 50% probability level. H atoms are presented as a small spheres of arbitrary radius.

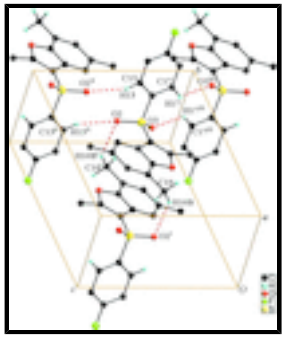


Fig. 2. C—H···O interactions (dotted lines) in the crystal structure of the title compound. [Symmetry codes: (i) - x + 1, - y + 1, - z + 1; (ii) - x + 1, - y + 2, - z + 1; (iii) - x + 1, - y + 2, - z.]

3-(4-Fluorophenylsulfonyl)-2,5,7-trimethyl-1-benzofuran

Crystal data

$C_{17}H_{15}FO_3S$	Z = 2
M_r = 318.35	F(000) = 332
Triclinic, $P\overline{1}$	D_x = 1.413 Mg m^{-3}
Hall symbol: -P 1	Mo $K\alpha$ radiation, λ = 0.71069 Å
a = 8.2851 (2) Å	Cell parameters from 7810 reflections
b = 9.3762 (2) Å	θ = 2.4–27.5°
c = 11.2241 (3) Å	μ = 0.24 mm^{-1}
α = 70.441 (1)°	T = 173 K
β = 71.177 (1)°	Block, colourless
γ = 69.407 (1)°	0.23 × 0.21 × 0.19 mm
V = 748.07 (3) Å^3	

Data collection

Bruker SMART APEXII CCD diffractometer	3449 independent reflections
Radiation source: rotating anode	3097 reflections with $I > 2\sigma(I)$
graphite multilayer	R_{int} = 0.026
Detector resolution: 10.0 pixels mm^{-1}	θ_{max} = 27.6°, θ_{min} = 2.0°
φ and ω scans	h = −10→10
Absorption correction: multi-scan (*SADABS*; Bruker, 2009)	k = −12→12
T_{min} = 0.948, T_{max} = 0.957	l = −14→14
13476 measured reflections	

Refinement

Refinement on F^2	Primary atom site location: structure-invariant direct methods
Least-squares matrix: full	Secondary atom site location: difference Fourier map
$R[F^2 > 2\sigma(F^2)] = 0.038$	Hydrogen site location: difference Fourier map
$wR(F^2) = 0.105$	H-atom parameters constrained
$S = 1.04$	$w = 1/[\sigma^2(F_o^2) + (0.0536P)^2 + 0.3586P]$ where $P = (F_o^2 + 2F_c^2)/3$
3449 reflections	$(\Delta/\sigma)_{max} < 0.001$
202 parameters	$\Delta\rho_{max} = 0.28$ e Å^{-3}
0 restraints	$\Delta\rho_{min} = -0.38$ e Å^{-3}

Special details

Geometry. All esds (except the esd in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell esds are taken into account individually in the estimation of esds in distances, angles and torsion angles; correlations between esds in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell esds is used for estimating esds involving l.s. planes.

Refinement. Refinement of F^2 against ALL reflections. The weighted R-factor wR and goodness of fit S are based on F^2, conventional R-factors R are based on F, with F set to zero for negative F^2. The threshold expression of $F^2 > 2$sigma(F^2) is used only for calculating R-factors(gt) etc. and is not relevant to the choice of reflections for refinement. R-factors based on F^2 are statistically about twice as large as those based on F, and R- factors based on ALL data will be even larger.

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å^2)

	x	*y*	*z*	U_{iso}*/U_{eq}
S	0.48710 (5)	0.89687 (4)	0.29416 (3)	0.02449 (12)
F	0.98555 (17)	1.27225 (14)	−0.00227 (13)	0.0583 (3)
O1	0.75715 (15)	0.45344 (12)	0.32852 (11)	0.0300 (2)
O2	0.39991 (14)	0.94794 (13)	0.41216 (10)	0.0304 (2)
O3	0.38323 (15)	0.91207 (14)	0.20728 (11)	0.0328 (3)
C1	0.60789 (19)	0.70192 (17)	0.33737 (14)	0.0254 (3)
C2	0.67369 (19)	0.62533 (16)	0.45489 (14)	0.0242 (3)
C3	0.6664 (2)	0.66868 (17)	0.56438 (14)	0.0271 (3)
H3	0.6038	0.7718	0.5750	0.033*
C4	0.7533 (2)	0.55674 (19)	0.65748 (15)	0.0299 (3)
C5	0.8449 (2)	0.40466 (18)	0.63998 (15)	0.0315 (3)
H5	0.9044	0.3309	0.7046	0.038*
C6	0.8531 (2)	0.35680 (17)	0.53365 (15)	0.0292 (3)
C7	0.76463 (19)	0.47267 (17)	0.44329 (14)	0.0262 (3)
C8	0.6618 (2)	0.59417 (18)	0.26597 (15)	0.0278 (3)
C9	0.7515 (3)	0.5984 (2)	0.77707 (17)	0.0415 (4)
H9A	0.7024	0.7123	0.7667	0.062*
H9B	0.8728	0.5666	0.7883	0.062*
H9C	0.6782	0.5434	0.8537	0.062*

C10	0.9501 (2)	0.19388 (19)	0.51553 (18)	0.0373 (4)
H10A	1.0603	0.1967	0.4485	0.056*
H10B	0.8753	0.1551	0.4886	0.056*
H10C	0.9779	0.1236	0.5977	0.056*
C11	0.6407 (3)	0.5985 (2)	0.13829 (17)	0.0382 (4)
H11A	0.7576	0.5774	0.0786	0.057*
H11B	0.5679	0.7027	0.1022	0.057*
H11C	0.5829	0.5183	0.1498	0.057*
C12	0.64455 (19)	1.00421 (17)	0.20516 (14)	0.0251 (3)
C13	0.7224 (2)	1.05360 (19)	0.27106 (15)	0.0309 (3)
H13	0.6959	1.0257	0.3634	0.037*
C14	0.8396 (2)	1.1442 (2)	0.20033 (18)	0.0381 (4)
H14	0.8957	1.1787	0.2429	0.046*
C15	0.8722 (2)	1.1827 (2)	0.06712 (18)	0.0386 (4)
C16	0.7969 (2)	1.1347 (2)	−0.00004 (17)	0.0400 (4)
H16	0.8233	1.1638	−0.0924	0.048*
C17	0.6816 (2)	1.0430 (2)	0.07044 (15)	0.0333 (3)
H17	0.6283	1.0068	0.0270	0.040*

Atomic displacement parameters (Å^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
S	0.02610 (19)	0.02512 (19)	0.02153 (19)	−0.00398 (14)	−0.00822 (13)	−0.00554 (13)
F	0.0579 (7)	0.0490 (7)	0.0633 (8)	−0.0316 (6)	−0.0054 (6)	0.0012 (6)
O1	0.0343 (6)	0.0252 (5)	0.0327 (6)	−0.0066 (4)	−0.0092 (5)	−0.0100 (4)
O2	0.0309 (6)	0.0314 (6)	0.0254 (5)	−0.0035 (4)	−0.0054 (4)	−0.0092 (4)
O3	0.0340 (6)	0.0364 (6)	0.0301 (6)	−0.0077 (5)	−0.0148 (5)	−0.0058 (5)
C1	0.0276 (7)	0.0249 (7)	0.0237 (7)	−0.0065 (6)	−0.0074 (6)	−0.0056 (5)
C2	0.0247 (7)	0.0234 (7)	0.0237 (7)	−0.0078 (5)	−0.0057 (5)	−0.0034 (5)
C3	0.0296 (7)	0.0255 (7)	0.0252 (7)	−0.0068 (6)	−0.0066 (6)	−0.0055 (6)
C4	0.0329 (8)	0.0324 (8)	0.0235 (7)	−0.0116 (6)	−0.0075 (6)	−0.0022 (6)
C5	0.0325 (8)	0.0285 (8)	0.0289 (8)	−0.0109 (6)	−0.0100 (6)	0.0040 (6)
C6	0.0277 (7)	0.0221 (7)	0.0346 (8)	−0.0089 (6)	−0.0072 (6)	−0.0011 (6)
C7	0.0269 (7)	0.0246 (7)	0.0278 (7)	−0.0097 (6)	−0.0052 (6)	−0.0057 (6)
C8	0.0292 (7)	0.0273 (7)	0.0286 (7)	−0.0079 (6)	−0.0078 (6)	−0.0080 (6)
C9	0.0522 (11)	0.0445 (10)	0.0285 (8)	−0.0108 (8)	−0.0172 (8)	−0.0051 (7)
C10	0.0373 (9)	0.0231 (7)	0.0476 (10)	−0.0058 (6)	−0.0124 (7)	−0.0041 (7)
C11	0.0475 (10)	0.0396 (9)	0.0335 (9)	−0.0092 (8)	−0.0130 (7)	−0.0157 (7)
C12	0.0280 (7)	0.0223 (7)	0.0228 (7)	−0.0032 (5)	−0.0076 (5)	−0.0050 (5)
C13	0.0356 (8)	0.0306 (8)	0.0267 (7)	−0.0066 (6)	−0.0091 (6)	−0.0084 (6)
C14	0.0407 (9)	0.0346 (9)	0.0448 (10)	−0.0121 (7)	−0.0116 (8)	−0.0137 (7)
C15	0.0380 (9)	0.0279 (8)	0.0437 (10)	−0.0123 (7)	−0.0055 (7)	−0.0015 (7)
C16	0.0442 (10)	0.0428 (10)	0.0263 (8)	−0.0140 (8)	−0.0071 (7)	0.0010 (7)
C17	0.0381 (8)	0.0368 (8)	0.0248 (7)	−0.0100 (7)	−0.0109 (6)	−0.0042 (6)

Geometric parameters (Å, °)

S—O2	1.4384 (11)	C9—H9A	0.9800
S—O3	1.4402 (11)	C9—H9B	0.9800

S—C1	1.7351 (15)	C9—H9C	0.9800
S—C12	1.7669 (15)	C10—H10A	0.9800
F—C15	1.3561 (19)	C10—H10B	0.9800
O1—C8	1.3647 (19)	C10—H10C	0.9800
O1—C7	1.3823 (18)	C11—H11A	0.9800
C1—C8	1.362 (2)	C11—H11B	0.9800
C1—C2	1.452 (2)	C11—H11C	0.9800
C2—C7	1.392 (2)	C12—C17	1.387 (2)
C2—C3	1.396 (2)	C12—C13	1.388 (2)
C3—C4	1.390 (2)	C13—C14	1.387 (2)
C3—H3	0.9500	C13—H13	0.9500
C4—C5	1.406 (2)	C14—C15	1.373 (3)
C4—C9	1.513 (2)	C14—H14	0.9500
C5—C6	1.384 (2)	C15—C16	1.374 (3)
C5—H5	0.9500	C16—C17	1.383 (2)
C6—C7	1.389 (2)	C16—H16	0.9500
C6—C10	1.503 (2)	C17—H17	0.9500
C8—C11	1.484 (2)		
O2—S—O3	119.38 (7)	C4—C9—H9C	109.5
O2—S—C1	107.27 (7)	H9A—C9—H9C	109.5
O3—S—C1	109.18 (7)	H9B—C9—H9C	109.5
O2—S—C12	107.00 (7)	C6—C10—H10A	109.5
O3—S—C12	107.22 (7)	C6—C10—H10B	109.5
C1—S—C12	106.04 (7)	H10A—C10—H10B	109.5
C8—O1—C7	107.03 (11)	C6—C10—H10C	109.5
C8—C1—C2	107.63 (13)	H10A—C10—H10C	109.5
C8—C1—S	126.31 (12)	H10B—C10—H10C	109.5
C2—C1—S	126.04 (11)	C8—C11—H11A	109.5
C7—C2—C3	119.44 (13)	C8—C11—H11B	109.5
C7—C2—C1	104.30 (13)	H11A—C11—H11B	109.5
C3—C2—C1	136.26 (14)	C8—C11—H11C	109.5
C4—C3—C2	118.13 (14)	H11A—C11—H11C	109.5
C4—C3—H3	120.9	H11B—C11—H11C	109.5
C2—C3—H3	120.9	C17—C12—C13	121.50 (15)
C3—C4—C5	120.01 (14)	C17—C12—S	118.94 (12)
C3—C4—C9	120.21 (15)	C13—C12—S	119.50 (11)
C5—C4—C9	119.77 (15)	C14—C13—C12	119.12 (15)
C6—C5—C4	123.49 (14)	C14—C13—H13	120.4
C6—C5—H5	118.3	C12—C13—H13	120.4
C4—C5—H5	118.3	C15—C14—C13	118.22 (16)
C5—C6—C7	114.38 (14)	C15—C14—H14	120.9
C5—C6—C10	123.44 (15)	C13—C14—H14	120.9
C7—C6—C10	122.18 (15)	F—C15—C14	118.37 (16)
O1—C7—C6	124.84 (14)	F—C15—C16	118.03 (16)
O1—C7—C2	110.61 (13)	C14—C15—C16	123.59 (16)
C6—C7—C2	124.53 (14)	C15—C16—C17	118.18 (16)
C1—C8—O1	110.43 (13)	C15—C16—H16	120.9
C1—C8—C11	134.21 (15)	C17—C16—H16	120.9
O1—C8—C11	115.35 (13)	C16—C17—C12	119.37 (15)

C4—C9—H9A	109.5	C16—C17—H17	120.3
C4—C9—H9B	109.5	C12—C17—H17	120.3
H9A—C9—H9B	109.5		
O2—S—C1—C8	157.19 (13)	C1—C2—C7—O1	−0.13 (16)
O3—S—C1—C8	26.50 (16)	C3—C2—C7—C6	−0.8 (2)
C12—S—C1—C8	−88.73 (15)	C1—C2—C7—C6	178.84 (14)
O2—S—C1—C2	−24.51 (15)	C2—C1—C8—O1	0.16 (17)
O3—S—C1—C2	−155.21 (12)	S—C1—C8—O1	178.72 (10)
C12—S—C1—C2	89.57 (13)	C2—C1—C8—C11	−179.06 (17)
C8—C1—C2—C7	−0.02 (16)	S—C1—C8—C11	−0.5 (3)
S—C1—C2—C7	−178.58 (11)	C7—O1—C8—C1	−0.25 (16)
C8—C1—C2—C3	179.48 (16)	C7—O1—C8—C11	179.14 (13)
S—C1—C2—C3	0.9 (3)	O2—S—C12—C17	−147.39 (12)
C7—C2—C3—C4	0.8 (2)	O3—S—C12—C17	−18.20 (14)
C1—C2—C3—C4	−178.62 (15)	C1—S—C12—C17	98.35 (13)
C2—C3—C4—C5	−0.1 (2)	O2—S—C12—C13	29.85 (14)
C2—C3—C4—C9	179.17 (14)	O3—S—C12—C13	159.04 (12)
C3—C4—C5—C6	−0.8 (2)	C1—S—C12—C13	−84.41 (13)
C9—C4—C5—C6	179.94 (15)	C17—C12—C13—C14	0.2 (2)
C4—C5—C6—C7	0.9 (2)	S—C12—C13—C14	−176.95 (12)
C4—C5—C6—C10	−179.56 (15)	C12—C13—C14—C15	0.7 (2)
C8—O1—C7—C6	−178.73 (14)	C13—C14—C15—F	179.52 (15)
C8—O1—C7—C2	0.24 (16)	C13—C14—C15—C16	−0.9 (3)
C5—C6—C7—O1	178.75 (13)	F—C15—C16—C17	179.80 (16)
C10—C6—C7—O1	−0.8 (2)	C14—C15—C16—C17	0.2 (3)
C5—C6—C7—C2	−0.1 (2)	C15—C16—C17—C12	0.7 (3)
C10—C6—C7—C2	−179.66 (14)	C13—C12—C17—C16	−0.9 (2)
C3—C2—C7—O1	−179.73 (12)	S—C12—C17—C16	176.28 (13)

Hydrogen-bond geometry (Å, °)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
C10—H10B···O2^{i}	0.98	2.56	3.363 (2)	139
C13—H13···O2^{ii}	0.95	2.45	3.365 (2)	160
C17—H17···O3^{iii}	0.95	2.50	3.198 (2)	130

Symmetry codes: (i) −*x*+1, −*y*+1, −*z*+1; (ii) −*x*+1, −*y*+2, −*z*+1; (iii) −*x*+1, −*y*+2, −*z*.

Fig. 1

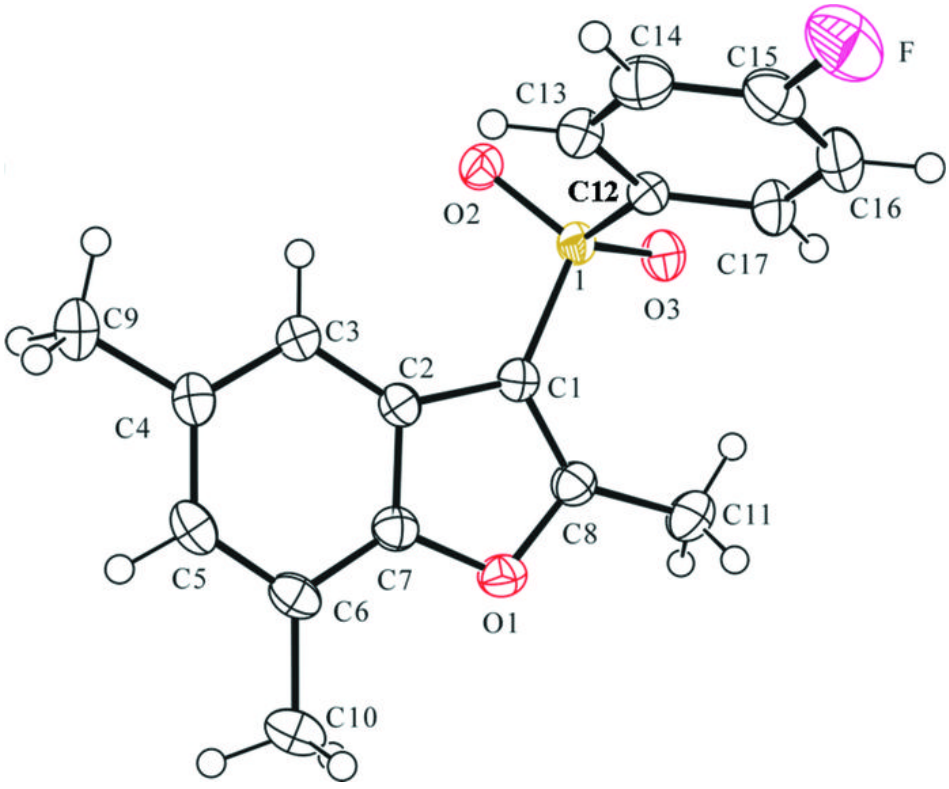
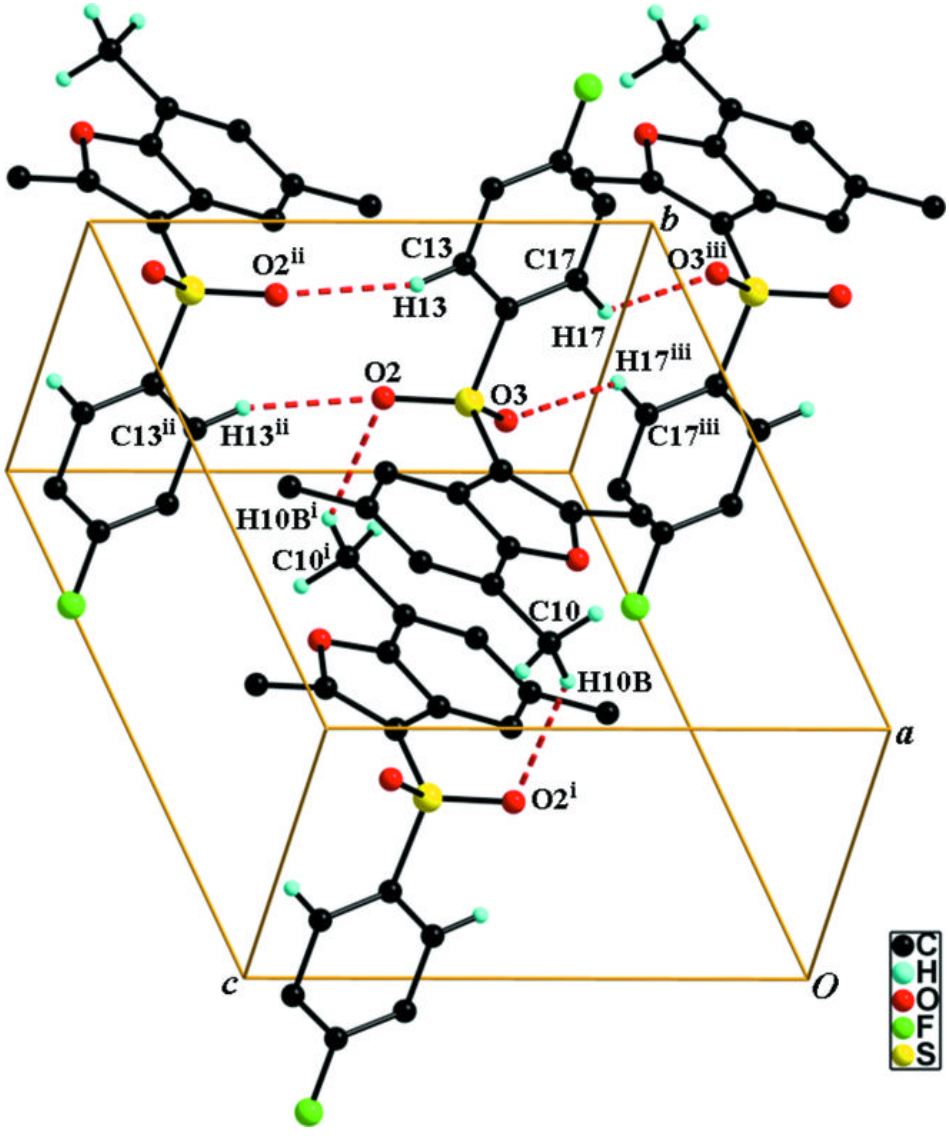

C14
C15
F
C13
C12
O2
C16
I
O3
C17
C9
C3
C2
C1
C4
C11
C8
C5
C7
O1
C6
C10

Fig. 2


O2ii
C13
C17
O3iii
H13
H17
H17iii
O2
O3
C13ii
H13ii
C17iii
H10Bi
C10i
C10
H10B
O2i
b
a
c
O
C
H
O
F
S

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Hexaaquazinc(II) bis(2,4,5-tricarboxybenzoate) 4,5-diazafluoren-9-one disolvate dihydrate

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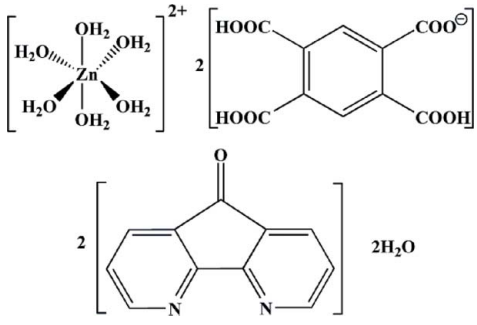
Key indicators: single-crystal X-ray study; T = 293 K; mean σ(C–C) = 0.002 Å; R factor = 0.031; wR factor = 0.086; data-to-parameter ratio = 14.8.

The asymmetric unit of the title complex, $[Zn(H_2O)_6](C_{10}H_5O_8)_2\cdot 2C_{11}H_6N_2O\cdot 2H_2O$, contains one half of the complex cation with the Zn^{II} ion located on an inversion center, a monovalent 2,4,5-tricarboxybenzoate (1,2,4,5-BTC) counter-anion, a 4,5-diazafluoren-9-one (DAFO) molecule and an uncoordinated water molecule. In the crystal structure, O—H···O and O—H···N hydrogen bonds link the cations, anions and water molecules into a three-dimensional network.

Related literature

For ZnII complexes, see: Rochon & Massarweh (2000); Si *et al.* (2003). For a related structure, see: Zhu *et al.* (2009).



Experimental

Crystal data

$[Zn(H_2O)_6](C_{10}H_5O_8)_2\cdot 2C_{11}H_6N_2O\cdot 2H_2O$
M_r = 1080.13
Triclinic, $P\overline{1}$
a = 8.380 (5) Å
b = 9.757 (5) Å
c = 14.107 (5) Å
α = 77.964 (5)°
β = 77.709 (5)°
γ = 89.948 (5)°
V = 1101.1 (9) Å^3
Z = 1
Mo $K\alpha$ radiation
μ = 0.66 mm^{-1}
T = 293 K
0.28 × 0.23 × 0.19 mm

Data collection

Rigaku R-AXIS RAPID diffractometer
Absorption correction: multi-scan (*ABSCOR*; Higashi, 1995)
T_{min} = 0.836, T_{max} = 0.885
6855 measured reflections
5060 independent reflections
4670 reflections with $I > 2\sigma(I)$
R_{int} = 0.014

Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.031
$wR(F^2)$ = 0.086
S = 1.06
5060 reflections
343 parameters
H atoms treated by a mixture of independent and constrained refinement
$\Delta\rho_{max}$ = 0.28 e Å^{-3}
$\Delta\rho_{min}$ = −0.34 e Å^{-3}

Table 1
Selected geometric parameters (Å, °).

Zn1—O9	2.0550 (15)	Zn1—O11	2.0755 (12)
Zn1—O10	2.0712 (13)		
O9^{i}—Zn1—O10	89.81 (6)	O9—Zn1—O11	93.35 (5)
O9—Zn1—O10	90.19 (6)	O10^{i}—Zn1—O11	89.23 (6)
O9^{i}—Zn1—O11	86.65 (5)	O10—Zn1—O11	90.77 (6)

Symmetry code: (i) $-x, -y+1, -z+1$.

Table 2
Hydrogen-bond geometry (Å, °).

D—H···A	D—H	H···A	D···A	D—H···A
O1W—H1A···O12^{ii}	0.86	2.12	2.8342 (19)	141
O1W—H1B···O5^{iii}	0.89	1.94	2.815 (2)	168
O9—H9A···O1W^{ii}	0.75	2.13	2.8526 (19)	161
O9—H9B···O5^{iii}	0.83	1.87	2.6929 (18)	177
O10—H10A···O1^{iv}	0.82	1.96	2.7860 (18)	174
O11—H11B···N1^{v}	0.80	2.10	2.880 (2)	166
O11—H11A···O6^{iii}	0.76	2.05	2.7725 (17)	160
O10—H10B···N2^{vi}	0.88	1.88	2.747 (2)	171
O3—H3O···O6^{vii}	0.94 (3)	1.55 (3)	2.4883 (18)	173 (3)
O2—H2O···O1W	0.86 (3)	1.83 (3)	2.6747 (19)	167 (2)
O8—H8O···O4^{viii}	0.85 (3)	1.83 (3)	2.670 (2)	171 (3)

Symmetry codes: (ii) $-x+1, -y+1, -z+1$; (iii) $-x+1, -y+1, -z+2$; (iv) $x-1, y, z$; (v) $x-1, y-1, z$; (vi) $-x+1, -y+2, -z+1$; (vii) $-x+2, -y+1, -z+2$; (viii) $x, y+1, z$.

Data collection: *PROCESS-AUTO* (Rigaku, 1998); cell refinement: *PROCESS-AUTO*; data reduction: *PROCESS-AUTO*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *SHELXTL-Plus* (Sheldrick, 2008); software used to prepare material for publication: *SHELXL97*.

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Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: ER2077).

References

Higashi, T. (1995). *ABSCOR*. Rigaku Corporation, Tokyo, Japan.
Rigaku (1998). *PROCESS-AUTO*. Rigaku Corporation, Tokyo, Japan.
Rochon, F.-D. & Massarweh, G. (2000). *Inorg. Chim. Acta*, **304**, 190–198.
Sheldrick, G. M. (2008). *Acta Cryst.* A**64**, 112–122.
Si, S.-F., Wang, R.-J. & Li, Y.-D. (2003). *Inorg. Chem. Commun.* **6**, 1152–1155.
Zhu, Z.-B., Gao, S. & Ng, S. W. (2009). *Acta Cryst.* E**65**, m1345.

supplementary materials

Acta Cryst. (2010). E**66**, m804 [**doi:10.1107/S1600536810021641**]

Hexaaquazinc(II) bis(2,4,5-tricarboxybenzoate) 4,5-diazafluoren-9-one disolvate dihydrate

G.-F. Yang and Y.-H. Zhao

Comment

Single-crystal X-ray diffraction analyses revealed Zn^{II} is hexa-coordinated and exhibits octahedral coordintion environment supplied by six water molecules (Fig. 1). The O atoms from four coordinated water molecules in the equatorial plane around the Zn^{II} ion form a slightly distorted square-planar arrangement with an average Zn—O bond length of 2.073 (1) Å; the slightly distorted octahedral coordination is completed by the other O atoms at a slightly shorter distance [2.055 (2) Å] in the axial positions. benzene-1,2,4,5-tetracarboxylate (1,2,4,5-BTC) counter-anion, and DAFO molecule are both uncoordinated. Intermolecular hydrogen bonds, O—H···O and O—H···N, extend the ion complex into a three-dimensional supramolecular network structure (Fig. 2, Table 1).

Experimental

Zinc(II) acetate dihydrate (0.066 g, 0.3 mol), benzene-1,2,4,5-tetracarboxylate (0.055 g, 0.2 mmol), 4, 5-diazafluoren-9-one (0.036 g, 0.2 mmol), sodium hydroxide (0.016 g, 0.4 mmol) and water (14 ml) were placed in a 23 ml Teflon-lined autoclave, and the autoclave was heated at 423 K for 3 d. After cooling slowly to room temperature at a rate of 10 K h^{-1}, colorless crystals were obtained.

Refinement

C-bound H atoms were treated as riding, with C—H = 0.93Å and U_{iso}(H) = 1.2 times U_{eq}(C). O-bound H atoms were located in a difference Fourier map and refined as riding in their as-found relative positions; U_{iso}(H) = 1.5U_{eq}(O).

Figures

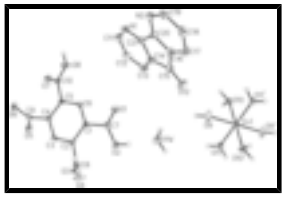


Fig. 1. View of the local coordination of Zn^{II} with the atomic numbering scheme. Displacement ellipsoids are drawn at the 30% probability level.

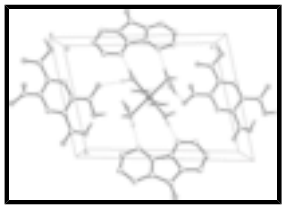


Fig. 2. A packing diagram for the three-dimensional supramolecular framework *via* O—H···O interactions. The view direction is parallel to the *a* axis. Hydrogen bonds are indicated by dashed lines.

Hexaaquazinc(II) bis(2,4,5-tricarboxybenzoate) 4,5-diazafluoren-9-one disolvate dihydrate

Crystal data

$[Zn(H_2O)_6](C_{10}H_5O_8)_2{\cdot}2C_{11}H_6N_2O{\cdot}2H_2O$	$Z = 1$
$M_r = 1080.13$	$F(000) = 556$
Triclinic, $P\overline{1}$	$D_x = 1.629$ Mg m^{-3}
$a = 8.380$ (5) Å	Mo $K\alpha$ radiation, $\lambda = 0.71069$ Å
$b = 9.757$ (5) Å	Cell parameters from 6265 reflections
$c = 14.107$ (5) Å	$\theta = 2.1$–$28.2°$
$\alpha = 77.964$ (5)°	$\mu = 0.66$ mm^{-1}
$\beta = 77.709$ (5)°	$T = 293$ K
$\gamma = 89.948$ (5)°	Block, colorless
$V = 1101.1$ (9) Å^3	0.28 × 0.23 × 0.19 mm

Data collection

Rigaku R-AXIS RAPID diffractometer	5060 independent reflections
Radiation source: fine-focus sealed tube	4670 reflections with $I > 2\sigma(I)$
graphite	$R_{int} = 0.014$
Detector resolution: 10 pixels mm^{-1}	$\theta_{max} = 28.3°$, $\theta_{min} = 1.5°$
ω scan	$h = -11 \rightarrow 4$
Absorption correction: multi-scan (*ABSCOR*; Higashi, 1995)	$k = -12 \rightarrow 12$
$T_{min} = 0.836$, $T_{max} = 0.885$	$l = -18 \rightarrow 16$
6855 measured reflections	

Refinement

Refinement on F^2	Primary atom site location: structure-invariant direct methods
Least-squares matrix: full	Secondary atom site location: difference Fourier map
$R[F^2 > 2\sigma(F^2)] = 0.031$	Hydrogen site location: inferred from neighbouring sites
$wR(F^2) = 0.086$	H atoms treated by a mixture of independent and constrained refinement
$S = 1.06$	$w = 1/[\sigma^2(F_o^2) + (0.0461P)^2 + 0.2811P]$ where $P = (F_o^2 + 2F_c^2)/3$
5060 reflections	$(\Delta/\sigma)_{max} = 0.001$
343 parameters	$\Delta\rho_{max} = 0.28$ e Å^{-3}
0 restraints	$\Delta\rho_{min} = -0.34$ e Å^{-3}

Special details

Geometry. All e.s.d.'s (except the e.s.d. in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell e.s.d.'s are taken into account individually in the estimation of e.s.d.'s in distances, angles and torsion angles; correlations

between e.s.d.'s in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell e.s.d.'s is used for estimating e.s.d.'s involving l.s. planes.

Refinement. Refinement of F^2 against ALL reflections. The weighted *R*-factor *wR* and goodness of fit *S* are based on F^2, conventional *R*-factors *R* are based on *F*, with *F* set to zero for negative F^2. The threshold expression of $F^2 > \sigma(F^2)$ is used only for calculating *R*-factors(gt) *etc*. and is not relevant to the choice of reflections for refinement. *R*-factors based on F^2 are statistically about twice as large as those based on *F*, and *R*- factors based on ALL data will be even larger.

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters ($Å^2$)

	x	*y*	*z*	U_{iso}*/U_{eq}
Zn1	0.0000	0.5000	0.5000	0.02688 (8)
O1	0.70290 (17)	0.59156 (12)	0.76405 (8)	0.0414 (3)
O2	0.64715 (15)	0.36226 (11)	0.82062 (9)	0.0356 (2)
O3	0.89652 (15)	0.20199 (11)	0.90798 (9)	0.0374 (3)
O4	0.68585 (18)	0.13427 (11)	1.03103 (9)	0.0510 (4)
O5	0.72889 (14)	0.45006 (13)	1.28469 (8)	0.0394 (3)
O6	0.93948 (14)	0.60062 (13)	1.21458 (8)	0.0371 (3)
O7	0.68773 (16)	0.79402 (12)	1.15402 (8)	0.0408 (3)
O8	0.7470 (2)	0.88143 (12)	0.99083 (9)	0.0521 (4)
O12	0.55282 (18)	0.75220 (15)	0.47805 (12)	0.0579 (4)
N1	0.76786 (17)	1.09551 (14)	0.61753 (10)	0.0354 (3)
N2	0.93283 (18)	1.14163 (15)	0.39355 (10)	0.0372 (3)
C1	0.72961 (16)	0.49108 (14)	0.92716 (10)	0.0235 (3)
C2	0.76421 (17)	0.37449 (13)	0.99478 (10)	0.0241 (3)
C3	0.78982 (18)	0.39158 (14)	1.08567 (10)	0.0269 (3)
H3	0.8115	0.3136	1.1309	0.032*
C4	0.78401 (16)	0.52197 (14)	1.11107 (10)	0.0239 (3)
C5	0.74847 (17)	0.63815 (13)	1.04361 (10)	0.0240 (3)
C6	0.72178 (17)	0.62128 (14)	0.95285 (10)	0.0254 (3)
H6	0.6981	0.6990	0.9082	0.030*
C7	0.69319 (17)	0.48682 (14)	0.82862 (10)	0.0267 (3)
C8	0.77793 (19)	0.22755 (14)	0.97678 (10)	0.0293 (3)
C9	0.81864 (17)	0.52666 (14)	1.21153 (10)	0.0260 (3)
C10	0.72500 (18)	0.77881 (14)	1.07017 (11)	0.0280 (3)
C11	0.6757 (2)	1.05207 (18)	0.71039 (13)	0.0422 (4)
H11	0.6890	1.1019	0.7579	0.051*
C12	0.5640 (2)	0.9399 (2)	0.74011 (14)	0.0462 (4)
H12	0.5047	0.9166	0.8054	0.055*
C13	0.5404 (2)	0.86182 (18)	0.67221 (14)	0.0432 (4)
H13	0.4665	0.7850	0.6900	0.052*
C14	0.63219 (19)	0.90423 (16)	0.57714 (13)	0.0349 (3)
C15	0.6374 (2)	0.84773 (18)	0.48618 (14)	0.0401 (4)
C16	0.7622 (2)	0.93733 (17)	0.40690 (13)	0.0371 (3)
C17	0.8169 (2)	0.9358 (2)	0.30764 (14)	0.0477 (4)
H17	0.7787	0.8677	0.2796	0.057*
C18	0.9305 (3)	1.0392 (2)	0.25193 (14)	0.0503 (5)
H18	0.9710	1.0421	0.1848	0.060*
C19	0.9840 (2)	1.1388 (2)	0.29631 (13)	0.0456 (4)

H19	1.0600	1.2081	0.2569	0.055*
C20	0.82315 (18)	1.04143 (15)	0.44622 (12)	0.0315 (3)
C21	0.74262 (18)	1.01997 (15)	0.55338 (11)	0.0304 (3)
O1W	0.54813 (14)	0.40373 (14)	0.64908 (9)	0.0427 (3)
H1A	0.5031	0.3305	0.6388	0.064*
H1B	0.4692	0.4612	0.6658	0.064*
O9	0.21520 (14)	0.55344 (16)	0.53380 (9)	0.0485 (3)
H9A	0.2906	0.5561	0.4935	0.073*
H9B	0.2308	0.5549	0.5895	0.073*
O10	−0.11749 (14)	0.65168 (12)	0.56875 (8)	0.0378 (3)
H10A	−0.1723	0.6286	0.6259	0.057*
H11B	−0.0987	0.2735	0.6240	0.057*
O11	−0.06978 (15)	0.34898 (12)	0.63034 (8)	0.0389 (3)
H11A	−0.0226	0.3459	0.6709	0.058*
H10B	−0.0502	0.7156	0.5757	0.058*
H3O	0.957 (3)	0.281 (3)	0.865 (2)	0.083 (9)*
H2O	0.629 (3)	0.369 (3)	0.7620 (19)	0.063 (7)*
H8O	0.732 (3)	0.959 (3)	1.0088 (19)	0.071 (8)*

Atomic displacement parameters (Å^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Zn1	0.03260 (13)	0.02768 (13)	0.02240 (12)	0.00010 (9)	−0.00775 (9)	−0.00810 (9)
O1	0.0733 (8)	0.0291 (6)	0.0246 (5)	0.0058 (5)	−0.0168 (5)	−0.0054 (4)
O2	0.0530 (7)	0.0292 (5)	0.0304 (6)	−0.0027 (5)	−0.0169 (5)	−0.0114 (4)
O3	0.0468 (6)	0.0257 (5)	0.0383 (6)	0.0047 (5)	0.0001 (5)	−0.0130 (5)
O4	0.0778 (9)	0.0201 (5)	0.0433 (7)	−0.0077 (5)	0.0147 (6)	−0.0091 (5)
O5	0.0452 (6)	0.0485 (7)	0.0221 (5)	−0.0104 (5)	−0.0067 (4)	−0.0030 (5)
O6	0.0418 (6)	0.0449 (6)	0.0264 (5)	−0.0096 (5)	−0.0109 (4)	−0.0080 (5)
O7	0.0630 (8)	0.0324 (6)	0.0323 (6)	0.0055 (5)	−0.0105 (5)	−0.0182 (5)
O8	0.1023 (11)	0.0172 (5)	0.0347 (6)	0.0055 (6)	−0.0075 (7)	−0.0088 (5)
O12	0.0530 (8)	0.0509 (8)	0.0825 (11)	−0.0060 (6)	−0.0266 (7)	−0.0304 (7)
N1	0.0454 (7)	0.0281 (6)	0.0353 (7)	0.0025 (5)	−0.0097 (6)	−0.0120 (5)
N2	0.0451 (7)	0.0342 (7)	0.0343 (7)	0.0042 (6)	−0.0091 (6)	−0.0114 (5)
C1	0.0307 (6)	0.0199 (6)	0.0202 (6)	0.0004 (5)	−0.0046 (5)	−0.0060 (5)
C2	0.0326 (7)	0.0175 (6)	0.0224 (6)	0.0002 (5)	−0.0041 (5)	−0.0065 (5)
C3	0.0387 (7)	0.0195 (6)	0.0227 (6)	0.0041 (5)	−0.0080 (5)	−0.0034 (5)
C4	0.0293 (6)	0.0231 (6)	0.0200 (6)	0.0007 (5)	−0.0053 (5)	−0.0066 (5)
C5	0.0322 (7)	0.0189 (6)	0.0221 (6)	0.0007 (5)	−0.0053 (5)	−0.0077 (5)
C6	0.0370 (7)	0.0187 (6)	0.0210 (6)	0.0027 (5)	−0.0071 (5)	−0.0045 (5)
C7	0.0333 (7)	0.0259 (7)	0.0227 (7)	0.0036 (5)	−0.0059 (5)	−0.0098 (5)
C8	0.0452 (8)	0.0177 (6)	0.0257 (7)	0.0021 (5)	−0.0066 (6)	−0.0072 (5)
C9	0.0330 (7)	0.0258 (6)	0.0219 (6)	0.0045 (5)	−0.0081 (5)	−0.0089 (5)
C10	0.0378 (7)	0.0200 (6)	0.0281 (7)	0.0012 (5)	−0.0077 (6)	−0.0091 (5)
C11	0.0540 (10)	0.0377 (9)	0.0363 (9)	0.0072 (7)	−0.0071 (7)	−0.0140 (7)
C12	0.0472 (10)	0.0423 (9)	0.0427 (10)	0.0068 (7)	0.0013 (7)	−0.0061 (7)
C13	0.0366 (8)	0.0335 (8)	0.0564 (11)	0.0027 (6)	−0.0066 (7)	−0.0062 (7)
C14	0.0323 (7)	0.0285 (7)	0.0480 (9)	0.0064 (6)	−0.0134 (6)	−0.0127 (6)

C15	0.0373 (8)	0.0347 (8)	0.0584 (11)	0.0077 (6)	−0.0223 (7)	−0.0204 (7)
C16	0.0394 (8)	0.0374 (8)	0.0447 (9)	0.0100 (6)	−0.0205 (7)	−0.0199 (7)
C17	0.0554 (11)	0.0535 (11)	0.0506 (11)	0.0162 (9)	−0.0277 (9)	−0.0311 (9)
C18	0.0615 (12)	0.0607 (12)	0.0353 (9)	0.0172 (9)	−0.0156 (8)	−0.0203 (8)
C19	0.0546 (10)	0.0469 (10)	0.0351 (9)	0.0076 (8)	−0.0080 (7)	−0.0099 (7)
C20	0.0364 (7)	0.0280 (7)	0.0360 (8)	0.0087 (6)	−0.0145 (6)	−0.0131 (6)
C21	0.0337 (7)	0.0255 (7)	0.0355 (8)	0.0073 (5)	−0.0111 (6)	−0.0108 (6)
O1W	0.0379 (6)	0.0548 (7)	0.0407 (7)	0.0006 (5)	−0.0088 (5)	−0.0221 (6)
O9	0.0346 (6)	0.0857 (10)	0.0278 (6)	−0.0111 (6)	−0.0068 (5)	−0.0177 (6)
O10	0.0448 (6)	0.0351 (6)	0.0336 (6)	0.0016 (5)	−0.0024 (5)	−0.0140 (5)
O11	0.0550 (7)	0.0349 (6)	0.0283 (6)	−0.0069 (5)	−0.0156 (5)	−0.0031 (4)

Geometric parameters (Å, °)

Zn1—O9^{i}	2.0550 (15)	C4—C9	1.5156 (19)
Zn1—O9	2.0550 (15)	C5—C6	1.3879 (19)
Zn1—O10^{i}	2.0712 (13)	C5—C10	1.4983 (19)
Zn1—O10	2.0712 (13)	C6—H6	0.9300
Zn1—O11^{i}	2.0755 (12)	C11—C12	1.376 (3)
Zn1—O11	2.0755 (12)	C11—H11	0.9300
O1—C7	1.2088 (18)	C12—C13	1.386 (3)
O2—C7	1.3097 (18)	C12—H12	0.9300
O2—H2O	0.86 (3)	C13—C14	1.375 (3)
O3—C8	1.2968 (18)	C13—H13	0.9300
O3—H3O	0.94 (3)	C14—C21	1.399 (2)
O4—C8	1.2119 (19)	C14—C15	1.491 (2)
O5—C9	1.2402 (18)	C15—C16	1.485 (3)
O6—C9	1.2573 (19)	C16—C17	1.381 (3)
O7—C10	1.1978 (18)	C16—C20	1.399 (2)
O8—C10	1.3169 (19)	C17—C18	1.376 (3)
O8—H8O	0.85 (3)	C17—H17	0.9300
O12—C15	1.210 (2)	C18—C19	1.383 (3)
N1—C21	1.329 (2)	C18—H18	0.9300
N1—C11	1.353 (2)	C19—H19	0.9300
N2—C20	1.327 (2)	C20—C21	1.489 (2)
N2—C19	1.354 (2)	O1W—H1A	0.8602
C1—C6	1.3897 (19)	O1W—H1B	0.8916
C1—C2	1.3974 (19)	O9—H9A	0.7509
C1—C7	1.4939 (19)	O9—H9B	0.8266
C2—C3	1.3871 (19)	O10—H10A	0.8240
C2—C8	1.5075 (19)	O10—H10B	0.8756
C3—C4	1.390 (2)	O11—H11B	0.8033
C3—H3	0.9300	O11—H11A	0.7581
C4—C5	1.3962 (19)		
O9^{i}—Zn1—O9	180.00 (6)	O7—C10—O8	124.78 (13)
O9^{i}—Zn1—O10^{i}	90.19 (6)	O7—C10—C5	123.23 (13)
O9—Zn1—O10^{i}	89.81 (6)	O8—C10—C5	111.97 (12)

$O9^{i}$—Zn1—O10	89.81 (6)	N1—C11—C12	125.12 (17)
O9—Zn1—O10	90.19 (6)	N1—C11—H11	117.4
$O10^{i}$—Zn1—O10	180.000 (1)	C12—C11—H11	117.4
$O9^{i}$—Zn1—$O11^{i}$	93.35 (5)	C11—C12—C13	119.65 (17)
O9—Zn1—$O11^{i}$	86.65 (5)	C11—C12—H12	120.2
$O10^{i}$—Zn1—$O11^{i}$	90.77 (6)	C13—C12—H12	120.2
O10—Zn1—$O11^{i}$	89.23 (6)	C14—C13—C12	116.35 (16)
$O9^{i}$—Zn1—O11	86.65 (5)	C14—C13—H13	121.8
O9—Zn1—O11	93.35 (5)	C12—C13—H13	121.8
$O10^{i}$—Zn1—O11	89.23 (6)	C13—C14—C21	120.15 (15)
O10—Zn1—O11	90.77 (6)	C13—C14—C15	131.05 (16)
$O11^{i}$—Zn1—O11	180.0	C21—C14—C15	108.79 (15)
C7—O2—H2O	108.3 (17)	O12—C15—C16	127.32 (18)
C8—O3—H3O	116.1 (17)	O12—C15—C14	126.97 (18)
C10—O8—H8O	109.1 (18)	C16—C15—C14	105.65 (13)
C21—N1—C11	114.33 (14)	C17—C16—C20	119.59 (17)
C20—N2—C19	115.56 (15)	C17—C16—C15	131.56 (16)
C6—C1—C2	119.02 (12)	C20—C16—C15	108.80 (15)
C6—C1—C7	116.07 (12)	C18—C17—C16	117.23 (17)
C2—C1—C7	124.86 (12)	C18—C17—H17	121.4
C3—C2—C1	119.25 (12)	C16—C17—H17	121.4
C3—C2—C8	115.88 (12)	C17—C18—C19	119.64 (17)
C1—C2—C8	124.87 (12)	C17—C18—H18	120.2
C2—C3—C4	121.84 (12)	C19—C18—H18	120.2
C2—C3—H3	119.1	N2—C19—C18	124.07 (18)
C4—C3—H3	119.1	N2—C19—H19	118.0
C3—C4—C5	118.79 (12)	C18—C19—H19	118.0
C3—C4—C9	116.48 (12)	N2—C20—C16	123.90 (15)
C5—C4—C9	124.73 (12)	N2—C20—C21	127.60 (14)
C6—C5—C4	119.52 (12)	C16—C20—C21	108.50 (14)
C6—C5—C10	118.91 (12)	N1—C21—C14	124.40 (15)
C4—C5—C10	121.39 (12)	N1—C21—C20	127.36 (14)
C5—C6—C1	121.57 (12)	C14—C21—C20	108.24 (13)
C5—C6—H6	119.2	H1A—O1W—H1B	107.9
C1—C6—H6	119.2	Zn1—O9—H9A	115.7
O1—C7—O2	124.26 (14)	Zn1—O9—H9B	126.9
O1—C7—C1	121.57 (13)	H9A—O9—H9B	115.9
O2—C7—C1	114.14 (12)	Zn1—O10—H10A	119.5
O4—C8—O3	121.35 (13)	Zn1—O10—H10B	113.2
O4—C8—C2	119.60 (13)	H10A—O10—H10B	100.6
O3—C8—C2	118.84 (12)	Zn1—O11—H11B	115.8
O5—C9—O6	124.96 (13)	Zn1—O11—H11A	119.0
O5—C9—C4	116.40 (13)	H11B—O11—H11A	114.1
O6—C9—C4	118.52 (12)		
C6—C1—C2—C3	0.0 (2)	N1—C11—C12—C13	0.3 (3)
C7—C1—C2—C3	−177.52 (13)	C11—C12—C13—C14	−0.5 (3)
C6—C1—C2—C8	−179.46 (13)	C12—C13—C14—C21	0.3 (2)

C7—C1—C2—C8	3.0 (2)	C12—C13—C14—C15	−179.10 (16)
C1—C2—C3—C4	−0.8 (2)	C13—C14—C15—O12	3.2 (3)
C8—C2—C3—C4	178.71 (13)	C21—C14—C15—O12	−176.28 (17)
C2—C3—C4—C5	1.2 (2)	C13—C14—C15—C16	−179.47 (17)
C2—C3—C4—C9	−178.42 (13)	C21—C14—C15—C16	1.10 (17)
C3—C4—C5—C6	−0.7 (2)	O12—C15—C16—C17	−1.6 (3)
C9—C4—C5—C6	178.82 (13)	C14—C15—C16—C17	−178.92 (17)
C3—C4—C5—C10	174.23 (13)	O12—C15—C16—C20	175.75 (17)
C9—C4—C5—C10	−6.2 (2)	C14—C15—C16—C20	−1.62 (17)
C4—C5—C6—C1	0.0 (2)	C20—C16—C17—C18	−0.2 (2)
C10—C5—C6—C1	−175.12 (13)	C15—C16—C17—C18	176.91 (18)
C2—C1—C6—C5	0.4 (2)	C16—C17—C18—C19	−0.2 (3)
C7—C1—C6—C5	178.14 (12)	C20—N2—C19—C18	−0.7 (3)
C6—C1—C7—O1	20.5 (2)	C17—C18—C19—N2	0.6 (3)
C2—C1—C7—O1	−161.92 (15)	C19—N2—C20—C16	0.4 (2)
C6—C1—C7—O2	−157.94 (13)	C19—N2—C20—C21	−178.61 (15)
C2—C1—C7—O2	19.6 (2)	C17—C16—C20—N2	0.0 (2)
C3—C2—C8—O4	61.2 (2)	C15—C16—C20—N2	−177.65 (14)
C1—C2—C8—O4	−119.33 (18)	C17—C16—C20—C21	179.20 (14)
C3—C2—C8—O3	−113.59 (16)	C15—C16—C20—C21	1.52 (17)
C1—C2—C8—O3	65.9 (2)	C11—N1—C21—C14	−0.4 (2)
C3—C4—C9—O5	−57.77 (18)	C11—N1—C21—C20	179.48 (15)
C5—C4—C9—O5	122.67 (16)	C13—C14—C21—N1	0.2 (2)
C3—C4—C9—O6	118.48 (15)	C15—C14—C21—N1	179.69 (14)
C5—C4—C9—O6	−61.1 (2)	C13—C14—C21—C20	−179.72 (14)
C6—C5—C10—O7	152.54 (15)	C15—C14—C21—C20	−0.21 (17)
C4—C5—C10—O7	−22.5 (2)	N2—C20—C21—N1	−1.6 (3)
C6—C5—C10—O8	−26.2 (2)	C16—C20—C21—N1	179.28 (15)
C4—C5—C10—O8	158.82 (15)	N2—C20—C21—C14	178.31 (15)
C21—N1—C11—C12	0.2 (3)	C16—C20—C21—C14	−0.83 (17)

Symmetry codes: (i) −*x*, −*y*+1, −*z*+1.

Hydrogen-bond geometry (Å, °)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
O1W—H1A···O12^{ii}	0.86	2.12	2.8342 (19)	141.
O1W—H1B···O5^{iii}	0.89	1.94	2.815 (2)	168.
O9—H9A···O1W^{ii}	0.75	2.13	2.8526 (19)	161.
O9—H9B···O5^{iii}	0.83	1.87	2.6929 (18)	177.
O10—H10A···O1^{iv}	0.82	1.96	2.7860 (18)	174.
O11—H11B···N1^{v}	0.80	2.10	2.880 (2)	166.
O11—H11A···O6^{iii}	0.76	2.05	2.7725 (17)	160.
O10—H10B···N2^{vi}	0.88	1.88	2.747 (2)	171.
O3—H3O···O6^{vii}	0.94 (3)	1.55 (3)	2.4883 (18)	173 (3)
O2—H2O···O1W	0.86 (3)	1.83 (3)	2.6747 (19)	167 (2)
O8—H8O···O4^{viii}	0.85 (3)	1.83 (3)	2.670 (2)	171 (3)

Symmetry codes: (ii) −*x*+1, −*y*+1, −*z*+1; (iii) −*x*+1, −*y*+1, −*z*+2; (iv) *x*−1, *y*, *z*; (v) *x*−1, *y*−1, *z*; (vi) −*x*+1, −*y*+2, −*z*+1; (vii) −*x*+2, −*y*+1, −*z*+2; (viii) *x*, *y*+1, *z*.

Fig. 1

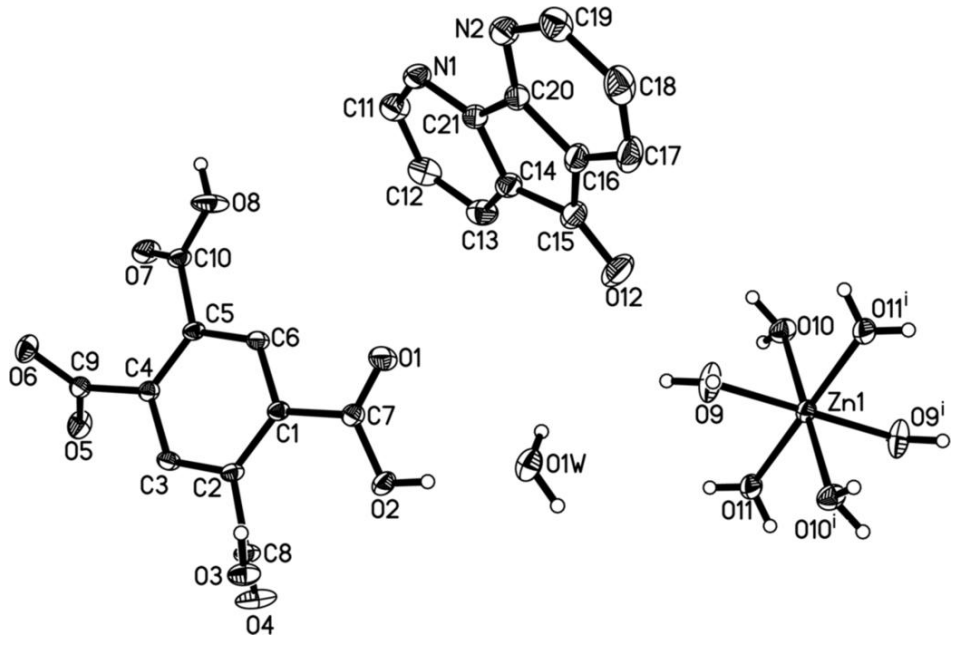
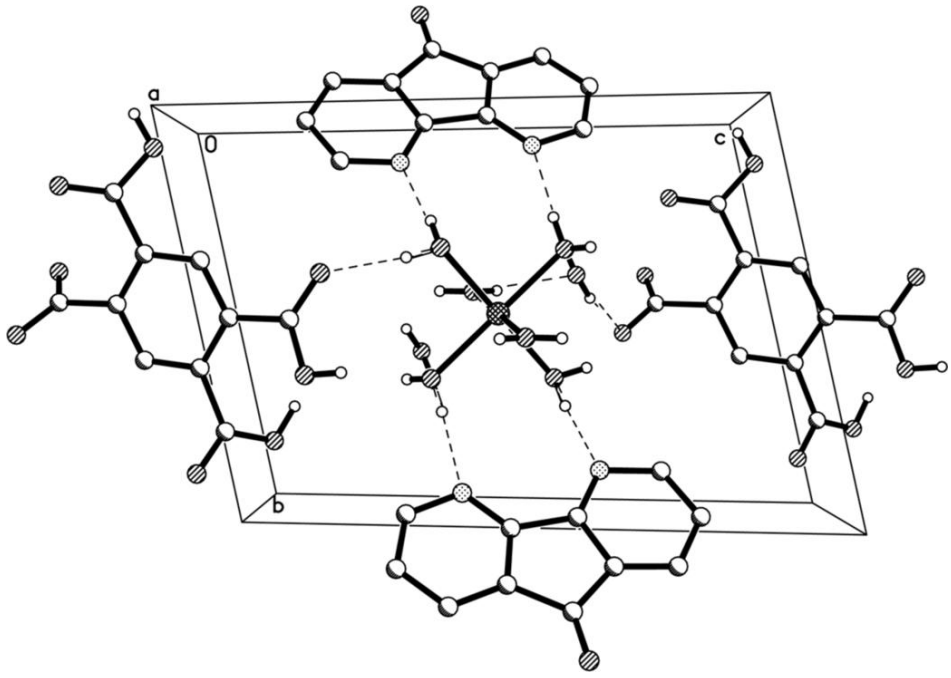


Fig. 2



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catena-Poly[[[(2-phenylacetato-κO)-zinc(II)]bis[μ-4,4′-(disulfanediyl)-dipyridine-κ^2N:N']] monohydrate]

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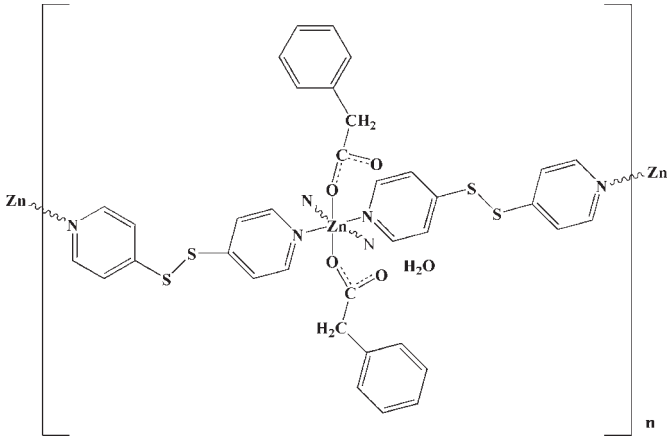
Key indicators: single-crystal X-ray study; T = 295 K; mean σ(C–C) = 0.004 Å; R factor = 0.035; wR factor = 0.092; data-to-parameter ratio = 17.4.

In the title compound, $\{[Zn(C_8H_7O_2)_2(C_{10}H_8N_2S_2)_2]\cdot H_2O\}_n$, the Zn^{II} atom is coordinated by four N atoms from four 4,4′-(disulfanediyl)dipyridine (bpds) ligands and two O atoms from two 2-phenylacetate anions in a distorted octahedral coordination geometry. The two bpds ligands of the same axial chirality bridge Zn^{II} atoms, generating repeated rhomboidal chains, which are linked by O—H···O hydrogen bonds into a ladder structure.

Related literature

For coordination chemistry based on pyridyl donor ligands, see: Biradha *et al.* (2006); Liu *et al.* (2008); Hernández-Ahuactzi *et al.* (2008); Ma, Wang, Wang *et al.* (2009). For bpds compounds, see: Horikoshi & Mochida (2006); Carballo *et al.* (2008); Ma, Wang, Hu *et al.* (2009); Horikoshi & Mikuriya (2005). For compounds containing phenylacetic acid, see: Johnston *et al.* (2008).



Experimental

Crystal data

$[Zn(C_8H_7O_2)_2(C_{10}H_8N_2S_2)_2]\cdot H_2O$
M_r = 794.27
Triclinic, $P\overline{1}$
a = 9.851 (2) Å
b = 11.130 (2) Å
c = 18.319 (4) Å
α = 90.38 (3)°
β = 98.88 (3)°
γ = 115.89 (3)°
V = 1779.0 (6) Å^3
Z = 2
Mo $K\alpha$ radiation
μ = 0.97 mm^{-1}
T = 295 K
0.51 × 0.41 × 0.36 mm

Data collection

Rigaku R-AXIS RAPID diffractometer
Absorption correction: multi-scan (*ABSCOR*; Higashi, 1995)
T_{min} = 0.623, T_{max} = 0.701
16701 measured reflections
7859 independent reflections
6036 reflections with $I > 2\sigma(I)$
R_{int} = 0.038

Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.035
$wR(F^2)$ = 0.092
S = 1.07
7859 reflections
451 parameters
H-atom parameters constrained
$\Delta\rho_{max}$ = 0.43 e Å^{-3}
$\Delta\rho_{min}$ = −0.34 e Å^{-3}

Table 1
Hydrogen-bond geometry (Å, °).

D—H···A	D—H	H···A	D···A	D—H···A
O5—H5c···O4^{i}	0.81	2.20	2.970 (3)	158
O5—H5d···O4	0.80	2.15	2.945 (3)	169

Symmetry code: (i) $-x+1, -y, -z$.

Data collection: *RAPID-AUTO* (Rigaku, 1998); cell refinement: *RAPID-AUTO*; data reduction: *CrystalStructure* (Rigaku/MSC, 2004); program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *SHELXTL* (Sheldrick, 2008); software used to prepare material for publication: *SHELXL97*.

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Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: ER2078).

References

Biradha, K., Sarkar, M. & Rajput, L. (2006). *Chem. Commun.* pp. 4169–4179.
Carballo, R., Covelo, B., Fernández-Fermida, N., García-Martinez, E., Lago, A. B. & Vázquez-Löpez, E. M. (2008). *Cryst. Growth Des.* **8**, 995–1004.
Hernández-Ahuactzi, I. F., Höpfl, H., Barba, V., Román-Bravo, P., Zamudio-Rivera, L. S. & Beltrán, H. I. (2008). *Eur. J. Inorg. Chem.* pp. 2746–2755.
Higashi, T. (1995). *ABSCOR*. Rigaku Corporation, Tokyo, Japan.
Horikoshi, R. & Mikuriya, M. (2005). *Cryst. Growth Des.* pp. 223–230.
Horikoshi, R. & Mochida, T. (2006). *Coord. Chem. Rev.* **250**, 2595–2609.
Johnston, L. L., Brown, K. A., Martin, D. P. & LaDuca, R. L. (2008). *J. Mol. Struct.* **882**, 80–87.
Liu, J. Q., Wang, Y. Y., Ma, L. F., Zhang, W. H., Zeng, X. R., Shi, Q. Z. & Peng, S. M. (2008). *Inorg. Chim. Acta*, **361**, 2327–2334.
Ma, L. F., Wang, L. Y., Hu, J. L., Wang, Y. Y., Batten, S. R. & Wang, J. G. (2009). *CrystEngComm*, **11**, 777–783.

Ma, L. F., Wang, L. Y., Wang, Y. Y., Du, M. & Wang, J. G. (2009). *CrystEngComm*, **11**, 109–117.
Rigaku (1998). *RAPID-AUTO*. Rigaku Corporation, Tokyo, Japan.
Rigaku/MSC (2004). *CrystalStructure*. Rigaku/MSC Inc., The Woodlands, Texas, USA.
Sheldrick, G. M. (2008). *Acta Cryst.* A**64**, 112–122.

supplementary materials

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catena-Poly[[[(2-phenylacetato-κO)zinc(II)]bis[μ-4,4'-(disulfanediyl)dipyridine-$\kappa^2 N$:N']] monohydrate\]

J. Zhang and W. Xu

Comment

Recently, a variety of pyridyl-donor ligands have been widely employ to construct coordination polymers with intriguing topologies and unexpected properties (Biradha *et al.*, 2006; Liu *et al.*, 2008; Hernández-Ahuactzi *et al.*, 2008; Ma, Wang, Hu *et al.*, 2009). 4,4'-dipyridyl disulfide (bpds) is a bipyridyl-type ligand with a twisted structuret. Addtionally, bpds ligand has axial chirality. A number of coordination polymers containing bpds ligand have been reported (Horikoshi *et al.*, 2006; Carballo *et al.*, 2008; Ma, Wang, Wang *et al.*, 2009). Phenylacetic acid is one of the most common carboxylate ligands and can adopt different coordination modes (Johnston *et al.*, 2008). However, the coordination polymers based on mixed bpds and phenylacetate anion have not been reported to date. In this paper, we report the title Znic polymeric compound, $[\{Zn(bpds)_2(C_6H_5CH_2COO)_2\}.H_2O]_n$ with a 1D repeated rhomboidal chain structure. The unsymmetrical unit of the title compound consisits of one Zn^{2+} cation, two bpds molecules of the same chirality, two phenylacetate anions and one lattice water molecule (Fig.1).The *M*- and *P*- bpds molecules act as bis-monodentate bridging ligands with the C—S—S—C torsion angle being 97.10 (1)° and 93.40 (1)°, respectively, and the corresponding py ring planes form dihedral angles of 89.06 (6)° and 79.42 (6)°. Both crystallographically distinct phenylacetate anions monodentately coordinate to the metal atoms.The Zn atom has a distorted octahedral environment, being surrounded by two nitrogen atoms from two *M*-bpds and two nitrogen atoms from two *P*-bpds in the equatorial plane, and by two oxygen atoms from two crystallographically distinct phenylacetate anions occupying the axial positions. The corresponding bond distances range from 2.111 (2)Å to 2.202 (2) Å, and the bond angles in the region 84.12 (7)—175.94 (7)° deviate from the values of 90° and 180° for an ideal octahedron (table 1). Along the [110] direction, the two bpds ligands of the same chirality bridge Zn atoms to form 1D repeated rhomboidal chains(Fig. 2), which is similar with the structures of the reported zinc coordination polymers based on bpds ligand (Horikoshi *et al.*, 2005). The Zn···Zn separation through bpds ligands is 11.187 Å. The lattice water form hydrogen bonds to the uncoordinated carboxylate oxygen atoms of two different phenylacetate anions. In this way, the adjacent chains are linked by water molecules to give a ladder structure.

Experimental

0.0750 g (0.25 mmol) $Zn(NO_3)_2.6H_2O$ and 0.0345 g (0.25 mmol) phenylacetic acid were succesively dissolved in a stirred aqueous ethanolic solution consisting of 5 ml EtOH and 10 ml H_2O, to which 0.5 ml 1.0 M NaOH was added. The formed white suspension was stirred at 80°C for 30 min and then added was an ethanolic solution of 0.0570 g (0.25 mmol) 4,4'-dipyridyldisulfide in 5 ml EtOH. The final mixture was further stirred at 75°C for 1 h and filtered off. The colorless filtrate (pH=6.02) was left standing at room temperature for one week affording colorless block-like crystals (yield: 4 mg).

Refinement

H atoms bonded to C atoms were palced in geometrically calculated position and were refined using a riding model, with U_{iso}(H) = 1.2 Ueq(C). H atoms attached to O atoms were found in a difference Fourier synthesis and were refined using a riding model, with the O—H distances fixed as initially found and with U_{iso}(H) values set at 1.2 *U*eq(O).

Figures

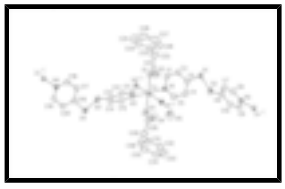


Fig. 1. View of the molecular of the title compound, Displacement ellipsoids are drawn at the 45% probability level.

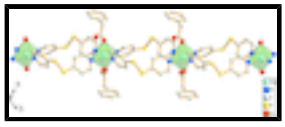


Fig. 2. 1D repeated rhomboidal chains in the title compound.

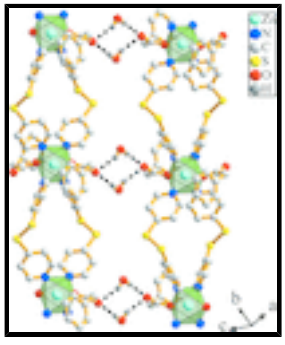


Fig. 3. The ladder structure of the title compound.

catena-Poly[[[(2-phenylacetato-κ*O*)zinc(II)]bis[μ-4,4'- (disulfanediyl)dipyridine-κ^2*N*:*N*']] monohydrate]

Crystal data

$[Zn(C_8H_7O_2)_2(C_{10}H_8N_2S_2)_2]\cdot H_2O$	$Z = 2$
$M_r = 794.27$	$F(000) = 820$
Triclinic, $P\overline{1}$	$D_x = 1.483$ Mg m^{-3}
Hall symbol: -P 1	Mo *K*α radiation, λ = 0.71073 Å
a = 9.851 (2) Å	Cell parameters from 16701 reflections
b = 11.130 (2) Å	θ = 3.1–27.5°
c = 18.319 (4) Å	μ = 0.97 mm^{-1}
α = 90.38 (3)°	*T* = 295 K
β = 98.88 (3)°	Block, colorless
γ = 115.89 (3)°	0.51 × 0.41 × 0.36 mm
V = 1779.0 (6) Å^3	

Data collection

Rigaku R-AXIS RAPID diffractometer	7859 independent reflections
Radiation source: fine-focus sealed tube	6036 reflections with $I > 2\sigma(I)$
graphite	$R_{int} = 0.038$
Detector resolution: 0 pixels mm^{-1}	$\theta_{max} = 27.5°$, $\theta_{min} = 3.1°$
ω scans	$h = -12 \rightarrow 12$
Absorption correction: multi-scan (*ABSCOR*; Higashi, 1995)	$k = -11 \rightarrow 14$
$T_{min} = 0.623$, $T_{max} = 0.701$	$l = -23 \rightarrow 23$
16701 measured reflections	

Refinement

Refinement on F^2	Primary atom site location: structure-invariant direct methods
Least-squares matrix: full	Secondary atom site location: difference Fourier map
$R[F^2 > 2\sigma(F^2)] = 0.035$	Hydrogen site location: inferred from neighbouring sites
$wR(F^2) = 0.092$	H-atom parameters constrained
$S = 1.07$	$w = 1/[\sigma^2(F_o^2) + (0.0395P)^2 + 0.3693P]$ where $P = (F_o^2 + 2F_c^2)/3$
7859 reflections	$(\Delta/\sigma)_{max} = 0.001$
451 parameters	$\Delta\rho_{max} = 0.43$ e Å^{-3}
0 restraints	$\Delta\rho_{min} = -0.34$ e Å^{-3}

Special details

Geometry. All esds (except the esd in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell esds are taken into account individually in the estimation of esds in distances, angles and torsion angles; correlations between esds in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell esds is used for estimating esds involving l.s. planes.

Refinement. Refinement of F^2 against ALL reflections. The weighted *R*-factor wR and goodness of fit *S* are based on F^2, conventional *R*-factors *R* are based on *F*, with *F* set to zero for negative F^2. The threshold expression of $F^2 > \sigma(F^2)$ is used only for calculating *R*-factors(gt) etc. and is not relevant to the choice of reflections for refinement. *R*-factors based on F^2 are statistically about twice as large as those based on *F*, and *R*- factors based on ALL data will be even larger.

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å^2)

	x	*y*	*z*	U_{iso}*/U_{eq}
Zn	0.42078 (3)	0.23364 (2)	0.254511 (13)	0.03328 (8)
N1	0.21801 (19)	0.10323 (18)	0.17515 (9)	0.0351 (4)
C1	0.1234 (2)	0.1508 (2)	0.14209 (11)	0.0353 (5)
H1A	0.1526	0.2422	0.1492	0.042*
C2	−0.0162 (2)	0.0710 (2)	0.09761 (12)	0.0355 (5)

H2A	−0.0790	0.1081	0.0755	0.043*
C3	−0.0604 (2)	−0.0650 (2)	0.08669 (11)	0.0336 (5)
C4	0.0375 (3)	−0.1155 (2)	0.12028 (14)	0.0457 (6)
H4A	0.0115	−0.2064	0.1141	0.055*
C5	0.1747 (3)	−0.0276 (2)	0.16317 (14)	0.0463 (6)
H5A	0.2407	−0.0617	0.1850	0.056*
S1	−0.24164 (6)	−0.16230 (6)	0.03032 (3)	0.03988 (14)
S2	−0.24204 (6)	−0.34128 (6)	0.00746 (3)	0.04027 (14)
C6	−0.3406 (2)	−0.4474 (2)	0.07251 (11)	0.0344 (5)
C7	−0.3961 (3)	−0.4103 (2)	0.12877 (13)	0.0476 (6)
H7A	−0.3824	−0.3226	0.1357	0.057*
C8	−0.4725 (3)	−0.5053 (2)	0.17481 (13)	0.0466 (6)
H8A	−0.5116	−0.4795	0.2118	0.056*
N2	−0.4932 (2)	−0.63104 (18)	0.16917 (9)	0.0339 (4)
C9	−0.4425 (2)	−0.6675 (2)	0.11302 (12)	0.0377 (5)
H9A	−0.4595	−0.7563	0.1069	0.045*
C10	−0.3665 (2)	−0.5801 (2)	0.06409 (12)	0.0377 (5)
H10A	−0.3330	−0.6094	0.0260	0.045*
N3	0.61670 (19)	0.37405 (18)	0.33457 (10)	0.0355 (4)
C11	0.5949 (2)	0.4081 (2)	0.40060 (12)	0.0358 (5)
H11A	0.4977	0.3640	0.4128	0.043*
C12	0.7090 (2)	0.5050 (2)	0.45119 (12)	0.0359 (5)
H12A	0.6889	0.5262	0.4962	0.043*
C13	0.8547 (2)	0.5704 (2)	0.43370 (11)	0.0335 (5)
C14	0.8780 (2)	0.5378 (2)	0.36502 (12)	0.0398 (5)
H14A	0.9735	0.5818	0.3509	0.048*
C15	0.7571 (2)	0.4390 (2)	0.31818 (12)	0.0415 (5)
H15A	0.7740	0.4163	0.2726	0.050*
S3	0.99682 (6)	0.69153 (6)	0.50235 (3)	0.04202 (15)
S4	1.20007 (6)	0.72797 (6)	0.47202 (3)	0.04384 (15)
C16	1.2462 (2)	0.8675 (2)	0.41869 (11)	0.0339 (5)
C17	1.1450 (2)	0.9135 (2)	0.38416 (12)	0.0379 (5)
H17A	1.0420	0.8714	0.3883	0.046*
C18	1.2001 (2)	1.0225 (2)	0.34368 (13)	0.0402 (5)
H18A	1.1317	1.0540	0.3214	0.048*
N4	1.34608 (19)	1.08651 (18)	0.33422 (10)	0.0357 (4)
C19	1.4430 (2)	1.0421 (2)	0.36901 (12)	0.0393 (5)
H19A	1.5457	1.0869	0.3644	0.047*
C20	1.3994 (2)	0.9344 (2)	0.41103 (12)	0.0381 (5)
H20A	1.4707	0.9066	0.4339	0.046*
O1	0.29666 (17)	0.33877 (16)	0.27800 (8)	0.0414 (4)
O2	0.2410 (2)	0.3097 (2)	0.39220 (9)	0.0544 (5)
C21	0.2319 (3)	0.3518 (2)	0.33031 (13)	0.0389 (5)
C22	0.1335 (4)	0.4250 (4)	0.31603 (16)	0.0678 (9)
H22A	0.0295	0.3630	0.3204	0.081*
H22B	0.1692	0.4966	0.3551	0.081*
C23	0.1282 (3)	0.4843 (3)	0.24333 (15)	0.0494 (6)
C24	0.2307 (3)	0.6123 (3)	0.23429 (19)	0.0666 (8)
H24A	0.3012	0.6656	0.2750	0.080*

C25	0.2315 (5)	0.6642 (4)	0.1657 (2)	0.0866 (11)
H25A	0.3032	0.7509	0.1605	0.104*
C26	0.1280 (6)	0.5887 (6)	0.1063 (2)	0.0942 (13)
H26A	0.1294	0.6230	0.0601	0.113*
C27	0.0224 (5)	0.4634 (5)	0.1139 (2)	0.0892 (12)
H27A	−0.0500	0.4121	0.0732	0.107*
C28	0.0224 (4)	0.4120 (3)	0.18197 (19)	0.0687 (8)
H28A	−0.0513	0.3259	0.1866	0.082*
O3	0.57013 (19)	0.14005 (17)	0.23618 (8)	0.0453 (4)
O4	0.5095 (3)	0.0218 (2)	0.12864 (11)	0.0731 (6)
C29	0.5861 (3)	0.0632 (2)	0.19184 (13)	0.0426 (5)
C30	0.7158 (4)	0.0237 (3)	0.21550 (17)	0.0652 (8)
H30A	0.7119	−0.0377	0.1765	0.078*
H30B	0.8123	0.1035	0.2188	0.078*
C31	0.7172 (3)	−0.0404 (3)	0.28744 (15)	0.0469 (6)
C32	0.6281 (3)	−0.1760 (3)	0.28977 (17)	0.0618 (7)
H32A	0.5654	−0.2267	0.2466	0.074*
C33	0.6295 (4)	−0.2379 (3)	0.35429 (19)	0.0706 (8)
H33A	0.5680	−0.3294	0.3543	0.085*
C34	0.7211 (4)	−0.1654 (3)	0.41871 (18)	0.0663 (8)
H34A	0.7226	−0.2070	0.4625	0.080*
C35	0.8096 (4)	−0.0319 (3)	0.41752 (18)	0.0669 (8)
H35A	0.8717	0.0182	0.4610	0.080*
C36	0.8088 (3)	0.0305 (3)	0.35277 (17)	0.0605 (7)
H36A	0.8710	0.1219	0.3532	0.073*
O5	0.3132 (3)	−0.1386 (2)	−0.00858 (12)	0.0856 (7)
H5C	0.3720	−0.0885	−0.0334	0.128*
H5D	0.3676	−0.1044	0.0305	0.128*

Atomic displacement parameters (Å^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Zn	0.03625 (14)	0.03132 (15)	0.02738 (13)	0.01058 (10)	0.00539 (10)	0.00328 (10)
N1	0.0369 (9)	0.0334 (10)	0.0314 (9)	0.0130 (8)	0.0037 (7)	0.0012 (8)
C1	0.0399 (11)	0.0305 (12)	0.0318 (11)	0.0115 (9)	0.0082 (9)	0.0051 (9)
C2	0.0368 (11)	0.0356 (13)	0.0333 (11)	0.0150 (9)	0.0071 (9)	0.0074 (9)
C3	0.0330 (10)	0.0357 (12)	0.0280 (10)	0.0101 (9)	0.0095 (8)	0.0065 (9)
C4	0.0469 (13)	0.0306 (13)	0.0532 (15)	0.0148 (10)	−0.0018 (11)	−0.0016 (11)
C5	0.0451 (13)	0.0415 (15)	0.0502 (15)	0.0213 (11)	−0.0035 (11)	−0.0019 (11)
S1	0.0346 (3)	0.0371 (3)	0.0383 (3)	0.0079 (2)	0.0035 (2)	0.0064 (2)
S2	0.0414 (3)	0.0367 (3)	0.0326 (3)	0.0064 (2)	0.0119 (2)	0.0028 (2)
C6	0.0305 (10)	0.0361 (12)	0.0299 (11)	0.0087 (8)	0.0052 (8)	0.0044 (9)
C7	0.0703 (16)	0.0278 (12)	0.0451 (14)	0.0171 (11)	0.0255 (12)	0.0053 (10)
C8	0.0664 (16)	0.0365 (14)	0.0415 (13)	0.0211 (11)	0.0271 (12)	0.0061 (11)
N2	0.0400 (9)	0.0293 (10)	0.0302 (9)	0.0128 (7)	0.0085 (7)	0.0043 (7)
C9	0.0453 (12)	0.0363 (13)	0.0319 (11)	0.0186 (10)	0.0064 (9)	0.0033 (9)
C10	0.0437 (12)	0.0403 (13)	0.0323 (11)	0.0198 (10)	0.0117 (9)	0.0034 (10)
N3	0.0365 (9)	0.0358 (11)	0.0327 (10)	0.0151 (8)	0.0049 (7)	0.0008 (8)

C11	0.0371 (11)	0.0359 (12)	0.0329 (11)	0.0138 (9)	0.0086 (9)	0.0051 (9)
C12	0.0457 (12)	0.0333 (12)	0.0289 (11)	0.0169 (9)	0.0088 (9)	0.0050 (9)
C13	0.0400 (11)	0.0277 (11)	0.0313 (11)	0.0148 (9)	0.0026 (9)	0.0064 (9)
C14	0.0337 (11)	0.0425 (14)	0.0389 (12)	0.0129 (9)	0.0066 (9)	0.0007 (10)
C15	0.0382 (12)	0.0495 (15)	0.0356 (12)	0.0177 (10)	0.0084 (9)	−0.0034 (10)
S3	0.0443 (3)	0.0374 (3)	0.0313 (3)	0.0071 (2)	0.0037 (2)	0.0024 (2)
S4	0.0408 (3)	0.0383 (3)	0.0477 (3)	0.0154 (2)	0.0009 (2)	0.0144 (3)
C16	0.0394 (11)	0.0294 (12)	0.0305 (11)	0.0140 (9)	0.0036 (9)	0.0038 (9)
C17	0.0320 (11)	0.0377 (13)	0.0421 (13)	0.0129 (9)	0.0085 (9)	0.0107 (10)
C18	0.0376 (11)	0.0454 (14)	0.0421 (13)	0.0218 (10)	0.0088 (10)	0.0140 (11)
N4	0.0365 (9)	0.0342 (10)	0.0350 (10)	0.0136 (8)	0.0084 (8)	0.0078 (8)
C19	0.0312 (10)	0.0495 (15)	0.0341 (12)	0.0149 (10)	0.0062 (9)	0.0055 (10)
C20	0.0348 (11)	0.0452 (14)	0.0362 (12)	0.0203 (10)	0.0035 (9)	0.0070 (10)
O1	0.0494 (9)	0.0504 (10)	0.0324 (8)	0.0286 (8)	0.0101 (7)	0.0016 (7)
O2	0.0647 (11)	0.0735 (13)	0.0402 (10)	0.0405 (10)	0.0204 (8)	0.0146 (9)
C21	0.0413 (12)	0.0386 (13)	0.0377 (12)	0.0171 (10)	0.0113 (10)	0.0019 (10)
C22	0.092 (2)	0.087 (2)	0.0610 (18)	0.0650 (19)	0.0367 (17)	0.0286 (16)
C23	0.0567 (15)	0.0557 (17)	0.0517 (15)	0.0366 (13)	0.0176 (12)	0.0113 (13)
C24	0.0659 (18)	0.060 (2)	0.073 (2)	0.0278 (15)	0.0109 (15)	0.0058 (16)
C25	0.103 (3)	0.067 (2)	0.111 (3)	0.048 (2)	0.043 (3)	0.041 (2)
C26	0.134 (4)	0.133 (4)	0.068 (2)	0.102 (3)	0.028 (3)	0.033 (3)
C27	0.093 (3)	0.123 (4)	0.065 (2)	0.068 (3)	−0.0098 (19)	−0.012 (2)
C28	0.0663 (18)	0.060 (2)	0.081 (2)	0.0295 (15)	0.0121 (16)	−0.0011 (17)
O3	0.0613 (10)	0.0496 (10)	0.0361 (9)	0.0325 (8)	0.0156 (8)	0.0069 (8)
O4	0.0900 (15)	0.0695 (15)	0.0499 (12)	0.0298 (11)	0.0025 (10)	−0.0152 (10)
C29	0.0546 (14)	0.0338 (13)	0.0398 (13)	0.0164 (10)	0.0189 (11)	0.0083 (10)
C30	0.080 (2)	0.072 (2)	0.0706 (19)	0.0493 (17)	0.0411 (16)	0.0242 (16)
C31	0.0523 (14)	0.0432 (15)	0.0565 (15)	0.0286 (11)	0.0183 (12)	0.0071 (12)
C32	0.0708 (18)	0.0469 (17)	0.0577 (18)	0.0215 (14)	−0.0027 (14)	−0.0036 (14)
C33	0.086 (2)	0.0390 (17)	0.078 (2)	0.0230 (14)	0.0032 (17)	0.0111 (15)
C34	0.081 (2)	0.075 (2)	0.0628 (19)	0.0527 (18)	0.0094 (16)	0.0146 (17)
C35	0.0722 (19)	0.070 (2)	0.0612 (19)	0.0390 (17)	−0.0052 (15)	−0.0109 (16)
C36	0.0598 (16)	0.0419 (16)	0.075 (2)	0.0192 (12)	0.0097 (14)	−0.0055 (15)
O5	0.0779 (14)	0.0842 (17)	0.0699 (15)	0.0144 (12)	0.0105 (11)	−0.0102 (12)

Geometric parameters (Å, °)

Zn—O1	2.1105 (15)	C17—C18	1.371 (3)
Zn—N4^{i}	2.160 (2)	C17—H17A	0.9300
Zn—N1	2.180 (2)	C18—N4	1.338 (3)
Zn—N2^{ii}	2.1808 (19)	C18—H18A	0.9300
Zn—N3	2.186 (2)	N4—C19	1.338 (3)
Zn—O3	2.2019 (16)	N4—Zn^{ii}	2.160 (2)
N1—C5	1.332 (3)	C19—C20	1.371 (3)
N1—C1	1.333 (3)	C19—H19A	0.9300
C1—C2	1.386 (3)	C20—H20A	0.9300
C1—H1A	0.9300	O1—C21	1.270 (2)
C2—C3	1.383 (3)	O2—C21	1.235 (3)

C2—H2A	0.9300	C21—C22	1.512 (4)
C3—C4	1.385 (3)	C22—C23	1.494 (4)
C3—S1	1.776 (2)	C22—H22A	0.9700
C4—C5	1.381 (3)	C22—H22B	0.9700
C4—H4A	0.9300	C23—C24	1.369 (4)
C5—H5A	0.9300	C23—C28	1.375 (4)
S1—S2	2.0311 (10)	C24—C25	1.387 (5)
S2—C6	1.770 (2)	C24—H24A	0.9300
C6—C7	1.377 (3)	C25—C26	1.351 (6)
C6—C10	1.387 (3)	C25—H25A	0.9300
C7—C8	1.381 (3)	C26—C27	1.351 (6)
C7—H7A	0.9300	C26—H26A	0.9300
C8—N2	1.324 (3)	C27—C28	1.376 (5)
C8—H8A	0.9300	C27—H27A	0.9300
N2—C9	1.343 (3)	C28—H28A	0.9300
N2—Zn^{i}	2.1808 (19)	O3—C29	1.251 (3)
C9—C10	1.376 (3)	O4—C29	1.242 (3)
C9—H9A	0.9300	C29—C30	1.528 (4)
C10—H10A	0.9300	C30—C31	1.504 (4)
N3—C15	1.335 (3)	C30—H30A	0.9700
N3—C11	1.341 (3)	C30—H30B	0.9700
C11—C12	1.375 (3)	C31—C36	1.379 (4)
C11—H11A	0.9300	C31—C32	1.380 (4)
C12—C13	1.387 (3)	C32—C33	1.373 (4)
C12—H12A	0.9300	C32—H32A	0.9300
C13—C14	1.387 (3)	C33—C34	1.372 (4)
C13—S3	1.773 (2)	C33—H33A	0.9300
C14—C15	1.376 (3)	C34—C35	1.357 (4)
C14—H14A	0.9300	C34—H34A	0.9300
C15—H15A	0.9300	C35—C36	1.379 (4)
S3—S4	2.0294 (10)	C35—H35A	0.9300
S4—C16	1.764 (2)	C36—H36A	0.9300
C16—C17	1.382 (3)	O5—H5C	0.8098
C16—C20	1.392 (3)	O5—H5D	0.8029
O1—Zn—N4^{i}	97.17 (7)	C17—C16—S4	126.14 (17)
O1—Zn—N1	87.04 (7)	C20—C16—S4	115.38 (17)
N4^{i}—Zn—N1	88.63 (7)	C18—C17—C16	118.5 (2)
O1—Zn—N2^{ii}	88.99 (7)	C18—C17—H17A	120.7
N4^{i}—Zn—N2^{ii}	173.74 (7)	C16—C17—H17A	120.7
N1—Zn—N2^{ii}	90.57 (7)	N4—C18—C17	124.0 (2)
O1—Zn—N3	88.99 (7)	N4—C18—H18A	118.0
N4^{i}—Zn—N3	92.71 (7)	C17—C18—H18A	118.0
N1—Zn—N3	175.94 (7)	C19—N4—C18	116.7 (2)
N2^{ii}—Zn—N3	88.51 (7)	C19—N4—Zn^{ii}	119.65 (14)
O1—Zn—O3	174.45 (6)	C18—N4—Zn^{ii}	122.96 (15)
N4^{i}—Zn—O3	84.12 (7)	N4—C19—C20	123.7 (2)
N1—Zn—O3	98.39 (7)	N4—C19—H19A	118.2

$N2^{ii}$—Zn—O3	89.85 (7)	C20—C19—H19A	118.2
N3—Zn—O3	85.56 (7)	C19—C20—C16	118.6 (2)
C5—N1—C1	117.18 (19)	C19—C20—H20A	120.7
C5—N1—Zn	122.60 (15)	C16—C20—H20A	120.7
C1—N1—Zn	119.88 (15)	C21—O1—Zn	137.60 (16)
N1—C1—C2	123.3 (2)	O2—C21—O1	126.2 (2)
N1—C1—H1A	118.4	O2—C21—C22	116.3 (2)
C2—C1—H1A	118.4	O1—C21—C22	117.5 (2)
C3—C2—C1	118.7 (2)	C23—C22—C21	117.5 (2)
C3—C2—H2A	120.6	C23—C22—H22A	107.9
C1—C2—H2A	120.6	C21—C22—H22A	107.9
C2—C3—C4	118.5 (2)	C23—C22—H22B	107.9
C2—C3—S1	116.61 (17)	C21—C22—H22B	107.9
C4—C3—S1	124.88 (18)	H22A—C22—H22B	107.2
C5—C4—C3	118.4 (2)	C24—C23—C28	116.9 (3)
C5—C4—H4A	120.8	C24—C23—C22	121.5 (3)
C3—C4—H4A	120.8	C28—C23—C22	121.6 (3)
N1—C5—C4	123.9 (2)	C23—C24—C25	121.4 (3)
N1—C5—H5A	118.1	C23—C24—H24A	119.3
C4—C5—H5A	118.1	C25—C24—H24A	119.3
C3—S1—S2	104.60 (9)	C26—C25—C24	119.9 (4)
C6—S2—S1	105.51 (8)	C26—C25—H25A	120.1
C7—C6—C10	118.0 (2)	C24—C25—H25A	120.1
C7—C6—S2	125.76 (19)	C25—C26—C27	120.2 (4)
C10—C6—S2	116.21 (16)	C25—C26—H26A	119.9
C6—C7—C8	119.0 (2)	C27—C26—H26A	119.9
C6—C7—H7A	120.5	C26—C27—C28	119.8 (4)
C8—C7—H7A	120.5	C26—C27—H27A	120.1
N2—C8—C7	123.7 (2)	C28—C27—H27A	120.1
N2—C8—H8A	118.2	C23—C28—C27	121.9 (3)
C7—C8—H8A	118.2	C23—C28—H28A	119.1
C8—N2—C9	117.00 (19)	C27—C28—H28A	119.1
$C8—N2—Zn^{i}$	121.68 (14)	C29—O3—Zn	143.09 (17)
$C9—N2—Zn^{i}$	120.90 (15)	O4—C29—O3	125.0 (2)
N2—C9—C10	123.3 (2)	O4—C29—C30	117.4 (2)
N2—C9—H9A	118.4	O3—C29—C30	117.5 (2)
C10—C9—H9A	118.4	C31—C30—C29	117.2 (2)
C9—C10—C6	118.9 (2)	C31—C30—H30A	108.0
C9—C10—H10A	120.5	C29—C30—H30A	108.0
C6—C10—H10A	120.5	C31—C30—H30B	108.0
C15—N3—C11	117.28 (19)	C29—C30—H30B	108.0
C15—N3—Zn	122.71 (14)	H30A—C30—H30B	107.3
C11—N3—Zn	119.66 (14)	C36—C31—C32	117.1 (3)
N3—C11—C12	123.3 (2)	C36—C31—C30	122.5 (3)
N3—C11—H11A	118.4	C32—C31—C30	120.3 (3)
C12—C11—H11A	118.4	C33—C32—C31	121.7 (3)
C11—C12—C13	118.72 (19)	C33—C32—H32A	119.2
C11—C12—H12A	120.6	C31—C32—H32A	119.2

C13—C12—H12A	120.6	C34—C33—C32	120.3 (3)
C14—C13—C12	118.5 (2)	C34—C33—H33A	119.9
C14—C13—S3	125.30 (17)	C32—C33—H33A	119.9
C12—C13—S3	116.18 (16)	C35—C34—C33	118.9 (3)
C15—C14—C13	118.6 (2)	C35—C34—H34A	120.6
C15—C14—H14A	120.7	C33—C34—H34A	120.6
C13—C14—H14A	120.7	C34—C35—C36	120.9 (3)
N3—C15—C14	123.5 (2)	C34—C35—H35A	119.5
N3—C15—H15A	118.2	C36—C35—H35A	119.5
C14—C15—H15A	118.2	C31—C36—C35	121.1 (3)
C13—S3—S4	105.43 (8)	C31—C36—H36A	119.5
C16—S4—S3	106.12 (8)	C35—C36—H36A	119.5
C17—C16—C20	118.5 (2)	H5C—O5—H5D	95.1

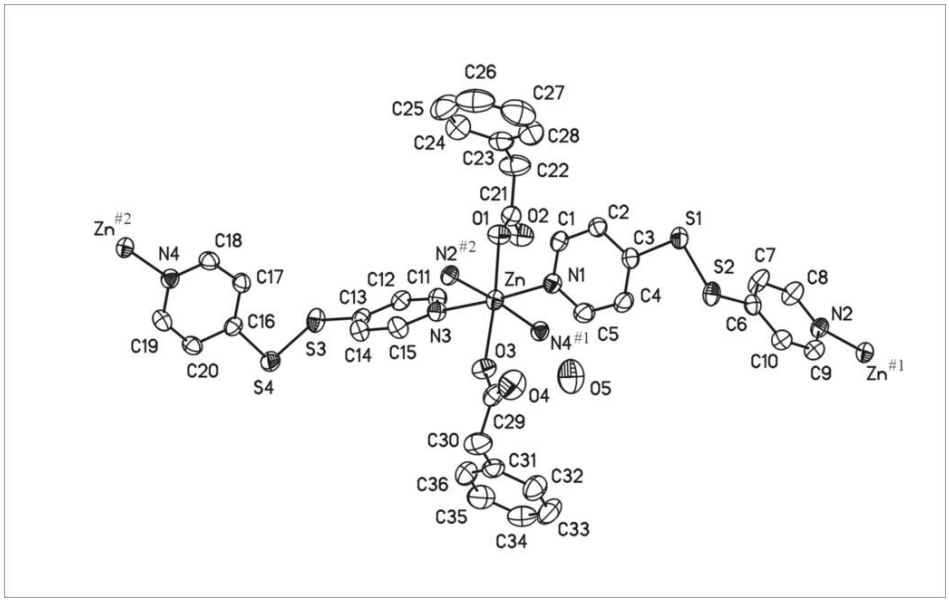
Symmetry codes: (i) $x-1, y-1, z$; (ii) $x+1, y+1, z$.

Hydrogen-bond geometry (Å, °)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
O5—H5c···O4^{iii}	0.81	2.20	2.970 (3)	158
O5—H5d···O4	0.80	2.15	2.945 (3)	169

Symmetry codes: (iii) $-x+1, -y, -z$.

Fig. 1


C26
C27
C25
C28
C24
C23
C22
C21
O1
O2
C1
C2
S1
Zn#2
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C18
N2#2
C3
C7
C17
C12
C11
Zn
N1
S2
C8
C13
C4
C16
C6
N2
N3
N4#1
C5
C19
S3
C14
C15
O3
C10
C9
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O5
C29
C30
C31
C32
C36
C35
C33
C34

Fig. 2

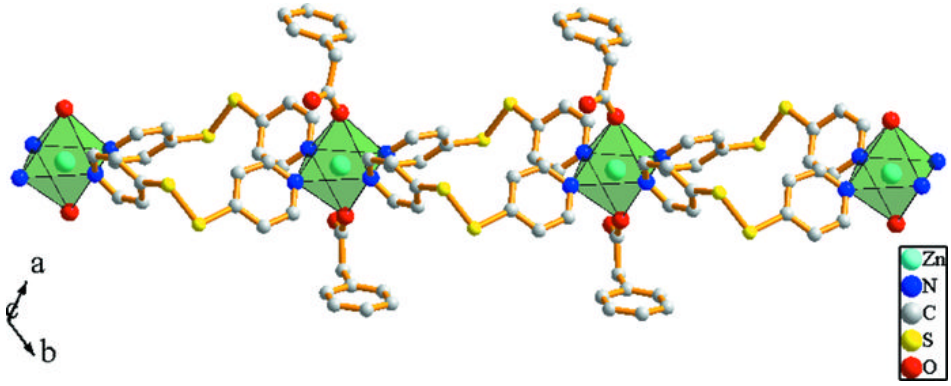
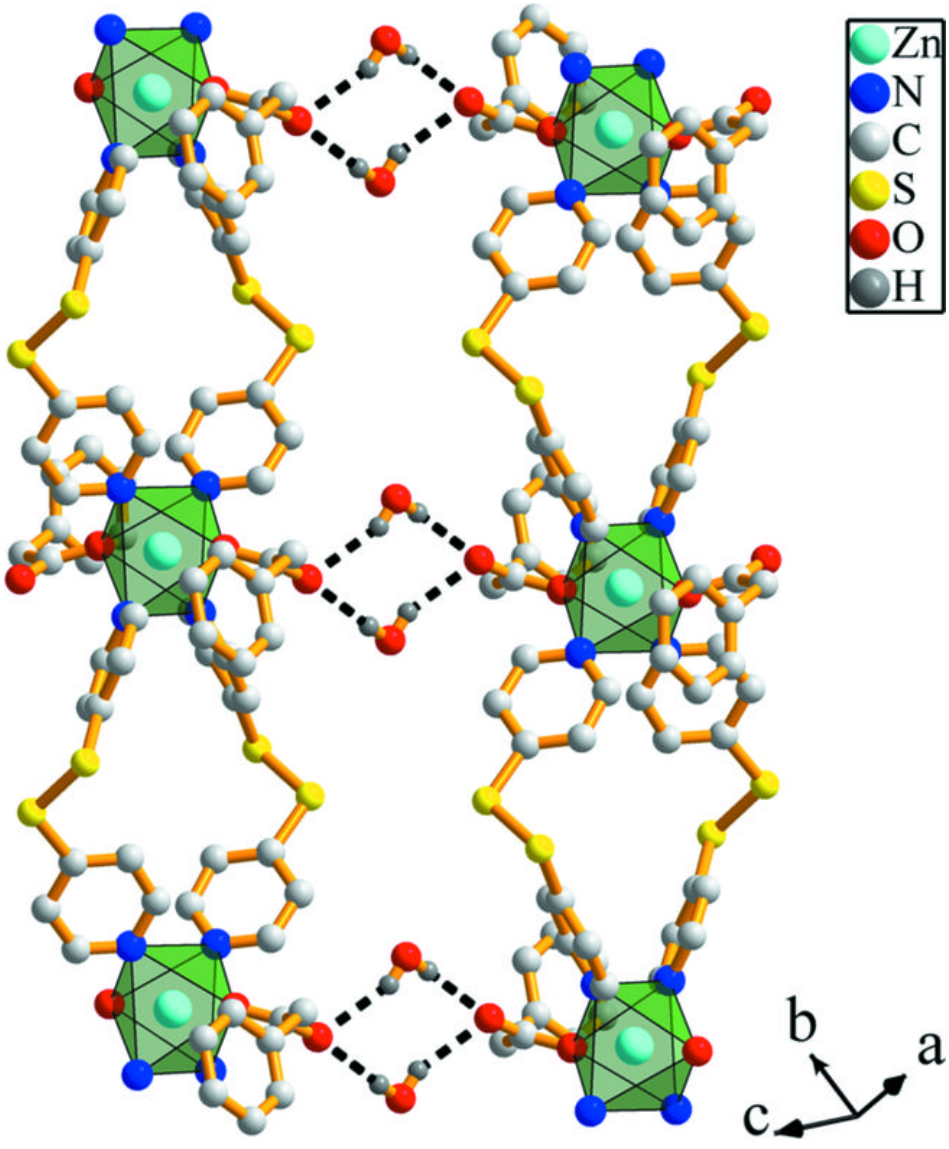


Fig. 3



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catena-Poly[[dichloridozinc(II)]-μ-1,1′-(butane-1,4-diyl)diimidazole-$\kappa^2N^3:N^{3'}$]

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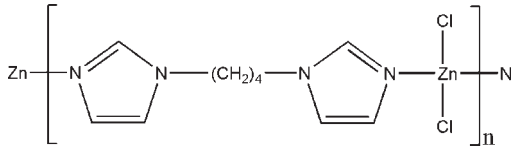
Key indicators: single-crystal X-ray study; T = 185 K; mean σ(C–C) = 0.007 Å; R factor = 0.051; wR factor = 0.107; data-to-parameter ratio = 18.3.

The title compound, $[ZnCl_2(C_{10}H_{14}N_4)]_n$, is a coordination polymer consisting of zigzag chains propagating in [001], in which the metal cation exhibits a distorted tetrahedral $ZnCl_2N_2$ coordination. Adjacent chains are linked by intermolecular C—H···Cl hydrogen bonds, forming a three-dimensional supramolecular network.

Related literature

For general background to metal complexes of *N*-heterocyclic compounds, see: Hu *et al.* (2003); Ohmori *et al.* (2005); Chen *et al.* (2004); Hu *et al.* (2005). For related structures, see: Li *et al.* (2006); Liu *et al.* (2007); Jin *et al.* (2007); Yang *et al.* (2009); Qi *et al.* (2008).



Experimental

Crystal data

$[ZnCl_2(C_{10}H_{14}N_4)]$
M_r = 326.52
Monoclinic, $P2_1/c$
a = 7.8090 (9) Å
b = 11.6001 (13) Å
c = 15.8047 (18) Å
β = 92.908 (2)°
V = 1429.8 (3) Å^3
Z = 4
Mo $K\alpha$ radiation
μ = 2.08 mm^{-1}
T = 185 K
0.29 × 0.22 × 0.15 mm

Data collection

Bruker SMART APEX CCD diffractometer
Absorption correction: multi-scan (*SADABS*; Sheldrick, 1996)
T_{min} = 0.585, T_{max} = 0.742
7827 measured reflections
2820 independent reflections
2174 reflections with $I > 2\sigma(I)$
R_{int} = 0.054

Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.051
$wR(F^2)$ = 0.107
S = 1.06
2820 reflections
154 parameters
H-atom parameters constrained
$\Delta\rho_{max}$ = 0.68 e Å^{-3}
$\Delta\rho_{min}$ = −0.36 e Å^{-3}

Table 1
Hydrogen-bond geometry (Å, °).

D—H···A	D—H	H···A	D···A	D—H···A
C3—H3···Cl1^{i}	0.93	2.63	3.538 (2)	166
C5—H5···Cl2^{ii}	0.93	2.78	3.599 (5)	147

Symmetry codes: (i) $-x+1, y+\frac{1}{2}, -z+\frac{1}{2}$; (ii) $x, -y+\frac{3}{2}, z+\frac{1}{2}$.

Data collection: *SMART* (Bruker, 2007); cell refinement: *SAINT* (Bruker, 2007); data reduction: *SAINT*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *SHELXTL* (Sheldrick, 2008) and *Mercury* (Macrae *et al.*, 2006); software used to prepare material for publication: *SHELXTL*.

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Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: EZ2200).

References

Bruker (2007). *SMART* and *SAINT*. Bruker AXS Inc., Madison, Wisconsin, USA.
Chen, Y.-B., Kang, Y., Qin, Y.-Y., Li, Z.-J., Cheng, J.-K., Hu, R.-F., Wen, Y.-H. & Yao, Y.-G. (2004). *Acta Cryst.* C**60**, m168–m169.
Hu, S., Chen, J.-C., Tong, M.-L., Wang, B., Yan, Y.-X. & Batten, S. R. (2005). *Angew. Chem. Int. Ed.* **44**, 5471–5475.
Hu, X.-L., Tang, Y.-J., Gantzel, P. & Meyer, K. (2003). *J. Am. Chem. Soc.* **22**, 612–614.
Jin, S.-W., Wang, D.-Q. & Chen, W.-Z. (2007). *Inorg. Chem. Commun.* **10**, 685–689.
Li, F.-F., Ma, J.-F., Song, S.-Y., Yang, J., Jia, H. Q. & Hu, N.-H. (2006). *Cryst. Growth Des.* **6**, 209–215.
Liu, Y.-Y., Ma, J.-F. & Zhang, L.-P. (2007). *Acta Cryst.* E**63**, m2317.
Macrae, C. F., Edgington, P. R., McCabe, P., Pidcock, E., Shields, G. P., Taylor, R., Towler, M. & van de Streek, J. (2006). *J. Appl. Cryst.* **39**, 453–457.
Ohmori, O., Kawano, M. & Fujita, M. (2005). *Angew. Chem. Int. Ed.* **44**, 1962–1964.
Qi, Y., Luo, F., Batten, S. R., Che, Y.-X. & Zheng, J.-M. (2008). *Cryst. Growth Des.* **8**, 2806–2813.
Sheldrick, G. M. (1996). *SADABS*. University of Göttingen, Germany.
Sheldrick, G. M. (2008). *Acta Cryst.* A**64**, 112–122.
Yang, J., Ma, J.-F., Liu, Y.-Y. & Batten, S. R. (2009). *CrystEngComm*, **11**, 151–159.

supplementary materials

Acta Cryst. (2010). E**66**, m750 [**doi:10.1107/S1600536810018246**]

catena-Poly[[dichloridozinc(II)]-μ-1,1'-(butane-1,4-diyl)diimidazole-$\kappa^2N^3:N^{3'}$]

R.-L. He, F.-J. Meng, G.-H. Wang, W. Yang and J.-W. Xu

Comment

N-heterocyclic compounds have been extensively studied in coordination chemistry research for their excellent bridging ability (Hu *et al.*, 2003; Ohmori *et al.*, 2005; Chen *et al.*, 2004; Hu *et al.*, 2005). The compound 1,1'-(1,4-butanediyl)bis(imidazole) (bbi), as a flexible nitrogenous ligand with a long -$CH_2CH_2CH_2CH_2$- spacer, can link discrete clusters into an extended network and is a good candidate to form highly connected 3D frameworks. A number of metal-bbi coordination polymers have been reported (Li *et al.*, 2006; Liu *et al.*, 2007; Jin *et al.*, 2007; Yang *et al.*, 2009; Qi *et al.*, 2008). Here we present a new polymeric compound, $[ZnCl_2(bbi)]_n$, (I), with a zigzag chain structure, synthesized under solvothermal conditions.

In the title compound, (I), the Zn centers are four-coordinated by two N atoms from two bbi ligands [Zn(1)—N(1) = 2.005 (3) Å and Zn(1)—N(3) = 2.013 (3) Å] and two Cl atoms [Zn(1)—Cl(1) = 2.2557 (11) Å and Zn(1)—Cl(2) =2.2321 (12) Å], resulting in a distorted tetrahedral geometry (Fig. 1). Each bbi coordinates to two Zn atoms through its two aromatic N atoms and acts as a bridging bidentate ligand to form a one-dimensional zigzag chain (Fig. 2). The adjacent Zn···Zn distance is 14.290 Å, which is similar to that observed in $[Cu_2(bbi)_2Cl_2]$ (Qi *et al.*, 2008). In addition, these one-dimensional chains are further connected by weak intermolecular C—H···Cl hydrogen bonds to construct a three-dimensional supramolecular network (Fig. 2).

Experimental

The title compound was solvothermally prepared from a reaction mixture of $ZnCl_2$ (0.3 mmol), bbi (0.1 mmol), ethanol (3 ml) and distilled water (7 ml); the pH value was adjusted to 4.5 with triethylamine and acetic acid. The mixture was stirred for 20 min at room temperature, then sealed in a 20 ml teflon-lined stainless steel autoclave and heated at 433 K for 72 h under autogenous pressure. After cooling to room temperature, colorless block crystals were obtained (yield 83% based on Zn).

Refinement

H atoms were positioned geometrically and refined with fixed individual displacement parameters [$U_{iso}(H) = 1.2U_{eq}(C)$], using a riding model, with C—H distances of 0.93 Å for Csp^2 and 0.97 Å for CH_2.

Figures

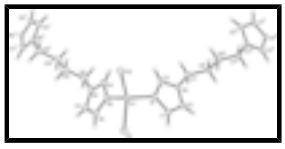


Fig. 1. Partial molecular structure of the title compound showing the atom numbering scheme. Displacement ellipsoids are drawn at the 30% probability level. Atoms marked with i or ii are at the symmetry positions (x+2, y+5/2, 3/2-z) and (x, y+5/2, 1/2-z) respectively.

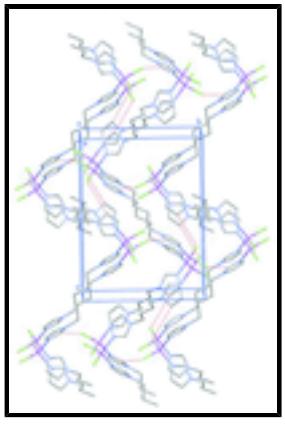


Fig. 2. The zigzag polymeric chain structure of the title compound. Dashed lines denote hydrogen bonds.

catena-Poly[[dichloridozinc(II)]-μ-1,1'-(butane-1,4-diyl)diimidazole- $\kappa^2N^3:N^{3'}$]

Crystal data

$[ZnCl_2(C_{10}H_{14}N_4)]$	$F(000) = 664$
$M_r = 326.52$	$D_x = 1.517$ Mg m^{-3}
Monoclinic, $P2_1/c$	Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å
Hall symbol: -P 2ybc	Cell parameters from 2763 reflections
$a = 7.8090$ (9) Å	$\theta = 2.2$–$26.1°$
$b = 11.6001$ (13) Å	$\mu = 2.08$ mm^{-1}
$c = 15.8047$ (18) Å	$T = 185$ K
$\beta = 92.908$ (2)°	Block, colorless
$V = 1429.8$ (3) Å^3	0.29 × 0.22 × 0.15 mm
$Z = 4$	

Data collection

Bruker SMART APEX CCD diffractometer	2820 independent reflections
Radiation source: fine-focus sealed tube	2174 reflections with $I > 2\sigma(I)$
graphite	$R_{int} = 0.054$
φ and ω scans	$\theta_{max} = 26.1°$, $\theta_{min} = 2.2°$
Absorption correction: multi-scan (*SADABS*; Sheldrick, 1996)	$h = -9 \rightarrow 9$
$T_{min} = 0.585$, $T_{max} = 0.742$	$k = -11 \rightarrow 14$
7827 measured reflections	$l = -19 \rightarrow 19$

Refinement

Refinement on F^2	Primary atom site location: structure-invariant direct methods
Least-squares matrix: full	Secondary atom site location: difference Fourier map
$R[F^2 > 2\sigma(F^2)] = 0.051$	Hydrogen site location: inferred from neighbouring sites
$wR(F^2) = 0.107$	H-atom parameters constrained

S = 1.06	$w = 1/[\sigma^2(F_o^2) + (0.0437P)^2 + 0.2952P]$ where $P = (F_o^2 + 2F_c^2)/3$
2820 reflections	$(\Delta/\sigma)_{max} < 0.001$
154 parameters	$\Delta\rho_{max} = 0.68$ e Å^{-3}
0 restraints	$\Delta\rho_{min} = -0.36$ e Å^{-3}

Special details

Geometry. All esds (except the esd in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell esds are taken into account individually in the estimation of esds in distances, angles and torsion angles; correlations between esds in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell esds is used for estimating esds involving l.s. planes.

Refinement. Refinement of F^2 against ALL reflections. The weighted *R*-factor wR and goodness of fit *S* are based on F^2, conventional *R*-factors *R* are based on *F*, with *F* set to zero for negative F^2. The threshold expression of $F^2 > \sigma(F^2)$ is used only for calculating *R*-factors(gt) etc. and is not relevant to the choice of reflections for refinement. *R*-factors based on F^2 are statistically about twice as large as those based on *F*, and *R*- factors based on ALL data will be even larger.

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å^2)

	x	*y*	*z*	U_{iso}*/U_{eq}
Zn1	0.46384 (6)	0.61215 (4)	0.27801 (3)	0.02355 (16)
Cl1	0.33311 (13)	0.46729 (9)	0.34476 (7)	0.0299 (3)
Cl2	0.67102 (14)	0.55460 (11)	0.19540 (7)	0.0370 (3)
N2	0.1432 (4)	0.8426 (3)	0.1480 (2)	0.0244 (8)
N1	0.2770 (4)	0.6993 (3)	0.2141 (2)	0.0249 (8)
N3	0.5563 (4)	0.7158 (3)	0.3717 (2)	0.0289 (9)
N4	0.6711 (5)	0.8617 (3)	0.4421 (2)	0.0341 (10)
C1	0.1030 (5)	0.6818 (4)	0.2160 (3)	0.0319 (11)
H1	0.0509	0.6195	0.2413	0.038*
C2	0.0202 (6)	0.7689 (4)	0.1755 (3)	0.0342 (11)
H2	−0.0980	0.7776	0.1676	0.041*
C3	0.2941 (5)	0.7974 (4)	0.1726 (3)	0.0283 (10)
H3	0.3992	0.8307	0.1620	0.034*
C6	0.5363 (6)	0.6995 (4)	0.4562 (3)	0.0384 (12)
H6	0.4815	0.6368	0.4796	0.046*
C5	0.6077 (6)	0.7875 (4)	0.5003 (3)	0.0423 (13)
H5	0.6131	0.7965	0.5589	0.051*
C4	0.6379 (6)	0.8141 (4)	0.3661 (3)	0.0359 (11)
H4	0.6688	0.8468	0.3153	0.043*
C7	0.1145 (6)	0.9520 (4)	0.1043 (3)	0.0302 (11)
H7A	0.2243	0.9890	0.0974	0.036*
H7B	0.0478	1.0018	0.1393	0.036*
C8	0.0227 (5)	0.9402 (4)	0.0186 (3)	0.0261 (10)
H8A	−0.0814	0.8957	0.0238	0.031*
H8B	0.0952	0.8993	−0.0194	0.031*
C9	0.7655 (6)	0.9682 (4)	0.4623 (3)	0.0438 (13)
H9A	0.7132	1.0070	0.5089	0.053*

H9B	0.7574	1.0192	0.4136	0.053*
C10	0.9514 (6)	0.9456 (4)	0.4862 (3)	0.0423 (13)
H10A	1.0055	0.9121	0.4380	0.051*
H10B	0.9591	0.8899	0.5320	0.051*

Atomic displacement parameters (Å^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Zn1	0.0249 (3)	0.0224 (3)	0.0230 (3)	−0.0008 (2)	−0.00252 (19)	0.0021 (2)
Cl1	0.0288 (6)	0.0250 (6)	0.0366 (6)	−0.0026 (5)	0.0069 (5)	0.0052 (5)
Cl2	0.0349 (6)	0.0457 (8)	0.0311 (6)	0.0052 (6)	0.0072 (5)	0.0077 (5)
N2	0.0253 (19)	0.024 (2)	0.0237 (18)	0.0029 (16)	−0.0019 (15)	0.0046 (15)
N1	0.0265 (19)	0.023 (2)	0.0247 (19)	0.0014 (16)	−0.0006 (15)	0.0043 (16)
N3	0.031 (2)	0.028 (2)	0.027 (2)	−0.0034 (17)	−0.0035 (16)	0.0027 (16)
N4	0.039 (2)	0.031 (2)	0.031 (2)	−0.0085 (18)	−0.0086 (18)	−0.0007 (17)
C1	0.028 (2)	0.034 (3)	0.034 (3)	−0.001 (2)	0.002 (2)	0.015 (2)
C2	0.022 (2)	0.038 (3)	0.043 (3)	−0.002 (2)	0.003 (2)	0.012 (2)
C3	0.026 (2)	0.031 (3)	0.028 (2)	−0.003 (2)	−0.0038 (18)	0.004 (2)
C6	0.048 (3)	0.040 (3)	0.028 (3)	−0.018 (3)	0.000 (2)	0.001 (2)
C5	0.054 (3)	0.048 (3)	0.024 (2)	−0.011 (3)	−0.001 (2)	0.001 (2)
C4	0.045 (3)	0.035 (3)	0.027 (2)	−0.007 (2)	−0.006 (2)	0.005 (2)
C7	0.036 (3)	0.022 (3)	0.032 (3)	−0.001 (2)	−0.002 (2)	0.005 (2)
C8	0.024 (2)	0.030 (3)	0.025 (2)	0.005 (2)	0.0043 (18)	0.0050 (19)
C9	0.057 (3)	0.037 (3)	0.037 (3)	−0.018 (3)	−0.007 (2)	0.003 (2)
C10	0.052 (3)	0.034 (3)	0.039 (3)	−0.017 (3)	−0.008 (2)	0.002 (2)

Geometric parameters (Å, °)

Zn1—N1	2.005 (3)	C3—H3	0.9300
Zn1—N3	2.013 (3)	C6—C5	1.342 (7)
Zn1—Cl2	2.2321 (12)	C6—H6	0.9300
Zn1—Cl1	2.2557 (11)	C5—H5	0.9300
N2—C3	1.330 (5)	C4—H4	0.9300
N2—C2	1.373 (5)	C7—C8	1.506 (6)
N2—C7	1.457 (5)	C7—H7A	0.9700
N1—C3	1.323 (5)	C7—H7B	0.9700
N1—C1	1.375 (5)	C8—C8^{i}	1.540 (8)
N3—C4	1.312 (6)	C8—H8A	0.9700
N3—C6	1.364 (5)	C8—H8B	0.9700
N4—C4	1.336 (5)	C9—C10	1.504 (6)
N4—C5	1.369 (6)	C9—H9A	0.9700
N4—C9	1.466 (6)	C9—H9B	0.9700
C1—C2	1.344 (6)	C10—C10^{ii}	1.524 (9)
C1—H1	0.9300	C10—H10A	0.9700
C2—H2	0.9300	C10—H10B	0.9700
N1—Zn1—N3	107.13 (14)	C6—C5—N4	106.5 (4)
N1—Zn1—Cl2	112.74 (10)	C6—C5—H5	126.8
N3—Zn1—Cl2	111.43 (11)	N4—C5—H5	126.8

N1—Zn1—Cl1	106.02 (10)	N3—C4—N4	111.7 (4)
N3—Zn1—Cl1	104.75 (11)	N3—C4—H4	124.1
Cl2—Zn1—Cl1	114.17 (5)	N4—C4—H4	124.1
C3—N2—C2	106.6 (4)	N2—C7—C8	113.7 (4)
C3—N2—C7	126.6 (4)	N2—C7—H7A	108.8
C2—N2—C7	126.8 (4)	C8—C7—H7A	108.8
C3—N1—C1	105.2 (4)	N2—C7—H7B	108.8
C3—N1—Zn1	126.4 (3)	C8—C7—H7B	108.8
C1—N1—Zn1	127.5 (3)	H7A—C7—H7B	107.7
C4—N3—C6	105.5 (4)	C7—C8—C8^{i}	110.6 (5)
C4—N3—Zn1	128.8 (3)	C7—C8—H8A	109.5
C6—N3—Zn1	125.6 (3)	C8^{i}—C8—H8A	109.5
C4—N4—C5	106.5 (4)	C7—C8—H8B	109.5
C4—N4—C9	128.0 (4)	C8^{i}—C8—H8B	109.5
C5—N4—C9	125.3 (4)	H8A—C8—H8B	108.1
C2—C1—N1	109.3 (4)	N4—C9—C10	112.1 (4)
C2—C1—H1	125.3	N4—C9—H9A	109.2
N1—C1—H1	125.3	C10—C9—H9A	109.2
C1—C2—N2	106.9 (4)	N4—C9—H9B	109.2
C1—C2—H2	126.5	C10—C9—H9B	109.2
N2—C2—H2	126.5	H9A—C9—H9B	107.9
N1—C3—N2	112.0 (4)	C9—C10—C10^{ii}	112.8 (5)
N1—C3—H3	124.0	C9—C10—H10A	109.0
N2—C3—H3	124.0	C10^{ii}—C10—H10A	109.0
C5—C6—N3	109.7 (4)	C9—C10—H10B	109.0
C5—C6—H6	125.1	C10^{ii}—C10—H10B	109.0
N3—C6—H6	125.1	H10A—C10—H10B	107.8

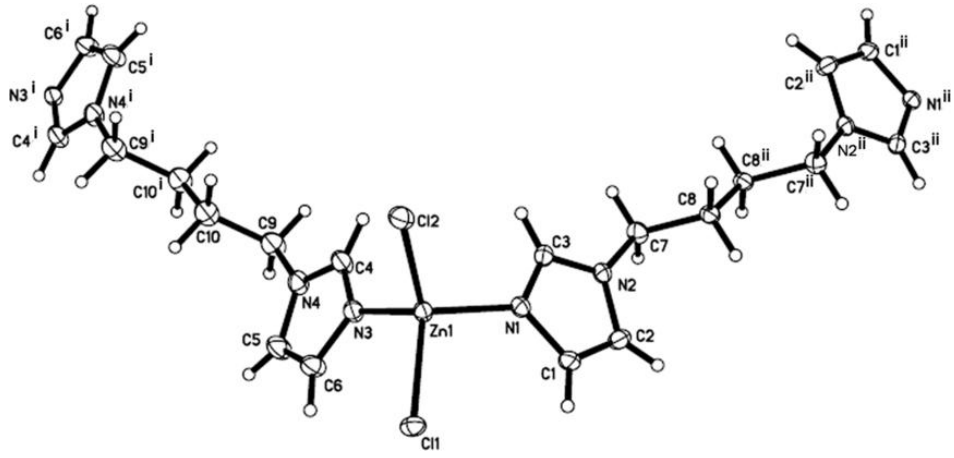
Symmetry codes: (i) −*x*, −*y*+2, −*z*; (ii) −*x*+2, −*y*+2, −*z*+1.

Hydrogen-bond geometry (Å, °)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
C3—H3···Cl1^{iii}	0.93	2.63	3.538 (2)	166
C5—H5···Cl2^{iv}	0.93	2.78	3.599 (5)	147

Symmetry codes: (iii) −*x*+1, *y*+1/2, −*z*+1/2; (iv) *x*, −*y*+3/2, *z*+1/2.

Fig. 1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N1
C5
C6
Cl1
C3
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N1ii
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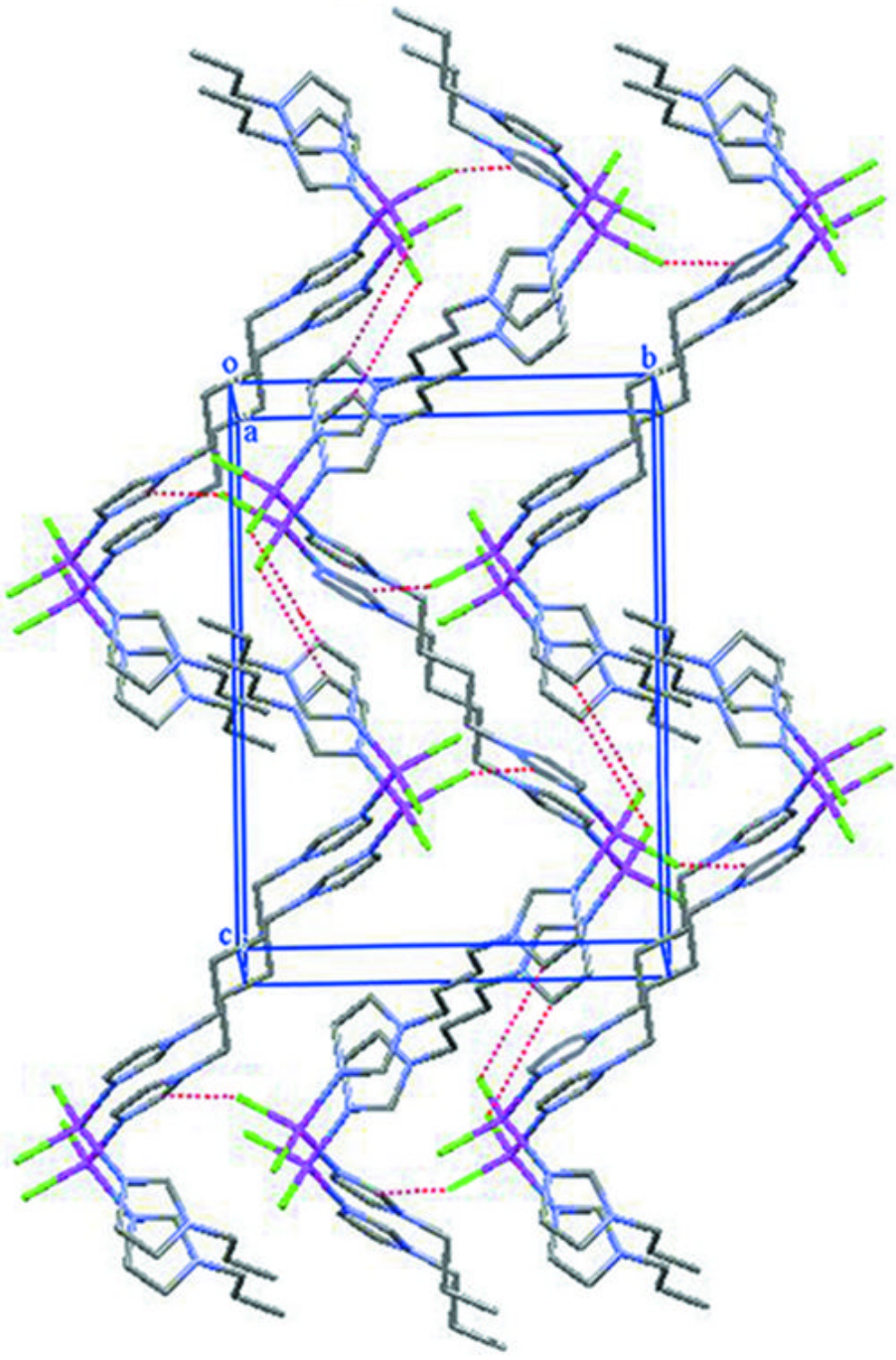
C2
C1

Fig. 2



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Trichloridobis(ethyldiphenylphosphine)-(tetrahydrofuran)molybdenum(III)

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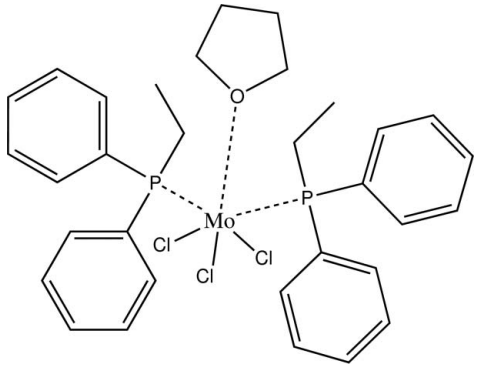
Key indicators: single-crystal X-ray study; T = 120 K; mean σ(C–C) = 0.010 Å; disorder in main residue; R factor = 0.044; wR factor = 0.115; data-to-parameter ratio = 18.2.

In the mononuclear title compound, $[MoCl_3(C_4H_8O)(C_{14}H_{15}P)_2]$, obtained by the reaction of trichlorotris(tetrahydrofuran)molybdenum(III) and ethyldiphenylphosphine in tetrahydrofuran (THF) solution, the Mo^{III} atom is six-coordinated by one O atom of a THF molecule, two P atoms from two ethyldiphenylphosphine ligands and three Cl atoms in a distorted octahedral geometry. The C atoms of the THF molecule are disordered over two positions in a 0.55 (2): 0.45 (2) ratio.

Related literature

For the structures of similar molybdenum complexes and for bond-length data, see: Cotton & Jianrui (1996); Cotton & Vidyasagar (1995); Hofacker *et al.* (1989); Borgmann *et al.* (1997). For the synthesis, see: Anker *et al.* (1975).



Experimental

Crystal data

$[MoCl_3(C_4H_8O)(C_{14}H_{15}P)_2]$
M_r = 702.85
Monoclinic, $P2_1/c$
a = 15.437 Å
b = 13.356 Å
c = 20.229 Å
β = 128.87°
V = 3247.1 Å^3
Z = 4
Mo $K\alpha$ radiation
μ = 0.77 mm^{-1}
T = 120 K
0.13 × 0.10 × 0.04 mm

Data collection

Oxford Diffraction KM-4/Xcalibur diffractometer with a Sapphire2 detector
Absorption correction: analytical [*CrysAlis RED* (Oxford Diffraction, 2006). based on expressions derived by Clark & Reid (1995)]
T_{min} = 0.937, T_{max} = 0.970
25240 measured reflections
7022 independent reflections
2985 reflections with $I > 2\sigma(I)$
R_{int} = 0.089

Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.044
$wR(F^2)$ = 0.115
S = 0.81
7022 reflections
385 parameters
H-atom parameters constrained
$\Delta\rho_{max}$ = 0.70 e Å^{-3}
$\Delta\rho_{min}$ = −0.54 e Å^{-3}

Table 1
Selected bond lengths (Å).

Mo1—O1	2.206 (3)	Mo1—Cl3	2.4126 (13)
Mo1—Cl1	2.3871 (13)	Mo1—P1	2.5964 (14)
Mo1—Cl2	2.3822 (13)	Mo1—P2	2.5974 (13)

Data collection: *CrysAlis CCD* (Oxford Diffraction, 2006); cell refinement: *CrysAlis RED* (Oxford Diffraction, 2006); data reduction: *CrysAlis RED*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *ORTEP-3 for Windows* (Farrugia, 1997); software used to prepare material for publication: *WinGX* (Farrugia, 1999).

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Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: EZ2211).

References

Anker, M. W., Chatt, J., Leigh, G. J. & Wedd, A. G. (1975). *J. Chem. Soc. Dalton Trans.* pp. 2639–2645.
Borgmann, C., Limberg, C. & Driess, A. (1997). *J. Organomet. Chem.* **541**, 367–375.
Clark, R. C. & Reid, J. S. (1995). *Acta Cryst.* A**51**, 887–897.
Cotton, F. A. & Jianrui, S. (1996). *Inorg. Chim. Acta*, **251**, 101–104.
Cotton, F. A. & Vidyasagar, K. (1995). *Polyhedron*, **14**, 3077–3085.
Farrugia, L. J. (1997). *J. Appl. Cryst.* **30**, 565.
Farrugia, L. J. (1999). *J. Appl. Cryst.* **32**, 837–838.
Hofacker, P., Friebel, C., Debhnicke, K., Bauml, P., Hiller, W. & Strähle, J. (1989). *Z. Naturforsch. Teil B*, **44**, 1161–1166.
Oxford Diffraction (2006). *CrysAlis CCD* and *CrysAlis RED*. Oxford Diffraction Ltd, Abingdon, England.
Sheldrick, G. M. (2008). *Acta Cryst.* A**64**, 112–122.

supplementary materials

Acta Cryst. (2010). E**66**, m786 [**doi:10.1107/S1600536810021690**]

Trichloridobis(ethyldiphenylphosphine)(tetrahydrofuran)molybdenum(III)

T. Kruczynski, J. Pikies and L. Ponikiewski

Comment

The title molecule [$MoCl_3(PEtPh_2)(THF)$] was prepared as a potential adduct for synthesis with lithium phosphanides of the formula R_2P—$P(SiMe_3)Li$ (R = ^{t}Bu, ^{i}Pr, Et_2N, $^i Pr_2N$).

The Mo^{III} atom resides in a distorted $MoCl_3OP_2$ octahedral environment. The equatorial positions are occupied by three Cl atoms and one O atom from the THF, while the axial positions are occupied by P atoms from two ethyldiphenylphosphine residues. The Mo—Cl bond length [2.3871 (13) Å, 2.3822 (13) Å, 2.4126 (13) Å], the Mo—P bond length [2.5964 (14) Å, 2.5974 (13) Å] and the Mo—O bond length [2.206 (3) Å] are very similar to the previously reported molybdenum complexes (Cotton & Vidyasagar, 1995; Cotton & Jianrui, 1996; Hofacker *et al.*, 1989; Borgmann *et al.*, 1997).

Atoms C29, C30, C31, C32 from the THF molecule were disordered over two positions. During the refinement process the disorder models were refined with occupancies of 0.55 (2) and 0.45 (2).

Experimental

The title compound was prepared according to the previously published method (Anker *et al.*, 1975)

Refinement

Atoms C29, C30, C31, C32 were disordered over two positions. During the refinement process the disorder models were refined with occupancies of 0.55 (2) and 0.45 (2). H atoms bonded to C were included in calculated positions and refined as riding on their parent C atom with C—H = 0.95 Å, U_{iso}(H) = 1.2 U_{eq}(C) for aromatic; C—H = 0.99 Å, U_{iso}(H) = 1.2 U_{eq}(C) for methylene; and C—H = 0.98 Å, U_{iso}(H) = 1.5 U_{eq}(C) for methyl atoms.

Figures

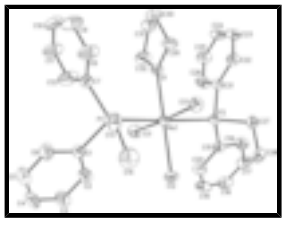


Fig. 1. The molecular structure of the title compound showing the atomic numbering scheme. Displacement ellipsoids are drawn at the 50% probability level. For clarity, all H atoms and the minor component of the disorder have been omitted.

Trichloridobis(ethyldiphenylphosphine)(tetrahydrofuran)molybdenum(III)

Crystal data

$[MoCl_3(C_4H_8O)(C_{14}H_{15}P)_2]$	$F(000) = 1444$
$M_r = 702.85$	$D_x = 1.438$ Mg m^{-3}
Monoclinic, $P2_1/c$	Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å
Hall symbol: -P 2ybc	Cell parameters from 5220 reflections
$a = 15.437$ Å	$\theta = 2.0$–$28.9°$
$b = 13.356$ Å	$\mu = 0.77$ mm^{-1}
$c = 20.229$ Å	$T = 120$ K
$\beta = 128.87°$	Block, orange
$V = 3247.1$ Å^3	0.13 × 0.1 × 0.04 mm
$Z = 4$	

Data collection

Oxford Diffraction KM-4/Xcalibur diffractometer with a Sapphire2 (large Be window) detector	7022 independent reflections
graphite	2985 reflections with $I > 2\sigma(I)$
Detector resolution: 8.1883 pixels mm^{-1}	$R_{int} = 0.089$
ω scans	$\theta_{max} = 27°$, $\theta_{min} = 2°$
Absorption correction: analytical [*CrysAlis RED* (Oxford Diffraction, 2006). based on expressions derived by Clark & Reid (1995)]	$h = -15 \rightarrow 19$
$T_{min} = 0.937$, $T_{max} = 0.97$	$k = -16 \rightarrow 17$
25240 measured reflections	$l = -25 \rightarrow 22$

Refinement

Refinement on F^2	Primary atom site location: structure-invariant direct methods
Least-squares matrix: full	Secondary atom site location: difference Fourier map
$R[F^2 > 2\sigma(F^2)] = 0.044$	Hydrogen site location: inferred from neighbouring sites
$wR(F^2) = 0.115$	H-atom parameters constrained
$S = 0.81$	$w = 1/[\sigma^2(F_o^2) + (0.0551P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
7022 reflections	$(\Delta/\sigma)_{max} = 0.001$
385 parameters	$\Delta\rho_{max} = 0.70$ e Å^{-3}
0 restraints	$\Delta\rho_{min} = -0.54$ e Å^{-3}

Special details

Experimental. CrysAlis RED (Oxford Diffraction, 2006) Analytical numeric absorption correction using a multifaceted crystal model based on expressions derived by Clark & Reid (1995)

Geometry. All e.s.d.'s (except the e.s.d. in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell e.s.d.'s are taken into account individually in the estimation of e.s.d.'s in distances, angles and torsion angles; correlations between e.s.d.'s in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell e.s.d.'s is used for estimating e.s.d.'s involving l.s. planes.

Refinement. Refinement of F^2 against ALL reflections. The weighted *R*-factor *wR* and goodness of fit *S* are based on F^2, conventional *R*-factors *R* are based on *F*, with *F* set to zero for negative F^2. The threshold expression of $F^2 > \sigma(F^2)$ is used only for calculating *R*-factors(gt) *etc*. and is not relevant to the choice of reflections for refinement. *R*-factors based on F^2 are statistically about twice as large as those based on *F*, and *R*- factors based on ALL data will be even larger.

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å^2)

	x	*y*	*z*	U_{iso}*/U_{eq}	Occ. (<1)
Mo1	0.57979 (3)	0.74957 (4)	0.63166 (2)	0.03356 (12)	
Cl1	0.53421 (13)	0.92350 (10)	0.61183 (10)	0.0612 (4)	
Cl2	0.62891 (9)	0.74919 (11)	0.76928 (7)	0.0511 (3)	
Cl3	0.62090 (10)	0.57325 (9)	0.64269 (9)	0.0488 (3)	
P1	0.78469 (10)	0.78721 (10)	0.69759 (9)	0.0415 (3)	
P2	0.37606 (10)	0.70228 (10)	0.56343 (8)	0.0370 (3)	
O1	0.5361 (2)	0.7484 (3)	0.50482 (18)	0.0411 (7)	
C1	0.8589 (4)	0.8883 (4)	0.7753 (3)	0.0495 (14)	
C2	0.8104 (5)	0.9421 (5)	0.8018 (4)	0.075 (2)	
H2A	0.7358	0.9277	0.7785	0.09*	
C3	0.8682 (6)	1.0174 (6)	0.8621 (5)	0.099 (3)	
H3A	0.8334	1.0547	0.8797	0.118*	
C4	0.9750 (6)	1.0370 (5)	0.8957 (4)	0.084 (2)	
H4A	1.0161	1.0871	0.938	0.101*	
C5	1.0232 (5)	0.9849 (5)	0.8687 (4)	0.0711 (19)	
H5A	1.0976	1	0.8918	0.085*	
C6	0.9674 (4)	0.9118 (4)	0.8095 (4)	0.0645 (17)	
H6A	1.0026	0.8765	0.7913	0.077*	
C7	0.8016 (4)	0.8198 (4)	0.6187 (3)	0.0462 (13)	
C8	0.8262 (6)	0.7500 (6)	0.5828 (4)	0.0873 (15)	
H8A	0.8389	0.6826	0.6018	0.105*	
C9	0.8329 (5)	0.7744 (6)	0.5206 (4)	0.084 (2)	
H9A	0.8507	0.7242	0.4977	0.101*	
C10	0.8145 (5)	0.8694 (6)	0.4914 (4)	0.080 (2)	
H10A	0.8208	0.8866	0.449	0.096*	
C11	0.7871 (6)	0.9387 (5)	0.5234 (4)	0.0873 (15)	
H11A	0.7712	1.0052	0.5021	0.105*	
C12	0.7820 (7)	0.9141 (5)	0.5872 (5)	0.098 (2)	
H12A	0.7641	0.9649	0.6097	0.117*	
C13	0.8800 (4)	0.6808 (4)	0.7548 (4)	0.0563 (16)	
H13A	0.85	0.6221	0.7166	0.068*	
H13B	0.9529	0.6977	0.7698	0.068*	
C14	0.8976 (5)	0.6530 (5)	0.8342 (4)	0.084 (2)	
H14A	0.9562	0.6022	0.8654	0.126*	
H14B	0.8283	0.6261	0.8194	0.126*	

H14C	0.9198	0.7126	0.87	0.126*	
C15	0.2980 (4)	0.7756 (3)	0.5873 (3)	0.0414 (13)	
C16	0.1881 (4)	0.7565 (4)	0.5442 (3)	0.0572 (14)	
H16A	0.1526	0.705	0.5026	0.069*	
C17	0.1273 (5)	0.8118 (5)	0.5608 (4)	0.0656 (17)	
H17A	0.051	0.7972	0.5318	0.079*	
C18	0.1780 (5)	0.8869 (5)	0.6187 (4)	0.0639 (17)	
H18A	0.1364	0.9264	0.6291	0.077*	
C19	0.2870 (5)	0.9059 (5)	0.6615 (4)	0.0675 (18)	
H19A	0.3217	0.9584	0.7021	0.081*	
C20	0.3483 (4)	0.8502 (4)	0.6471 (3)	0.0524 (14)	
H20A	0.4255	0.8633	0.6785	0.063*	
C21	0.2853 (4)	0.7107 (4)	0.4475 (3)	0.0416 (13)	
C22	0.2670 (4)	0.6302 (4)	0.3982 (3)	0.0497 (14)	
H22A	0.2983	0.567	0.4241	0.06*	
C23	0.2041 (4)	0.6398 (5)	0.3121 (3)	0.0594 (16)	
H23A	0.1927	0.5835	0.2787	0.071*	
C24	0.1579 (4)	0.7294 (5)	0.2740 (3)	0.0630 (18)	
H24A	0.1137	0.7357	0.2141	0.076*	
C25	0.1750 (4)	0.8081 (5)	0.3209 (4)	0.0621 (16)	
H25A	0.1427	0.8707	0.2942	0.075*	
C26	0.2390 (4)	0.8001 (4)	0.4079 (4)	0.0599 (16)	
H26A	0.2509	0.8574	0.4405	0.072*	
C27	0.3571 (4)	0.5747 (4)	0.5836 (3)	0.0466 (13)	
H27A	0.2765	0.5598	0.5468	0.056*	
H27B	0.3913	0.5281	0.5678	0.056*	
C28	0.4074 (4)	0.5557 (4)	0.6752 (3)	0.0624 (16)	
H28A	0.3979	0.485	0.6824	0.094*	
H28B	0.3699	0.5977	0.6901	0.094*	
H28C	0.4868	0.5721	0.7123	0.094*	
C29	0.542 (4)	0.6602 (15)	0.4672 (19)	0.064 (3)	0.55 (2)
H29A	0.4819	0.6128	0.4502	0.077*	0.55 (2)
H29B	0.6146	0.6263	0.5077	0.077*	0.55 (2)
C30	0.5284 (16)	0.6963 (11)	0.3911 (10)	0.066 (3)	0.55 (2)
H30A	0.4919	0.6449	0.3458	0.079*	0.55 (2)
H30B	0.6012	0.7139	0.4062	0.079*	0.55 (2)
C31	0.4556 (16)	0.7877 (16)	0.3635 (13)	0.073 (5)	0.55 (2)
H31A	0.4697	0.8363	0.3343	0.088*	0.55 (2)
H31B	0.3758	0.7691	0.325	0.088*	0.55 (2)
C32	0.488 (5)	0.8294 (17)	0.4431 (19)	0.068 (7)	0.55 (2)
H32A	0.5427	0.8838	0.4634	0.081*	0.55 (2)
H32B	0.4218	0.857	0.4344	0.081*	0.55 (2)
C29A	0.541 (5)	0.6650 (18)	0.461 (2)	0.056 (3)	0.45 (2)
H29C	0.5087	0.604	0.4656	0.067*	0.45 (2)
H29D	0.6191	0.6509	0.4857	0.067*	0.45 (2)
C30A	0.474 (2)	0.6981 (14)	0.3695 (13)	0.075 (4)	0.45 (2)
H30C	0.4962	0.6617	0.3397	0.091*	0.45 (2)
H30D	0.393	0.6895	0.3382	0.091*	0.45 (2)
C31A	0.506 (2)	0.8069 (16)	0.3820 (17)	0.063 (4)	0.45 (2)

H31C	0.4502	0.8462	0.3304	0.076*	0.45 (2)
H31D	0.5797	0.8153	0.3959	0.076*	0.45 (2)
C32A	0.510 (6)	0.839 (2)	0.455 (3)	0.064 (7)	0.45 (2)
H32C	0.5683	0.8906	0.4901	0.077*	0.45 (2)
H32D	0.4375	0.867	0.4346	0.077*	0.45 (2)

Atomic displacement parameters (Å^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Mo1	0.0421 (2)	0.0281 (2)	0.0318 (2)	0.00186 (18)	0.02382 (17)	0.0012 (2)
Cl1	0.0978 (11)	0.0283 (8)	0.0685 (10)	0.0094 (7)	0.0575 (9)	0.0041 (7)
Cl2	0.0565 (7)	0.0651 (8)	0.0343 (6)	−0.0004 (7)	0.0297 (6)	0.0013 (8)
Cl3	0.0583 (8)	0.0320 (7)	0.0577 (9)	0.0070 (6)	0.0372 (7)	0.0059 (6)
P1	0.0426 (8)	0.0390 (8)	0.0446 (8)	−0.0019 (5)	0.0281 (7)	−0.0007 (6)
P2	0.0405 (7)	0.0363 (8)	0.0323 (8)	0.0025 (5)	0.0220 (6)	−0.0010 (6)
O1	0.0568 (19)	0.0352 (18)	0.0328 (16)	0.0028 (17)	0.0288 (15)	0.0022 (19)
C1	0.057 (4)	0.048 (4)	0.045 (3)	−0.008 (2)	0.032 (3)	−0.005 (3)
C2	0.076 (4)	0.081 (5)	0.086 (5)	−0.033 (3)	0.060 (4)	−0.042 (4)
C3	0.109 (6)	0.114 (6)	0.105 (6)	−0.055 (5)	0.083 (5)	−0.069 (5)
C4	0.088 (5)	0.074 (5)	0.069 (5)	−0.040 (4)	0.039 (4)	−0.031 (4)
C5	0.055 (4)	0.062 (5)	0.075 (5)	−0.018 (3)	0.031 (4)	−0.012 (4)
C6	0.060 (4)	0.057 (4)	0.080 (5)	−0.013 (3)	0.046 (4)	−0.011 (3)
C7	0.049 (3)	0.046 (4)	0.053 (3)	−0.004 (2)	0.036 (3)	−0.004 (3)
C8	0.154 (5)	0.060 (3)	0.093 (4)	0.013 (3)	0.099 (4)	0.013 (3)
C9	0.100 (5)	0.096 (6)	0.086 (5)	0.038 (4)	0.073 (4)	0.009 (4)
C10	0.114 (5)	0.085 (6)	0.089 (5)	0.006 (4)	0.087 (5)	0.007 (4)
C11	0.154 (5)	0.060 (3)	0.093 (4)	0.013 (3)	0.099 (4)	0.013 (3)
C12	0.204 (8)	0.041 (4)	0.116 (6)	0.005 (4)	0.133 (6)	0.006 (4)
C13	0.048 (3)	0.049 (4)	0.066 (4)	0.003 (2)	0.033 (3)	0.014 (3)
C14	0.074 (4)	0.084 (5)	0.067 (5)	0.013 (3)	0.031 (4)	0.029 (4)
C15	0.046 (3)	0.042 (4)	0.033 (3)	0.007 (2)	0.024 (3)	0.002 (2)
C16	0.051 (3)	0.067 (4)	0.057 (3)	0.003 (3)	0.036 (3)	−0.008 (3)
C17	0.058 (4)	0.086 (5)	0.064 (4)	0.018 (3)	0.044 (4)	0.009 (4)
C18	0.072 (4)	0.069 (5)	0.061 (4)	0.028 (3)	0.047 (4)	0.010 (3)
C19	0.079 (5)	0.070 (5)	0.056 (4)	0.011 (3)	0.044 (4)	−0.011 (3)
C20	0.051 (3)	0.061 (4)	0.042 (3)	0.004 (3)	0.028 (3)	−0.005 (3)
C21	0.040 (3)	0.044 (3)	0.036 (3)	0.002 (2)	0.022 (3)	−0.006 (2)
C22	0.054 (3)	0.050 (4)	0.048 (3)	0.005 (2)	0.033 (3)	0.001 (3)
C23	0.060 (4)	0.072 (5)	0.035 (3)	0.003 (3)	0.024 (3)	−0.012 (3)
C24	0.056 (4)	0.089 (5)	0.030 (3)	0.013 (3)	0.020 (3)	−0.005 (3)
C25	0.067 (4)	0.061 (4)	0.047 (4)	0.022 (3)	0.030 (3)	0.013 (3)
C26	0.076 (4)	0.047 (4)	0.047 (4)	0.014 (3)	0.034 (3)	0.002 (3)
C27	0.051 (3)	0.040 (3)	0.052 (3)	−0.004 (2)	0.034 (3)	0.001 (3)
C28	0.077 (4)	0.059 (4)	0.058 (4)	−0.004 (3)	0.045 (3)	0.014 (3)
C29	0.089 (5)	0.066 (4)	0.053 (5)	−0.004 (4)	0.052 (5)	−0.013 (4)
C30	0.084 (6)	0.076 (5)	0.053 (6)	−0.004 (5)	0.051 (6)	−0.011 (4)
C31	0.086 (14)	0.083 (10)	0.040 (9)	−0.014 (9)	0.035 (11)	0.004 (7)
C32	0.094 (19)	0.057 (6)	0.049 (8)	0.010 (8)	0.043 (12)	0.020 (6)

C29A	0.086 (5)	0.055 (5)	0.052 (5)	−0.005 (4)	0.056 (5)	−0.012 (4)
C30A	0.094 (7)	0.077 (6)	0.058 (6)	−0.003 (6)	0.049 (6)	−0.014 (5)
C31A	0.076 (14)	0.085 (10)	0.036 (10)	−0.011 (9)	0.039 (12)	0.003 (7)
C32A	0.092 (19)	0.055 (6)	0.047 (8)	0.008 (8)	0.044 (12)	0.020 (6)

Geometric parameters (Å, °)

Mo1—O1	2.206 (3)	C16—H16A	0.95
Mo1—Cl1	2.3871 (13)	C17—C18	1.356 (8)
Mo1—Cl2	2.3822 (13)	C17—H17A	0.95
Mo1—Cl3	2.4126 (13)	C18—C19	1.348 (7)
Mo1—P1	2.5964 (14)	C18—H18A	0.95
Mo1—P2	2.5974 (13)	C19—C20	1.371 (7)
P1—C7	1.824 (6)	C19—H19A	0.95
P1—C1	1.830 (5)	C20—H20A	0.95
P1—C13	1.840 (5)	C21—C26	1.364 (7)
P2—C27	1.818 (5)	C21—C22	1.370 (7)
P2—C21	1.830 (5)	C22—C23	1.368 (7)
P2—C15	1.838 (5)	C22—H22A	0.95
O1—C29	1.434 (15)	C23—C24	1.358 (8)
O1—C29A	1.453 (16)	C23—H23A	0.95
O1—C32	1.455 (15)	C24—C25	1.326 (7)
O1—C32A	1.459 (17)	C24—H24A	0.95
C1—C2	1.366 (7)	C25—C26	1.380 (7)
C1—C6	1.389 (7)	C25—H25A	0.95
C2—C3	1.390 (8)	C26—H26A	0.95
C2—H2A	0.95	C27—C28	1.514 (7)
C3—C4	1.358 (9)	C27—H27A	0.99
C3—H3A	0.95	C27—H27B	0.99
C4—C5	1.359 (9)	C28—H28A	0.98
C4—H4A	0.95	C28—H28B	0.98
C5—C6	1.355 (8)	C28—H28C	0.98
C5—H5A	0.95	C29—C30	1.499 (17)
C6—H6A	0.95	C29—H29A	0.99
C7—C12	1.358 (8)	C29—H29B	0.99
C7—C8	1.373 (8)	C30—C31	1.510 (16)
C8—C9	1.364 (9)	C30—H30A	0.99
C8—H8A	0.95	C30—H30B	0.99
C9—C10	1.352 (9)	C31—C32	1.464 (16)
C9—H9A	0.95	C31—H31A	0.99
C10—C11	1.341 (8)	C31—H31B	0.99
C10—H10A	0.95	C32—H32A	0.99
C11—C12	1.381 (9)	C32—H32B	0.99
C11—H11A	0.95	C29A—C30A	1.514 (18)
C12—H12A	0.95	C29A—H29C	0.99
C13—C14	1.498 (8)	C29A—H29D	0.99
C13—H13A	0.99	C30A—C31A	1.506 (17)
C13—H13B	0.99	C30A—H30C	0.99
C14—H14A	0.98	C30A—H30D	0.99

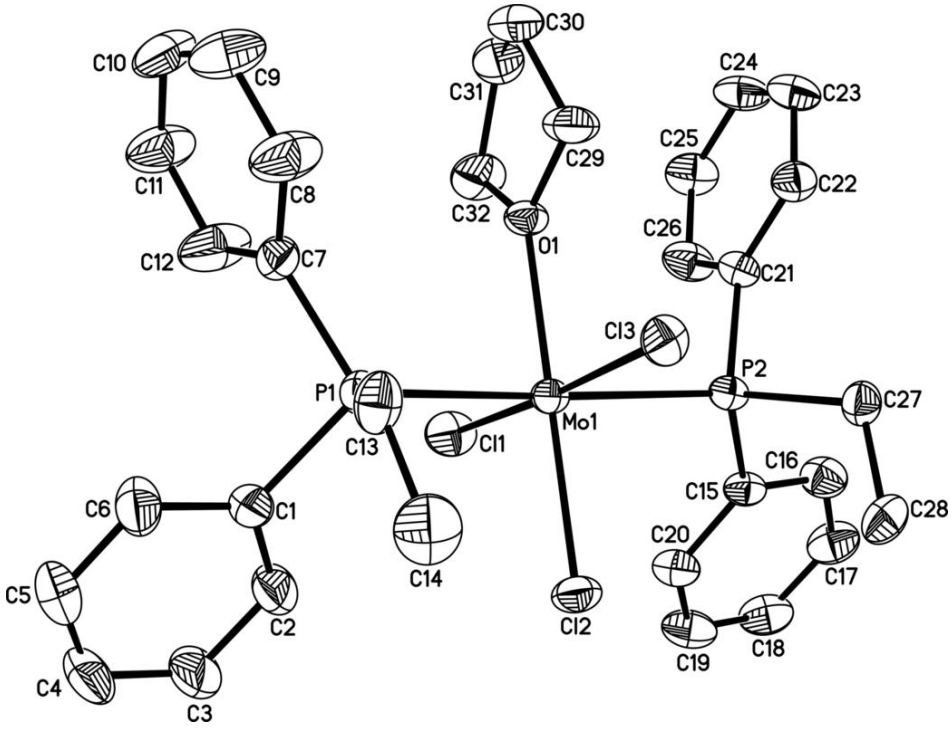
C14—H14B	0.98	C31A—C32A	1.509 (18)
C14—H14C	0.98	C31A—H31C	0.99
C15—C16	1.359 (7)	C31A—H31D	0.99
C15—C20	1.371 (7)	C32A—H32C	0.99
C16—C17	1.391 (7)	C32A—H32D	0.99
O1—Mo1—Cl2	179.21 (10)	C18—C17—H17A	120.3
O1—Mo1—Cl1	88.22 (10)	C16—C17—H17A	120.3
Cl2—Mo1—Cl1	92.44 (5)	C19—C18—C17	120.3 (5)
O1—Mo1—Cl3	88.34 (10)	C19—C18—H18A	119.8
Cl2—Mo1—Cl3	91.01 (5)	C17—C18—H18A	119.8
Cl1—Mo1—Cl3	176.50 (6)	C18—C19—C20	120.8 (6)
O1—Mo1—P1	89.05 (9)	C18—C19—H19A	119.6
Cl2—Mo1—P1	90.49 (5)	C20—C19—H19A	119.6
Cl1—Mo1—P1	91.92 (5)	C19—C20—C15	119.8 (5)
Cl3—Mo1—P1	88.66 (4)	C19—C20—H20A	120.1
O1—Mo1—P2	89.76 (8)	C15—C20—H20A	120.1
Cl2—Mo1—P2	90.67 (4)	C26—C21—C22	117.8 (5)
Cl1—Mo1—P2	90.94 (5)	C26—C21—P2	120.3 (4)
Cl3—Mo1—P2	88.41 (4)	C22—C21—P2	121.8 (4)
P1—Mo1—P2	176.87 (5)	C23—C22—C21	120.8 (5)
C7—P1—C1	102.7 (2)	C23—C22—H22A	119.6
C7—P1—C13	103.8 (3)	C21—C22—H22A	119.6
C1—P1—C13	101.9 (3)	C24—C23—C22	120.4 (6)
C7—P1—Mo1	113.20 (16)	C24—C23—H23A	119.8
C1—P1—Mo1	119.23 (19)	C22—C23—H23A	119.8
C13—P1—Mo1	114.15 (18)	C25—C24—C23	119.6 (6)
C27—P2—C21	104.1 (2)	C25—C24—H24A	120.2
C27—P2—C15	102.5 (2)	C23—C24—H24A	120.2
C21—P2—C15	101.7 (2)	C24—C25—C26	120.9 (6)
C27—P2—Mo1	114.84 (16)	C24—C25—H25A	119.6
C21—P2—Mo1	111.36 (16)	C26—C25—H25A	119.6
C15—P2—Mo1	120.40 (17)	C21—C26—C25	120.6 (6)
C29—O1—C32	108.9 (15)	C21—C26—H26A	119.7
C29A—O1—C32	104.0 (14)	C25—C26—H26A	119.7
C29—O1—C32A	113.6 (15)	C28—C27—P2	113.6 (4)
C29A—O1—C32A	108.5 (16)	C28—C27—H27A	108.8
C29—O1—Mo1	123.2 (9)	P2—C27—H27A	108.8
C29A—O1—Mo1	128.2 (10)	C28—C27—H27B	108.8
C32—O1—Mo1	127.6 (11)	P2—C27—H27B	108.8
C32A—O1—Mo1	122.9 (12)	H27A—C27—H27B	107.7
C2—C1—C6	118.3 (5)	C27—C28—H28A	109.5
C2—C1—P1	121.5 (4)	C27—C28—H28B	109.5
C6—C1—P1	120.2 (4)	H28A—C28—H28B	109.5
C1—C2—C3	121.1 (6)	C27—C28—H28C	109.5
C1—C2—H2A	119.5	H28A—C28—H28C	109.5
C3—C2—H2A	119.5	H28B—C28—H28C	109.5
C4—C3—C2	119.2 (7)	O1—C29—C30	105.5 (14)
C4—C3—H3A	120.4	O1—C29—H29A	110.6
C2—C3—H3A	120.4	C30—C29—H29A	110.6

C5—C4—C3	120.0 (6)	O1—C29—H29B	110.6
C5—C4—H4A	120	C30—C29—H29B	110.6
C3—C4—H4A	120	H29A—C29—H29B	108.8
C6—C5—C4	121.3 (6)	C29—C30—C31	103.3 (18)
C6—C5—H5A	119.3	C29—C30—H30A	111.1
C4—C5—H5A	119.3	C31—C30—H30A	111.1
C5—C6—C1	120.1 (6)	C29—C30—H30B	111.1
C5—C6—H6A	120	C31—C30—H30B	111.1
C1—C6—H6A	120	H30A—C30—H30B	109.1
C12—C7—C8	115.8 (6)	C32—C31—C30	104.0 (19)
C12—C7—P1	121.3 (5)	C32—C31—H31A	111
C8—C7—P1	122.7 (4)	C30—C31—H31A	111
C9—C8—C7	122.1 (7)	C32—C31—H31B	111
C9—C8—H8A	118.9	C30—C31—H31B	111
C7—C8—H8A	118.9	H31A—C31—H31B	109
C10—C9—C8	120.7 (7)	O1—C32—C31	107.4 (17)
C10—C9—H9A	119.7	O1—C32—H32A	110.2
C8—C9—H9A	119.7	C31—C32—H32A	110.2
C11—C10—C9	118.7 (7)	O1—C32—H32B	110.2
C11—C10—H10A	120.7	C31—C32—H32B	110.2
C9—C10—H10A	120.7	H32A—C32—H32B	108.5
C10—C11—C12	120.4 (6)	O1—C29A—C30A	105.3 (18)
C10—C11—H11A	119.8	O1—C29A—H29C	110.7
C12—C11—H11A	119.8	C30A—C29A—H29C	110.7
C7—C12—C11	122.2 (7)	O1—C29A—H29D	110.7
C7—C12—H12A	118.9	C30A—C29A—H29D	110.7
C11—C12—H12A	118.9	H29C—C29A—H29D	108.8
C14—C13—P1	113.7 (4)	C31A—C30A—C29A	100 (2)
C14—C13—H13A	108.8	C31A—C30A—H30C	111.8
P1—C13—H13A	108.8	C29A—C30A—H30C	111.8
C14—C13—H13B	108.8	C31A—C30A—H30D	111.8
P1—C13—H13B	108.8	C29A—C30A—H30D	111.8
H13A—C13—H13B	107.7	H30C—C30A—H30D	109.5
C13—C14—H14A	109.5	C30A—C31A—C32A	104 (2)
C13—C14—H14B	109.5	C30A—C31A—H31C	110.9
H14A—C14—H14B	109.5	C32A—C31A—H31C	110.9
C13—C14—H14C	109.5	C30A—C31A—H31D	110.9
H14A—C14—H14C	109.5	C32A—C31A—H31D	110.9
H14B—C14—H14C	109.5	H31C—C31A—H31D	108.9
C16—C15—C20	119.4 (5)	O1—C32A—C31A	105 (2)
C16—C15—P2	119.5 (4)	O1—C32A—H32C	110.7
C20—C15—P2	121.1 (4)	C31A—C32A—H32C	110.7
C15—C16—C17	120.3 (6)	O1—C32A—H32D	110.7
C15—C16—H16A	119.8	C31A—C32A—H32D	110.7
C17—C16—H16A	119.8	H32C—C32A—H32D	108.8
C18—C17—C16	119.4 (6)		
O1—Mo1—P1—C7	11.0 (2)	P1—C7—C8—C9	176.5 (5)
Cl2—Mo1—P1—C7	−169.7 (2)	C7—C8—C9—C10	−0.5 (12)
Cl1—Mo1—P1—C7	−77.2 (2)	C8—C9—C10—C11	−1.4 (11)

Cl3—Mo1—P1—C7	99.3 (2)	C9—C10—C11—C12	2.3 (11)
O1—Mo1—P1—C1	131.9 (2)	C8—C7—C12—C11	−0.5 (11)
Cl2—Mo1—P1—C1	−48.8 (2)	P1—C7—C12—C11	−175.6 (6)
Cl1—Mo1—P1—C1	43.7 (2)	C10—C11—C12—C7	−1.4 (12)
Cl3—Mo1—P1—C1	−139.8 (2)	C7—P1—C13—C14	168.8 (4)
O1—Mo1—P1—C13	−107.4 (2)	C1—P1—C13—C14	62.4 (5)
Cl2—Mo1—P1—C13	71.9 (2)	Mo1—P1—C13—C14	−67.6 (5)
Cl1—Mo1—P1—C13	164.4 (2)	C27—P2—C15—C16	−58.1 (5)
Cl3—Mo1—P1—C13	−19.1 (2)	C21—P2—C15—C16	49.4 (5)
O1—Mo1—P2—C27	108.1 (2)	Mo1—P2—C15—C16	173.0 (4)
Cl2—Mo1—P2—C27	−71.3 (2)	C27—P2—C15—C20	122.9 (4)
Cl1—Mo1—P2—C27	−163.7 (2)	C21—P2—C15—C20	−129.7 (4)
Cl3—Mo1—P2—C27	19.7 (2)	Mo1—P2—C15—C20	−6.1 (5)
O1—Mo1—P2—C21	−9.9 (2)	C20—C15—C16—C17	−0.2 (8)
Cl2—Mo1—P2—C21	170.76 (18)	P2—C15—C16—C17	−179.3 (4)
Cl1—Mo1—P2—C21	78.31 (18)	C15—C16—C17—C18	1.8 (9)
Cl3—Mo1—P2—C21	−98.26 (18)	C16—C17—C18—C19	−1.9 (9)
O1—Mo1—P2—C15	−128.8 (2)	C17—C18—C19—C20	0.3 (9)
Cl2—Mo1—P2—C15	51.90 (18)	C18—C19—C20—C15	1.3 (9)
Cl1—Mo1—P2—C15	−40.55 (18)	C16—C15—C20—C19	−1.3 (8)
Cl3—Mo1—P2—C15	142.89 (18)	P2—C15—C20—C19	177.8 (4)
Cl1—Mo1—O1—C29	−180 (2)	C27—P2—C21—C26	150.8 (5)
Cl3—Mo1—O1—C29	0(2)	C15—P2—C21—C26	44.6 (5)
P1—Mo1—O1—C29	89 (2)	Mo1—P2—C21—C26	−84.9 (5)
P2—Mo1—O1—C29	−89 (2)	C27—P2—C21—C22	−33.3 (5)
Cl1—Mo1—O1—C29A	179 (3)	C15—P2—C21—C22	−139.5 (4)
Cl3—Mo1—O1—C29A	−2(3)	Mo1—P2—C21—C22	91.0 (4)
P1—Mo1—O1—C29A	87 (3)	C26—C21—C22—C23	−0.1 (8)
P2—Mo1—O1—C29A	−90 (3)	P2—C21—C22—C23	−176.1 (4)
Cl1—Mo1—O1—C32	−6(3)	C21—C22—C23—C24	−0.6 (9)
Cl3—Mo1—O1—C32	173 (3)	C22—C23—C24—C25	0.7 (9)
P1—Mo1—O1—C32	−98 (3)	C23—C24—C25—C26	−0.1 (9)
P2—Mo1—O1—C32	85 (3)	C22—C21—C26—C25	0.7 (8)
Cl1—Mo1—O1—C32A	7(4)	P2—C21—C26—C25	176.7 (4)
Cl3—Mo1—O1—C32A	−173 (4)	C24—C25—C26—C21	−0.6 (9)
P1—Mo1—O1—C32A	−85 (4)	C21—P2—C27—C28	−169.0 (4)
P2—Mo1—O1—C32A	98 (4)	C15—P2—C27—C28	−63.3 (4)
C7—P1—C1—C2	128.5 (5)	Mo1—P2—C27—C28	69.0 (4)
C13—P1—C1—C2	−124.3 (5)	C32—O1—C29—C30	17 (4)
Mo1—P1—C1—C2	2.4 (6)	C32A—O1—C29—C30	5(5)
C7—P1—C1—C6	−52.0 (5)	Mo1—O1—C29—C30	−168.8 (15)
C13—P1—C1—C6	55.3 (5)	O1—C29—C30—C31	−30 (4)
Mo1—P1—C1—C6	−178.0 (4)	C29—C30—C31—C32	33 (4)
C6—C1—C2—C3	−0.9 (10)	C29—O1—C32—C31	4(5)
P1—C1—C2—C3	178.7 (6)	C29A—O1—C32—C31	6(5)
C1—C2—C3—C4	−0.6 (12)	C32A—O1—C32—C31	120 (18)
C2—C3—C4—C5	1.6 (12)	Mo1—O1—C32—C31	−170.0 (17)
C3—C4—C5—C6	−1.2 (11)	C30—C31—C32—O1	−23 (4)
C4—C5—C6—C1	−0.3 (10)	C32—O1—C29A—C30A	−11 (4)

C2—C1—C6—C5	1.3 (9)	C32A—O1—C29A—C30A	−22 (5)
P1—C1—C6—C5	−178.2 (5)	Mo1—O1—C29A—C30A	165.2 (15)
C1—P1—C7—C12	−47.7 (6)	O1—C29A—C30A—C31A	38 (4)
C13—P1—C7—C12	−153.6 (5)	C29A—C30A—C31A—C32A	−39 (4)
Mo1—P1—C7—C12	82.1 (5)	C29—O1—C32A—C31A	−4(6)
C1—P1—C7—C8	137.5 (5)	C29A—O1—C32A—C31A	−3(6)
C13—P1—C7—C8	31.6 (6)	C32—O1—C32A—C31A	−73 (13)
Mo1—P1—C7—C8	−92.7 (5)	Mo1—O1—C32A—C31A	170 (2)
C12—C7—C8—C9	1.4 (10)	C30A—C31A—C32A—O1	27 (5)

Fig. 1


C30
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C22
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Cl1
C16
C15
C6
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C28
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C2
Cl2
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(Acetato-κ^2O,O')bis(1,10-phenanthroline-κ^2N,N')copper(II) trifluoroacetate tetrahydrate

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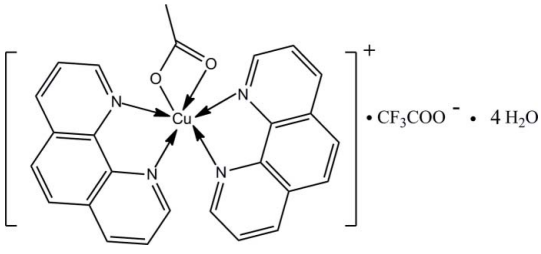
Key indicators: single-crystal X-ray study; T = 293 K; mean σ(C–C) = 0.008 Å; disorder in solvent or counterion; R factor = 0.051; wR factor = 0.159; data-to-parameter ratio = 12.0.

In the title compound, $[Cu(CH_3CO_2)(C_{12}H_8N_2)_2](CF_3CO_2)\cdot 4H_2O$, the Cu^{II} atom shows a distorted octahedral coordination with four N atoms [Cu—N = 2.015 (3)–2.244 (3) Å] from the two phenanthroline ligands and two O atoms from the acetate [Cu—O = 1.953 (3) and 2.764 (3) Å]. Strong intermolecular O—H···O hydrogen-bonding interactions consolidate the crystal packing. The F atoms of the anion are disordered over two positions in a 0.5233 (3):0.4767 (3) ratio.

Related literature

For metal–1,10-phenanthroline complexes with carboxylates, see: Sun *et al.* (2007); Liu *et al.* (2009).



Experimental

Crystal data

$[Cu(C_2H_3O_2)(C_{12}H_8N_2)_2](C_2F_3O_2)\cdot 4H_2O$
M_r = 668.08
Triclinic, $P\overline{1}$
a = 8.9019 (7) Å
b = 11.6662 (9) Å
c = 15.698 (1) Å
α = 101.619 (1)°
β = 101.512 (1)°
γ = 108.514 (1)°
V = 1451.98 (19) Å^3
Z = 2
Mo $K\alpha$ radiation
μ = 0.83 mm^{-1}
T = 293 K
0.28 × 0.25 × 0.19 mm

Data collection

Bruker SMART APEX diffractometer
Absorption correction: multi-scan (*SADABS*; Bruker, 2005)
T_{min} = 0.801, T_{max} = 0.859
7689 measured reflections
5112 independent reflections
4389 reflections with $I > 2\sigma(I)$
R_{int} = 0.043

Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.051
$wR(F^2)$ = 0.159
S = 1.02
5112 reflections
425 parameters
103 restraints
H-atom parameters constrained
$\Delta\rho_{max}$ = 1.04 e Å^{-3}
$\Delta\rho_{min}$ = −0.87 e Å^{-3}

Table 1
Selected geometric parameters (Å, °).

Cu1—O1	1.953 (3)	Cu1—N2	2.037 (3)
Cu1—N1	2.015 (3)	Cu1—N3	2.244 (3)
Cu1—N4	2.022 (3)		
O1—Cu1—N1	91.55 (13)	N4—Cu1—N2	92.78 (14)
O1—Cu1—N4	93.66 (13)	O1—Cu1—N3	93.94 (12)
N1—Cu1—N4	169.21 (13)	N1—Cu1—N3	110.64 (13)
O1—Cu1—N2	171.51 (12)	N4—Cu1—N3	78.44 (13)
N1—Cu1—N2	81.21 (14)	N2—Cu1—N3	92.75 (13)

Table 2
Hydrogen-bond geometry (Å, °).

D—H···A	D—H	H···A	D···A	D—H···A
O7—H7A···O5	0.85	1.95	2.787 (8)	168
O7—H7B···O4	0.85	2.11	2.854 (8)	145
O6—H6A···O1	0.85	2.00	2.844 (5)	170
O6—H6B···O4^{i}	0.85	2.03	2.881 (7)	175
O8—H8B···O3^{ii}	0.85	2.03	2.868 (10)	171
O8—H8A···O6^{iii}	0.85	2.17	2.809 (9)	132

Symmetry codes: (i) $x, y-1, z$; (ii) $x+1, y, z$; (iii) $x, y+1, z$.

Data collection: *SMART* (Bruker, 2005); cell refinement: *SAINT* (Bruker, 2005); data reduction: *SAINT*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *XP* in *SHELXTL* (Sheldrick, 2008); software used to prepare material for publication: *SHELXL97*.

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Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: EZ2212).

References

Bruker (2005). *SMART*, *SAINT* and *SADABS*. Bruker AXS Inc., Madison, Wisconsin, USA.
Liu, Y., Ning, J., Sun, J. & Zhang, C. (2009). *Acta Cryst.* E**65**, m113.
Sheldrick, G. M. (2008). *Acta Cryst.* A**64**, 112–122.
Sun, J., Ma, C. & Zhang, R. (2007). *Acta Cryst.* E**63**, m2691–m2692.

supplementary materials

Acta Cryst. (2010). E**66**, m865 [**doi:10.1107/S1600536810024359**]

(Acetato-κ^2O,O')bis(1,10-phenanthroline-κ^2N,N')copper(II) trifluoroacetate tetrahydrate

J. Wang and Z. Jin

Comment

Metal complexes with carboxylates are among the most investigated complexes in the field of coordination chemistry, in which metal-1,10-phenanthroline complexes and their derivatives have also attracted much attention during recent decades because of their interesting features (Sun *et al.*, 2007; Liu *et al.*, 2009). In this work, the title compound was obtained by the reaction of trifluoroacetic acid and cupric acetate in the presence of 1,10-phenanthroline as co-ligand.

The molecular structure of the title complex is shown in Fig. 1. The Cu^{II} atom exhibits a six-coordinate distorted octahedral geometry with four N atoms [Cu—N 2.015 (3) Å–2.244 (3) Å] from two phenanthroline ligands and two O atoms from the acetate ligand [Cu—O 1.953 (3), 2.764 (3) Å]. Three N atoms and one O atom occupy the equatorial positions with a slight departure from the ideal plane by 0.0563 (2) Å, while one O atom and one N atom lie in the apical positions with an axis angle of 140.63 (10)°, showing a large deviation from the expected 180°. Strong intermolecular O—H···O hydrogen bonding interactions exist.

Experimental

The reaction was carried out by the solvothermal method. Trifluoroacetic acid (0.114 g,1 mmol) and cupric acetate (0.199 g, 1 mmol) and 1,10-phenanthroline (0.312 g, 2 mmol) were added to an airtight vessel with the 21 ml of a 2:1 ethanol-water mixture. The resulting blue solution was filtered. Upon standing, the filtrate yielded blue block-shaped crystals after several days.

The yield is 76% and elemental analysis: calc. for $C_{28}H_{27}CuF_3N_4O_8$: C 50.34, H 4.07, N 8.39; found: C 50.52, H 4.29, N 8.53. The elemental analyses were performed with PERKIN ELMER MODEL 2400 SERIES II.

Refinement

The U_{iso}(H) values were set at 1.2U_{eq}(C—H) for the H atoms from the phen rings and waters, 1.5U_{eq}(C—H) for the methyl moiety. As the diffraction intensities were of high quality, the H atoms could be located in difference Fourier maps and refined using the riding model. Three disordered F atoms were treated as statistically disordered between two positions with the refined occupancies of 0.5233 (3) and 0.4767 (3), respectively.

Figures

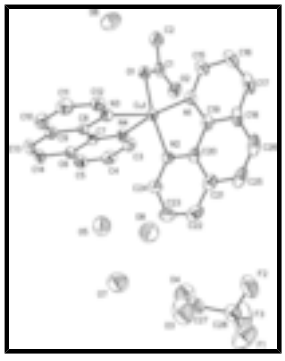


Fig. 1. The molecular structure of title compound, with atom labels and 30% probability displacement ellipsoids for non-H atoms.

(Acetato-κ^2*O*,*O*')bis(1,10-phenanthroline- κ^2*N*,*N*')copper(II) trifluoroacetate tetrahydrate

Crystal data

$[Cu(C_2H_3O_2)(C_{12}H_8N_2)_2](C_2F_3O_2)\cdot 4H_2O$	$Z = 2$
$M_r = 668.08$	$F(000) = 686$
Triclinic, $P\overline{1}$	$D_x = 1.528$ Mg m^{-3}
$a = 8.9019$ (7) Å	Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å
$b = 11.6662$ (9) Å	Cell parameters from 4430 reflections
$c = 15.698$ (1) Å	$\theta = 2.5$–$27.8°$
$\alpha = 101.619$ (1)°	$\mu = 0.83$ mm^{-1}
$\beta = 101.512$ (1)°	$T = 293$ K
$\gamma = 108.514$ (1)°	Block, blue
$V = 1451.98$ (19) Å^3	0.28 × 0.25 × 0.19 mm

Data collection

Bruker SMART APEX diffractometer	5112 independent reflections
Radiation source: fine-focus sealed tube	4389 reflections with $I > 2\sigma(I)$
graphite	$R_{int} = 0.043$
phi and ω scans	$\theta_{max} = 25.1°$, $\theta_{min} = 2.5°$
Absorption correction: multi-scan (*SADABS*; Bruker, 2005)	$h = -10 \rightarrow 10$
$T_{min} = 0.801$, $T_{max} = 0.859$	$k = -13 \rightarrow 13$
7689 measured reflections	$l = -18 \rightarrow 17$

Refinement

Refinement on F^2	Primary atom site location: structure-invariant direct methods
Least-squares matrix: full	Secondary atom site location: difference Fourier map
$R[F^2 > 2\sigma(F^2)] = 0.051$	Hydrogen site location: inferred from neighbouring sites

$wR(F^2) = 0.159$	H-atom parameters constrained
$S = 1.02$	$w = 1/[\sigma^2(F_o^2) + (0.108P)^2 + 0.7243P]$ where $P = (F_o^2 + 2F_c^2)/3$
5112 reflections	$(\Delta/\sigma)_{max} = 0.002$
425 parameters	$\Delta\rho_{max} = 1.04$ e Å^{-3}
103 restraints	$\Delta\rho_{min} = -0.86$ e Å^{-3}

Special details

Geometry. All e.s.d.'s (except the e.s.d. in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell e.s.d.'s are taken into account individually in the estimation of e.s.d.'s in distances, angles and torsion angles; correlations between e.s.d.'s in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell e.s.d.'s is used for estimating e.s.d.'s involving l.s. planes.

Refinement. Refinement of F^2 against ALL reflections. The weighted *R*-factor *wR* and goodness of fit *S* are based on F^2, conventional *R*-factors *R* are based on *F*, with *F* set to zero for negative F^2. The threshold expression of $F^2 > \sigma(F^2)$ is used only for calculating *R*-factors(gt) *etc*. and is not relevant to the choice of reflections for refinement. *R*-factors based on F^2 are statistically about twice as large as those based on *F*, and *R*- factors based on ALL data will be even larger.

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å^2)

	x	*y*	*z*	U_{iso}*/U_{eq}	Occ. (<1)
Cu1	0.70769 (5)	0.42710 (4)	0.71713 (3)	0.0397 (2)	
F1	0.083 (2)	0.9968 (17)	0.6171 (10)	0.133 (4)	0.52 (2)
F2	0.138 (2)	0.8377 (11)	0.5566 (10)	0.118 (4)	0.52 (2)
F3	0.3252 (15)	1.0243 (15)	0.6021 (9)	0.121 (4)	0.52 (2)
F1'	0.0317 (13)	0.9385 (17)	0.5837 (12)	0.120 (4)	0.48 (2)
F2'	0.206 (2)	0.8680 (17)	0.5546 (10)	0.117 (4)	0.48 (2)
F3'	0.263 (2)	1.0720 (11)	0.6148 (9)	0.116 (4)	0.48 (2)
N1	0.5545 (4)	0.3202 (3)	0.5937 (2)	0.0432 (8)	
N2	0.5668 (4)	0.5324 (3)	0.6982 (2)	0.0440 (8)	
N3	0.6031 (4)	0.3667 (3)	0.8268 (2)	0.0439 (8)	
N4	0.8712 (4)	0.5606 (3)	0.8296 (2)	0.0428 (8)	
O1	0.8368 (4)	0.3195 (3)	0.7158 (2)	0.0491 (7)	
O2	0.9846 (4)	0.4555 (4)	0.6563 (2)	0.0676 (9)	
O3	0.1324 (9)	0.8811 (7)	0.7380 (5)	0.146 (2)	
O4	0.3983 (7)	0.9689 (5)	0.7462 (4)	0.1105 (16)	
O5	0.7803 (6)	0.8614 (5)	0.9518 (4)	0.1055 (15)	
H5A	0.8130	0.8679	0.9051	0.127*	
H5B	0.8480	0.9207	0.9978	0.127*	
O6	0.7421 (6)	0.0847 (4)	0.7568 (4)	0.0954 (14)	
H6A	0.7587	0.1508	0.7392	0.115*	
H6B	0.6419	0.0542	0.7570	0.115*	
O7	0.5361 (8)	0.9627 (7)	0.9249 (4)	0.139 (2)	
H7A	0.6116	0.9327	0.9256	0.166*	
H7B	0.5276	0.9963	0.8818	0.166*	
O8	0.9949 (10)	1.0217 (8)	0.8494 (5)	0.176 (3)	

H8A	0.8909	0.9997	0.8294	0.211*
H8B	1.0276	0.9799	0.8113	0.211*
C1	0.9569 (5)	0.3597 (5)	0.6812 (3)	0.0505 (10)
C2	1.0606 (7)	0.2817 (6)	0.6725 (4)	0.0720 (15)
H2A	1.0192	0.2109	0.6951	0.108*
H2B	1.1731	0.3315	0.7071	0.108*
H2C	1.0556	0.2522	0.6099	0.108*
C3	1.0023 (6)	0.6569 (4)	0.8305 (3)	0.0539 (11)
H3	1.0226	0.6644	0.7757	0.065*
C4	1.1096 (6)	0.7466 (4)	0.9102 (4)	0.0624 (13)
H4	1.1998	0.8126	0.9082	0.075*
C5	1.0821 (6)	0.7371 (4)	0.9907 (3)	0.0583 (12)
H5	1.1533	0.7966	1.0444	0.070*
C6	0.9449 (5)	0.6366 (4)	0.9928 (3)	0.0497 (10)
C7	0.8417 (5)	0.5507 (4)	0.9101 (3)	0.0402 (9)
C8	0.6997 (5)	0.4478 (4)	0.9087 (3)	0.0401 (9)
C9	0.6667 (6)	0.4339 (4)	0.9899 (3)	0.0511 (11)
C10	0.5254 (7)	0.3300 (5)	0.9842 (4)	0.0659 (14)
H10	0.4985	0.3174	1.0368	0.079*
C11	0.4303 (7)	0.2496 (5)	0.9031 (4)	0.0676 (14)
H11	0.3378	0.1809	0.8992	0.081*
C12	0.4720 (6)	0.2712 (4)	0.8253 (3)	0.0544 (11)
H12	0.4047	0.2153	0.7694	0.065*
C13	0.7751 (7)	0.5228 (5)	1.0731 (3)	0.0633 (13)
H13	0.7536	0.5136	1.1274	0.076*
C14	0.9071 (7)	0.6189 (5)	1.0746 (3)	0.0627 (13)
H14	0.9755	0.6753	1.1301	0.075*
C15	0.5530 (6)	0.2158 (4)	0.5418 (3)	0.0566 (11)
H15	0.6303	0.1826	0.5631	0.068*
C16	0.4407 (7)	0.1531 (5)	0.4566 (3)	0.0685 (14)
H16	0.4453	0.0806	0.4214	0.082*
C17	0.3246 (7)	0.1982 (6)	0.4250 (3)	0.0719 (16)
H17	0.2476	0.1556	0.3687	0.086*
C18	0.3210 (5)	0.3089 (5)	0.4771 (3)	0.0568 (12)
C19	0.4408 (5)	0.3674 (4)	0.5617 (3)	0.0446 (9)
C20	0.4465 (5)	0.4808 (4)	0.6192 (3)	0.0435 (9)
C21	0.3284 (5)	0.5328 (5)	0.5919 (3)	0.0549 (11)
C22	0.3376 (7)	0.6413 (6)	0.6535 (4)	0.0709 (15)
H22	0.2617	0.6788	0.6392	0.085*
C23	0.4577 (8)	0.6925 (5)	0.7343 (4)	0.0720 (15)
H23	0.4622	0.7637	0.7757	0.086*
C24	0.5729 (6)	0.6375 (5)	0.7545 (3)	0.0585 (12)
H24	0.6565	0.6751	0.8090	0.070*
C25	0.2096 (6)	0.4726 (6)	0.5058 (4)	0.0689 (16)
H25	0.1326	0.5073	0.4870	0.083*
C26	0.2068 (6)	0.3658 (7)	0.4505 (4)	0.0698 (16)
H26	0.1285	0.3295	0.3941	0.084*
C27	0.2466 (9)	0.9333 (5)	0.7120 (4)	0.0738 (16)
C28	0.1951 (7)	0.9529 (5)	0.6193 (4)	0.0709 (14)

Atomic displacement parameters (Å^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Cu1	0.0400 (3)	0.0424 (3)	0.0318 (3)	0.0131 (2)	0.0061 (2)	0.0079 (2)
F1	0.127 (8)	0.135 (8)	0.138 (8)	0.076 (6)	−0.004 (6)	0.033 (6)
F2	0.108 (8)	0.122 (6)	0.075 (5)	−0.001 (6)	0.009 (6)	0.010 (5)
F3	0.109 (7)	0.130 (7)	0.119 (6)	0.005 (6)	0.049 (5)	0.070 (6)
F1'	0.071 (6)	0.127 (8)	0.130 (8)	0.013 (6)	0.004 (5)	0.032 (6)
F2'	0.118 (8)	0.148 (8)	0.071 (5)	0.060 (7)	0.024 (6)	−0.015 (6)
F3'	0.127 (8)	0.102 (7)	0.094 (6)	0.006 (6)	0.018 (6)	0.050 (5)
N1	0.0406 (18)	0.0477 (19)	0.0347 (17)	0.0091 (15)	0.0117 (14)	0.0089 (15)
N2	0.0454 (19)	0.0455 (19)	0.0408 (18)	0.0165 (15)	0.0121 (15)	0.0125 (15)
N3	0.0445 (19)	0.0401 (18)	0.0436 (19)	0.0126 (15)	0.0115 (15)	0.0108 (15)
N4	0.0416 (18)	0.0445 (18)	0.0366 (17)	0.0123 (15)	0.0057 (14)	0.0110 (15)
O1	0.0505 (17)	0.0550 (17)	0.0462 (16)	0.0231 (14)	0.0162 (13)	0.0159 (14)
O2	0.072 (2)	0.080 (2)	0.066 (2)	0.0317 (19)	0.0306 (18)	0.038 (2)
O3	0.175 (6)	0.155 (6)	0.132 (5)	0.042 (5)	0.091 (5)	0.077 (5)
O4	0.098 (4)	0.090 (3)	0.113 (4)	0.023 (3)	−0.004 (3)	0.020 (3)
O5	0.093 (3)	0.131 (4)	0.099 (3)	0.045 (3)	0.031 (3)	0.038 (3)
O6	0.090 (3)	0.075 (3)	0.127 (4)	0.027 (2)	0.034 (3)	0.044 (3)
O7	0.136 (5)	0.190 (6)	0.109 (4)	0.102 (5)	0.023 (4)	0.029 (4)
O8	0.203 (8)	0.259 (9)	0.161 (7)	0.159 (7)	0.096 (6)	0.099 (7)
C1	0.051 (2)	0.068 (3)	0.034 (2)	0.025 (2)	0.0098 (18)	0.016 (2)
C2	0.076 (3)	0.102 (4)	0.062 (3)	0.053 (3)	0.032 (3)	0.030 (3)
C3	0.051 (3)	0.051 (2)	0.051 (3)	0.009 (2)	0.008 (2)	0.018 (2)
C4	0.047 (3)	0.045 (3)	0.074 (3)	0.004 (2)	0.001 (2)	0.012 (2)
C5	0.053 (3)	0.048 (3)	0.052 (3)	0.015 (2)	−0.007 (2)	−0.003 (2)
C6	0.052 (2)	0.052 (2)	0.042 (2)	0.026 (2)	0.0027 (19)	0.0063 (19)
C7	0.044 (2)	0.043 (2)	0.0327 (19)	0.0205 (18)	0.0040 (16)	0.0087 (16)
C8	0.045 (2)	0.044 (2)	0.038 (2)	0.0233 (18)	0.0126 (17)	0.0132 (17)
C9	0.062 (3)	0.062 (3)	0.046 (2)	0.036 (2)	0.023 (2)	0.021 (2)
C10	0.075 (3)	0.078 (4)	0.068 (3)	0.035 (3)	0.041 (3)	0.037 (3)
C11	0.066 (3)	0.060 (3)	0.083 (4)	0.019 (3)	0.036 (3)	0.029 (3)
C12	0.054 (3)	0.044 (2)	0.061 (3)	0.012 (2)	0.020 (2)	0.014 (2)
C13	0.086 (4)	0.079 (4)	0.036 (2)	0.043 (3)	0.022 (2)	0.017 (2)
C14	0.075 (3)	0.078 (3)	0.033 (2)	0.039 (3)	0.005 (2)	0.004 (2)
C15	0.058 (3)	0.053 (3)	0.048 (3)	0.010 (2)	0.018 (2)	0.004 (2)
C16	0.070 (3)	0.063 (3)	0.049 (3)	0.005 (3)	0.020 (2)	−0.003 (2)
C17	0.056 (3)	0.086 (4)	0.034 (2)	−0.008 (3)	0.005 (2)	−0.002 (2)
C18	0.041 (2)	0.078 (3)	0.037 (2)	0.001 (2)	0.0096 (18)	0.019 (2)
C19	0.034 (2)	0.056 (2)	0.038 (2)	0.0049 (18)	0.0116 (16)	0.0184 (19)
C20	0.036 (2)	0.055 (2)	0.042 (2)	0.0124 (18)	0.0152 (17)	0.0231 (19)
C21	0.043 (2)	0.071 (3)	0.064 (3)	0.022 (2)	0.022 (2)	0.039 (3)
C22	0.066 (3)	0.079 (4)	0.096 (4)	0.043 (3)	0.035 (3)	0.050 (3)
C23	0.086 (4)	0.062 (3)	0.083 (4)	0.041 (3)	0.032 (3)	0.022 (3)
C24	0.068 (3)	0.056 (3)	0.055 (3)	0.029 (2)	0.017 (2)	0.013 (2)
C25	0.039 (2)	0.108 (5)	0.071 (3)	0.024 (3)	0.015 (2)	0.056 (4)

C26	0.037 (2)	0.115 (5)	0.047 (3)	0.010 (3)	0.005 (2)	0.038 (3)
C27	0.094 (4)	0.050 (3)	0.073 (4)	0.018 (3)	0.036 (3)	0.010 (3)
C28	0.069 (3)	0.065 (3)	0.074 (4)	0.015 (3)	0.028 (3)	0.020 (3)

Geometric parameters (Å, °)

Cu1—O1	1.953 (3)	C4—H4	0.9300
Cu1—N1	2.015 (3)	C5—C6	1.410 (7)
Cu1—N4	2.022 (3)	C5—H5	0.9300
Cu1—N2	2.037 (3)	C6—C7	1.397 (6)
Cu1—N3	2.244 (3)	C6—C14	1.428 (7)
F1—C28	1.256 (11)	C7—C8	1.433 (6)
F2—C28	1.367 (12)	C8—C9	1.392 (6)
F3—C28	1.308 (10)	C9—C10	1.415 (7)
F1'—C28	1.393 (12)	C9—C13	1.425 (7)
F2'—C28	1.311 (12)	C10—C11	1.343 (8)
F3'—C28	1.351 (11)	C10—H10	0.9301
N1—C15	1.317 (6)	C11—C12	1.392 (7)
N1—C19	1.357 (5)	C11—H11	0.9300
N2—C24	1.337 (6)	C12—H12	0.9300
N2—C20	1.344 (5)	C13—C14	1.334 (8)
N3—C12	1.326 (6)	C13—H13	0.9300
N3—C8	1.357 (5)	C14—H14	0.9300
N4—C3	1.333 (6)	C15—C16	1.389 (7)
N4—C7	1.361 (5)	C15—H15	0.9300
O1—C1	1.294 (5)	C16—C17	1.355 (8)
O2—C1	1.226 (6)	C16—H16	0.9300
O3—C27	1.202 (8)	C17—C18	1.396 (8)
O4—C27	1.245 (8)	C17—H17	0.9300
O5—H5A	0.8500	C18—C19	1.406 (6)
O5—H5B	0.8500	C18—C26	1.422 (8)
O6—H6A	0.8501	C19—C20	1.423 (6)
O6—H6B	0.8500	C20—C21	1.410 (6)
O7—H7A	0.8500	C21—C22	1.397 (8)
O7—H7B	0.8501	C21—C25	1.419 (7)
O8—H8A	0.8500	C22—C23	1.363 (8)
O8—H8B	0.8500	C22—H22	0.9300
C1—C2	1.494 (7)	C23—C24	1.391 (7)
C2—H2A	0.9600	C23—H23	0.9300
C2—H2B	0.9600	C24—H24	0.9300
C2—H2C	0.9600	C25—C26	1.356 (8)
C3—C4	1.390 (7)	C25—H25	0.9300
C3—H3	0.9300	C26—H26	0.9300
C4—C5	1.353 (8)	C27—C28	1.521 (9)
O1—Cu1—N1	91.55 (13)	C14—C13—C9	121.3 (4)
O1—Cu1—N4	93.66 (13)	C14—C13—H13	119.3
N1—Cu1—N4	169.21 (13)	C9—C13—H13	119.4
O1—Cu1—N2	171.51 (12)	C13—C14—C6	121.3 (4)
N1—Cu1—N2	81.21 (14)	C13—C14—H14	119.2

N4—Cu1—N2	92.78 (14)	C6—C14—H14	119.6
O1—Cu1—N3	93.94 (12)	N1—C15—C16	122.8 (5)
N1—Cu1—N3	110.64 (13)	N1—C15—H15	118.5
N4—Cu1—N3	78.44 (13)	C16—C15—H15	118.7
N2—Cu1—N3	92.75 (13)	C17—C16—C15	119.6 (5)
C15—N1—C19	117.9 (4)	C17—C16—H16	120.2
C15—N1—Cu1	129.2 (3)	C15—C16—H16	120.2
C19—N1—Cu1	112.9 (3)	C16—C17—C18	120.0 (4)
C24—N2—C20	118.2 (4)	C16—C17—H17	120.1
C24—N2—Cu1	129.2 (3)	C18—C17—H17	120.0
C20—N2—Cu1	112.5 (3)	C17—C18—C19	116.7 (5)
C12—N3—C8	117.7 (4)	C17—C18—C26	124.9 (5)
C12—N3—Cu1	132.8 (3)	C19—C18—C26	118.4 (5)
C8—N3—Cu1	109.5 (2)	N1—C19—C18	123.0 (4)
C3—N4—C7	118.3 (4)	N1—C19—C20	116.5 (4)
C3—N4—Cu1	125.3 (3)	C18—C19—C20	120.5 (4)
C7—N4—Cu1	116.4 (3)	N2—C20—C21	123.5 (4)
C1—O1—Cu1	110.9 (3)	N2—C20—C19	116.9 (4)
H5A—O5—H5B	109.6	C21—C20—C19	119.6 (4)
H6A—O6—H6B	109.6	C22—C21—C20	116.4 (4)
H7A—O7—H7B	109.8	C22—C21—C25	124.8 (5)
H8A—O8—H8B	108.6	C20—C21—C25	118.8 (5)
O2—C1—O1	122.5 (4)	C23—C22—C21	120.3 (5)
O2—C1—C2	121.4 (4)	C23—C22—H22	119.8
O1—C1—C2	116.0 (4)	C21—C22—H22	119.9
C1—C2—H2A	109.0	C22—C23—C24	119.6 (5)
C1—C2—H2B	109.7	C22—C23—H23	120.1
H2A—C2—H2B	109.5	C24—C23—H23	120.3
C1—C2—H2C	109.8	N2—C24—C23	122.0 (5)
H2A—C2—H2C	109.5	N2—C24—H24	119.3
H2B—C2—H2C	109.5	C23—C24—H24	118.7
N4—C3—C4	122.7 (4)	C26—C25—C21	121.3 (5)
N4—C3—H3	118.7	C26—C25—H25	119.6
C4—C3—H3	118.7	C21—C25—H25	119.2
C5—C4—C3	119.5 (5)	C25—C26—C18	121.4 (5)
C5—C4—H4	120.3	C25—C26—H26	119.1
C3—C4—H4	120.2	C18—C26—H26	119.5
C4—C5—C6	119.7 (4)	O3—C27—O4	130.9 (7)
C4—C5—H5	120.2	O3—C27—C28	113.8 (7)
C6—C5—H5	120.1	O4—C27—C28	115.2 (6)
C7—C6—C5	117.6 (4)	F1—C28—F3	113.6 (9)
C7—C6—C14	118.9 (4)	F1—C28—F2'	127.6 (11)
C5—C6—C14	123.5 (4)	F3—C28—F2'	81.4 (9)
N4—C7—C6	122.2 (4)	F1—C28—F3'	74.3 (9)
N4—C7—C8	118.1 (3)	F3—C28—F3'	40.5 (6)
C6—C7—C8	119.6 (4)	F2'—C28—F3'	113.5 (10)
N3—C8—C9	122.7 (4)	F1—C28—F2	110.5 (9)
N3—C8—C7	117.6 (3)	F3—C28—F2	106.9 (8)
C9—C8—C7	119.7 (4)	F2'—C28—F2	26.1 (8)

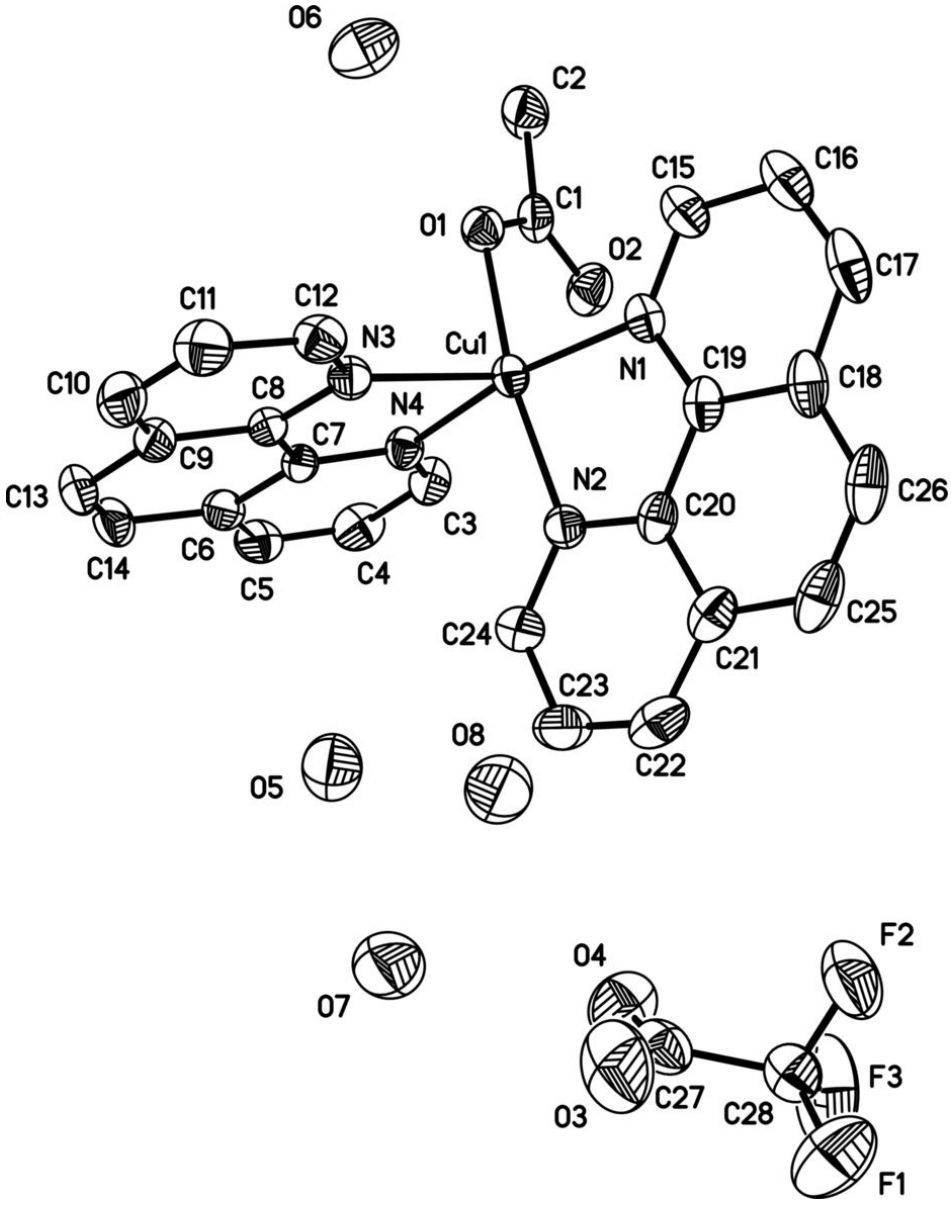
C8—C9—C10	117.2 (4)	F3'—C28—F2	132.9 (10)
C8—C9—C13	119.1 (4)	F1—C28—F1'	30.7 (7)
C10—C9—C13	123.7 (4)	F3—C28—F1'	126.8 (10)
C11—C10—C9	120.0 (5)	F2'—C28—F1'	99.2 (9)
C11—C10—H10	120.0	F3'—C28—F1'	96.1 (9)
C9—C10—H10	120.0	F2—C28—F1'	79.8 (9)
C10—C11—C12	119.0 (5)	F1—C28—C27	109.3 (8)
C10—C11—H11	120.3	F3—C28—C27	109.3 (8)
C12—C11—H11	120.7	F2'—C28—C27	112.0 (9)
N3—C12—C11	123.4 (5)	F3'—C28—C27	115.4 (7)
N3—C12—H12	118.3	F2—C28—C27	107.1 (8)
C11—C12—H12	118.3	F1'—C28—C27	119.0 (8)

Hydrogen-bond geometry (Å, °)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
O7—H7A···O5	0.85	1.95	2.787 (8)	168
O7—H7B···O4	0.85	2.11	2.854 (8)	145
O6—H6A···O1	0.85	2.00	2.844 (5)	170
O6—H6B···O4^{i}	0.85	2.03	2.881 (7)	175
O8—H8B···O3^{ii}	0.85	2.03	2.868 (10)	171
O8—H8A···O6^{iii}	0.85	2.17	2.809 (9)	132

Symmetry codes: (i) *x*, *y*−1, *z*; (ii) *x*+1, *y*, *z*; (iii) *x*, *y*+1, *z*.

Fig. 1


O6
C2
C15
C16
C1
O1
O2
C17
C11
C12
N3
Cu1
N1
C19
C18
C10
C8
N4
C7
C9
N2
C26
C13
C3
C20
C6
C14
C5
C4
C24
C25
C21
C23
O8
C22
O5
F2
O4
O7
F3
C27
O3
C28
F1

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(4-Chlorophenyl)(3,6-dibromo-2-hydroxy-7-methoxy-1-naphthyl)methanone

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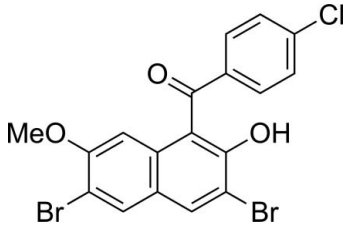
Key indicators: single-crystal X-ray study; T = 193 K; mean σ(C–C) = 0.004 Å; R factor = 0.031; wR factor = 0.081; data-to-parameter ratio = 14.4.

The asymmetric unit of the title compound, $C_{18}H_{11}Br_2ClO_3$, contains two crystallographically independent molecules in which the dihedral angles between the naphthalene ring systems and the benzene rings are 55.64 (11) and 60.50 (11)°. In each molecule, an intramolecular O—H···O=C hydrogen bond generates a six-membered ring. In the crystal structure, intermolecular C—H···O and C—H···Cl hydrogen bonds and two different Br···O halogen bonds [2.9850 (19) and 3.2169 (19) Å] are observed.

Related literature

For the structures of closely related compounds, see: Mitsui *et al.* (2008*a*,*b*, 2009, 2010*a*,*b*,*c*). For a review of halogen bonding, see: Politzer *et al.* (2007).



Experimental

Crystal data

$C_{18}H_{11}Br_2ClO_3$
M_r = 470.54
Monoclinic, $C2/c$
a = 32.1178 (6) Å
b = 11.1814 (2) Å
c = 19.7078 (4) Å
β = 104.687 (1)°
V = 6846.2 (2) Å^3
Z = 16
Cu $K\alpha$ radiation
μ = 7.57 mm^{-1}
T = 193 K
0.30 × 0.30 × 0.10 mm

Data collection

Rigaku R-AXIS RAPID diffractometer
Absorption correction: numerical (*NUMABS*; Higashi, 1999)
T_{min} = 0.135, T_{max} = 0.469
60758 measured reflections
6263 independent reflections
5929 reflections with $I > 2\sigma(I)$
R_{int} = 0.036

Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.031
$wR(F^2)$ = 0.081
S = 1.14
6263 reflections
435 parameters
H-atom parameters constrained
$\Delta\rho_{max}$ = 0.85 e Å^{-3}
$\Delta\rho_{min}$ = −1.08 e Å^{-3}

Table 1
Hydrogen-bond geometry (Å, °).

D—H···A	D—H	H···A	D···A	D—H···A
O2—H2*O*···O1	0.79	1.77	2.497 (3)	153
O5—H5*O*···O4	0.78	1.85	2.568 (3)	153
C4—H4···O4^{i}	0.95	2.42	3.338 (3)	162
C18—H18*A*···Cl2^{ii}	0.98	2.81	3.406 (3)	120
C34—H34···O2^{iii}	0.95	2.49	3.397 (4)	160

Symmetry codes: (i) $x, -y+1, z-\frac{1}{2}$; (ii) $-x+\frac{1}{2}, -y+\frac{1}{2}, -z+1$; (iii) $x, -y, z+\frac{1}{2}$.

Data collection: *PROCESS-AUTO* (Rigaku, 1998); cell refinement: *PROCESS-AUTO*; data reduction: *CrystalStructure* (Rigaku/MSC, 2004); program(s) used to solve structure: *SIR2004* (Burla *et al.*, 2005); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *ORTEPIII* (Burnett & Johnson, 1996); software used to prepare material for publication: *SHELXL97*.

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Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: EZ2214).

References

Burla, M. C., Caliandro, R., Camalli, M., Carrozzini, B., Cascarano, G. L., De Caro, L., Giacovazzo, C., Polidori, G. & Spagna, R. (2005). *J. Appl. Cryst.* **38**, 381–388.
Burnett, M. N. & Johnson, C. K. (1996). *ORTEPIII*. Report ORNL-6895. Oak Ridge National Laboratory. Tennessee, USA.
Higashi, T. (1999). *NUMABS*. Rigaku Corporation, Tokyo, Japan.
Mitsui, R., Nagasawa, A., Watanabe, S., Okamoto, A. & Yonezawa, N. (2010*b*). *Acta Cryst.* E**66**, o873.
Mitsui, R., Nakaema, K., Nagasawa, A., Noguchi, K. & Yonezawa, N. (2010*a*). *Acta Cryst.* E**66**, o676.
Mitsui, R., Nakaema, K., Noguchi, K., Okamoto, A. & Yonezawa, N. (2008*a*). *Acta Cryst.* E**64**, o1278.
Mitsui, R., Nakaema, K., Noguchi, K. & Yonezawa, N. (2008*b*). *Acta Cryst.* E**64**, o2497.
Mitsui, R., Noguchi, K. & Yonezawa, N. (2009). *Acta Cryst.* E**65**, o543.
Mitsui, R., Watanabe, S., Nagasawa, A., Okamoto, A. & Yonezawa, N. (2010*c*). *Acta Cryst.* E**66**, o1304.
Politzer, P., Lane, P., Concha, M. C., Ma, Y. & Murray, J. S. (2007). *J. Mol. Model.* **13**, 305–311.
Rigaku (1998). *PROCESS-AUTO*. Rigaku Corporation, Tokyo, Japan.
Rigaku/MSC (2004). *CrystalStructure*. Rigaku/MSC, The Woodlands, Texas, USA.
Sheldrick, G. M. (2008). *Acta Cryst.* A**64**, 112–122.

supplementary materials

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(4-Chlorophenyl)(3,6-dibromo-2-hydroxy-7-methoxy-1-naphthyl)methanone

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Comment

Recently, we reported the crystal structures of 1-aroylated 2,7-dimethoxynaphthalenes, 1-(4-chlorobenzoyl)-2,7-dimethoxynaphthalene (Mitsui *et al.*, 2008*a*), (4-chlorophenyl)(2-hydroxy-7-methoxynaphthalen-1-yl)methanone (Mitsui *et al.*, 2008*b*), (4-chlorophenyl)(2-ethoxy-7-methoxynaphthalen-1-yl)methanone (Mitsui *et al.*, 2009), 1-bromo-8-(4-chlorobenzoyl)-7-hydroxy-2-methoxynaphthalene (Mitsui *et al.*, 2010*a*), (8-bromo-2,7-dimethoxy-1-naphthyl)(4-chlorophenyl)methanone (Mitsui *et al.*, 2010*b*) and (4-chlorophenyl)(3,8-dibromo-2-hydroxy-7-methoxy-1-naphthyl)methanone (Mitsui *et al.*, 2010*c*). As a part of our ongoing studies on the synthesis and crystal structure analysis of aroylated naphthalene derivatives, we prepared and analysed the structure of a single crystal of 2,7-dibromo-4-(4-chlorobenzoyl)-3-hydroxy-6-methoxynaphthalene, (I). The title compound was prepared by electrophilic aromatic bromination reaction of (4-chlorophenyl)(2-hydroxy-7-methoxynaphthalen-1-yl)methanone with bromine.

An *ORTEPIII* (Burnett & Johnson, 1996) plot of (I) is shown in Fig. 1. The title compound crystallizes in the monoclinic crystal system such that there are two molecules in the asymmetric unit, molecules *A* and *B*, respectively. In *A*, the dihedral angle between the naphthalene ring (C1–C10) and the benzene ring (C12–C17) is 55.64 (11)°, and the central carbonyl C—(C═O)—C group is relatively coplanar to the naphthalene ring [9.72 (15)°]. In *B*, by contrast, the dihedral angle between the naphthalene ring (C19–C28) and the benzene ring (C30–C35) is 60.50 (11)°, and the central carbonyl C—(C═O)—C group is twisted away from the naphthalene ring [23.73 (15)°]. In each molecule, the hydroxy groups are involved in O—H···O═C hydrogen bond generates a six-membered ring (Fig. 1 and Table 1).

In the crystal structure, intermolecular C—H···O and C—H···Cl hydrogen bonding interactions contribute to the stabilization of the molecular and crystal structures (Figs. 2 and 3, Table 1). Additionally, the contact distances Br2···O1 and Br3···O6 are 2.9850 (19) and 3.2169 (19) Å, respectively (Figs. 2 and 3). These contacts are shorter than the sum of their van der Waals radii (3.37 Å), and arranged nearly linearly [C7—Br2···O1 = 172.24 (10)°, C21—Br3···O6 = 142.02 (9)°], suggesting that there is a possibility for halogen bonding, which further contributes to crystal packing stability (Politzer *et al.*, 2007).

Experimental

To a solution of (4-chlorophenyl)(2-hydroxy-7-methoxynaphthalen-1-yl)methanone (313 mg, 1.00 mmol) in chloroform (5 ml) was added Br_2 (646 mg, 4.04 mmol) drop-wise at 0 °C. The reaction mixture was stirred for 12 h at 0 °C, then poured into aqueous 2 *M* $Na_2S_2O_3$ (10 ml), and the aqueous layer was extracted with $CHCl_3$ (3 × 10 ml). The combined organic layers were washed with 2 *M* $Na_2S_2O_3$ (3 × 30 ml) and brine (3 × 30 ml), and dried over $MgSO_4$ overnight. The solvent was removed *in vacuo* and the crude material was purified by column chromatography (silica gel, $CHCl_3$) to give the title compound (yield 409 mg, 87%). Single crystals suitable for X-ray diffraction analysis were obtained from $CHCl_3$ as yellow blocks (m.p. 431.5–432.0 K).

Spectroscopic Data: ^{1}H NMR (300 MHz, $CDCl_3$) δ 10.10 (s, 1H), 8.04 (s, 1H), 7.88 (s, 1H), 7.63 (d, 2H), 7.43 (d, 2H), 6.62 (s, 1H), 3.49 (s, 3H); ^{13}C NMR (75 MHz, DMSO-d_6) δ 194.2, 154.0, 149.2, 138.4, 135.9, 132.3, 131.3, 130.6, 130.5, 128.6, 124.7, 121.0, 111.6, 110.8, 102.8, 55.7; IR (KBr): 1662, 1607, 1591, 1486, 1240, 1211, 1093, 843; HRMS (*m/z*): $[M + H]^+$ calcd for $C_{18}H_{12}Br_2ClO_3$, 468.8842 found, 468.8839. Anal. Calcd for $C_{18}H_{11}Br_2ClO_3$: C 45.95, H 2.36. Found: C 46.10, H 2.32.

Refinement

All the H atoms could be located in difference Fourier maps. All the H atoms were subsequently refined as riding atoms, with O2—H2O = 0.792, O5—H5O = 0.783, C—H = 0.950 (aromatic) and 0.980 (methyl) Å, and U_{iso}(H) = 1.2U_{eq}(C).

Figures

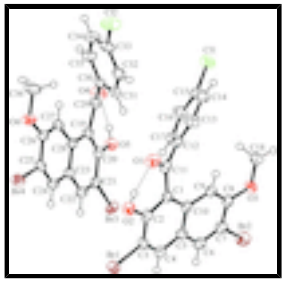


Fig. 1. The asymmetric unit of compound (I), showing 50% probability displacement ellipsoids. The intramolecular hydrogen bond is shown as a dashed line.

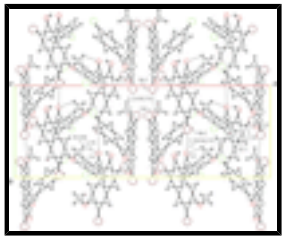


Fig. 2. Partial crystal packing diagram of compound (I), viewed down the *c* axis. Intermolecular C—H···O hydrogen bonds and Br···O halogen bonds are shown as dashed lines.

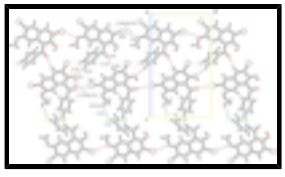


Fig. 3. Partial crystal packing diagram of compound (I), viewed down the *a* axis. Intermolecular C—H···O, C—H···Cl hydrogen bonds and Br···O halogen bonds are shown as dashed lines.

(4-Chlorophenyl)(3,6-dibromo-2-hydroxy-7-methoxy-1-naphthyl)methanone

Crystal data

$C_{18}H_{11}Br_2ClO_3$	$F(000) = 3680$
$M_r = 470.54$	$D_x = 1.826$ Mg m^{-3}
Monoclinic, *C*2/*c*	Melting point = 431.5–432.0 K
Hall symbol: -C 2yc	Cu *Kα* radiation, λ = 1.54187 Å
a = 32.1178 (6) Å	Cell parameters from 39111 reflections
b = 11.1814 (2) Å	θ = 3.2–68.2°
c = 19.7078 (4) Å	μ = 7.57 mm^{-1}

β = 104.687 (1)°	T = 193 K
V = 6846.2 (2) Å^3	Block, yellow
Z = 16	0.30 × 0.30 × 0.10 mm

Data collection

Rigaku R-AXIS RAPID diffractometer	6263 independent reflections
Radiation source: rotating anode	5929 reflections with $I > 2\sigma(I)$
graphite	R_{int} = 0.036
Detector resolution: 10.00 pixels mm^{-1}	θ_{max} = 68.2°, θ_{min} = 4.2°
ω scans	h = −38→38
Absorption correction: numerical (*NUMABS*; Higashi, 1999)	k = −13→13
T_{min} = 0.135, T_{max} = 0.469	l = −23→23
60758 measured reflections	

Refinement

Refinement on F^2	Primary atom site location: structure-invariant direct methods
Least-squares matrix: full	Secondary atom site location: difference Fourier map
$R[F^2 > 2\sigma(F^2)]$ = 0.031	Hydrogen site location: difference Fourier map
$wR(F^2)$ = 0.081	H-atom parameters constrained
S = 1.14	$w = 1/[\sigma^2(F_o^2) + (0.0417P)^2 + 12.8149P]$ where $P = (F_o^2 + 2F_c^2)/3$
6263 reflections	$(\Delta/\sigma)_{max}$ = 0.001
435 parameters	$\Delta\rho_{max}$ = 0.85 e Å^{-3}
0 restraints	$\Delta\rho_{min}$ = −1.08 e Å^{-3}

Special details

Geometry. All e.s.d.'s (except the e.s.d. in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell e.s.d.'s are taken into account individually in the estimation of e.s.d.'s in distances, angles and torsion angles; correlations between e.s.d.'s in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell e.s.d.'s is used for estimating e.s.d.'s involving l.s. planes.

Refinement. Refinement of F^2 against ALL reflections. The weighted R-factor wR and goodness of fit S are based on F^2, conventional R-factors R are based on F, with F set to zero for negative F^2. The threshold expression of $F^2 > \sigma(F^2)$ is used only for calculating R-factors(gt) *etc*. and is not relevant to the choice of reflections for refinement. R-factors based on F^2 are statistically about twice as large as those based on F, and R- factors based on ALL data will be even larger.

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å^2)

	x	y	z	U_{iso}*/U_{eq}
Br1	0.072488 (11)	0.38461 (3)	−0.022815 (15)	0.04538 (10)
Br2	0.173873 (12)	0.97541 (3)	0.193709 (18)	0.04571 (10)
Br3	0.038818 (9)	0.53557 (2)	0.168208 (16)	0.03360 (9)

Br4	0.023492 (11)	−0.17162 (3)	0.074334 (14)	0.03793 (9)
Cl1	0.21994 (3)	0.46769 (8)	0.54028 (4)	0.0503 (2)
Cl2	0.19143 (3)	−0.20130 (9)	0.48243 (5)	0.0581 (2)
O1	0.17220 (7)	0.23655 (17)	0.22437 (11)	0.0403 (5)
O2	0.12506 (6)	0.26173 (17)	0.10327 (10)	0.0357 (4)
H2O	0.1405	0.2323	0.1369	0.043*
O3	0.22492 (6)	0.79766 (17)	0.28983 (10)	0.0356 (4)
O4	0.06859 (7)	0.28669 (18)	0.41182 (10)	0.0393 (5)
O5	0.05702 (6)	0.44299 (16)	0.31336 (10)	0.0303 (4)
H5O	0.0593	0.4145	0.3504	0.036*
O6	0.04818 (7)	−0.19587 (17)	0.22873 (10)	0.0372 (5)
C1	0.15660 (8)	0.4293 (2)	0.17549 (13)	0.0258 (5)
C2	0.13115 (8)	0.3794 (2)	0.11283 (14)	0.0288 (6)
C3	0.10935 (8)	0.4552 (3)	0.05777 (13)	0.0309 (6)
C4	0.11292 (8)	0.5753 (3)	0.06312 (14)	0.0320 (6)
H4	0.0970	0.6244	0.0262	0.038*
C5	0.14024 (8)	0.6289 (2)	0.12333 (13)	0.0277 (5)
C6	0.14426 (9)	0.7552 (3)	0.12782 (14)	0.0322 (6)
H6	0.1279	0.8037	0.0910	0.039*
C7	0.17117 (9)	0.8070 (2)	0.18417 (15)	0.0308 (6)
C8	0.19743 (8)	0.7369 (2)	0.23794 (14)	0.0285 (5)
C9	0.19403 (8)	0.6138 (2)	0.23409 (13)	0.0268 (5)
H9	0.2125	0.5664	0.2692	0.032*
C10	0.16371 (8)	0.5568 (2)	0.17917 (13)	0.0251 (5)
C11	0.17185 (8)	0.3462 (2)	0.23443 (14)	0.0292 (6)
C12	0.18475 (8)	0.3844 (2)	0.30934 (13)	0.0265 (5)
C13	0.22110 (9)	0.3333 (3)	0.35338 (15)	0.0345 (6)
H13	0.2381	0.2788	0.3348	0.041*
C14	0.23289 (9)	0.3612 (3)	0.42463 (15)	0.0384 (7)
H14	0.2585	0.3295	0.4545	0.046*
C15	0.20650 (9)	0.4361 (3)	0.45078 (14)	0.0328 (6)
C16	0.16946 (9)	0.4855 (3)	0.40839 (15)	0.0328 (6)
H16	0.1514	0.5353	0.4278	0.039*
C17	0.15917 (8)	0.4610 (2)	0.33720 (14)	0.0288 (5)
H17	0.1345	0.4967	0.3071	0.035*
C18	0.24891 (9)	0.7304 (3)	0.34889 (15)	0.0358 (6)
H18A	0.2668	0.7849	0.3832	0.043*
H18B	0.2674	0.6724	0.3332	0.043*
H18C	0.2290	0.6879	0.3707	0.043*
C19	0.06148 (7)	0.2314 (2)	0.29361 (13)	0.0245 (5)
C20	0.05402 (7)	0.3492 (2)	0.27021 (13)	0.0251 (5)
C21	0.04405 (8)	0.3740 (2)	0.19710 (14)	0.0261 (5)
C22	0.03838 (8)	0.2840 (2)	0.14929 (13)	0.0271 (5)
H22	0.0319	0.3025	0.1007	0.033*
C23	0.04202 (8)	0.1626 (2)	0.17117 (13)	0.0256 (5)
C24	0.03339 (8)	0.0696 (2)	0.12090 (13)	0.0273 (5)
H24	0.0256	0.0885	0.0723	0.033*
C25	0.03620 (8)	−0.0467 (2)	0.14174 (13)	0.0275 (5)
C26	0.04715 (8)	−0.0773 (2)	0.21398 (13)	0.0264 (5)

C27	0.05499 (8)	0.0121 (2)	0.26305 (13)	0.0259 (5)
H27	0.0614	−0.0085	0.3114	0.031*
C28	0.05375 (7)	0.1344 (2)	0.24380 (13)	0.0231 (5)
C29	0.07782 (8)	0.2141 (2)	0.37033 (13)	0.0276 (5)
C30	0.10722 (8)	0.1132 (2)	0.39876 (13)	0.0273 (5)
C31	0.14023 (8)	0.0807 (3)	0.36814 (13)	0.0296 (6)
H31	0.1446	0.1245	0.3292	0.035*
C32	0.16668 (9)	−0.0151 (3)	0.39424 (15)	0.0346 (6)
H32	0.1893	−0.0377	0.3738	0.042*
C33	0.15938 (9)	−0.0772 (3)	0.45092 (15)	0.0367 (6)
C34	0.12720 (10)	−0.0470 (3)	0.48230 (15)	0.0391 (7)
H34	0.1228	−0.0917	0.5209	0.047*
C35	0.10132 (10)	0.0504 (3)	0.45627 (14)	0.0345 (6)
H35	0.0794	0.0743	0.4780	0.041*
C36	0.06237 (12)	−0.2311 (3)	0.30100 (15)	0.0438 (8)
H36A	0.0619	−0.3185	0.3043	0.053*
H36B	0.0431	−0.1969	0.3273	0.053*
H36C	0.0917	−0.2020	0.3207	0.053*

Atomic displacement parameters (Å^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Br1	0.05153 (19)	0.0532 (2)	0.02754 (16)	−0.02078 (15)	0.00293 (13)	−0.00796 (13)
Br2	0.0600 (2)	0.01933 (17)	0.0526 (2)	−0.00021 (13)	0.00479 (16)	0.00278 (13)
Br3	0.04039 (16)	0.02086 (15)	0.04206 (17)	0.00226 (11)	0.01511 (13)	0.00746 (11)
Br4	0.05632 (19)	0.02872 (17)	0.02572 (15)	−0.00679 (13)	0.00481 (13)	−0.00455 (11)
Cl1	0.0497 (4)	0.0711 (6)	0.0289 (3)	−0.0060 (4)	0.0077 (3)	−0.0068 (3)
Cl2	0.0671 (5)	0.0552 (5)	0.0506 (5)	0.0325 (4)	0.0123 (4)	0.0199 (4)
O1	0.0628 (13)	0.0182 (10)	0.0390 (11)	0.0006 (9)	0.0116 (10)	−0.0024 (8)
O2	0.0475 (11)	0.0254 (10)	0.0342 (10)	−0.0079 (8)	0.0105 (9)	−0.0082 (8)
O3	0.0414 (11)	0.0228 (10)	0.0359 (10)	−0.0052 (8)	−0.0023 (8)	−0.0017 (8)
O4	0.0536 (12)	0.0319 (11)	0.0301 (10)	0.0092 (9)	0.0064 (9)	−0.0065 (8)
O5	0.0364 (10)	0.0221 (9)	0.0325 (9)	0.0025 (8)	0.0087 (8)	−0.0022 (7)
O6	0.0603 (13)	0.0202 (10)	0.0264 (10)	−0.0037 (9)	0.0025 (9)	0.0017 (7)
C1	0.0290 (12)	0.0217 (13)	0.0282 (13)	−0.0018 (10)	0.0103 (10)	−0.0019 (10)
C2	0.0323 (13)	0.0268 (14)	0.0307 (13)	−0.0056 (11)	0.0140 (11)	−0.0069 (11)
C3	0.0315 (13)	0.0377 (16)	0.0233 (12)	−0.0089 (11)	0.0062 (10)	−0.0056 (11)
C4	0.0316 (13)	0.0373 (16)	0.0258 (13)	−0.0028 (12)	0.0050 (11)	0.0014 (11)
C5	0.0297 (12)	0.0272 (14)	0.0263 (12)	−0.0013 (10)	0.0072 (10)	−0.0003 (10)
C6	0.0358 (14)	0.0268 (14)	0.0319 (14)	0.0016 (11)	0.0049 (11)	0.0058 (11)
C7	0.0375 (14)	0.0164 (13)	0.0382 (15)	−0.0007 (10)	0.0088 (12)	0.0012 (11)
C8	0.0302 (13)	0.0231 (13)	0.0307 (13)	−0.0021 (10)	0.0052 (10)	−0.0014 (10)
C9	0.0291 (12)	0.0227 (13)	0.0280 (13)	−0.0007 (10)	0.0063 (10)	0.0009 (10)
C10	0.0276 (12)	0.0227 (13)	0.0266 (12)	−0.0011 (10)	0.0100 (10)	−0.0009 (10)
C11	0.0320 (13)	0.0219 (14)	0.0353 (14)	−0.0027 (10)	0.0113 (11)	−0.0012 (11)
C12	0.0322 (13)	0.0197 (13)	0.0291 (13)	−0.0025 (10)	0.0103 (10)	0.0028 (10)
C13	0.0402 (15)	0.0302 (15)	0.0356 (15)	0.0088 (12)	0.0142 (12)	0.0044 (12)
C14	0.0360 (14)	0.0437 (18)	0.0345 (15)	0.0067 (13)	0.0074 (12)	0.0077 (13)

C15	0.0367 (14)	0.0371 (16)	0.0253 (13)	−0.0060 (12)	0.0095 (11)	−0.0009 (11)
C16	0.0331 (14)	0.0329 (15)	0.0354 (14)	0.0000 (11)	0.0140 (12)	−0.0044 (12)
C17	0.0268 (12)	0.0265 (14)	0.0333 (14)	0.0008 (10)	0.0080 (10)	0.0016 (11)
C18	0.0401 (15)	0.0295 (15)	0.0329 (14)	−0.0026 (12)	0.0003 (12)	−0.0015 (12)
C19	0.0213 (11)	0.0252 (13)	0.0265 (12)	0.0018 (9)	0.0050 (9)	0.0007 (10)
C20	0.0213 (11)	0.0226 (13)	0.0316 (13)	−0.0006 (9)	0.0069 (10)	−0.0015 (10)
C21	0.0256 (12)	0.0186 (12)	0.0347 (14)	0.0019 (9)	0.0086 (10)	0.0051 (10)
C22	0.0283 (12)	0.0271 (14)	0.0265 (12)	0.0012 (10)	0.0078 (10)	0.0051 (10)
C23	0.0251 (12)	0.0242 (13)	0.0267 (13)	−0.0001 (10)	0.0051 (10)	0.0025 (10)
C24	0.0323 (13)	0.0281 (14)	0.0203 (12)	−0.0018 (11)	0.0044 (10)	0.0007 (10)
C25	0.0331 (13)	0.0252 (14)	0.0224 (12)	−0.0043 (10)	0.0036 (10)	−0.0045 (10)
C26	0.0314 (12)	0.0211 (13)	0.0250 (12)	−0.0014 (10)	0.0037 (10)	0.0012 (10)
C27	0.0293 (12)	0.0241 (13)	0.0223 (12)	0.0000 (10)	0.0030 (10)	0.0024 (10)
C28	0.0221 (11)	0.0222 (13)	0.0244 (12)	0.0007 (9)	0.0047 (9)	−0.0003 (10)
C29	0.0310 (13)	0.0237 (13)	0.0266 (13)	−0.0019 (10)	0.0046 (10)	−0.0027 (10)
C30	0.0316 (13)	0.0261 (14)	0.0206 (12)	0.0000 (10)	−0.0002 (10)	−0.0031 (10)
C31	0.0278 (12)	0.0351 (15)	0.0242 (12)	−0.0025 (11)	0.0034 (10)	0.0039 (11)
C32	0.0283 (13)	0.0399 (16)	0.0334 (14)	0.0045 (12)	0.0037 (11)	0.0016 (12)
C33	0.0413 (15)	0.0332 (16)	0.0301 (14)	0.0108 (12)	−0.0008 (12)	0.0053 (12)
C34	0.0527 (17)	0.0389 (17)	0.0254 (13)	0.0080 (14)	0.0094 (12)	0.0071 (12)
C35	0.0442 (15)	0.0342 (16)	0.0259 (13)	0.0070 (13)	0.0108 (12)	0.0016 (11)
C36	0.071 (2)	0.0263 (15)	0.0273 (14)	0.0007 (14)	−0.0002 (14)	0.0052 (11)

Geometric parameters (Å, °)

Br1—C3	1.896 (3)	C14—H14	0.9500
Br2—C7	1.892 (3)	C15—C16	1.384 (4)
Br3—C21	1.889 (2)	C16—C17	1.385 (4)
Br4—C25	1.899 (3)	C16—H16	0.9500
Cl1—C15	1.743 (3)	C17—H17	0.9500
Cl2—C33	1.745 (3)	C18—H18A	0.9800
O1—C11	1.243 (3)	C18—H18B	0.9800
O2—C2	1.336 (3)	C18—H18C	0.9800
O2—H2O	0.7916	C19—C20	1.396 (4)
O3—C8	1.353 (3)	C19—C28	1.441 (3)
O3—C18	1.435 (3)	C19—C29	1.482 (3)
O4—C29	1.240 (3)	C20—C21	1.422 (4)
O5—C20	1.338 (3)	C21—C22	1.359 (4)
O5—H5O	0.7825	C22—C23	1.419 (4)
O6—C26	1.356 (3)	C22—H22	0.9500
O6—C36	1.436 (3)	C23—C24	1.414 (4)
C1—C2	1.412 (4)	C23—C28	1.420 (3)
C1—C10	1.442 (4)	C24—C25	1.360 (4)
C1—C11	1.471 (4)	C24—H24	0.9500
C2—C3	1.415 (4)	C25—C26	1.419 (3)
C3—C4	1.350 (4)	C26—C27	1.369 (4)
C4—C5	1.417 (4)	C27—C28	1.417 (4)
C4—H4	0.9500	C27—H27	0.9500
C5—C10	1.417 (4)	C29—C30	1.487 (4)

C5—C6	1.419 (4)	C30—C35	1.386 (4)
C6—C7	1.353 (4)	C30—C31	1.394 (4)
C6—H6	0.9500	C31—C32	1.383 (4)
C7—C8	1.413 (4)	C31—H31	0.9500
C8—C9	1.381 (4)	C32—C33	1.385 (4)
C9—C10	1.411 (4)	C32—H32	0.9500
C9—H9	0.9500	C33—C34	1.374 (4)
C11—C12	1.491 (4)	C34—C35	1.387 (4)
C12—C13	1.389 (4)	C34—H34	0.9500
C12—C17	1.392 (4)	C35—H35	0.9500
C13—C14	1.394 (4)	C36—H36A	0.9800
C13—H13	0.9500	C36—H36B	0.9800
C14—C15	1.381 (4)	C36—H36C	0.9800
C2—O2—H2O	104.6	H18A—C18—H18C	109.5
C8—O3—C18	117.6 (2)	H18B—C18—H18C	109.5
C20—O5—H5O	104.4	C20—C19—C28	119.9 (2)
C26—O6—C36	117.7 (2)	C20—C19—C29	116.5 (2)
C2—C1—C10	118.9 (2)	C28—C19—C29	123.5 (2)
C2—C1—C11	116.4 (2)	O5—C20—C19	123.4 (2)
C10—C1—C11	124.6 (2)	O5—C20—C21	116.9 (2)
O2—C2—C1	123.0 (3)	C19—C20—C21	119.6 (2)
O2—C2—C3	117.1 (2)	C22—C21—C20	121.0 (2)
C1—C2—C3	119.9 (2)	C22—C21—Br3	120.9 (2)
C4—C3—C2	121.4 (2)	C20—C21—Br3	118.16 (19)
C4—C3—Br1	120.2 (2)	C21—C22—C23	120.7 (2)
C2—C3—Br1	118.4 (2)	C21—C22—H22	119.6
C3—C4—C5	120.6 (3)	C23—C22—H22	119.6
C3—C4—H4	119.7	C24—C23—C22	120.2 (2)
C5—C4—H4	119.7	C24—C23—C28	119.8 (2)
C4—C5—C10	120.3 (2)	C22—C23—C28	119.9 (2)
C4—C5—C6	120.0 (3)	C25—C24—C23	120.4 (2)
C10—C5—C6	119.7 (2)	C25—C24—H24	119.8
C7—C6—C5	120.4 (3)	C23—C24—H24	119.8
C7—C6—H6	119.8	C24—C25—C26	120.9 (2)
C5—C6—H6	119.8	C24—C25—Br4	120.40 (19)
C6—C7—C8	120.9 (2)	C26—C25—Br4	118.62 (19)
C6—C7—Br2	120.8 (2)	O6—C26—C27	124.9 (2)
C8—C7—Br2	118.3 (2)	O6—C26—C25	115.9 (2)
O3—C8—C9	124.7 (2)	C27—C26—C25	119.1 (2)
O3—C8—C7	116.0 (2)	C26—C27—C28	121.9 (2)
C9—C8—C7	119.2 (2)	C26—C27—H27	119.1
C8—C9—C10	121.4 (2)	C28—C27—H27	119.1
C8—C9—H9	119.3	C27—C28—C23	117.8 (2)
C10—C9—H9	119.3	C27—C28—C19	123.7 (2)
C9—C10—C5	117.8 (2)	C23—C28—C19	118.4 (2)
C9—C10—C1	123.7 (2)	O4—C29—C19	120.4 (2)
C5—C10—C1	118.5 (2)	O4—C29—C30	118.9 (2)
O1—C11—C1	120.8 (2)	C19—C29—C30	120.7 (2)
O1—C11—C12	115.4 (2)	C35—C30—C31	119.9 (2)

C1—C11—C12	123.7 (2)	C35—C30—C29	119.1 (2)
C13—C12—C17	119.5 (2)	C31—C30—C29	121.0 (2)
C13—C12—C11	118.7 (2)	C32—C31—C30	120.2 (3)
C17—C12—C11	121.5 (2)	C32—C31—H31	119.9
C12—C13—C14	120.5 (3)	C30—C31—H31	119.9
C12—C13—H13	119.7	C31—C32—C33	118.3 (3)
C14—C13—H13	119.7	C31—C32—H32	120.8
C15—C14—C13	118.4 (3)	C33—C32—H32	120.8
C15—C14—H14	120.8	C34—C33—C32	122.7 (3)
C13—C14—H14	120.8	C34—C33—Cl2	118.6 (2)
C14—C15—C16	122.1 (3)	C32—C33—Cl2	118.7 (2)
C14—C15—Cl1	118.9 (2)	C33—C34—C35	118.4 (3)
C16—C15—Cl1	119.0 (2)	C33—C34—H34	120.8
C15—C16—C17	118.7 (3)	C35—C34—H34	120.8
C15—C16—H16	120.6	C30—C35—C34	120.4 (3)
C17—C16—H16	120.6	C30—C35—H35	119.8
C16—C17—C12	120.6 (2)	C34—C35—H35	119.8
C16—C17—H17	119.7	O6—C36—H36A	109.5
C12—C17—H17	119.7	O6—C36—H36B	109.5
O3—C18—H18A	109.5	H36A—C36—H36B	109.5
O3—C18—H18B	109.5	O6—C36—H36C	109.5
H18A—C18—H18B	109.5	H36A—C36—H36C	109.5
O3—C18—H18C	109.5	H36B—C36—H36C	109.5
C10—C1—C2—O2	175.8 (2)	C28—C19—C20—O5	174.3 (2)
C11—C1—C2—O2	−7.9 (4)	C29—C19—C20—O5	−6.4 (3)
C10—C1—C2—C3	−6.8 (4)	C28—C19—C20—C21	−7.9 (3)
C11—C1—C2—C3	169.6 (2)	C29—C19—C20—C21	171.4 (2)
O2—C2—C3—C4	178.8 (2)	O5—C20—C21—C22	−176.9 (2)
C1—C2—C3—C4	1.2 (4)	C19—C20—C21—C22	5.1 (4)
O2—C2—C3—Br1	1.8 (3)	O5—C20—C21—Br3	3.0 (3)
C1—C2—C3—Br1	−175.81 (19)	C19—C20—C21—Br3	−174.94 (18)
C2—C3—C4—C5	2.7 (4)	C20—C21—C22—C23	0.4 (4)
Br1—C3—C4—C5	179.7 (2)	Br3—C21—C22—C23	−179.53 (19)
C3—C4—C5—C10	−0.9 (4)	C21—C22—C23—C24	176.0 (2)
C3—C4—C5—C6	179.0 (3)	C21—C22—C23—C28	−3.1 (4)
C4—C5—C6—C7	−178.1 (3)	C22—C23—C24—C25	−179.0 (2)
C10—C5—C6—C7	1.7 (4)	C28—C23—C24—C25	0.1 (4)
C5—C6—C7—C8	3.2 (4)	C23—C24—C25—C26	1.0 (4)
C5—C6—C7—Br2	−175.7 (2)	C23—C24—C25—Br4	178.73 (19)
C18—O3—C8—C9	−7.1 (4)	C36—O6—C26—C27	−6.0 (4)
C18—O3—C8—C7	173.8 (2)	C36—O6—C26—C25	175.3 (3)
C6—C7—C8—O3	176.3 (3)	C24—C25—C26—O6	178.7 (2)
Br2—C7—C8—O3	−4.7 (3)	Br4—C25—C26—O6	0.9 (3)
C6—C7—C8—C9	−2.9 (4)	C24—C25—C26—C27	−0.1 (4)
Br2—C7—C8—C9	176.1 (2)	Br4—C25—C26—C27	−177.86 (19)
O3—C8—C9—C10	178.3 (2)	O6—C26—C27—C28	179.4 (2)
C7—C8—C9—C10	−2.6 (4)	C25—C26—C27—C28	−1.9 (4)
C8—C9—C10—C5	7.3 (4)	C26—C27—C28—C23	2.9 (4)
C8—C9—C10—C1	−175.2 (2)	C26—C27—C28—C19	179.5 (2)

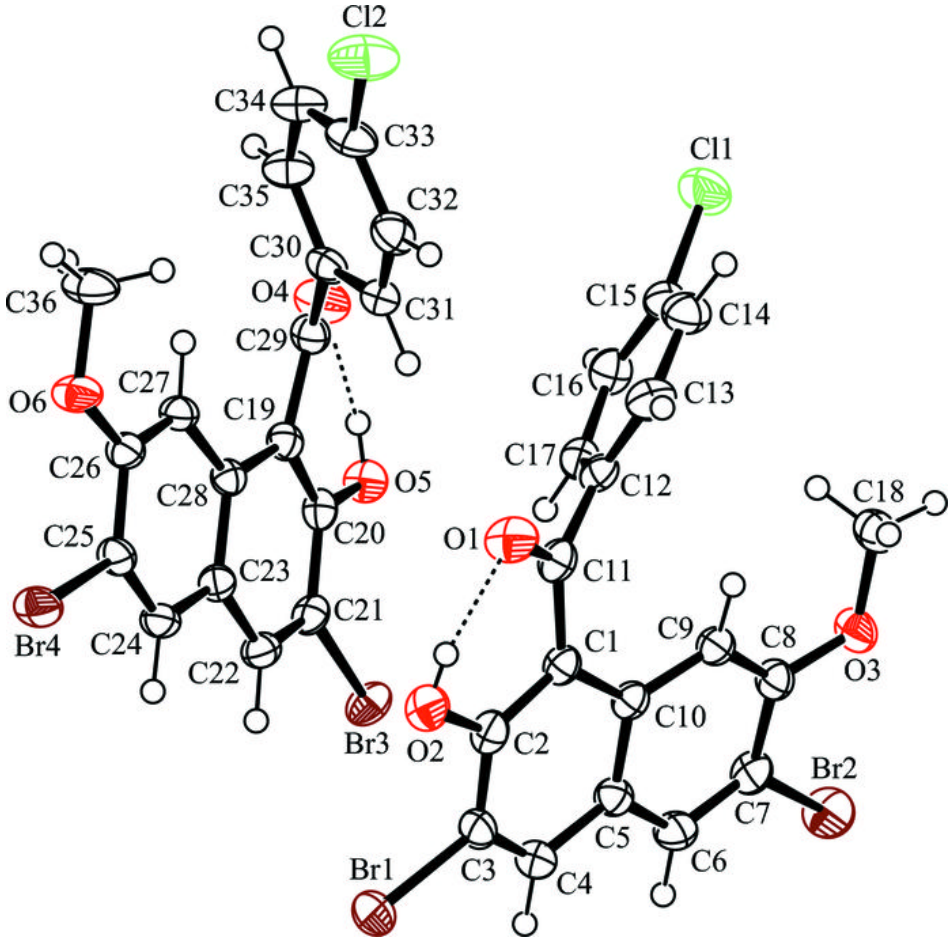
C4—C5—C10—C9	173.0 (2)	C24—C23—C28—C27	−2.0 (3)
C6—C5—C10—C9	−6.9 (4)	C22—C23—C28—C27	177.1 (2)
C4—C5—C10—C1	−4.6 (4)	C24—C23—C28—C19	−178.8 (2)
C6—C5—C10—C1	175.5 (2)	C22—C23—C28—C19	0.3 (3)
C2—C1—C10—C9	−169.1 (2)	C20—C19—C28—C27	−171.4 (2)
C11—C1—C10—C9	14.9 (4)	C29—C19—C28—C27	9.4 (4)
C2—C1—C10—C5	8.4 (4)	C20—C19—C28—C23	5.2 (3)
C11—C1—C10—C5	−167.6 (2)	C29—C19—C28—C23	−174.0 (2)
C2—C1—C11—O1	18.4 (4)	C20—C19—C29—O4	29.0 (4)
C10—C1—C11—O1	−165.5 (3)	C28—C19—C29—O4	−151.7 (3)
C2—C1—C11—C12	−157.1 (2)	C20—C19—C29—C30	−147.9 (2)
C10—C1—C11—C12	19.0 (4)	C28—C19—C29—C30	31.3 (4)
O1—C11—C12—C13	45.9 (4)	O4—C29—C30—C35	44.2 (4)
C1—C11—C12—C13	−138.4 (3)	C19—C29—C30—C35	−138.8 (3)
O1—C11—C12—C17	−128.2 (3)	O4—C29—C30—C31	−136.2 (3)
C1—C11—C12—C17	47.5 (4)	C19—C29—C30—C31	40.8 (4)
C17—C12—C13—C14	−2.2 (4)	C35—C30—C31—C32	1.0 (4)
C11—C12—C13—C14	−176.3 (3)	C29—C30—C31—C32	−178.5 (2)
C12—C13—C14—C15	3.1 (4)	C30—C31—C32—C33	0.2 (4)
C13—C14—C15—C16	−1.2 (5)	C31—C32—C33—C34	−0.4 (5)
C13—C14—C15—Cl1	177.9 (2)	C31—C32—C33—Cl2	177.9 (2)
C14—C15—C16—C17	−1.5 (4)	C32—C33—C34—C35	−0.6 (5)
Cl1—C15—C16—C17	179.4 (2)	Cl2—C33—C34—C35	−178.9 (2)
C15—C16—C17—C12	2.5 (4)	C31—C30—C35—C34	−2.0 (4)
C13—C12—C17—C16	−0.7 (4)	C29—C30—C35—C34	177.6 (3)
C11—C12—C17—C16	173.3 (2)	C33—C34—C35—C30	1.8 (5)

Hydrogen-bond geometry (Å, °)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
O2—H2O···O1	0.79	1.77	2.497 (3)	153
O5—H5O···O4	0.78	1.85	2.568 (3)	153
C4—H4···O4^{i}	0.95	2.42	3.338 (3)	162
C18—H18A···Cl2^{ii}	0.98	2.81	3.406 (3)	120
C34—H34···O2^{iii}	0.95	2.49	3.397 (4)	160

Symmetry codes: (i) *x*, −*y*+1, *z*−1/2; (ii) −*x*+1/2, −*y*+1/2, −*z*+1; (iii) *x*, −*y*, *z*+1/2.

Fig. 1


Cl2
C34
C33
C35
C32
C30
O4
C31
C36
C29
C27
O6
C19
C26
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C28
C20
C25
C23
C21
Br4
C24
C22
Br3
Cl1
C15
C14
C16
C13
C17
C12
O1
C11
C18
C1
C9
C8
O3
O2
C2
C10
Br2
C7
C5
C6
Br1
C3
C4

Fig. 2

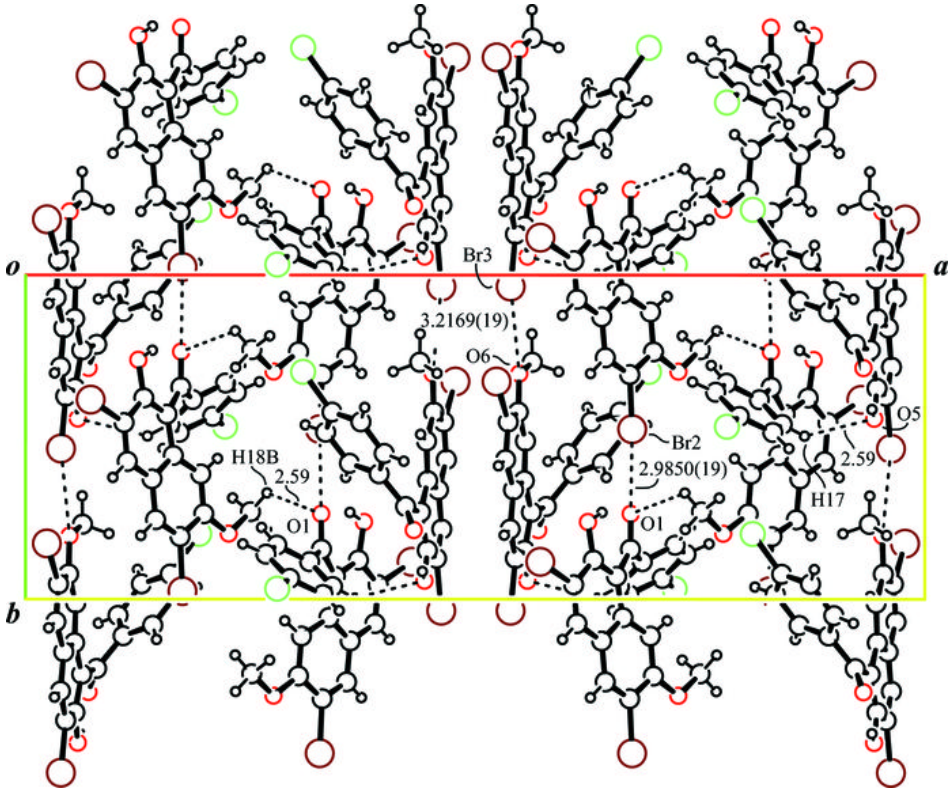
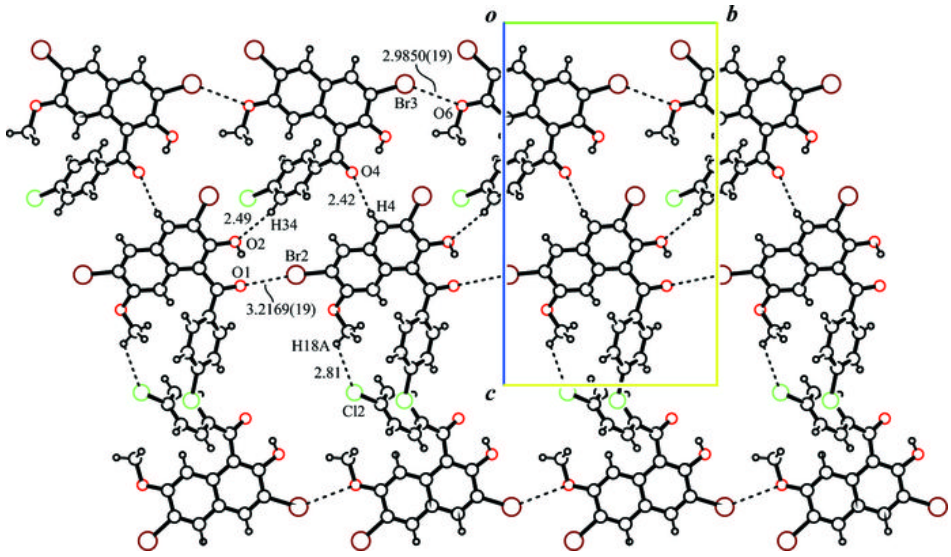


Fig. 3


o
b
c
2.9850(19)
Br3
O6
O4
2.42
H4
2.49
H34
O2
Br2
O1
3.2169(19)
H18A
2.81
Cl2

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1-(2-Phenylethyl)adamantane

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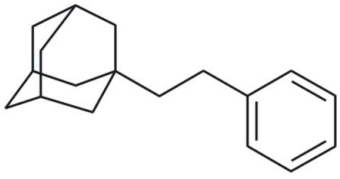
Key indicators: single-crystal X-ray study; T = 120 K; mean σ(C–C) = 0.004 Å; R factor = 0.042; wR factor = 0.127; data-to-parameter ratio = 8.9.

In the title compound, $C_{18}H_{24}$, the adamantane cage consists of three fused cyclohexane rings in almost ideal chair conformations, with C—C—C angles in the range 108.0 (14)–111.1 (15)°. The phenyl and 1-adamantyl substituents adopt *anti* orientations with a C—C—C—C torsion angle of 177.10 (16)°. In the crystal packing, the molecules are linked by weak C—H$\cdots\pi$ interactions into chains along the *a* axis.

Related literature

The title compound was prepared according to a modified procedure of Adkins & Billica (1948). For some important properties of compounds bearing the adamantane scaffold, see: van der Schyf *et al.* (2009); van Bommel *et al.* (2001). For a related structure, see: Raine *et al.* (2002).



Experimental

Crystal data

$C_{18}H_{24}$
M_r = 240.37
Orthorhombic, $P2_12_12_1$
a = 6.4844 (5) Å
b = 7.5109 (5) Å
c = 28.5305 (19) Å
V = 1389.55 (17) Å^3
Z = 4
Mo $K\alpha$ radiation
μ = 0.06 mm^{-1}
T = 120 K
0.40 × 0.20 × 0.20 mm

Data collection

Kuma KM-4-CCD diffractometer
Absorption correction: multi-scan (*CrysAlis RED*; Oxford Diffraction, 2009)
T_{min} = 0.924, T_{max} = 1.000
11994 measured reflections
1452 independent reflections
1277 reflections with $I > 2\sigma(I)$
R_{int} = 0.043

Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.042
$wR(F^2)$ = 0.127
S = 1.30
1452 reflections
163 parameters
H-atom parameters constrained
$\Delta\rho_{max}$ = 0.24 e Å^{-3}
$\Delta\rho_{min}$ = −0.15 e Å^{-3}

Table 1
Hydrogen-bond geometry (Å, °).

*Cg*1 is the centroid of the C13–C18 ring.

D—H$\cdots A$	D—H	H$\cdots A$	$D\cdots A$	D—H$\cdots A$
C18—H18$\cdots$*Cg*1^{i}	0.95	2.64	3.529 (3)	156

Symmetry code: (i) $x-\frac{1}{2}, -y+\frac{3}{2}, -z$.

Data collection: *CrysAlis CCD* (Oxford Diffraction, 2009); cell refinement: *CrysAlis RED* (Oxford Diffraction, 2009); data reduction: *CrysAlis RED*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *ORTEP-3* (Farrugia, 1997) and *Mercury* (Macrae *et al.*, 2008); software used to prepare material for publication: *SHELXL97*.

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Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: EZ2215).

References

Adkins, H. & Billica, H. R. (1948). *J. Am. Chem. Soc.* **70**, 695–698.
Bommel, K. J. C. van, Metselaar, M. A., Werboom, W. & Reinhoudt, D. N. (2001). *J. Org. Chem.* **66**, 5405–5412.
Farrugia, L. J. (1997). *J. Appl. Cryst.* **30**, 565.
Macrae, C. F., Bruno, I. J., Chisholm, J. A., Edgington, P. R., McCabe, P., Pidcock, E., Rodriguez-Monge, L., Taylor, R., van de Streek, J. & Wood, P. A. (2008). *J. Appl. Cryst.* **41**, 466–470.
Oxford Diffraction (2009). *CrysAlis CCD* and *CrysAlis RED*. Oxford Diffraction Ltd, Yarnton, England.
Raine, A. L., Williams, C. M. & Bernhardt, P. V. (2002). *Acta Cryst.* E**58**, o1439–o1440.
Schyf, C. J. van der & Geldenhuys, W. J. (2009). *Neurotherapeutics*, **6**, 175–186.
Sheldrick, G. M. (2008). *Acta Cryst.* A**64**, 112–122.

supplementary materials

Acta Cryst. (2010). E**66**, o1736 [**doi:10.1107/S1600536810023251**]

1-(2-Phenylethyl)adamantane

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Comment

Adamantane is a molecule with an elegant structure and unique properties. The addition of the highly lipophilic adamantane cage to a known biologically active compound can significantly improve the pharmacokinetic profile of the resulting molecule, *e.g.* its oral bioavailability (van der Schyf *et al.* 2009). Moreover, the relatively stable host–guest interactions of the adamantane scaffold with β-cyclodextrin might increase the solubility of non-polar substances in polar media (van Bommel *et al.* 2001). Both these characteristics have an important role in drug design. This structure represents one of the few low-molecular-weight molecules bearing an adamantane moiety that has no polar function group. Therefore, this compound may be used as a standard molecule for investigations of non-polar interactions.

The asymmetric unit of the title compound consists of a single molecule (Fig. 1). The benzene ring is nearly planar with a maximum deviation from the best plane being 0.007 (2) Å for C16. The torsion angles describing mutual alignment of the 1-adamantyl and phenyl substituents C18—C13—C12—C11, C13—C12—C11—C1 and C12—C11—C1—C2 are -73.4 (2), -177.10 (16) and 179.59 (16)°, respectively. In the crystal packing, the molecules are arranged into chains parallel to the *a*-axis linked by weak C—H···π interactions (Fig. 2, Table 1).

Experimental

The title compound was prepared according to a modified literature procedure published by Adkins & Billica (1948). 2-(1-Adamantyl)-2-benzyl-1,3-dithiane (0.33 mmol, 114 mg) was dissolved in 5 ml of dioxane and a large excess of Raney nickel catalyst was added to this solution. The reaction mixture was stirred and refluxed under Ar atmosphere. Further portions of Raney nickel were added until the starting material was completely consumed (monitored by GC). Subsequently, the Raney nickel was filtered off, the filtrate was diluted with water and extracted with diethyl ether. The combined organic layers were washed twice with brine and dried over Na_2SO_4. The required product was obtained after evaporation of solvent in vacuum as a colorless crystalline powder (72 mg, 91%, mp 318–324 K). The crystal used for data collection was grown by spontaneous evaporation from deuterochloroform at room temperature.

Refinement

Hydrogen atoms were positioned geometrically and refined as riding using standard *SHELXTL* constraints, with their U_{iso} set to either $1.2U_{eq}$ of their parent atoms. In the absence of significant anomalous scattering, Friedel pairs were merged.

Figures

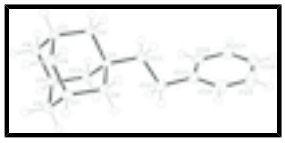


Fig. 1. *ORTEP* diagram of the asymmetric unit showing the atom labelling scheme with atoms represented as 50% probability ellipsoids.

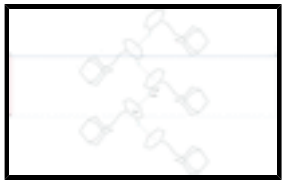


Fig. 2. A partial view of the crystal packing viewed along the *b*-axis showing the arrangement of the molecules into chains parallel to the *a*-axis stabilized by weak C—H···π interactions (dotted lines). *Cg*1 is the center of gravity of C13–C18. H-atoms (except those which are involved in H-bonding) have been omitted for clarity. Symmetry codes: (i) -*x* + 1.5, -*y* + 1, *z* + 1/2; (ii) –x+2, *y* - 1/2, -*z* + 1/2.

1-(2-Phenylethyl)adamantane

Crystal data

$C_{18}H_{24}$	D_x = 1.149 Mg m^{-3}
M_r = 240.37	Melting point: 321 K
Orthorhombic, $P2_12_12_1$	Mo $K\alpha$ radiation, λ = 0.71073 Å
Hall symbol: P 2ac 2ab	Cell parameters from 5446 reflections
a = 6.4844 (5) Å	θ = 3.1–27.2°
b = 7.5109 (5) Å	μ = 0.06 mm^{-1}
c = 28.5305 (19) Å	*T* = 120 K
V = 1389.55 (17) Å^3	Block, colourless
Z = 4	0.40 × 0.20 × 0.20 mm
F(000) = 528	

Data collection

Kuma KM-4-CCD diffractometer	1452 independent reflections
Radiation source: fine-focus sealed tube	1277 reflections with $I > 2\sigma(I)$
graphite	R_{int} = 0.043
Detector resolution: 0.06 mm pixels mm^{-1}	θ_{max} = 25.0°, θ_{min} = 3.1°
ω scan	*h* = −5→7
Absorption correction: multi-scan (*CrysAlis RED*; Oxford Diffraction, 2009)	*k* = −8→8
T_{min} = 0.924, T_{max} = 1.000	*l* = −33→33
11994 measured reflections	

Refinement

Refinement on F^2	Primary atom site location: structure-invariant direct methods
Least-squares matrix: full	Secondary atom site location: difference Fourier map
$R[F^2 > 2\sigma(F^2)]$ = 0.042	Hydrogen site location: inferred from neighbouring sites
$wR(F^2)$ = 0.127	H-atom parameters constrained
S = 1.30	$w = 1/[\sigma^2(F_o^2) + (0.0705P)^2 + 0.0787P]$ where $P = (F_o^2 + 2F_c^2)/3$
1452 reflections	$(\Delta/\sigma)_{max} < 0.001$
163 parameters	$\Delta\rho_{max}$ = 0.24 e Å^{-3}
0 restraints	$\Delta\rho_{min}$ = −0.15 e Å^{-3}

Special details

Geometry. All e.s.d.'s (except the e.s.d. in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell e.s.d.'s are taken into account individually in the estimation of e.s.d.'s in distances, angles and torsion angles; correlations between e.s.d.'s in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell e.s.d.'s is used for estimating e.s.d.'s involving l.s. planes.

Refinement. Refinement of F^2 against ALL reflections. The weighted *R*-factor *wR* and goodness of fit *S* are based on F^2, conventional *R*-factors *R* are based on *F*, with *F* set to zero for negative F^2. The threshold expression of $F^2 > 2\sigma(F^2)$ is used only for calculating *R*-factors(gt) *etc*. and is not relevant to the choice of reflections for refinement. *R*-factors based on F^2 are statistically about twice as large as those based on *F*, and *R*- factors based on ALL data will be even larger.

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters ($Å^2$)

	x	*y*	*z*	U_{iso}*/U_{eq}
C1	0.8116 (4)	0.4428 (3)	0.14870 (8)	0.0172 (6)
C2	0.6166 (4)	0.4772 (3)	0.17845 (9)	0.0207 (6)
H2A	0.6402	0.5812	0.1991	0.025*
H2B	0.4993	0.5052	0.1575	0.025*
C3	0.5633 (4)	0.3148 (3)	0.20840 (8)	0.0206 (6)
H3	0.4366	0.3400	0.2272	0.025*
C4	0.5236 (4)	0.1543 (3)	0.17589 (9)	0.0232 (6)
H4A	0.4887	0.0482	0.1949	0.028*
H4B	0.4059	0.1803	0.1549	0.028*
C5	0.7167 (4)	0.1176 (3)	0.14680 (8)	0.0212 (6)
H5	0.6913	0.0137	0.1257	0.025*
C6	0.8974 (4)	0.0749 (3)	0.17999 (9)	0.0222 (6)
H6A	0.8640	−0.0316	0.1990	0.027*
H6B	1.0230	0.0490	0.1615	0.027*
C7	0.9363 (4)	0.2344 (3)	0.21230 (8)	0.0195 (6)
H7	1.0545	0.2072	0.2337	0.023*
C8	0.9892 (4)	0.3977 (3)	0.18208 (8)	0.0182 (6)
H8A	1.0171	0.5010	0.2027	0.022*
H8B	1.1154	0.3731	0.1637	0.022*
C9	0.7437 (4)	0.2729 (4)	0.24146 (8)	0.0217 (6)
H9A	0.7693	0.3756	0.2624	0.026*
H9B	0.7097	0.1683	0.2611	0.026*
C10	0.7703 (4)	0.2808 (3)	0.11744 (9)	0.0208 (6)
H10A	0.6548	0.3076	0.0959	0.025*
H10B	0.8941	0.2554	0.0983	0.025*
C11	0.8577 (4)	0.6112 (3)	0.12008 (8)	0.0219 (6)
H11A	0.7359	0.6377	0.1004	0.026*
H11B	0.8750	0.7118	0.1421	0.026*
C12	1.0478 (5)	0.6040 (4)	0.08826 (9)	0.0283 (7)
H12A	1.1701	0.5727	0.1073	0.034*
H12B	1.0284	0.5092	0.0646	0.034*
C13	1.0866 (5)	0.7775 (4)	0.06375 (8)	0.0234 (6)
C14	1.2499 (5)	0.8876 (4)	0.07581 (8)	0.0302 (7)

H14	1.3389	0.8539	0.1007	0.036*
C15	1.2855 (5)	1.0453 (4)	0.05228 (9)	0.0349 (8)
H15	1.3969	1.1197	0.0615	0.042*
C16	1.1596 (5)	1.0957 (4)	0.01530 (9)	0.0317 (7)
H16	1.1860	1.2027	−0.0014	0.038*
C17	0.9961 (5)	0.9891 (4)	0.00311 (9)	0.0285 (7)
H17	0.9071	1.0238	−0.0217	0.034*
C18	0.9604 (5)	0.8312 (4)	0.02684 (9)	0.0275 (7)
H18	0.8477	0.7581	0.0178	0.033*

Atomic displacement parameters (Å^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
C1	0.0173 (14)	0.0180 (13)	0.0163 (11)	−0.0001 (11)	0.0018 (10)	−0.0003 (10)
C2	0.0141 (13)	0.0236 (14)	0.0244 (13)	0.0037 (11)	0.0005 (12)	−0.0009 (11)
C3	0.0150 (14)	0.0257 (14)	0.0212 (12)	0.0006 (11)	0.0051 (11)	0.0004 (11)
C4	0.0187 (15)	0.0262 (14)	0.0247 (12)	−0.0028 (12)	−0.0013 (12)	0.0051 (11)
C5	0.0238 (15)	0.0188 (13)	0.0210 (12)	−0.0015 (12)	−0.0036 (11)	−0.0037 (11)
C6	0.0196 (14)	0.0202 (13)	0.0269 (13)	0.0012 (12)	0.0022 (12)	0.0028 (11)
C7	0.0157 (14)	0.0246 (14)	0.0184 (12)	0.0004 (12)	−0.0023 (11)	0.0037 (11)
C8	0.0155 (13)	0.0214 (13)	0.0177 (11)	−0.0004 (11)	0.0010 (11)	−0.0020 (11)
C9	0.0196 (15)	0.0278 (15)	0.0176 (11)	−0.0020 (13)	0.0016 (11)	0.0017 (10)
C10	0.0199 (15)	0.0237 (14)	0.0187 (11)	0.0010 (12)	−0.0007 (11)	−0.0012 (10)
C11	0.0216 (14)	0.0217 (14)	0.0223 (12)	0.0016 (12)	−0.0002 (12)	0.0007 (11)
C12	0.0275 (16)	0.0289 (15)	0.0284 (13)	0.0014 (14)	0.0050 (13)	0.0058 (12)
C13	0.0252 (16)	0.0248 (14)	0.0201 (12)	−0.0005 (12)	0.0029 (11)	0.0015 (11)
C14	0.0302 (16)	0.0415 (18)	0.0190 (12)	−0.0061 (15)	−0.0020 (12)	0.0030 (12)
C15	0.040 (2)	0.0352 (17)	0.0291 (14)	−0.0181 (15)	−0.0039 (14)	−0.0028 (13)
C16	0.0468 (19)	0.0250 (14)	0.0235 (13)	−0.0047 (15)	0.0047 (13)	0.0029 (12)
C17	0.0307 (17)	0.0317 (15)	0.0232 (13)	0.0030 (14)	−0.0002 (14)	0.0046 (11)
C18	0.0237 (16)	0.0283 (15)	0.0306 (14)	−0.0033 (13)	−0.0027 (12)	0.0000 (12)

Geometric parameters (Å, °)

C1—C10	1.532 (3)	C8—H8B	0.9900
C1—C8	1.532 (3)	C9—H9A	0.9900
C1—C11	1.535 (3)	C9—H9B	0.9900
C1—C2	1.544 (3)	C10—H10A	0.9900
C2—C3	1.529 (3)	C10—H10B	0.9900
C2—H2A	0.9900	C11—C12	1.532 (4)
C2—H2B	0.9900	C11—H11A	0.9900
C3—C9	1.535 (4)	C11—H11B	0.9900
C3—C4	1.542 (3)	C12—C13	1.500 (4)
C3—H3	1.0000	C12—H12A	0.9900
C4—C5	1.527 (4)	C12—H12B	0.9900
C4—H4A	0.9900	C13—C14	1.387 (4)
C4—H4B	0.9900	C13—C18	1.393 (4)
C5—C10	1.525 (3)	C14—C15	1.381 (4)
C5—C6	1.540 (4)	C14—H14	0.9500

C5—H5	1.0000	C15—C16	1.387 (4)
C6—C7	1.533 (3)	C15—H15	0.9500
C6—H6A	0.9900	C16—C17	1.373 (4)
C6—H6B	0.9900	C16—H16	0.9500
C7—C9	1.528 (4)	C17—C18	1.385 (4)
C7—C8	1.538 (3)	C17—H17	0.9500
C7—H7	1.0000	C18—H18	0.9500
C8—H8A	0.9900		
C10—C1—C8	108.5 (2)	C1—C8—H8B	109.5
C10—C1—C11	112.24 (18)	C7—C8—H8B	109.5
C8—C1—C11	111.5 (2)	H8A—C8—H8B	108.0
C10—C1—C2	108.1 (2)	C7—C9—C3	109.08 (18)
C8—C1—C2	108.09 (18)	C7—C9—H9A	109.9
C11—C1—C2	108.3 (2)	C3—C9—H9A	109.9
C3—C2—C1	111.0 (2)	C7—C9—H9B	109.9
C3—C2—H2A	109.4	C3—C9—H9B	109.9
C1—C2—H2A	109.4	H9A—C9—H9B	108.3
C3—C2—H2B	109.4	C5—C10—C1	110.99 (19)
C1—C2—H2B	109.4	C5—C10—H10A	109.4
H2A—C2—H2B	108.0	C1—C10—H10A	109.4
C2—C3—C9	109.5 (2)	C5—C10—H10B	109.4
C2—C3—C4	108.97 (18)	C1—C10—H10B	109.4
C9—C3—C4	109.7 (2)	H10A—C10—H10B	108.0
C2—C3—H3	109.6	C12—C11—C1	116.3 (2)
C9—C3—H3	109.6	C12—C11—H11A	108.2
C4—C3—H3	109.6	C1—C11—H11A	108.2
C5—C4—C3	109.3 (2)	C12—C11—H11B	108.2
C5—C4—H4A	109.8	C1—C11—H11B	108.2
C3—C4—H4A	109.8	H11A—C11—H11B	107.4
C5—C4—H4B	109.8	C13—C12—C11	112.4 (2)
C3—C4—H4B	109.8	C13—C12—H12A	109.1
H4A—C4—H4B	108.3	C11—C12—H12A	109.1
C10—C5—C4	109.9 (2)	C13—C12—H12B	109.1
C10—C5—C6	109.4 (2)	C11—C12—H12B	109.1
C4—C5—C6	109.09 (18)	H12A—C12—H12B	107.9
C10—C5—H5	109.5	C14—C13—C18	117.6 (2)
C4—C5—H5	109.5	C14—C13—C12	122.0 (2)
C6—C5—H5	109.5	C18—C13—C12	120.4 (3)
C7—C6—C5	109.4 (2)	C15—C14—C13	121.2 (3)
C7—C6—H6A	109.8	C15—C14—H14	119.4
C5—C6—H6A	109.8	C13—C14—H14	119.4
C7—C6—H6B	109.8	C14—C15—C16	120.4 (3)
C5—C6—H6B	109.8	C14—C15—H15	119.8
H6A—C6—H6B	108.2	C16—C15—H15	119.8
C9—C7—C6	109.9 (2)	C17—C16—C15	119.2 (3)
C9—C7—C8	109.7 (2)	C17—C16—H16	120.4
C6—C7—C8	108.84 (18)	C15—C16—H16	120.4
C9—C7—H7	109.5	C16—C17—C18	120.3 (3)
C6—C7—H7	109.5	C16—C17—H17	119.9

C8—C7—H7	109.5	C18—C17—H17	119.9
C1—C8—C7	110.9 (2)	C17—C18—C13	121.3 (3)
C1—C8—H8A	109.5	C17—C18—H18	119.4
C7—C8—H8A	109.5	C13—C18—H18	119.4

Hydrogen-bond geometry (Å, °)

*Cg*1 is the centroid of the C13–C18 ring.

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
C18—H18···Cg1^{i}	0.95	2.64	3.529 (3)	156

Symmetry codes: (i) *x*−1/2, −*y*+3/2, −*z*.

Fig. 1

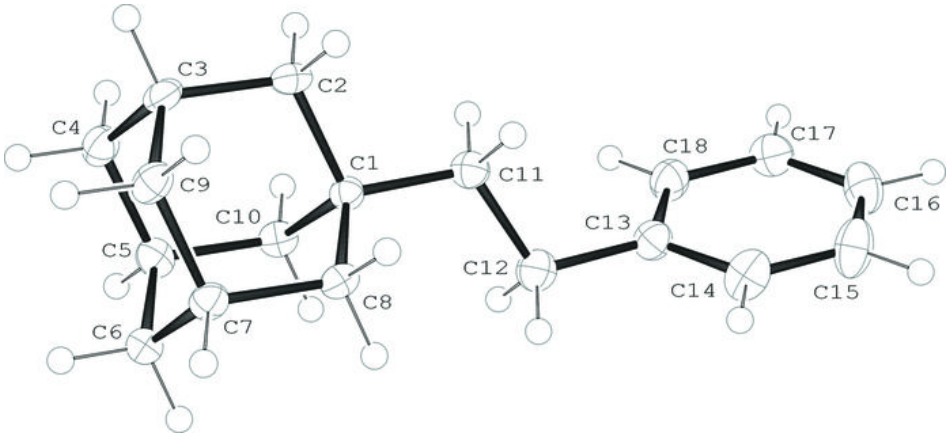
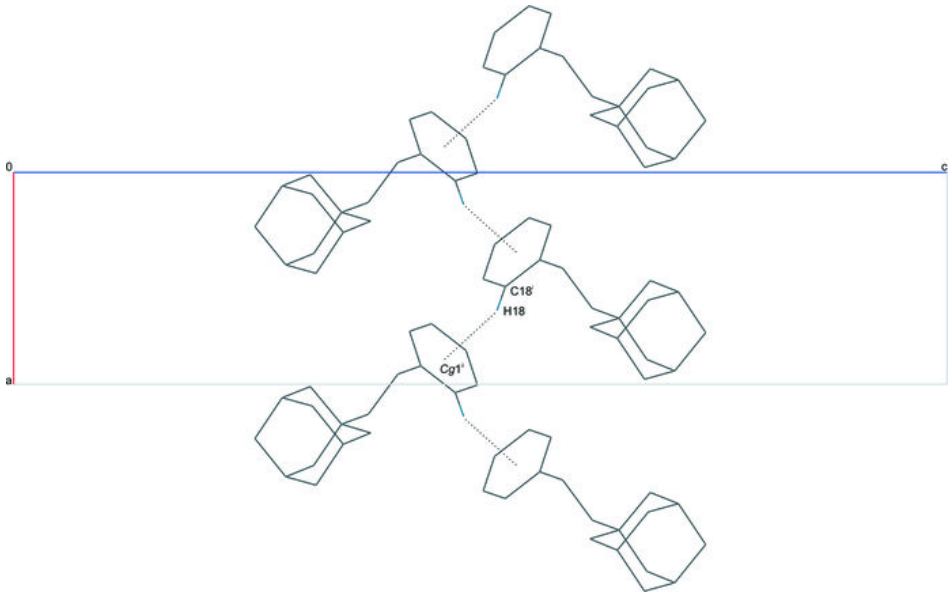


Fig. 2



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3β-Hydroxylup-20(29)-en-28-yl 1*H*-imidazole-1-carboxylate

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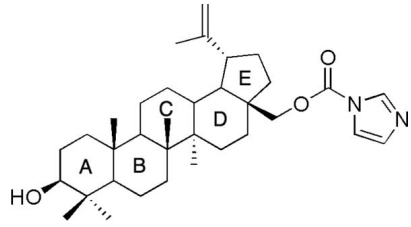
Key indicators: single-crystal X-ray study; T = 293 K; mean σ(C–C) = 0.005 Å; R factor = 0.049; wR factor = 0.119; data-to-parameter ratio = 8.7.

The title triterpene, $C_{34}H_{52}N_2O_3$, is a C-28 carbamate derivative of betulin prepared in a one-step reaction from the commercially available 1,1′-carbonyldiimidazole (CDI). All rings are fused *trans*. The X-ray study shows the retention of the configuration of C-28 with respect to the known chiral centres of the molecule. In the crystal, the molecules are O—H···O hydrogen bonded *via* the hydroxy group and the carbonyl group of the carbamate function into chains running along the *c* axis. A quantum-mechanical *ab initio* Roothaan Hartree–Fock calculation of the equilibrium geometry of the isolated molecule gives values for bond-lengths and valency angles close to the experimental values. The calculations also reproduce the molecular conformation well, with calculated puckering parameters that agree well with the observed values.

Related literature

For the synthesis of the title compound, see: Santos *et al.* (2009). For the biological activity of betulin and betulinic acid, see: Dzubak *et al.* (2006); Tolstikova *et al.* (2006); Petronelli *et al.* (2009). For plant triterpenes as potential anti-cancer drugs, see: Kinghorn *et al.* (2004); Setzer & Setzer (2003). For products afforded by the reaction of CDI with alcohols and phenols, see: Tang *et al.* (2004); Totleben *et al.* (1997); Herbez & Fischer (2005); Moreira *et al.* (2008); Ramos Silva *et al.* (2007). For puckering and asymmetry parameters, see: Cremer & Pople (1975); Duax & Norton (1975). The quantum chemical calculations were performed with the computer program *GAMESS* (Schmidt *et al.*, 1993).



Experimental

Crystal data

$C_{34}H_{52}N_2O_3$
M_r = 536.78
Orthorhombic, $P2_12_12_1$
a = 8.2575 (2) Å
b = 12.3909 (4) Å
c = 29.0992 (8) Å
V = 2977.37 (15) Å^3
Z = 4
Mo $K\alpha$ radiation
μ = 0.08 mm^{-1}
T = 293 K
0.25 × 0.22 × 0.18 mm

Data collection

Bruker APEXII CCD area-detector diffractometer
Absorption correction: multi-scan (*SADABS*; Sheldrick, 2000)
T_{min} = 0.898, T_{max} = 1.0
54547 measured reflections
3117 independent reflections
2106 reflections with $I > 2\sigma(I)$
R_{int} = 0.111

Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.049
$wR(F^2)$ = 0.119
S = 1.02
3117 reflections
360 parameters
H-atom parameters constrained
$\Delta\rho_{max}$ = 0.17 e Å^{-3}
$\Delta\rho_{min}$ = −0.20 e Å^{-3}

Table 1
Hydrogen-bond geometry (Å, °).

D—H···A	D—H	H···A	D···A	D—H···A
O3A—H3A···O28B^{i}	0.82	2.13	2.920 (4)	162

Symmetry code: (i) $-x+\frac{3}{2}, -y+2, z-\frac{1}{2}$.

Data collection: *APEX2* (Bruker, 2006); cell refinement: *SAINT* (Bruker, 2006); data reduction: *SAINT*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *PLATON* (Spek, 2009); software used to prepare material for publication: *SHELXL97*.

This work was supported by the Fundação para a Ciência e Tecnologia. RCS thanks the FCT for a grant (SFRH/BD/23700/2005). We gratefully acknowledge the LCA-UC for granting computer time in the Milipeia cluster and Mr Carlos Pereira for help in the analysis of the output of the GAMESS code.

Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: EZ2217).

References

Bruker (2006). *APEX2* and *SAINT*. Bruker AXS Inc., Madison, Wisconsin, USA.
Cremer, D. & Pople, J. A. (1975). *J. Am. Chem. Soc.* **97**, 1354–1358.

Duax, W. L. & Norton, D. A. (1975). *Atlas of Steroid Structure*. New York: Plenum Press.
Dzubak, P., Hajduch, M., Vydra, D., Hustova, A., Kvasnica, M., Biedermann, D., Markova, L., Urban, M. & Sarek, J. (2006). *Nat. Prod. Rep.* **23**, 294–411.
Herbez, V. & Fischer, F. (2005). *Tetrahedron Lett.* **46**, 6797–6799.
Kinghorn, A. D., Su, B. N., Jang, D. S., Chang, L. C., Lee, D., Gu, J. Q., Carcache-Blanco, E. J., Powlus, A. D., Lee, S. K., Park, E. J., Cuendet, M., Gills, J. J., Bhat, K., Park, H. S., Mata-Greenwood, E., Song, L. L., Jong, M. H. & Pezzuto, J. M. (2004). *Planta Med.* **70**, 691–705.
Moreira, V. M. A., Vasaitis, T. S., Guo, Z. Y., Njar, V. C. O. & Salvador, J. A. R. (2008). *Steroids*, **73**, 1217–1227.
Petronelli, A., Pannitteri, G. & Testa, U. (2009). *Anticancer Drugs*, **20**, 880–892.
Santos, R. C., Salvador, J. A. R., Marín, S. & Cascante, M. (2009). *Bioorg. Med. Chem.* **17**, 6241–6250.
Schmidt, M. W., Baldrige, K. K., Boatz, J. A., Elbert, S. T., Gordon, M. S., Jensen, J. J., Koseki, S., Matsunaga, N., Nguyen, K. A., Sue, S., Windus, T. L., Dupuis, M. & Montgomery, J. A. (1993). *J. Comput. Chem.* **14**, 1347–1363.
Setzer, W. N. & Setzer, M. C. (2003). *Mini Rev. Med. Chem.* **3**, 540–556.
Sheldrick, G. M. (2000). *SADABS*. University of Göttingen, Germany.
Sheldrick, G. M. (2008). *Acta Cryst.* A**64**, 112–122.
Ramos Silva, M., Matos Beja, A., Moreira, V. M., Santos, R. C. & Salvador, J. A. R. (2007). (2007). *Acta Cryst.* E**63**, o4824.
Spek, A. L. (2009). *Acta Cryst.* D**65**, 148–155.
Tang, Y. Q., Dong, Y. X. & Vennerstrom, J. L. (2004). *Synthesis*, pp. 2540–2544.
Tolstikova, T. G., Sorokina, I. V., Tolstikov, G. A., Tolstikov, A. G. & Flekhter, O. B. (2006). *Russ. J. Bioorg. Chem.* **32**, 37–49.
Totleben, M. J., Freeman, J. P. & Szmuszkovicz, J. (1997). *J. Org. Chem.* **62**, 7319–7323.

supplementary materials

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3β-Hydroxylup-20(29)-en-28-yl 1*H*-imidazole-1-carboxylate

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Comment

Cancer is the second most important disease leading to death in both the developing and developed countries nowadays. Numerous experimental and epidemiological studies have shown that several plant derived natural products may serve as effective anticancer drugs, among which are plant triterpenes (Kinghorn *et al.*, 2004 and Setzer *et al.*, 2003). Betulin and betulinic acid, two pentacyclic lupane triterpenes were reported to display several biological effects including anti-inflammatory, antiviral, antimalarial and in particular anticancer (Dzubak *et al.*, 2006 and Tolstikova *et al.*, 2006). The therapeutic characteristics of betulinic acid regarding specificity and mode of action make it a promising anticancer agent presently under evaluation in phase I studies (Petronelli *et al.*, 2009).

As part of our current interest in the synthesis of new triterpenoid derivatives with cytotoxic activity, we have recently reported the synthesis and evaluation of novel carbamates and *N*-acylheterocyclic derivatives of betulin and betulinic acid for potential use as chemotherapeutic agents (Santos *et al.*, 2009).

The general procedure for the synthesis of the novel lupane derivatives involved dissolution of the corresponding lupanes and CDI, in THF at reflux, under N_2. The reaction of CDI with alcohols and phenols has been reported to afford either *N*-alkylimidazoles (Tang *et al.*, 2004 and Totleben *et al.*, 1997) or imidazole carboxylic esters (carbamates) (Herbez *et al.*, 2005; Moreira *et al.*, 2008; Ramos Silva *et al.*, 2007; Tang *et al.*, 2004 and Totleben *et al.*, 1997) depending both on alcohol type and on the reaction conditions used. In this case the reaction afforded the carbamate derivative 3β-hydroxy-lup-20 (29)-en-28-yl-1*H*-imidazole-1-carboxylate in good yield. This compound had been found to induce a selective dose-dependent decrease in the viability of HepG2, HeLa and Jurkat cells after 72 h of treatment according to the determined IC_{50} values (4.2 µ M, 7.6 µ M and 16.3µ M, respectively), which were 2–8 times lower than that obtained with betulinic acid.

Mindful of the biological and synthetic importance of such molecules, we report in this communication the molecular structure of the 3β-hydroxy-lup-20 (29)-en-28-yl-1*H*-imidazole-1-carboxylate determined by single-crystal X-ray diffraction, and compare it with that of the free molecule as given by a quantum mechanical *ab initio* calculation. The structure of this compound with the corresponding atomic numbering scheme is shown in Fig. 1. This triterpenoid compound is a lupane-type with an imidazole carbonyloxy at C-28. The retention of configuration of C-28 was unequivocally demonstrated by this X-ray crystallographic study.

Bond lengths and valency angles have typical values for this type of compounds. All rings are fused *trans* as shown by the angle between the least-squares planes of the rings [rings A and B: 14.63 (18)°, B and C: 10.63 (18)°, C and D: 6.67 (18)°, D and E: 4.6 (2)°]. Rings A and C have conformations close to chair while rings B and D have conformations slightly distorted from chair towards half-chair as shown by the Cremer & Pople (1975) parameters [ring A: Q = 0.545 (4) Å, θ = 5.4 (4)° and φ = 36 (5)°; B: Q = 0.571 (4) Å, θ = 11.3 (4)° and φ = 1.0 (19)°; C: Q = 0.601 (4) Å, θ = 5.7 (4)° and φ = 338 (3)°; D: Q = 0.569 (4) Å, θ = 171.1 (4)° and φ = 90 (2)°]. Ring E has a twisted conformation along the C17–C18 bond [q_2 = 0.443 (4) Å and φ_2 = 9.0 (5)° and asymmetry parameters (Duax & Norton, 1975) ΔC_2(C21) = ΔC_2(C17,18) = 11.7 (4)°].

The molecules are hydrogen bonded involving the hydroxyl group at C3 and the carbonyl group of the carbamate moiety, forming infinite chains running along the *c* axis. In addition, two short distances between C16—H16A and C28—H28B and the O28A and O28B atoms, respectively may be due to weak intramolecular C—H···O interactions.

In order to gain some insight on how the crystal packing of (I) might affect the molecular geometry we have performed a quantum chemical calculation on the equilibrium geometry of the free molecule. These calculations were performed with the computer program GAMESS (Schmidt *et al.*, 1993).

The *ab initio* calculations reproduce the observed experimental bond lengths and valency angles of the molecule well, with the exception of the bond C20—C30 for which the calculations gave a distance of 1.5103 Å instead of the observed value of 1.433 (6) Å. Also, the calculated conformations of the rings are very close to the experimental values, with the exception of ring E for which the calculations gave a conformation closer to envelope on C17, instead of the observed twisted conformation around C17–C18.

Experimental

All reagents were obtained from Sigma-Aldrich Co. THF was dried and purified before use according to standard procedures. A solution of betulin (200 mg, 0.45 mmol) and CDI (219 mg, 1.35 mmol) was refluxed in anyhdrous THF (8 ml). After 7 h the reaction was complete (TLC control). Water (30 ml) was added to the mixture and the resulting precipitate was dissolved in ethyl ether (50 ml). The aqueous phase was extracted twice with diethyl ether (2 *x* 30 ml). The organic phase was then washed with water (30 ml), brine (30 ml), dried with anhydrous Na_2SO_4, filtered, and concentrated under reduced pressure to give a yellowish solid. This solid was submitted to f.c.c. with petroleum ether 40–60°C/ethyl acetate (3:2) and afforded the title compound (246 mg, 82%). Full analytical details for this compound (MS, IR, ^{1}H and ^{13}C NMR spectroscopy data) can be found in Santos *et al.*, 2009. Recrystallization from acetone at room temperature gave colourless single crystals suitable for X-ray diffraction.

Ab initio calculations were based on a molecular orbital Roothaan Hartree-Fock method using an extended 6–31 G(d,p) basis set. Tight conditions for convergence of both the self-consistent field cycles and maximum density and energy gradient variations were imposed (10^{-6} atomic units). The program was run on the Milipeia cluster of UC-LCA (using 16 Opteron cores at 2.2 GHz, runing Linux).

Refinement

All H atoms attached to C atoms were refined as riding on their parent atoms using *SHELXL97* defaults. The H atom of the hydroxyl group was refined using an HFIX 147 instruction with U_{iso}= 1.5 U_{eq} of the O atom. The absolute configuration was not determined from the X-ray data, as the molecule lacks any strong anomalous scatterers at the Mo Kα wavelength, but was known from the synthetic route. Friedel pairs were merged for the refinement.

Figures

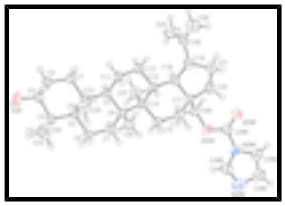


Fig. 1. *ORTEPII* plot of the title compound showing the atomic numbering scheme. Displacement ellipsoids are drawn at the 50% level.

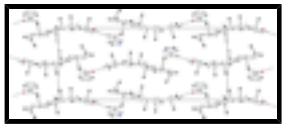


Fig. 2. Packing diagram (view along the *a* axis) showing the hydrogen bonding network.

Fig. 3. The formation of the title compound.

3β-Hydroxylup-20 (29)-en-28-yl 1*H*-imidazole-1-carboxylate

Crystal data

$C_{34}H_{52}N_2O_3$	D_x = 1.197 Mg m^{-3}
M_r = 536.78	Melting point: 476 K
Orthorhombic, $P2_12_12_1$	Mo $K\alpha$ radiation, λ = 0.71073 Å
Hall symbol: P 2ac 2ab	Cell parameters from 3394 reflections
a = 8.2575 (2) Å	θ = 2.6–19.6°
b = 12.3909 (4) Å	μ = 0.08 mm^{-1}
c = 29.0992 (8) Å	T = 293 K
V = 2977.37 (15) Å^3	Block, colourless
Z = 4	0.25 × 0.22 × 0.18 mm
F(000) = 1176	

Data collection

Bruker APEXII CCD area-detector diffractometer	3117 independent reflections
Radiation source: fine-focus sealed tube	2106 reflections with $I > 2\sigma(I)$
graphite	R_{int} = 0.111
φ and ω scans	θ_{max} = 25.4°, θ_{min} = 1.4°
Absorption correction: multi-scan (*SADABS*; Sheldrick, 2000)	h = −9→9
T_{min} = 0.898, T_{max} = 1.0	k = −14→14
54547 measured reflections	l = −35→35

Refinement

Refinement on F^2	Secondary atom site location: difference Fourier map
Least-squares matrix: full	Hydrogen site location: inferred from neighbouring sites

$R[F^2 > 2\sigma(F^2)] = 0.049$	H-atom parameters constrained
$wR(F^2) = 0.119$	$w = 1/[\sigma^2(F_o^2) + (0.0588P)^2 + 0.259P]$ where $P = (F_o^2 + 2F_c^2)/3$
$S = 1.02$	$(\Delta/\sigma)_{max} < 0.001$
3117 reflections	$\Delta\rho_{max} = 0.17$ e Å^{-3}
360 parameters	$\Delta\rho_{min} = -0.19$ e Å^{-3}
0 restraints	Extinction correction: *SHELXL97* (Sheldrick, 2008), $Fc^*=kFc[1+0.001xFc^2\lambda^3/\sin(2\theta)]^{-1/4}$
Primary atom site location: structure-invariant direct methods	Extinction coefficient: 0.0030 (6)

Special details

Geometry. All e.s.d.'s (except the e.s.d. in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell e.s.d.'s are taken into account individually in the estimation of e.s.d.'s in distances, angles and torsion angles; correlations between e.s.d.'s in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell e.s.d.'s is used for estimating e.s.d.'s involving l.s. planes.

Refinement. Refinement of F^2 against ALL reflections. The weighted *R*-factor *wR* and goodness of fit *S* are based on F^2, conventional *R*-factors *R* are based on *F*, with *F* set to zero for negative F^2. The threshold expression of $F^2 > \sigma(F^2)$ is used only for calculating *R*-factors(gt) *etc*. and is not relevant to the choice of reflections for refinement. *R*-factors based on F^2 are statistically about twice as large as those based on *F*, and *R*- factors based on ALL data will be even larger.

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å^2)

	x	*y*	*z*	U_{iso}*/U_{eq}
O3A	1.2324 (3)	0.9802 (3)	−0.21004 (8)	0.0692 (9)
H3A	1.1856	0.9476	−0.2307	0.104*
O28A	0.3667 (3)	1.0883 (2)	0.12637 (8)	0.0487 (7)
O28B	0.3861 (3)	1.1078 (3)	0.20317 (9)	0.0608 (8)
N28A	0.1558 (3)	1.1559 (2)	0.16449 (11)	0.0456 (8)
N28B	−0.0758 (4)	1.2165 (3)	0.13709 (15)	0.0720 (11)
C1	1.1881 (4)	0.9825 (3)	−0.08289 (11)	0.0431 (10)
H1A	1.2619	1.0103	−0.0598	0.052*
H1B	1.1784	0.9052	−0.0782	0.052*
C2	1.2598 (4)	1.0030 (4)	−0.13052 (11)	0.0472 (10)
H2A	1.2766	1.0799	−0.1346	0.057*
H2B	1.3643	0.9676	−0.1328	0.057*
C3	1.1511 (4)	0.9619 (3)	−0.16763 (11)	0.0447 (9)
H3	1.1410	0.8837	−0.1636	0.054*
C4	0.9786 (4)	1.0102 (3)	−0.16640 (12)	0.0403 (9)
C5	0.9112 (4)	0.9973 (3)	−0.11667 (11)	0.0351 (8)
H5	0.9023	0.9191	−0.1124	0.042*
C6	0.7385 (4)	1.0385 (3)	−0.11032 (11)	0.0449 (10)
H6A	0.7396	1.1166	−0.1081	0.054*
H6B	0.6739	1.0187	−0.1369	0.054*
C7	0.6626 (4)	0.9911 (3)	−0.06708 (11)	0.0452 (10)
H7A	0.6511	0.9138	−0.0711	0.054*

H7B	0.5549	1.0211	−0.0634	0.054*
C8	0.7600 (4)	1.0123 (3)	−0.02291 (11)	0.0354 (8)
C9	0.9435 (4)	0.9876 (3)	−0.03140 (11)	0.0342 (8)
H9	0.9479	0.9092	−0.0358	0.041*
C10	1.0205 (4)	1.0351 (3)	−0.07616 (11)	0.0350 (8)
C11	1.0414 (4)	1.0077 (3)	0.01245 (11)	0.0421 (9)
H11A	1.1537	0.9890	0.0069	0.051*
H11B	1.0369	1.0839	0.0200	0.051*
C12	0.9792 (4)	0.9427 (3)	0.05311 (11)	0.0390 (9)
H12A	1.0394	0.9628	0.0804	0.047*
H12B	0.9980	0.8666	0.0474	0.047*
C13	0.7987 (4)	0.9610 (3)	0.06169 (10)	0.0334 (8)
H13	0.7858	1.0383	0.0678	0.040*
C14	0.6979 (4)	0.9367 (3)	0.01754 (11)	0.0346 (8)
C15	0.5141 (4)	0.9542 (3)	0.02663 (12)	0.0455 (10)
H15A	0.4933	1.0311	0.0280	0.055*
H15B	0.4539	0.9255	0.0007	0.055*
C16	0.4497 (4)	0.9020 (3)	0.07071 (12)	0.0470 (10)
H16A	0.3380	0.9237	0.0754	0.056*
H16B	0.4520	0.8241	0.0674	0.056*
C17	0.5496 (4)	0.9344 (3)	0.11233 (12)	0.0376 (9)
C18	0.7289 (4)	0.9020 (3)	0.10367 (11)	0.0365 (9)
H18	0.7282	0.8250	0.0959	0.044*
C19	0.8096 (4)	0.9114 (3)	0.15107 (11)	0.0403 (9)
H19	0.8379	0.9874	0.1560	0.048*
C20	0.9578 (5)	0.8441 (3)	0.16120 (13)	0.0477 (10)
C21	0.6699 (5)	0.8817 (4)	0.18491 (13)	0.0552 (11)
H21A	0.6939	0.8144	0.2005	0.066*
H21B	0.6571	0.9379	0.2079	0.066*
C22	0.5159 (4)	0.8707 (3)	0.15669 (13)	0.0466 (10)
H22A	0.4240	0.9008	0.1730	0.056*
H22B	0.4938	0.7955	0.1499	0.056*
C23	0.9800 (6)	1.1274 (3)	−0.18353 (14)	0.0609 (12)
H23A	1.0188	1.1295	−0.2146	0.091*
H23B	1.0499	1.1699	−0.1643	0.091*
H23C	0.8722	1.1563	−0.1824	0.091*
C24	0.8719 (5)	0.9437 (4)	−0.19920 (12)	0.0549 (11)
H24A	0.7664	0.9760	−0.2012	0.082*
H24B	0.8620	0.8714	−0.1877	0.082*
H24C	0.9206	0.9422	−0.2291	0.082*
C25	1.0456 (5)	1.1586 (3)	−0.07340 (13)	0.0534 (11)
H25A	1.0781	1.1780	−0.0428	0.080*
H25B	0.9461	1.1946	−0.0809	0.080*
H25C	1.1282	1.1799	−0.0948	0.080*
C26	0.7317 (5)	1.1319 (3)	−0.01023 (12)	0.0494 (10)
H26A	0.7605	1.1768	−0.0358	0.074*
H26B	0.7974	1.1505	0.0158	0.074*
H26C	0.6196	1.1427	−0.0028	0.074*
C27	0.7156 (5)	0.8154 (3)	0.00488 (12)	0.0455 (10)

H27A	0.6582	0.7723	0.0269	0.068*
H27B	0.8281	0.7959	0.0051	0.068*
H27C	0.6715	0.8031	−0.0252	0.068*
C28	0.5360 (4)	1.0553 (3)	0.12224 (13)	0.0461 (10)
H28A	0.5927	1.0719	0.1506	0.055*
H28B	0.5870	1.0956	0.0976	0.055*
C28A	0.3144 (4)	1.1153 (3)	0.16739 (14)	0.0452 (9)
C28B	0.0639 (5)	1.1753 (3)	0.12673 (15)	0.0536 (11)
H28C	0.0974	1.1608	0.0968	0.064*
C28C	−0.0750 (6)	1.2231 (4)	0.18384 (19)	0.0810 (16)
H28D	−0.1615	1.2487	0.2012	0.097*
C28D	0.0650 (5)	1.1884 (4)	0.20191 (16)	0.0702 (14)
H28E	0.0945	1.1867	0.2327	0.084*
C29	0.9945 (6)	0.7521 (4)	0.13855 (17)	0.0801 (15)
H29A	1.0819	0.7103	0.1480	0.096*
H29B	0.9324	0.7306	0.1135	0.096*
C30	1.0532 (6)	0.8776 (4)	0.19981 (16)	0.0818 (16)
H30A	1.1456	0.8311	0.2028	0.123*
H30B	0.9890	0.8735	0.2273	0.123*
H30C	1.0889	0.9506	0.1953	0.123*

Atomic displacement parameters (Å^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
O3A	0.0532 (18)	0.118 (3)	0.0366 (15)	−0.0123 (18)	0.0124 (13)	−0.0020 (16)
O28A	0.0432 (15)	0.0619 (18)	0.0411 (15)	0.0164 (13)	0.0093 (12)	−0.0033 (14)
O28B	0.0542 (17)	0.083 (2)	0.0449 (17)	0.0161 (16)	−0.0023 (14)	0.0079 (16)
N28A	0.0382 (16)	0.0482 (19)	0.0505 (19)	0.0132 (15)	0.0066 (16)	0.0009 (17)
N28B	0.054 (2)	0.071 (3)	0.091 (3)	0.020 (2)	−0.016 (2)	−0.009 (2)
C1	0.0292 (18)	0.063 (3)	0.038 (2)	−0.0043 (19)	−0.0011 (15)	0.0032 (19)
C2	0.034 (2)	0.070 (3)	0.038 (2)	−0.005 (2)	0.0047 (16)	0.001 (2)
C3	0.041 (2)	0.060 (3)	0.034 (2)	−0.0035 (18)	0.0061 (18)	0.0000 (19)
C4	0.043 (2)	0.048 (2)	0.0300 (19)	−0.0036 (18)	−0.0006 (17)	0.0017 (18)
C5	0.0328 (18)	0.040 (2)	0.0322 (19)	−0.0014 (17)	−0.0038 (15)	0.0012 (17)
C6	0.038 (2)	0.058 (3)	0.039 (2)	0.0024 (19)	−0.0030 (17)	0.0054 (19)
C7	0.0283 (17)	0.065 (3)	0.042 (2)	0.0008 (19)	−0.0018 (16)	−0.001 (2)
C8	0.0311 (18)	0.039 (2)	0.0362 (19)	0.0052 (16)	−0.0016 (15)	−0.0024 (17)
C9	0.0282 (17)	0.043 (2)	0.0319 (19)	−0.0013 (16)	−0.0053 (15)	−0.0007 (16)
C10	0.0297 (19)	0.040 (2)	0.035 (2)	−0.0021 (16)	0.0007 (16)	−0.0016 (16)
C11	0.0297 (18)	0.065 (3)	0.0313 (19)	−0.0065 (19)	−0.0005 (15)	−0.0022 (19)
C12	0.0309 (18)	0.052 (2)	0.034 (2)	0.0016 (18)	−0.0033 (16)	−0.0058 (17)
C13	0.0308 (18)	0.038 (2)	0.0311 (18)	−0.0021 (15)	0.0020 (15)	−0.0038 (16)
C14	0.0269 (17)	0.042 (2)	0.0349 (19)	−0.0031 (16)	0.0042 (15)	−0.0044 (16)
C15	0.0309 (19)	0.062 (3)	0.043 (2)	0.0027 (18)	−0.0013 (17)	−0.0008 (19)
C16	0.0302 (18)	0.060 (3)	0.050 (2)	0.0003 (19)	0.0032 (18)	−0.002 (2)
C17	0.036 (2)	0.036 (2)	0.041 (2)	0.0021 (17)	0.0088 (17)	−0.0011 (17)
C18	0.0317 (18)	0.040 (2)	0.038 (2)	0.0027 (16)	0.0008 (16)	−0.0015 (17)
C19	0.042 (2)	0.040 (2)	0.039 (2)	−0.0010 (17)	−0.0004 (17)	−0.0028 (18)

C20	0.044 (2)	0.056 (3)	0.043 (2)	−0.002 (2)	0.004 (2)	0.016 (2)
C21	0.060 (3)	0.062 (3)	0.045 (2)	0.002 (2)	0.007 (2)	0.005 (2)
C22	0.043 (2)	0.045 (2)	0.051 (2)	0.0038 (18)	0.0128 (19)	0.0057 (19)
C23	0.070 (3)	0.060 (3)	0.053 (3)	0.003 (2)	−0.002 (2)	0.021 (2)
C24	0.049 (2)	0.076 (3)	0.040 (2)	−0.008 (2)	−0.0032 (19)	0.000 (2)
C25	0.063 (3)	0.048 (3)	0.049 (2)	−0.015 (2)	0.003 (2)	−0.006 (2)
C26	0.050 (2)	0.049 (3)	0.050 (2)	0.006 (2)	0.0109 (19)	0.0034 (19)
C27	0.045 (2)	0.045 (2)	0.046 (2)	−0.0104 (19)	−0.0012 (19)	−0.0084 (18)
C28	0.038 (2)	0.052 (3)	0.047 (2)	0.0067 (19)	0.0117 (18)	0.0009 (19)
C28A	0.042 (2)	0.044 (2)	0.050 (3)	0.0037 (19)	0.005 (2)	0.005 (2)
C28B	0.057 (3)	0.050 (3)	0.054 (3)	0.002 (2)	−0.010 (2)	−0.004 (2)
C28C	0.057 (3)	0.098 (4)	0.088 (4)	0.033 (3)	0.009 (3)	−0.011 (3)
C28D	0.061 (3)	0.095 (4)	0.054 (3)	0.024 (3)	0.008 (2)	−0.009 (3)
C29	0.076 (3)	0.069 (3)	0.095 (4)	0.028 (3)	−0.025 (3)	−0.018 (3)
C30	0.064 (3)	0.110 (4)	0.072 (3)	0.004 (3)	−0.010 (3)	−0.004 (3)

Geometric parameters (Å, °)

O3A—C3	1.423 (4)	C14—C15	1.555 (4)
O3A—H3A	0.8200	C15—C16	1.532 (5)
O28A—C28A	1.312 (4)	C15—H15A	0.9700
O28A—C28	1.462 (4)	C15—H15B	0.9700
O28B—C28A	1.201 (4)	C16—C17	1.520 (5)
N28A—C28B	1.357 (5)	C16—H16A	0.9700
N28A—C28D	1.382 (5)	C16—H16B	0.9700
N28A—C28A	1.406 (5)	C17—C28	1.529 (5)
N28B—C28B	1.297 (5)	C17—C22	1.539 (5)
N28B—C28C	1.363 (6)	C17—C18	1.555 (5)
C1—C2	1.528 (4)	C18—C19	1.536 (4)
C1—C10	1.543 (5)	C18—H18	0.9800
C1—H1A	0.9700	C19—C20	1.510 (5)
C1—H1B	0.9700	C19—C21	1.561 (5)
C2—C3	1.494 (5)	C19—H19	0.9800
C2—H2A	0.9700	C20—C29	1.352 (6)
C2—H2B	0.9700	C20—C30	1.433 (6)
C3—C4	1.546 (5)	C21—C22	1.520 (5)
C3—H3	0.9800	C21—H21A	0.9700
C4—C23	1.535 (5)	C21—H21B	0.9700
C4—C24	1.539 (5)	C22—H22A	0.9700
C4—C5	1.559 (5)	C22—H22B	0.9700
C5—C6	1.526 (5)	C23—H23A	0.9600
C5—C10	1.557 (5)	C23—H23B	0.9600
C5—H5	0.9800	C23—H23C	0.9600
C6—C7	1.524 (4)	C24—H24A	0.9600
C6—H6A	0.9700	C24—H24B	0.9600
C6—H6B	0.9700	C24—H24C	0.9600
C7—C8	1.539 (5)	C25—H25A	0.9600
C7—H7A	0.9700	C25—H25B	0.9600
C7—H7B	0.9700	C25—H25C	0.9600

C8—C26	1.545 (5)	C26—H26A	0.9600
C8—C9	1.566 (4)	C26—H26B	0.9600
C8—C14	1.590 (5)	C26—H26C	0.9600
C9—C11	1.531 (4)	C27—H27A	0.9600
C9—C10	1.565 (4)	C27—H27B	0.9600
C9—H9	0.9800	C27—H27C	0.9600
C10—C25	1.547 (5)	C28—H28A	0.9700
C11—C12	1.520 (4)	C28—H28B	0.9700
C11—H11A	0.9700	C28B—H28C	0.9300
C11—H11B	0.9700	C28C—C28D	1.341 (6)
C12—C13	1.528 (4)	C28C—H28D	0.9300
C12—H12A	0.9700	C28D—H28E	0.9300
C12—H12B	0.9700	C29—H29A	0.9300
C13—C18	1.536 (4)	C29—H29B	0.9300
C13—C14	1.560 (4)	C30—H30A	0.9600
C13—H13	0.9800	C30—H30B	0.9600
C14—C27	1.554 (5)	C30—H30C	0.9600
C3—O3A—H3A	109.5	C17—C16—C15	111.5 (3)
C28A—O28A—C28	117.4 (3)	C17—C16—H16A	109.3
C28B—N28A—C28D	106.5 (3)	C15—C16—H16A	109.3
C28B—N28A—C28A	129.3 (4)	C17—C16—H16B	109.3
C28D—N28A—C28A	124.2 (4)	C15—C16—H16B	109.3
C28B—N28B—C28C	104.6 (4)	H16A—C16—H16B	108.0
C2—C1—C10	113.1 (3)	C16—C17—C28	111.7 (3)
C2—C1—H1A	109.0	C16—C17—C22	115.8 (3)
C10—C1—H1A	109.0	C28—C17—C22	109.3 (3)
C2—C1—H1B	109.0	C16—C17—C18	108.6 (3)
C10—C1—H1B	109.0	C28—C17—C18	110.7 (3)
H1A—C1—H1B	107.8	C22—C17—C18	100.1 (3)
C3—C2—C1	111.5 (3)	C13—C18—C19	121.0 (3)
C3—C2—H2A	109.3	C13—C18—C17	111.3 (3)
C1—C2—H2A	109.3	C19—C18—C17	104.4 (3)
C3—C2—H2B	109.3	C13—C18—H18	106.4
C1—C2—H2B	109.3	C19—C18—H18	106.4
H2A—C2—H2B	108.0	C17—C18—H18	106.4
O3A—C3—C2	106.8 (3)	C20—C19—C18	119.0 (3)
O3A—C3—C4	113.1 (3)	C20—C19—C21	110.2 (3)
C2—C3—C4	113.9 (3)	C18—C19—C21	103.2 (3)
O3A—C3—H3	107.6	C20—C19—H19	108.0
C2—C3—H3	107.6	C18—C19—H19	108.0
C4—C3—H3	107.6	C21—C19—H19	108.0
C23—C4—C24	108.0 (3)	C29—C20—C30	120.2 (4)
C23—C4—C3	110.6 (3)	C29—C20—C19	123.5 (4)
C24—C4—C3	107.8 (3)	C30—C20—C19	116.0 (4)
C23—C4—C5	113.7 (3)	C22—C21—C19	107.4 (3)
C24—C4—C5	108.4 (3)	C22—C21—H21A	110.2
C3—C4—C5	108.1 (3)	C19—C21—H21A	110.2
C6—C5—C10	110.4 (3)	C22—C21—H21B	110.2
C6—C5—C4	114.3 (3)	C19—C21—H21B	110.2

C10—C5—C4	117.7 (3)	H21A—C21—H21B	108.5
C6—C5—H5	104.2	C21—C22—C17	104.8 (3)
C10—C5—H5	104.2	C21—C22—H22A	110.8
C4—C5—H5	104.2	C17—C22—H22A	110.8
C7—C6—C5	110.8 (3)	C21—C22—H22B	110.8
C7—C6—H6A	109.5	C17—C22—H22B	110.8
C5—C6—H6A	109.5	H22A—C22—H22B	108.9
C7—C6—H6B	109.5	C4—C23—H23A	109.5
C5—C6—H6B	109.5	C4—C23—H23B	109.5
H6A—C6—H6B	108.1	H23A—C23—H23B	109.5
C6—C7—C8	114.1 (3)	C4—C23—H23C	109.5
C6—C7—H7A	108.7	H23A—C23—H23C	109.5
C8—C7—H7A	108.7	H23B—C23—H23C	109.5
C6—C7—H7B	108.7	C4—C24—H24A	109.5
C8—C7—H7B	108.7	C4—C24—H24B	109.5
H7A—C7—H7B	107.6	H24A—C24—H24B	109.5
C7—C8—C26	106.5 (3)	C4—C24—H24C	109.5
C7—C8—C9	109.9 (3)	H24A—C24—H24C	109.5
C26—C8—C9	111.8 (3)	H24B—C24—H24C	109.5
C7—C8—C14	110.4 (3)	C10—C25—H25A	109.5
C26—C8—C14	109.9 (3)	C10—C25—H25B	109.5
C9—C8—C14	108.3 (3)	H25A—C25—H25B	109.5
C11—C9—C10	114.7 (3)	C10—C25—H25C	109.5
C11—C9—C8	110.3 (3)	H25A—C25—H25C	109.5
C10—C9—C8	116.8 (3)	H25B—C25—H25C	109.5
C11—C9—H9	104.5	C8—C26—H26A	109.5
C10—C9—H9	104.5	C8—C26—H26B	109.5
C8—C9—H9	104.5	H26A—C26—H26B	109.5
C1—C10—C25	107.8 (3)	C8—C26—H26C	109.5
C1—C10—C5	107.2 (3)	H26A—C26—H26C	109.5
C25—C10—C5	114.5 (3)	H26B—C26—H26C	109.5
C1—C10—C9	108.1 (3)	C14—C27—H27A	109.5
C25—C10—C9	112.6 (3)	C14—C27—H27B	109.5
C5—C10—C9	106.3 (3)	H27A—C27—H27B	109.5
C12—C11—C9	112.6 (3)	C14—C27—H27C	109.5
C12—C11—H11A	109.1	H27A—C27—H27C	109.5
C9—C11—H11A	109.1	H27B—C27—H27C	109.5
C12—C11—H11B	109.1	O28A—C28—C17	111.1 (3)
C9—C11—H11B	109.1	O28A—C28—H28A	109.4
H11A—C11—H11B	107.8	C17—C28—H28A	109.4
C11—C12—C13	112.2 (3)	O28A—C28—H28B	109.4
C11—C12—H12A	109.2	C17—C28—H28B	109.4
C13—C12—H12A	109.2	H28A—C28—H28B	108.0
C11—C12—H12B	109.2	O28B—C28A—O28A	127.3 (3)
C13—C12—H12B	109.2	O28B—C28A—N28A	122.6 (4)
H12A—C12—H12B	107.9	O28A—C28A—N28A	110.1 (3)
C12—C13—C18	115.1 (3)	N28B—C28B—N28A	112.2 (4)
C12—C13—C14	110.9 (3)	N28B—C28B—H28C	123.9
C18—C13—C14	111.3 (3)	N28A—C28B—H28C	123.9

C12—C13—H13	106.3	C28D—C28C—N28B	112.1 (4)
C18—C13—H13	106.3	C28D—C28C—H28D	124.0
C14—C13—H13	106.3	N28B—C28C—H28D	124.0
C27—C14—C15	105.5 (3)	C28C—C28D—N28A	104.6 (4)
C27—C14—C13	109.4 (3)	C28C—C28D—H28E	127.7
C15—C14—C13	110.7 (3)	N28A—C28D—H28E	127.7
C27—C14—C8	111.4 (3)	C20—C29—H29A	120.0
C15—C14—C8	111.0 (3)	C20—C29—H29B	120.0
C13—C14—C8	108.9 (3)	H29A—C29—H29B	120.0
C16—C15—C14	115.0 (3)	C20—C30—H30A	109.5
C16—C15—H15A	108.5	C20—C30—H30B	109.5
C14—C15—H15A	108.5	H30A—C30—H30B	109.5
C16—C15—H15B	108.5	C20—C30—H30C	109.5
C14—C15—H15B	108.5	H30A—C30—H30C	109.5
H15A—C15—H15B	107.5	H30B—C30—H30C	109.5
C10—C1—C2—C3	−58.5 (4)	C9—C8—C14—C27	−60.7 (3)
C1—C2—C3—O3A	−177.2 (3)	C7—C8—C14—C15	−57.6 (4)
C1—C2—C3—C4	57.1 (4)	C26—C8—C14—C15	59.6 (4)
O3A—C3—C4—C23	−48.1 (4)	C9—C8—C14—C15	−178.0 (3)
C2—C3—C4—C23	74.1 (4)	C7—C8—C14—C13	−179.7 (3)
O3A—C3—C4—C24	69.8 (4)	C26—C8—C14—C13	−62.5 (3)
C2—C3—C4—C24	−168.0 (3)	C9—C8—C14—C13	59.9 (3)
O3A—C3—C4—C5	−173.2 (3)	C27—C14—C15—C16	70.6 (4)
C2—C3—C4—C5	−51.0 (4)	C13—C14—C15—C16	−47.6 (4)
C23—C4—C5—C6	58.6 (4)	C8—C14—C15—C16	−168.6 (3)
C24—C4—C5—C6	−61.6 (4)	C14—C15—C16—C17	52.6 (4)
C3—C4—C5—C6	−178.2 (3)	C15—C16—C17—C28	65.0 (4)
C23—C4—C5—C10	−73.5 (4)	C15—C16—C17—C22	−169.0 (3)
C24—C4—C5—C10	166.3 (3)	C15—C16—C17—C18	−57.4 (4)
C3—C4—C5—C10	49.7 (4)	C12—C13—C18—C19	51.4 (4)
C10—C5—C6—C7	−63.2 (4)	C14—C13—C18—C19	178.7 (3)
C4—C5—C6—C7	161.3 (3)	C12—C13—C18—C17	174.4 (3)
C5—C6—C7—C8	56.1 (4)	C14—C13—C18—C17	−58.3 (4)
C6—C7—C8—C26	75.0 (4)	C16—C17—C18—C13	61.6 (4)
C6—C7—C8—C9	−46.3 (4)	C28—C17—C18—C13	−61.4 (4)
C6—C7—C8—C14	−165.7 (3)	C22—C17—C18—C13	−176.7 (3)
C7—C8—C9—C11	−179.6 (3)	C16—C17—C18—C19	−166.3 (3)
C26—C8—C9—C11	62.3 (4)	C28—C17—C18—C19	70.7 (4)
C14—C8—C9—C11	−58.9 (4)	C22—C17—C18—C19	−44.6 (3)
C7—C8—C9—C10	47.0 (4)	C13—C18—C19—C20	−79.6 (4)
C26—C8—C9—C10	−71.1 (4)	C17—C18—C19—C20	154.2 (3)
C14—C8—C9—C10	167.7 (3)	C13—C18—C19—C21	158.0 (3)
C2—C1—C10—C25	−70.7 (4)	C17—C18—C19—C21	31.8 (4)
C2—C1—C10—C5	53.0 (4)	C18—C19—C20—C29	−22.7 (5)
C2—C1—C10—C9	167.4 (3)	C21—C19—C20—C29	96.1 (5)
C6—C5—C10—C1	175.3 (3)	C18—C19—C20—C30	163.0 (4)
C4—C5—C10—C1	−51.0 (4)	C21—C19—C20—C30	−78.2 (4)
C6—C5—C10—C25	−65.2 (4)	C20—C19—C21—C22	−134.8 (3)
C4—C5—C10—C25	68.5 (4)	C18—C19—C21—C22	−6.7 (4)

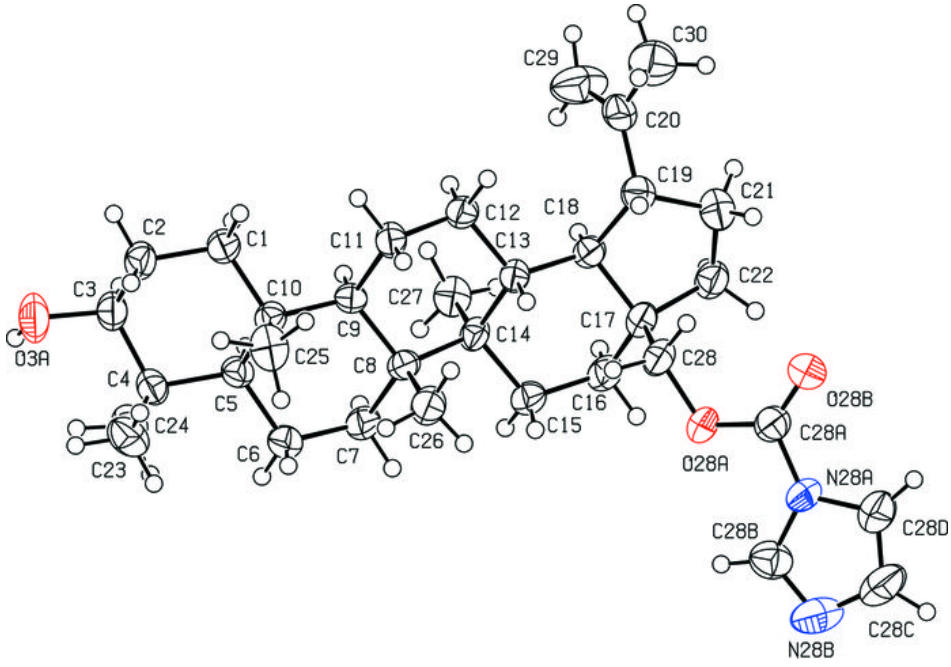
C6—C5—C10—C9	59.8 (4)	C19—C21—C22—C17	−21.2 (4)
C4—C5—C10—C9	−166.5 (3)	C16—C17—C22—C21	156.3 (3)
C11—C9—C10—C1	60.2 (4)	C28—C17—C22—C21	−76.5 (4)
C8—C9—C10—C1	−168.4 (3)	C18—C17—C22—C21	39.8 (4)
C11—C9—C10—C25	−58.7 (4)	C28A—O28A—C28—C17	109.7 (4)
C8—C9—C10—C25	72.7 (4)	C16—C17—C28—O28A	53.7 (4)
C11—C9—C10—C5	175.1 (3)	C22—C17—C28—O28A	−75.7 (4)
C8—C9—C10—C5	−53.5 (4)	C18—C17—C28—O28A	174.9 (3)
C10—C9—C11—C12	−169.2 (3)	C28—O28A—C28A—O28B	−6.5 (6)
C8—C9—C11—C12	56.4 (4)	C28—O28A—C28A—N28A	173.6 (3)
C9—C11—C12—C13	−54.2 (4)	C28B—N28A—C28A—O28B	175.4 (4)
C11—C12—C13—C18	−177.3 (3)	C28D—N28A—C28A—O28B	−1.8 (6)
C11—C12—C13—C14	55.2 (4)	C28B—N28A—C28A—O28A	−4.7 (5)
C12—C13—C14—C27	63.5 (4)	C28D—N28A—C28A—O28A	178.1 (4)
C18—C13—C14—C27	−66.0 (3)	C28C—N28B—C28B—N28A	−0.6 (5)
C12—C13—C14—C15	179.4 (3)	C28D—N28A—C28B—N28B	−0.3 (5)
C18—C13—C14—C15	49.8 (4)	C28A—N28A—C28B—N28B	−177.9 (4)
C12—C13—C14—C8	−58.4 (4)	C28B—N28B—C28C—C28D	1.3 (7)
C18—C13—C14—C8	172.1 (3)	N28B—C28C—C28D—N28A	−1.4 (6)
C7—C8—C14—C27	59.6 (4)	C28B—N28A—C28D—C28C	1.0 (5)
C26—C8—C14—C27	176.9 (3)	C28A—N28A—C28D—C28C	178.8 (4)

Hydrogen-bond geometry (Å, °)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
O3A—H3A···O28B^{i}	0.82	2.13	2.920 (4)	162

Symmetry codes: (i) −*x*+3/2, −*y*+2, *z*−1/2.

Fig. 1


C30
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C4
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C16
O28B
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C7
N28A
C28D
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C28C
N28B

Fig. 2

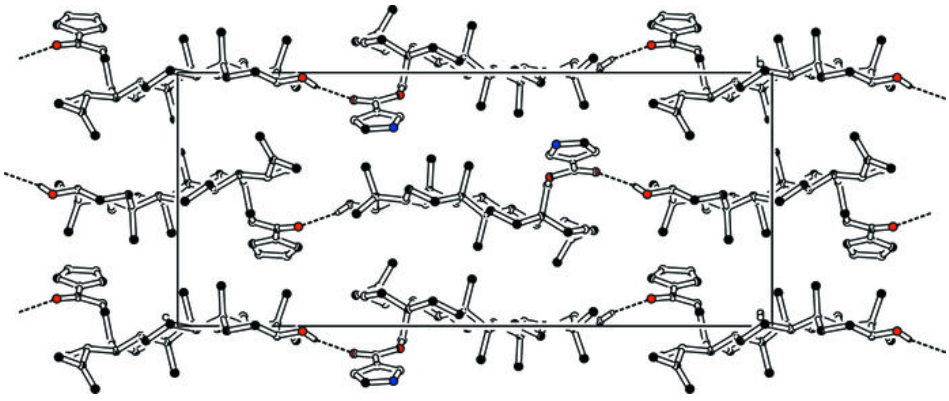
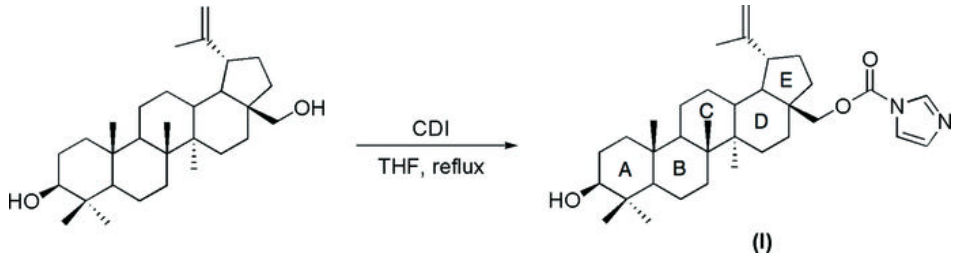


Fig. 3



(I)

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3,9-Bis(2,4-dichlorophenyl)-2,4,8,10-tetraoxaspiro[5.5]undecane

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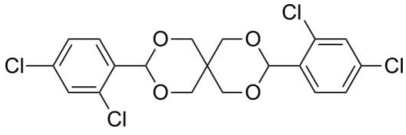
Key indicators: single-crystal X-ray study; T = 295 K; mean σ(C–C) = 0.003 Å; R factor = 0.035; wR factor = 0.160; data-to-parameter ratio = 13.7.

In the title compound, $C_{19}H_{16}Cl_4O_4$, the two halves of the molecule are related by a crystallographic twofold rotation axis passing through the central spiro-C atom. The two non-planar six-membered heterocycles both adopt chair conformations, and the dihedral angle between the two benzene rings is 76.6 (1)°. In the crystal structure, intermolecular C—H···O hydrogen bonds link the molecules into chains along the c axis.

Related literature

For general background to spiranes, see: Cismaş *et al.* (2005); Mihiş *et al.* (2008); Sun *et al.* (2010).



Experimental

Crystal data

$C_{19}H_{16}Cl_4O_4$
M_r = 450.12
Monoclinic, $P2/c$
a = 14.365 (2) Å
b = 5.7397 (9) Å
c = 11.7464 (19) Å
β = 93.275 (3)°
V = 966.9 (3) Å^3
Z = 2
Mo $K\alpha$ radiation
μ = 0.64 mm^{-1}
T = 295 K
0.21 × 0.21 × 0.16 mm

Data collection

Bruker APEXII CCD diffractometer
Absorption correction: multi-scan (*SADABS*; Bruker, 2000)
T_{min} = 0.878, T_{max} = 0.905
5044 measured reflections
1686 independent reflections
1444 reflections with $I > 2\sigma(I)$
R_{int} = 0.022

Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.035
$wR(F^2)$ = 0.160
S = 1.02
1686 reflections
123 parameters
H-atom parameters constrained
$\Delta\rho_{max}$ = 0.35 e Å^{-3}
$\Delta\rho_{min}$ = −0.40 e Å^{-3}

Table 1
Hydrogen-bond geometry (Å, °).

D—H···A	D—H	H···A	D···A	D—H···A
C5—H5···O2^{i}	0.93	2.58	3.425 (3)	152

Symmetry code: (i) $x, -y+1, z+\frac{1}{2}$.

Data collection: *SMART* (Bruker, 2000); cell refinement: *SAINT* (Bruker, 2000); data reduction: *SAINT*; program(s) used to solve structure: *SHELXTL* (Sheldrick, 2008); program(s) used to refine structure: *SHELXTL*; molecular graphics: *SHELXTL* (Sheldrick, 2008); software used to prepare material for publication: *SHELXTL*.

We gratefully acknowledge financial support from the Natural Science Foundation of China (No. 20872051).

Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: EZ2218).

References

Bruker (2000). *SAINT*, *SMART* and *SADABS*. Bruker AXS Inc., Madison, Wisconsin, USA.
Cismaş, C., Terec, A., Mager, S. & Grosu, I. (2005). *Curr. Org. Chem.* **9**, 1287–1314.
Mihiş, A., Condamine, E., Bogdan, E., Terec, A., Kurtán, T. & Grosu, I. (2008). *Molecules*, **13**, 2848–2858.
Sheldrick, G. M. (2008). *Acta Cryst.* A**64**, 112–122.
Sun, X., Yu, S.-L., Li, Z.-Y. & Yang, Y. (2010). *J. Mol. Struct.* **973**, 152–156.

supplementary materials

Acta Cryst. (2010). E**66**, o1864 [**doi:10.1107/S1600536810024712**]

3,9-Bis(2,4-dichlorophenyl)-2,4,8,10-tetraoxaspiro[5.5]undecane

Z. Li, Q. Tang, K. Wu, S. Yu and X. Sun

Comment

Owing to their characteristic axial and helical chirality, the stereochemistry of spiranes with six-membered rings has been extensively studied (Cismaş *et al.*, 2005). In the past three decades, most of these investigations were carried out with spiranes containing 1,3-dioxane units (Mihiş *et al.*, 2008; Sun *et al.*, 2010). We herein present the structure of 3,9-bis(2,4-dichlorophenyl)-2,4,8,10-tetraoxaspiro[5.5]undecane (Fig. 1).

In the title compound, a 2-fold rotation axis passes through the central spiro-C atom (C9). The two non-planar six-membered heterocycles [(O1, O2 and C7–C10) and (O1A, O2A and C7A–C10A)] both adopt chair conformations, and the dihedral angle between the two benzene rings (C1–C6 and C1A–C6A) is 76.6 (1)°. In the crystal structure, intermolecular C—H···O hydrogen bonds link the molecules to form one-dimensional chain along the *c* axis (Fig. 2).

Experimental

To a solution of 2,4-dichlorobenzaldehyde (5 mmol, 0.88 g) and pentaerythritol (3 mmol, 0.41 g) in toluene (25 ml), phosphotungstic acid (1 mol%, 16.5 mg) was added as catalyst. The mixture was refluxed for 6 h to complete the reaction. After reaction, the mixture was allowed to cool to room temperature, and dichloromethane (25 ml) was added to dissolve the product. The insoluble residues were filtered off and the filtrate was dried over anhydrous Na_2SO_4. The solvent was evaporated under vacuum and the product recrystallized from ethanol to afford a white solid (71% yield, m.p. 469–470 K). Single crystals suitable for X-ray diffraction were also obtained by evaporation of an ethanol solution.

Refinement

All H atoms were placed in geometrically idealized positions and constrained to ride on their parent atoms, with C—H distances of 0.93–0.98 Å, and with $U_{iso}(H) = 1.2U_{eq}(C)$.

Figures

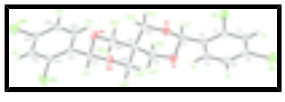


Fig. 1. The molecular structure of the title compound showing the atom numbering scheme. Displacement ellipsoids are drawn at the 30% probability level [Symmetry code: -*x* + 1, *y*, -*z* + 1/2].

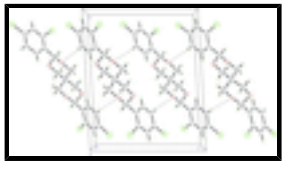


Fig. 2. One-dimensional stack running along the *c* axis. Hydrogen bonds are shown as dashed lines.

3,9-Bis(2,4-dichlorophenyl)-2,4,8,10-tetraoxaspiro[5.5]undecane

Crystal data

$C_{19}H_{16}Cl_4O_4$	$F(000) = 460$
$M_r = 450.12$	$D_x = 1.546$ Mg m^{-3}
Monoclinic, $P2/c$	Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å
$a = 14.365$ (2) Å	Cell parameters from 2876 reflections
$b = 5.7397$ (9) Å	$\theta = 2.8$–$29.5°$
$c = 11.7464$ (19) Å	$\mu = 0.64$ mm^{-1}
$\beta = 93.275$ (3)°	$T = 295$ K
$V = 966.9$ (3) Å^3	Block, colorless
$Z = 2$	0.21 × 0.21 × 0.16 mm

Data collection

Bruker APEXII CCD diffractometer	1686 independent reflections
Radiation source: fine-focus sealed tube	1444 reflections with $I > 2\sigma(I)$
graphite	$R_{int} = 0.022$
φ and ω scans	$\theta_{max} = 25.0°$, $\theta_{min} = 1.4°$
Absorption correction: multi-scan (*SADABS*; Bruker, 2000)	$h = -17 \rightarrow 17$
$T_{min} = 0.878$, $T_{max} = 0.905$	$k = -6 \rightarrow 6$
5044 measured reflections	$l = -13 \rightarrow 8$

Refinement

Refinement on F^2	Primary atom site location: structure-invariant direct methods
Least-squares matrix: full	Secondary atom site location: difference Fourier map
$R[F^2 > 2\sigma(F^2)] = 0.035$	Hydrogen site location: inferred from neighbouring sites
$wR(F^2) = 0.160$	H-atom parameters constrained
$S = 1.02$	$w = 1/[\sigma^2(F_o^2) + (0.133P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
1686 reflections	$(\Delta/\sigma)_{max} = 0.001$
123 parameters	$\Delta\rho_{max} = 0.35$ e Å^{-3}
0 restraints	$\Delta\rho_{min} = -0.40$ e Å^{-3}

Special details

Geometry. All e.s.d.'s (except the e.s.d. in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell e.s.d.'s are taken into account individually in the estimation of e.s.d.'s in distances, angles and torsion angles; correlations between e.s.d.'s in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell e.s.d.'s is used for estimating e.s.d.'s involving l.s. planes.

Refinement. Refinement of F^2 against ALL reflections. The weighted *R*-factor *wR* and goodness of fit *S* are based on F^2, conventional *R*-factors *R* are based on *F*, with *F* set to zero for negative F^2. The threshold expression of $F^2 > \sigma(F^2)$ is used only for calculating *R*-factors(gt) *etc*. and is not relevant to the choice of reflections for refinement. *R*-factors based on F^2 are statistically about twice as large as those based on *F*, and *R*- factors based on ALL data will be even larger.

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å^2)

	x	*y*	*z*	U_{iso}*/U_{eq}
Cl1	0.11833 (4)	1.10777 (11)	0.35541 (6)	0.0638 (3)
Cl2	0.09727 (5)	0.41534 (13)	0.65874 (6)	0.0751 (3)
O1	0.39049 (10)	1.0814 (2)	0.40196 (12)	0.0428 (4)
O2	0.37013 (9)	0.7923 (2)	0.26477 (12)	0.0414 (4)
C1	0.12123 (14)	0.7578 (4)	0.50648 (19)	0.0483 (6)
H1	0.0599	0.7995	0.5178	0.058*
C2	0.17289 (14)	0.8801 (3)	0.43034 (18)	0.0415 (5)
C3	0.26501 (12)	0.8219 (3)	0.41278 (16)	0.0361 (5)
C4	0.30282 (15)	0.6348 (4)	0.47363 (19)	0.0455 (5)
H4	0.3642	0.5922	0.4629	0.055*
C5	0.25309 (15)	0.5092 (4)	0.5495 (2)	0.0498 (6)
H5	0.2801	0.3841	0.5894	0.060*
C6	0.16219 (16)	0.5739 (4)	0.56487 (19)	0.0469 (6)
C7	0.32422 (14)	0.9531 (3)	0.33360 (17)	0.0388 (5)
H7	0.2855	1.0590	0.2857	0.047*
C8	0.44930 (15)	1.2158 (4)	0.3327 (2)	0.0492 (6)
H8A	0.4948	1.2992	0.3814	0.059*
H8B	0.4118	1.3298	0.2898	0.059*
C9	0.5000	1.0610 (4)	0.2500	0.0365 (6)
C10	0.42682 (15)	0.9102 (4)	0.18627 (17)	0.0427 (5)
H10A	0.3877	1.0073	0.1357	0.051*
H10B	0.4575	0.7965	0.1402	0.051*

Atomic displacement parameters (Å^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Cl1	0.0494 (4)	0.0675 (5)	0.0753 (6)	0.0257 (3)	0.0111 (3)	0.0162 (3)
Cl2	0.0745 (6)	0.0858 (6)	0.0674 (6)	−0.0222 (3)	0.0251 (4)	0.0137 (3)
O1	0.0476 (9)	0.0412 (8)	0.0411 (9)	−0.0055 (6)	0.0148 (7)	−0.0084 (5)
O2	0.0405 (8)	0.0478 (8)	0.0371 (8)	−0.0064 (6)	0.0124 (6)	−0.0095 (6)
C1	0.0344 (10)	0.0593 (13)	0.0524 (14)	0.0033 (9)	0.0125 (9)	−0.0040 (10)
C2	0.0357 (10)	0.0456 (12)	0.0435 (12)	0.0069 (8)	0.0048 (8)	−0.0030 (8)
C3	0.0316 (10)	0.0439 (10)	0.0331 (10)	0.0029 (8)	0.0033 (8)	−0.0044 (8)
C4	0.0355 (11)	0.0532 (13)	0.0480 (13)	0.0095 (8)	0.0043 (9)	0.0047 (9)
C5	0.0486 (12)	0.0515 (12)	0.0491 (13)	0.0040 (10)	0.0016 (10)	0.0098 (10)
C6	0.0476 (13)	0.0525 (12)	0.0414 (12)	−0.0086 (9)	0.0108 (9)	−0.0005 (9)
C7	0.0348 (10)	0.0474 (11)	0.0347 (11)	0.0071 (8)	0.0052 (8)	0.0018 (8)
C8	0.0559 (14)	0.0384 (11)	0.0554 (14)	−0.0039 (9)	0.0225 (11)	−0.0064 (9)
C9	0.0404 (15)	0.0340 (13)	0.0362 (15)	0.000	0.0114 (11)	0.000

C10	0.0417 (11)	0.0554 (12)	0.0315 (11)	−0.0013 (8)	0.0082 (9)	−0.0012 (8)

Geometric parameters (Å, °)

Cl1—C2	1.737 (2)	C4—H4	0.9300
Cl2—C6	1.741 (2)	C5—C6	1.379 (3)
O1—C7	1.417 (3)	C5—H5	0.9300
O1—C8	1.431 (2)	C7—H7	0.9800
O2—C7	1.414 (2)	C8—C9	1.531 (2)
O2—C10	1.434 (2)	C8—H8A	0.9700
C1—C6	1.373 (3)	C8—H8B	0.9700
C1—C2	1.386 (3)	C9—C10^{i}	1.525 (2)
C1—H1	0.9300	C9—C10	1.525 (2)
C2—C3	1.391 (3)	C9—C8^{i}	1.531 (2)
C3—C4	1.384 (3)	C10—H10A	0.9700
C3—C7	1.499 (3)	C10—H10B	0.9700
C4—C5	1.378 (3)		
C7—O1—C8	110.95 (15)	O1—C7—C3	107.23 (15)
C7—O2—C10	111.11 (15)	O2—C7—H7	110.1
C6—C1—C2	118.81 (19)	O1—C7—H7	110.1
C6—C1—H1	120.6	C3—C7—H7	110.1
C2—C1—H1	120.6	O1—C8—C9	111.43 (16)
C1—C2—C3	121.53 (19)	O1—C8—H8A	109.3
C1—C2—Cl1	117.74 (15)	C9—C8—H8A	109.3
C3—C2—Cl1	120.73 (16)	O1—C8—H8B	109.3
C4—C3—C2	117.28 (19)	C9—C8—H8B	109.3
C4—C3—C7	119.37 (17)	H8A—C8—H8B	108.0
C2—C3—C7	123.34 (17)	C10^{i}—C9—C10	110.8 (2)
C5—C4—C3	122.52 (19)	C10^{i}—C9—C8^{i}	107.54 (12)
C5—C4—H4	118.7	C10—C9—C8^{i}	110.94 (12)
C3—C4—H4	118.7	C10^{i}—C9—C8	110.94 (12)
C4—C5—C6	118.3 (2)	C10—C9—C8	107.54 (12)
C4—C5—H5	120.9	C8^{i}—C9—C8	109.1 (2)
C6—C5—H5	120.9	O2—C10—C9	110.67 (14)
C1—C6—C5	121.6 (2)	O2—C10—H10A	109.5
C1—C6—Cl2	119.24 (17)	C9—C10—H10A	109.5
C5—C6—Cl2	119.17 (18)	O2—C10—H10B	109.5
O2—C7—O1	110.06 (16)	C9—C10—H10B	109.5
O2—C7—C3	109.08 (16)	H10A—C10—H10B	108.1
C6—C1—C2—C3	−0.6 (3)	C8—O1—C7—O2	62.5 (2)
C6—C1—C2—Cl1	178.60 (17)	C8—O1—C7—C3	−179.01 (15)
C1—C2—C3—C4	0.7 (3)	C4—C3—C7—O2	47.8 (2)
Cl1—C2—C3—C4	−178.44 (16)	C2—C3—C7—O2	−133.17 (19)
C1—C2—C3—C7	−178.38 (19)	C4—C3—C7—O1	−71.4 (2)
Cl1—C2—C3—C7	2.5 (3)	C2—C3—C7—O1	107.7 (2)
C2—C3—C4—C5	−0.4 (3)	C7—O1—C8—C9	−57.8 (2)
C7—C3—C4—C5	178.70 (19)	O1—C8—C9—C10^{i}	−69.6 (2)

C3—C4—C5—C6	0.0 (4)	O1—C8—C9—C10	51.7 (2)
C2—C1—C6—C5	0.1 (3)	O1—C8—C9—C8^{i}	172.1 (2)
C2—C1—C6—Cl2	−178.77 (16)	C7—O2—C10—C9	59.2 (2)
C4—C5—C6—C1	0.2 (3)	C10^{i}—C9—C10—O2	69.36 (13)
C4—C5—C6—Cl2	179.05 (17)	C8^{i}—C9—C10—O2	−171.24 (15)
C10—O2—C7—O1	−63.4 (2)	C8—C9—C10—O2	−52.1 (2)
C10—O2—C7—C3	179.21 (15)		

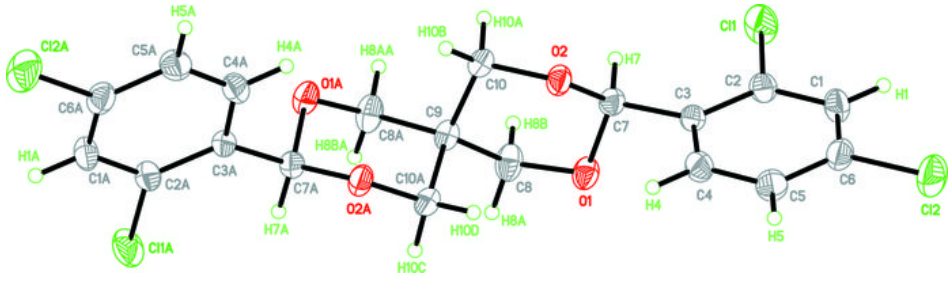
Symmetry codes: (i) −*x*+1, *y*, −*z*+1/2.

Hydrogen-bond geometry (Å, °)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
C5—H5···O2^{ii}	0.93	2.58	3.425 (3)	152
C7—H7···Cl1	0.98	2.60	3.113 (2)	113

Symmetry codes: (ii) *x*, −*y*+1, *z*+1/2.

Fig. 1


H5A
Cl2A
C5A
C4A
H4A
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H10A
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O1A
O2
H7
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C1
H1
C6A
C9
C8A
C3
H8B
C7
H8BA
H1A
C1A
C2A
C3A
C7A
C10A
C8
O1
C4
C5
C6
Cl2
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H10D
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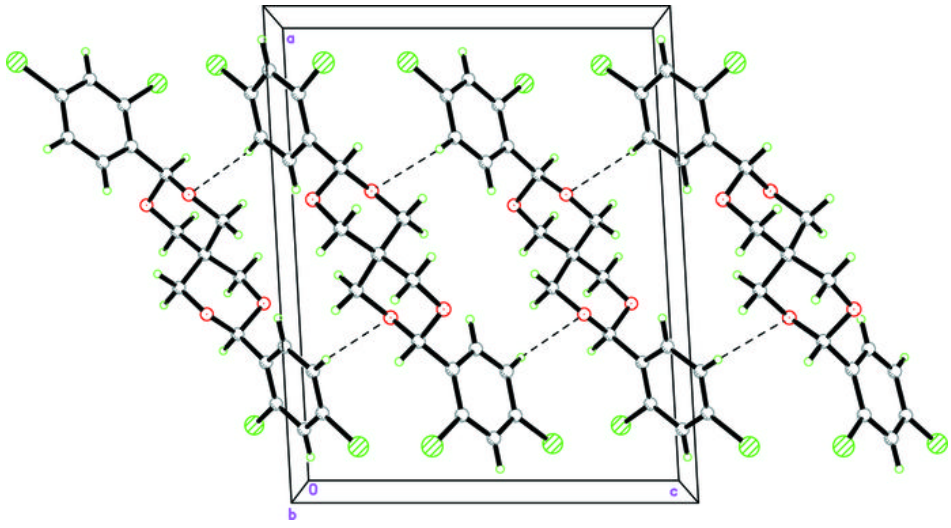
Cl1A
H10C

Fig. 2



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1,1′-(Ethane-1,2-diyl)bis(indoline-2,3-dione)

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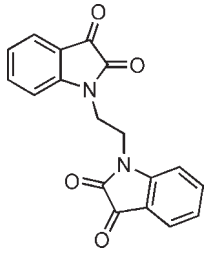
Received 6 February 2010; accepted 20 May 2010

Key indicators: single-crystal X-ray study; T = 296 K; mean σ(C–C) = 0.002 Å; R factor = 0.040; wR factor = 0.102; data-to-parameter ratio = 15.6.

The molecule of the title compound, $C_{18}H_{12}N_2O_4$, is situated on a crystallographic centre of symmetry. The molecule has a zigzag structure, with two parallel symmetry-related indoline-2,3-dione fragments linked by an ethylene group at each N atom. In the crystal, the molecules stack in columns along the b axis. There are two such columns in the structure. The molecules within each column are parallel; however, the molecules in the two columns differ in the respective orientation of the indoline-2,3-dione fragments. In one column, they are approximately parallel to (112), while in the other they are approximately parallel to ($\bar{1}$12). The interplanar angle between the indoline-2,3-dione fragments in the two columns is 80.83 (3)°. The molecules within each column are related by mutual displacement of their centres of symmetry, that is (0, ±1/2, ±1/2). The packing between the molecules is provided by weak interactions only, *viz*. C—H···O hydrogen bonds and π–π [centroid–centroid distance = 3.8745 (8) Å] and C═O···π interactions.

Related literature

For the biological and pharmacological activity of 1,2-bis-[(indolin-2,3-dion)-1-yl]ethane and its analogues, see: Breinholt *et al.* (1996); Norman (1996); Rajopadhye & Popp (1988). For details of the synthesis, see: Hyatt *et al.* (2007). For the melting point, see: Schmidt *et al.* (2008)·For a description of the Cambridge Structural Database, see: Allen (2002).



Experimental

Crystal data

$C_{18}H_{12}N_2O_4$
M_r = 320.30
Monoclinic, $P2_1/c$
a = 12.2572 (3) Å
b = 5.2314 (1) Å
c = 12.5122 (3) Å
β = 115.747 (1)°
V = 722.66 (3) Å^3
Z = 2
Mo $K\alpha$ radiation
μ = 0.11 mm^{-1}
T = 296 K
0.45 × 0.32 × 0.25 mm

Data collection

Bruker APEXII CCD area-detector diffractometer
Absorption correction: multi-scan (*SADABS*; Bruker, 2007)
T_{min} = 0.723, T_{max} = 0.893
13976 measured reflections
1714 independent reflections
1496 reflections with $I > 2\sigma(I)$
R_{int} = 0.028

Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.040
$wR(F^2)$ = 0.102
S = 1.05
1714 reflections
110 parameters
H-atom parameters constrained
$\Delta\rho_{max}$ = 0.19 e Å^{-3}
$\Delta\rho_{min}$ = −0.16 e Å^{-3}

Table 1
Hydrogen-bond geometry (Å, °).

D—H···A	D—H	H···A	D···A	D—H···A
C9—H9A···O1^{i}	0.97	2.47	3.262 (2)	139

Symmetry code: (i) $x, -y+\frac{1}{2}, z-\frac{1}{2}$.

Table 2
C═O···π interactions (Å, °).

*Cg*1 and *Cg*2 are the centroids of the N1,C1,C6–C8 pyrrole and C1—C6 benzene rings, respectively.

C═O···*Cg*	O···*Cg*	C···*Cg*	C═O···*Cg*
C8—O2···*Cg*1	3.8207 (12)	4.4046 (12)	111.34 (10)
C8—O2···*Cg*1	3.6269 (15)	4.6449 (17)	142.86 (10)
C8—O2···*Cg*2	3.5874 (14)	3.5278 (14)	77.47 (9)

Symmetry codes: (i) $x, 1+y, z$; (ii) $-x, \frac{1}{2}+y, \frac{3}{2}-z$; (iii) $x, 1+y, z$.

Data collection: *APEX2* (Bruker, 2007); cell refinement: *APEX2* and *SAINT* (Bruker, 2007); data reduction: *SAINT*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *SHELXTL* (Sheldrick, 2008); software used to prepare material for publication: *SHELXTL* and *PLATON* (Spek, 2009).

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Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: FB2183).

References

Allen, F. H. (2002). *Acta Cryst.* B**58**, 380–388.
Breinholt, J., Demuth, H., Heide, M., Jensen, G. W., Moller, I. L., Nielson, R. I., Olsen, C. E. & Rosendahl, C. N. (1996). *Acta Chem. Scand.* **50**, 443–445.
Bruker (2007). *APEX2*, *SADABS* and *SAINT*. Bruker AXS Inc., Madison, Wisconsin, USA.
Hyatt, J. L., Moak, T., Hatfield, M. J., Tsurkan, L., Edwards, C. C., Wierdl, M., Danks, M. K., Wadkins, R. M. & Potter, P. M. (2007). *J. Med. Chem.* **50**, 1876–1885.
Norman, T. R. (1996). *Med. Sci. Res.* **24**, 153–154.
Rajopadhye, M. & Popp, F. D. (1988). *J. Med. Chem.* **31**, 1001–1005.
Sheldrick, G. M. (2008). *Acta Cryst.* A**64**, 112–122.
Schmidt, M. S., Reverdito, A. M., Kremenchuzky, L., Perillo, I. A. & Blanco, M. M. (2008). *Molecules*, **13**, 831–840.
Spek, A. L. (2009). *Acta Cryst.* D**65**, 148–155.

supplementary materials

Acta Cryst. (2010). E**66**, o1569-o1570 [**doi:10.1107/S1600536810018957**]

1,1'-(Ethane-1,2-diyl)bis(indoline-2,3-dione)

Y. Wang, S.-L. Cao, C.-Q. Wan and J.-L. Yuan

Comment

Isatins present a wide range of important biological and pharmacological activities. Fungicide (Breinholt *et al.*, 1996), antianxiety (Norman, 1996; Breinholt *et al.*, 1996) and anticonvulsant ones (Rajopadhye & Popp, 1988) are among them. In particular, the title compound, 1,2-bis[(indolin-2,3-dion)-1-yl]ethane, and related 1,1-bis{4-[(2,3-dioxoindolin-1-yl)methyl]phenyl}methane and 1-(3,4-dichlorobenzyl)indoline-2,3-dione (Hyatt *et al.*, 2007) have been considered as potent and selective carboxylesterase inhibitors (Hyatt *et al.*, 2007). Herein, we report the structure of the title compound.

The centrosymmetric molecule takes a zigzag fashion, with two symmetric parallel indoline-2,3-dione fragments being linked by the ethylene group to the N atoms (Fig. 1). There are only weak intermolecular interactions in the structure: a π-electron—π-electron ring interaction between N1\C1\C6\C7\C8 (pyrrole) and C1\C2\C3\C4\C5\C6 (benzene) rings (symmetry code: x, y+1, z) with the distance between the respective centroids equal to 3.8745 (8) Å. A C-H···O bond is given in Tab. 1 while C═O···π-electron ring interactions are listed in Tab. 2.

The distance C7-C8 (1.5554 (19) Å) corresponds well to the pertinent distances previously observed in well determined structures with the indoline-2,3-dione fragment. The search in the Cambridge Structural Database (Allen, 2002; Cambridge Structural Database, version 5.31 and addenda up to 26 February 2010) yielded 12 hits with structures determined with R_{val}<0.05. The corresponding extremal distances from this search equalled to 1.531 and 1.578 Å for JOBDEG and NAQRAY, respectively.

Experimental

A mixture of indoline-2,3-dione (1.47 g, 10 mmol), 1,2-dibromoethane (5.64 g, 30 mmol) and K_2CO_3 (2 g, 14.5 mmol) in *N,N*-dimethylformamide (20 ml) was heated at 100-120 °C for 3 h. After cooling to room temperature, the reaction mixture was poured into 0°C water (100 ml). The resulting precipitate was separated by filtration, dried in air and then it was purified by column chromatography on a silica gel with dichloromethane/methanol = 95:5, v/v, as an eluent. The precipitate included the prevailing product 1-(2-bromoethyl)indoline-2,3-dione (R_f = 0.77, m.p. 131-132°C; yield 60.9%) as well as the the title product 1,2-bis[(indolin-2,3-dion)-1-yl]ethane (R_f = 0.64, m.p. 296-297°C; yield 13.1%). The prevailing product, 1-(2-bromoethyl)indoline-2,3-dione, has been determined by a mass spectrometric analysis while its melting point (131-132°C) corresponded to 131°C reported by Schmidt *et al.* (2008). The orange crystals of the title compound that measured 0.40 × 0.30 × 0.20 mm on average were obtained by slow evaporation from the solution of dichloromethane *N,N*-dimethylformamide 50:50 (v/v).

Refinement

All the H atoms were discernible in the difference electron density maps. Nevertheless, the hydrogen atoms were placed into the idealized positions and allowed to ride on the carrier atoms, with C—H = 0.93 and 0.97 Å for aryl and methylene hydrogens, respectively. $U_{iso}(H) = 1.2U_{eq}(C)_{aryl/methylene}$.

Figures

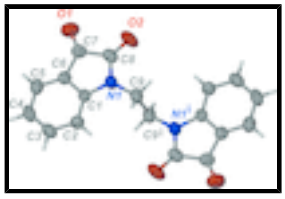


Fig. 1. The title molecule with the atomic numbering scheme. The displacement ellipsoids are shown at the 50% probability level. Symmetry code: (i): *-x*, *-y*, *-z*+1.

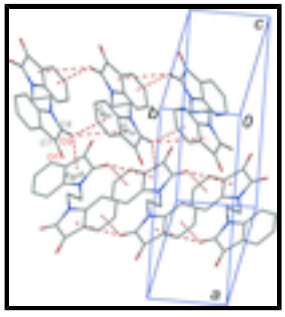


Fig. 2. The column motifs of the molecules of the title compound. The π-electron ring···π-electron ring interactions are shown as a red dashed lines. Cg1, Cg2 are the centroids of the N1-C1-C6-C7-C8 (pyrrole) and C1-C2-C3-C4-C5-C6 (benzene) rings, respectively. Symmetry codes: (i): *x*, 1+*y*, *z*; (ii): *-x*, 1/2+*y*, 3/2-*z*.

1,1'-(Ethane-1,2-diyl)bis(indoline-2,3-dione)

Crystal data

$C_{18}H_{12}N_2O_4$	$F(000) = 332$
$M_r = 320.30$	$D_x = 1.472$ Mg m^{-3}
Monoclinic, $P2_1/c$	Melting point = 569–570 K
Hall symbol: -P 2ybc	Mo $K\alpha$ radiation, λ = 0.71073 Å
$a = 12.2572$ (3) Å	Cell parameters from 243 reflections
$b = 5.2314$ (1) Å	θ = 1.8–27.2°
$c = 12.5122$ (3) Å	μ = 0.11 mm^{-1}
β = 115.747 (1)°	$T = 296$ K
$V = 722.66$ (3) Å^3	Block, orange
$Z = 2$	0.45 × 0.32 × 0.25 mm

Data collection

Bruker APEXII CCD area-detector diffractometer	1714 independent reflections
Radiation source: fine-focus sealed tube	1496 reflections with $I > 2\sigma(I)$
graphite	$R_{int} = 0.028$
ω scans	$\theta_{max} = 27.9°$, $\theta_{min} = 1.8°$

Absorption correction: multi-scan (*SADABS*; Bruker, 2007)
T_{min} = 0.723, T_{max} = 0.893
13976 measured reflections

h = −16→16
k = −6→6
l = −16→16

Refinement

Refinement on F^2
Least-squares matrix: full
$R[F^2 > 2\sigma(F^2)]$ = 0.040
$wR(F^2)$ = 0.102
S = 1.05
1714 reflections
110 parameters
0 restraints
24 constraints
Primary atom site location: structure-invariant direct methods
Secondary atom site location: difference Fourier map
Hydrogen site location: difference Fourier map
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.0422P)^2 + 0.1818P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max}$ = 0.19 e Å^{-3}
$\Delta\rho_{min}$ = −0.16 e Å^{-3}
Extinction correction: *SHELXL97* (Sheldrick, 2008), $Fc^* = kFc[1+0.001xFc^2\lambda^3/\sin(2\theta)]^{-1/4}$
Extinction coefficient: 0.060 (5)

Special details

Geometry. All esds (except the esd in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell esds are taken into account individually in the estimation of esds in distances, angles and torsion angles; correlations between esds in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell esds is used for estimating esds involving l.s. planes.

Refinement. Refinement of F^2 against ALL reflections. The weighted *R*-factor wR and goodness of fit *S* are based on F^2, conventional *R*-factors *R* are based on *F*, with *F* set to zero for negative F^2. The threshold expression of $F^2 > \sigma(F^2)$ is used only for calculating *R*-factors(gt) etc. and is not relevant to the choice of reflections for refinement. *R*-factors based on F^2 are statistically about twice as large as those based on *F*, and *R*- factors based on ALL data will be even larger.

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å^2)

	x	*y*	*z*	U_{iso}*/U_{eq}
C1	0.22945 (10)	−0.0885 (2)	0.68434 (10)	0.0390 (3)
C2	0.26127 (11)	−0.2721 (3)	0.62433 (12)	0.0474 (3)
H5	0.2193	−0.2905	0.5425	0.057*
C3	0.35869 (12)	−0.4288 (3)	0.69112 (14)	0.0539 (4)
H4	0.3818	−0.5550	0.6527	0.065*
C4	0.42235 (12)	−0.4035 (3)	0.81260 (14)	0.0566 (4)
H3	0.4875	−0.5110	0.8545	0.068*
C5	0.38964 (12)	−0.2189 (3)	0.87211 (12)	0.0526 (3)
H2	0.4318	−0.2010	0.9540	0.063*
C6	0.29262 (11)	−0.0609 (2)	0.80716 (11)	0.0429 (3)
C7	0.23681 (12)	0.1498 (3)	0.84203 (12)	0.0478 (3)
C8	0.13013 (12)	0.2405 (2)	0.72484 (12)	0.0488 (3)

C9	0.04837 (11)	0.1014 (3)	0.51355 (11)	0.0484 (3)
H9A	0.0900	0.0746	0.4639	0.058*
H9B	0.0108	0.2689	0.4955	0.058*
N1	0.13504 (9)	0.0917 (2)	0.63726 (9)	0.0448 (3)
O2	0.05930 (10)	0.4097 (2)	0.71384 (11)	0.0696 (4)
O1	0.26316 (11)	0.2447 (2)	0.93787 (9)	0.0691 (4)

Atomic displacement parameters (Å^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
C1	0.0363 (5)	0.0370 (6)	0.0449 (6)	−0.0013 (5)	0.0187 (5)	0.0035 (5)
C2	0.0446 (6)	0.0499 (8)	0.0498 (7)	−0.0001 (5)	0.0223 (5)	−0.0031 (6)
C3	0.0506 (7)	0.0464 (8)	0.0736 (9)	0.0055 (6)	0.0352 (7)	0.0004 (7)
C4	0.0436 (7)	0.0509 (8)	0.0731 (9)	0.0099 (6)	0.0232 (7)	0.0159 (7)
C5	0.0471 (7)	0.0550 (8)	0.0488 (7)	−0.0009 (6)	0.0145 (6)	0.0106 (6)
C6	0.0442 (6)	0.0403 (6)	0.0449 (6)	−0.0024 (5)	0.0200 (5)	0.0030 (5)
C7	0.0573 (7)	0.0441 (7)	0.0500 (7)	−0.0051 (6)	0.0306 (6)	−0.0006 (6)
C8	0.0546 (7)	0.0393 (7)	0.0623 (8)	0.0022 (6)	0.0344 (6)	0.0042 (6)
C9	0.0438 (6)	0.0483 (7)	0.0494 (7)	0.0030 (6)	0.0169 (6)	0.0149 (6)
N1	0.0425 (5)	0.0424 (6)	0.0477 (6)	0.0057 (4)	0.0179 (5)	0.0044 (5)
O2	0.0796 (7)	0.0511 (6)	0.0934 (9)	0.0219 (5)	0.0518 (7)	0.0109 (6)
O1	0.0868 (8)	0.0726 (8)	0.0564 (6)	−0.0037 (6)	0.0390 (6)	−0.0127 (5)

Geometric parameters (Å, °)

C1—C2	1.3757 (17)	C5—H2	0.9300
C1—C6	1.3958 (17)	C6—C7	1.4605 (18)
C1—N1	1.4081 (15)	C7—O1	1.2051 (16)
C2—C3	1.3892 (19)	C7—C8	1.5554 (19)
C2—H5	0.9300	C8—O2	1.2053 (16)
C3—C4	1.381 (2)	C8—N1	1.3665 (17)
C3—H4	0.9300	C9—N1	1.4486 (16)
C4—C5	1.381 (2)	C9—C9^{i}	1.515 (3)
C4—H3	0.9300	C9—H9A	0.9700
C5—C6	1.3847 (18)	C9—H9B	0.9700
C2—C1—C6	121.32 (11)	C1—C6—C7	107.40 (11)
C2—C1—N1	127.98 (11)	O1—C7—C6	130.57 (14)
C6—C1—N1	110.70 (11)	O1—C7—C8	124.38 (13)
C1—C2—C3	117.20 (12)	C6—C7—C8	105.05 (10)
C1—C2—H5	121.4	O2—C8—N1	127.39 (14)
C3—C2—H5	121.4	O2—C8—C7	126.91 (13)
C4—C3—C2	122.18 (13)	N1—C8—C7	105.69 (11)
C4—C3—H4	118.9	N1—C9—C9^{i}	110.73 (13)
C2—C3—H4	118.9	N1—C9—H9A	109.5
C3—C4—C5	120.21 (13)	C9^{i}—C9—H9A	109.5
C3—C4—H3	119.9	N1—C9—H9B	109.5
C5—C4—H3	119.9	C9^{i}—C9—H9B	109.5
C4—C5—C6	118.51 (13)	H9A—C9—H9B	108.1

C4—C5—H2	120.7	C8—N1—C1	111.12 (10)
C6—C5—H2	120.7	C8—N1—C9	124.73 (11)
C5—C6—C1	120.58 (12)	C1—N1—C9	123.94 (11)
C5—C6—C7	132.02 (12)		
C6—C1—C2—C3	0.09 (18)	O1—C7—C8—O2	−1.6 (2)
N1—C1—C2—C3	−179.95 (12)	C6—C7—C8—O2	179.12 (13)
C1—C2—C3—C4	−0.3 (2)	O1—C7—C8—N1	177.33 (13)
C2—C3—C4—C5	0.4 (2)	C6—C7—C8—N1	−1.95 (13)
C3—C4—C5—C6	−0.3 (2)	O2—C8—N1—C1	−179.26 (13)
C4—C5—C6—C1	0.07 (19)	C7—C8—N1—C1	1.81 (13)
C4—C5—C6—C7	−179.40 (13)	O2—C8—N1—C9	−4.4 (2)
C2—C1—C6—C5	0.03 (18)	C7—C8—N1—C9	176.68 (11)
N1—C1—C6—C5	−179.94 (11)	C2—C1—N1—C8	179.03 (12)
C2—C1—C6—C7	179.61 (11)	C6—C1—N1—C8	−1.01 (14)
N1—C1—C6—C7	−0.36 (13)	C2—C1—N1—C9	4.11 (19)
C5—C6—C7—O1	1.7 (2)	C6—C1—N1—C9	−175.93 (11)
C1—C6—C7—O1	−177.84 (14)	C9^{i}—C9—N1—C8	−95.50 (17)
C5—C6—C7—C8	−179.10 (13)	C9^{i}—C9—N1—C1	78.73 (17)
C1—C6—C7—C8	1.38 (13)		

Symmetry codes: (i) −*x*, −*y*, −*z*+1.

Hydrogen-bond geometry (Å, °)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
C9—H9A···O1^{ii}	0.97	2.47	3.262 (2)	139

Symmetry codes: (ii) *x*, −*y*+1/2, *z*−1/2.

Table 2

C═O···π interactions (Å, °)

Cg1 and Cg2 are the centroids of the N1,C1,C6–C8 pyrrole and C1—C6 benzene rings, respectively.

C═O···Cg	O···Cg	C···Cg	C═O···Cg
C8—O2···Cg1	3.8207 (12)	4.4046 (12)	111.34 (10)
C8—O2···Cg1	3.6269 (15)	4.6449 (17)	142.86 (10)
C8—O2···Cg2	3.5874 (14)	3.5278 (14)	77.47 (9)

Symmetry codes: (i) *x*, 1+*y*, *z*; (ii) -x, 1/2+*y*, 3/2-*z*; (iii) *x*, 1+*y*, *z*.

Fig. 1

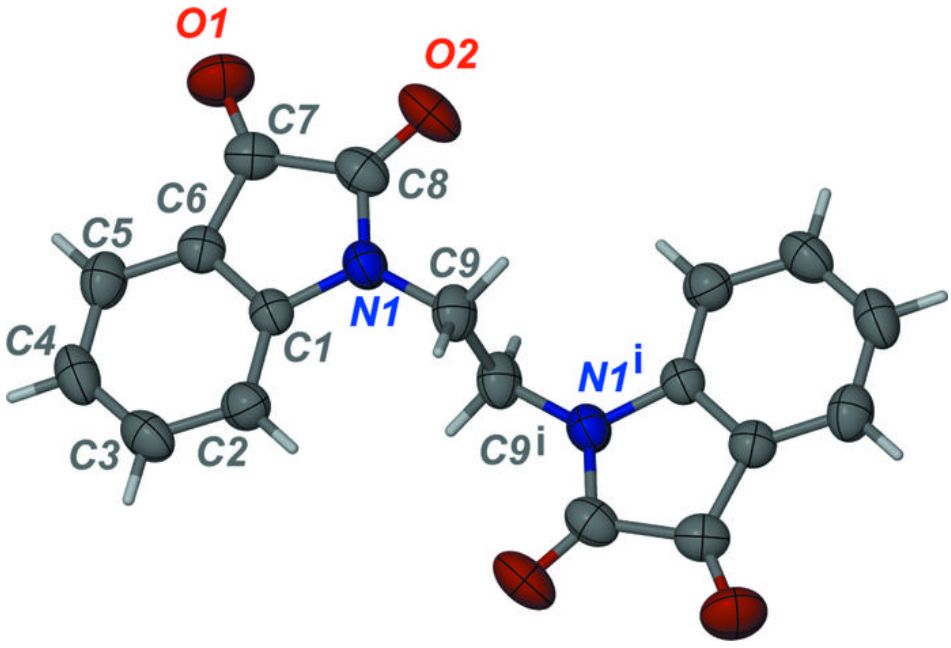
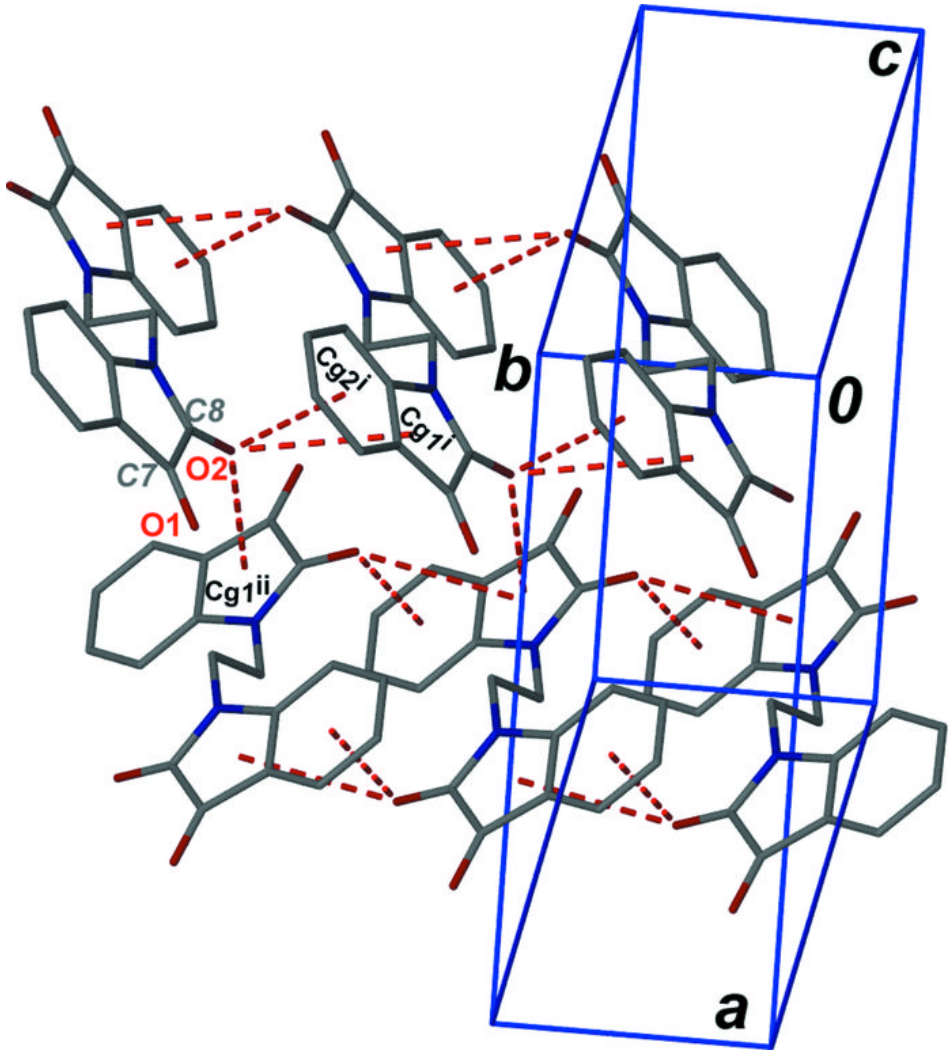


Fig. 2



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1-{6-Chloro-2-[(2-chloro-3-quinolyl)methoxy]-4-phenyl-3-quinolyl}ethan-1-one

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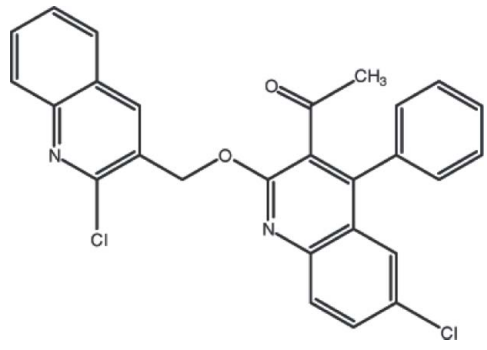
Key indicators: single-crystal X-ray study; T = 295 K; mean σ(C–C) = 0.003 Å; R factor = 0.040; wR factor = 0.109; data-to-parameter ratio = 16.4.

In the title compound, $C_{27}H_{18}Cl_2N_2O_2$, the 2-chloroquinoline and 6-chloroquinoline rings are almost planar, with maximum deviations from their mean planes of 0.072 (1) and 0.044 (1) Å, respectively, for the Cl atoms. The interplanar angle between these rings is 14.36 (5)°. The interplanar angle between the 6-chloroquinoline and phenyl rings is 66.00 (8)°. In the crystal, molecules are interlinked by weak C—H···O, C—H···π and π–π stacking [centroid–centroid distances = 3.7453 (10) and 3.7557 (9) Å] interactions.

Related literature

For a related crystal structure containing 2-quinolone, see: Khan *et al.* (2010). For the biological activity, such as antibacterial, anticancer, antiviral and cardiotonic activity of compounds containing 2-quinolone, see: Ukita & Mizuno (1960); Jayashree *et al.* (2010); Joseph *et al.* (2002); Xiao *et al.* (2001); Roopan & Khan (2009).



Experimental

Crystal data

$C_{27}H_{18}Cl_2N_2O_2$
M_r = 473.33
Triclinic, $P\overline{1}$
a = 9.2694 (3) Å
b = 10.8862 (4) Å
c = 13.0490 (5) Å
α = 100.615 (3)°
β = 103.570 (3)°
γ = 111.894 (4)°
V = 1132.51 (9) Å^3
Z = 2
Mo $K\alpha$ radiation
μ = 0.32 mm^{-1}
T = 295 K
0.25 × 0.21 × 0.14 mm

Data collection

Oxford Xcalibur Eos (Nova) CCD detector diffractometer
Absorption correction: multi-scan (*CrysAlis PRO RED*; Oxford Diffraction, 2009)
T_{min} = 0.925, T_{max} = 0.957
24246 measured reflections
4918 independent reflections
3250 reflections with $I > 2\sigma(I)$
R_{int} = 0.037

Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.040
$wR(F^2)$ = 0.109
S = 1.05
4918 reflections
300 parameters
H-atom parameters constrained
$\Delta\rho_{max}$ = 0.27 e Å^{-3}
$\Delta\rho_{min}$ = −0.35 e Å^{-3}

Table 1
Hydrogen-bond geometry (Å, °).

*Cg*1 is the centroid of the N1/C1–C3/C8/C9 ring.

D—H···A	D—H	H···A	D···A	D—H···A
C3—H3···O1	0.93	2.36	2.703 (2)	101
C6—H6···O2^{i}	0.93	2.52	3.296 (3)	142
C22—H22···*Cg*1^{ii}	0.93	2.95	3.683 (3)	137

Symmetry codes: (i) $-x+2, -y+1, -z+1$; (ii) $x-1, y-1, z$.

Data collection: *CrysAlis PRO CCD* (Oxford Diffraction, 2009); cell refinement: *CrysAlis PRO CCD*; data reduction: *CrysAlis PRO RED* (Oxford Diffraction, 2009); program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *ORTEP-3 for Windows* (Farrugia, 1997); software used to prepare material for publication: *WinGX* (Farrugia, 1999).

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Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: FB2195).

References

Farrugia, L. J. (1997). *J. Appl. Cryst.* **30**, 565.
Farrugia, L. J. (1999). *J. Appl. Cryst.* **32**, 837–838.
Jayashree, B. S., Thomas, S. & Nayak, Y. (2010). *Med. Chem. Res.* **19**, 193–209.
Joseph, B., Darro, F., Behard, A., Lesur, B., Collignon, F., Decaestecker, C., Frydman, A., Guillaumet, G. & Kiss, R. (2002). *J. Med. Chem.* **45**, 2543–2555.
Khan, F. N., Roopan, S. M., Hathwar, V. R. & Akkurt, M. (2010). *Acta Cryst.* E**66**, o972–o973.

Oxford Diffraction (2009). *CrysAlis PRO CCD* and *CrysAlis PRO RED*. Oxford Diffraction Ltd, Yarnton, England.
Roopan, S. M. & Khan, F. N. (2009). *ARKIVOC*, **xiii**, 161–169.
Sheldrick, G. M. (2008). *Acta Cryst.* A**64**, 112–122.
Ukita, C. & Mizuno, D. (1960). *Chem. Pharm. Bull.* **8**, 1016–1020.
Xiao, Z., Waters, N. C., Woodard, C. L., Li, Z. & Li, P. K. (2001). *Bioorg. Med. Chem. Lett.* **11**, 2875–2878.

supplementary materials

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1-{6-Chloro-2-[(2-chloro-3-quinolyl)methoxy]-4-phenyl-3-quinolyl}ethan-1-one

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Comment

Quinolones have emerged as one of the important classes among chemotherapeutic drugs for treatment of various bacterial infections. The quinolones, precisely the compounds with 2-quinolone moiety, show interesting biologic activities such as antibacterial, anticancer, antiviral and cardiotonic ones (Ukita & Mizuno, 1960; Jayashree *et al.*, 2010; Joseph *et al.*, 2002; Xiao *et al.*, 2001). In continuation of our previous work (Roopan *et al.*, 2009; Khan *et al.*, 2010), we report the structure of a new compound, 3-acetyl-2(2-chloroquinolin-3-yl)methoxy-6-chloro-4-phenylquinoline.

In the title molecule, as shown in Fig. 1, the 2-chloroquinoline (N1/C1–C9/Cl2) and 6-chloroquinoline (N2/C11—C19/Cl1) rings are almost planar, with maximal deviations from their mean planes of 0.072 (1) and of 0.044 (1) Å for Cl1 and Cl2 atoms, respectively. The interplanar angle between these rings is 14.36 (5)°. The interplanar angle between the quinoline (N2/C11—C19) and the phenyl (C20–C25) rings equals to 66.00 (8)° while the dihedral angle between the quinoline ring (N2/C11—C19) and the acetaldehyde (C26/C27/O2) group equals to 76.41 (9)°.

The molecules are linked by intermolecular C—H···O interactions (Tab. 1). The crystal structure is further stabilized by C—H···π-electron ring interactions (Tab. 1) and by π-electron···π-electron ring interactions between the pyridine ring (N2/C11– C19; its centroid is Cg1) with each of the benzene rings (C4–C9; its centroid is Cg2) and (C14–C19; its centroid is Cg3). The distances between these centroids of the respective rings are: Cg1···Cg2(1-*x*, 1-*y*, 1-*z*) = 3.7453 (10) Å and Cg1···Cg3 (1-*x*, 1-*y*, 2-*z*) = 3.7557 (9) Å.

Experimental

To a solution of 3-acetyl-6-chloro-2-hydroxy-4-phenylquinoline (297 mg, 1 mmol) in 5 ml of dimethylsulphoxide) were added solid 2-chloro-3-chloromethylquinoline (211 mg, 1 mmol) and powder Ag_2SO_4 (30 mg, 0.1 mmol). Then the mixture was refluxed at 383 K. The reaction was completed in 20 min, having been monitored by the thin layer chromatography using petroleum ether/ethyl acetate (95:5) as an eluant. The reaction mixture was then filtered to remove the catalyst, Ag_2SO_4. The filtrate liquid was added dropwise into 50 g of crushed ice. The solution was neutralized by 20 ml of 2N HCl. The precipitate was filtered, dried and re-crystallized from 10 ml of ethanol. The solution was kept for a day after which the resulting crystals were isolated and dried. Colourless block-shaped crystals measured about 0.20 mm in each direction.

Refinement

All the hydrogens were discernible in the difference electron density maps. However, they were constrained by the riding model approximation: C—$H_{methylene}$=0.97 Å; C—H_{methyl}=0.96 Å; C—H_{aryl}=0.93 Å; $U_{iso}(H_{methylene/aryl})=1.2U_{eq}(C_{methylene/aryl})$; $U_{iso}H_{(methyl)}=1.5U_{eq}(C_{methyl})$.

Figures

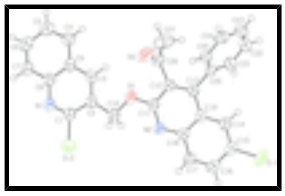


Fig. 1. A view of the title molecule, showing the atom-numbering scheme. The displacement ellipsoids are drawn at the 50% probability level.

1-{6-Chloro-2-[(2-chloro-3-quinolyl)methoxy]-4-phenyl-3-quinolyl}ethan-1-one

Crystal data

$C_{27}H_{18}Cl_2N_2O_2$	$Z = 2$
$M_r = 473.33$	$F(000) = 488$
Triclinic, $P\overline{1}$	$D_x = 1.388$ Mg m^{-3}
Hall symbol: -P 1	Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å
$a = 9.2694$ (3) Å	Cell parameters from 1523 reflections
$b = 10.8862$ (4) Å	$\theta = 1.9$–$21.4°$
$c = 13.0490$ (5) Å	$\mu = 0.32$ mm^{-1}
$\alpha = 100.615$ (3)°	$T = 295$ K
$\beta = 103.570$ (3)°	Block, colourless
$\gamma = 111.894$ (4)°	0.25 × 0.21 × 0.14 mm
$V = 1132.51$ (9) Å^3	

Data collection

Oxford Xcalibur Eos (Nova) CCD detector diffractometer	4918 independent reflections
Radiation source: Enhance (Mo) X-ray Source	3250 reflections with $I > 2\sigma(I)$
graphite	$R_{int} = 0.037$
ω scans	$\theta_{max} = 27.0°$, $\theta_{min} = 3.1°$
Absorption correction: multi-scan (*CrysAlis PRO* RED; Oxford Diffraction, 2009)	$h = -11 \rightarrow 11$
$T_{min} = 0.925$, $T_{max} = 0.957$	$k = -13 \rightarrow 13$
24246 measured reflections	$l = -16 \rightarrow 16$

Refinement

Refinement on F^2	Secondary atom site location: difference Fourier map
Least-squares matrix: full	Hydrogen site location: difference Fourier map
$R[F^2 > 2\sigma(F^2)] = 0.040$	H-atom parameters constrained
$wR(F^2) = 0.109$	$w = 1/[\sigma^2(F_o^2) + (0.0549P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
$S = 1.05$	$(\Delta/\sigma)_{max} = 0.001$
4918 reflections	$\Delta\rho_{max} = 0.27$ e Å^{-3}
300 parameters	$\Delta\rho_{min} = -0.35$ e Å^{-3}

0 restraints

71 constraints

Primary atom site location: structure-invariant direct methods

Extinction correction: *SHELXL97* (Sheldrick, 2008), $FC^*=KFC[1+0.001XFC^2\Lambda^3/SIN(2\Theta)]^{-1/4}$

Extinction coefficient: 0.0099 (17)

Special details

Geometry. Bond distances, angles etc. have been calculated using the rounded fractional coordinates. All su's are estimated from the variances of the (full) variance-covariance matrix. The cell esds are taken into account in the estimation of distances, angles and torsion angles

Refinement. Refinement on F^2 for ALL reflections except those flagged by the user for potential systematic errors. Weighted *R*-factors wR and all goodnesses of fit *S* are based on F^2, conventional *R*-factors *R* are based on *F*, with *F* set to zero for negative F^2. The observed criterion of $F^2 > \sigma(F^2)$ is used only for calculating -*R*-factor-obs etc. and is not relevant to the choice of reflections for refinement. *R*-factors based on F^2 are statistically about twice as large as those based on *F*, and *R*-factors based on ALL data will be even larger.

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å^2)

	x	*y*	*z*	U_{iso}*/U_{eq}
Cl1	−0.01220 (6)	0.20006 (6)	1.04669 (4)	0.0754 (2)
Cl2	0.74140 (7)	0.93000 (5)	0.71360 (5)	0.0840 (2)
O1	0.59905 (14)	0.49825 (11)	0.72135 (10)	0.0560 (4)
O2	0.74428 (17)	0.29669 (16)	0.77583 (12)	0.0814 (6)
N1	0.84627 (17)	0.84682 (14)	0.56079 (12)	0.0521 (5)
N2	0.43430 (15)	0.49906 (13)	0.82893 (10)	0.0430 (4)
C1	0.7687 (2)	0.80443 (17)	0.62730 (14)	0.0484 (6)
C2	0.70647 (18)	0.66777 (16)	0.63617 (13)	0.0432 (5)
C3	0.73284 (19)	0.57472 (16)	0.56702 (13)	0.0453 (5)
C4	0.8507 (2)	0.52185 (18)	0.42066 (13)	0.0520 (6)
C5	0.9361 (2)	0.56806 (19)	0.35310 (14)	0.0564 (6)
C6	0.9910 (2)	0.7072 (2)	0.35350 (15)	0.0575 (7)
C7	0.9603 (2)	0.79738 (19)	0.42130 (14)	0.0560 (6)
C8	0.87261 (19)	0.75263 (16)	0.49223 (13)	0.0445 (5)
C9	0.81637 (19)	0.61318 (16)	0.49267 (13)	0.0428 (5)
C10	0.6179 (2)	0.63335 (16)	0.71731 (14)	0.0486 (6)
C11	0.50542 (19)	0.43665 (16)	0.77951 (13)	0.0431 (5)
C12	0.49480 (18)	0.30284 (15)	0.77809 (12)	0.0416 (5)
C13	0.39256 (18)	0.22631 (15)	0.82609 (12)	0.0388 (5)
C14	0.19783 (18)	0.21883 (17)	0.93163 (13)	0.0459 (5)
C15	0.12456 (19)	0.28562 (18)	0.98332 (14)	0.0495 (6)
C16	0.1567 (2)	0.42295 (19)	0.98914 (14)	0.0530 (6)
C17	0.25945 (19)	0.49098 (17)	0.93803 (13)	0.0485 (6)
C18	0.33581 (18)	0.42562 (15)	0.88126 (12)	0.0390 (5)
C19	0.30637 (17)	0.28760 (15)	0.87940 (12)	0.0385 (5)
C20	0.37473 (19)	0.08368 (15)	0.82266 (13)	0.0416 (5)
C21	0.2255 (2)	−0.03105 (17)	0.76412 (15)	0.0575 (6)
C22	0.2112 (3)	−0.16304 (18)	0.75627 (17)	0.0661 (7)

C23	0.3442 (3)	−0.18296 (19)	0.80755 (16)	0.0639 (8)
C24	0.4922 (3)	−0.0704 (2)	0.86684 (15)	0.0587 (7)
C25	0.5077 (2)	0.06250 (17)	0.87376 (13)	0.0481 (6)
C26	0.6008 (2)	0.25390 (17)	0.72580 (14)	0.0506 (6)
C27	0.5199 (3)	0.1518 (2)	0.61324 (16)	0.0879 (9)
H3	0.69470	0.48340	0.56900	0.0540*
H4	0.81460	0.42950	0.41950	0.0620*
H5	0.95820	0.50720	0.30630	0.0680*
H6	1.04900	0.73760	0.30680	0.0690*
H7	0.99740	0.88930	0.42100	0.0670*
H10A	0.68150	0.70080	0.78980	0.0580*
H10B	0.51100	0.63400	0.69340	0.0580*
H14	0.17640	0.12800	0.93070	0.0550*
H16	0.10850	0.46760	1.02750	0.0640*
H17	0.27950	0.58200	0.94070	0.0580*
H21	0.13420	−0.01860	0.72980	0.0690*
H22	0.11080	−0.23920	0.71600	0.0790*
H23	0.33410	−0.27240	0.80220	0.0770*
H24	0.58240	−0.08340	0.90250	0.0700*
H25	0.60880	0.13830	0.91330	0.0580*
H27A	0.59860	0.12490	0.59180	0.1320*
H27B	0.47890	0.19330	0.56160	0.1320*
H27C	0.43000	0.07140	0.61380	0.1320*

Atomic displacement parameters (Å^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Cl1	0.0653 (3)	0.0939 (4)	0.0895 (4)	0.0336 (3)	0.0538 (3)	0.0437 (3)
Cl2	0.1264 (5)	0.0624 (3)	0.1087 (4)	0.0548 (3)	0.0834 (4)	0.0406 (3)
O1	0.0692 (8)	0.0515 (7)	0.0724 (8)	0.0302 (6)	0.0473 (7)	0.0353 (6)
O2	0.0569 (9)	0.1003 (11)	0.0888 (10)	0.0354 (8)	0.0381 (8)	0.0119 (8)
N1	0.0597 (9)	0.0463 (8)	0.0640 (9)	0.0239 (7)	0.0349 (8)	0.0269 (7)
N2	0.0441 (7)	0.0441 (7)	0.0467 (8)	0.0205 (6)	0.0192 (6)	0.0191 (6)
C1	0.0508 (10)	0.0473 (10)	0.0576 (10)	0.0235 (8)	0.0273 (9)	0.0226 (8)
C2	0.0393 (9)	0.0438 (9)	0.0487 (9)	0.0154 (7)	0.0179 (8)	0.0202 (8)
C3	0.0451 (9)	0.0393 (9)	0.0506 (10)	0.0130 (7)	0.0182 (8)	0.0200 (8)
C4	0.0587 (11)	0.0490 (10)	0.0487 (10)	0.0233 (9)	0.0189 (9)	0.0149 (8)
C5	0.0596 (11)	0.0669 (12)	0.0506 (10)	0.0324 (10)	0.0236 (9)	0.0183 (9)
C6	0.0560 (11)	0.0721 (13)	0.0551 (11)	0.0276 (10)	0.0299 (9)	0.0286 (10)
C7	0.0620 (11)	0.0554 (11)	0.0622 (11)	0.0240 (9)	0.0333 (10)	0.0306 (9)
C8	0.0427 (9)	0.0471 (9)	0.0485 (10)	0.0187 (8)	0.0200 (8)	0.0210 (8)
C9	0.0398 (9)	0.0454 (9)	0.0421 (9)	0.0160 (7)	0.0130 (7)	0.0173 (7)
C10	0.0521 (10)	0.0461 (9)	0.0573 (10)	0.0214 (8)	0.0278 (9)	0.0247 (8)
C11	0.0455 (9)	0.0442 (9)	0.0465 (9)	0.0181 (8)	0.0242 (8)	0.0205 (7)
C12	0.0438 (9)	0.0427 (9)	0.0432 (9)	0.0199 (7)	0.0200 (8)	0.0146 (7)
C13	0.0396 (8)	0.0387 (8)	0.0385 (8)	0.0159 (7)	0.0151 (7)	0.0122 (7)
C14	0.0429 (9)	0.0471 (9)	0.0511 (10)	0.0171 (8)	0.0210 (8)	0.0209 (8)
C15	0.0413 (9)	0.0642 (11)	0.0512 (10)	0.0229 (8)	0.0248 (8)	0.0240 (9)

C16	0.0511 (10)	0.0722 (12)	0.0533 (10)	0.0377 (9)	0.0273 (9)	0.0218 (9)
C17	0.0523 (10)	0.0517 (10)	0.0517 (10)	0.0297 (9)	0.0207 (9)	0.0189 (8)
C18	0.0372 (8)	0.0431 (9)	0.0385 (8)	0.0177 (7)	0.0139 (7)	0.0144 (7)
C19	0.0353 (8)	0.0423 (9)	0.0387 (8)	0.0158 (7)	0.0140 (7)	0.0139 (7)
C20	0.0476 (9)	0.0400 (9)	0.0433 (9)	0.0183 (8)	0.0248 (8)	0.0153 (7)
C21	0.0534 (11)	0.0467 (10)	0.0685 (12)	0.0185 (9)	0.0195 (9)	0.0165 (9)
C22	0.0716 (13)	0.0425 (10)	0.0789 (14)	0.0162 (10)	0.0322 (11)	0.0158 (10)
C23	0.0994 (16)	0.0485 (11)	0.0689 (12)	0.0401 (12)	0.0496 (12)	0.0287 (10)
C24	0.0805 (14)	0.0709 (13)	0.0551 (11)	0.0502 (12)	0.0367 (11)	0.0312 (10)
C25	0.0533 (10)	0.0525 (10)	0.0452 (9)	0.0253 (8)	0.0228 (8)	0.0164 (8)
C26	0.0604 (11)	0.0532 (10)	0.0562 (11)	0.0298 (9)	0.0356 (10)	0.0249 (9)
C27	0.1010 (17)	0.1078 (18)	0.0619 (13)	0.0604 (15)	0.0312 (13)	0.0040 (12)

Geometric parameters (Å, °)

Cl1—C15	1.747 (2)	C17—C18	1.408 (3)
Cl2—C1	1.7394 (19)	C18—C19	1.418 (2)
O1—C10	1.427 (2)	C20—C21	1.386 (3)
O1—C11	1.357 (2)	C20—C25	1.378 (3)
O2—C26	1.196 (3)	C21—C22	1.375 (3)
N1—C1	1.295 (2)	C22—C23	1.371 (4)
N1—C8	1.365 (2)	C23—C24	1.372 (3)
N2—C11	1.298 (2)	C24—C25	1.383 (3)
N2—C18	1.374 (2)	C26—C27	1.488 (3)
C1—C2	1.419 (2)	C3—H3	0.9300
C2—C3	1.361 (2)	C4—H4	0.9300
C2—C10	1.503 (2)	C5—H5	0.9300
C3—C9	1.406 (2)	C6—H6	0.9300
C4—C5	1.360 (3)	C7—H7	0.9300
C4—C9	1.416 (3)	C10—H10A	0.9700
C5—C6	1.405 (3)	C10—H10B	0.9700
C6—C7	1.354 (3)	C14—H14	0.9300
C7—C8	1.407 (3)	C16—H16	0.9300
C8—C9	1.411 (2)	C17—H17	0.9300
C11—C12	1.419 (2)	C21—H21	0.9300
C12—C13	1.366 (2)	C22—H22	0.9300
C12—C26	1.512 (3)	C23—H23	0.9300
C13—C19	1.433 (2)	C24—H24	0.9300
C13—C20	1.490 (2)	C25—H25	0.9300
C14—C15	1.359 (3)	C27—H27A	0.9600
C14—C19	1.409 (2)	C27—H27B	0.9600
C15—C16	1.395 (3)	C27—H27C	0.9600
C16—C17	1.362 (3)		
Cl1···C22^{i}	3.497 (3)	C26···C25	3.120 (2)
Cl2···C24^{ii}	3.391 (3)	C27···C20	3.400 (3)
Cl1···H10A^{iii}	2.9500	C1···H27B^{v}	2.9600
Cl2···H10A	2.7700	C1···H21^{vi}	3.0100
Cl2···H10B	3.0500	C4···H10B^{v}	2.9700

O1···O2	3.076 (2)	C4···H4^{iv}	3.1000
O2···O1	3.076 (2)	C12···H25	3.0200
O2···C25	3.360 (2)	C14···H21	3.1000
O2···C6^{iv}	3.296 (3)	C15···H10A^{iii}	3.0300
O1···H3	2.3600	C16···H16^{x}	3.0900
O2···H25	2.8900	C20···H14	2.6900
O2···H6^{iv}	2.5200	C20···H27C	2.8800
O2···H16^{iii}	2.8900	C21···H14	2.7600
N2···C5^{v}	3.410 (2)	C26···H25	2.9500
N1···H21^{vi}	2.7000	H3···O1	2.3600
N1···H7^{vii}	2.6300	H3···H4	2.5400
N1···H27B^{v}	2.8900	H4···H3	2.5400
N2···H10A	2.7500	H4···C4^{iv}	3.1000
N2···H10B	2.5600	H6···O2^{iv}	2.5200
C4···C4^{iv}	3.291 (3)	H7···N1^{vii}	2.6300
C5···C18^{v}	3.507 (2)	H10A···Cl2	2.7700
C5···N2^{v}	3.410 (2)	H10A···N2	2.7500
C6···C18^{v}	3.376 (2)	H10A···Cl1^{iii}	2.9500
C6···O2^{iv}	3.296 (3)	H10A···C15^{iii}	3.0300
C11···C17^{iii}	3.583 (2)	H10B···Cl2	3.0500
C11···C16^{iii}	3.399 (2)	H10B···N2	2.5600
C14···C21	3.292 (3)	H10B···C4^{v}	2.9700
C16···C11^{iii}	3.399 (2)	H14···C20	2.6900
C17···C11^{iii}	3.583 (2)	H14···C21	2.7600
C18···C5^{v}	3.507 (2)	H16···O2^{iii}	2.8900
C18···C6^{v}	3.376 (2)	H16···C16^{x}	3.0900
C18···C18^{iii}	3.397 (2)	H16···H16^{x}	2.3700
C20···C27	3.400 (3)	H21···N1^{xi}	2.7000
C21···C14	3.292 (3)	H21···C1^{xi}	3.0100
C22···Cl1^{i}	3.497 (3)	H21···C14	3.1000
C24···C24^{viii}	3.476 (3)	H25···O2	2.8900
C24···C25^{viii}	3.370 (3)	H25···C12	3.0200
C24···Cl2^{ix}	3.391 (3)	H25···C26	2.9500
C25···O2	3.360 (2)	H27B···N1^{v}	2.8900
C25···C24^{viii}	3.370 (3)	H27B···C1^{v}	2.9600
C25···C26	3.120 (2)	H27C···C20	2.8800
C10—O1—C11	118.10 (14)	C20—C21—C22	120.62 (19)
C1—N1—C8	117.82 (15)	C21—C22—C23	120.4 (2)
C11—N2—C18	116.19 (14)	C22—C23—C24	119.7 (2)
Cl2—C1—N1	115.52 (14)	C23—C24—C25	120.1 (2)
Cl2—C1—C2	118.16 (14)	C20—C25—C24	120.63 (18)
N1—C1—C2	126.32 (17)	O2—C26—C12	119.55 (16)

C1—C2—C3	115.29 (16)	O2—C26—C27	122.6 (2)
C1—C2—C10	120.45 (15)	C12—C26—C27	117.83 (18)
C3—C2—C10	124.27 (15)	C2—C3—H3	119.00
C2—C3—C9	121.62 (16)	C9—C3—H3	119.00
C5—C4—C9	120.58 (17)	C5—C4—H4	120.00
C4—C5—C6	120.40 (18)	C9—C4—H4	120.00
C5—C6—C7	120.58 (18)	C4—C5—H5	120.00
C6—C7—C8	120.27 (18)	C6—C5—H5	120.00
N1—C8—C7	118.72 (16)	C5—C6—H6	120.00
N1—C8—C9	121.43 (16)	C7—C6—H6	120.00
C7—C8—C9	119.84 (16)	C6—C7—H7	120.00
C3—C9—C4	124.14 (16)	C8—C7—H7	120.00
C3—C9—C8	117.52 (16)	O1—C10—H10A	110.00
C4—C9—C8	118.32 (16)	O1—C10—H10B	110.00
O1—C10—C2	106.79 (14)	C2—C10—H10A	110.00
O1—C11—N2	120.52 (15)	C2—C10—H10B	110.00
O1—C11—C12	113.48 (15)	H10A—C10—H10B	109.00
N2—C11—C12	126.00 (16)	C15—C14—H14	120.00
C11—C12—C13	118.51 (16)	C19—C14—H14	120.00
C11—C12—C26	118.07 (15)	C15—C16—H16	120.00
C13—C12—C26	123.40 (15)	C17—C16—H16	120.00
C12—C13—C19	118.23 (15)	C16—C17—H17	119.00
C12—C13—C20	119.71 (16)	C18—C17—H17	120.00
C19—C13—C20	122.06 (15)	C20—C21—H21	120.00
C15—C14—C19	119.79 (16)	C22—C21—H21	120.00
Cl1—C15—C14	119.98 (15)	C21—C22—H22	120.00
Cl1—C15—C16	118.08 (15)	C23—C22—H22	120.00
C14—C15—C16	121.94 (18)	C22—C23—H23	120.00
C15—C16—C17	119.32 (18)	C24—C23—H23	120.00
C16—C17—C18	121.02 (17)	C23—C24—H24	120.00
N2—C18—C17	117.92 (15)	C25—C24—H24	120.00
N2—C18—C19	123.13 (15)	C20—C25—H25	120.00
C17—C18—C19	118.95 (15)	C24—C25—H25	120.00
C13—C19—C14	123.33 (15)	C26—C27—H27A	109.00
C13—C19—C18	117.73 (15)	C26—C27—H27B	109.00
C14—C19—C18	118.92 (15)	C26—C27—H27C	109.00
C13—C20—C21	120.60 (16)	H27A—C27—H27B	110.00
C13—C20—C25	120.80 (15)	H27A—C27—H27C	109.00
C21—C20—C25	118.55 (16)	H27B—C27—H27C	109.00
C10—O1—C11—C12	179.97 (14)	C11—C12—C13—C20	178.02 (14)
C10—O1—C11—N2	0.6 (2)	C26—C12—C13—C19	175.94 (15)
C11—O1—C10—C2	−172.51 (14)	C26—C12—C13—C20	−3.5 (2)
C1—N1—C8—C7	−178.41 (17)	C11—C12—C26—O2	77.7 (2)
C1—N1—C8—C9	0.5 (3)	C11—C12—C26—C27	−103.07 (19)
C8—N1—C1—C2	−0.3 (3)	C13—C12—C26—O2	−100.8 (2)
C8—N1—C1—Cl2	179.24 (13)	C13—C12—C26—C27	78.5 (2)
C18—N2—C11—O1	177.01 (14)	C12—C13—C19—C14	180.00 (15)
C18—N2—C11—C12	−2.3 (2)	C12—C13—C19—C18	−1.5 (2)
C11—N2—C18—C17	178.56 (15)	C20—C13—C19—C14	−0.5 (2)

C11—N2—C18—C19	−2.3 (2)	C20—C13—C19—C18	177.98 (14)
N1—C1—C2—C3	0.0 (3)	C12—C13—C20—C21	−114.4 (2)
Cl2—C1—C2—C3	−179.53 (14)	C12—C13—C20—C25	63.0 (2)
Cl2—C1—C2—C10	0.7 (2)	C19—C13—C20—C21	66.2 (2)
N1—C1—C2—C10	−179.77 (18)	C19—C13—C20—C25	−116.50 (19)
C1—C2—C3—C9	0.1 (3)	C19—C14—C15—Cl1	179.18 (13)
C10—C2—C3—C9	179.87 (17)	C19—C14—C15—C16	−1.8 (3)
C3—C2—C10—O1	11.0 (2)	C15—C14—C19—C13	178.00 (16)
C1—C2—C10—O1	−169.28 (15)	C15—C14—C19—C18	−0.5 (2)
C2—C3—C9—C4	178.49 (17)	Cl1—C15—C16—C17	−178.30 (14)
C2—C3—C9—C8	0.1 (3)	C14—C15—C16—C17	2.6 (3)
C9—C4—C5—C6	−0.3 (3)	C15—C16—C17—C18	−1.2 (3)
C5—C4—C9—C3	−178.26 (18)	C16—C17—C18—N2	178.19 (16)
C5—C4—C9—C8	0.1 (3)	C16—C17—C18—C19	−1.0 (2)
C4—C5—C6—C7	0.2 (3)	N2—C18—C19—C13	4.1 (2)
C5—C6—C7—C8	−0.1 (3)	N2—C18—C19—C14	−177.32 (15)
C6—C7—C8—C9	0.0 (3)	C17—C18—C19—C13	−176.73 (15)
C6—C7—C8—N1	178.91 (17)	C17—C18—C19—C14	1.9 (2)
N1—C8—C9—C3	−0.4 (3)	C13—C20—C21—C22	176.68 (18)
N1—C8—C9—C4	−178.90 (16)	C25—C20—C21—C22	−0.7 (3)
C7—C8—C9—C3	178.51 (17)	C13—C20—C25—C24	−177.52 (17)
C7—C8—C9—C4	0.0 (3)	C21—C20—C25—C24	−0.1 (3)
O1—C11—C12—C13	−174.57 (14)	C20—C21—C22—C23	0.8 (3)
O1—C11—C12—C26	6.9 (2)	C21—C22—C23—C24	−0.1 (3)
N2—C11—C12—C13	4.7 (3)	C22—C23—C24—C25	−0.8 (3)
N2—C11—C12—C26	−173.79 (16)	C23—C24—C25—C20	0.9 (3)
C11—C12—C13—C19	−2.5 (2)		

Symmetry codes: (i) −*x*, −*y*, −*z*+2; (ii) *x*, *y*+1, *z*; (iii) −*x*+1, −*y*+1, −*z*+2; (iv) −*x*+2, −*y*+1, −*z*+1; (v) −*x*+1, −*y*+1, −*z*+1; (vi) *x*+1, *y*+1, *z*; (vii) −*x*+2, −*y*+2, −*z*+1; (viii) −*x*+1, −*y*, −*z*+2; (ix) *x*, *y*−1, *z*; (x) −*x*, −*y*+1, −*z*+2; (xi) *x*−1, *y*−1, *z*.

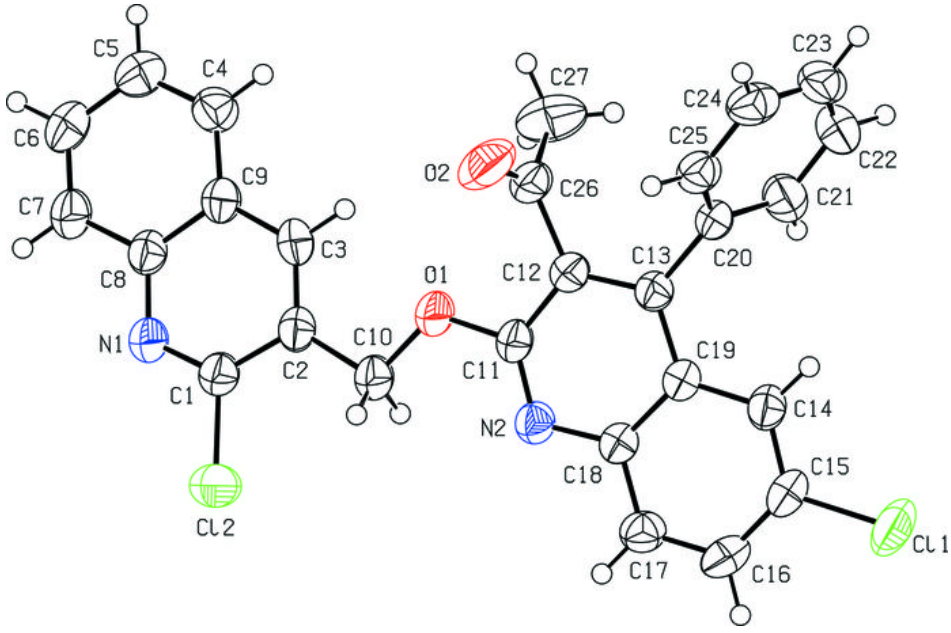
Hydrogen-bond geometry (Å, °)

Cg1 is the centroid of the N1/C1–C3/C8/C9 ring.

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
C3—H3···O1	0.93	2.36	2.703 (2)	101
C6—H6···O2^{iv}	0.93	2.52	3.296 (3)	142
C22—H22···Cg1^{xi}	0.93	2.95	3.683 (3)	137

Symmetry codes: (iv) −*x*+2, −*y*+1, −*z*+1; (xi) *x*−1, *y*−1, *z*.

Fig. 1


C5
C4
C6
C9
C7
C3
C8
O1
C12
C13
C20
N1
C10
C2
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C19
C1
C14
N2
C18
C15
Cl2
Cl1
C17
C16
C27
C23
C24
C25
C22
O2
C26
C21

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(*Z*)-2-Amino-5-[2,4-dimethoxy-6-(4-methoxystyryl)benzylidene]-1,3-thiazol-4(5*H*)-one methanol solvate

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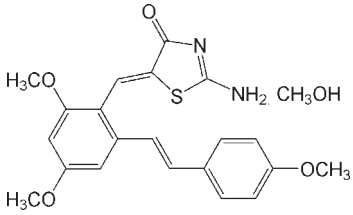
Key indicators: single-crystal X-ray study; T = 90 K; mean σ(C–C) = 0.003 Å; R factor = 0.043; wR factor = 0.112; data-to-parameter ratio = 14.2.

In the crystal structure of the title compound, $C_{21}H_{20}N_2O_4S\cdot CH_3OH$, molecules are linked into chains by a series of intermolecular N—H···O, N—H···N and O—H···O hydrogen bonds. The molecular structure shows a double bond with Z geometry, connecting the thiazolone and resveratrol units. The dihedral angle between the thiazolone ring and the nearest dimethoxybenzene ring is 53.02 (7)°.

Related literature

For related structure–activitystudies, see; Aggarwal *et al.* (2004); Pettit *et al.* (1995); Cushman *et al.* (1991).



Experimental

Crystal data

$C_{21}H_{20}N_2O_4S\cdot CH_4O$ M_r = 428.49
Monoclinic, $P2_1/c$
a = 10.6243 (2) Å
b = 22.2530 (5) Å
c = 9.0562 (2) Å
β = 93.028 (1)°
V = 2138.10 (8) Å^3
Z = 4
Cu $K\alpha$ radiation
μ = 1.65 mm^{-1}
T = 90 K
0.15 × 0.08 × 0.02 mm

Data collection

Bruker X8 Proteum diffractometer
Absorption correction: multi-scan (*SADABS*; Bruker, 2006)
T_{min} = 0.777, T_{max} = 0.968
31098 measured reflections
3911 independent reflections
3631 reflections with $I > 2\sigma(I)$
R_{int} = 0.044

Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.043
$wR(F^2)$ = 0.112
S = 1.13
3911 reflections
276 parameters
H-atom parameters constrained
$\Delta\rho_{max}$ = 0.51 e Å^{-3}
$\Delta\rho_{min}$ = −0.30 e Å^{-3}

Table 1
Hydrogen-bond geometry (Å, °).

D—H···A	D—H	H···A	D···A	D—H···A
N2—H2A···O4^{i}	0.88	2.07	2.926 (2)	163
N2—H2A···N1^{i}	0.88	2.64	3.175 (2)	120
N2—H2B···O1S^{ii}	0.88	2.05	2.872 (2)	154
O1S—H1S···O4	0.84	1.88	2.716 (2)	172

Symmetry codes: (i) $x, -y+\frac{3}{2}, z+\frac{1}{2}$; (ii) $x, y, z+1$.

Data collection: *APEX2* (Bruker, 2006); cell refinement: *SAINT* (Bruker, 2006); data reduction: *SAINT*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *XP* in *SHELXTL* (Sheldrick, 2008); software used to prepare material for publication: *SHELXL97* and local procedures.

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Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: FJ2286).

References

Aggarwal, B. B., Bhardwaj, A., Aggarwal, R. S., Seeram, N. P., Shishodia, S. & Takada, Y. (2004). *Anticancer Res.* **24**, 2783–2840.
Bruker (2006). *APEX2*, *SAINT* and *SADABS*. Bruker AXS Inc., Madison, Wisconsin, USA.
Cushman, M., Nagarathnam, D., Gopal, D., Chakraborti, A. K., Lin, C. M. & Hamel, E. (1991). *J. Med. Chem.* **34**, 2579–2588.
Pettit, G. R., Singh, S. B., Boyd, M. R., Hamel, E., Pettit, R. K., Schmidt, J. M. & Hogan, F. (1995). *J. Med. Chem.* **38**, 1666–1672.
Sheldrick, G. M. (2008). *Acta Cryst.* A**64**, 112–122.

supplementary materials

Acta Cryst. (2010). E**66**, o1792 [**doi:10.1107/S1600536810018520**]

(*Z*)-2-Amino-5-[2,4-dimethoxy-6-(4-methoxystyryl)benzylidene]-1,3-thiazol-4(5*H*)-one methanol solvate

N. R. Madadi, T. R. Y. Reddy, N. R. Penthala, S. Parkin and P. A. Crooks

Comment

Many natural products possessing a trimethoxybenzene ring, e.g., colchicines, and podophyllotoxins, are potent cytotoxic agents and exert their antitumor properties by their antitubulin activity. In view of the activity of such trimethoxybenzenes, similar structurally related stilbene moieties have been studied. The trihydroxy compound, resveratrol, a naturally occurring phytoalexin (trans-3, 4, 5-trihydroxystilbene) present in grapes, berries, peanuts,and red wine [Aggarwal *et al.*,2004, Pettit *et al.*, 1995) is reported to be a potential cancer chemotherapeutic agent based on its striking inhibitory effects on cellular events associated with cancer initiation, promotion, and progression. (Cushman *et al.*, 1991). These observations encouraged us to design and synthesise a series of novel trimethoxy resveratrol analogs that were expected to function as potent cytotoxic agents against lung and breast cancer cells. The structural characterization of the title compound by x-ray analysis was performed to determine the geometry (*E* vs *Z*) of the double bond connecting the thiozolone ring and the resveratrol moiety, which cannot be easily determined by NMR spectroscopic analysis, and to obtain detailed information on the structural conformation of the molecule, that may be useful in structure-activity relationship (SAR) analysis. The title compound was synthesized in two steps. In step one, the formylation of (*E*)-1, 3-dimethoxy-5- (4-methoxystyryl)benzene with a slight excess of phosphorous oxychloride in dimethylformamide at 0 °C resulted the formation of trans-2-formyl-3, 4', 5-trimethoxystilbene. In step two, the reaction of trans-2-formyl-3, 4', 5-trimethoxystilbene with the active methelene compound, 2-aminothiazol-4(*5H*)-one in presence of ammonium acetate in acetic acid under microwave irradiation conditions yielded the title compound, (*Z*)-2-amino-5-[2,4-dimethoxy-6- (4-methoxystyryl)benzylidene]thiazol-4(*5H*)-one in 90% yield. The x-ray analysis studies revealed that the double bond connecting the thiazolone and resveratrol moieties has the *Z* geometry. The dihedral angle between the plane of the thiazolone ring and the plane of the nearest phenyl ring is 53.02 (7)°. The crystal packing is stabilized by a series of N—H···O, N—H···N and O—H···O intermolecular hydrogen bonds.

Experimental

A mixture of trans-2-formyl-3,4',5-trimethoxystilbene (50 mg, 1 mmol), 2-aminothiazol-4(5*H*)-one (20.44 mg, 1.1 mmol), ammonium acetate (13.56 mg, 1.1 mmol) and acetic acid (0.25 ml) was irradiated in a domestic microwave oven for 60 sec with intermittent cooling to room temperature every 20 sec. The reaction mixture was allowed to cool to room temperature, and treated with saturated aqueous sodium bicarbonate solution. The precipitate thus obtained was collected by filtration, washed with cold water and dried, to afford the crude product. Crystallization from methanol gave a white crystalline product of (*Z*)-2-amino-5-[2,4-dimethoxy-6-(4-methoxystyryl) benzylidene]thiazol-4(5*H*)-one methanolate, which was suitable for x-ray analysis. ^{1}H NMR (DMSO-d_6): δ 3.77 (*s*, 3H, -OCH_3), 3.82 (*s*, 3H, -OCH_3), 3.86 (*s*, 3H, -OCH_3), 6.54-6.55 (*d*, *J*=2 Hz, 1H), 6.90-6.91 (*m*, 1H), 6.93-6.95 (*d*, *J*=2 Hz, 3H), 7.20-7.23 (*d*, *J*=16 Hz, 1H), 7.47-7.49 (*d*, *J*=9 Hz, 2H), 7.61 (*s*, 1H), 8.83 (*s*, 1H), 9.12 (*s*, 1H) ppm. ^{13}C NMR (DMSO-d_6): δ 55.6, 55.9, 56.3, 98.1, 102.8, 114.9, 115.9, 124.2,125.7, 128.6, 130.2, 131.6, 134.6, 138.4, 150.5, 158.9, 159.9, 161.6, 176.6, 180.3, 181.3. M. P: 172-175 °C

Refinement

H atoms were found in difference Fourier maps and subsequently placed in idealized positions with constrained distances of 0.98 Å (RCH_3), 0.95 Å ($C_{Ar}H$), and with $U_{iso}(H)$ values set to either $1.2U_{eq}$ or $1.5U_{eq}$ (RCH_3, OH) of the attached atom.

Figures

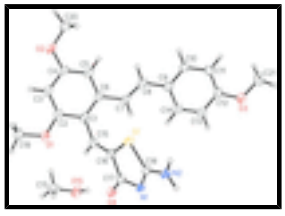


Fig. 1. A view of the molecule with the atom numbering scheme. Displacement ellipsoids are drawn at the 50% probability level.

(*Z*)-2-Amino-5-[2,4-dimethoxy-6-(4-methoxystyryl)benzylidene]-1,3- thiazol-4(5*H*)-one methanol solvate

Crystal data

$C_{21}H_{20}N_2O_4S·CH_4O$	$F(000) = 904$
$M_r = 428.49$	$D_x = 1.331$ Mg m^{-3}
Monoclinic, $P2_1/c$	Cu $K\alpha$ radiation, $\lambda = 1.54178$ Å
Hall symbol: -P 2ybc	Cell parameters from 9054 reflections
$a = 10.6243$ (2) Å	$\theta = 4.0$–$68.4°$
$b = 22.2530$ (5) Å	$\mu = 1.65$ mm^{-1}
$c = 9.0562$ (2) Å	$T = 90$ K
$\beta = 93.028$ (1)°	Lath, yellow
$V = 2138.10$ (8) Å^3	0.15 × 0.08 × 0.02 mm
$Z = 4$	

Data collection

Bruker X8 Proteum diffractometer	3911 independent reflections
Radiation source: fine-focus rotating anode	3631 reflections with $I > 2\sigma(I)$
graded multilayer optics	$R_{int} = 0.044$
Detector resolution: 5.6 pixels mm^{-1}	$\theta_{max} = 68.4°$, $\theta_{min} = 4.0°$
φ and ω scans	$h = -12 \rightarrow 12$
Absorption correction: multi-scan (*SADABS*; Bruker, 2006)	$k = -26 \rightarrow 26$
$T_{min} = 0.777$, $T_{max} = 0.968$	$l = -10 \rightarrow 10$
31098 measured reflections	

Refinement

Refinement on F^2	Primary atom site location: structure-invariant direct methods

Least-squares matrix: full	Secondary atom site location: difference Fourier map
$R[F^2 > 2\sigma(F^2)] = 0.043$	Hydrogen site location: inferred from neighbouring sites
$wR(F^2) = 0.112$	H-atom parameters constrained
$S = 1.13$	$w = 1/[\sigma^2(F_o^2) + (0.0357P)^2 + 2.3067P]$ where $P = (F_o^2 + 2F_c^2)/3$
3911 reflections	$(\Delta/\sigma)_{max} < 0.001$
276 parameters	$\Delta\rho_{max} = 0.51$ e Å^{-3}
0 restraints	$\Delta\rho_{min} = -0.30$ e Å^{-3}

Special details

Geometry. All esds (except the esd in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell esds are taken into account individually in the estimation of esds in distances, angles and torsion angles; correlations between esds in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell esds is used for estimating esds involving l.s. planes.

Refinement. Refinement of F^2 against ALL reflections. The weighted *R*-factor wR and goodness of fit *S* are based on F^2, conventional *R*-factors *R* are based on *F*, with *F* set to zero for negative F^2. The threshold expression of $F^2 > 2\sigma(F^2)$ is used only for calculating *R*-factors(gt) etc. and is not relevant to the choice of reflections for refinement. *R*-factors based on F^2 are statistically about twice as large as those based on *F*, and *R*- factors based on ALL data will be even larger.

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å^2)

	x	*y*	*z*	U_{iso}*/U_{eq}
S1	0.73380 (5)	0.59495 (2)	0.83763 (5)	0.02575 (15)
O1	0.84106 (14)	0.45171 (6)	0.46089 (17)	0.0294 (3)
N1	0.79198 (16)	0.69625 (7)	0.70367 (18)	0.0233 (4)
C1	0.67303 (19)	0.48654 (9)	0.5941 (2)	0.0230 (4)
O2	0.56944 (16)	0.31027 (7)	0.6733 (2)	0.0401 (4)
N2	0.78786 (18)	0.70133 (8)	0.95934 (19)	0.0288 (4)
H2A	0.8067	0.7398	0.9591	0.035*
H2B	0.7766	0.6828	1.0435	0.035*
C2	0.73882 (19)	0.43671 (9)	0.5382 (2)	0.0247 (4)
O3	0.15908 (16)	0.72923 (7)	1.04700 (19)	0.0379 (4)
C3	0.7014 (2)	0.37874 (9)	0.5646 (2)	0.0287 (5)
H3	0.7459	0.3457	0.5260	0.034*
O4	0.79309 (15)	0.66720 (6)	0.46217 (15)	0.0276 (3)
C4	0.5968 (2)	0.36913 (9)	0.6495 (2)	0.0285 (5)
C5	0.5283 (2)	0.41643 (9)	0.7024 (2)	0.0254 (4)
H5	0.4560	0.4090	0.7571	0.031*
C6	0.56614 (19)	0.47574 (9)	0.6748 (2)	0.0227 (4)
C7	0.49002 (19)	0.52638 (9)	0.7237 (2)	0.0230 (4)
H7	0.4958	0.5629	0.6702	0.028*
C8	0.41358 (19)	0.52599 (9)	0.8360 (2)	0.0252 (4)
H8	0.4032	0.4890	0.8861	0.030*
C9	0.34427 (19)	0.57835 (9)	0.8881 (2)	0.0249 (4)
C10	0.2585 (2)	0.57198 (10)	0.9977 (2)	0.0280 (5)

H10	0.2434	0.5330	1.0359	0.034*
C11	0.1938 (2)	0.62079 (10)	1.0535 (2)	0.0296 (5)
H11	0.1356	0.6150	1.1283	0.036*
C12	0.2153 (2)	0.67762 (10)	0.9992 (2)	0.0296 (5)
C13	0.2998 (2)	0.68532 (10)	0.8890 (3)	0.0363 (5)
H13	0.3138	0.7243	0.8502	0.044*
C14	0.3634 (2)	0.63662 (10)	0.8357 (3)	0.0325 (5)
H14	0.4219	0.6428	0.7614	0.039*
C15	0.71662 (18)	0.54678 (9)	0.5548 (2)	0.0223 (4)
H15	0.7306	0.5531	0.4533	0.027*
C16	0.73910 (19)	0.59395 (9)	0.6445 (2)	0.0224 (4)
C17	0.77662 (18)	0.65520 (9)	0.5932 (2)	0.0218 (4)
C18	0.77655 (19)	0.67159 (9)	0.8345 (2)	0.0227 (4)
C19	0.9131 (2)	0.40406 (10)	0.4010 (3)	0.0352 (5)
H19A	0.9469	0.3783	0.4815	0.053*
H19B	0.9829	0.4211	0.3480	0.053*
H19C	0.8590	0.3802	0.3326	0.053*
C20	0.4740 (2)	0.29656 (11)	0.7742 (3)	0.0427 (6)
H20A	0.4925	0.3177	0.8678	0.064*
H20B	0.4726	0.2531	0.7921	0.064*
H20C	0.3917	0.3095	0.7316	0.064*
C21	0.0789 (2)	0.72365 (12)	1.1677 (3)	0.0387 (6)
H21A	0.0098	0.6959	1.1407	0.058*
H21B	0.0443	0.7631	1.1909	0.058*
H21C	0.1276	0.7081	1.2543	0.058*
O1S	0.80228 (17)	0.61397 (7)	0.19308 (17)	0.0374 (4)
H1S	0.7956	0.6277	0.2787	0.056*
C1S	0.8883 (2)	0.56477 (11)	0.1984 (3)	0.0355 (5)
H1S1	0.9573	0.5731	0.2717	0.053*
H1S2	0.9226	0.5593	0.1009	0.053*
H1S3	0.8442	0.5281	0.2262	0.053*

Atomic displacement parameters (Å^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
S1	0.0407 (3)	0.0184 (3)	0.0178 (3)	−0.0068 (2)	−0.0021 (2)	0.00092 (18)
O1	0.0325 (8)	0.0229 (7)	0.0330 (8)	0.0030 (6)	0.0050 (6)	−0.0030 (6)
N1	0.0327 (9)	0.0184 (8)	0.0185 (8)	−0.0006 (7)	−0.0005 (7)	0.0005 (6)
C1	0.0286 (10)	0.0183 (10)	0.0215 (10)	0.0002 (8)	−0.0055 (8)	−0.0022 (8)
O2	0.0421 (9)	0.0152 (7)	0.0638 (12)	−0.0006 (6)	0.0108 (8)	0.0004 (7)
N2	0.0457 (11)	0.0208 (9)	0.0196 (9)	−0.0054 (8)	−0.0004 (8)	−0.0007 (7)
C2	0.0267 (10)	0.0236 (10)	0.0232 (10)	0.0020 (8)	−0.0036 (8)	−0.0015 (8)
O3	0.0432 (9)	0.0266 (8)	0.0448 (10)	0.0034 (7)	0.0121 (7)	−0.0054 (7)
C3	0.0316 (11)	0.0203 (10)	0.0337 (12)	0.0045 (8)	−0.0033 (9)	−0.0026 (9)
O4	0.0431 (9)	0.0214 (7)	0.0185 (7)	−0.0005 (6)	0.0018 (6)	0.0010 (5)
C4	0.0326 (11)	0.0160 (10)	0.0363 (12)	−0.0020 (8)	−0.0043 (9)	0.0008 (8)
C5	0.0273 (10)	0.0201 (10)	0.0284 (11)	−0.0008 (8)	−0.0032 (8)	−0.0001 (8)
C6	0.0276 (10)	0.0184 (9)	0.0211 (10)	0.0008 (8)	−0.0071 (8)	−0.0023 (8)

C7	0.0264 (10)	0.0162 (9)	0.0256 (11)	−0.0015 (8)	−0.0059 (8)	−0.0007 (8)
C8	0.0295 (11)	0.0190 (10)	0.0263 (11)	−0.0028 (8)	−0.0047 (8)	0.0000 (8)
C9	0.0279 (10)	0.0236 (10)	0.0227 (10)	−0.0024 (8)	−0.0028 (8)	−0.0019 (8)
C10	0.0356 (11)	0.0236 (11)	0.0244 (11)	−0.0031 (9)	−0.0015 (9)	0.0018 (8)
C11	0.0312 (11)	0.0348 (12)	0.0230 (11)	−0.0035 (9)	0.0022 (8)	−0.0023 (9)
C12	0.0322 (11)	0.0238 (11)	0.0325 (12)	0.0008 (9)	−0.0002 (9)	−0.0076 (9)
C13	0.0440 (13)	0.0215 (11)	0.0446 (14)	−0.0035 (10)	0.0121 (11)	−0.0015 (10)
C14	0.0364 (12)	0.0229 (11)	0.0390 (13)	−0.0042 (9)	0.0098 (10)	−0.0040 (9)
C15	0.0259 (10)	0.0215 (10)	0.0192 (10)	0.0014 (8)	−0.0020 (8)	0.0012 (8)
C16	0.0249 (10)	0.0188 (10)	0.0232 (10)	−0.0005 (8)	−0.0015 (8)	0.0023 (8)
C17	0.0252 (10)	0.0195 (10)	0.0206 (10)	0.0012 (8)	−0.0010 (8)	0.0011 (8)
C18	0.0258 (10)	0.0186 (9)	0.0234 (10)	−0.0023 (8)	−0.0001 (8)	−0.0017 (8)
C19	0.0337 (12)	0.0319 (12)	0.0401 (13)	0.0067 (10)	0.0038 (10)	−0.0053 (10)
C20	0.0417 (14)	0.0210 (11)	0.0662 (18)	−0.0025 (10)	0.0092 (12)	0.0090 (11)
C21	0.0366 (13)	0.0387 (13)	0.0413 (14)	0.0073 (10)	0.0058 (10)	−0.0064 (11)
O1S	0.0644 (11)	0.0277 (8)	0.0199 (8)	0.0013 (8)	0.0020 (7)	0.0003 (6)
C1S	0.0409 (13)	0.0380 (13)	0.0275 (12)	−0.0060 (10)	0.0017 (10)	−0.0014 (10)

Geometric parameters (Å, °)

S1—C16	1.753 (2)	C9—C10	1.390 (3)
S1—C18	1.765 (2)	C9—C14	1.399 (3)
O1—C2	1.365 (3)	C10—C11	1.394 (3)
O1—C19	1.431 (3)	C10—H10	0.9500
N1—C18	1.324 (3)	C11—C12	1.380 (3)
N1—C17	1.358 (3)	C11—H11	0.9500
C1—C6	1.403 (3)	C12—C13	1.388 (3)
C1—C2	1.418 (3)	C13—C14	1.378 (3)
C1—C15	1.468 (3)	C13—H13	0.9500
O2—C4	1.362 (3)	C14—H14	0.9500
O2—C20	1.433 (3)	C15—C16	1.341 (3)
N2—C18	1.310 (3)	C15—H15	0.9500
N2—H2A	0.8800	C16—C17	1.501 (3)
N2—H2B	0.8800	C19—H19A	0.9800
C2—C3	1.375 (3)	C19—H19B	0.9800
O3—C12	1.375 (3)	C19—H19C	0.9800
O3—C21	1.426 (3)	C20—H20A	0.9800
C3—C4	1.401 (3)	C20—H20B	0.9800
C3—H3	0.9500	C20—H20C	0.9800
O4—C17	1.237 (2)	C21—H21A	0.9800
C4—C5	1.380 (3)	C21—H21B	0.9800
C5—C6	1.406 (3)	C21—H21C	0.9800
C5—H5	0.9500	O1S—C1S	1.425 (3)
C6—C7	1.469 (3)	O1S—H1S	0.8400
C7—C8	1.334 (3)	C1S—H1S1	0.9800
C7—H7	0.9500	C1S—H1S2	0.9800
C8—C9	1.470 (3)	C1S—H1S3	0.9800
C8—H8	0.9500		
C16—S1—C18	88.54 (9)	C14—C13—C12	120.2 (2)

C2—O1—C19	118.01 (17)	C14—C13—H13	119.9
C18—N1—C17	111.41 (17)	C12—C13—H13	119.9
C6—C1—C2	118.67 (18)	C13—C14—C9	121.8 (2)
C6—C1—C15	123.84 (18)	C13—C14—H14	119.1
C2—C1—C15	117.36 (18)	C9—C14—H14	119.1
C4—O2—C20	118.05 (18)	C16—C15—C1	128.05 (19)
C18—N2—H2A	120.0	C16—C15—H15	116.0
C18—N2—H2B	120.0	C1—C15—H15	116.0
H2A—N2—H2B	120.0	C15—C16—C17	124.40 (18)
O1—C2—C3	124.34 (19)	C15—C16—S1	126.89 (16)
O1—C2—C1	114.37 (18)	C17—C16—S1	108.69 (14)
C3—C2—C1	121.28 (19)	O4—C17—N1	122.94 (18)
C12—O3—C21	117.11 (18)	O4—C17—C16	123.11 (18)
C2—C3—C4	118.93 (19)	N1—C17—C16	113.95 (17)
C2—C3—H3	120.5	N2—C18—N1	123.57 (18)
C4—C3—H3	120.5	N2—C18—S1	119.09 (15)
O2—C4—C5	123.9 (2)	N1—C18—S1	117.32 (15)
O2—C4—C3	114.60 (19)	O1—C19—H19A	109.5
C5—C4—C3	121.50 (19)	O1—C19—H19B	109.5
C4—C5—C6	119.6 (2)	H19A—C19—H19B	109.5
C4—C5—H5	120.2	O1—C19—H19C	109.5
C6—C5—H5	120.2	H19A—C19—H19C	109.5
C1—C6—C5	120.01 (18)	H19B—C19—H19C	109.5
C1—C6—C7	119.95 (18)	O2—C20—H20A	109.5
C5—C6—C7	119.97 (19)	O2—C20—H20B	109.5
C8—C7—C6	126.26 (19)	H20A—C20—H20B	109.5
C8—C7—H7	116.9	O2—C20—H20C	109.5
C6—C7—H7	116.9	H20A—C20—H20C	109.5
C7—C8—C9	125.10 (19)	H20B—C20—H20C	109.5
C7—C8—H8	117.5	O3—C21—H21A	109.5
C9—C8—H8	117.5	O3—C21—H21B	109.5
C10—C9—C14	116.7 (2)	H21A—C21—H21B	109.5
C10—C9—C8	120.47 (19)	O3—C21—H21C	109.5
C14—C9—C8	122.80 (19)	H21A—C21—H21C	109.5
C9—C10—C11	122.3 (2)	H21B—C21—H21C	109.5
C9—C10—H10	118.9	C1S—O1S—H1S	109.5
C11—C10—H10	118.9	O1S—C1S—H1S1	109.5
C12—C11—C10	119.4 (2)	O1S—C1S—H1S2	109.5
C12—C11—H11	120.3	H1S1—C1S—H1S2	109.5
C10—C11—H11	120.3	O1S—C1S—H1S3	109.5
O3—C12—C11	124.8 (2)	H1S1—C1S—H1S3	109.5
O3—C12—C13	115.6 (2)	H1S2—C1S—H1S3	109.5
C11—C12—C13	119.7 (2)		
C19—O1—C2—C3	1.1 (3)	C9—C10—C11—C12	−0.2 (3)
C19—O1—C2—C1	179.79 (18)	C21—O3—C12—C11	4.0 (3)
C6—C1—C2—O1	179.80 (17)	C21—O3—C12—C13	−175.4 (2)
C15—C1—C2—O1	3.9 (3)	C10—C11—C12—O3	−178.8 (2)
C6—C1—C2—C3	−1.5 (3)	C10—C11—C12—C13	0.6 (3)
C15—C1—C2—C3	−177.44 (19)	O3—C12—C13—C14	178.5 (2)

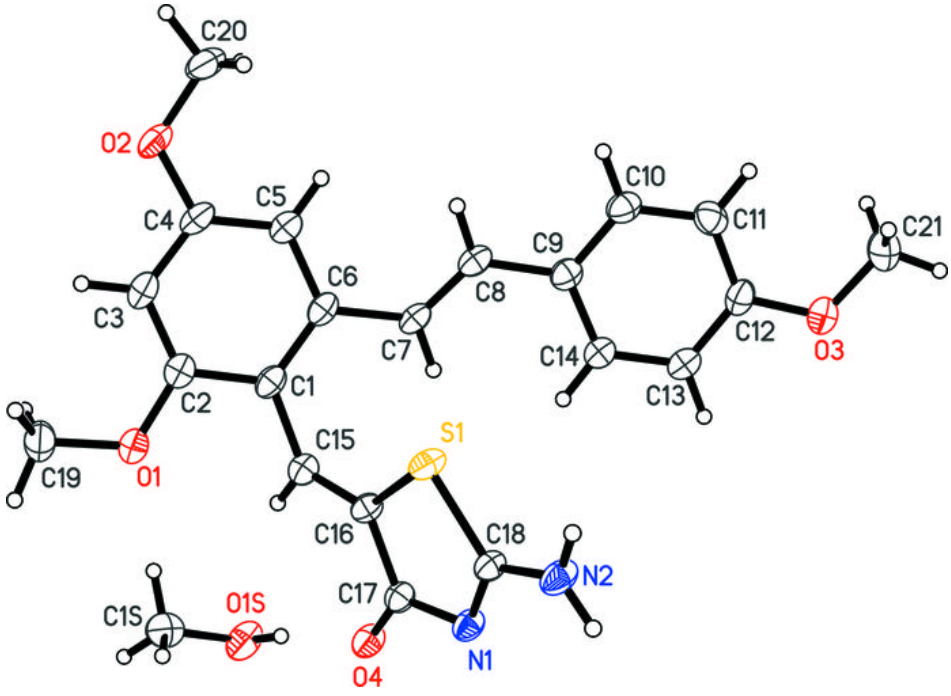
O1—C2—C3—C4	178.09 (19)	C11—C12—C13—C14	−1.0 (4)
C1—C2—C3—C4	−0.5 (3)	C12—C13—C14—C9	1.0 (4)
C20—O2—C4—C5	−8.1 (3)	C10—C9—C14—C13	−0.5 (3)
C20—O2—C4—C3	172.3 (2)	C8—C9—C14—C13	−178.2 (2)
C2—C3—C4—O2	−178.10 (19)	C6—C1—C15—C16	52.1 (3)
C2—C3—C4—C5	2.3 (3)	C2—C1—C15—C16	−132.2 (2)
O2—C4—C5—C6	178.4 (2)	C1—C15—C16—C17	−176.34 (19)
C3—C4—C5—C6	−2.0 (3)	C1—C15—C16—S1	5.2 (3)
C2—C1—C6—C5	1.8 (3)	C18—S1—C16—C15	179.4 (2)
C15—C1—C6—C5	177.43 (19)	C18—S1—C16—C17	0.77 (14)
C2—C1—C6—C7	−175.00 (18)	C18—N1—C17—O4	−176.10 (19)
C15—C1—C6—C7	0.7 (3)	C18—N1—C17—C16	3.4 (2)
C4—C5—C6—C1	−0.1 (3)	C15—C16—C17—O4	−1.8 (3)
C4—C5—C6—C7	176.70 (19)	S1—C16—C17—O4	176.94 (16)
C1—C6—C7—C8	−157.3 (2)	C15—C16—C17—N1	178.79 (19)
C5—C6—C7—C8	25.9 (3)	S1—C16—C17—N1	−2.5 (2)
C6—C7—C8—C9	176.15 (18)	C17—N1—C18—N2	179.14 (19)
C7—C8—C9—C10	174.4 (2)	C17—N1—C18—S1	−2.8 (2)
C7—C8—C9—C14	−8.0 (3)	C16—S1—C18—N2	179.25 (18)
C14—C9—C10—C11	0.1 (3)	C16—S1—C18—N1	1.12 (17)
C8—C9—C10—C11	177.91 (19)		

Hydrogen-bond geometry (Å, °)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
N2—H2A···O4^{i}	0.88	2.07	2.926 (2)	163
N2—H2A···N1^{i}	0.88	2.64	3.175 (2)	120
N2—H2B···O1S^{ii}	0.88	2.05	2.872 (2)	154
O1S—H1S···O4	0.84	1.88	2.716 (2)	172

Symmetry codes: (i) *x*, −*y*+3/2, *z*+1/2; (ii) *x*, *y*, *z*+1.

Fig. 1


C20
O2
C4
C5
C6
C3
C2
C1
C19
O1
C15
S1
C16
C18
N2
C17
O4
N1
C1S
O1S
C7
C8
C9
C10
C11
C12
O3
C21
C14
C13

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Acanthoic acid

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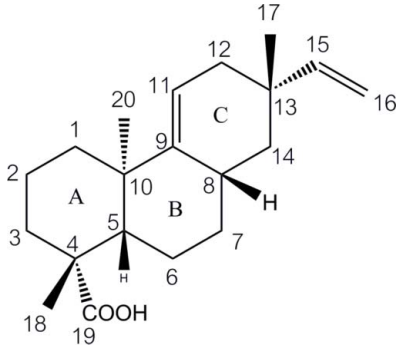
Key indicators: single-crystal X-ray study; T = 100 K; mean σ(C–C) = 0.005 Å; R factor = 0.056; wR factor = 0.158; data-to-parameter ratio = 11.9.

The title compound [systematic name: (1*R*,4a*R*,7*S*,8a*S*,10a*S*)-1,4a,7-trimethyl-7-vinyl-1,2,3,4,4a,6,7,8,8a,9,10,10a-dodecahydrophenanthrene-1-carboxylic acid], $C_{20}H_{30}O_2$, is a pimarane-type diterpene extracted from *Croton oblongifolius*. There are two independent molecules in the asymmetric unit. In both of these, the six-membered rings *A*, *B* and *C* adopt chair, boat and half-chair conformations, respectively. Rings *A* and *B* are *trans*-fused. The two molecules in the asymmetric unit form O—H···O hydrogen-bonded $R_2^2(8)$ dimers. The absolute configuration was assigned on the basis of the published literature on analogous structures.

Related literature

For background to the structure of acanthoic acid, see: Kim *et al.* (1998); Ling *et al.* (2001); Suh *et al.* (2001). For the related absolute configuration, see: Ling *et al.* (2000). For puckering parameters, see: Cremer & Pople (1975).



Experimental

Crystal data

$C_{20}H_{30}O_2$
M_r = 302.44
Tetragonal, $P4_3$
a = 12.8697 (16) Å
c = 21.768 (2) Å
V = 3605.5 (7) Å^3
Z = 8
Mo $K\alpha$ radiation
μ = 0.07 mm^{-1}
T = 100 K
0.40 × 0.20 × 0.02 mm

Data collection

Bruker SMART APEXII CCD area-detector diffractometer
21616 measured reflections
4824 independent reflections
3830 reflections with $I > 2\sigma(I)$
R_{int} = 0.050

Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.056
$wR(F^2)$ = 0.158
S = 1.02
4824 reflections
405 parameters
1 restraint
H-atom parameters constrained
$\Delta\rho_{max}$ = 0.37 e Å^{-3}
$\Delta\rho_{min}$ = −0.29 e Å^{-3}

Table 1
Hydrogen-bond geometry (Å, °).

D—H···A	D—H	H···A	D···A	D—H···A
O2′—H2′···O1	0.82	1.87	2.687 (3)	177
O2—H2···O1′	0.82	1.83	2.649 (3)	175

Data collection: *APEX2* (Bruker, 2008); cell refinement: *SAINT* (Bruker, 2008); data reduction: *SAINT*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *ORTEP-3* (Farrugia, 1997); software used to prepare material for publication: *publCIF* (Westrip, 2010).

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Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: FJ2300).

References

Bruker (2008). *APEX2*, *SADABS* and *SAINT*. Bruker AXS Inc., Madison, Wisconsin, USA.
Cremer, D. & Pople, J. A. (1975). *J. Am. Chem. Soc.* **97**, 1354–1358.
Farrugia, L. J. (1997). *J. Appl. Cryst.* **30**, 565.
Kim, Y. H., Chung, B. S. & Sankawa, U. (1998). *J. Nat. Prod.* **51**, 1080–1083.
Ling, T., Chowdhury, C., Kramer, B. A., Vong, B. G., Palladino, M. A. & Theodorakis, E. A. (2001). *J. Org. Chem.* **66**, 8843–8853.
Ling, T., Kramer, B. A., Palladino, M. A. & Theodorakis, E. A. (2000). *Org. Lett.* **2**, 2073–2076.
Sheldrick, G. M. (2008). *Acta Cryst.* A**64**, 112–122.
Suh, Y. G., Kim, Y. H., Park, M. H., Choi, Y. H., Lee, H. K., Moon, J. Y., Min, K. H., Shin, D. Y., Jung, J. K., Park, O. H., Jeon, R. O., Park, H. S. & Kang, S. A. (2001). *Bioorg. Med. Chem. Lett.* **11**, 559–562.
Westrip, S. P. (2010). *J. Appl. Cryst.* **43**. Submitted.

supplementary materials

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Acanthoic acid

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Comment

Acanthoic acid is a pimarane-type diterpene. It was first isolated from root bark of *Acanthopanax koreanum* Nakai (Araliaceae) (Kim *et al.*, 1998) which has been used for treatment of neuralgia, hypertension, rheumatism and diabetes (Ling *et al.*, 2001). This natural product exhibits anti-inflammatory activity (Suh *et al.*, 2001). In this work, acanthoic acid was isolated in high yield from stem bark of *Croton oblongifolius* from Ratchaburi Province, Thailand.

There are two independent molecules in the asymmetric unit. In both independent molecules, the six memberred rings A, B and C adopts a chair, boat and half-chair conformations, respectively with the puckering parameters: Q = 0.546 Å, θ = 179.5° and φ = -107.0° for A, Q = 0.766 Å, θ = 89.9° and φ = -73.3° for B and Q = 0.493 Å, θ = 128.4° and φ = 35.2° for C. Rings A/B is *trans*-fused. The ethylene group substituted at C13 is in an equatorial position. The two molecules in the asymmetric unit form O—H···O hydrogen-bonded $R_2^2(8)$ dimers. The absolute configuration was assigned by comparison with the crystal structure of *p*-bromobenzoate ester-acanthoic derivative (Ling *et al.*, 2000).

Experimental

Dried powder of stem bark of *Croton oblongifolius* Roxb. (5.23 kg) from Ratchaburi province was extracted with hexane (4Lx5). The hexane crude extract was obtained as viscous yellow brown oil. This crude extract was purified by quick column chromatography on silica gel using a mixture of hexane and ethyl acetate (100:0-0:100). Fractions with similar components were combined according to TLC profile. The combined fraction eluted with a 7:3 mixture of hexane and ethyl acetate was crystallized in hexane and ethyl acetate to give colourless crystals (5.5% yield).

mp. 140-142^{o}C; $[a]^{25}_{D}$ -36.1 (*c* = 0.42, benzene); ^{1}H-NMR (400 MHz, $CDCl_3$) *d* 5.81 (dd, 1H, *J*=10.6, 17.4 Hz, H-15), 5.39 (m, 1H, H-11), 4.93 (dd, 1H, *J*=1.2, 17.4 Hz, H-16 *trans*), 4.86 (dd, 1H, *J*=1.2, 10.6 Hz, H-16 *cis*), 2.31 (m, 1H, H-8), 2.21 (m, 1H, H-2 b), 2.15 (m, 1H, H-3a), 2.01 (m, 1H, H-12a), 1.93 (m, 1H, H-2a), 1.89 (m, 1H, H-6 b), 1.81 (m, 1H, H-1a), 1.77 (m, 1H, H-12 b), 1.73 (m, 1H, H-7a), 1.66 (dd, 1H, *J*=6.2, 13.0 Hz, H-5), 1.48 (m, 1H, H-6a), 1.45 (m, 1H, H-14a), 1.28 (m, 1H, H-1 b), 1.25 (s, 3H, H-18), 1.21 (m, 1H, H-7 b), 1.05 (m, 1H, H-3 b), 1.03 (m, 1H, H-14 b), 0.99 (s, 3H, H-20), 0.96 (s, 3H, H-17); ^{13}C NMR (100 MHz, $CDCl_3$) *d* 184.60 (C-19), 150.23 (C-15), 149.85 (C-9), 116.59 (C-11), 109.16 (C-16), 47.99 (C-5), 44.21 (C-4), 41.92 (C-1), 41.80 (C-14), 38.43 (C-10), 38.08 (C-3), 37.47 (C-12), 34.86 (C-13), 28.67 (C-8), 28.56 (C-18), 27.76 (C-7), 22.40 (C-20), 22.17 (C-17), 20.34 (C-6), 18.91 (C-2)

Refinement

Non-H atoms were refined anisotropically. H atoms were treated as riding atoms with distances C—H = 0.96 Å (CH_3), 0.97 Å (CH_2), 0.93 Å (CH), and *U*iso(H) = 1.20 *U*eq(C) for methylene and aromatic, 1.50 *U*eq(C) for methyl. The absolute structure could not be determined from the X-ray analysis, but it is known from earlier work on related compounds (Ling

et al., 2000). In the absence of significant anomalous scattering effects, 3,697 Friedel pairs were therefore merged before the final refinement.

Figures

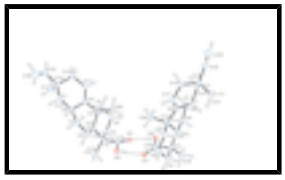


Fig. 1. The asymmetric unit of the title compound showing two independent molecules. Displacement ellipsoids for non-H atoms are drawn at the 30% probability level. Hydrogen bonds are shown as dashed lines.

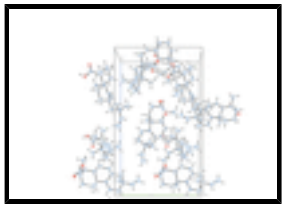


Fig. 2. The crystal structure of the title compound viewed along the *a*-axis.

(1*R*,4a*R*,7*S*,8a*S*,10a*S*)-1,4a,7-trimethyl-7- vinyl-1,2,3,4,4a,6,7,8,8a,9,10,10a-dodecahydrophenanthrene-1-carboxylic acid

Crystal data

$C_{20}H_{30}O_2$	$D_x = 1.114$ Mg m^{-3}
$M_r = 302.44$	Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å
Tetragonal, $P4_3$	Cell parameters from 9639 reflections
Hall symbol: P 4cw	$\theta = 1.6$–$30.2°$
$a = 12.8697$ (16) Å	$\mu = 0.07$ mm^{-1}
$c = 21.768$ (2) Å	$T = 100$ K
$V = 3605.5$ (7) Å^3	Needle, colourless
$Z = 8$	0.40 × 0.20 × 0.02 mm
$F(000) = 1328$	

Data collection

Bruker SMART APEXII CCD area-detector diffractometer	3830 reflections with $I > 2\sigma(I)$
Radiation source: Mo	$R_{int} = 0.050$
graphite	$\theta_{max} = 30.2°$, $\theta_{min} = 1.6°$
φ and ω scans	$h = -16\rightarrow16$
21616 measured reflections	$k = -17\rightarrow17$
4824 independent reflections	$l = -25\rightarrow28$

Refinement

Refinement on F^2	1 restraint
Least-squares matrix: full	H-atom parameters constrained
$R[F^2 > 2\sigma(F^2)] = 0.056$	$w = 1/[\sigma^2(F_o^2) + (0.0853P)^2 + 1.0669P]$

where $P = (F_o^2 + 2F_c^2)/3$

$wR(F^2) = 0.158$

$(\Delta/\sigma)_{max} = 0.002$

$S = 1.02$

$\Delta\rho_{max} = 0.37$ e Å^{-3}

4824 reflections

$\Delta\rho_{min} = -0.29$ e Å^{-3}

405 parameters

Special details

Geometry. All esds (except the esd in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell esds are taken into account individually in the estimation of esds in distances, angles and torsion angles; correlations between esds in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell esds is used for estimating esds involving l.s. planes.

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å^2)

	x	*y*	*z*	U_{iso}*/U_{eq}
C1	0.2020 (3)	0.6538 (3)	0.07071 (16)	0.0369 (7)
H1A	0.133	0.6753	0.0833	0.044*
H1B	0.208	0.6659	0.0269	0.044*
C2	0.2143 (3)	0.5365 (3)	0.08320 (18)	0.0395 (8)
H2A	0.1582	0.4991	0.0633	0.047*
H2B	0.2793	0.5125	0.0657	0.047*
C3	0.2130 (3)	0.5131 (3)	0.15123 (18)	0.0389 (7)
H3A	0.2246	0.4393	0.157	0.047*
H3B	0.1446	0.5293	0.1673	0.047*
C4	0.2946 (2)	0.5735 (2)	0.18865 (14)	0.0283 (6)
C5	0.2819 (2)	0.6927 (2)	0.17370 (13)	0.0257 (6)
H5	0.2117	0.7103	0.1876	0.031*
C6	0.3540 (2)	0.7641 (2)	0.21113 (15)	0.0332 (6)
H6A	0.4256	0.7438	0.2041	0.04*
H6B	0.3393	0.7553	0.2545	0.04*
C7	0.3407 (3)	0.8792 (3)	0.19396 (17)	0.0384 (7)
H7A	0.3387	0.9204	0.2313	0.046*
H7B	0.4005	0.9015	0.1703	0.046*
C8	0.2417 (2)	0.9002 (2)	0.15664 (15)	0.0309 (6)
H8	0.182	0.8755	0.1805	0.037*
C9	0.2483 (2)	0.8366 (2)	0.09816 (14)	0.0307 (6)
C10	0.2833 (2)	0.7217 (2)	0.10447 (13)	0.0261 (6)
C11	0.2242 (3)	0.8779 (3)	0.04395 (17)	0.0439 (8)
H11	0.2322	0.8361	0.0094	0.053*
C12	0.1851 (4)	0.9870 (3)	0.03404 (18)	0.0535 (10)
H12A	0.1287	0.9856	0.0045	0.064*
H12B	0.2406	1.0289	0.0169	0.064*
C13	0.1463 (3)	1.0377 (3)	0.09429 (18)	0.0481 (9)
C14	0.2265 (3)	1.0152 (3)	0.14356 (18)	0.0436 (8)
H14A	0.2055	1.0496	0.1812	0.052*
H14B	0.2925	1.0447	0.131	0.052*
C15	0.1282 (5)	1.1516 (4)	0.0829 (2)	0.0853 (19)

H15	0.0933	1.1636	0.0461	0.102*
C16	0.1472 (8)	1.2286 (4)	0.1089 (3)	0.123 (3)
H16A	0.182	1.2263	0.1463	0.147*
H16B	0.1275	1.2921	0.0922	0.147*
C17	0.0409 (3)	0.9895 (4)	0.1120 (2)	0.0610 (12)
H17A	0.0484	0.9156	0.1159	0.092*
H17B	−0.0093	1.0047	0.0806	0.092*
H17C	0.018	1.0181	0.1504	0.092*
C18	0.2726 (3)	0.5543 (3)	0.25738 (17)	0.0429 (8)
H18A	0.2051	0.5811	0.2676	0.064*
H18B	0.3243	0.5888	0.2817	0.064*
H18C	0.2745	0.481	0.2656	0.064*
C19	0.4032 (2)	0.5295 (2)	0.17572 (14)	0.0312 (6)
C20	0.3915 (2)	0.7082 (2)	0.07483 (14)	0.0332 (7)
H20A	0.3909	0.7371	0.0342	0.05*
H20B	0.4083	0.6356	0.0726	0.05*
H20C	0.4427	0.7434	0.0993	0.05*
O1	0.42045 (17)	0.46242 (17)	0.13726 (11)	0.0352 (5)
O2	0.47604 (18)	0.5668 (2)	0.21170 (12)	0.0437 (6)
H2	0.532	0.5404	0.2027	0.066*
C1'	0.8991 (3)	0.6408 (3)	0.09529 (17)	0.0415 (8)
H1'1	0.9703	0.6216	0.086	0.05*
H1'2	0.8959	0.716	0.0969	0.05*
C2'	0.8713 (3)	0.5981 (3)	0.15830 (16)	0.0468 (9)
H2'1	0.9222	0.6216	0.1881	0.056*
H2'2	0.8039	0.6248	0.1706	0.056*
C3'	0.8682 (3)	0.4805 (3)	0.15808 (16)	0.0429 (8)
H3'1	0.8463	0.4564	0.1983	0.051*
H3'2	0.9377	0.4542	0.1507	0.051*
C4'	0.7945 (2)	0.4360 (2)	0.10933 (15)	0.0322 (6)
C5'	0.8256 (2)	0.4816 (2)	0.04527 (14)	0.0271 (6)
H5'	0.8981	0.4603	0.0397	0.033*
C6'	0.7679 (2)	0.4328 (2)	−0.00971 (15)	0.0316 (6)
H6'1	0.7876	0.3603	−0.0131	0.038*
H6'2	0.6937	0.4357	−0.0021	0.038*
C7'	0.7919 (2)	0.4880 (2)	−0.07080 (14)	0.0299 (6)
H7'1	0.7984	0.4365	−0.1031	0.036*
H7'2	0.7342	0.5333	−0.0813	0.036*
C8'	0.8922 (2)	0.5526 (2)	−0.06797 (13)	0.0257 (6)
H8'	0.9494	0.5068	−0.0557	0.031*
C9'	0.8790 (2)	0.6354 (2)	−0.01921 (15)	0.0301 (6)
C10'	0.8288 (2)	0.6029 (2)	0.04225 (14)	0.0285 (6)
C11'	0.9096 (3)	0.7328 (2)	−0.02861 (17)	0.0402 (8)
H11'	0.8987	0.7801	0.003	0.048*
C12'	0.9605 (3)	0.7729 (3)	−0.08629 (19)	0.0435 (8)
H12C	1.018	0.8177	−0.0751	0.052*
H12D	0.9106	0.8144	−0.109	0.052*
C13'	1.0012 (2)	0.6844 (3)	−0.12842 (16)	0.0355 (7)
C14'	0.9179 (2)	0.5993 (2)	−0.13061 (14)	0.0332 (6)

H14C	0.8549	0.6283	−0.1481	0.04*
H14D	0.9414	0.5442	−0.1576	0.04*
C15'	1.0229 (3)	0.7320 (3)	−0.1906 (2)	0.0536 (10)
H15'	1.0743	0.7829	−0.1908	0.064*
C16'	0.9827 (4)	0.7138 (5)	−0.2418 (2)	0.0762 (15)
H16C	0.9307	0.664	−0.2453	0.091*
H16D	1.0047	0.7502	−0.2763	0.091*
C17'	1.1037 (2)	0.6415 (3)	−0.10289 (17)	0.0401 (8)
H17D	1.1267	0.5847	−0.128	0.06*
H17E	1.0932	0.6176	−0.0616	0.06*
H17F	1.1553	0.6954	−0.1031	0.06*
C18'	0.8066 (3)	0.3167 (3)	0.10861 (19)	0.0447 (8)
H18D	0.7936	0.2897	0.149	0.067*
H18E	0.876	0.2989	0.0963	0.067*
H18F	0.7579	0.2872	0.0801	0.067*
C19'	0.6819 (2)	0.4561 (2)	0.12987 (15)	0.0318 (6)
C20'	0.7191 (2)	0.6510 (2)	0.04652 (16)	0.0338 (7)
H20D	0.723	0.7242	0.0383	0.051*
H20E	0.6916	0.6401	0.087	0.051*
H20F	0.6743	0.6185	0.0169	0.051*
O1'	0.66053 (17)	0.4932 (2)	0.17988 (11)	0.0402 (5)
O2'	0.61042 (16)	0.42401 (18)	0.09132 (11)	0.0362 (5)
H2'	0.5527	0.4336	0.1063	0.054*

Atomic displacement parameters (Å^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
C1	0.0352 (16)	0.0399 (17)	0.0356 (17)	0.0035 (13)	−0.0104 (13)	−0.0085 (13)
C2	0.0300 (15)	0.0364 (17)	0.052 (2)	−0.0012 (13)	−0.0083 (14)	−0.0164 (15)
C3	0.0293 (15)	0.0311 (15)	0.056 (2)	−0.0040 (12)	0.0048 (14)	−0.0024 (15)
C4	0.0268 (13)	0.0308 (14)	0.0273 (14)	0.0015 (11)	0.0060 (11)	0.0024 (11)
C5	0.0238 (12)	0.0294 (14)	0.0241 (14)	0.0008 (10)	0.0007 (10)	−0.0004 (11)
C6	0.0321 (15)	0.0382 (16)	0.0292 (15)	−0.0013 (12)	−0.0035 (12)	−0.0085 (13)
C7	0.0365 (16)	0.0379 (17)	0.0408 (19)	−0.0064 (13)	−0.0014 (14)	−0.0107 (14)
C8	0.0306 (14)	0.0302 (14)	0.0320 (15)	−0.0015 (11)	0.0090 (12)	−0.0022 (12)
C9	0.0304 (14)	0.0284 (14)	0.0333 (16)	0.0010 (11)	0.0095 (12)	0.0000 (12)
C10	0.0267 (13)	0.0283 (13)	0.0232 (14)	0.0010 (10)	0.0013 (10)	−0.0035 (11)
C11	0.056 (2)	0.0450 (19)	0.0308 (17)	0.0130 (16)	0.0074 (15)	0.0021 (14)
C12	0.070 (3)	0.050 (2)	0.041 (2)	0.0220 (19)	0.0139 (18)	0.0119 (17)
C13	0.064 (2)	0.0360 (17)	0.044 (2)	0.0177 (16)	0.0181 (18)	0.0112 (15)
C14	0.054 (2)	0.0311 (16)	0.046 (2)	0.0001 (14)	0.0140 (16)	−0.0039 (14)
C15	0.152 (5)	0.046 (3)	0.057 (3)	0.037 (3)	0.043 (3)	0.019 (2)
C16	0.259 (10)	0.047 (3)	0.063 (4)	0.002 (4)	0.052 (5)	0.001 (3)
C17	0.049 (2)	0.066 (3)	0.068 (3)	0.019 (2)	0.007 (2)	0.017 (2)
C18	0.0443 (19)	0.0463 (19)	0.0381 (19)	0.0087 (15)	0.0151 (15)	0.0136 (15)
C19	0.0302 (14)	0.0334 (15)	0.0301 (16)	0.0031 (12)	0.0049 (12)	0.0063 (12)
C20	0.0337 (15)	0.0368 (16)	0.0290 (16)	0.0009 (12)	0.0090 (12)	−0.0002 (12)
O1	0.0297 (11)	0.0339 (11)	0.0420 (13)	0.0043 (9)	0.0057 (9)	−0.0020 (9)

O2	0.0306 (11)	0.0593 (16)	0.0413 (14)	0.0109 (11)	−0.0038 (10)	−0.0125 (12)
C1'	0.0365 (17)	0.0484 (19)	0.0395 (18)	−0.0164 (14)	0.0051 (14)	−0.0145 (15)
C2'	0.0376 (18)	0.070 (2)	0.0332 (18)	−0.0149 (17)	0.0003 (14)	−0.0156 (17)
C3'	0.0282 (15)	0.070 (2)	0.0309 (17)	−0.0012 (15)	0.0022 (13)	−0.0002 (16)
C4'	0.0258 (14)	0.0394 (16)	0.0312 (16)	0.0013 (12)	0.0038 (12)	0.0000 (12)
C5'	0.0217 (12)	0.0287 (13)	0.0309 (15)	−0.0003 (10)	0.0043 (11)	−0.0007 (11)
C6'	0.0336 (15)	0.0293 (14)	0.0319 (16)	−0.0072 (12)	0.0048 (12)	−0.0071 (12)
C7'	0.0295 (14)	0.0318 (14)	0.0284 (15)	−0.0045 (11)	−0.0005 (11)	−0.0061 (12)
C8'	0.0259 (13)	0.0252 (13)	0.0261 (14)	0.0008 (10)	0.0033 (11)	−0.0027 (11)
C9'	0.0251 (13)	0.0291 (14)	0.0363 (16)	−0.0030 (11)	0.0088 (12)	−0.0072 (12)
C10'	0.0255 (13)	0.0261 (13)	0.0337 (16)	−0.0048 (10)	0.0063 (11)	−0.0087 (11)
C11'	0.0442 (18)	0.0266 (15)	0.050 (2)	−0.0019 (13)	0.0177 (15)	−0.0090 (14)
C12'	0.0411 (18)	0.0291 (16)	0.060 (2)	−0.0036 (13)	0.0171 (16)	0.0034 (15)
C13'	0.0319 (15)	0.0380 (16)	0.0366 (17)	−0.0001 (12)	0.0098 (13)	0.0089 (13)
C14'	0.0330 (15)	0.0371 (16)	0.0296 (15)	0.0026 (12)	0.0022 (12)	0.0000 (12)
C15'	0.045 (2)	0.063 (2)	0.053 (3)	0.0037 (17)	0.0147 (18)	0.022 (2)
C16'	0.079 (3)	0.111 (4)	0.039 (3)	0.004 (3)	0.008 (2)	0.013 (2)
C17'	0.0322 (16)	0.0484 (19)	0.0398 (19)	−0.0012 (13)	0.0072 (14)	0.0047 (15)
C18'	0.0447 (19)	0.0415 (18)	0.048 (2)	0.0055 (15)	0.0097 (16)	0.0135 (16)
C19'	0.0259 (14)	0.0368 (16)	0.0328 (16)	−0.0006 (11)	0.0042 (12)	0.0027 (12)
C20'	0.0332 (15)	0.0296 (14)	0.0387 (17)	0.0017 (12)	0.0126 (13)	−0.0055 (13)
O1'	0.0287 (11)	0.0606 (15)	0.0312 (12)	0.0039 (10)	0.0038 (9)	−0.0057 (11)
O2'	0.0251 (10)	0.0459 (13)	0.0374 (12)	−0.0053 (9)	0.0070 (9)	−0.0049 (10)

Geometric parameters (Å, °)

C1—C2	1.542 (5)	C1'—C2'	1.520 (5)
C1—C10	1.548 (4)	C1'—C10'	1.545 (4)
C1—H1A	0.97	C1'—H1'1	0.97
C1—H1B	0.97	C1'—H1'2	0.97
C2—C3	1.511 (6)	C2'—C3'	1.514 (6)
C2—H2A	0.97	C2'—H2'1	0.97
C2—H2B	0.97	C2'—H2'2	0.97
C3—C4	1.540 (4)	C3'—C4'	1.534 (5)
C3—H3A	0.97	C3'—H3'1	0.97
C3—H3B	0.97	C3'—H3'2	0.97
C4—C19	1.534 (4)	C4'—C19'	1.538 (4)
C4—C18	1.543 (4)	C4'—C18'	1.544 (5)
C4—C5	1.577 (4)	C4'—C5'	1.565 (4)
C5—C6	1.539 (4)	C5'—C6'	1.542 (4)
C5—C10	1.553 (4)	C5'—C10'	1.563 (4)
C5—H5	0.98	C5'—H5'	0.98
C6—C7	1.537 (5)	C6'—C7'	1.539 (4)
C6—H6A	0.97	C6'—H6'1	0.97
C6—H6B	0.97	C6'—H6'2	0.97
C7—C8	1.535 (5)	C7'—C8'	1.536 (4)
C7—H7A	0.97	C7'—H7'1	0.97
C7—H7B	0.97	C7'—H7'2	0.97
C8—C9	1.515 (4)	C8'—C9'	1.514 (4)

C8—C14	1.520 (4)	C8'—C14'	1.526 (4)
C8—H8	0.98	C8'—H8'	0.98
C9—C11	1.331 (5)	C9'—C11'	1.329 (4)
C9—C10	1.552 (4)	C9'—C10'	1.544 (4)
C10—C20	1.545 (4)	C10'—C20'	1.545 (4)
C11—C12	1.507 (5)	C11'—C12'	1.507 (5)
C11—H11	0.93	C11'—H11'	0.93
C12—C13	1.548 (5)	C12'—C13'	1.553 (5)
C12—H12A	0.97	C12'—H12C	0.97
C12—H12B	0.97	C12'—H12D	0.97
C13—C15	1.505 (5)	C13'—C15'	1.511 (5)
C13—C14	1.516 (6)	C13'—C17'	1.534 (5)
C13—C17	1.540 (6)	C13'—C14'	1.534 (5)
C14—H14A	0.97	C14'—H14C	0.97
C14—H14B	0.97	C14'—H14D	0.97
C15—C16	1.167 (8)	C15'—C16'	1.251 (7)
C15—H15	0.93	C15'—H15'	0.93
C16—H16A	0.93	C16'—H16C	0.93
C16—H16B	0.93	C16'—H16D	0.93
C17—H17A	0.96	C17'—H17D	0.96
C17—H17B	0.96	C17'—H17E	0.96
C17—H17C	0.96	C17'—H17F	0.96
C18—H18A	0.96	C18'—H18D	0.96
C18—H18B	0.96	C18'—H18E	0.96
C18—H18C	0.96	C18'—H18F	0.96
C19—O1	1.223 (4)	C19'—O1'	1.220 (4)
C19—O2	1.313 (4)	C19'—O2'	1.312 (4)
C20—H20A	0.96	C20'—H20D	0.96
C20—H20B	0.96	C20'—H20E	0.96
C20—H20C	0.96	C20'—H20F	0.96
O2—H2	0.82	O2'—H2'	0.82
C2—C1—C10	113.6 (3)	C2'—C1'—C10'	115.0 (3)
C2—C1—H1A	108.9	C2'—C1'—H1'1	108.5
C10—C1—H1A	108.9	C10'—C1'—H1'1	108.5
C2—C1—H1B	108.9	C2'—C1'—H1'2	108.5
C10—C1—H1B	108.9	C10'—C1'—H1'2	108.5
H1A—C1—H1B	107.7	H1'1—C1'—H1'2	107.5
C3—C2—C1	111.5 (3)	C3'—C2'—C1'	111.4 (3)
C3—C2—H2A	109.3	C3'—C2'—H2'1	109.4
C1—C2—H2A	109.3	C1'—C2'—H2'1	109.4
C3—C2—H2B	109.3	C3'—C2'—H2'2	109.4
C1—C2—H2B	109.3	C1'—C2'—H2'2	109.4
H2A—C2—H2B	108	H2'1—C2'—H2'2	108
C2—C3—C4	114.2 (3)	C2'—C3'—C4'	113.1 (3)
C2—C3—H3A	108.7	C2'—C3'—H3'1	109
C4—C3—H3A	108.7	C4'—C3'—H3'1	109
C2—C3—H3B	108.7	C2'—C3'—H3'2	109
C4—C3—H3B	108.7	C4'—C3'—H3'2	109
H3A—C3—H3B	107.6	H3'1—C3'—H3'2	107.8

C19—C4—C3	109.8 (3)	C3'—C4'—C19'	108.6 (3)
C19—C4—C18	106.6 (2)	C3'—C4'—C18'	108.4 (3)
C3—C4—C18	107.9 (3)	C19'—C4'—C18'	105.4 (3)
C19—C4—C5	114.6 (2)	C3'—C4'—C5'	108.6 (2)
C3—C4—C5	108.1 (2)	C19'—C4'—C5'	115.9 (3)
C18—C4—C5	109.7 (2)	C18'—C4'—C5'	109.8 (3)
C6—C5—C10	111.3 (2)	C6'—C5'—C10'	112.8 (2)
C6—C5—C4	114.2 (2)	C6'—C5'—C4'	114.6 (2)
C10—C5—C4	115.6 (2)	C10'—C5'—C4'	114.8 (2)
C6—C5—H5	104.8	C6'—C5'—H5'	104.4
C10—C5—H5	104.8	C10'—C5'—H5'	104.4
C4—C5—H5	104.8	C4'—C5'—H5'	104.4
C5—C6—C7	112.3 (2)	C7'—C6'—C5'	112.7 (2)
C5—C6—H6A	109.1	C7'—C6'—H6'1	109
C7—C6—H6A	109.1	C5'—C6'—H6'1	109
C5—C6—H6B	109.1	C7'—C6'—H6'2	109
C7—C6—H6B	109.1	C5'—C6'—H6'2	109
H6A—C6—H6B	107.9	H6'1—C6'—H6'2	107.8
C8—C7—C6	113.0 (2)	C8'—C7'—C6'	112.5 (2)
C8—C7—H7A	109	C8'—C7'—H7'1	109.1
C6—C7—H7A	109	C6'—C7'—H7'1	109.1
C8—C7—H7B	109	C8'—C7'—H7'2	109.1
C6—C7—H7B	109	C6'—C7'—H7'2	109.1
H7A—C7—H7B	107.8	H7'1—C7'—H7'2	107.8
C9—C8—C14	112.0 (3)	C9'—C8'—C14'	111.9 (2)
C9—C8—C7	107.7 (3)	C9'—C8'—C7'	108.4 (2)
C14—C8—C7	112.1 (3)	C14'—C8'—C7'	111.1 (2)
C9—C8—H8	108.3	C9'—C8'—H8'	108.5
C14—C8—H8	108.3	C14'—C8'—H8'	108.5
C7—C8—H8	108.3	C7'—C8'—H8'	108.5
C11—C9—C8	121.1 (3)	C11'—C9'—C8'	121.5 (3)
C11—C9—C10	121.8 (3)	C11'—C9'—C10'	120.9 (3)
C8—C9—C10	117.1 (3)	C8'—C9'—C10'	117.6 (2)
C20—C10—C1	110.3 (3)	C20'—C10'—C9'	109.0 (3)
C20—C10—C9	109.4 (2)	C20'—C10'—C1'	111.3 (2)
C1—C10—C9	107.5 (2)	C9'—C10'—C1'	108.5 (2)
C20—C10—C5	112.8 (2)	C20'—C10'—C5'	111.9 (2)
C1—C10—C5	108.5 (2)	C9'—C10'—C5'	108.6 (2)
C9—C10—C5	108.1 (2)	C1'—C10'—C5'	107.4 (3)
C9—C11—C12	125.2 (3)	C9'—C11'—C12'	125.5 (3)
C9—C11—H11	117.4	C9'—C11'—H11'	117.3
C12—C11—H11	117.4	C12'—C11'—H11'	117.3
C11—C12—C13	112.3 (3)	C11'—C12'—C13'	112.8 (3)
C11—C12—H12A	109.1	C11'—C12'—H12C	109
C13—C12—H12A	109.1	C13'—C12'—H12C	109
C11—C12—H12B	109.1	C11'—C12'—H12D	109
C13—C12—H12B	109.1	C13'—C12'—H12D	109
H12A—C12—H12B	107.9	H12C—C12'—H12D	107.8
C15—C13—C14	114.1 (4)	C15'—C13'—C17'	108.1 (3)

C15—C13—C17	107.3 (4)	C15'—C13'—C14'	113.0 (3)
C14—C13—C17	110.2 (3)	C17'—C13'—C14'	110.8 (3)
C15—C13—C12	108.7 (3)	C15'—C13'—C12'	107.1 (3)
C14—C13—C12	107.4 (3)	C17'—C13'—C12'	109.9 (3)
C17—C13—C12	109.0 (4)	C14'—C13'—C12'	107.8 (3)
C13—C14—C8	114.0 (3)	C8'—C14'—C13'	113.9 (3)
C13—C14—H14A	108.8	C8'—C14'—H14C	108.8
C8—C14—H14A	108.8	C13'—C14'—H14C	108.8
C13—C14—H14B	108.8	C8'—C14'—H14D	108.8
C8—C14—H14B	108.8	C13'—C14'—H14D	108.8
H14A—C14—H14B	107.7	H14C—C14'—H14D	107.7
C16—C15—C13	135.5 (7)	C16'—C15'—C13'	130.2 (4)
C16—C15—H15	112.2	C16'—C15'—H15'	114.9
C13—C15—H15	112.2	C13'—C15'—H15'	114.9
C15—C16—H16A	120	C15'—C16'—H16C	120
C15—C16—H16B	120	C15'—C16'—H16D	120
H16A—C16—H16B	120	H16C—C16'—H16D	120
C13—C17—H17A	109.5	C13'—C17'—H17D	109.5
C13—C17—H17B	109.5	C13'—C17'—H17E	109.5
H17A—C17—H17B	109.5	H17D—C17'—H17E	109.5
C13—C17—H17C	109.5	C13'—C17'—H17F	109.5
H17A—C17—H17C	109.5	H17D—C17'—H17F	109.5
H17B—C17—H17C	109.5	H17E—C17'—H17F	109.5
C4—C18—H18A	109.5	C4'—C18'—H18D	109.5
C4—C18—H18B	109.5	C4'—C18'—H18E	109.5
H18A—C18—H18B	109.5	H18D—C18'—H18E	109.5
C4—C18—H18C	109.5	C4'—C18'—H18F	109.5
H18A—C18—H18C	109.5	H18D—C18'—H18F	109.5
H18B—C18—H18C	109.5	H18E—C18'—H18F	109.5
O1—C19—O2	122.5 (3)	O1'—C19'—O2'	122.4 (3)
O1—C19—C4	123.5 (3)	O1'—C19'—C4'	122.5 (3)
O2—C19—C4	114.0 (3)	O2'—C19'—C4'	114.9 (3)
C10—C20—H20A	109.5	C10'—C20'—H20D	109.5
C10—C20—H20B	109.5	C10'—C20'—H20E	109.5
H20A—C20—H20B	109.5	H20D—C20'—H20E	109.5
C10—C20—H20C	109.5	C10'—C20'—H20F	109.5
H20A—C20—H20C	109.5	H20D—C20'—H20F	109.5
H20B—C20—H20C	109.5	H20E—C20'—H20F	109.5
C19—O2—H2	109.5	C19'—O2'—H2'	109.5
C10—C1—C2—C3	54.8 (4)	C10'—C1'—C2'—C3'	54.7 (4)
C1—C2—C3—C4	−55.4 (4)	C1'—C2'—C3'—C4'	−55.4 (4)
C2—C3—C4—C19	−72.7 (3)	C2'—C3'—C4'—C19'	−72.1 (3)
C2—C3—C4—C18	171.5 (3)	C2'—C3'—C4'—C18'	173.9 (3)
C2—C3—C4—C5	52.9 (3)	C2'—C3'—C4'—C5'	54.7 (3)
C19—C4—C5—C6	−61.0 (3)	C3'—C4'—C5'—C6'	172.2 (3)
C3—C4—C5—C6	176.2 (3)	C19'—C4'—C5'—C6'	−65.4 (3)
C18—C4—C5—C6	58.8 (3)	C18'—C4'—C5'—C6'	53.8 (3)
C19—C4—C5—C10	70.1 (3)	C3'—C4'—C5'—C10'	−55.0 (3)
C3—C4—C5—C10	−52.7 (3)	C19'—C4'—C5'—C10'	67.5 (3)

C18—C4—C5—C10	−170.1 (3)	C18'—C4'—C5'—C10'	−173.3 (3)
C10—C5—C6—C7	45.5 (3)	C10'—C5'—C6'—C7'	39.9 (3)
C4—C5—C6—C7	178.7 (2)	C4'—C5'—C6'—C7'	173.7 (2)
C5—C6—C7—C8	14.7 (4)	C5'—C6'—C7'—C8'	19.4 (4)
C6—C7—C8—C9	−59.8 (3)	C6'—C7'—C8'—C9'	−61.1 (3)
C6—C7—C8—C14	176.4 (3)	C6'—C7'—C8'—C14'	175.6 (2)
C14—C8—C9—C11	−11.1 (4)	C14'—C8'—C9'—C11'	−13.8 (4)
C7—C8—C9—C11	−134.9 (3)	C7'—C8'—C9'—C11'	−136.6 (3)
C14—C8—C9—C10	169.4 (3)	C14'—C8'—C9'—C10'	166.3 (3)
C7—C8—C9—C10	45.6 (3)	C7'—C8'—C9'—C10'	43.5 (3)
C2—C1—C10—C20	71.9 (4)	C11'—C9'—C10'—C20'	71.0 (4)
C2—C1—C10—C9	−169.0 (3)	C8'—C9'—C10'—C20'	−109.2 (3)
C2—C1—C10—C5	−52.2 (3)	C11'—C9'—C10'—C1'	−50.4 (4)
C11—C9—C10—C20	68.8 (4)	C8'—C9'—C10'—C1'	129.4 (3)
C8—C9—C10—C20	−111.7 (3)	C11'—C9'—C10'—C5'	−166.9 (3)
C11—C9—C10—C1	−51.0 (4)	C8'—C9'—C10'—C5'	13.0 (3)
C8—C9—C10—C1	128.5 (3)	C2'—C1'—C10'—C20'	70.8 (4)
C11—C9—C10—C5	−168.0 (3)	C2'—C1'—C10'—C9'	−169.3 (3)
C8—C9—C10—C5	11.6 (3)	C2'—C1'—C10'—C5'	−52.1 (4)
C6—C5—C10—C20	62.5 (3)	C6'—C5'—C10'—C20'	64.1 (3)
C4—C5—C10—C20	−70.0 (3)	C4'—C5'—C10'—C20'	−69.6 (3)
C6—C5—C10—C1	−174.9 (2)	C6'—C5'—C10'—C9'	−56.3 (3)
C4—C5—C10—C1	52.6 (3)	C4'—C5'—C10'—C9'	170.0 (2)
C6—C5—C10—C9	−58.7 (3)	C6'—C5'—C10'—C1'	−173.5 (2)
C4—C5—C10—C9	168.9 (2)	C4'—C5'—C10'—C1'	52.8 (3)
C8—C9—C11—C12	−2.4 (6)	C8'—C9'—C11'—C12'	−0.6 (6)
C10—C9—C11—C12	177.1 (3)	C10'—C9'—C11'—C12'	179.2 (3)
C9—C11—C12—C13	−16.0 (6)	C9'—C11'—C12'—C13'	−15.2 (5)
C11—C12—C13—C15	169.3 (4)	C11'—C12'—C13'—C15'	165.0 (3)
C11—C12—C13—C14	45.4 (5)	C11'—C12'—C13'—C17'	−77.8 (4)
C11—C12—C13—C17	−74.0 (4)	C11'—C12'—C13'—C14'	43.1 (4)
C15—C13—C14—C8	177.8 (3)	C9'—C8'—C14'—C13'	45.2 (3)
C17—C13—C14—C8	57.1 (4)	C7'—C8'—C14'—C13'	166.5 (3)
C12—C13—C14—C8	−61.6 (4)	C15'—C13'—C14'—C8'	−178.1 (3)
C9—C8—C14—C13	44.4 (4)	C17'—C13'—C14'—C8'	60.3 (4)
C7—C8—C14—C13	165.6 (3)	C12'—C13'—C14'—C8'	−60.0 (4)
C14—C13—C15—C16	−15.6 (10)	C17'—C13'—C15'—C16'	124.4 (5)
C17—C13—C15—C16	106.8 (9)	C14'—C13'—C15'—C16'	1.3 (6)
C12—C13—C15—C16	−135.4 (8)	C12'—C13'—C15'—C16'	−117.2 (5)
C3—C4—C19—O1	5.7 (4)	C3'—C4'—C19'—O1'	−6.0 (4)
C18—C4—C19—O1	122.2 (3)	C18'—C4'—C19'—O1'	110.0 (4)
C5—C4—C19—O1	−116.2 (3)	C5'—C4'—C19'—O1'	−128.4 (3)
C3—C4—C19—O2	−171.4 (3)	C3'—C4'—C19'—O2'	178.4 (3)
C18—C4—C19—O2	−54.8 (3)	C18'—C4'—C19'—O2'	−65.6 (3)
C5—C4—C19—O2	66.8 (3)	C5'—C4'—C19'—O2'	55.9 (4)

Hydrogen-bond geometry (Å, °)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*

O2'—H2'···O1	0.82	1.87	2.687 (3)	177
O2—H2···O1'	0.82	1.83	2.649 (3)	175

Fig. 1

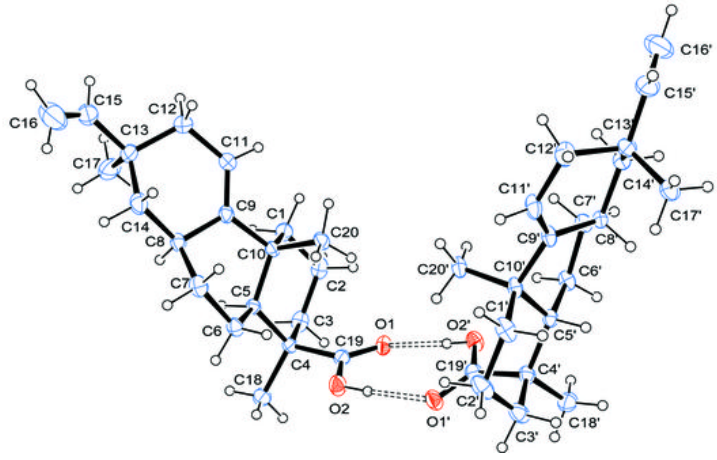
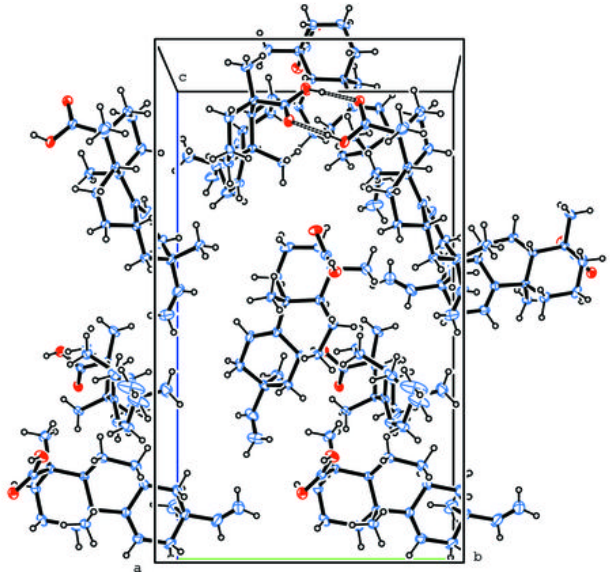


Fig. 2



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1,3-Dibenzyl-1,2,3,4-tetrahydroquinazoline-2,4-dione

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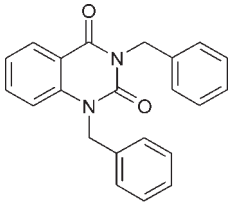
Key indicators: single-crystal X-ray study; T = 293 K; mean σ(C–C) = 0.003 Å; R factor = 0.041; wR factor = 0.112; data-to-parameter ratio = 15.1.

The asymmetric unit of the title compound, $C_{22}H_{18}N_2O_2$, contains two independent molecules, which differ in the orientations of the benzyl groups with respect to the planar (r.m.s. deviations of 0.031 and 0.020 Å) quinazoline-2,4-dione skeletons [dihedral angles of 73.97 (4) and 70.07 (4)° in the first molecule and 75.63 (4) and 63.52 (3)° in the second]. The crystal structure is stabilized by weak intermolecular C—H···O and C—H···π interactions and aromatic π–π stacking interactions [centroid–centroid distance = 3.735 (2) Å].

Related literature

For the synthesis of the title compound, see: Hedayatullah (1981). For the synthesis of quinazoline-2,4-dione derivatives, see: Shi *et al.* (2007); Kuryazov *et al.* (2008). For the biological activity of quinazoline-2,4-dione derivatives, see: Colottaa *et al.* (2004); Yakhontov *et al.* (1977). For related structures, see: Mazza *et al.* (1988). For bond-length data, see: Allen *et al.* (1987).



Experimental

Crystal data

$C_{22}H_{18}N_2O_2$
M_r = 342.38
Orthorhombic, *Pbca*
a = 17.8989 (4) Å
b = 14.0071 (4) Å
c = 27.7222 (6) Å
V = 6950.3 (3) Å^3
Z = 16
Cu $K\alpha$ radiation
μ = 0.68 mm^{-1}
T = 293 K
0.5 × 0.4 × 0.35 mm

Data collection

Oxford Diffraction Xcalibur Ruby diffractometer
Absorption correction: multi-scan (*CrysAlis PRO*; Oxford Diffraction, 2009)
T_{min} = 0.804, T_{max} = 1.000
18947 measured reflections
7088 independent reflections
4141 reflections with $I > 2\sigma(I)$
R_{int} = 0.030

Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.041
$wR(F^2)$ = 0.112
S = 0.90
7088 reflections
470 parameters
H-atom parameters constrained
$\Delta\rho_{max}$ = 0.28 e Å^{-3}
$\Delta\rho_{min}$ = −0.14 e Å^{-3}

Table 1
Hydrogen-bond geometry (Å, °).

*Cg*4 and *Cg*8 are the centroids of the C17*A*–C22*A* and C10*B*–C15*B* rings, respectively.

D—H···A	D—H	H···A	D···A	D—H···A
C19*A*—H19*A*···O2b^{i}	0.93	2.70	3.419 (3)	134
C6*B*—H6*B*···C11a^{ii}	0.93	2.89	3.604 (3)	134
C21*B*—H21*B*···C11a^{iii}	0.93	2.80	3.600 (3)	145
C19*A*—H19*A*···O2b^{i}	0.93	2.70	3.419 (3)	134
C7*B*—H7*B*···*Cg*4	0.93	2.78	3.586 (2)	146
C5*A*—H5*A*···*Cg*8^{ii}	0.93	2.90	3.641 (2)	138

Symmetry codes: (i) $x+\frac{1}{2}, y, -z+\frac{3}{2}$; (ii) $-x+\frac{3}{2}, y-\frac{1}{2}, z$; (iii) $x-\frac{1}{2}, y, -z+\frac{3}{2}$.

Data collection: *CrysAlis PRO* (Oxford Diffraction, 2009); cell refinement: *CrysAlis PRO*; data reduction: *CrysAlis PRO*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *XP* in *SHELXTL* (Sheldrick, 2008); software used to prepare material for publication: *SHELXL97*.

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Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: FJ2301).

References

Allen, F. H., Kennard, O., Watson, D. G., Brammer, L., Orpen, G. & Taylor, R. (1987). *J. Chem. Soc. Perkin Trans. 2*, pp. S1–19.
Colottaa, V., Catarzia, D., Varanoa, F., Calabria, F. R., Filacchionia, G., Costaglib, C. & Gallib, A. (2004). *Bioorg. Med. Chem. Lett.* **14**, 2345–2349.
Hedayatullah, M. (1981). *J. Heterocycl. Chem.* **18**, 339–342.
Kuryazov, R. Sh., Mukhamedov, N. S. & Shakhidoyatov, Kh. M. (2008). *Chem. Heterocycl. Compd*, **44**, 324–329.
Mazza, F., Pochetti, G., Pinnen, F. & Lucente, G. (1988). *Acta Cryst.* C**44**, 1014–1017.
Oxford Diffraction (2009). *CrysAlis PRO*. Oxford Diffraction Ltd, Yarnton, England.
Sheldrick, G. M. (2008). *Acta Cryst.* A**64**, 112–122.
Shi, D.-Q., Dou, G.-L., Li, Z.-Y., Ni, S.-N., Li, X.-Y., Wang, X.-S., Wu, H. & Ji, S.-J. (2007). *Tetrahedron*, **63**, 9764–9773.
Yakhontov, L. N., Liberman, S. S., Zhikhareva, G. P. & Kuzmina, K. K. (1977). *Pharm. Chem. J.* **11**, 598–612.

supplementary materials

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1,3-Dibenzyl-1,2,3,4-tetrahydroquinazoline-2,4-dione

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Comment

Quinazoline-2,4-diones have been frequently used as intermediates and synthetic precursors for the preparation of a wide variety of heterocyclic compounds (Kuryazov *et al.*, 2008). In addition, they possess different biological activities (Colottaa *et al.*, 2004; Yakhontov *et al.*, 1977).

The title compound consists of a quinazoline-2,4-dione skeleton with two benzyl groups. The asymmetric unit contains two molecules of 1,2,3,4-tetrahydro-1,3-dibenzylquinazoline-2,4-dione (Fig.1). Orientation of benzyl groups with respect to the planar quinazoline-2,4-dione skeletons are different for independent molecules. Dihedral angles between planar quinazoline-2,4-dione system and benzyl group planes are 73.97 (4)° and 70.07 (4)° (for molecule A) and 75.63 (4)° and 63.52 (3)° (for molecule B). Torsion angles responsible for orientation of benzyl groups are shown in table 1. (In order compare torsions between A and B independent molecules must be taken absolute values of torsion angles).

Quinazoline-2,4-dione system of the molecules are packed into sheets along *b* axis by a aromatic π–π stacking interaction. The benzene rings in the quinazoline-2,4-dione system standing nearly parallel (molecules A and B) are separated with distance of 3.477 (2) Å and benzene ring-centroid separation is 3.735 (2) Å with ring offset of 1.364 (2) Å. This distances for molecules of A at (*x*,*y*,*z*) and B at (1.5 - *x*, 1/2 + *y*, *z*) are 3.493 (2) Å, 3.791 (2) Å and 1.473 (2) Å.

The observed structure is stabilized by weak C—H···O and C—H···C_{ar} type hydrogen bonds (Table 2). The bond distances and angles in organic compound molecules are in normal ranges (Allen *et al.*, 1987).

Experimental

To suspension of 1*H*-quinazoline-2,4-dione (1.62 g) in 40 ml benzene was added 10% aqueous solution of sodium hydroxide (40 ml), tetrabutylammonium bromide (1.29 g, 4 mmol) and benzyl chloride (3.80 g, 30 mmol). The mixture was heated until 60° C and helded out for 6 h (Hedayatullah, 1981). The organic layer was separated, washed with water until neutral reaction and dryed with Na_2SO_4, benzene was evaporated. Residue was recrystallized from benzene and obtained in 88% yield (3.02 g) of title compound. Colorless crystals suitable for X-ray analysis were obtained from dimethylformamide by slow evaporation.

Refinement

Carbon-bound H atoms were positioned geometrically and treated as riding on their C atoms, with C—H distances of 0.93 Å (aromatic) and 0.97 Å (CH_2) and were refined with U_{iso}(H)=1.2Ueq(C).

Figures

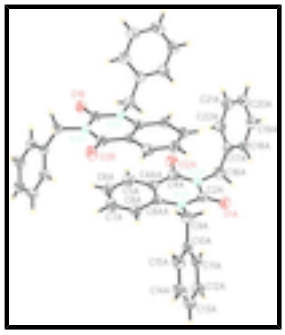


Fig. 1. Asymmetric unit of cell with atom labels and 30% probability displacement ellipsoids for non-H atoms.

1,3-Dibenzyl-1,2,3,4-tetrahydroquinazoline-2,4-dione

Crystal data

$C_{22}H_{18}N_2O_2$	D_x = 1.309 Mg m^{-3}
M_r = 342.38	Melting point: 398(2) K
Orthorhombic, *Pbca*	Cu *K*α radiation, λ = 1.54184 Å
Hall symbol: -P 2ac 2ab	Cell parameters from 2463 reflections
a = 17.8989 (4) Å	θ = 3.5–35.8°
b = 14.0071 (4) Å	μ = 0.68 mm^{-1}
c = 27.7222 (6) Å	*T* = 293 K
V = 6950.3 (3) Å^3	Prism, colourless
Z = 16	0.5 × 0.4 × 0.35 mm
F(000) = 2880	

Data collection

Oxford Diffraction Xcalibur Ruby diffractometer	7088 independent reflections
Radiation source: Enhance (Cu) X-ray Source	4141 reflections with $I > 2\sigma(I)$
graphite	R_{int} = 0.030
Detector resolution: 10.2576 pixels mm^{-1}	θ_{max} = 75.8°, θ_{min} = 4.0°
ω scans	*h* = −22→18
Absorption correction: multi-scan (*CrysAlis PRO*; Oxford Diffraction, 2009)	*k* = −11→17
T_{min} = 0.804, T_{max} = 1.000	*l* = −31→34
18947 measured reflections	

Refinement

Refinement on F^2	Secondary atom site location: difference Fourier map
Least-squares matrix: full	Hydrogen site location: inferred from neighbouring sites
$R[F^2 > 2\sigma(F^2)]$ = 0.041	H-atom parameters constrained
$wR(F^2)$ = 0.112	$w = 1/[\sigma^2(F_o^2) + (0.0587P)^2]$

	where $P = (F_o^2 + 2F_c^2)/3$
$S = 0.90$	$(\Delta/\sigma)_{max} = 0.002$
7088 reflections	$\Delta\rho_{max} = 0.28$ e Å^{-3}
470 parameters	$\Delta\rho_{min} = -0.14$ e Å^{-3}
0 restraints	Extinction correction: *SHELXL97* (Sheldrick, 2008), $Fc^*=kFc[1+0.001xFc^2\lambda^3/\sin(2\theta)]^{-1/4}$
Primary atom site location: structure-invariant direct methods	Extinction coefficient: 0.00081 (5)

Special details

Geometry. All e.s.d.'s (except the e.s.d. in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell e.s.d.'s are taken into account individually in the estimation of e.s.d.'s in distances, angles and torsion angles; correlations between e.s.d.'s in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell e.s.d.'s is used for estimating e.s.d.'s involving l.s. planes.

Refinement. Refinement of F^2 against ALL reflections. The weighted *R*-factor *wR* and goodness of fit *S* are based on F^2, conventional *R*-factors *R* are based on *F*, with *F* set to zero for negative F^2. The threshold expression of $F^2 > \sigma(F^2)$ is used only for calculating *R*-factors(gt) *etc*. and is not relevant to the choice of reflections for refinement. *R*-factors based on F^2 are statistically about twice as large as those based on *F*, and *R*- factors based on ALL data will be even larger.

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å^2)

	x	*y*	*z*	U_{iso}*/U_{eq}
O1A	0.90039 (7)	0.27786 (11)	0.72998 (5)	0.0745 (4)
O2A	0.85328 (8)	0.30319 (11)	0.89063 (5)	0.0770 (4)
N1A	0.77945 (8)	0.27259 (10)	0.75417 (5)	0.0498 (4)
N3A	0.87693 (8)	0.29234 (10)	0.81052 (6)	0.0531 (4)
C2A	0.85450 (10)	0.28112 (13)	0.76252 (7)	0.0538 (5)
C4A	0.82872 (11)	0.29654 (13)	0.84973 (7)	0.0542 (5)
C4AA	0.74920 (10)	0.29394 (11)	0.83793 (6)	0.0476 (4)
C5A	0.69582 (11)	0.30185 (13)	0.87449 (7)	0.0596 (5)
H5A	0.7113	0.3091	0.9063	0.072*
C6A	0.62102 (11)	0.29916 (14)	0.86422 (8)	0.0639 (5)
H6A	0.5859	0.3033	0.8888	0.077*
C7A	0.59835 (11)	0.29017 (13)	0.81658 (8)	0.0627 (5)
H7A	0.5476	0.2894	0.8094	0.075*
C8A	0.64939 (10)	0.28232 (13)	0.77977 (7)	0.0563 (5)
H8A	0.6332	0.2767	0.7480	0.068*
C8AA	0.72575 (9)	0.28287 (11)	0.79034 (6)	0.0454 (4)
C9A	0.75706 (10)	0.24198 (13)	0.70537 (6)	0.0531 (4)
H9AA	0.7164	0.1965	0.7084	0.064*
H9AB	0.7988	0.2089	0.6906	0.064*
C10A	0.73253 (9)	0.32101 (13)	0.67192 (6)	0.0480 (4)
C11A	0.76693 (11)	0.40913 (13)	0.67155 (7)	0.0583 (5)
H11A	0.8039	0.4228	0.6941	0.070*
C12A	0.74673 (12)	0.47754 (15)	0.63777 (8)	0.0722 (6)
H12A	0.7701	0.5368	0.6377	0.087*

C13A	0.69229 (13)	0.45750 (18)	0.60452 (8)	0.0775 (7)
H13A	0.6785	0.5035	0.5820	0.093*
C14A	0.65844 (13)	0.37067 (19)	0.60429 (8)	0.0801 (7)
H14A	0.6220	0.3572	0.5814	0.096*
C15A	0.67784 (11)	0.30240 (16)	0.63795 (7)	0.0671 (5)
H15A	0.6539	0.2434	0.6378	0.081*
C16A	0.95826 (10)	0.29432 (13)	0.81973 (8)	0.0627 (5)
H16A	0.9681	0.3332	0.8480	0.075*
H16C	0.9834	0.3235	0.7925	0.075*
C17A	0.98951 (9)	0.19523 (13)	0.82771 (7)	0.0530 (4)
C18A	1.00645 (10)	0.13649 (14)	0.78927 (8)	0.0617 (5)
H18A	1.0011	0.1593	0.7579	0.074*
C19A	1.03111 (11)	0.04455 (16)	0.79674 (9)	0.0748 (6)
H19A	1.0409	0.0049	0.7706	0.090*
C20A	1.04120 (12)	0.01171 (18)	0.84297 (10)	0.0873 (7)
H20A	1.0579	−0.0503	0.8481	0.105*
C21A	1.02667 (12)	0.07020 (18)	0.88159 (9)	0.0853 (7)
H21A	1.0346	0.0482	0.9128	0.102*
C22A	1.00042 (10)	0.16140 (16)	0.87410 (7)	0.0684 (6)
H22A	0.9900	0.2005	0.9004	0.082*
O1B	0.61180 (7)	0.06448 (9)	0.98324 (5)	0.0633 (4)
O2B	0.54505 (7)	0.03102 (10)	0.82607 (5)	0.0668 (4)
N1B	0.70512 (7)	0.06323 (10)	0.92718 (5)	0.0467 (3)
N3B	0.57889 (7)	0.04627 (9)	0.90467 (5)	0.0455 (3)
C2B	0.63124 (9)	0.05873 (12)	0.94108 (7)	0.0480 (4)
C4AB	0.67396 (9)	0.04264 (11)	0.84349 (6)	0.0444 (4)
C4B	0.59496 (9)	0.03999 (12)	0.85581 (6)	0.0476 (4)
C5B	0.69580 (10)	0.03363 (12)	0.79517 (6)	0.0542 (5)
H5B	0.6597	0.0278	0.7712	0.065*
C6B	0.76984 (11)	0.03330 (13)	0.78293 (7)	0.0599 (5)
H6B	0.7842	0.0264	0.7509	0.072*
C7B	0.82289 (10)	0.04332 (13)	0.81853 (7)	0.0576 (5)
H7B	0.8732	0.0429	0.8102	0.069*
C8AB	0.72776 (9)	0.05321 (11)	0.87922 (6)	0.0435 (4)
C8B	0.80291 (9)	0.05388 (12)	0.86611 (7)	0.0533 (4)
H8B	0.8396	0.0615	0.8896	0.064*
C9B	0.76085 (10)	0.07851 (12)	0.96557 (6)	0.0545 (5)
H9B	0.7359	0.1041	0.9938	0.065*
H9D	0.7968	0.1257	0.9547	0.065*
C10B	0.80190 (10)	−0.01121 (13)	0.97963 (6)	0.0498 (4)
C11B	0.76367 (11)	−0.08904 (13)	0.99740 (7)	0.0588 (5)
H11B	0.7120	−0.0862	1.0005	0.071*
C12B	0.80122 (13)	−0.17137 (15)	1.01063 (8)	0.0711 (6)
H12B	0.7749	−0.2229	1.0233	0.085*
C13B	0.87748 (13)	−0.17699 (17)	1.00508 (8)	0.0769 (6)
H13B	0.9026	−0.2329	1.0131	0.092*
C14B	0.91636 (12)	−0.09989 (17)	0.98765 (8)	0.0736 (6)
H14B	0.9679	−0.1035	0.9840	0.088*
C15B	0.87924 (10)	−0.01730 (15)	0.97548 (7)	0.0617 (5)

H15B	0.9061	0.0351	0.9644	0.074*
C16B	0.50000 (9)	0.03632 (12)	0.91967 (7)	0.0511 (4)
H16B	0.4981	−0.0001	0.9494	0.061*
H16D	0.4733	0.0004	0.8952	0.061*
C17B	0.46085 (8)	0.13002 (12)	0.92738 (6)	0.0458 (4)
C18B	0.44536 (10)	0.16354 (14)	0.97336 (7)	0.0588 (5)
H18B	0.4611	0.1286	1.0000	0.071*
C19B	0.40708 (11)	0.24777 (15)	0.98023 (8)	0.0698 (6)
H19B	0.3966	0.2689	1.0113	0.084*
C20B	0.38446 (11)	0.30048 (14)	0.94116 (8)	0.0667 (6)
H20B	0.3591	0.3577	0.9456	0.080*
C21B	0.39945 (10)	0.26832 (14)	0.89542 (8)	0.0636 (5)
H21B	0.3841	0.3040	0.8689	0.076*
C22B	0.43716 (10)	0.18334 (13)	0.88838 (7)	0.0546 (4)
H22B	0.4466	0.1620	0.8572	0.066*

Atomic displacement parameters (Å^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
O1A	0.0545 (8)	0.1060 (12)	0.0629 (9)	0.0081 (8)	0.0042 (7)	0.0195 (8)
O2A	0.0782 (10)	0.0927 (11)	0.0600 (8)	0.0061 (8)	−0.0186 (8)	−0.0133 (8)
N1A	0.0497 (8)	0.0526 (8)	0.0470 (8)	−0.0007 (7)	−0.0019 (7)	0.0021 (7)
N3A	0.0485 (8)	0.0514 (9)	0.0592 (9)	−0.0013 (7)	−0.0091 (7)	0.0050 (7)
C2A	0.0508 (10)	0.0543 (11)	0.0564 (11)	0.0043 (8)	−0.0011 (9)	0.0129 (9)
C4A	0.0613 (11)	0.0454 (10)	0.0558 (11)	0.0007 (9)	−0.0080 (10)	−0.0016 (9)
C4AA	0.0562 (10)	0.0357 (8)	0.0509 (10)	0.0001 (8)	−0.0025 (8)	−0.0001 (8)
C5A	0.0755 (13)	0.0490 (11)	0.0544 (11)	−0.0009 (10)	0.0017 (10)	−0.0074 (9)
C6A	0.0621 (12)	0.0599 (12)	0.0699 (13)	−0.0041 (10)	0.0134 (11)	−0.0085 (10)
C7A	0.0521 (11)	0.0594 (12)	0.0765 (14)	−0.0048 (9)	0.0008 (10)	−0.0087 (11)
C8A	0.0519 (10)	0.0581 (11)	0.0589 (11)	−0.0027 (9)	−0.0024 (9)	−0.0011 (10)
C8AA	0.0496 (9)	0.0364 (8)	0.0501 (10)	−0.0015 (7)	0.0003 (8)	0.0025 (8)
C9A	0.0567 (10)	0.0526 (10)	0.0500 (10)	0.0017 (9)	−0.0012 (9)	−0.0030 (9)
C10A	0.0447 (9)	0.0556 (10)	0.0436 (9)	0.0055 (8)	0.0024 (8)	−0.0033 (8)
C11A	0.0571 (11)	0.0617 (12)	0.0561 (11)	0.0052 (9)	−0.0041 (9)	−0.0008 (10)
C12A	0.0811 (15)	0.0588 (12)	0.0766 (14)	0.0096 (11)	0.0074 (12)	0.0109 (11)
C13A	0.0798 (15)	0.0928 (17)	0.0599 (13)	0.0336 (14)	0.0013 (12)	0.0178 (13)
C14A	0.0747 (15)	0.1002 (18)	0.0653 (14)	0.0219 (14)	−0.0215 (12)	−0.0031 (14)
C15A	0.0579 (11)	0.0750 (14)	0.0684 (13)	0.0040 (10)	−0.0115 (10)	−0.0061 (11)
C16A	0.0493 (10)	0.0628 (12)	0.0758 (14)	−0.0107 (9)	−0.0113 (10)	0.0083 (10)
C17A	0.0356 (8)	0.0619 (11)	0.0616 (11)	−0.0065 (8)	−0.0052 (8)	0.0112 (10)
C18A	0.0470 (10)	0.0761 (14)	0.0621 (12)	−0.0012 (10)	0.0051 (9)	0.0156 (11)
C19A	0.0567 (12)	0.0811 (15)	0.0867 (16)	0.0119 (11)	0.0168 (11)	0.0081 (13)
C20A	0.0631 (14)	0.0857 (17)	0.113 (2)	0.0246 (12)	0.0145 (14)	0.0336 (16)
C21A	0.0695 (14)	0.110 (2)	0.0764 (16)	0.0181 (14)	0.0016 (12)	0.0386 (15)
C22A	0.0568 (12)	0.0878 (15)	0.0607 (12)	0.0031 (11)	−0.0043 (10)	0.0106 (12)
O1B	0.0576 (8)	0.0803 (9)	0.0520 (8)	0.0075 (7)	0.0021 (6)	0.0003 (7)
O2B	0.0490 (7)	0.0854 (10)	0.0661 (8)	−0.0013 (7)	−0.0096 (7)	−0.0101 (7)
N1B	0.0412 (7)	0.0463 (8)	0.0525 (8)	0.0014 (6)	−0.0047 (6)	−0.0038 (7)

N3B	0.0388 (7)	0.0430 (8)	0.0545 (9)	0.0020 (6)	−0.0008 (6)	0.0011 (7)
C2B	0.0468 (9)	0.0414 (9)	0.0558 (11)	0.0049 (8)	−0.0025 (8)	0.0012 (8)
C4AB	0.0451 (9)	0.0342 (8)	0.0539 (10)	0.0011 (7)	−0.0002 (8)	−0.0014 (8)
C4B	0.0430 (9)	0.0424 (9)	0.0573 (11)	0.0001 (8)	−0.0052 (8)	−0.0026 (8)
C5B	0.0563 (11)	0.0509 (10)	0.0556 (11)	0.0017 (9)	−0.0021 (9)	−0.0032 (9)
C6B	0.0647 (12)	0.0540 (11)	0.0610 (12)	0.0016 (9)	0.0103 (10)	0.0006 (10)
C7B	0.0469 (10)	0.0493 (10)	0.0766 (14)	−0.0005 (8)	0.0122 (9)	0.0075 (10)
C8AB	0.0410 (9)	0.0329 (8)	0.0567 (10)	−0.0001 (7)	−0.0021 (8)	0.0006 (8)
C8B	0.0426 (9)	0.0503 (10)	0.0670 (12)	−0.0011 (8)	−0.0036 (9)	0.0051 (9)
C9B	0.0515 (10)	0.0515 (10)	0.0605 (11)	0.0012 (8)	−0.0098 (9)	−0.0124 (9)
C10B	0.0493 (10)	0.0514 (10)	0.0486 (10)	0.0019 (8)	−0.0101 (8)	−0.0098 (8)
C11B	0.0569 (11)	0.0610 (12)	0.0584 (11)	0.0023 (9)	−0.0048 (9)	−0.0066 (10)
C12B	0.0818 (15)	0.0609 (13)	0.0704 (13)	0.0033 (11)	−0.0094 (12)	0.0060 (11)
C13B	0.0835 (16)	0.0728 (15)	0.0745 (15)	0.0234 (13)	−0.0169 (13)	0.0020 (12)
C14B	0.0555 (12)	0.0895 (16)	0.0759 (14)	0.0186 (12)	−0.0117 (11)	0.0002 (13)
C15B	0.0499 (11)	0.0696 (13)	0.0654 (12)	0.0003 (10)	−0.0100 (9)	−0.0030 (10)
C16B	0.0393 (9)	0.0478 (10)	0.0662 (12)	−0.0032 (8)	0.0020 (8)	0.0087 (9)
C17B	0.0338 (8)	0.0465 (10)	0.0570 (10)	−0.0023 (7)	0.0011 (8)	0.0081 (8)
C18B	0.0556 (11)	0.0633 (12)	0.0574 (12)	0.0069 (9)	0.0038 (9)	0.0122 (10)
C19B	0.0674 (13)	0.0741 (14)	0.0679 (14)	0.0142 (11)	0.0075 (11)	−0.0061 (12)
C20B	0.0549 (11)	0.0543 (12)	0.0908 (16)	0.0124 (9)	0.0031 (11)	−0.0005 (11)
C21B	0.0558 (11)	0.0586 (12)	0.0764 (14)	0.0083 (9)	−0.0088 (10)	0.0154 (11)
C22B	0.0502 (10)	0.0575 (11)	0.0561 (11)	0.0037 (9)	−0.0032 (9)	0.0078 (9)

Geometric parameters (Å, °)

O1A—C2A	1.221 (2)	O1B—C2B	1.222 (2)
O2A—C4A	1.220 (2)	O2B—C4B	1.2222 (19)
N1A—C2A	1.368 (2)	N1B—C2B	1.379 (2)
N1A—C8AA	1.397 (2)	N1B—C8AB	1.397 (2)
N1A—C9A	1.474 (2)	N1B—C9B	1.474 (2)
N3A—C4A	1.389 (2)	N3B—C4B	1.387 (2)
N3A—C2A	1.399 (2)	N3B—C2B	1.388 (2)
N3A—C16A	1.478 (2)	N3B—C16B	1.479 (2)
C4A—C4AA	1.461 (2)	C4AB—C8AB	1.389 (2)
C4AA—C8AA	1.393 (2)	C4AB—C5B	1.401 (2)
C4AA—C5A	1.397 (2)	C4AB—C4B	1.455 (2)
C5A—C6A	1.369 (3)	C5B—C6B	1.368 (2)
C5A—H5A	0.9300	C5B—H5B	0.9300
C6A—C7A	1.387 (3)	C6B—C7B	1.377 (3)
C6A—H6A	0.9300	C6B—H6B	0.9300
C7A—C8A	1.374 (2)	C7B—C8B	1.375 (2)
C7A—H7A	0.9300	C7B—H7B	0.9300
C8A—C8AA	1.398 (2)	C8AB—C8B	1.393 (2)
C8A—H8A	0.9300	C8B—H8B	0.9300
C9A—C10A	1.510 (2)	C9B—C10B	1.507 (2)
C9A—H9AA	0.9700	C9B—H9B	0.9700
C9A—H9AB	0.9700	C9B—H9D	0.9700
C10A—C11A	1.379 (2)	C10B—C11B	1.378 (2)

C10A—C15A	1.383 (2)	C10B—C15B	1.392 (2)
C11A—C12A	1.388 (3)	C11B—C12B	1.384 (3)
C11A—H11A	0.9300	C11B—H11B	0.9300
C12A—C13A	1.370 (3)	C12B—C13B	1.376 (3)
C12A—H12A	0.9300	C12B—H12B	0.9300
C13A—C14A	1.359 (3)	C13B—C14B	1.373 (3)
C13A—H13A	0.9300	C13B—H13B	0.9300
C14A—C15A	1.380 (3)	C14B—C15B	1.376 (3)
C14A—H14A	0.9300	C14B—H14B	0.9300
C15A—H15A	0.9300	C15B—H15B	0.9300
C16A—C17A	1.513 (2)	C16B—C17B	1.503 (2)
C16A—H16A	0.9700	C16B—H16B	0.9700
C16A—H16C	0.9700	C16B—H16D	0.9700
C17A—C18A	1.380 (3)	C17B—C22B	1.381 (2)
C17A—C22A	1.384 (3)	C17B—C18B	1.386 (2)
C18A—C19A	1.377 (3)	C18B—C19B	1.378 (2)
C18A—H18A	0.9300	C18B—H18B	0.9300
C19A—C20A	1.374 (3)	C19B—C20B	1.372 (3)
C19A—H19A	0.9300	C19B—H19B	0.9300
C20A—C21A	1.373 (3)	C20B—C21B	1.372 (3)
C20A—H20A	0.9300	C20B—H20B	0.9300
C21A—C22A	1.377 (3)	C21B—C22B	1.382 (2)
C21A—H21A	0.9300	C21B—H21B	0.9300
C22A—H22A	0.9300	C22B—H22B	0.9300
C2A—N1A—C8AA	123.03 (15)	C2B—N1B—C8AB	122.66 (14)
C2A—N1A—C9A	116.58 (15)	C2B—N1B—C9B	116.98 (14)
C8AA—N1A—C9A	120.11 (14)	C8AB—N1B—C9B	120.36 (14)
C4A—N3A—C2A	124.81 (15)	C4B—N3B—C2B	125.30 (14)
C4A—N3A—C16A	118.42 (15)	C4B—N3B—C16B	117.80 (14)
C2A—N3A—C16A	116.68 (16)	C2B—N3B—C16B	116.87 (14)
O1A—C2A—N1A	122.15 (17)	O1B—C2B—N1B	122.51 (16)
O1A—C2A—N3A	120.93 (17)	O1B—C2B—N3B	120.76 (16)
N1A—C2A—N3A	116.91 (16)	N1B—C2B—N3B	116.73 (15)
O2A—C4A—N3A	120.45 (18)	C8AB—C4AB—C5B	119.85 (16)
O2A—C4A—C4AA	124.14 (18)	C8AB—C4AB—C4B	120.59 (16)
N3A—C4A—C4AA	115.41 (16)	C5B—C4AB—C4B	119.56 (16)
C8AA—C4AA—C5A	119.31 (16)	O2B—C4B—N3B	120.91 (15)
C8AA—C4AA—C4A	120.56 (16)	O2B—C4B—C4AB	123.68 (17)
C5A—C4AA—C4A	120.13 (16)	N3B—C4B—C4AB	115.40 (15)
C6A—C5A—C4AA	121.04 (18)	C6B—C5B—C4AB	120.52 (17)
C6A—C5A—H5A	119.5	C6B—C5B—H5B	119.7
C4AA—C5A—H5A	119.5	C4AB—C5B—H5B	119.7
C5A—C6A—C7A	119.11 (19)	C5B—C6B—C7B	119.34 (18)
C5A—C6A—H6A	120.4	C5B—C6B—H6B	120.3
C7A—C6A—H6A	120.4	C7B—C6B—H6B	120.3
C8A—C7A—C6A	121.32 (18)	C8B—C7B—C6B	121.30 (18)
C8A—C7A—H7A	119.3	C8B—C7B—H7B	119.4
C6A—C7A—H7A	119.3	C6B—C7B—H7B	119.4
C7A—C8A—C8AA	119.60 (18)	C4AB—C8AB—C8B	118.93 (16)

C7A—C8A—H8A	120.2	C4AB—C8AB—N1B	119.22 (15)
C8AA—C8A—H8A	120.2	C8B—C8AB—N1B	121.84 (15)
C4AA—C8AA—N1A	118.95 (15)	C7B—C8B—C8AB	120.05 (17)
C4AA—C8AA—C8A	119.60 (17)	C7B—C8B—H8B	120.0
N1A—C8AA—C8A	121.45 (16)	C8AB—C8B—H8B	120.0
N1A—C9A—C10A	115.43 (14)	N1B—C9B—C10B	113.29 (14)
N1A—C9A—H9AA	108.4	N1B—C9B—H9B	108.9
C10A—C9A—H9AA	108.4	C10B—C9B—H9B	108.9
N1A—C9A—H9AB	108.4	N1B—C9B—H9D	108.9
C10A—C9A—H9AB	108.4	C10B—C9B—H9D	108.9
H9AA—C9A—H9AB	107.5	H9B—C9B—H9D	107.7
C11A—C10A—C15A	118.66 (18)	C11B—C10B—C15B	118.35 (17)
C11A—C10A—C9A	122.06 (16)	C11B—C10B—C9B	120.66 (16)
C15A—C10A—C9A	119.08 (17)	C15B—C10B—C9B	120.98 (17)
C10A—C11A—C12A	120.43 (19)	C10B—C11B—C12B	120.85 (19)
C10A—C11A—H11A	119.8	C10B—C11B—H11B	119.6
C12A—C11A—H11A	119.8	C12B—C11B—H11B	119.6
C13A—C12A—C11A	119.9 (2)	C13B—C12B—C11B	120.0 (2)
C13A—C12A—H12A	120.1	C13B—C12B—H12B	120.0
C11A—C12A—H12A	120.1	C11B—C12B—H12B	120.0
C14A—C13A—C12A	120.2 (2)	C14B—C13B—C12B	119.8 (2)
C14A—C13A—H13A	119.9	C14B—C13B—H13B	120.1
C12A—C13A—H13A	119.9	C12B—C13B—H13B	120.1
C13A—C14A—C15A	120.3 (2)	C13B—C14B—C15B	120.2 (2)
C13A—C14A—H14A	119.8	C13B—C14B—H14B	119.9
C15A—C14A—H14A	119.8	C15B—C14B—H14B	119.9
C14A—C15A—C10A	120.5 (2)	C14B—C15B—C10B	120.8 (2)
C14A—C15A—H15A	119.7	C14B—C15B—H15B	119.6
C10A—C15A—H15A	119.7	C10B—C15B—H15B	119.6
N3A—C16A—C17A	111.85 (14)	N3B—C16B—C17B	113.76 (13)
N3A—C16A—H16A	109.2	N3B—C16B—H16B	108.8
C17A—C16A—H16A	109.2	C17B—C16B—H16B	108.8
N3A—C16A—H16C	109.2	N3B—C16B—H16D	108.8
C17A—C16A—H16C	109.2	C17B—C16B—H16D	108.8
H16A—C16A—H16C	107.9	H16B—C16B—H16D	107.7
C18A—C17A—C22A	118.84 (19)	C22B—C17B—C18B	118.39 (16)
C18A—C17A—C16A	121.02 (17)	C22B—C17B—C16B	120.26 (16)
C22A—C17A—C16A	120.13 (19)	C18B—C17B—C16B	121.31 (16)
C19A—C18A—C17A	120.79 (19)	C19B—C18B—C17B	121.10 (18)
C19A—C18A—H18A	119.6	C19B—C18B—H18B	119.5
C17A—C18A—H18A	119.6	C17B—C18B—H18B	119.5
C20A—C19A—C18A	119.7 (2)	C20B—C19B—C18B	119.9 (2)
C20A—C19A—H19A	120.1	C20B—C19B—H19B	120.0
C18A—C19A—H19A	120.1	C18B—C19B—H19B	120.0
C21A—C20A—C19A	120.2 (2)	C19B—C20B—C21B	119.68 (18)
C21A—C20A—H20A	119.9	C19B—C20B—H20B	120.2
C19A—C20A—H20A	119.9	C21B—C20B—H20B	120.2
C20A—C21A—C22A	120.1 (2)	C20B—C21B—C22B	120.58 (19)
C20A—C21A—H21A	120.0	C20B—C21B—H21B	119.7

C22A—C21A—H21A	120.0	C22B—C21B—H21B	119.7
C21A—C22A—C17A	120.4 (2)	C17B—C22B—C21B	120.34 (18)
C21A—C22A—H22A	119.8	C17B—C22B—H22B	119.8
C17A—C22A—H22A	119.8	C21B—C22B—H22B	119.8
C8AA—N1A—C2A—O1A	−175.32 (16)	C8AB—N1B—C2B—O1B	177.61 (15)
C9A—N1A—C2A—O1A	10.7 (3)	C9B—N1B—C2B—O1B	−1.9 (2)
C8AA—N1A—C2A—N3A	5.7 (3)	C8AB—N1B—C2B—N3B	−1.8 (2)
C9A—N1A—C2A—N3A	−168.28 (14)	C9B—N1B—C2B—N3B	178.73 (13)
C4A—N3A—C2A—O1A	−179.83 (17)	C4B—N3B—C2B—O1B	179.24 (16)
C16A—N3A—C2A—O1A	−3.4 (3)	C16B—N3B—C2B—O1B	−2.5 (2)
C4A—N3A—C2A—N1A	−0.8 (3)	C4B—N3B—C2B—N1B	−1.4 (2)
C16A—N3A—C2A—N1A	175.60 (15)	C16B—N3B—C2B—N1B	176.87 (13)
C2A—N3A—C4A—O2A	177.49 (17)	C2B—N3B—C4B—O2B	−178.43 (16)
C16A—N3A—C4A—O2A	1.1 (3)	C16B—N3B—C4B—O2B	3.4 (2)
C2A—N3A—C4A—C4AA	−3.4 (3)	C2B—N3B—C4B—C4AB	2.9 (2)
C16A—N3A—C4A—C4AA	−179.81 (14)	C16B—N3B—C4B—C4AB	−175.28 (13)
O2A—C4A—C4AA—C8AA	−177.75 (17)	C8AB—C4AB—C4B—O2B	179.88 (16)
N3A—C4A—C4AA—C8AA	3.2 (2)	C5B—C4AB—C4B—O2B	−0.7 (3)
O2A—C4A—C4AA—C5A	1.8 (3)	C8AB—C4AB—C4B—N3B	−1.5 (2)
N3A—C4A—C4AA—C5A	−177.27 (15)	C5B—C4AB—C4B—N3B	177.94 (15)
C8AA—C4AA—C5A—C6A	−0.2 (3)	C8AB—C4AB—C5B—C6B	1.3 (3)
C4A—C4AA—C5A—C6A	−179.71 (17)	C4B—C4AB—C5B—C6B	−178.20 (16)
C4AA—C5A—C6A—C7A	−1.2 (3)	C4AB—C5B—C6B—C7B	−0.9 (3)
C5A—C6A—C7A—C8A	1.1 (3)	C5B—C6B—C7B—C8B	−0.2 (3)
C6A—C7A—C8A—C8AA	0.3 (3)	C5B—C4AB—C8AB—C8B	−0.5 (2)
C5A—C4AA—C8AA—N1A	−178.40 (15)	C4B—C4AB—C8AB—C8B	178.98 (15)
C4A—C4AA—C8AA—N1A	1.1 (2)	C5B—C4AB—C8AB—N1B	179.26 (15)
C5A—C4AA—C8AA—C8A	1.6 (3)	C4B—C4AB—C8AB—N1B	−1.3 (2)
C4A—C4AA—C8AA—C8A	−178.84 (16)	C2B—N1B—C8AB—C4AB	3.1 (2)
C2A—N1A—C8AA—C4AA	−5.9 (2)	C9B—N1B—C8AB—C4AB	−177.48 (14)
C9A—N1A—C8AA—C4AA	167.91 (15)	C2B—N1B—C8AB—C8B	−177.20 (15)
C2A—N1A—C8AA—C8A	174.10 (16)	C9B—N1B—C8AB—C8B	2.3 (2)
C9A—N1A—C8AA—C8A	−12.1 (2)	C6B—C7B—C8B—C8AB	0.9 (3)
C7A—C8A—C8AA—C4AA	−1.7 (3)	C4AB—C8AB—C8B—C7B	−0.6 (2)
C7A—C8A—C8AA—N1A	178.33 (16)	N1B—C8AB—C8B—C7B	179.66 (15)
C2A—N1A—C9A—C10A	−99.51 (18)	C2B—N1B—C9B—C10B	102.55 (18)
C8AA—N1A—C9A—C10A	86.33 (19)	C8AB—N1B—C9B—C10B	−76.95 (19)
N1A—C9A—C10A—C11A	38.0 (2)	N1B—C9B—C10B—C11B	−60.1 (2)
N1A—C9A—C10A—C15A	−147.14 (17)	N1B—C9B—C10B—C15B	120.61 (18)
C15A—C10A—C11A—C12A	0.1 (3)	C15B—C10B—C11B—C12B	−0.2 (3)
C9A—C10A—C11A—C12A	174.99 (16)	C9B—C10B—C11B—C12B	−179.58 (17)
C10A—C11A—C12A—C13A	0.0 (3)	C10B—C11B—C12B—C13B	−1.5 (3)
C11A—C12A—C13A—C14A	−0.5 (3)	C11B—C12B—C13B—C14B	1.8 (3)
C12A—C13A—C14A—C15A	0.9 (3)	C12B—C13B—C14B—C15B	−0.4 (3)
C13A—C14A—C15A—C10A	−0.8 (3)	C13B—C14B—C15B—C10B	−1.4 (3)
C11A—C10A—C15A—C14A	0.3 (3)	C11B—C10B—C15B—C14B	1.7 (3)
C9A—C10A—C15A—C14A	−174.73 (18)	C9B—C10B—C15B—C14B	−178.98 (17)
C4A—N3A—C16A—C17A	88.4 (2)	C4B—N3B—C16B—C17B	−97.31 (18)
C2A—N3A—C16A—C17A	−88.3 (2)	C2B—N3B—C16B—C17B	84.33 (18)

N3A—C16A—C17A—C18A	81.3 (2)	N3B—C16B—C17B—C22B	76.8 (2)
N3A—C16A—C17A—C22A	−97.6 (2)	N3B—C16B—C17B—C18B	−105.44 (19)
C22A—C17A—C18A—C19A	2.4 (3)	C22B—C17B—C18B—C19B	0.2 (3)
C16A—C17A—C18A—C19A	−176.51 (17)	C16B—C17B—C18B—C19B	−177.63 (17)
C17A—C18A—C19A—C20A	−2.0 (3)	C17B—C18B—C19B—C20B	−0.8 (3)
C18A—C19A—C20A—C21A	0.1 (3)	C18B—C19B—C20B—C21B	0.7 (3)
C19A—C20A—C21A—C22A	1.4 (4)	C19B—C20B—C21B—C22B	0.0 (3)
C20A—C21A—C22A—C17A	−0.9 (3)	C18B—C17B—C22B—C21B	0.5 (3)
C18A—C17A—C22A—C21A	−1.0 (3)	C16B—C17B—C22B—C21B	178.34 (16)
C16A—C17A—C22A—C21A	177.99 (18)	C20B—C21B—C22B—C17B	−0.6 (3)

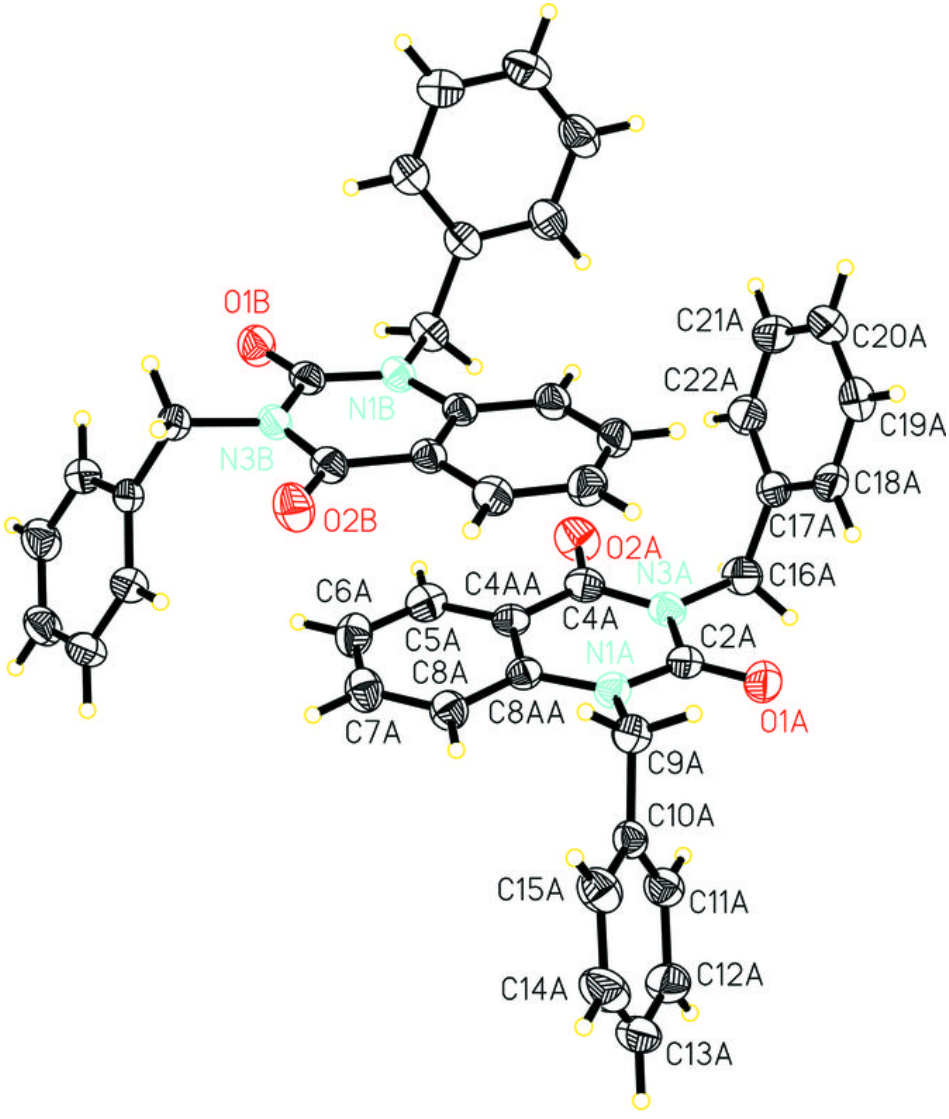
Hydrogen-bond geometry (Å, °)

Cg4 and Cg8 are the centroids of the C17A–C22A and C10B–C15B rings, respectively.

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
C19A—H19A···O2b^{i}	0.93	2.70	3.419 (3)	134
C6B—H6B···C11a^{ii}	0.93	2.89	3.604 (3)	134
C21B—H21B···C11a^{iii}	0.93	2.80	3.600 (3)	145
C19A—H19A···O2b^{i}	0.93	2.70	3.419 (3)	134
C7B—H7B···Cg4	0.93	2.78	3.586 (2)	146
C5A—H5A···Cg8^{ii}	0.93	2.90	3.641 (2)	138

Symmetry codes: (i) *x*+1/2, *y*, −*z*+3/2; (ii) −*x*+3/2, *y*−1/2, *z*; (iii) *x*−1/2, *y*, −*z*+3/2.

Fig. 1


O1B
N1B
N3B
O2B
O2A
N3A
C21A
C20A
C22A
C19A
C18A
C17A
C16A
C6A
C4AA
C4A
C5A
N1A
C2A
C8A
C8AA
O1A
C7A
C9A
C10A
C15A
C11A
C14A
C12A
C13A

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Chloridotris[μ_2-2-(dimethylamino)-ethanolato]-μ_3-hydroxido-tri-μ_2-trifluoroacetato-tetracopper(II) tetrahydrofuran solvate

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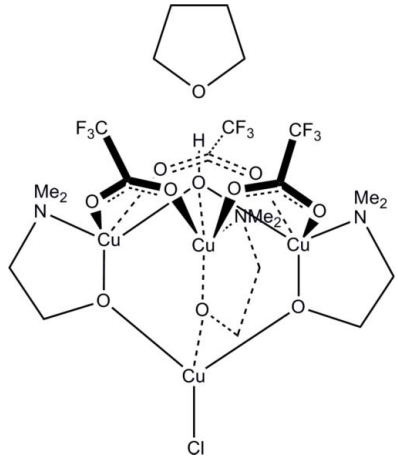
Key indicators: single-crystal X-ray study; T = 100 K; mean σ(C–C) = 0.005 Å; disorder in main residue; R factor = 0.043; wR factor = 0.103; data-to-parameter ratio = 22.0.

The title compound, $[Cu_4(C_2F_3O_2)_3(C_4H_{10}NO)_3Cl(OH)]\cdot C_4H_8O$ or $[Cu_4(TFA)_3(dmae)_3Cl(OH)]\cdot THF$ (dmae is dimethylaminoethanolate, TFA is trifluoroacetate and THF is tetrahydrofuran), has an approximate molecular threefold symmetry with three equivalent {Cu(dmae)(TFA)} units bridging between a Cu—Cl and a hydroxide unit, with the latter two lying on the molecular threefold axis. However, in the solid state, the tetranuclear complex has C_i symmetry. The Cu atom bonded to the Cl atom has a distorted tetrahedral geometry. The other three Cu atoms have distorted square-pyramidal geometries with an NO_4 coordination environment. The bonds within the $CuNO_3$ base of the pyramid range from 1.953 (2) to 2.033 (3) Å, while the apical Cu—O bonds are significantly longer, ranging from 2.286 (2) to 2.377 (2) Å. The square-pyramidal geometries are augmented by weak interactions towards a sixth O atom, forming a highly distorted octahedral coordination environment [long Cu—O distances = 2.712 (2)–2.824 (2) Å]. The hydroxide group is hydrogen bonded to the tetrahydrofuran solvent molecule. One of the $-CF_3$ groups shows minor disorder over two positions, with a refined occupancy ratio of 0.894 (4):0.106 (5).

Related literature

For the synthesis of $[Cu(dmae)Cl]_4$, used as starting material for title compound, see: Anwander *et al.* (1997). For general background to copper(II) complexes, see: Coastamagna *et al.* (1992). For related structures, see: Tahir *et al.* (2008); Shahid *et al.* (2009).



Experimental

Crystal data

$[Cu_4(C_2F_3O_2)_3(C_4H_{10}NO)_3Cl(OH)]\cdot C_4H_8O$
M_r = 982.21
Monoclinic, $C2/c$
a = 16.4353 (14) Å
b = 12.1893 (12) Å
c = 35.547 (3) Å
β = 94.678 (2)°
V = 7097.7 (11) Å^3
Z = 8
Mo $K\alpha$ radiation
μ = 2.54 mm^{-1}
T = 100 K
0.41 × 0.38 × 0.28 mm

Data collection

Bruker SMART APEX CCD diffractometer
Absorption correction: multi-scan (*SADABS*; Bruker, 2008)
T_{min} = 0.673, T_{max} = 0.746
20465 measured reflections
10267 independent reflections
7515 reflections with $I > 2\sigma(I)$
R_{int} = 0.035

Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.043
$wR(F^2)$ = 0.103
S = 1.01
10267 reflections
467 parameters
15 restraints
H-atom parameters constrained
$\Delta\rho_{max}$ = 0.92 e Å^{-3}
$\Delta\rho_{min}$ = −0.69 e Å^{-3}

Table 1
Hydrogen-bond geometry (Å, °).

D—H···A	D—H	H···A	D···A	D—H···A
O10—H10···O11	1.00	1.73	2.723 (3)	174

Data collection: *APEX2* (Bruker, 2008); cell refinement: *SAINT* (Bruker, 2008); data reduction: *SAINT*; program(s) used to solve structure: *SHELXTL* (Sheldrick, 2008); program(s) used to refine structure: *SHELXTL*; molecular graphics: *Mercury* (Macrae *et al.*, 2008); software used to prepare material for publication: *SHELXTL* and *publCIF* (Westrip, 2010).

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Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: FJ2302).

References

Anwander, R., Munck, F. C., Priermeier, T., Scherer, W., Runte, O. & Herrmann, W. A. (1997). *Inorg. Chem.* **36**, 3545–3552.

Bruker (2008). *APEX2*, *SAINT* and *SADABS*. Bruker AXS Inc, Madison, Wisconsin, USA.

Coastamagna, J., Vargas, J., Latorre, R. & Alvarado, A. (1992). *Coord. Chem. Rev.* **119**, 67–88.

Macrae, C. F., Bruno, I. J., Chisholm, J. A., Edgington, P. R., McCabe, P., Pidcock, E., Rodriguez-Monge, L., Taylor, R., van de Streek, J. & Wood, P. A. (2008). *J. Appl. Cryst.* **41**, 466–470.

Shahid, M., Mazhar, M., Zeller, M. & Hunter, A. D. (2009). *Acta Cryst.* E**65**, m345–m346.

Sheldrick, G. M. (2008). *Acta Cryst.* A**64**, 112–122.

Tahir, A. A., Hamid, M., Mazhar, M., Zeller, M., Hunter, A. D., Nadeem, M. & Akhtar, M. J. (2008). *Dalton Trans.* pp. 1224–1232.

Westrip, S. P. (2010). *J. Appl. Cryst.* **43**. Submitted.

supplementary materials

Acta Cryst. (2010). E**66**, m814-m815 [**doi:10.1107/S1600536810022877**]

Chloridotris[μ_2-2-(dimethylamino)ethanolato]-μ_3-hydroxido-tri-μ_2-trifluoroacetato-tetracopper(II) tetrahydrofuran solvate

S. T. Hussain, S. A. Bakar, M. Mazhar and M. Zeller

Comment

In recent years, there has been a considerable interest towards the synthesis of copper complexes; these complexes are extensively used in catalysis, enzymatic reactions, magnetism and molecular architecture (Coastamagna, Vargas *et al.*, 1992). The present work is a continuation of earlier studies for the preparation and structure eludication of copper (II) complexes (Shahid *et al.*, 2009). The motivation behind the synthesis of the title compound was to use it as a starting material for the synthesis of single source precursors for the deposition of thin films of copper oxides using aerosol assisted chemical vapor deposition (AACVD). We present here the synthesis and crystal structure of the title compound, $[Cu_4((CH_3)_2NCH_2CH_2O)_3(F_3CCOO)_3(OH)Cl]$ or $[Cu_4(dmae)_3(TFA)_3(OH)Cl]$ (dmae = dimethylaminoethanolate, TFA = trifluoroacetate), which crystallized from THF as the mono solvate with the THF molecule tightly hydrogen bonded to the hydroxyl group.

The title compound has a slightly distorted molecular three fold symmetry with three equivalent Cu(dmae)(TFA) units bridging *via* their alcoholate oxygen atoms between a Cu—Cl and an hydroxyl unit with the latter two lying on a molecular pseudo threefold axis. The Cu atom bonded to the chlorine has a distorted tetrahedral geometry. The other three copper atoms have distorted square pyramidal geometries with a CNO_4 coordination environment from the dmae O and N atoms, the hydroxyl O atom and two TFA anions. The TFA anions are bridging between two neighboring copper ions with one of the oxygen atoms being part of the base of the pyramid of one copper ion, and the other being in the apical position of the neighboring copper ion. The bonds within the $CuNO_3$ bases of the pyramids are strong and quite similar in length with distances between 1.953 (2) and 2.033 (3) Å. The apical Cu—O bonds are significantly longer and between 2.286 (2) and 2.377 (2) Å, thus rendering the μ_2-bridge of the TFA ions asymmetric. The square pyramidal geometries are augmented by weak interactions towards a fifth oxygen atom to form a highly distorted octahedral coordination environment (Cu—O distances: O3—Cu3 = 2.712 (2), O2—Cu2 = 2.780 (2), O1—Cu4 = 2.8240 (2) Å).

A similar motif as in the title compound was previously observed for two mixed metal copper-titanium complexes (Tahir *et al.*, 2008). In these complexes the TFA anions were replaced by benzoate or 2-methyl-benzoate ligands, and the Cu—Cl unit was replaced by a titanium atom, which in turn was bonded to another larger Cu—Ti cluster. The $[Cu_3(dmae)_3(TFA)_3(OH)]$ unit in the title compound and the $[Cu_3((CH_3)_2NCH_2CH_2O)_3(O_2C—C_6H_5R)_3(OH)]$ units in the Cu—Ti complexes (*R* = H, Me) are quite similar. In the 2-methyl-benzoate complexes the $[Cu_3((CH_3)_2NCH_2CH_2O)_3(O_2C—C_6H_5Me)_3(OH)]$ unit is located on an actual crystallographic three fold axis. The carboxylate anions show coordination modes differing slightly from those observed in the title compound with some of the oxygen atoms being detached from the copper ions and interactions to the fifth oxygen atom, which are very weak in the title compound, being strengthened instead. The overall coordination environment - distorted square pyramidal CNO_4 geometries with an additional weak interaction towards a fifth oxygen atom - is however the same in all three compounds, which shows the idiosyncracy commonly observed for copper(II) to form strongly distorted and highly flexible octahedral geometries with a set of four strong bonds in a square planar arrangement and two apical ligands at variable distances. Indi-

vidual ligand atoms in these kinds of complexes can easily switch from tightly bound to only weakly coordinated as long as the overall coordination environment of the metal center is retained, and energy differences and activation barriers between the different arrangements that can be achieved that way are quite small. The difference in bonding arrangement in the three complexes in the solid state does thus probably not translate into a different chemical nature for the three complexes as the bonding environment around Cu(II) is very flexible and it can be assumed that in solution (*i.e.* upon release of packing effects) all complexes will attain the same connectivity pattern.

In the title compound the hydroxyl group is O—H···O hydrogen bonded to a tetrahydrofuran molecule (Table 1), which is embedded in a bowl shaped cleft of the complex formed by the three TFA ligands. No such host–guest behavior was observed for the other two related compounds (Tahir *et al.*, 2008).

Experimental

Tetrameric *N*,*N*-dimethylaminoethanolato copper(II) chloride, $[Cu(dmae)Cl]_4$ was prepared according to a literature method (Anwander *et al.*, 1997). The title compound was prepared as follows: 1.25 g (1.67 mmole) of $[Cu(dmae)Cl]_4$ in 20 ml THF were combined with 1.77 g (6.66 mmole) of $Cu(F_3CCOO)_2$ in 10 ml THF followed by the addition of 0.297 g (3.33 mmole) *N*,*N*-dimethylaminoethanol. The reaction mixture was stirred for 3 h and filtered through a cannula to remove any undissolved species. The filtrate was evaporated to dryness under vacuum, the solid was re-dissolved in 5 ml THF and placed in a vial with rubber seal at room temperature for one week to give blue crystals suitable for single-crystal X-ray diffraction analysis. Yield: 86% m.p. 393–394 K. Elemental Analysis for $Cu_4((CH_3)_2NCH_2CH_2O)_3(F_3CCOO)_3(OH)Cl$ % calc: C, 21.99 H, 3.97 N, 4.27, % found: C, 22.10 H, 3.90 N, 4.53.

Refinement

The fluorine atoms bonded to C14 were refined as disordered over two mutually exclusive positions with a refined occupancy ratio of 0.894 (4) to 0.106 (5). C—F bond distances within this CF_3 group were restrained to be the same within a standard uncertaincy of 0.02 Å and ADPs of the minor F atoms were constrained to be identical to those of the major moiety F atom opposite their position.

All hydrogen atoms were added in calculated positions with a C—H bond distances of 0.97 (methylene), 0.96 (methyl) and 1.00 Å (OH). They were refined with isotropic displacement parameteres U_{iso} of 1.5 (methyl, OH) or 1.2 times U_{eq} (methylene) of the adjacent carbon or oxygen atom.

Figures

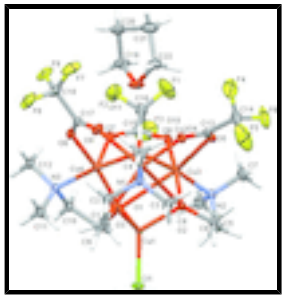


Fig. 1. Perspective view of the title compound with the atom numbering scheme. The displacement ellipsoids are at the 50% probability level and H atoms are drawn as small spheres of arbitrary radii.

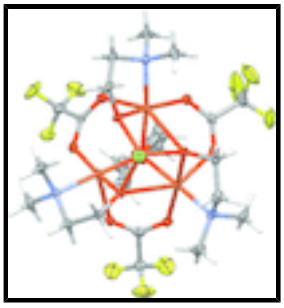


Fig. 2. Perspective view of the title compound, view down the pseudo three fold axis. The displacement ellipsoids are at the 50% probability level and H atoms are drawn as small spheres of arbitrary radii.

Chloridotris[μ$_2$-2-(dimethylamino)ethanolato]-μ$_3$-hydroxido-tri-μ$_2$- trifluoroacetato-tetracopper(II) tetrahydrofuran solvate

Crystal data

$[Cu_4(C_2F_3O_2)_3(C_4H_{10}NO)_3Cl(OH)]\cdot C_4H_8O$	$F(000) = 3952$
$M_r = 982.21$	$D_x = 1.838$ Mg m^{-3}
Monoclinic, $C2/c$	Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å
Hall symbol: -C 2yc	Cell parameters from 1722 reflections
$a = 16.4353$ (14) Å	$\theta = 2.4$–$30.1°$
$b = 12.1893$ (12) Å	$\mu = 2.54$ mm^{-1}
$c = 35.547$ (3) Å	$T = 100$ K
$\beta = 94.678$ (2)°	Block, blue
$V = 7097.7$ (11) Å^3	0.41 × 0.38 × 0.28 mm
$Z = 8$	

Data collection

Bruker SMART APEX CCD diffractometer	10267 independent reflections
Radiation source: fine-focus sealed tube	7515 reflections with $I > 2\sigma(I)$
graphite	$R_{int} = 0.035$
ω scans	$\theta_{max} = 31.6°$, $\theta_{min} = 1.2°$
Absorption correction: multi-scan (*SADABS*; Bruker, 2008)	$h = -12\rightarrow22$
$T_{min} = 0.673$, $T_{max} = 0.746$	$k = -15\rightarrow17$
20465 measured reflections	$l = -37\rightarrow50$

Refinement

Refinement on F^2	Primary atom site location: structure-invariant direct methods
Least-squares matrix: full	Secondary atom site location: difference Fourier map
$R[F^2 > 2\sigma(F^2)] = 0.043$	Hydrogen site location: inferred from neighbouring sites
$wR(F^2) = 0.103$	H-atom parameters constrained
$S = 1.01$	$w = 1/[\sigma^2(F_o^2) + (0.0396P)^2 + 12.2423P]$ where $P = (F_o^2 + 2F_c^2)/3$

10267 reflections	$(\Delta/\sigma)_{max} = 0.001$
467 parameters	$\Delta\rho_{max} = 0.92$ e Å^{-3}
15 restraints	$\Delta\rho_{min} = -0.69$ e Å^{-3}

Special details

Experimental. The fluorine atoms bonded to C14 were refined as disordered over two mutually exclusive positions with a refined occupancy ratio of 0.894 (4) to 0.106 (5). C-f bond distances within this CF3 group were restrained to be the same within a standard uncertaincy of 0.02 Angstrom and ADPs of the minor F atoms were constrained to be identical to those of the major moiety F atom opposite their position.

Geometry. All e.s.d.'s (except the e.s.d. in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell e.s.d.'s are taken into account individually in the estimation of e.s.d.'s in distances, angles and torsion angles; correlations between e.s.d.'s in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell e.s.d.'s is used for estimating e.s.d.'s involving l.s. planes.

Refinement. Refinement of F^2 against ALL reflections. The weighted *R*-factor *wR* and goodness of fit *S* are based on F^2, conventional *R*-factors *R* are based on *F*, with *F* set to zero for negative F^2. The threshold expression of $F^2 > \sigma(F^2)$ is used only for calculating *R*-factors(gt) *etc*. and is not relevant to the choice of reflections for refinement. *R*-factors based on F^2 are statistically about twice as large as those based on *F*, and *R*- factors based on ALL data will be even larger.

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å^2)

	x	*y*	*z*	U_{iso}*/U_{eq}	Occ. (<1)
C1	0.3487 (2)	0.6333 (3)	0.27202 (8)	0.0213 (7)	
H1A	0.2955	0.6699	0.2659	0.026*	
H1B	0.3614	0.5884	0.2500	0.026*	
C2	0.41488 (18)	0.7186 (3)	0.28039 (9)	0.0188 (7)	
H2A	0.4693	0.6841	0.2796	0.023*	
H2B	0.4097	0.7771	0.2610	0.023*	
C3	0.3331 (2)	0.8365 (3)	0.31874 (10)	0.0253 (8)	
H3A	0.3358	0.8958	0.3003	0.038*	
H3B	0.3303	0.8679	0.3440	0.038*	
H3C	0.2843	0.7919	0.3123	0.038*	
C4	0.4799 (2)	0.8341 (3)	0.32982 (10)	0.0240 (7)	
H4A	0.4845	0.8938	0.3117	0.036*	
H4B	0.5289	0.7881	0.3305	0.036*	
H4C	0.4745	0.8649	0.3550	0.036*	
C5	0.16045 (19)	0.6242 (3)	0.37865 (9)	0.0203 (7)	
H5A	0.1270	0.6612	0.3580	0.024*	
H5B	0.1718	0.6772	0.3995	0.024*	
C6	0.11552 (19)	0.5262 (3)	0.39231 (10)	0.0234 (7)	
H6A	0.0666	0.5508	0.4045	0.028*	
H6B	0.0974	0.4787	0.3706	0.028*	
C7	0.1697 (2)	0.5093 (3)	0.45818 (10)	0.0283 (8)	
H7A	0.1147	0.5027	0.4668	0.042*	
H7B	0.1853	0.5868	0.4578	0.042*	
H7C	0.2085	0.4690	0.4754	0.042*	
C8	0.1435 (2)	0.3471 (3)	0.42013 (11)	0.0274 (8)	

H8A	0.0861	0.3437	0.4256	0.041*	
H8B	0.1769	0.3067	0.4396	0.041*	
H8C	0.1498	0.3141	0.3954	0.041*	
C9	0.24516 (18)	0.2700 (3)	0.31588 (9)	0.0180 (6)	
H9A	0.2240	0.2915	0.2901	0.022*	
H9B	0.2000	0.2358	0.3285	0.022*	
C10	0.31478 (18)	0.1882 (3)	0.31392 (9)	0.0175 (6)	
H10A	0.3235	0.1482	0.3381	0.021*	
H10B	0.3008	0.1341	0.2937	0.021*	
C11	0.3849 (2)	0.2949 (3)	0.26740 (9)	0.0238 (7)	
H11A	0.3777	0.2355	0.2489	0.036*	
H11B	0.4350	0.3355	0.2634	0.036*	
H11C	0.3380	0.3448	0.2644	0.036*	
C12	0.46108 (19)	0.1720 (3)	0.31080 (10)	0.0237 (7)	
H12A	0.4524	0.1108	0.2930	0.036*	
H12B	0.4661	0.1437	0.3367	0.036*	
H12C	0.5112	0.2110	0.3058	0.036*	
C13	0.37061 (18)	0.7122 (3)	0.42640 (9)	0.0166 (6)	
C14	0.3775 (2)	0.8151 (3)	0.45127 (10)	0.0294 (8)	
C15	0.36846 (19)	0.2779 (3)	0.42436 (9)	0.0194 (6)	
C16	0.3779 (2)	0.1874 (3)	0.45482 (10)	0.0252 (7)	
C17	0.55106 (18)	0.4851 (3)	0.34328 (8)	0.0157 (6)	
C18	0.6447 (2)	0.4702 (3)	0.34677 (10)	0.0244 (7)	
C19	0.5583 (2)	0.3809 (3)	0.44361 (11)	0.0290 (8)	
H19A	0.5641	0.3255	0.4236	0.035*	
H19B	0.5265	0.3485	0.4633	0.035*	
C20	0.6412 (2)	0.4186 (4)	0.46031 (11)	0.0331 (9)	
H20A	0.6634	0.3684	0.4805	0.040*	
H20B	0.6805	0.4245	0.4407	0.040*	
C21	0.6219 (2)	0.5295 (4)	0.47598 (13)	0.0426 (11)	
H21A	0.6701	0.5785	0.4767	0.051*	
H21B	0.6036	0.5231	0.5017	0.051*	
C22	0.5532 (2)	0.5721 (3)	0.44827 (11)	0.0330 (9)	
H22A	0.5109	0.6091	0.4620	0.040*	
H22B	0.5747	0.6252	0.4305	0.040*	
Cl1	0.13236 (5)	0.50928 (7)	0.27516 (2)	0.02051 (16)	
Cu1	0.23798 (2)	0.50916 (3)	0.317137 (10)	0.01044 (8)	
Cu2	0.39464 (2)	0.63387 (3)	0.350823 (10)	0.01304 (8)	
Cu3	0.28392 (2)	0.48008 (3)	0.401847 (10)	0.01366 (9)	
Cu4	0.39472 (2)	0.37149 (3)	0.343178 (10)	0.01343 (8)	
F1	0.38789 (19)	0.2286 (2)	0.48959 (7)	0.0616 (8)	
F2	0.44062 (16)	0.1223 (2)	0.45106 (7)	0.0499 (7)	
F3	0.31145 (16)	0.1262 (2)	0.45306 (9)	0.0618 (8)	
F4	0.45195 (17)	0.8352 (4)	0.46438 (13)	0.0738 (15)	0.894 (5)
F5	0.3505 (3)	0.9028 (2)	0.43088 (9)	0.0678 (12)	0.894 (5)
F6	0.3305 (2)	0.8121 (3)	0.47923 (9)	0.0526 (10)	0.894 (5)
F4B	0.418 (2)	0.8966 (17)	0.4377 (8)	0.0526 (10)	0.106 (5)
F5B	0.3162 (13)	0.855 (3)	0.4664 (11)	0.0738 (15)	0.106 (5)
F6B	0.420 (2)	0.788 (2)	0.4834 (6)	0.0678 (12)	0.106 (5)

F7	0.68329 (13)	0.5493 (2)	0.36747 (8)	0.0452 (7)
F8	0.67280 (13)	0.4751 (2)	0.31263 (7)	0.0474 (7)
F9	0.66948 (11)	0.37600 (18)	0.36251 (6)	0.0329 (5)
N1	0.40701 (15)	0.7666 (2)	0.31829 (7)	0.0158 (5)
N2	0.17040 (16)	0.4632 (2)	0.41990 (7)	0.0195 (6)
N3	0.39102 (15)	0.2481 (2)	0.30606 (7)	0.0163 (5)
O1	0.34445 (12)	0.56503 (18)	0.30425 (6)	0.0159 (4)
O2	0.23492 (12)	0.58621 (18)	0.36547 (6)	0.0155 (4)
O3	0.27429 (12)	0.36447 (17)	0.33646 (6)	0.0141 (4)
O4	0.40721 (13)	0.72338 (18)	0.39660 (6)	0.0187 (5)
O5	0.33254 (13)	0.6340 (2)	0.43810 (6)	0.0211 (5)
O6	0.32578 (13)	0.35798 (19)	0.43373 (6)	0.0192 (5)
O7	0.40130 (13)	0.25998 (19)	0.39509 (6)	0.0189 (5)
O8	0.51284 (12)	0.39551 (19)	0.34027 (6)	0.0196 (5)
O9	0.52741 (13)	0.58004 (19)	0.34305 (7)	0.0213 (5)
O10	0.38614 (12)	0.49500 (16)	0.37767 (6)	0.0122 (4)
H10	0.4325	0.4905	0.3976	0.018*
O11	0.51928 (15)	0.4780 (2)	0.42819 (8)	0.0318 (6)

Atomic displacement parameters (Å^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
C1	0.0238 (17)	0.0301 (18)	0.0103 (14)	−0.0031 (14)	0.0035 (12)	0.0015 (13)
C2	0.0169 (15)	0.0227 (17)	0.0180 (15)	0.0011 (12)	0.0087 (12)	0.0044 (13)
C3	0.0224 (17)	0.0220 (18)	0.0321 (19)	0.0076 (14)	0.0060 (14)	0.0069 (15)
C4	0.0229 (17)	0.0194 (17)	0.0296 (18)	−0.0061 (13)	0.0021 (14)	0.0040 (14)
C5	0.0201 (16)	0.0214 (17)	0.0199 (15)	0.0065 (13)	0.0046 (12)	0.0013 (13)
C6	0.0168 (15)	0.0282 (19)	0.0250 (17)	0.0009 (13)	0.0007 (13)	−0.0003 (14)
C7	0.0271 (17)	0.040 (2)	0.0189 (17)	−0.0023 (16)	0.0088 (14)	−0.0038 (15)
C8	0.0244 (18)	0.028 (2)	0.0312 (19)	−0.0064 (14)	0.0074 (15)	0.0034 (15)
C9	0.0167 (15)	0.0161 (15)	0.0212 (16)	−0.0021 (12)	0.0008 (12)	−0.0019 (13)
C10	0.0178 (15)	0.0175 (16)	0.0171 (15)	−0.0017 (12)	0.0009 (12)	−0.0018 (12)
C11	0.0274 (18)	0.0251 (18)	0.0197 (16)	−0.0027 (14)	0.0075 (14)	−0.0045 (14)
C12	0.0168 (16)	0.0243 (18)	0.0297 (18)	0.0062 (13)	0.0010 (13)	−0.0089 (15)
C13	0.0161 (15)	0.0173 (15)	0.0156 (15)	0.0034 (12)	−0.0033 (12)	−0.0047 (12)
C14	0.036 (2)	0.0260 (19)	0.0273 (19)	−0.0043 (16)	0.0099 (16)	−0.0086 (16)
C15	0.0195 (16)	0.0184 (16)	0.0197 (16)	−0.0030 (13)	−0.0031 (12)	0.0024 (13)
C16	0.035 (2)	0.0217 (18)	0.0199 (17)	0.0028 (15)	0.0053 (14)	0.0050 (14)
C17	0.0125 (13)	0.0211 (16)	0.0139 (14)	0.0018 (12)	0.0036 (11)	0.0025 (12)
C18	0.0166 (15)	0.0246 (18)	0.0324 (19)	0.0038 (13)	0.0054 (14)	0.0113 (15)
C19	0.0284 (19)	0.029 (2)	0.0283 (19)	0.0025 (15)	−0.0032 (15)	0.0047 (16)
C20	0.0233 (18)	0.048 (3)	0.0270 (19)	0.0037 (17)	−0.0060 (15)	0.0058 (18)
C21	0.032 (2)	0.049 (3)	0.044 (3)	−0.0038 (19)	−0.0155 (19)	−0.007 (2)
C22	0.029 (2)	0.030 (2)	0.037 (2)	0.0000 (16)	−0.0118 (16)	−0.0089 (17)
Cl1	0.0180 (3)	0.0238 (4)	0.0185 (4)	0.0001 (3)	−0.0054 (3)	0.0021 (3)
Cu1	0.01002 (16)	0.01276 (18)	0.00839 (16)	−0.00009 (13)	−0.00024 (12)	0.00033 (13)
Cu2	0.01405 (18)	0.01354 (18)	0.01150 (17)	−0.00088 (14)	0.00094 (13)	0.00082 (14)
Cu3	0.01306 (17)	0.01724 (19)	0.01080 (17)	0.00010 (14)	0.00167 (13)	0.00157 (14)

Cu4	0.01185 (18)	0.01471 (18)	0.01367 (17)	0.00029 (14)	0.00071 (13)	−0.00261 (14)
F1	0.115 (2)	0.0484 (17)	0.0214 (13)	0.0182 (16)	0.0036 (13)	0.0092 (12)
F2	0.0589 (17)	0.0486 (16)	0.0429 (15)	0.0237 (13)	0.0085 (12)	0.0191 (13)
F3	0.0555 (17)	0.0442 (17)	0.086 (2)	−0.0120 (13)	0.0071 (15)	0.0327 (16)
F4	0.0287 (16)	0.099 (3)	0.093 (3)	−0.0140 (17)	0.0005 (16)	−0.075 (3)
F5	0.121 (4)	0.0276 (16)	0.056 (2)	0.0143 (18)	0.012 (2)	−0.0113 (15)
F6	0.061 (2)	0.056 (2)	0.0442 (19)	−0.0053 (16)	0.0264 (16)	−0.0278 (16)
F4B	0.061 (2)	0.056 (2)	0.0442 (19)	−0.0053 (16)	0.0264 (16)	−0.0278 (16)
F5B	0.0287 (16)	0.099 (3)	0.093 (3)	−0.0140 (17)	0.0005 (16)	−0.075 (3)
F6B	0.121 (4)	0.0276 (16)	0.056 (2)	0.0143 (18)	0.012 (2)	−0.0113 (15)
F7	0.0210 (11)	0.0334 (13)	0.0787 (19)	−0.0063 (10)	−0.0113 (11)	0.0017 (13)
F8	0.0272 (12)	0.075 (2)	0.0427 (15)	0.0169 (12)	0.0203 (10)	0.0258 (13)
F9	0.0180 (10)	0.0303 (12)	0.0505 (14)	0.0051 (8)	0.0039 (9)	0.0172 (11)
N1	0.0137 (12)	0.0168 (13)	0.0173 (13)	0.0012 (10)	0.0034 (10)	0.0015 (10)
N2	0.0181 (13)	0.0260 (15)	0.0148 (13)	−0.0005 (11)	0.0039 (10)	0.0009 (11)
N3	0.0154 (12)	0.0155 (13)	0.0180 (13)	0.0011 (10)	0.0011 (10)	−0.0029 (11)
O1	0.0160 (11)	0.0204 (11)	0.0114 (10)	−0.0034 (9)	0.0026 (8)	0.0016 (9)
O2	0.0151 (10)	0.0186 (11)	0.0128 (10)	0.0018 (9)	0.0018 (8)	0.0002 (9)
O3	0.0128 (10)	0.0139 (10)	0.0153 (10)	0.0000 (8)	−0.0006 (8)	−0.0019 (8)
O4	0.0204 (11)	0.0191 (12)	0.0168 (11)	−0.0024 (9)	0.0022 (9)	−0.0016 (9)
O5	0.0227 (12)	0.0260 (13)	0.0147 (11)	−0.0046 (10)	0.0018 (9)	−0.0039 (10)
O6	0.0211 (12)	0.0200 (12)	0.0165 (11)	0.0013 (9)	0.0021 (9)	0.0037 (9)
O7	0.0222 (11)	0.0179 (11)	0.0167 (11)	0.0023 (9)	0.0020 (9)	0.0009 (9)
O8	0.0138 (11)	0.0213 (12)	0.0242 (12)	0.0000 (9)	0.0048 (9)	−0.0032 (10)
O9	0.0155 (11)	0.0201 (12)	0.0285 (13)	0.0027 (9)	0.0030 (9)	0.0045 (10)
O10	0.0122 (9)	0.0135 (10)	0.0109 (9)	−0.0005 (8)	0.0002 (7)	−0.0007 (8)
O11	0.0296 (14)	0.0249 (14)	0.0373 (15)	0.0007 (11)	−0.0193 (11)	−0.0005 (12)

Geometric parameters (Å, °)

C1—O1	1.422 (4)	C14—F6	1.308 (4)
C1—C2	1.516 (5)	C14—F4B	1.310 (14)
C1—H1A	0.9900	C14—F6B	1.333 (15)
C1—H1B	0.9900	C14—F5	1.346 (5)
C2—N1	1.484 (4)	C15—O7	1.230 (4)
C2—H2A	0.9900	C15—O6	1.263 (4)
C2—H2B	0.9900	C15—C16	1.545 (5)
C3—N1	1.485 (4)	C16—F2	1.316 (4)
C3—H3A	0.9800	C16—F3	1.319 (4)
C3—H3B	0.9800	C16—F1	1.332 (4)
C3—H3C	0.9800	C17—O9	1.221 (4)
C4—N1	1.484 (4)	C17—O8	1.260 (4)
C4—H4A	0.9800	C17—C18	1.545 (4)
C4—H4B	0.9800	C18—F9	1.326 (4)
C4—H4C	0.9800	C18—F8	1.334 (4)
C5—O2	1.423 (3)	C18—F7	1.340 (4)
C5—C6	1.505 (5)	C19—O11	1.434 (4)
C5—H5A	0.9900	C19—C20	1.512 (5)
C5—H5B	0.9900	C19—H19A	0.9900

C6—N2	1.490 (4)	C19—H19B	0.9900
C6—H6A	0.9900	C20—C21	1.506 (6)
C6—H6B	0.9900	C20—H20A	0.9900
C7—N2	1.473 (4)	C20—H20B	0.9900
C7—H7A	0.9800	C21—C22	1.528 (5)
C7—H7B	0.9800	C21—H21A	0.9900
C7—H7C	0.9800	C21—H21B	0.9900
C8—N2	1.483 (4)	C22—O11	1.439 (4)
C8—H8A	0.9800	C22—H22A	0.9900
C8—H8B	0.9800	C22—H22B	0.9900
C8—H8C	0.9800	Cl1—Cu1	2.1948 (8)
C9—O3	1.426 (4)	Cu1—O2	1.962 (2)
C9—C10	1.523 (4)	Cu1—O1	1.966 (2)
C9—H9A	0.9900	Cu1—O3	1.968 (2)
C9—H9B	0.9900	Cu2—O10	1.954 (2)
C10—N3	1.496 (4)	Cu2—O4	1.956 (2)
C10—H10A	0.9900	Cu2—O1	1.975 (2)
C10—H10B	0.9900	Cu2—N1	2.009 (3)
C11—N3	1.484 (4)	Cu2—O9	2.317 (2)
C11—H11A	0.9800	Cu3—O2	1.956 (2)
C11—H11B	0.9800	Cu3—O10	1.957 (2)
C11—H11C	0.9800	Cu3—O6	1.961 (2)
C12—N3	1.478 (4)	Cu3—N2	2.032 (3)
C12—H12A	0.9800	Cu3—O5	2.377 (2)
C12—H12B	0.9800	Cu4—O10	1.954 (2)
C12—H12C	0.9800	Cu4—O8	1.974 (2)
C13—O5	1.231 (4)	Cu4—O3	1.976 (2)
C13—O4	1.267 (4)	Cu4—N3	1.998 (3)
C13—C14	1.533 (5)	Cu4—O7	2.287 (2)
C14—F5B	1.278 (15)	O10—H10	0.9990
C14—F4	1.296 (4)		
O1—C1—C2	109.0 (2)	F8—C18—C17	109.7 (3)
O1—C1—H1A	109.9	F7—C18—C17	112.5 (3)
C2—C1—H1A	109.9	O11—C19—C20	105.1 (3)
O1—C1—H1B	109.9	O11—C19—H19A	110.7
C2—C1—H1B	109.9	C20—C19—H19A	110.7
H1A—C1—H1B	108.3	O11—C19—H19B	110.7
N1—C2—C1	109.5 (2)	C20—C19—H19B	110.7
N1—C2—H2A	109.8	H19A—C19—H19B	108.8
C1—C2—H2A	109.8	C21—C20—C19	102.0 (3)
N1—C2—H2B	109.8	C21—C20—H20A	111.4
C1—C2—H2B	109.8	C19—C20—H20A	111.4
H2A—C2—H2B	108.2	C21—C20—H20B	111.4
N1—C3—H3A	109.5	C19—C20—H20B	111.4
N1—C3—H3B	109.5	H20A—C20—H20B	109.2
H3A—C3—H3B	109.5	C20—C21—C22	103.5 (3)
N1—C3—H3C	109.5	C20—C21—H21A	111.1
H3A—C3—H3C	109.5	C22—C21—H21A	111.1
H3B—C3—H3C	109.5	C20—C21—H21B	111.1

N1—C4—H4A	109.5	C22—C21—H21B	111.1
N1—C4—H4B	109.5	H21A—C21—H21B	109.0
H4A—C4—H4B	109.5	O11—C22—C21	106.5 (3)
N1—C4—H4C	109.5	O11—C22—H22A	110.4
H4A—C4—H4C	109.5	C21—C22—H22A	110.4
H4B—C4—H4C	109.5	O11—C22—H22B	110.4
O2—C5—C6	107.8 (3)	C21—C22—H22B	110.4
O2—C5—H5A	110.1	H22A—C22—H22B	108.6
C6—C5—H5A	110.1	O2—Cu1—O1	97.18 (9)
O2—C5—H5B	110.1	O2—Cu1—O3	98.75 (9)
C6—C5—H5B	110.1	O1—Cu1—O3	98.13 (9)
H5A—C5—H5B	108.5	O2—Cu1—Cl1	121.31 (6)
N2—C6—C5	109.6 (3)	O1—Cu1—Cl1	120.73 (7)
N2—C6—H6A	109.8	O3—Cu1—Cl1	116.00 (6)
C5—C6—H6A	109.8	O10—Cu2—O4	94.81 (9)
N2—C6—H6B	109.8	O10—Cu2—O1	89.98 (9)
C5—C6—H6B	109.8	O4—Cu2—O1	160.49 (9)
H6A—C6—H6B	108.2	O10—Cu2—N1	173.56 (9)
N2—C7—H7A	109.5	O4—Cu2—N1	91.20 (10)
N2—C7—H7B	109.5	O1—Cu2—N1	85.10 (10)
H7A—C7—H7B	109.5	O10—Cu2—O9	85.32 (8)
N2—C7—H7C	109.5	O4—Cu2—O9	102.75 (9)
H7A—C7—H7C	109.5	O1—Cu2—O9	96.48 (8)
H7B—C7—H7C	109.5	N1—Cu2—O9	91.08 (9)
N2—C8—H8A	109.5	O2—Cu3—O10	88.29 (8)
N2—C8—H8B	109.5	O2—Cu3—O6	172.03 (9)
H8A—C8—H8B	109.5	O10—Cu3—O6	92.93 (9)
N2—C8—H8C	109.5	O2—Cu3—N2	86.38 (10)
H8A—C8—H8C	109.5	O10—Cu3—N2	172.39 (10)
H8B—C8—H8C	109.5	O6—Cu3—N2	91.62 (10)
O3—C9—C10	109.3 (2)	O2—Cu3—O5	86.47 (9)
O3—C9—H9A	109.8	O10—Cu3—O5	84.38 (8)
C10—C9—H9A	109.8	O6—Cu3—O5	101.48 (9)
O3—C9—H9B	109.8	N2—Cu3—O5	100.69 (10)
C10—C9—H9B	109.8	O10—Cu4—O8	92.30 (9)
H9A—C9—H9B	108.3	O10—Cu4—O3	89.22 (8)
N3—C10—C9	109.5 (3)	O8—Cu4—O3	168.40 (9)
N3—C10—H10A	109.8	O10—Cu4—N3	173.88 (9)
C9—C10—H10A	109.8	O8—Cu4—N3	93.10 (10)
N3—C10—H10B	109.8	O3—Cu4—N3	84.91 (9)
C9—C10—H10B	109.8	O10—Cu4—O7	87.29 (8)
H10A—C10—H10B	108.2	O8—Cu4—O7	98.53 (9)
N3—C11—H11A	109.5	O3—Cu4—O7	93.03 (8)
N3—C11—H11B	109.5	N3—Cu4—O7	94.73 (9)
H11A—C11—H11B	109.5	C4—N1—C2	110.0 (2)
N3—C11—H11C	109.5	C4—N1—C3	108.8 (3)
H11A—C11—H11C	109.5	C2—N1—C3	111.6 (2)
H11B—C11—H11C	109.5	C4—N1—Cu2	113.88 (19)
N3—C12—H12A	109.5	C2—N1—Cu2	103.03 (19)

N3—C12—H12B	109.5	C3—N1—Cu2	109.54 (19)
H12A—C12—H12B	109.5	C7—N2—C8	109.5 (3)
N3—C12—H12C	109.5	C7—N2—C6	111.2 (3)
H12A—C12—H12C	109.5	C8—N2—C6	109.3 (3)
H12B—C12—H12C	109.5	C7—N2—Cu3	109.3 (2)
O5—C13—O4	130.9 (3)	C8—N2—Cu3	112.3 (2)
O5—C13—C14	117.0 (3)	C6—N2—Cu3	105.17 (19)
O4—C13—C14	112.1 (3)	C12—N3—C11	109.9 (2)
F4—C14—F6	109.3 (4)	C12—N3—C10	109.2 (3)
F5B—C14—F4B	108 (2)	C11—N3—C10	111.5 (2)
F5B—C14—F6B	96 (2)	C12—N3—Cu4	114.56 (19)
F4B—C14—F6B	105 (2)	C11—N3—Cu4	108.6 (2)
F4—C14—F5	107.6 (4)	C10—N3—Cu4	103.00 (18)
F6—C14—F5	104.0 (3)	C1—O1—Cu1	119.59 (18)
F4—C14—C13	112.7 (3)	C1—O1—Cu2	112.44 (19)
F6—C14—C13	113.2 (3)	Cu1—O1—Cu2	105.70 (9)
F4B—C14—C13	115.1 (10)	C5—O2—Cu3	108.43 (17)
F6B—C14—C13	107.4 (12)	C5—O2—Cu1	121.87 (18)
F5—C14—C13	109.4 (3)	Cu3—O2—Cu1	102.93 (10)
O7—C15—O6	130.7 (3)	C9—O3—Cu1	117.73 (17)
O7—C15—C16	116.1 (3)	C9—O3—Cu4	112.83 (17)
O6—C15—C16	113.2 (3)	Cu1—O3—Cu4	106.00 (10)
F2—C16—F3	107.9 (3)	C13—O4—Cu2	127.6 (2)
F2—C16—F1	106.5 (3)	C13—O5—Cu3	125.9 (2)
F3—C16—F1	107.2 (3)	C15—O6—Cu3	127.6 (2)
F2—C16—C15	113.2 (3)	C15—O7—Cu4	125.6 (2)
F3—C16—C15	109.6 (3)	C17—O8—Cu4	127.6 (2)
F1—C16—C15	112.2 (3)	C17—O9—Cu2	124.8 (2)
O9—C17—O8	131.7 (3)	Cu2—O10—Cu4	110.45 (10)
O9—C17—C18	115.2 (3)	Cu2—O10—Cu3	113.15 (10)
O8—C17—C18	113.1 (3)	Cu4—O10—Cu3	108.20 (9)
F9—C18—F8	107.8 (3)	Cu2—O10—H10	108.2
F9—C18—F7	106.0 (3)	Cu4—O10—H10	108.3
F8—C18—F7	106.5 (3)	Cu3—O10—H10	108.4
F9—C18—C17	113.9 (3)	C19—O11—C22	109.0 (3)
O1—C1—C2—N1	−45.7 (3)	O10—Cu3—O2—C5	−165.02 (19)
O2—C5—C6—N2	52.7 (3)	N2—Cu3—O2—C5	20.4 (2)
O3—C9—C10—N3	−42.2 (3)	O5—Cu3—O2—C5	−80.55 (19)
O5—C13—C14—F5B	−46 (3)	O10—Cu3—O2—Cu1	64.62 (9)
O4—C13—C14—F5B	135 (3)	N2—Cu3—O2—Cu1	−109.95 (11)
O5—C13—C14—F4	114.5 (4)	O5—Cu3—O2—Cu1	149.09 (9)
O4—C13—C14—F4	−64.8 (5)	O1—Cu1—O2—C5	146.6 (2)
O5—C13—C14—F6	−10.3 (5)	O3—Cu1—O2—C5	−113.9 (2)
O4—C13—C14—F6	170.4 (3)	Cl1—Cu1—O2—C5	13.8 (2)
O5—C13—C14—F4B	−179.5 (19)	O1—Cu1—O2—Cu3	−91.71 (10)
O4—C13—C14—F4B	1.2 (19)	O3—Cu1—O2—Cu3	7.71 (10)
O5—C13—C14—F6B	63.9 (19)	Cl1—Cu1—O2—Cu3	135.49 (6)
O4—C13—C14—F6B	−115.4 (19)	C10—C9—O3—Cu1	138.4 (2)
O5—C13—C14—F5	−125.8 (4)	C10—C9—O3—Cu4	14.3 (3)

O4—C13—C14—F5	54.9 (4)	O2—Cu1—O3—C9	146.95 (19)
O7—C15—C16—F2	21.6 (4)	O1—Cu1—O3—C9	−114.43 (19)
O6—C15—C16—F2	−160.1 (3)	Cl1—Cu1—O3—C9	15.7 (2)
O7—C15—C16—F3	−98.9 (4)	O2—Cu1—O3—Cu4	−85.68 (10)
O6—C15—C16—F3	79.5 (4)	O1—Cu1—O3—Cu4	12.93 (11)
O7—C15—C16—F1	142.1 (3)	Cl1—Cu1—O3—Cu4	143.02 (6)
O6—C15—C16—F1	−39.5 (4)	O10—Cu4—O3—C9	−171.33 (19)
O9—C17—C18—F9	153.1 (3)	O8—Cu4—O3—C9	91.0 (5)
O8—C17—C18—F9	−28.5 (4)	N3—Cu4—O3—C9	10.4 (2)
O9—C17—C18—F8	−86.0 (4)	O7—Cu4—O3—C9	−84.08 (19)
O8—C17—C18—F8	92.4 (3)	O10—Cu4—O3—Cu1	58.43 (10)
O9—C17—C18—F7	32.4 (4)	O8—Cu4—O3—Cu1	−39.2 (5)
O8—C17—C18—F7	−149.2 (3)	N3—Cu4—O3—Cu1	−119.84 (11)
O11—C19—C20—C21	36.9 (4)	O7—Cu4—O3—Cu1	145.67 (9)
C19—C20—C21—C22	−33.5 (4)	O5—C13—O4—Cu2	17.2 (5)
C20—C21—C22—O11	19.0 (4)	C14—C13—O4—Cu2	−163.6 (2)
C1—C2—N1—C4	169.3 (3)	O10—Cu2—O4—C13	−39.4 (3)
C1—C2—N1—C3	−69.9 (3)	O1—Cu2—O4—C13	64.3 (4)
C1—C2—N1—Cu2	47.6 (3)	N1—Cu2—O4—C13	142.9 (3)
O4—Cu2—N1—C4	51.0 (2)	O9—Cu2—O4—C13	−125.7 (3)
O1—Cu2—N1—C4	−148.2 (2)	O4—C13—O5—Cu3	−15.7 (5)
O9—Cu2—N1—C4	−51.8 (2)	C14—C13—O5—Cu3	165.1 (2)
O4—Cu2—N1—C2	170.02 (17)	O2—Cu3—O5—C13	−51.2 (3)
O1—Cu2—N1—C2	−29.17 (17)	O10—Cu3—O5—C13	37.4 (3)
O9—Cu2—N1—C2	67.24 (17)	O6—Cu3—O5—C13	129.2 (3)
O4—Cu2—N1—C3	−71.1 (2)	N2—Cu3—O5—C13	−136.9 (3)
O1—Cu2—N1—C3	89.7 (2)	O7—C15—O6—Cu3	8.0 (5)
O9—Cu2—N1—C3	−173.9 (2)	C16—C15—O6—Cu3	−170.1 (2)
C5—C6—N2—C7	84.5 (3)	O10—Cu3—O6—C15	−41.7 (3)
C5—C6—N2—C8	−154.5 (3)	N2—Cu3—O6—C15	132.2 (3)
C5—C6—N2—Cu3	−33.7 (3)	O5—Cu3—O6—C15	−126.6 (3)
O2—Cu3—N2—C7	−111.5 (2)	O6—C15—O7—Cu4	−1.2 (5)
O6—Cu3—N2—C7	76.2 (2)	C16—C15—O7—Cu4	176.9 (2)
O5—Cu3—N2—C7	−25.8 (2)	O10—Cu4—O7—C15	30.6 (3)
O2—Cu3—N2—C8	126.7 (2)	O8—Cu4—O7—C15	122.6 (3)
O6—Cu3—N2—C8	−45.5 (2)	O3—Cu4—O7—C15	−58.4 (3)
O5—Cu3—N2—C8	−147.5 (2)	N3—Cu4—O7—C15	−143.6 (3)
O2—Cu3—N2—C6	7.9 (2)	O9—C17—O8—Cu4	−12.4 (5)
O6—Cu3—N2—C6	−164.4 (2)	C18—C17—O8—Cu4	169.5 (2)
O5—Cu3—N2—C6	93.6 (2)	O10—Cu4—O8—C17	−30.2 (3)
C9—C10—N3—C12	170.1 (3)	O3—Cu4—O8—C17	67.2 (6)
C9—C10—N3—C11	−68.2 (3)	N3—Cu4—O8—C17	146.9 (3)
C9—C10—N3—Cu4	48.0 (3)	O7—Cu4—O8—C17	−117.8 (3)
O8—Cu4—N3—C12	41.2 (2)	O8—C17—O9—Cu2	15.4 (5)
O3—Cu4—N3—C12	−150.3 (2)	C18—C17—O9—Cu2	−166.5 (2)
O7—Cu4—N3—C12	−57.7 (2)	O10—Cu2—O9—C17	24.9 (3)
O8—Cu4—N3—C11	−82.1 (2)	O4—Cu2—O9—C17	118.8 (3)
O3—Cu4—N3—C11	86.44 (19)	O1—Cu2—O9—C17	−64.6 (3)
O7—Cu4—N3—C11	179.06 (19)	N1—Cu2—O9—C17	−149.8 (3)

O8—Cu4—N3—C10	159.62 (18)	O4—Cu2—O10—Cu4	−168.32 (10)
O3—Cu4—N3—C10	−31.84 (18)	O1—Cu2—O10—Cu4	30.61 (10)
O7—Cu4—N3—C10	60.78 (18)	O9—Cu2—O10—Cu4	−65.89 (10)
C2—C1—O1—Cu1	144.4 (2)	O4—Cu2—O10—Cu3	70.20 (11)
C2—C1—O1—Cu2	19.6 (3)	O1—Cu2—O10—Cu3	−90.86 (11)
O2—Cu1—O1—C1	−115.4 (2)	O9—Cu2—O10—Cu3	172.64 (11)
O3—Cu1—O1—C1	144.7 (2)	O8—Cu4—O10—Cu2	72.73 (11)
Cl1—Cu1—O1—C1	17.8 (2)	O3—Cu4—O10—Cu2	−95.76 (10)
O2—Cu1—O1—Cu2	12.61 (11)	O7—Cu4—O10—Cu2	171.17 (10)
O3—Cu1—O1—Cu2	−87.35 (10)	O8—Cu4—O10—Cu3	−162.91 (10)
Cl1—Cu1—O1—Cu2	145.78 (6)	O3—Cu4—O10—Cu3	28.60 (10)
O10—Cu2—O1—C1	−170.14 (19)	O7—Cu4—O10—Cu3	−64.47 (10)
O4—Cu2—O1—C1	85.4 (3)	O2—Cu3—O10—Cu2	23.58 (11)
N1—Cu2—O1—C1	5.7 (2)	O6—Cu3—O10—Cu2	−164.31 (11)
O9—Cu2—O1—C1	−84.9 (2)	O5—Cu3—O10—Cu2	−63.05 (10)
O10—Cu2—O1—Cu1	57.71 (10)	O2—Cu3—O10—Cu4	−99.15 (10)
O4—Cu2—O1—Cu1	−46.8 (3)	O6—Cu3—O10—Cu4	72.97 (11)
N1—Cu2—O1—Cu1	−126.46 (11)	O5—Cu3—O10—Cu4	174.22 (10)
O9—Cu2—O1—Cu1	143.00 (10)	C20—C19—O11—C22	−25.9 (4)
C6—C5—O2—Cu3	−44.1 (3)	C21—C22—O11—C19	4.2 (4)
C6—C5—O2—Cu1	74.9 (3)		

Hydrogen-bond geometry (Å, °)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
O10—H10···O11	1.00	1.73	2.723 (3)	174

Fig. 1

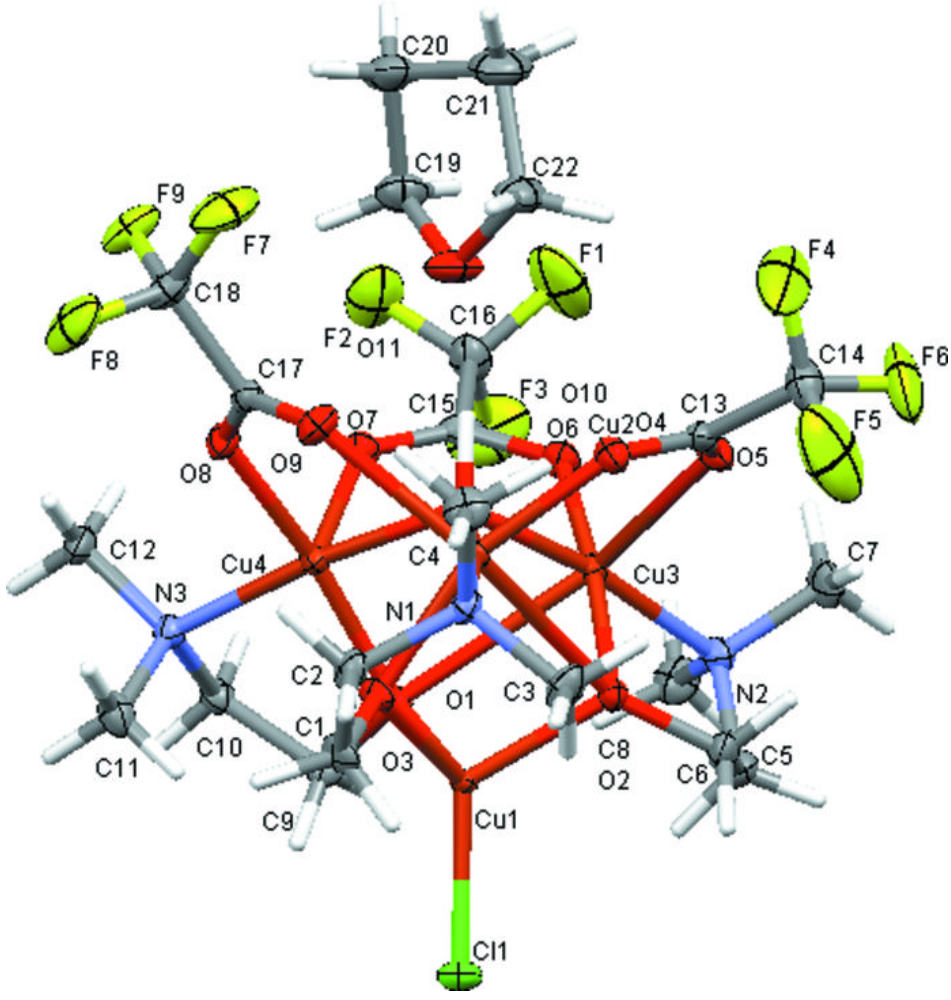
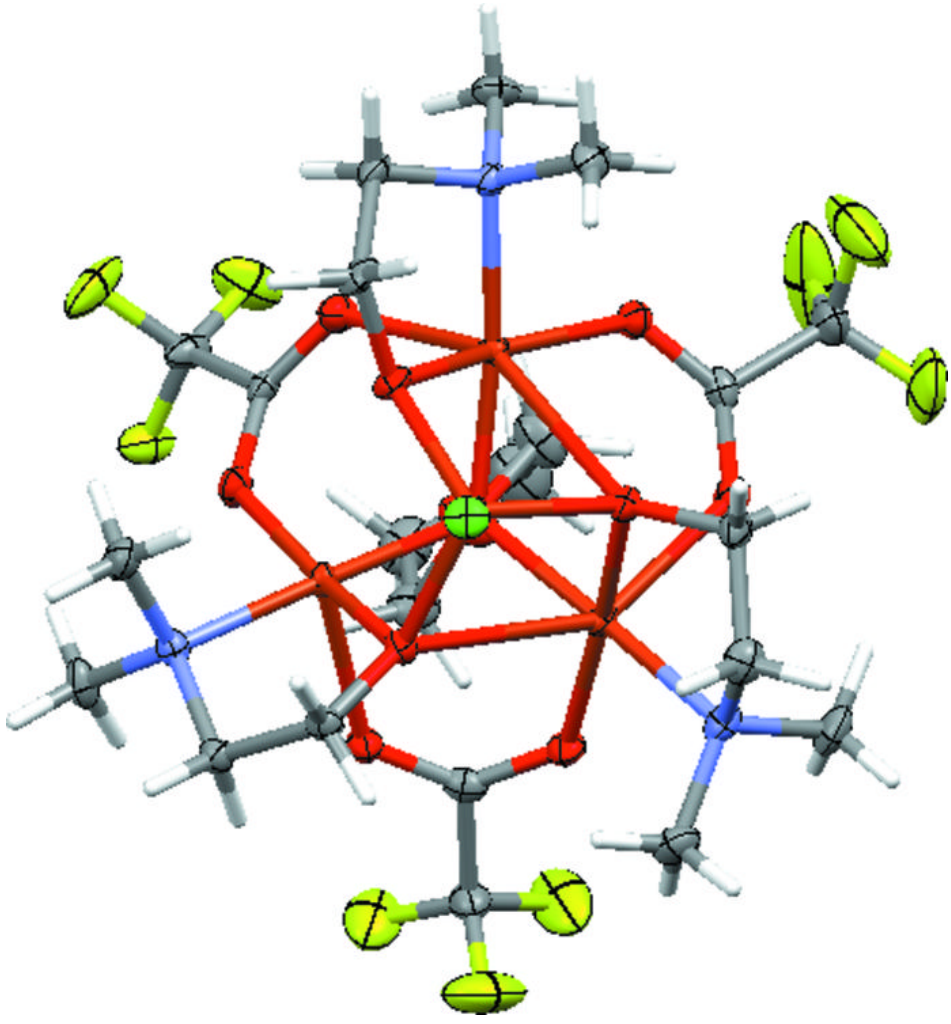

C20
C21
C19
C22
F9
F7
F1
F4
C18
F2
O11
C16
C14
F6
F8
C17
C15
F3
O10
C13
O7
O6
Cu2O4
F5
O8
O9
O5
C12
Cu4
C4
Cu3
C7
N3
N1
C2
O1
C3
N2
C1
C8
O2
C10
O3
C6
C5
C11
C9
Cu1
Cl1

Fig. 2



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4-Methylanilinium *p*-toluenesulfonate

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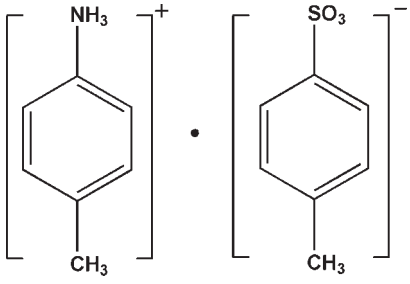
Key indicators: single-crystal X-ray study; T = 293 K; mean σ(C–C) = 0.004 Å; R factor = 0.041; wR factor = 0.093; data-to-parameter ratio = 18.0.

The crystal structure of the title compound, $C_7H_{10}N^+\cdot C_7H_7O_3S^-$, displays strong N—H···O and N—H···S hydrogen bonding between the ammonium group and the *p*-toluenesulfonate anion, linking the cations and anions into chains along the *b* axis.

Related literature

For background to dielectric–ferroelectric materials, see: Hang *et al.* (2009); Li *et al.* (2008).



Experimental

Crystal data

$C_7H_{10}N^+\cdot C_7H_7O_3S^-$
M_r = 279.35
Monoclinic, $P2_1$
a = 5.775 (4) Å
b = 9.026 (5) Å
c = 13.350 (8) Å
β = 96.344 (9)°
V = 691.6 (7) Å^3
Z = 2
Mo $K\alpha$ radiation
μ = 0.24 mm^{-1}
T = 293 K
0.2 × 0.2 × 0.2 mm

Data collection

Rigaku Mercury2 diffractometer
Absorption correction: multi-scan (*CrystalClear*; Rigaku, 2005)
T_{min} = 0.929, T_{max} = 1.000
6641 measured reflections
3136 independent reflections
2876 reflections with $I > 2\sigma(I)$
R_{int} = 0.029

Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.041
$wR(F^2)$ = 0.093
S = 0.99
3136 reflections
174 parameters
1 restraint
H-atom parameters constrained
$\Delta\rho_{max}$ = 0.18 e Å^{-3}
$\Delta\rho_{min}$ = −0.23 e Å^{-3}
Absolute structure: Flack (1983), 1448 Friedel pairs
Flack parameter: 0.05 (8)

Table 1
Hydrogen-bond geometry (Å, °).

D—H···A	D—H	H···A	D···A	D—H···A
N1—H1D···O1^{i}	0.89	2.31	3.170 (3)	164
N1—H1D···O2^{i}	0.89	2.33	2.824 (3)	115
N1—H1D···S1^{i}	0.89	2.81	3.570 (3)	144
N1—H1E···O1^{ii}	0.89	1.96	2.829 (3)	165
N1—H1F···O3^{iii}	0.89	2.02	2.785 (3)	143

Symmetry codes: (i) $-x-1, y-\frac{1}{2}, -z+1$; (ii) $x-1, y-1, z$; (iii) $-x, y-\frac{1}{2}, -z+1$.

Data collection: *CrystalClear* (Rigaku, 2005); cell refinement: *CrystalClear*; data reduction: *CrystalClear*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *SHELXTL* (Sheldrick, 2008); software used to prepare material for publication: *PRPKAPPA* (Ferguson, 1999).

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Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: FJ2307).

References

Ferguson, G. (1999). *PRPKAPPA*. University of Guelph, Canada.
Flack, H. D. (1983). *Acta Cryst.* A**39**, 876–881.
Hang, T., Fu, D. W., Ye, Q. & Xiong, R. G. (2009). *Cryst. Growth Des.* **5**, 2026–2029.
Li, X. Z., Qu, Z. R. & Xiong, R. G. (2008). *Chin. J. Chem.* **11**, 1959–1962.
Rigaku (2005). *CrystalClear*. Rigaku Corporation, Tokyo, Japan.
Sheldrick, G. M. (2008). *Acta Cryst.* A**64**, 112–122.

supplementary materials

Acta Cryst. (2010). E**66**, o1794 [**doi:10.1107/S1600536810021537**]

4-Methylanilinium *p*-toluenesulfonate

R. Xu

Comment

Dielectric-ferroelectric as an interesting class of materials, there are organic ligands (Li *et al.*, 2008), metal-organic coordination compounds (Hang *et al.*, 2009) and organic-inorganic hybrid. In this article, the preparation and crystal structure of the title compound have been presented. It should be not a real ferroelectrics or there may be no distinct phase transition occurred within the measured temperature range. Similarly, below the melting point (477 K) of the compound, the dielectric constant as a function of temperature also goes smoothly, and there is no dielectric anomaly observed.

The asymmetric unit of the title compound contains a (CH_3—C_6H_4—NH_3^+) cation and an (CH_3—C_6H_4—SO_3^-) anion (Fig.1). The strong N—H···S, N—H···O hydrogen bonds involving H1D and H1E (N1···S1 3.570 (3) Å and N1···O1 2.829 (3) Å) are beneficial to the stability of the crystal structure and link the cations and anions to chains along the *b* axis (Fig. 2 and Tab. 1).

Experimental

The title compound was obtained by the addition of *p*-toluenesulfonic acid (3.78 g, 0.022 mol) to a solution of 4-methylaniline (2.14 g, 0.02 mol) in ethanol, in the stoichiometric ratio 1.1:1. After two weeks, good quality single crystals were obtained by slow evaporation.

Refinement

Positional parameters of all the H atoms were calculated geometrically and the H atoms were set to ride on the C and N atoms to which they are bonded, with U_{iso}(H) = 1.2Ueq(C or N).

Figures

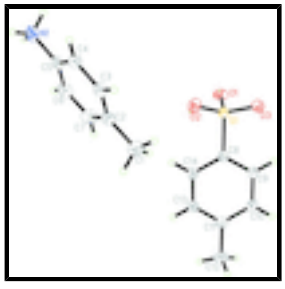


Fig. 1. The molecular structure of the title compound, showing the atomic numbering scheme. Displacement ellipsoids are drawn at the 30% probability level.

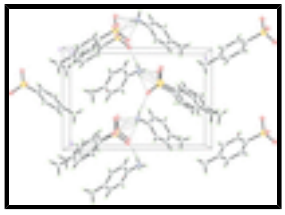


Fig. 2. A view of the packing of the title compound, stacking along the *b* axis. Dashed lines indicate hydrogen bonds.

4-Methylanilinium *p*-toluenesulfonate

Crystal data

$C_7H_{10}N^+·C_7H_7O_3S^-$	$F(000) = 296$
$M_r = 279.35$	$D_x = 1.341$ Mg m^{-3}
Monoclinic, $P2_1$	Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å
Hall symbol: P 2yb	Cell parameters from 3136 reflections
$a = 5.775$ (4) Å	$\theta = 3.6$–$27.5°$
$b = 9.026$ (5) Å	$\mu = 0.24$ mm^{-1}
$c = 13.350$ (8) Å	$T = 293$ K
$\beta = 96.344$ (9)°	Prism, colorless
$V = 691.6$ (7) Å^3	0.2 × 0.2 × 0.2 mm
$Z = 2$	

Data collection

Rigaku Mercury2 diffractometer	3136 independent reflections
Radiation source: fine-focus sealed tube	2876 reflections with $I > 2\sigma(I)$
graphite	$R_{int} = 0.029$
Detector resolution: 13.6612 pixels mm^{-1}	$\theta_{max} = 27.5°$, $\theta_{min} = 3.6°$
CCD_Profile_fitting scans	$h = -7 \rightarrow 7$
Absorption correction: multi-scan (*CrystalClear*; Rigaku, 2005)	$k = -11 \rightarrow 11$
$T_{min} = 0.929$, $T_{max} = 1.000$	$l = -17 \rightarrow 17$
6641 measured reflections	

Refinement

Refinement on F^2	Secondary atom site location: difference Fourier map
Least-squares matrix: full	Hydrogen site location: inferred from neighbouring sites
$R[F^2 > 2\sigma(F^2)] = 0.041$	H-atom parameters constrained
$wR(F^2) = 0.093$	$w = 1/[\sigma^2(F_o^2) + (0.0447P)^2 + 0.128P]$ where $P = (F_o^2 + 2F_c^2)/3$
$S = 0.99$	$(\Delta/\sigma)_{max} < 0.001$
3136 reflections	$\Delta\rho_{max} = 0.18$ e Å^{-3}
174 parameters	$\Delta\rho_{min} = -0.23$ e Å^{-3}

1 restraint	Absolute structure: Flack (1983), 1448 Friedel pairs
Primary atom site location: structure-invariant direct methods	Flack parameter: 0.05 (8)

Special details

Geometry. All e.s.d.'s (except the e.s.d. in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell e.s.d.'s are taken into account individually in the estimation of e.s.d.'s in distances, angles and torsion angles; correlations between e.s.d.'s in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell e.s.d.'s is used for estimating e.s.d.'s involving l.s. planes.

Refinement. Refinement of F^2 against ALL reflections. The weighted *R*-factor *wR* and goodness of fit *S* are based on F^2, conventional *R*-factors *R* are based on *F*, with *F* set to zero for negative F^2. The threshold expression of $F^2 > \sigma(F^2)$ is used only for calculating *R*-factors(gt) *etc*. and is not relevant to the choice of reflections for refinement. *R*-factors based on F^2 are statistically about twice as large as those based on *F*, and *R*- factors based on ALL data will be even larger.

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å^2)

	x	*y*	*z*	U_{iso}*/U_{eq}
S1	0.14320 (9)	−0.16236 (6)	0.34803 (4)	0.03362 (14)
O1	0.0753 (3)	−0.0673 (2)	0.42886 (12)	0.0456 (4)
O2	0.0234 (3)	−0.30349 (19)	0.34704 (14)	0.0481 (4)
O3	0.3936 (2)	−0.1756 (2)	0.34883 (12)	0.0485 (4)
C8	0.0436 (3)	−0.0720 (2)	0.23353 (15)	0.0302 (4)
C9	0.1872 (4)	0.0278 (3)	0.19156 (17)	0.0363 (5)
H9A	0.3372	0.0450	0.2223	0.044*
C10	0.1071 (4)	0.1023 (3)	0.10348 (19)	0.0420 (6)
H10A	0.2038	0.1701	0.0761	0.050*
C11	−0.1161 (4)	0.0769 (3)	0.05557 (17)	0.0394 (5)
C12	−0.2047 (5)	0.1588 (4)	−0.0397 (2)	0.0589 (8)
H12A	−0.3718	0.1546	−0.0491	0.071*
H12B	−0.1434	0.1134	−0.0962	0.071*
H12C	−0.1553	0.2603	−0.0343	0.071*
C13	−0.2562 (4)	−0.0238 (3)	0.09898 (18)	0.0405 (6)
H13A	−0.4056	−0.0420	0.0679	0.049*
C14	−0.1806 (4)	−0.0981 (3)	0.18702 (18)	0.0368 (5)
H14A	−0.2783	−0.1647	0.2149	0.044*
N1	−0.7130 (4)	−0.8010 (3)	0.50369 (16)	0.0513 (5)
H1D	−0.8346	−0.7437	0.5125	0.062*
H1E	−0.7621	−0.8925	0.4885	0.062*
H1F	−0.6154	−0.8026	0.5602	0.062*
C1	−0.2340 (5)	−0.5599 (4)	0.1861 (2)	0.0590 (7)
H1A	−0.2324	−0.4538	0.1911	0.071*
H1B	−0.3120	−0.5889	0.1218	0.071*
H1C	−0.0768	−0.5963	0.1926	0.071*
C2	−0.3611 (4)	−0.6242 (2)	0.26934 (18)	0.0408 (6)
C3	−0.2853 (4)	−0.7531 (3)	0.31786 (18)	0.0400 (5)
H3A	−0.1548	−0.8010	0.2985	0.048*
C4	−0.3986 (4)	−0.8132 (3)	0.39495 (18)	0.0392 (5)

H4A	−0.3448	−0.8996	0.4275	0.047*
C5	−0.5937 (4)	−0.7409 (3)	0.42196 (17)	0.0385 (5)
C6	−0.6736 (4)	−0.6122 (3)	0.3749 (2)	0.0485 (7)
H6A	−0.8047	−0.5645	0.3939	0.058*
C7	−0.5565 (5)	−0.5552 (3)	0.2994 (2)	0.0508 (6)
H7A	−0.6097	−0.4680	0.2677	0.061*

Atomic displacement parameters (Å^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
S1	0.0322 (2)	0.0360 (3)	0.0334 (3)	0.0060 (3)	0.00711 (18)	0.0046 (2)
O1	0.0537 (10)	0.0513 (11)	0.0326 (9)	0.0096 (9)	0.0085 (7)	−0.0025 (8)
O2	0.0532 (11)	0.0334 (9)	0.0589 (11)	0.0011 (8)	0.0121 (8)	0.0090 (8)
O3	0.0311 (7)	0.0656 (11)	0.0489 (9)	0.0115 (9)	0.0046 (6)	0.0178 (9)
C8	0.0276 (10)	0.0320 (11)	0.0315 (10)	0.0028 (9)	0.0058 (8)	−0.0017 (9)
C9	0.0309 (11)	0.0432 (13)	0.0349 (12)	−0.0018 (10)	0.0044 (9)	0.0023 (10)
C10	0.0416 (13)	0.0448 (14)	0.0409 (13)	−0.0050 (11)	0.0101 (10)	0.0068 (11)
C11	0.0438 (12)	0.0443 (13)	0.0303 (11)	0.0072 (11)	0.0042 (10)	0.0023 (10)
C12	0.0641 (18)	0.074 (2)	0.0371 (14)	0.0073 (16)	0.0010 (12)	0.0134 (14)
C13	0.0295 (11)	0.0532 (15)	0.0380 (12)	0.0016 (11)	−0.0004 (9)	−0.0003 (11)
C14	0.0305 (11)	0.0392 (12)	0.0415 (13)	−0.0011 (10)	0.0071 (9)	0.0019 (10)
N1	0.0401 (11)	0.0737 (14)	0.0412 (11)	−0.0133 (11)	0.0088 (9)	−0.0154 (11)
C1	0.0736 (19)	0.0558 (17)	0.0486 (16)	−0.0024 (16)	0.0105 (14)	0.0017 (14)
C2	0.0469 (13)	0.0390 (14)	0.0362 (12)	−0.0028 (10)	0.0027 (10)	−0.0083 (9)
C3	0.0349 (12)	0.0416 (14)	0.0444 (13)	0.0025 (10)	0.0085 (10)	−0.0099 (11)
C4	0.0392 (12)	0.0377 (12)	0.0402 (12)	0.0013 (10)	0.0026 (9)	−0.0019 (10)
C5	0.0310 (11)	0.0513 (14)	0.0333 (11)	−0.0057 (10)	0.0047 (9)	−0.0119 (11)
C6	0.0385 (13)	0.0572 (16)	0.0494 (15)	0.0153 (11)	0.0032 (11)	−0.0145 (12)
C7	0.0583 (16)	0.0456 (15)	0.0474 (14)	0.0186 (13)	0.0012 (12)	−0.0013 (12)

Geometric parameters (Å, °)

S1—O2	1.449 (2)	N1—C5	1.458 (3)
S1—O3	1.4500 (18)	N1—H1D	0.8903
S1—O1	1.4655 (18)	N1—H1E	0.8893
S1—C8	1.772 (2)	N1—H1F	0.8904
C8—C9	1.384 (3)	C1—C2	1.514 (4)
C8—C14	1.393 (3)	C1—H1A	0.9600
C9—C10	1.389 (3)	C1—H1B	0.9600
C9—H9A	0.9300	C1—H1C	0.9600
C10—C11	1.393 (4)	C2—C3	1.379 (3)
C10—H10A	0.9300	C2—C7	1.387 (4)
C11—C13	1.386 (3)	C3—C4	1.389 (3)
C11—C12	1.510 (3)	C3—H3A	0.9300
C12—H12A	0.9600	C4—C5	1.384 (3)
C12—H12B	0.9600	C4—H4A	0.9300
C12—H12C	0.9600	C5—C6	1.376 (4)
C13—C14	1.381 (3)	C6—C7	1.374 (4)
C13—H13A	0.9300	C6—H6A	0.9300

C14—H14A	0.9300	C7—H7A	0.9300
O2—S1—O3	113.73 (12)	C5—N1—H1D	109.1
O2—S1—O1	110.78 (11)	C5—N1—H1E	109.9
O3—S1—O1	113.02 (11)	H1D—N1—H1E	109.5
O2—S1—C8	106.72 (11)	C5—N1—H1F	109.4
O3—S1—C8	105.82 (10)	H1D—N1—H1F	109.4
O1—S1—C8	106.15 (11)	H1E—N1—H1F	109.5
C9—C8—C14	119.9 (2)	C2—C1—H1A	109.5
C9—C8—S1	119.82 (16)	C2—C1—H1B	109.5
C14—C8—S1	120.26 (17)	H1A—C1—H1B	109.5
C8—C9—C10	120.0 (2)	C2—C1—H1C	109.5
C8—C9—H9A	120.0	H1A—C1—H1C	109.5
C10—C9—H9A	120.0	H1B—C1—H1C	109.5
C9—C10—C11	120.9 (2)	C3—C2—C7	118.0 (2)
C9—C10—H10A	119.5	C3—C2—C1	120.9 (2)
C11—C10—H10A	119.5	C7—C2—C1	121.1 (2)
C13—C11—C10	118.0 (2)	C2—C3—C4	121.8 (2)
C13—C11—C12	120.9 (2)	C2—C3—H3A	119.1
C10—C11—C12	121.1 (2)	C4—C3—H3A	119.1
C11—C12—H12A	109.5	C5—C4—C3	118.2 (2)
C11—C12—H12B	109.5	C5—C4—H4A	120.9
H12A—C12—H12B	109.5	C3—C4—H4A	120.9
C11—C12—H12C	109.5	C6—C5—C4	121.4 (2)
H12A—C12—H12C	109.5	C6—C5—N1	119.6 (2)
H12B—C12—H12C	109.5	C4—C5—N1	119.0 (2)
C14—C13—C11	122.0 (2)	C7—C6—C5	118.9 (2)
C14—C13—H13A	119.0	C7—C6—H6A	120.5
C11—C13—H13A	119.0	C5—C6—H6A	120.5
C13—C14—C8	119.2 (2)	C6—C7—C2	121.8 (2)
C13—C14—H14A	120.4	C6—C7—H7A	119.1
C8—C14—H14A	120.4	C2—C7—H7A	119.1
O2—S1—C8—C9	−151.80 (18)	C11—C13—C14—C8	−0.4 (4)
O3—S1—C8—C9	−30.3 (2)	C9—C8—C14—C13	0.3 (3)
O1—S1—C8—C9	90.00 (19)	S1—C8—C14—C13	178.57 (18)
O2—S1—C8—C14	29.9 (2)	C7—C2—C3—C4	−0.2 (3)
O3—S1—C8—C14	151.35 (19)	C1—C2—C3—C4	179.5 (2)
O1—S1—C8—C14	−88.3 (2)	C2—C3—C4—C5	0.6 (3)
C14—C8—C9—C10	0.3 (3)	C3—C4—C5—C6	−0.6 (3)
S1—C8—C9—C10	−178.00 (19)	C3—C4—C5—N1	−179.1 (2)
C8—C9—C10—C11	−0.7 (4)	C4—C5—C6—C7	0.2 (4)
C9—C10—C11—C13	0.6 (4)	N1—C5—C6—C7	178.6 (2)
C9—C10—C11—C12	179.4 (2)	C5—C6—C7—C2	0.3 (4)
C10—C11—C13—C14	0.0 (4)	C3—C2—C7—C6	−0.2 (4)
C12—C11—C13—C14	−178.8 (2)	C1—C2—C7—C6	−179.9 (2)

Hydrogen-bond geometry (Å, °)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*

N1—H1D···O1^{i}	0.89	2.31	3.170 (3)	164
N1—H1D···O2^{i}	0.89	2.33	2.824 (3)	115
N1—H1D···S1^{i}	0.89	2.81	3.570 (3)	144
N1—H1E···O1^{ii}	0.89	1.96	2.829 (3)	165
N1—H1F···O3^{iii}	0.89	2.02	2.785 (3)	143

Symmetry codes: (i) −*x*−1, *y*−1/2, −*z*+1; (ii) *x*−1, *y*−1, *z*; (iii) −*x*, *y*−1/2, −*z*+1.

Fig. 1

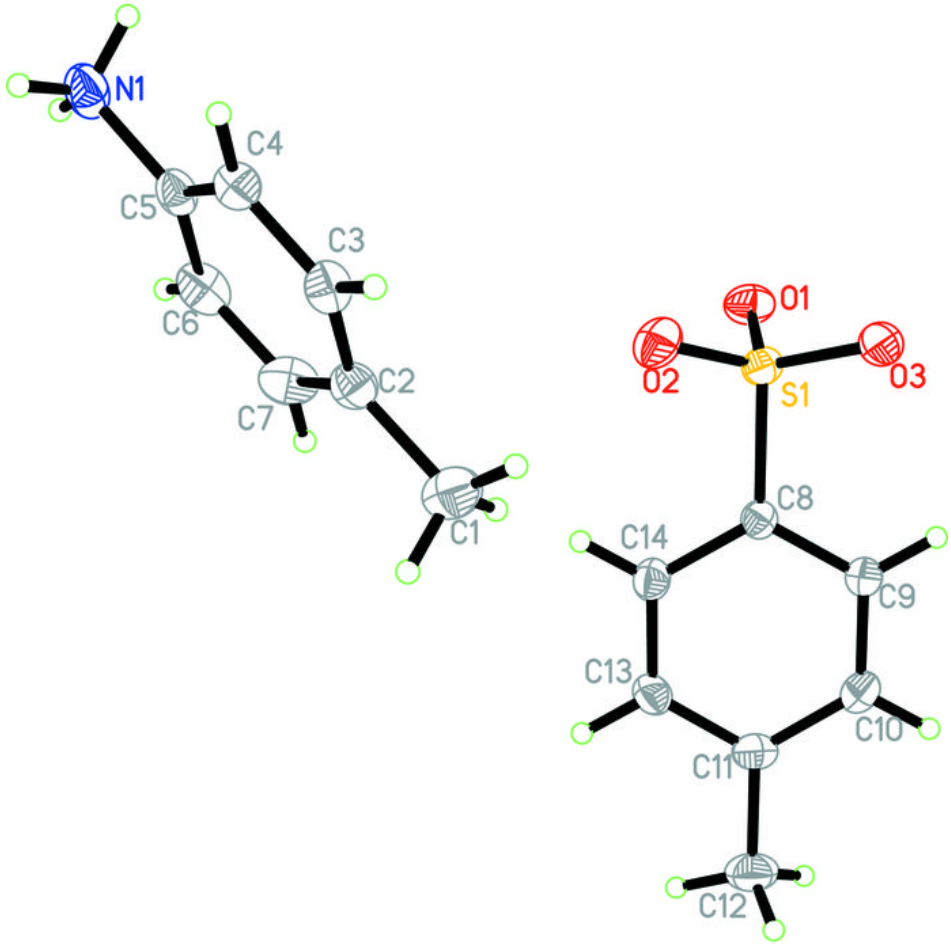
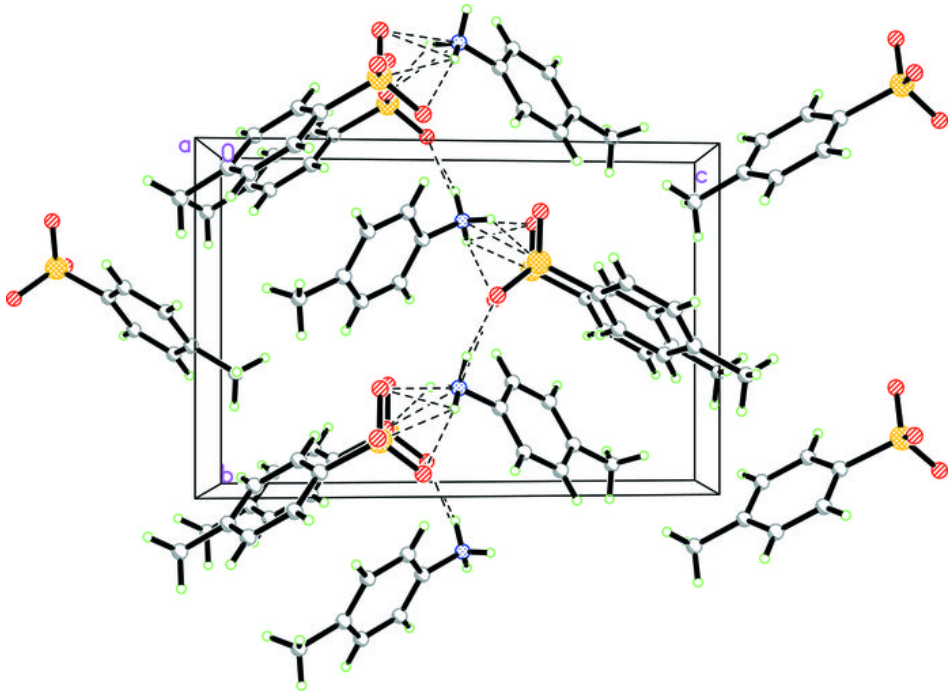


Fig. 2



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2-Amino-4,6-dimethylpyrimidin-1-ium 1-oxo-2,6,7-trioxa-1λ^5-phosphabicyclo-[2.2.2]octane-4-carboxylate

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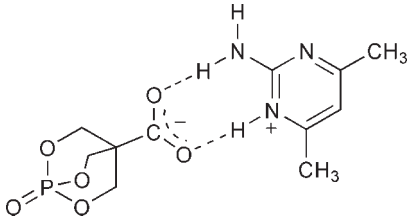
Key indicators: single-crystal X-ray study; T = 113 K; mean σ(C–C) = 0.001 Å; R factor = 0.039; wR factor = 0.107; data-to-parameter ratio = 32.0.

In the title compound, $C_6H_{10}N_3^+\cdot C_5H_6O_6P^-$, the cation and anion are linked by pairs of N—H···O hydrogen bonds. There are additional intermolecular N—H···N hydrogen bonds., which generate centrosymmetric tetramers of two cations and two anions

Related literature

For the applications of caged bicyclic phosphates, see: Li *et al.* (2000). For related structures, see: Meng *et al.* (2009); Guo & Zang (2008); Thakur & Desiraju (2008); Wang *et al.* (2007).



Experimental

Crystal data

$C_6H_{10}N_3^+\cdot C_5H_6O_6P^-$
M_r = 317.24
Monoclinic, $P2_1/c$
a = 9.5080 (13) Å
b = 6.1870 (8) Å
c = 23.974 (2) Å
β = 99.611 (5)°
V = 1390.5 (3) Å^3
Z = 4
Mo $K\alpha$ radiation
μ = 0.23 mm^{-1}
T = 113 K
0.24 × 0.22 × 0.14 mm

Data collection

Rigaku Saturn724 CCD diffractometer
Absorption correction: multi-scan (*CrystalClear*; Rigaku/MSC, 2009)
T_{min} = 0.947, T_{max} = 0.969
23989 measured reflections
6532 independent reflections
4883 reflections with $I > 2\sigma(I)$
R_{int} = 0.035

Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.039
$wR(F^2)$ = 0.107
S = 1.01
6532 reflections
204 parameters
H atoms treated by a mixture of independent and constrained refinement
$\Delta\rho_{max}$ = 0.54 e Å^{-3}
$\Delta\rho_{min}$ = −0.38 e Å^{-3}

Table 1
Hydrogen-bond geometry (Å, °).

D—H···A	D—H	H···A	D···A	D—H···A
N1—H1···O1	0.866 (15)	1.907 (15)	2.7719 (11)	176.4 (14)
N1—H2···N3^{i}	0.900 (14)	2.113 (15)	3.0114 (12)	176.3 (12)
N2—H3···O2	0.988 (15)	1.738 (16)	2.7170 (10)	170.4 (15)

Symmetry code: (i) $-x+1, -y, -z+1$.

Data collection: *CrystalClear-SM Expert* (Rigaku/MSC, 2009); cell refinement: *CrystalClear-SM Expert*; data reduction: *CrystalClear-SM Expert*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *CrystalStructure* (Rigaku/MSC, 2009); software used to prepare material for publication: *CrystalStructure*.

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Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: FJ2308).

References

Guo, M.-L. & Zang, H.-J. (2008). *Acta Cryst.* C**64**, m173–m175.
Li, X., Ou, Y.-X., Zhang, Y.-H. & Lian, D.-J. (2000). *Chin. Chem. Lett.* **11**, 887–890.
Meng, A.-L., Huang, J.-E., Zheng, B. & Li, Z.-J. (2009). *Acta Cryst.* E**65**, o1595.
Rigaku/MSC (2009). *CrystalClear-SM Expert* and *CrystalStructure*. Rigaku/MSC, The Woodlands, Texas, USA.
Sheldrick, G. M. (2008). *Acta Cryst.* A**64**, 112–122.
Thakur, T. S. & Desiraju, G. R. (2008). *Cryst. Growth Des.* **8**, 4031–4044.
Wang, Z., Zang, H.-J. & Guo, M.-L. (2007). *Acta Cryst.* E**63**, o3418.

supplementary materials

Acta Cryst. (2010). E**66**, o1528 [**doi:10.1107/S1600536810019896**]

2-Amino-4,6-dimethylpyrimidin-1-ium 1-oxo-2,6,7-trioxa-1λ^5-phosphabicyclo[2.2.2]octane-4-carboxylate

X.-F. Hou, G.-C. Li and P.-Y. Lai

Comment

Caged bicyclic phosphates are widely used as flame retardants or pesticides (Li *et al.* 2000). It can also serve as host–guest systems and have been studied in the context of hydrogen-bond patterns (Guo & Zang, 2008; Wang *et al.*, 2007). Aminopyrimidine derivatives are biologically important compounds as they occur in nature as components of nucleic acids (Meng *et al.*, 2009). The crystal structures of aminopyrimidine carboxylates have been reported (Thakur *et al.*, 2008). We report here the crystal structure of a new bicyclic phosphate cage compound.

In the title compound, $[C_6H_{10}N_3]^+$ $[C_5H_6O_6P]^-$, The cation and anion in the asymmetric unit are linked by N—H···O hydrogen bonds. There is also addition intermolecular N—H···N hydrogen bonds. (Fig. 2).

Experimental

The title compound was obtained by reaction of 1-oxo-2,6,7-trioxa-1-phosphabicyclo[2.2.2]octane-4-carboxylic acid (0.39 g, 0.2 mmol) and 2-amino-4,6-dimethylpyrimidine(0.25 g, 0.2 mmol) in refluxing acetone (50 ml). The solvent was evaporated *in vacuo*. The title compound was recrystallized from ethanol and single crystals of (I) were obtained by slow evaporation.

Refinement

All H atoms were placed in calculated positions, with C—H = 0.98 Å or 0.99 Å, and included in the final cycles of refinement using a riding model, with U_{iso}(H) = 1.2Ueq(C).

Figures

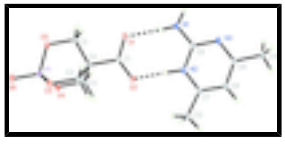


Fig. 1. The asymmetric unit of the title compound, (I), with displacement ellipsoids drawn at the 30% probability level.

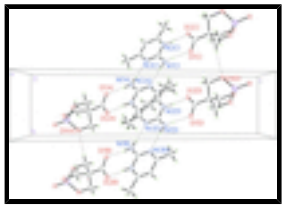


Fig. 2. The packing diagram of the title compound. Intermolecular hydrogen bonds are shown as dashed line.

2-Amino-4,6-dimethylpyrimidin-1-ium 1-oxo-2,6,7-trioxa-1λ^5-phosphabicyclo[2.2.2]octane-4-carboxylate

Crystal data

$C_6H_{10}N_3^+ \cdot C_5H_6O_6P^-$	$F(000) = 664$
$M_r = 317.24$	$D_x = 1.515$ Mg m^{-3}
Monoclinic, $P2_1/c$	Mo $K\alpha$ radiation, $\lambda = 0.71075$ Å
Hall symbol: -P 2ybc	Cell parameters from 5985 reflections
$a = 9.5080$ (13) Å	$\theta = 2.2$–$36.3°$
$b = 6.1870$ (8) Å	$\mu = 0.23$ mm^{-1}
$c = 23.974$ (2) Å	$T = 113$ K
$\beta = 99.611$ (5)°	Prism, colorless
$V = 1390.5$ (3) Å^3	0.24 × 0.22 × 0.14 mm
$Z = 4$	

Data collection

Rigaku Saturn724 CCD diffractometer	6532 independent reflections
Radiation source: rotating anode	4883 reflections with $I > 2\sigma(I)$
multilayer	$R_{int} = 0.035$
Detector resolution: 14.222 pixels mm^{-1}	$\theta_{max} = 36.5°$, $\theta_{min} = 1.7°$
ω scans	$h = -15 \rightarrow 14$
Absorption correction: multi-scan (*CrystalClear*; Rigaku/MSC, 2009)	$k = -10 \rightarrow 10$
$T_{min} = 0.947$, $T_{max} = 0.969$	$l = -36 \rightarrow 39$
23989 measured reflections	

Refinement

Refinement on F^2	Primary atom site location: structure-invariant direct methods
Least-squares matrix: full	Secondary atom site location: difference Fourier map
$R[F^2 > 2\sigma(F^2)] = 0.039$	Hydrogen site location: inferred from neighbouring sites
$wR(F^2) = 0.107$	H atoms treated by a mixture of independent and constrained refinement
$S = 1.01$	$w = 1/[\sigma^2(F_o^2) + (0.0615P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
6532 reflections	$(\Delta/\sigma)_{max} = 0.001$
204 parameters	$\Delta\rho_{max} = 0.54$ e Å^{-3}
0 restraints	$\Delta\rho_{min} = -0.38$ e Å^{-3}

Special details

Geometry. All e.s.d.'s (except the e.s.d. in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell e.s.d.'s are taken into account individually in the estimation of e.s.d.'s in distances, angles and torsion angles; correlations between e.s.d.'s in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell e.s.d.'s is used for estimating e.s.d.'s involving l.s. planes.

Refinement. Refinement of F^2 against ALL reflections. The weighted *R*-factor *wR* and goodness of fit *S* are based on F^2, conventional *R*-factors *R* are based on *F*, with *F* set to zero for negative F^2. The threshold expression of $F^2 > \sigma(F^2)$ is used only for calculating *R*-factors(gt) *etc*. and is not relevant to the choice of reflections for refinement. *R*-factors based on F^2 are statistically about twice as large as those based on *F*, and *R*- factors based on ALL data will be even larger.

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters ($Å^2$)

	x	*y*	*z*	U_{iso}*/U_{eq}
P1	0.14090 (2)	0.74372 (4)	0.157866 (9)	0.01584 (6)
O1	0.32415 (8)	0.33013 (12)	0.32735 (3)	0.02813 (17)
O2	0.46621 (8)	0.62093 (12)	0.33500 (3)	0.02544 (16)
O3	0.29862 (7)	0.67033 (12)	0.15596 (3)	0.02097 (14)
O4	0.15812 (7)	0.91396 (11)	0.20765 (3)	0.02023 (13)
O5	0.06923 (7)	0.54214 (12)	0.18168 (3)	0.02421 (15)
O6	0.06557 (8)	0.82445 (13)	0.10419 (3)	0.02619 (16)
N1	0.45629 (9)	0.17785 (15)	0.43177 (4)	0.02312 (17)
N2	0.61028 (8)	0.46847 (12)	0.43466 (3)	0.01702 (14)
N3	0.63811 (8)	0.21010 (14)	0.50821 (3)	0.01949 (15)
C1	0.36366 (9)	0.50774 (14)	0.31115 (4)	0.01674 (15)
C2	0.27993 (8)	0.59650 (13)	0.25498 (3)	0.01332 (14)
C3	0.37600 (9)	0.58891 (16)	0.20974 (4)	0.01990 (17)
H3A	0.4621	0.6782	0.2219	0.024*
H3B	0.4070	0.4383	0.2049	0.024*
C4	0.23414 (10)	0.83103 (15)	0.26188 (4)	0.02018 (17)
H4A	0.1711	0.8386	0.2908	0.024*
H4B	0.3193	0.9214	0.2749	0.024*
C5	0.14789 (10)	0.45860 (16)	0.23533 (4)	0.02254 (19)
H5A	0.1769	0.3072	0.2302	0.027*
H5B	0.0854	0.4605	0.2645	0.027*
C6	0.56840 (9)	0.28450 (15)	0.45830 (4)	0.01698 (15)
C7	0.72567 (10)	0.58213 (15)	0.45997 (4)	0.01896 (16)
C8	0.79892 (10)	0.51036 (16)	0.51086 (4)	0.02109 (17)
H8	0.8792	0.5871	0.5300	0.025*
C9	0.75166 (10)	0.32090 (16)	0.53356 (4)	0.01951 (17)
C10	0.76334 (12)	0.77807 (16)	0.42947 (5)	0.0264 (2)
H10A	0.8040	0.7342	0.3962	0.032*
H10B	0.8334	0.8642	0.4547	0.032*
H10C	0.6774	0.8647	0.4173	0.032*
C11	0.82793 (13)	0.22887 (19)	0.58813 (4)	0.0295 (2)
H11A	0.7581	0.1869	0.6120	0.035*
H11B	0.8927	0.3379	0.6079	0.035*

H11C	0.8828	0.1016	0.5803	0.035*
H1	0.4144 (16)	0.231 (2)	0.3998 (7)	0.033 (4)*
H2	0.4287 (15)	0.065 (2)	0.4512 (6)	0.039 (4)*
H3	0.5623 (16)	0.511 (3)	0.3965 (6)	0.052 (4)*

Atomic displacement parameters (Å^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
P1	0.01665 (11)	0.01722 (10)	0.01235 (10)	0.00168 (8)	−0.00133 (7)	0.00215 (7)
O1	0.0314 (4)	0.0245 (3)	0.0237 (3)	−0.0074 (3)	−0.0093 (3)	0.0116 (3)
O2	0.0232 (3)	0.0255 (3)	0.0229 (3)	−0.0060 (3)	−0.0101 (3)	0.0070 (3)
O3	0.0215 (3)	0.0277 (3)	0.0142 (3)	0.0069 (3)	0.0043 (2)	0.0034 (2)
O4	0.0265 (3)	0.0171 (3)	0.0155 (3)	0.0085 (2)	−0.0013 (2)	0.0013 (2)
O5	0.0211 (3)	0.0261 (3)	0.0213 (3)	−0.0082 (3)	−0.0087 (2)	0.0080 (3)
O6	0.0282 (4)	0.0310 (4)	0.0167 (3)	0.0031 (3)	−0.0042 (3)	0.0060 (3)
N1	0.0190 (4)	0.0305 (4)	0.0177 (4)	−0.0039 (3)	−0.0029 (3)	0.0094 (3)
N2	0.0183 (3)	0.0190 (3)	0.0127 (3)	0.0026 (3)	−0.0005 (2)	0.0021 (2)
N3	0.0171 (3)	0.0277 (4)	0.0127 (3)	0.0015 (3)	−0.0002 (3)	0.0054 (3)
C1	0.0161 (4)	0.0180 (4)	0.0149 (4)	0.0020 (3)	−0.0012 (3)	0.0028 (3)
C2	0.0126 (3)	0.0130 (3)	0.0134 (3)	0.0002 (3)	−0.0007 (3)	0.0011 (3)
C3	0.0157 (4)	0.0266 (4)	0.0171 (4)	0.0057 (3)	0.0018 (3)	0.0032 (3)
C4	0.0240 (4)	0.0190 (4)	0.0151 (4)	0.0073 (3)	−0.0040 (3)	−0.0018 (3)
C5	0.0200 (4)	0.0239 (4)	0.0203 (4)	−0.0077 (3)	−0.0065 (3)	0.0090 (3)
C6	0.0151 (4)	0.0231 (4)	0.0125 (3)	0.0028 (3)	0.0016 (3)	0.0034 (3)
C7	0.0219 (4)	0.0185 (4)	0.0157 (4)	0.0021 (3)	0.0009 (3)	−0.0016 (3)
C8	0.0231 (4)	0.0231 (4)	0.0154 (4)	0.0002 (3)	−0.0018 (3)	−0.0015 (3)
C9	0.0187 (4)	0.0273 (4)	0.0116 (3)	0.0031 (3)	−0.0002 (3)	0.0010 (3)
C10	0.0334 (5)	0.0182 (4)	0.0247 (5)	−0.0026 (4)	−0.0033 (4)	0.0018 (3)
C11	0.0280 (5)	0.0417 (6)	0.0151 (4)	−0.0023 (4)	−0.0070 (4)	0.0075 (4)

Geometric parameters (Å, °)

P1—O6	1.4529 (7)	C2—C3	1.5310 (12)
P1—O5	1.5734 (7)	C2—C4	1.5318 (12)
P1—O3	1.5748 (7)	C3—H3A	0.9900
P1—O4	1.5798 (7)	C3—H3B	0.9900
O1—C1	1.2443 (11)	C4—H4A	0.9900
O2—C1	1.2578 (11)	C4—H4B	0.9900
O3—C3	1.4631 (11)	C5—H5A	0.9900
O4—C4	1.4703 (10)	C5—H5B	0.9900
O5—C5	1.4694 (11)	C7—C8	1.3737 (12)
N1—C6	1.3227 (12)	C7—C10	1.4901 (14)
N1—H1	0.866 (15)	C8—C9	1.3977 (14)
N1—H2	0.900 (14)	C8—H8	0.9500
N2—C7	1.3580 (12)	C9—C11	1.4983 (13)
N2—C6	1.3603 (12)	C10—H10A	0.9800
N2—H3	0.988 (15)	C10—H10B	0.9800
N3—C9	1.3363 (12)	C10—H10C	0.9800
N3—C6	1.3484 (11)	C11—H11A	0.9800

C1—C2	1.5460 (11)	C11—H11B	0.9800
C2—C5	1.5260 (12)	C11—H11C	0.9800
O6—P1—O5	114.50 (4)	O4—C4—H4B	109.7
O6—P1—O3	113.86 (4)	C2—C4—H4B	109.7
O5—P1—O3	104.73 (4)	H4A—C4—H4B	108.2
O6—P1—O4	114.43 (4)	O5—C5—C2	110.24 (7)
O5—P1—O4	104.52 (4)	O5—C5—H5A	109.6
O3—P1—O4	103.59 (4)	C2—C5—H5A	109.6
C3—O3—P1	114.52 (5)	O5—C5—H5B	109.6
C4—O4—P1	114.14 (5)	C2—C5—H5B	109.6
C5—O5—P1	114.11 (5)	H5A—C5—H5B	108.1
C6—N1—H1	116.8 (10)	N1—C6—N3	119.58 (8)
C6—N1—H2	114.7 (9)	N1—C6—N2	119.05 (8)
H1—N1—H2	128.2 (13)	N3—C6—N2	121.37 (8)
C7—N2—C6	121.20 (7)	N2—C7—C8	118.78 (8)
C7—N2—H3	119.3 (10)	N2—C7—C10	116.39 (8)
C6—N2—H3	119.1 (10)	C8—C7—C10	124.83 (9)
C9—N3—C6	117.95 (8)	C7—C8—C9	117.94 (8)
O1—C1—O2	126.96 (8)	C7—C8—H8	121.0
O1—C1—C2	116.56 (7)	C9—C8—H8	121.0
O2—C1—C2	116.46 (7)	N3—C9—C8	122.75 (8)
C5—C2—C3	108.75 (7)	N3—C9—C11	116.02 (9)
C5—C2—C4	109.20 (7)	C8—C9—C11	121.23 (9)
C3—C2—C4	108.63 (7)	C7—C10—H10A	109.5
C5—C2—C1	110.36 (7)	C7—C10—H10B	109.5
C3—C2—C1	108.95 (7)	H10A—C10—H10B	109.5
C4—C2—C1	110.90 (7)	C7—C10—H10C	109.5
O3—C3—C2	110.00 (7)	H10A—C10—H10C	109.5
O3—C3—H3A	109.7	H10B—C10—H10C	109.5
C2—C3—H3A	109.7	C9—C11—H11A	109.5
O3—C3—H3B	109.7	C9—C11—H11B	109.5
C2—C3—H3B	109.7	H11A—C11—H11B	109.5
H3A—C3—H3B	108.2	C9—C11—H11C	109.5
O4—C4—C2	109.99 (7)	H11A—C11—H11C	109.5
O4—C4—H4A	109.7	H11B—C11—H11C	109.5
C2—C4—H4A	109.7		
O6—P1—O3—C3	179.91 (6)	C5—C2—C4—O4	−59.68 (9)
O5—P1—O3—C3	−54.29 (7)	C3—C2—C4—O4	58.79 (9)
O4—P1—O3—C3	55.00 (7)	C1—C2—C4—O4	178.50 (7)
O6—P1—O4—C4	179.86 (6)	P1—O5—C5—C2	1.39 (11)
O5—P1—O4—C4	53.84 (7)	C3—C2—C5—O5	−60.03 (10)
O3—P1—O4—C4	−55.60 (7)	C4—C2—C5—O5	58.35 (10)
O6—P1—O5—C5	178.68 (7)	C1—C2—C5—O5	−179.49 (7)
O3—P1—O5—C5	53.28 (8)	C9—N3—C6—N1	179.42 (9)
O4—P1—O5—C5	−55.34 (8)	C9—N3—C6—N2	−1.06 (13)
O1—C1—C2—C5	8.87 (11)	C7—N2—C6—N1	−179.24 (9)
O2—C1—C2—C5	−172.46 (9)	C7—N2—C6—N3	1.24 (13)
O1—C1—C2—C3	−110.46 (9)	C6—N2—C7—C8	−1.19 (13)

O2—C1—C2—C3	68.20 (10)	C6—N2—C7—C10	178.60 (8)
O1—C1—C2—C4	130.02 (9)	N2—C7—C8—C9	0.99 (13)
O2—C1—C2—C4	−51.31 (11)	C10—C7—C8—C9	−178.78 (9)
P1—O3—C3—C2	0.12 (9)	C6—N3—C9—C8	0.90 (14)
C5—C2—C3—O3	59.14 (9)	C6—N3—C9—C11	−178.44 (9)
C4—C2—C3—O3	−59.61 (9)	C7—C8—C9—N3	−0.89 (14)
C1—C2—C3—O3	179.47 (7)	C7—C8—C9—C11	178.42 (9)
P1—O4—C4—C2	1.10 (9)		

Hydrogen-bond geometry (Å, °)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
N1—H1···O1	0.866 (15)	1.907 (15)	2.7719 (11)	176.4 (14)
N1—H2···N3^{i}	0.900 (14)	2.113 (15)	3.0114 (12)	176.3 (12)
N2—H3···O2	0.988 (15)	1.738 (16)	2.7170 (10)	170.4 (15)

Symmetry codes: (i) −*x*+1, −*y*, −*z*+1.

Fig. 1

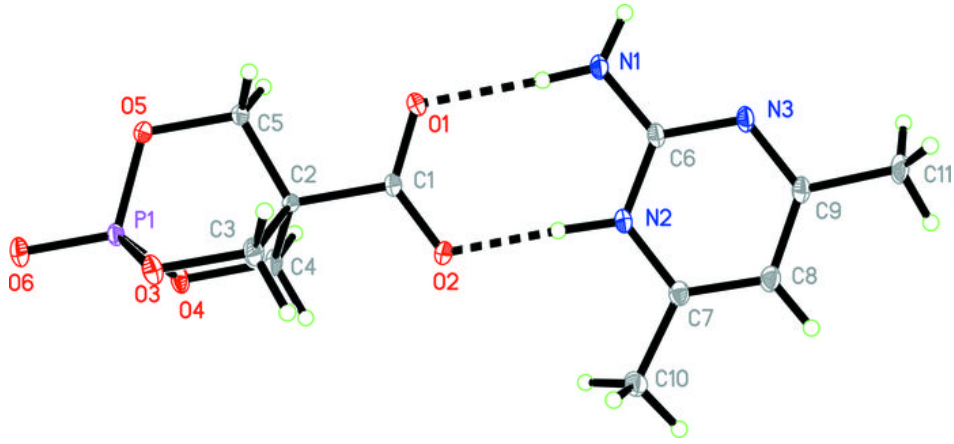
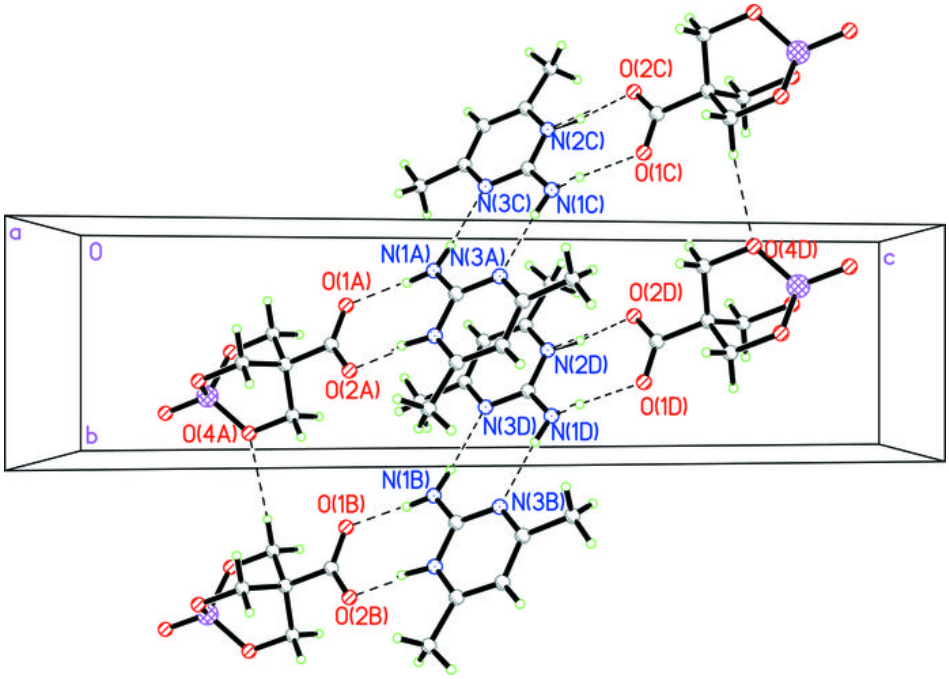


Fig. 2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b
c
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N(2C)
O(1C)
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N(1C)
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O(4A)
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N(1D)
N(1B)
O(1B)
N(3B)
O(2B)

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6-(Trifluoromethyl)pyrimidine-2,4(1*H*,3*H*)-dione monohydrate

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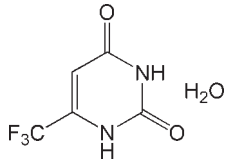
Key indicators: single-crystal X-ray study; T = 113 K; mean σ(C–C) = 0.002 Å; R factor = 0.036; wR factor = 0.100; data-to-parameter ratio = 13.0.

The title compound, $C_5H_3F_3N_2O_2\cdot H_2O$, was prepared by the reaction of ethyl 4,4,4-trifluoro-3-oxobutanoate with urea. In the crystal, the 6-(trifluoromethyl)pyrimidine-2,4(1*H*,3*H*)-dione and water molecules are linked by N—H···O and O—H···O hydrogen bonds. A ring dimer structure is formed by additional intermolecular N—H···O hydrogen bonds.

Related literature

For applications of pyrimidine derivatives as pesticides and pharmaceutical agents, see: Condon *et al.* (1993); as agrochemicals, see: Maeno *et al.* (1990); as antiviral agents, see: Gilchrist (1997); as herbicides, see: Selby *et al.* (2002).



Experimental

Crystal data

$C_5H_3F_3N_2O_2\cdot H_2O$
M_r = 198.11
Monoclinic, $P2_1/c$
a = 5.0250 (8) Å
b = 7.046 (1) Å
c = 20.769 (2) Å
β = 91.300 (7)°
V = 735.16 (17) Å^3
Z = 4
Mo $K\alpha$ radiation
μ = 0.19 mm^{-1}
T = 113 K
0.24 × 0.20 × 0.18 mm

Data collection

Rigaku Saturn724 CCD diffractometer
Absorption correction: multi-scan (*CrystalClear-SM Expert*; Rigaku/MSC, 2009)
T_{min} = 0.956, T_{max} = 0.966
6863 measured reflections
1747 independent reflections
1382 reflections with $I > 2\sigma(I)$
R_{int} = 0.029

Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.036
$wR(F^2)$ = 0.100
S = 1.07
1747 reflections
134 parameters
H atoms treated by a mixture of independent and constrained refinement
$\Delta\rho_{max}$ = 0.33 e Å^{-3}
$\Delta\rho_{min}$ = −0.21 e Å^{-3}

Table 1
Hydrogen-bond geometry (Å, °).

D—H···A	D—H	H···A	D···A	D—H···A
O3—H3B···O1^{i}	0.825 (17)	2.017 (18)	2.7815 (13)	153.9 (17)
O3—H3A···O2^{ii}	0.86 (2)	1.95 (2)	2.8066 (13)	176.0 (17)
N2—H2···O3	0.896 (17)	1.824 (17)	2.7191 (14)	177.9 (16)
N1—H1···O1^{iii}	0.954 (17)	1.896 (18)	2.8490 (14)	176.4 (16)

Symmetry codes: (i) $-x, -y+1, -z+1$; (ii) $x-1, y-1, z$; (iii) $-x+1, -y+2, -z+1$.

Data collection: *CrystalClear-SM Expert* (Rigaku/MSC, 2009); cell refinement: *CrystalClear-SM Expert*; data reduction: *CrystalClear-SM Expert*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *CrystalStructure* (Rigaku/MSC, 2009); software used to prepare material for publication: *CrystalStructure*.

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Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: FJ2309).

References

Condon, M. E., Brady, T. E., Feist, D., Malefyt, T., Marc, P., Quakenbush, L. S., Rodaway, S. J., Shaner, D. L. & Tecle, B. (1993). *Brighton Crop Protection Conference on Weeds*, pp. 41–46. Alton, Hampshire, England: BCPC Publications.
Gilchrist, T. L. (1997). *Heterocyclic Chemistry*, 3rd ed., pp. 261–276. Singapore: Addison Wesley Longman.
Maeno, S., Miura, I., Masuda, K. & Nagata, T. (1990). *Brighton Crop Protection Conference on Pests and Diseases*, pp. 415–422. Alton, Hampshire, England: BCPC Publications.
Rigaku/MSC (2009). *CrystalClear-SM Expert* and *CrystalStructure*. Rigaku/MSC, The Woodlands, Texas, USA.
Selby, T. P., Drumm, J. E., Coats, R. A., Coppo, F. T., Gee, S. K., Hay, J. V., Pasteris, R. J. & Stevenson, T. M. (2002). *ACS Symposium Series*, Vol. 800, *Synthesis and Chemistry of Agrochemicals VI*, pp. 74–84. Washington DC: American Chemical Society.
Sheldrick, G. M. (2008). *Acta Cryst.* A**64**, 112–122.

supplementary materials

Acta Cryst. (2010). E**66**, o1699 [**doi:10.1107/S1600536810022683**]

6-(Trifluoromethyl)pyrimidine-2,4(1*H*,3*H*)-dione monohydrate

G.-C. Li, H.-S. Wang, Y.-J. Niu and F.-L. Yang

Comment

Pyrimidine derivatives are very important molecules in biology and have many application in the areas of pesticide and pharmaceutical agents (Condon *et al.*, 1993). For example, imazosulfuron, ethirmol and mepanipyrim have been commercialized as agrochemicals (Maeno *et al.*, 1990). Pyrimidine derivatives have also been developed as antiviral agents, shch as AZT, which is the most widely used anti-AIDS drug (Gilchrist, 1997). Recently, a new series of highly active herbicides of substituted azolylpyrimidines were reported (Selby *et al.*, 2002). In order to discover further biologically active pyrimidine compounds, the title compound, (I), was synthesized and its crystal structure determined (Fig. 1).

In the crystal strucrure, The part of 6-(trifluoromethyl)pyrimidine-2,4(1*H*,3*H*)-dione and water molecule are linked by N—H···O and O—H···O hydrogen bonds. The ring dimer structure is formed by addition intermolecular N—H···O hydrogen bonds.

Experimental

To 35 ml absolute ethanol sodium (1.38 g, 60 mmol) was added. When sodium was dissppeared, ethyl 4,4,4-trifluoro-3-oxobutanoate(5.50 g, 30 mmol) and urea (1.80 g, 30 mmol) were added to the solution. The mixture was refluxed for 20 hr., The solvent was evaporated *in vacuo* and the residue was washed with water. The title compound was recrystallized from water and single crystals of (I) were obtained by slow evaporation.

Refinement

All H atoms were placed in calculated positions, with C—H = 0.95 Å, O—H = 0.86 Å or 0.825 Å, and included in the final cycles of refinement using a riding model, with U_{iso}(H) = 1.2Ueq(C).

Figures

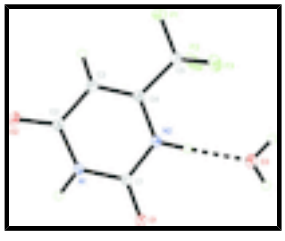


Fig. 1. The asymmetric unit of the title compound, (I), with displacement ellipsoids drawn at the 30% probability level.

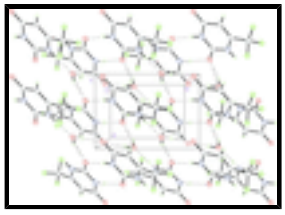


Fig. 2. The packing diagram of the title compound. Intermolecular hydrogen bonds are shown as dashed line.

6-(Trifluoromethyl)pyrimidine-2,4(1*H*,3*H*)-dione monohydrate

Crystal data

$C_5H_3F_3N_2O_2·H_2O$	$F(000) = 400$
$M_r = 198.11$	$D_x = 1.790$ Mg m^{-3}
Monoclinic, $P2_1/c$	Mo $K\alpha$ radiation, $\lambda = 0.71075$ Å
$a = 5.0250$ (8) Å	Cell parameters from 2492 reflections
$b = 7.046$ (1) Å	$\theta = 2.0$–$27.9°$
$c = 20.769$ (2) Å	$\mu = 0.19$ mm^{-1}
$\beta = 91.300$ (7)°	$T = 113$ K
$V = 735.16$ (17) Å^3	Prism, colorless
$Z = 4$	0.24 × 0.20 × 0.18 mm

Data collection

Rigaku Saturn724 CCD diffractometer	1747 independent reflections
Radiation source: rotating anode	1382 reflections with $I > 2\sigma(I)$
multilayer	$R_{int} = 0.029$
ω scans	$\theta_{max} = 27.9°$, $\theta_{min} = 2.0°$
Absorption correction: multi-scan (*CrystalClear*-SM Expert; Rigaku/MSC, 2009)	$h = -6 \rightarrow 6$
$T_{min} = 0.956$, $T_{max} = 0.966$	$k = -6 \rightarrow 9$
6863 measured reflections	$l = -27 \rightarrow 27$

Refinement

Refinement on F^2	Primary atom site location: structure-invariant direct methods
Least-squares matrix: full	Secondary atom site location: difference Fourier map
$R[F^2 > 2\sigma(F^2)] = 0.036$	Hydrogen site location: inferred from neighbouring sites
$wR(F^2) = 0.100$	H atoms treated by a mixture of independent and constrained refinement
$S = 1.07$	$w = 1/[\sigma^2(F_o^2) + (0.0589P)^2 + 0.0166P]$ where $P = (F_o^2 + 2F_c^2)/3$
1747 reflections	$(\Delta/\sigma)_{max} < 0.001$
134 parameters	$\Delta\rho_{max} = 0.33$ e Å^{-3}
0 restraints	$\Delta\rho_{min} = -0.21$ e Å^{-3}

Special details

Geometry. All e.s.d.'s (except the e.s.d. in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell e.s.d.'s are taken into account individually in the estimation of e.s.d.'s in distances, angles and torsion angles; correlations between e.s.d.'s in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell e.s.d.'s is used for estimating e.s.d.'s involving l.s. planes.

Refinement. Refinement of F^2 against ALL reflections. The weighted *R*-factor *wR* and goodness of fit *S* are based on F^2, conventional *R*-factors *R* are based on *F*, with *F* set to zero for negative F^2. The threshold expression of $F^2 > \sigma(F^2)$ is used only for calculating *R*-factors(gt) *etc*. and is not relevant to the choice of reflections for refinement. *R*-factors based on F^2 are statistically about twice as large as those based on *F*, and *R*- factors based on ALL data will be even larger.

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å^2)

	x	*y*	*z*	U_{iso}*/U_{eq}
F1	0.74748 (17)	0.37877 (12)	0.26992 (4)	0.0431 (3)
F2	0.33139 (17)	0.43344 (12)	0.28202 (4)	0.0433 (3)
F3	0.54045 (16)	0.25207 (11)	0.34843 (4)	0.0359 (2)
O1	0.32964 (16)	0.78481 (12)	0.48978 (4)	0.0247 (2)
O2	1.03039 (17)	0.99065 (12)	0.37275 (4)	0.0261 (2)
O3	0.09114 (19)	0.33980 (15)	0.43644 (5)	0.0299 (3)
N1	0.67605 (19)	0.88773 (14)	0.42979 (5)	0.0199 (2)
N2	0.46193 (19)	0.60395 (14)	0.40583 (5)	0.0187 (2)
C1	0.4798 (2)	0.76007 (17)	0.44449 (5)	0.0191 (3)
C2	0.8566 (2)	0.87123 (17)	0.38039 (6)	0.0193 (3)
C3	0.8191 (2)	0.70430 (17)	0.34028 (6)	0.0196 (3)
H3	0.9296	0.6828	0.3045	0.023*
C4	0.6262 (2)	0.58089 (16)	0.35448 (5)	0.0183 (3)
C5	0.5641 (2)	0.40964 (18)	0.31352 (6)	0.0237 (3)
H1	0.681 (3)	0.999 (2)	0.4561 (9)	0.048 (5)*
H2	0.340 (3)	0.518 (2)	0.4169 (8)	0.041 (5)*
H3A	0.081 (3)	0.234 (3)	0.4166 (10)	0.049 (5)*
H3B	−0.024 (3)	0.336 (3)	0.4642 (8)	0.043 (5)*

Atomic displacement parameters (Å^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
F1	0.0459 (5)	0.0380 (5)	0.0467 (5)	−0.0137 (4)	0.0277 (4)	−0.0219 (4)
F2	0.0400 (5)	0.0422 (6)	0.0467 (5)	0.0051 (4)	−0.0173 (4)	−0.0201 (4)
F3	0.0481 (5)	0.0177 (4)	0.0423 (5)	−0.0059 (4)	0.0095 (4)	−0.0025 (3)
O1	0.0267 (5)	0.0250 (5)	0.0229 (4)	−0.0091 (4)	0.0097 (4)	−0.0050 (3)
O2	0.0237 (5)	0.0225 (5)	0.0325 (5)	−0.0076 (4)	0.0092 (4)	−0.0012 (4)
O3	0.0307 (5)	0.0248 (6)	0.0347 (6)	−0.0110 (4)	0.0140 (4)	−0.0049 (4)
N1	0.0204 (5)	0.0192 (6)	0.0204 (5)	−0.0058 (4)	0.0042 (4)	−0.0025 (4)
N2	0.0191 (5)	0.0165 (5)	0.0208 (5)	−0.0046 (4)	0.0043 (4)	−0.0009 (4)
C1	0.0190 (6)	0.0193 (6)	0.0190 (5)	−0.0028 (4)	0.0014 (4)	0.0000 (5)
C2	0.0176 (5)	0.0187 (6)	0.0215 (6)	−0.0006 (5)	0.0023 (4)	0.0028 (4)

C3	0.0192 (6)	0.0195 (7)	0.0201 (6)	0.0010 (5)	0.0039 (4)	0.0010 (4)
C4	0.0185 (5)	0.0174 (6)	0.0191 (6)	0.0019 (4)	0.0013 (4)	0.0007 (5)
C5	0.0227 (6)	0.0216 (7)	0.0270 (6)	−0.0019 (5)	0.0064 (5)	−0.0038 (5)

Geometric parameters (Å, °)

F1—C5	1.3245 (14)	N1—H1	0.954 (17)
F2—C5	1.3374 (15)	N2—C1	1.3636 (15)
F3—C5	1.3328 (15)	N2—C4	1.3729 (14)
O1—C1	1.2317 (14)	N2—H2	0.896 (17)
O2—C2	1.2255 (14)	C2—C3	1.4512 (17)
O3—H3A	0.86 (2)	C3—C4	1.3400 (17)
O3—H3B	0.825 (17)	C3—H3	0.9500
N1—C1	1.3742 (15)	C4—C5	1.5050 (17)
N1—C2	1.3898 (15)		
H3A—O3—H3B	105.8 (17)	C4—C3—C2	119.01 (11)
C1—N1—C2	126.37 (10)	C4—C3—H3	120.5
C1—N1—H1	114.8 (11)	C2—C3—H3	120.5
C2—N1—H1	118.8 (11)	C3—C4—N2	123.00 (11)
C1—N2—C4	121.34 (10)	C3—C4—C5	122.52 (11)
C1—N2—H2	115.5 (11)	N2—C4—C5	114.42 (10)
C4—N2—H2	123.2 (11)	F1—C5—F3	107.89 (10)
O1—C1—N2	122.04 (10)	F1—C5—F2	107.48 (10)
O1—C1—N1	122.15 (11)	F3—C5—F2	106.44 (10)
N2—C1—N1	115.80 (10)	F1—C5—C4	112.30 (10)
O2—C2—N1	121.15 (11)	F3—C5—C4	112.34 (10)
O2—C2—C3	124.46 (11)	F2—C5—C4	110.10 (10)
N1—C2—C3	114.39 (10)		
C4—N2—C1—O1	178.24 (10)	C2—C3—C4—C5	176.73 (10)
C4—N2—C1—N1	−1.87 (16)	C1—N2—C4—C3	2.53 (18)
C2—N1—C1—O1	179.13 (11)	C1—N2—C4—C5	−174.89 (10)
C2—N1—C1—N2	−0.76 (17)	C3—C4—C5—F1	10.94 (17)
C1—N1—C2—O2	−177.49 (11)	N2—C4—C5—F1	−171.62 (10)
C1—N1—C2—C3	2.59 (16)	C3—C4—C5—F3	132.78 (12)
O2—C2—C3—C4	178.20 (11)	N2—C4—C5—F3	−49.78 (14)
N1—C2—C3—C4	−1.88 (16)	C3—C4—C5—F2	−108.79 (13)
C2—C3—C4—N2	−0.49 (18)	N2—C4—C5—F2	68.65 (13)

Hydrogen-bond geometry (Å, °)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
O3—H3B···O1^{i}	0.825 (17)	2.017 (18)	2.7815 (13)	153.9 (17)
O3—H3A···O2^{ii}	0.86 (2)	1.95 (2)	2.8066 (13)	176.0 (17)
N2—H2···O3	0.896 (17)	1.824 (17)	2.7191 (14)	177.9 (16)
N1—H1···O1^{iii}	0.954 (17)	1.896 (18)	2.8490 (14)	176.4 (16)

Symmetry codes: (i) −*x*, −*y*+1, −*z*+1; (ii) *x*−1, *y*−1, *z*; (iii) −*x*+1, −*y*+2, −*z*+1.

Fig. 1

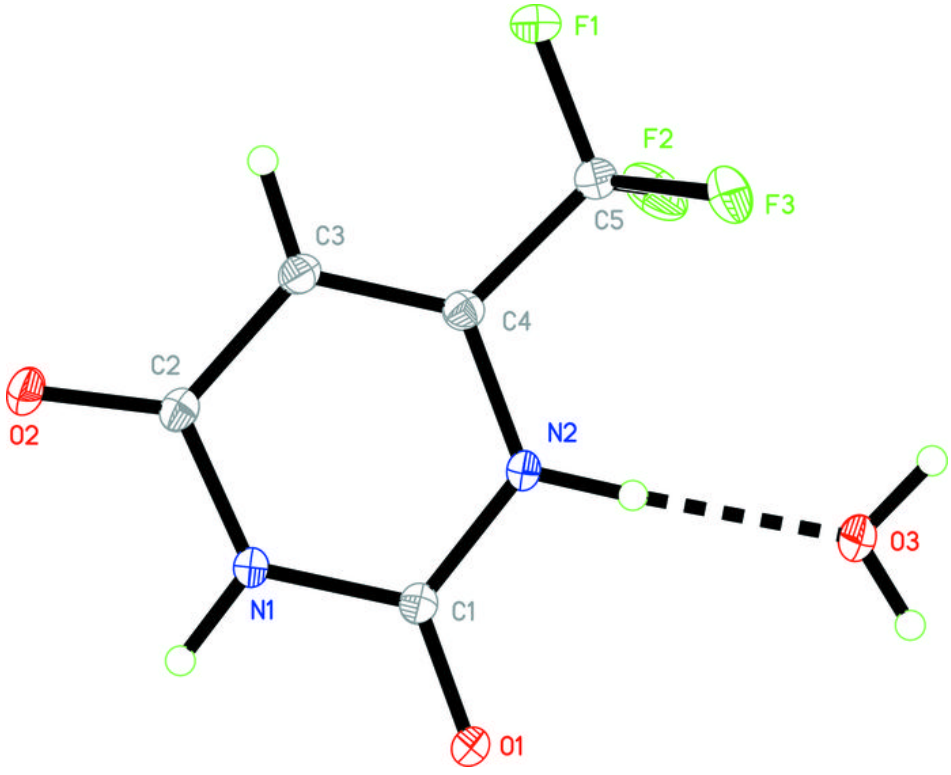
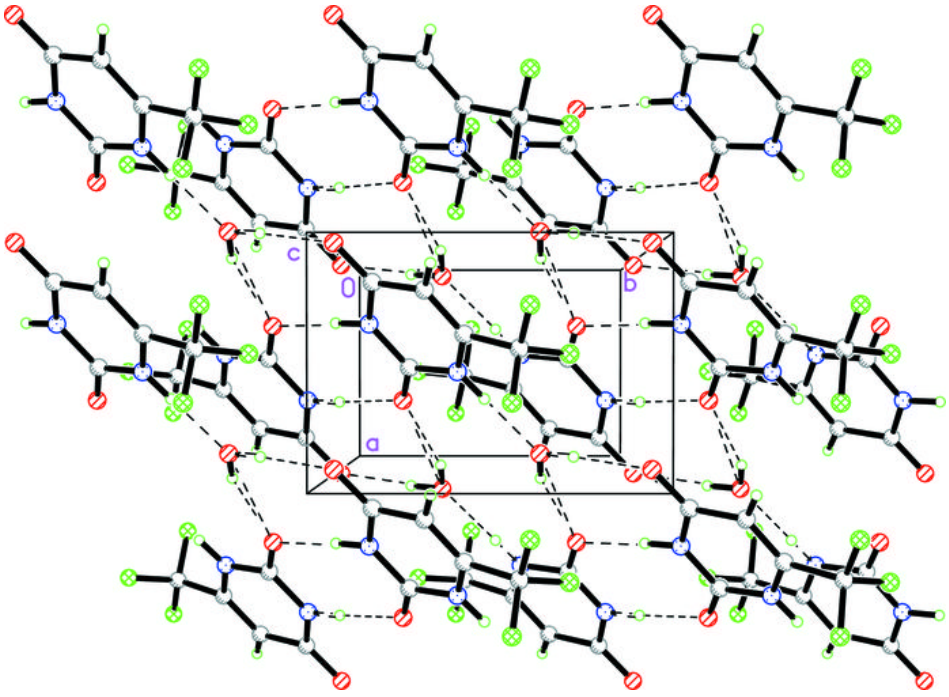


Fig. 2



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Bis(2-amino-4-methylpyridinium) *trans*-diaquabis(pyrazine-2,3-dicarboxylato)-cuprate(II) hexahydrate

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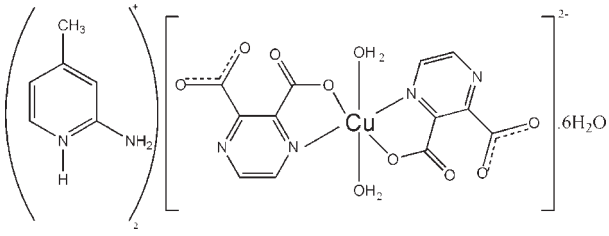
Key indicators: single-crystal X-ray study; T = 293 K; mean σ(C–C) = 0.002 Å; R factor = 0.036; wR factor = 0.092; data-to-parameter ratio = 17.5.

The title compound, $(C_6H_9N_2)_2[Cu(C_6H_2N_2O_4)_2(H_2O)_2]\cdot 6H_2O$, consists of a mononuclear *trans*-$[Cu(pzdc)_2(H_2O)_2]^{2-}$ dianion (pzdc is pyrazine-2,3-dicarboxylate) and two $[ampyH]^+$ cations (ampy is 2-amino-4-methylpyridine) with six water molecules of solvation. The Cu^{II} atom is hexacoordinated by two pzdc groups and two water molecules. The coordinated water molecules are in *trans*-diaxial positions and the pzdc dianion acts as a bidentate ligand through an O atom of the carboxylate group and the N atom of the pyrazine ring. There are diverse hydrogen-bonding interactions, such as N—H···O and O—H···O contacts, which lead to the formation of a three-dimensional supramolecular architecture.

Related literature

For the crystal structure of pyrazine-2,3-dicarboxylic acid ($pzdcH_2$), see: Takusagawa & Shimada (1973). For complexes of $pzdcH_2$ with manganese and zinc, see: Eshtiagh-Hosseini *et al.* (2010*a*,*b*). For the structure of bis(2,4,6-triamino-1,3,5-triazin-1-ium) pyrazine-2,3-dicarboxylate tetrahydrate, see: Eshtiagh-Hosseini *et al.* (2010*c*). For a review articleon water cluster chemistry, see: Aghabozorg *et al.* (2010).



Experimental

Crystal data

$(C_6H_9N_2)_2[Cu(C_6H_2N_2O_4)_2(H_2O)_2]\cdot 6H_2O$
M_r = 758.17
Triclinic, $P\overline{1}$
a = 6.9075 (14) Å
b = 8.4710 (17) Å
c = 14.505 (3) Å
α = 78.28 (3)°
β = 83.62 (3)°
γ = 85.81 (3)°
V = 824.8 (3) Å^3
Z = 1
Mo $K\alpha$ radiation
μ = 0.75 mm^{-1}
T = 293 K
0.3 × 0.2 × 0.1 mm

Data collection

Stoe IPDS 2 diffractometer
Absorption correction: for a sphere [modified Dwiggins (1975) interpolation procedure]
T_{min} = 0.743, T_{max} = 0.745
17015 measured reflections
4684 independent reflections
4282 reflections with $I > 2\sigma(I)$
R_{int} = 0.046

Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.036
$wR(F^2)$ = 0.092
S = 1.04
4684 reflections
268 parameters
H atoms treated by a mixture of independent and constrained refinement
$\Delta\rho_{max}$ = 0.36 e Å^{-3}
$\Delta\rho_{min}$ = −0.52 e Å^{-3}

Table 1
Hydrogen-bond geometry (Å, °).

D—H···A	D—H	H···A	D···A	D—H···A
N3—H13···O4^{i}	0.82	1.91	2.7221 (19)	169
N4—H14A···O8^{ii}	0.77	2.12	2.8879 (19)	177
N4—H14B···O3^{i}	0.84 (2)	2.07 (2)	2.903 (2)	168 (2)
O5—H5B···O7^{i}	0.79 (3)	1.92 (3)	2.703 (2)	173 (3)
O5—H5A···O4^{i}	0.82 (3)	2.09 (3)	2.8556 (18)	157 (3)
O8—H8B···O1^{iii}	0.76 (3)	2.03 (3)	2.7838 (18)	173 (3)
O6—H6B···O4^{iii}	0.81 (4)	2.06 (4)	2.839 (2)	162 (3)
O7—H17B···O8^{iv}	0.76 (4)	2.04 (4)	2.797 (2)	172 (4)

Symmetry codes: (i) $x, y-1, z$; (ii) $-x+1, -y, -z$; (iii) $x+1, y, z$; (iv) $x, y+1, z$.

Data collection: *X-AREA* (Stoe & Cie, 2009); cell refinement: *X-RED* (Stoe & Cie, 2009); data reduction: *X-RED*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *DIAMOND* (Crystal Impact, 2009); software used to prepare material for publication: *publCIF* (Westrip, 2010).

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Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: FJ2310).

References

Aghabozorg, H., Eshtiagh-Hosseini, H., Salimi, A. R. & Mirzaei, M. (2010). *J. Iran. Chem. Soc.* **7**, 289–300.
Crystal Impact (2009). *DIAMOND*. Crystal Impact GbR, Bonn, Germany.
Dwiggins, C. W. (1975). *Acta Cryst.* A**31**, 146–148.
Eshtiagh-Hosseini, H., Aghabozorg, H. & Mirzaei, M. (2010*a*). *Acta Cryst.* E**66**. Submitted. [XU2784]

Eshtiagh-Hosseini, H., Hassanpoor, A., Alfi, N., Mirzaei, M., Fromm, K. M., Shokrollahi, A., Gschwind, F. & Karami, E. (2010*b*). *J. Coord. Chem.* In the press.
Eshtiagh-Hosseini, H., Hassanpoor, A., Canadillas-Delgado, L. & Mirzaei, M. (2010*c*). *Acta Cryst.* E**66**, o1368–o1369.
Sheldrick, G. M. (2008). *Acta Cryst.* A**64**, 112–122.
Stoe & Cie (2009). *X-AREA* and *X-RED* Stoe & Cie, Darmstadt, Germany.
Takusagawa, F. & Shimada, A. (1973). *Chem. Lett.* pp. 1121–1123.
Westrip, S. P. (2010). *J. Appl. Cryst.* **43**. Submitted.

supplementary materials

Acta Cryst. (2010). E**66**, m826-m827 [**doi:10.1107/S1600536810023081**]

Bis(2-amino-4-methylpyridinium) *trans*-diaquabis(pyrazine-2,3-dicarboxylato)cuprate(II) hexahydrate

H. Eshtiagh-Hosseini, F. Gschwind, N. Alfi and M. Mirzaei

Comment

Dicarboxylate ligands are widely used to assemble supramolecular network organized by coordination bonds, hydrogen bonds and π –π stacking interaction. Due to the manifold N- and O-donors of pyridine or pyrazine-(di)carboxylic ligands, metal pyridine- or pyrazine dicarboxylates can contrast versatile structural motifs, which finally aggregate to generate various supramolecular architectures with interesting properties. As ones of the dicarboxylate ligands, $pzdcH_2$ have drawn extensive attentions. For the first time, Takusagawa & Shimada (1973) by single crystal X-ray diffraction, determined the structure of $pzdcH_2$. Continuing with our previous works on synthesizing coordination compounds *via* proton transfer mechanism including zinc atom (Eshtiagh-Hosseini *et al.*, 2010a), manganese atom (Eshtiagh-Hosseini *et al.*, 2010b), Bis(2,4,6-triamino-1,3,5-triazin-1-ium) pyrazine-2,3-dicarboxylate tetrahydrate (Eshtiagh-Hosseini *et al.*, 2010c), herein, we planned the reaction between $pzdcH_2$, ampy, and copper(II) choloride which resulted in the formation of $(ampy)_2[Cu(pzdc)_2(H_2O)_2].6H_2O$ (Fig. 1). Crystal packing diagram related to the title compound is also rendered in the Fig. 2. As you can see, the equatorial plane is occupied by two $(pzdc)^{2-}$ ligands coordinating through the pyridine nitrogen and one oxygen of the deprotonated carboxylate groups. The two coordinated water molecules occupy axial plane. This compound consists of an anionic moiety, *trans*-$[Cu(pzdc)_2(H_2O)_2]^{2-}$ complex, counter-ions, $(ampy)^+$, and six uncoordinated water molecules. The Cu—O and Cu—N bond distances related to $(pzdc)^{2-}$ ligand in herein presented compound are in the category of 1.9644 (13) Å , and 1.9840 (14) Å, respectively. These observerd bond lenghts are comprable with Zn(II) polymeric coordination compound which recently reported by our research group (Eshtiagh-Hosseini *et al.*, 2010a). In this polymeric compound which consist of only $(pzdc)^{2-}$ coordinative ligand, $\{(C_3H_{12}N_2)_2[Zn(C_{10}H_2O_8)_2]\}_n$, Zn—O and Zn—N bond distances are 2.0317 (15) to 2.2437 (15) Å, and 2.0901 (18) Å, respectively. These data show in this polymeric compound Zn—O bond distance is longer than herein presented compound. The intermolecular forces between the anionic and cationic parts in the title compound consist of hydrogen bonding and ion pairing interactions. Indeed, six uncoordinated water molecules increase the number of hydrogen bonds in the crystalline network and lead to the formation of $(H_2O)_n$ clusters throughout the crystalline network (see Review article by Aghabozorg *et al.* 2010).

Experimental

A solution of $pzdcH_2$ (0.18 mmol, 0.03 mg) in water (10 ml) refluxed for 1 hr, then a solution of $CuCl_2.6H_2O$ (0.02 mmol, 0.01 g) was added dropwise and continued refluxing for 6 hrs at 60°C. The obtained blue solution gave blue block like crystals of title compound after slow evaporation of solvent at room temperatur.

Refinement

The space group was confirmed by using PLATON software package. The structure was solved by direct methods using SHELXS-97 and refined using full matrix least-squares on F^2 with the SHELX-97 package. H-Atoms were constrained to the parent site using a rigid model. A final verification of possible voids was performed using the VOID routine on PLATON software.

Figures

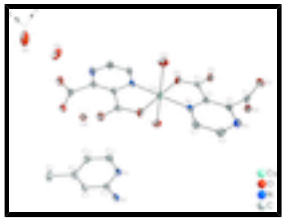


Fig. 1. Molecular structure of $(ampy)_2[Cu(pzdc)_2(H_2O)_2].6H_2O$. Ellipsoids are drawn at the 50% probability level. Hydrogen atoms are omitted for further clarity.

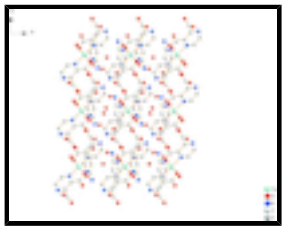


Fig. 2. Packing diagram of $(ampy)_2[Cu(pzdc)_2(H_2O)_2].6H_2O$.

Bis(2-amino-4-methylpyridinium) *trans*-diaquabis(pyrazine-2,3-dicarboxylato)cuprate(II) hexahydrate

Crystal data

$(C_6H_9N_2)_2[Cu(C_6H_2N_2O_4)_2(H_2O)_2]\cdot 6H_2O$	$Z = 1$
$M_r = 758.17$	$F(000) = 395.0$
Triclinic, $P\overline{1}$	$D_x = 1.526$ Mg m^{-3}
Hall symbol: -P 1	Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å
$a = 6.9075$ (14) Å	Cell parameters from 34097 reflections
$b = 8.4710$ (17) Å	$\theta = 3{,}8–59{,}7°$
$c = 14.505$ (3) Å	$\mu = 0.75$ mm^{-1}
$\alpha = 78.28$ (3)°	$T = 293$ K
$\beta = 83.62$ (3)°	Block, blue
$\gamma = 85.81$ (3)°	0.3 × 0.2 × 0.1 mm
$V = 824.8$ (3) Å^3	

Data collection

Stoe IPDS 2 diffractometer	4684 independent reflections
Radiation source: fine-focus sealed tube	4282 reflections with $I > 2\sigma(I)$
graphite	$R_{int} = 0.046$

Detector resolution: 6.67 pixels mm^{-1}	θ_{max} = 29.8°, θ_{min} = 2.5°
rotation method scans	h = −9→9
Absorption correction: for a sphere modified Dwiggins (1975) interpolation procedure	k = −11→11
T_{min} = 0.743, T_{max} = 0.745	l = −20→20
17015 measured reflections	

Refinement

Refinement on F^2	Primary atom site location: structure-invariant direct methods
Least-squares matrix: full	Secondary atom site location: difference Fourier map
$R[F^2 > 2\sigma(F^2)]$ = 0.036	Hydrogen site location: inferred from neighbouring sites
$wR(F^2)$ = 0.092	H atoms treated by a mixture of independent and constrained refinement
S = 1.03	$w = 1/[\sigma^2(F_o^2) + (0.0453P)^2 + 0.5453P]$ where $P = (F_o^2 + 2F_c^2)/3$
4684 reflections	$(\Delta/\sigma)_{max}$ = 0.001
268 parameters	$\Delta\rho_{max}$ = 0.36 e Å^{-3}
0 restraints	$\Delta\rho_{min}$ = −0.52 e Å^{-3}

Special details

Experimental. Absorption correction: Interpolation using Int. Tab. Vol. C (1992) p. 523, Tab. 6.3.3.3 for values of muR in the range 0-2.5, and Int. Tab. Vol. II (1959) p. 302; Table 5.3.6 B for muR in the range 2.6-10.0. The interpolation procedure of C. W. Dwiggins Jr is used with some modification.

Geometry. All s.u.'s (except the s.u. in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell s.u.'s are taken into account individually in the estimation of s.u.'s in distances, angles and torsion angles; correlations between s.u.'s in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell s.u.'s is used for estimating s.u.'s involving l.s. planes.

Refinement. Refinement of F^2 against ALL reflections. The weighted R-factor wR and goodness of fit S are based on F^2, conventional R-factors R are based on F, with F set to zero for negative F^2. The threshold expression of $F^2 > 2\sigma(F^2)$ is used only for calculating R-factors(gt) etc. and is not relevant to the choice of reflections for refinement. R-factors based on F^2 are statistically about twice as large as those based on F, and R- factors based on ALL data will be even larger.

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å^2)

	x	y	z	U_{iso}*/U_{eq}
Cu1	0.0000	0.0000	0.5000	0.01658 (8)
O3	0.30782 (17)	0.49841 (13)	0.17617 (8)	0.0195 (2)
O4	0.11843 (16)	0.64677 (13)	0.26546 (8)	0.0180 (2)
O1	−0.09643 (16)	0.33706 (13)	0.27415 (8)	0.0190 (2)
O5	0.1806 (2)	−0.17345 (17)	0.40519 (9)	0.0258 (3)
O2	−0.12649 (16)	0.11778 (13)	0.38957 (8)	0.0189 (2)
N1	0.19550 (18)	0.16670 (15)	0.45776 (8)	0.0147 (2)
N2	0.43093 (18)	0.41844 (16)	0.37769 (9)	0.0173 (2)

C1	−0.0415 (2)	0.24286 (17)	0.34432 (10)	0.0144 (2)
C2	0.1458 (2)	0.27423 (16)	0.38093 (9)	0.0134 (2)
C5	0.2651 (2)	0.40007 (17)	0.34084 (10)	0.0139 (2)
C4	0.4760 (2)	0.31081 (19)	0.45398 (11)	0.0187 (3)
H4	0.5897	0.3212	0.4806	0.022*
C3	0.3583 (2)	0.18338 (18)	0.49501 (10)	0.0171 (3)
H3	0.3936	0.1103	0.5483	0.021*
C6	0.2244 (2)	0.52402 (17)	0.25287 (10)	0.0148 (2)
N3	0.17729 (19)	−0.08982 (15)	0.12469 (9)	0.0175 (2)
H13	0.1634	−0.1765	0.1614	0.021*
N4	0.2985 (2)	−0.23942 (16)	0.01280 (10)	0.0200 (3)
H14A	0.3217	−0.2450	−0.0394	0.024*
C10	0.2467 (2)	−0.09571 (18)	0.03481 (10)	0.0160 (3)
C9	0.2613 (2)	0.05143 (19)	−0.03132 (11)	0.0184 (3)
C8	0.2056 (2)	0.19545 (18)	−0.00370 (11)	0.0197 (3)
C11	0.1206 (2)	0.05082 (19)	0.15352 (11)	0.0212 (3)
H11	0.0728	0.0489	0.2162	0.025*
C12	0.1332 (3)	0.19396 (19)	0.09169 (12)	0.0223 (3)
C7	0.2186 (3)	0.3528 (2)	−0.07308 (14)	0.0288 (4)
H7A	0.2698	0.4314	−0.0443	0.043*
H7B	0.0911	0.3898	−0.0912	0.043*
H7C	0.3034	0.3379	−0.1281	0.043*
O6	0.7121 (2)	0.67499 (18)	0.32078 (13)	0.0381 (4)
O7	0.4817 (2)	0.9530 (2)	0.28417 (12)	0.0385 (3)
O8	0.60159 (18)	0.25375 (14)	0.18411 (8)	0.0203 (2)
H12	0.097 (4)	0.287 (3)	0.1154 (19)	0.040 (7)*
H14B	0.289 (3)	−0.322 (3)	0.0565 (17)	0.024 (5)*
H9	0.311 (3)	0.045 (2)	−0.0939 (15)	0.017 (5)*
H5B	0.267 (4)	−0.130 (3)	0.372 (2)	0.040 (7)*
H5A	0.138 (4)	−0.236 (3)	0.377 (2)	0.040 (7)*
H8A	0.516 (4)	0.326 (3)	0.1824 (19)	0.039 (7)*
H8B	0.677 (4)	0.279 (3)	0.2116 (19)	0.034 (6)*
H6B	0.823 (5)	0.645 (4)	0.306 (2)	0.057 (9)*
H6A	0.632 (6)	0.606 (5)	0.333 (3)	0.076 (11)*
H17A	0.570 (5)	0.885 (4)	0.288 (2)	0.049 (8)*
H17B	0.524 (5)	1.032 (4)	0.259 (3)	0.062 (10)*

Atomic displacement parameters (Å^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Cu1	0.01841 (13)	0.01479 (13)	0.01464 (12)	−0.00519 (9)	−0.00398 (9)	0.00436 (9)
O3	0.0237 (5)	0.0173 (5)	0.0150 (5)	0.0014 (4)	0.0007 (4)	0.0003 (4)
O4	0.0203 (5)	0.0131 (5)	0.0190 (5)	0.0006 (4)	−0.0017 (4)	−0.0002 (4)
O1	0.0208 (5)	0.0176 (5)	0.0172 (5)	−0.0032 (4)	−0.0062 (4)	0.0032 (4)
O5	0.0265 (6)	0.0295 (6)	0.0239 (6)	−0.0017 (5)	−0.0016 (5)	−0.0116 (5)
O2	0.0193 (5)	0.0175 (5)	0.0185 (5)	−0.0068 (4)	−0.0056 (4)	0.0037 (4)
N1	0.0172 (5)	0.0131 (5)	0.0129 (5)	−0.0012 (4)	−0.0023 (4)	0.0003 (4)
N2	0.0158 (5)	0.0174 (6)	0.0179 (6)	−0.0020 (4)	−0.0023 (4)	−0.0007 (5)

C1	0.0154 (6)	0.0140 (6)	0.0134 (6)	−0.0015 (5)	−0.0013 (5)	−0.0014 (5)
C2	0.0149 (6)	0.0124 (6)	0.0121 (6)	−0.0004 (5)	−0.0013 (5)	−0.0006 (5)
C5	0.0149 (6)	0.0125 (6)	0.0133 (6)	0.0006 (5)	−0.0005 (5)	−0.0014 (5)
C4	0.0165 (6)	0.0196 (7)	0.0196 (7)	−0.0020 (5)	−0.0051 (5)	−0.0009 (5)
C3	0.0193 (6)	0.0165 (6)	0.0148 (6)	0.0005 (5)	−0.0044 (5)	−0.0006 (5)
C6	0.0154 (6)	0.0127 (6)	0.0154 (6)	−0.0035 (5)	−0.0015 (5)	0.0004 (5)
N3	0.0221 (6)	0.0146 (5)	0.0143 (5)	−0.0001 (4)	−0.0021 (4)	0.0007 (4)
N4	0.0262 (6)	0.0161 (6)	0.0162 (6)	0.0006 (5)	−0.0010 (5)	−0.0009 (5)
C10	0.0155 (6)	0.0175 (6)	0.0149 (6)	−0.0022 (5)	−0.0036 (5)	−0.0010 (5)
C9	0.0185 (6)	0.0192 (7)	0.0156 (6)	−0.0020 (5)	−0.0021 (5)	0.0014 (5)
C8	0.0194 (7)	0.0159 (7)	0.0223 (7)	−0.0034 (5)	−0.0057 (5)	0.0022 (5)
C11	0.0277 (8)	0.0199 (7)	0.0161 (6)	0.0016 (6)	−0.0033 (6)	−0.0043 (6)
C12	0.0282 (8)	0.0164 (7)	0.0232 (7)	−0.0002 (6)	−0.0067 (6)	−0.0044 (6)
C7	0.0340 (9)	0.0173 (7)	0.0308 (9)	−0.0031 (6)	−0.0035 (7)	0.0058 (6)
O6	0.0263 (7)	0.0240 (7)	0.0620 (10)	−0.0045 (5)	0.0142 (7)	−0.0127 (7)
O7	0.0273 (7)	0.0304 (7)	0.0498 (9)	−0.0033 (6)	−0.0024 (6)	0.0108 (7)
O8	0.0208 (5)	0.0204 (5)	0.0203 (5)	0.0013 (4)	−0.0044 (4)	−0.0051 (4)

Geometric parameters (Å, °)

Cu1—O2	1.9644 (13)	N3—C11	1.358 (2)
Cu1—O2^{i}	1.9644 (12)	N3—H13	0.8202
Cu1—N1	1.9840 (14)	N4—C10	1.335 (2)
Cu1—N1^{i}	1.9840 (14)	N4—H14A	0.7669
Cu1—O5	2.4038 (15)	N4—H14B	0.84 (2)
Cu1—O5^{i}	2.4038 (15)	C10—C9	1.412 (2)
O3—C6	1.2467 (18)	C9—C8	1.376 (2)
O4—C6	1.2597 (18)	C9—H9	0.95 (2)
O1—C1	1.2364 (18)	C8—C12	1.416 (2)
O5—H5B	0.79 (3)	C8—C7	1.500 (2)
O5—H5A	0.82 (3)	C11—C12	1.356 (2)
O2—C1	1.2732 (18)	C11—H11	0.9300
N1—C3	1.3291 (19)	C12—H12	0.93 (3)
N1—C2	1.3477 (18)	C7—H7A	0.9600
N2—C4	1.333 (2)	C7—H7B	0.9600
N2—C5	1.3486 (18)	C7—H7C	0.9600
C1—C2	1.5119 (19)	O6—H6B	0.81 (4)
C2—C5	1.387 (2)	O6—H6A	0.81 (4)
C5—C6	1.517 (2)	O7—H17A	0.80 (3)
C4—C3	1.393 (2)	O7—H17B	0.76 (4)
C4—H4	0.9300	O8—H8A	0.81 (3)
C3—H3	0.9300	O8—H8B	0.76 (3)
N3—C10	1.3475 (19)		
O2—Cu1—O2^{i}	180.00 (4)	N1—C3—H3	120.1
O2—Cu1—N1	83.31 (5)	C4—C3—H3	120.1
O2^{i}—Cu1—N1	96.69 (5)	O3—C6—O4	126.59 (14)
O2—Cu1—N1^{i}	96.69 (5)	O3—C6—C5	116.73 (13)

O2^{i}—Cu1—N1^{i}	83.31 (5)	O4—C6—C5	116.56 (13)
N1—Cu1—N1^{i}	180.00 (7)	C10—N3—C11	122.73 (14)
O2—Cu1—O5	90.70 (5)	C10—N3—H13	116.8
O2^{i}—Cu1—O5	89.30 (5)	C11—N3—H13	120.3
N1—Cu1—O5	90.80 (6)	C10—N4—H14A	119.0
N1^{i}—Cu1—O5	89.20 (6)	C10—N4—H14B	117.9 (15)
O2—Cu1—O5^{i}	89.30 (5)	H14A—N4—H14B	122.6
O2^{i}—Cu1—O5^{i}	90.70 (5)	N4—C10—N3	118.61 (14)
N1—Cu1—O5^{i}	89.20 (6)	N4—C10—C9	123.36 (14)
N1^{i}—Cu1—O5^{i}	90.80 (6)	N3—C10—C9	118.02 (14)
O5—Cu1—O5^{i}	180.00 (5)	C8—C9—C10	120.30 (14)
Cu1—O5—H5B	113 (2)	C8—C9—H9	123.0 (12)
Cu1—O5—H5A	127.8 (19)	C10—C9—H9	116.7 (12)
H5B—O5—H5A	107 (3)	C9—C8—C12	119.11 (14)
C1—O2—Cu1	114.87 (9)	C9—C8—C7	121.06 (15)
C3—N1—C2	119.43 (13)	C12—C8—C7	119.83 (15)
C3—N1—Cu1	129.00 (10)	C12—C11—N3	120.60 (15)
C2—N1—Cu1	111.57 (10)	C12—C11—H11	119.7
C4—N2—C5	117.45 (13)	N3—C11—H11	119.7
O1—C1—O2	126.27 (13)	C11—C12—C8	119.24 (15)
O1—C1—C2	118.40 (13)	C11—C12—H12	117.2 (17)
O2—C1—C2	115.33 (12)	C8—C12—H12	123.5 (17)
N1—C2—C5	120.04 (13)	C8—C7—H7A	109.5
N1—C2—C1	114.86 (12)	C8—C7—H7B	109.5
C5—C2—C1	125.09 (12)	H7A—C7—H7B	109.5
N2—C5—C2	121.23 (13)	C8—C7—H7C	109.5
N2—C5—C6	114.89 (13)	H7A—C7—H7C	109.5
C2—C5—C6	123.87 (13)	H7B—C7—H7C	109.5
N2—C4—C3	122.10 (14)	H6B—O6—H6A	117 (3)
N2—C4—H4	118.9	H17A—O7—H17B	107 (3)
C3—C4—H4	118.9	H8A—O8—H8B	105 (3)
N1—C3—C4	119.74 (14)		

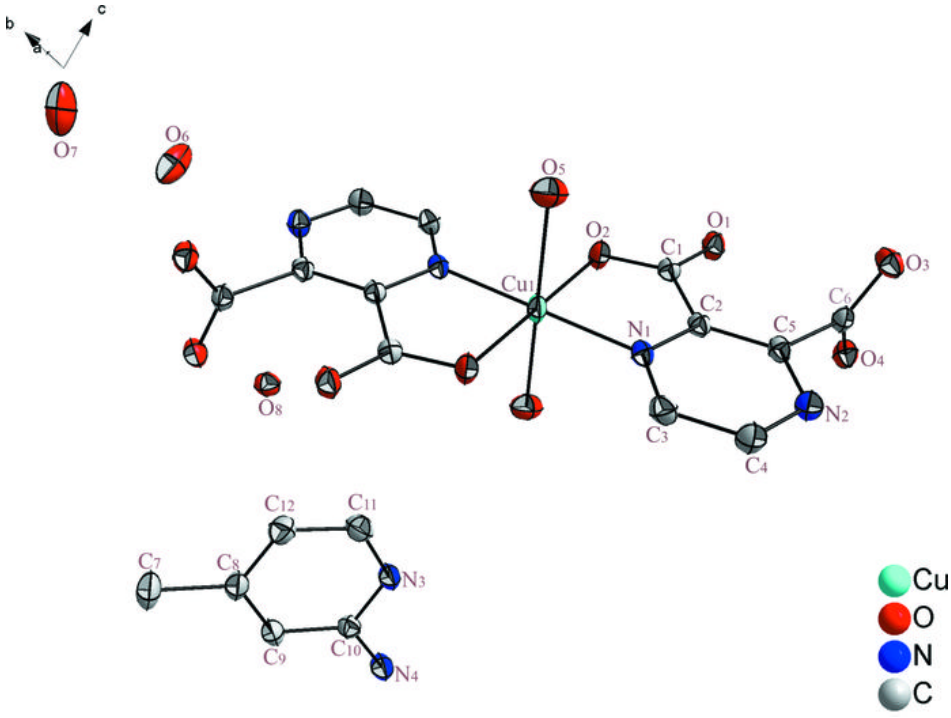
Symmetry codes: (i) −*x*, −*y*, −*z*+1.

Hydrogen-bond geometry (Å, °)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
N3—H13···O4^{ii}	0.82	1.91	2.7221 (19)	169
N4—H14A···O8^{iii}	0.77	2.12	2.8879 (19)	177
N4—H14B···O3^{ii}	0.84 (2)	2.07 (2)	2.903 (2)	168 (2)
O5—H5B···O7^{ii}	0.79 (3)	1.92 (3)	2.703 (2)	173 (3)
O5—H5A···O4^{ii}	0.82 (3)	2.09 (3)	2.8556 (18)	157 (3)
O8—H8B···O1^{iv}	0.76 (3)	2.03 (3)	2.7838 (18)	173 (3)
O6—H6B···O4^{iv}	0.81 (4)	2.06 (4)	2.839 (2)	162 (3)
O7—H17B···O8^{v}	0.76 (4)	2.04 (4)	2.797 (2)	172 (4)

Symmetry codes: (ii) *x*, *y*−1, *z*; (iii) −*x*+1, −*y*, −*z*; (iv) *x*+1, *y*, *z*; (v) *x*, *y*+1, *z*.

Fig. 1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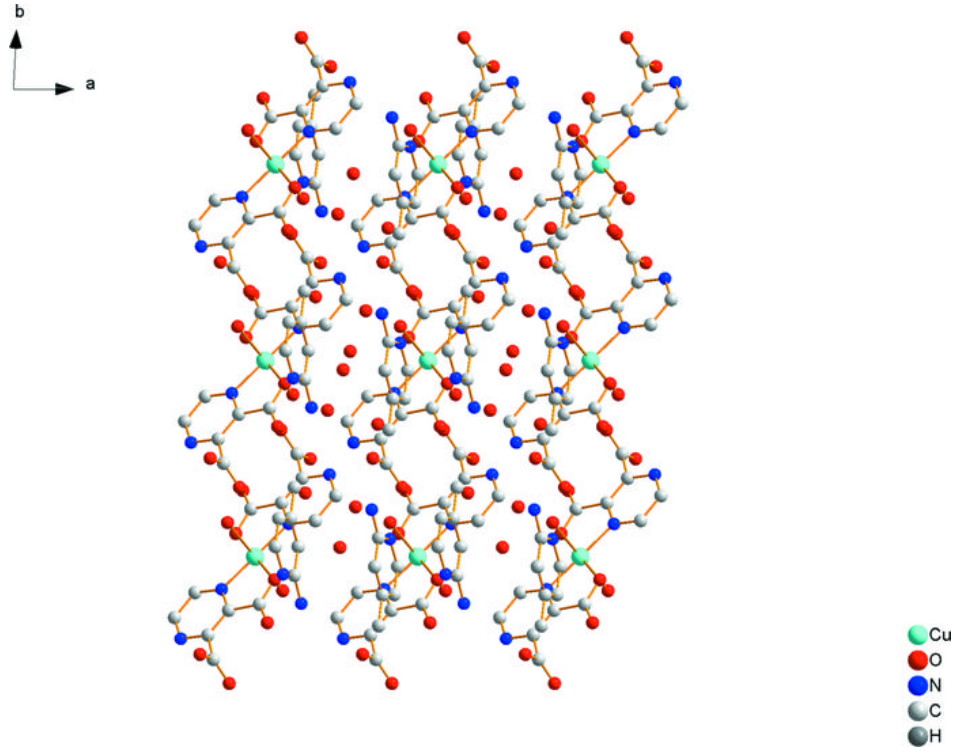
c
a
O7
O6
O5
O2
O1
C1
O3
Cu1
C2
C6
N1
C5
O4
O8
N2
C3
C4
C12
C11
C7
C8
N3
C9
C10
N4
Cu
O
N
C

Fig. 2



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4-(8-Ethoxy-2,3-dihydro-1*H*-cyclopenta-[*c*]quinolin-4-yl)butane-1-peroxol

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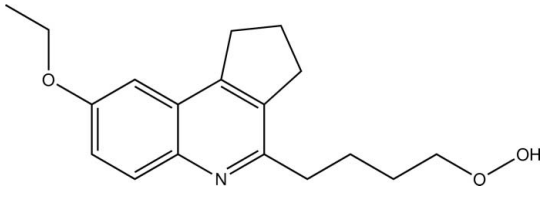
Key indicators: single-crystal X-ray study; T = 90 K; mean σ(C–C) = 0.002 Å; R factor = 0.036; wR factor = 0.110; data-to-parameter ratio = 13.9.

In the title molecule, $C_{18}H_{23}NO_3$, the hydroperoxybutyl substituent is nearly fully extended, with the four torsion angles in the range 170.23 (10)–178.71 (9)°. The O—O distance in the hydroperoxide group is 1.4690 (13) Å. This group acts as an intermolecular hydrogen-bond donor to a quinoline N atom. This results in dimeric units about the respective inversion centers, with graph-set notation $R_2^2(18)$.

Related literature

For a description of the Cambridge Structural Database, see: Allen (2002). For graph-set motifs, see: Etter (1990). For the biological activity of dihydroquinolines, see: Babiak *et al.* (1999); Cracknell *et al.* (1998); Dillard *et al.* (1973); Fotie *et al.* (2010); Lockhart *et al.* (2001); Shah *et al.* (2005); Takahashi *et al.* (2006); Thorisson *et al.* (1992). For related structures, see: Grignon-Dubois *et al.* (1993); Noland *et al.* (1996).



Experimental

Crystal data

$C_{18}H_{23}NO_3$
M_r = 301.37
Triclinic, $P\overline{1}$
a = 8.0113 (2) Å
b = 8.5091 (2) Å
c = 12.6334 (3) Å
α = 73.605 (1)°
β = 74.936 (1)°
γ = 78.136 (1)°
V = 789.63 (3) Å^3
Z = 2
Cu $K\alpha$ radiation
μ = 0.69 mm^{-1}
T = 90 K
0.19 × 0.17 × 0.15 mm

Data collection

Bruker APEXII CCD diffractometer
Absorption correction: multi-scan (*SADABS*; Sheldrick, 2004)
T_{min} = 0.880, T_{max} = 0.904
9369 measured reflections
2798 independent reflections
2400 reflections with $I > 2\sigma(I)$
R_{int} = 0.030

Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.036
$wR(F^2)$ = 0.110
S = 1.08
2798 reflections
202 parameters
H-atom parameters constrained
$\Delta\rho_{max}$ = 0.22 e Å^{-3}
$\Delta\rho_{min}$ = −0.27 e Å^{-3}

Table 1
Hydrogen-bond geometry (Å, °).

D—H···A	D—H	H···A	D···A	D—H···A
O2—H2···N1^{i}	0.84	1.93	2.7466 (14)	165

Symmetry code: (i) $-x+1, -y+1, -z+2$.

Data collection: *APEX2* (Bruker, 2006); cell refinement: *SAINT* (Bruker, 2006); data reduction: *SAINT*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *ORTEP-3 for Windows* (Farrugia, 1997); software used to prepare material for publication: *SHELXTL* (Sheldrick, 2008).

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Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: FJ2311).

References

Allen, F. H. (2002). *Acta Cryst.* B**58**, 380–388.
Babiak, J., Elokdah, H., Miller, C. & Sulkowski, T. (1999). US Patent 5 939 435.
Bruker (2006). *APEX2* and *SAINT*. Bruker AXS Inc., Madison, Wisconsin, USA.
Cracknell, M., Duriatti, A. & Kirby, N. (1998). World Patent WO 9805646.
Dillard, R., Pavey, D. & Benslay, D. (1973). *J. Med. Chem.* **16**, 251–253.
Etter, M. C. (1990). *Acc. Chem. Res.* **23**, 120–126.
Farrugia, L. J. (1997). *J. Appl. Cryst.* **30**, 565.
Fotie, J., Kaiser, M., Delfin, D. A., Manley, J., Reid, C. S., Paris, J. M., Wenzler, T., Maes, L., Mahasenan, K. V., Li, C. & Werbovetz, K. A. (2010). *J. Med. Chem.* **53**, 966–982.
Grignon-Dubois, M., Fialeix, M., Laguerre, M., Leger, J.-M. & Gauffre, J.-C. (1993). *J. Org. Chem.* **58**, 1926–1931.
Lockhart, B., Bonhomme, N., Roger, A., Dorey, G., Casara, P. & Lestage, P. (2001). *Eur. J. Pharmacol.* **416**, 59–68.
Noland, W. E., Konkel, M. J., Konkel, L. M. C., Pearce, B. C., Barnes, C. L. & Schlemper, E. O. (1996). *J. Org. Chem.* **61**, 451–454.
Shah, A., Pierson, J. & Pavlostathisa, S. (2005). *Water Res.* **39**, 4251–4263.
Sheldrick, G. M. (2004). *SADABS*. University of Göttingen, Germany.
Sheldrick, G. M. (2008). *Acta Cryst.* A**64**, 112–122.
Takahashi, H., Bekkali, Y., Capolino, A., Gilmore, T., Goldrick, S., Nelson, R., Terenzio, D., Wang, J., Zuvela-Jelaska, L., Proudfoot, J., Nabozny, G. & Thomson, D. (2006). *Bioorg. Med. Chem. Lett.* **16**, 1549–1552.
Thorisson, S., Gunstone, F. & Hardy, R. (1992). *J. Am. Oil Chem. Soc.* **69**, 806–809.

supplementary materials

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4-(8-Ethoxy-2,3-dihydro-1*H*-cyclopenta[*c*]quinolin-4-yl)butane-1-peroxol

J. Fotie, C. F. Fronczek, K. A. Burns, F. R. Fronczek, C. Bain, D. S. Bohle and F. P. Poudeu

Comment

Dihydroquinolines are mainly known for their antioxidant activity (Thorisson *et al.*, 1992, Lockhart *et al.*, 2001) although they have also been reported to possess anti-inflammatory (Dillard *et al.*, 1973), fungicidal (Cracknell *et al.*, 1998), antiatherosclerotic (Babiak *et al.*, 1999), and hormone receptor modulator (Takahashi *et al.*, 2006) properties. Furthermore, 6-ethoxy-1,2-dihydro-2,2,4-trimethylquinoline, also known as ethoxyquin, is a FDA approved antioxidant commonly used as a preservative in the food processing industry (Shah *et al.*, 2005). We have recently reported some dihydroquinoline derivatives with outstanding antitrypanosomal activity (Fotie *et al.*, 2010). In our effort to optimize the trypanocidal activity of this family of compound, we have synthesized the title compound, an unusual hydroperoxybutylquinoline derivative. Here we are reporting the characterization of that compound using ^{1}H– and ^{13}C-NMR spectroscopy, mass spectrometry, and single-crystal diffraction.

The molecular structure of the title compound is illustrated in Fig. 1. The 10-atom quinoline ring system is essentially planar, with mean deviation 0.009 Å and maximum deviation 0.017 (1) Å for both N1 and C11. The five-membered ring has the envelope conformation, with C9 at the flap position, 0.340 (2) Å out of the quinoline plane. The hydroperoxybutyl chain is extended, with torsion angle magnitudes in the range 170.23 (10) to 178.71 (9)°, and the best plane of its four C and two O atoms is approximately perpendicular to the quinoline plane, forming a dihedral angle of 89.53 (3)°. The hydroperoxy O—O distance, 1.4690 (13) Å agrees well with literature values for this group. The mean value of the 135 such distances in the Cambridge Structural Database (version 5.31, Nov. 2009; Allen 2002), after rejecting eight outliers, is 1.462 Å.

The hydroperoxide donates an intermolecular hydrogen bond to quinoline N1, with O···N distance 2.7466 (14) Å, forming discrete dimers having graph set (Etter, 1990) $R^2_2(18)$ about inversion centers, as illustrated in Fig. 2.

Experimental

The title compound was prepared by heating to reflux for three days, a mixture of *p*-phenitidine (500 mg, 3.6 mmol) and cyclopentanone (10 ml, large excess) in the presence of catalytic amounts of iodine (93 mg) and benzoyl peroxide (8.8 mg). After appropriate work-up, and purification on a silica gel column, crystals were carefully grown at room temperature, in a mixture of hexanes-dichloromethane, over the course of a week.

Mp: 131.3 - 131.6 °C. The melting point was recorded on a MEL-TEMP ELECTROTHERMAL digital melting point apparatus, and is not corrected.

ESIMS *m/z* (%): 316 (90) $[M + CH_3]^+$, 302 (43) $[M + H]^+$, 286 (100) $[M -16]^+$, 284 (94) $[M - H_2O]^+$. These fragment ions are consistent with a molecular formula of $C_{18}H_{23}NO_3$. The ESIMS spectrum was recorded on a Finnigan LCQDUO spectrometer.

NMR data were collected on a Bruker AC 300 Spectrometer. ^{1}H-NMR (300 MHz, $CDCl_3$) δ: 1.47 (3*H*, t, J = 6.7 Hz), 1.68 (2*H*, m), 1.85 (2*H*, m), 2.23 (2*H*, m), 3.04 (4*H*, t, J = 7.9 Hz), 3.13 (2*H*, t, J = 7.3 Hz), 4.10 (2*H*, t, 6.7 Hz), 4.15 (2*H*, q, J = 6.7 Hz), 6.90 (1*H*, d, J = 2.4 Hz), 7.23 (1*H*, dd, J = 9.2 Hz and 2,4 Hz), 7.83 (1*H*, d, 9.2 Hz), 13.6 (1*H*, brs). ^{13}C-NMR (75 MHz, $CDCl_3$) δ: 14.9, 24.0, 25.0, 25.9, 31.4, 31.5, 35.0, 63.8, 103.0, 121.1, 125.9, 129.2, 136.0, 141.6, 149.7, 155.9, 156.6. 162.3.

Refinement

H atoms on C were placed in idealized positions with C—H distances 0.95 - 1.00 Å and thereafter treated as riding. The OH H atom was located from a difference map in the expected circle. Torsional parameters were refined for the methyl and hydroperoxy OH groups. U_{iso} for H were assigned as 1.2 times U_{eq} of the attached atoms (1.5 for methyl and OH).

Figures

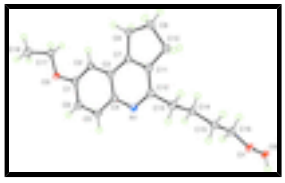


Fig. 1. Ellipsoids at the 50% level, with H atoms having arbitrary radius.

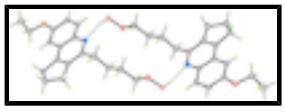


Fig. 2. The hydrogen-bonded dimer, with graph set $R^2_2(18)$.

4-(8-Ethoxy-2,3-dihydro-1*H*-cyclopenta[*c*]quinolin-4-yl)butane- 1-peroxol

Crystal data

$C_{18}H_{23}NO_3$	$Z = 2$
$M_r = 301.37$	$F(000) = 324$
Triclinic, $P\overline{1}$	$D_x = 1.268$ Mg m^{-3}
Hall symbol: -P 1	Cu *K*α radiation, λ = 1.54178 Å
$a = 8.0113$ (2) Å	Cell parameters from 4518 reflections
$b = 8.5091$ (2) Å	θ = 3.7–68.3°
$c = 12.6334$ (3) Å	μ = 0.69 mm^{-1}
α = 73.605 (1)°	$T = 90$ K
β = 74.936 (1)°	Prism, colourless
γ = 78.136 (1)°	0.19 × 0.17 × 0.15 mm
$V = 789.63$ (3) Å^3	

Data collection

Bruker APEXII CCD diffractometer	2798 independent reflections
Radiation source: fine-focus sealed tube	2400 reflections with $I > 2\sigma(I)$
graphite	$R_{int} = 0.030$
φ and ω scans	$\theta_{max} = 68.8°$, $\theta_{min} = 3.7°$

Absorption correction: multi-scan (*SADABS*; Sheldrick, 2004)

T_{min} = 0.880, T_{max} = 0.904

9369 measured reflections

$h = -9 \rightarrow 9$

$k = -9 \rightarrow 10$

$l = -15 \rightarrow 15$

Refinement

Refinement on F^2

Least-squares matrix: full

$R[F^2 > 2\sigma(F^2)] = 0.036$

$wR(F^2) = 0.110$

$S = 1.08$

2798 reflections

202 parameters

0 restraints

Primary atom site location: structure-invariant direct methods

Secondary atom site location: difference Fourier map

Hydrogen site location: inferred from neighbouring sites

H-atom parameters constrained

$w = 1/[\sigma^2(F_o^2) + (0.0626P)^2 + 0.1754P]$ where $P = (F_o^2 + 2F_c^2)/3$

$(\Delta/\sigma)_{max} < 0.001$

$\Delta\rho_{max} = 0.22$ e Å^{-3}

$\Delta\rho_{min} = -0.27$ e Å^{-3}

Extinction correction: *SHELXL97* (Sheldrick, 2008), $Fc^* = kFc[1+0.001xFc^2\lambda^3/\sin(2\theta)]^{-1/4}$

Extinction coefficient: 0.0023 (7)

Special details

Geometry. All e.s.d.'s (except the e.s.d. in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell e.s.d.'s are taken into account individually in the estimation of e.s.d.'s in distances, angles and torsion angles; correlations between e.s.d.'s in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell e.s.d.'s is used for estimating e.s.d.'s involving l.s. planes.

Refinement. Refinement of F^2 against ALL reflections. The weighted *R*-factor *wR* and goodness of fit *S* are based on F^2, conventional *R*-factors *R* are based on *F*, with *F* set to zero for negative F^2. The threshold expression of $F^2 > \sigma(F^2)$ is used only for calculating *R*-factors(gt) *etc*. and is not relevant to the choice of reflections for refinement. *R*-factors based on F^2 are statistically about twice as large as those based on *F*, and *R*- factors based on ALL data will be even larger.

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å^2)

	x	*y*	*z*	U_{iso}*/U_{eq}
O1	0.54940 (12)	0.44045 (11)	1.21141 (7)	0.0202 (2)
O2	0.43514 (12)	0.35072 (12)	1.31138 (8)	0.0233 (3)
H2	0.3429	0.4140	1.3292	0.035*
O3	0.98882 (12)	0.17854 (11)	0.27498 (8)	0.0201 (2)
N1	0.84064 (14)	0.40032 (13)	0.66551 (9)	0.0180 (3)
C1	0.96537 (17)	0.22269 (16)	0.37459 (11)	0.0177 (3)
C2	1.08402 (17)	0.17863 (16)	0.44285 (11)	0.0175 (3)
H2A	1.1914	0.1104	0.4233	0.021*
C3	1.04475 (17)	0.23589 (15)	0.54275 (11)	0.0166 (3)
C4	0.88489 (17)	0.33756 (16)	0.57160 (11)	0.0171 (3)
C5	0.76525 (17)	0.37924 (16)	0.49902 (11)	0.0184 (3)
H5	0.6573	0.4473	0.5172	0.022*

C6	0.80419 (17)	0.32234 (16)	0.40359 (11)	0.0198 (3)
H6	0.7225	0.3498	0.3562	0.024*
C7	1.15889 (17)	0.19861 (16)	0.61825 (11)	0.0173 (3)
C8	1.33845 (17)	0.09920 (17)	0.60806 (11)	0.0203 (3)
H8A	1.4123	0.1362	0.5321	0.024*
H8B	1.3323	−0.0203	0.6226	0.024*
C9	1.40947 (18)	0.13488 (18)	0.69997 (12)	0.0235 (3)
H9A	1.4726	0.0323	0.7404	0.028*
H9B	1.4909	0.2177	0.6656	0.028*
C10	1.25038 (18)	0.20199 (18)	0.78213 (12)	0.0229 (3)
H10A	1.2155	0.1143	0.8507	0.027*
H10B	1.2753	0.2956	0.8047	0.027*
C11	1.11048 (17)	0.25808 (16)	0.71348 (11)	0.0188 (3)
C12	0.95014 (17)	0.36144 (16)	0.73497 (11)	0.0184 (3)
C13	0.89624 (18)	0.43704 (17)	0.83518 (11)	0.0209 (3)
H13A	0.8268	0.5471	0.8139	0.025*
H13B	1.0025	0.4540	0.8543	0.025*
C14	0.78889 (17)	0.33287 (16)	0.94029 (11)	0.0186 (3)
H14A	0.6851	0.3105	0.9213	0.022*
H14B	0.8601	0.2254	0.9657	0.022*
C15	0.73048 (17)	0.42275 (16)	1.03551 (11)	0.0190 (3)
H15A	0.8351	0.4403	1.0561	0.023*
H15B	0.6655	0.5329	1.0079	0.023*
C16	0.61601 (18)	0.32967 (16)	1.13985 (11)	0.0194 (3)
H16A	0.5194	0.2962	1.1196	0.023*
H16B	0.6850	0.2291	1.1779	0.023*
C17	1.15683 (18)	0.09386 (16)	0.23380 (11)	0.0201 (3)
H17A	1.1735	−0.0203	0.2812	0.024*
H17B	1.2503	0.1526	0.2357	0.024*
C18	1.1631 (2)	0.09065 (18)	0.11403 (12)	0.0256 (3)
H18A	1.0682	0.0347	0.1132	0.038*
H18B	1.2755	0.0309	0.0835	0.038*
H18C	1.1496	0.2043	0.0676	0.038*

Atomic displacement parameters (Å^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
O1	0.0200 (5)	0.0214 (5)	0.0171 (5)	−0.0013 (4)	0.0010 (4)	−0.0070 (4)
O2	0.0197 (5)	0.0255 (5)	0.0176 (5)	0.0011 (4)	0.0027 (4)	−0.0033 (4)
O3	0.0201 (5)	0.0229 (5)	0.0180 (5)	0.0001 (4)	−0.0048 (4)	−0.0076 (4)
N1	0.0179 (6)	0.0168 (6)	0.0179 (6)	−0.0021 (4)	−0.0017 (4)	−0.0044 (4)
C1	0.0208 (7)	0.0161 (7)	0.0153 (6)	−0.0040 (5)	−0.0026 (5)	−0.0027 (5)
C2	0.0164 (7)	0.0150 (6)	0.0183 (7)	−0.0013 (5)	−0.0018 (5)	−0.0023 (5)
C3	0.0171 (7)	0.0141 (6)	0.0166 (7)	−0.0038 (5)	−0.0023 (5)	−0.0006 (5)
C4	0.0181 (7)	0.0141 (6)	0.0168 (7)	−0.0033 (5)	−0.0004 (5)	−0.0022 (5)
C5	0.0151 (7)	0.0165 (7)	0.0210 (7)	0.0002 (5)	−0.0027 (5)	−0.0029 (5)
C6	0.0187 (7)	0.0193 (7)	0.0199 (7)	−0.0030 (5)	−0.0051 (5)	−0.0017 (5)
C7	0.0173 (7)	0.0148 (6)	0.0175 (7)	−0.0039 (5)	−0.0023 (5)	−0.0003 (5)

C8	0.0176 (7)	0.0211 (7)	0.0201 (7)	0.0016 (5)	−0.0045 (5)	−0.0045 (5)
C9	0.0183 (7)	0.0282 (8)	0.0235 (7)	−0.0008 (6)	−0.0065 (6)	−0.0056 (6)
C10	0.0222 (7)	0.0259 (8)	0.0219 (7)	−0.0011 (6)	−0.0075 (6)	−0.0071 (6)
C11	0.0194 (7)	0.0180 (7)	0.0175 (7)	−0.0052 (5)	−0.0029 (5)	−0.0012 (5)
C12	0.0193 (7)	0.0164 (7)	0.0182 (7)	−0.0043 (5)	−0.0017 (5)	−0.0032 (5)
C13	0.0215 (7)	0.0203 (7)	0.0212 (7)	−0.0037 (5)	−0.0020 (6)	−0.0075 (6)
C14	0.0194 (7)	0.0188 (7)	0.0182 (7)	−0.0005 (5)	−0.0043 (5)	−0.0067 (5)
C15	0.0181 (7)	0.0203 (7)	0.0192 (7)	−0.0006 (5)	−0.0041 (5)	−0.0072 (5)
C16	0.0213 (7)	0.0195 (7)	0.0179 (7)	0.0005 (5)	−0.0043 (5)	−0.0075 (5)
C17	0.0214 (7)	0.0180 (7)	0.0197 (7)	−0.0001 (5)	−0.0029 (5)	−0.0058 (5)
C18	0.0307 (8)	0.0246 (8)	0.0226 (7)	−0.0005 (6)	−0.0046 (6)	−0.0106 (6)

Geometric parameters (Å, °)

O1—C16	1.4193 (15)	C9—H9B	0.9900
O1—O2	1.4690 (13)	C10—C11	1.5125 (18)
O2—H2	0.8400	C10—H10A	0.9900
O3—C1	1.3693 (15)	C10—H10B	0.9900
O3—C17	1.4319 (16)	C11—C12	1.4094 (19)
N1—C12	1.3288 (17)	C12—C13	1.5048 (18)
N1—C4	1.3709 (17)	C13—C14	1.5310 (18)
C1—C2	1.3729 (18)	C13—H13A	0.9900
C1—C6	1.4142 (19)	C13—H13B	0.9900
C2—C3	1.4166 (18)	C14—C15	1.5266 (17)
C2—H2A	0.9500	C14—H14A	0.9900
C3—C4	1.4147 (18)	C14—H14B	0.9900
C3—C7	1.4176 (18)	C15—C16	1.5122 (18)
C4—C5	1.4208 (18)	C15—H15A	0.9900
C5—C6	1.3628 (19)	C15—H15B	0.9900
C5—H5	0.9500	C16—H16A	0.9900
C6—H6	0.9500	C16—H16B	0.9900
C7—C11	1.3691 (19)	C17—C18	1.5087 (18)
C7—C8	1.5054 (18)	C17—H17A	0.9900
C8—C9	1.5420 (19)	C17—H17B	0.9900
C8—H8A	0.9900	C18—H18A	0.9800
C8—H8B	0.9900	C18—H18B	0.9800
C9—C10	1.5413 (19)	C18—H18C	0.9800
C9—H9A	0.9900		
C16—O1—O2	105.80 (9)	C7—C11—C12	120.33 (12)
O1—O2—H2	109.5	C7—C11—C10	111.14 (12)
C1—O3—C17	117.05 (10)	C12—C11—C10	128.50 (12)
C12—N1—C4	119.06 (11)	N1—C12—C11	121.27 (12)
O3—C1—C2	125.10 (12)	N1—C12—C13	116.62 (11)
O3—C1—C6	114.06 (11)	C11—C12—C13	122.09 (12)
C2—C1—C6	120.84 (12)	C12—C13—C14	114.07 (11)
C1—C2—C3	119.32 (12)	C12—C13—H13A	108.7
C1—C2—H2A	120.3	C14—C13—H13A	108.7
C3—C2—H2A	120.3	C12—C13—H13B	108.7
C4—C3—C2	120.22 (12)	C14—C13—H13B	108.7

C4—C3—C7	116.10 (12)	H13A—C13—H13B	107.6
C2—C3—C7	123.68 (12)	C15—C14—C13	110.73 (11)
N1—C4—C3	123.16 (12)	C15—C14—H14A	109.5
N1—C4—C5	118.20 (12)	C13—C14—H14A	109.5
C3—C4—C5	118.63 (12)	C15—C14—H14B	109.5
C6—C5—C4	120.53 (12)	C13—C14—H14B	109.5
C6—C5—H5	119.7	H14A—C14—H14B	108.1
C4—C5—H5	119.7	C16—C15—C14	113.20 (11)
C5—C6—C1	120.44 (12)	C16—C15—H15A	108.9
C5—C6—H6	119.8	C14—C15—H15A	108.9
C1—C6—H6	119.8	C16—C15—H15B	108.9
C11—C7—C3	120.02 (12)	C14—C15—H15B	108.9
C11—C7—C8	111.83 (11)	H15A—C15—H15B	107.8
C3—C7—C8	128.14 (12)	O1—C16—C15	106.06 (11)
C7—C8—C9	103.20 (11)	O1—C16—H16A	110.5
C7—C8—H8A	111.1	C15—C16—H16A	110.5
C9—C8—H8A	111.1	O1—C16—H16B	110.5
C7—C8—H8B	111.1	C15—C16—H16B	110.5
C9—C8—H8B	111.1	H16A—C16—H16B	108.7
H8A—C8—H8B	109.1	O3—C17—C18	107.10 (11)
C10—C9—C8	106.77 (11)	O3—C17—H17A	110.3
C10—C9—H9A	110.4	C18—C17—H17A	110.3
C8—C9—H9A	110.4	O3—C17—H17B	110.3
C10—C9—H9B	110.4	C18—C17—H17B	110.3
C8—C9—H9B	110.4	H17A—C17—H17B	108.6
H9A—C9—H9B	108.6	C17—C18—H18A	109.5
C11—C10—C9	103.12 (11)	C17—C18—H18B	109.5
C11—C10—H10A	111.1	H18A—C18—H18B	109.5
C9—C10—H10A	111.1	C17—C18—H18C	109.5
C11—C10—H10B	111.1	H18A—C18—H18C	109.5
C9—C10—H10B	111.1	H18B—C18—H18C	109.5
H10A—C10—H10B	109.1		
C17—O3—C1—C2	−6.48 (18)	C3—C7—C8—C9	168.11 (13)
C17—O3—C1—C6	173.01 (11)	C7—C8—C9—C10	18.58 (14)
O3—C1—C2—C3	178.62 (11)	C8—C9—C10—C11	−19.42 (14)
C6—C1—C2—C3	−0.8 (2)	C3—C7—C11—C12	−2.3 (2)
C1—C2—C3—C4	−0.07 (19)	C8—C7—C11—C12	176.70 (12)
C1—C2—C3—C7	−179.45 (12)	C3—C7—C11—C10	179.39 (11)
C12—N1—C4—C3	−1.71 (19)	C8—C7—C11—C10	−1.59 (16)
C12—N1—C4—C5	179.37 (11)	C9—C10—C11—C7	13.27 (15)
C2—C3—C4—N1	−178.41 (11)	C9—C10—C11—C12	−164.84 (13)
C7—C3—C4—N1	1.02 (19)	C4—N1—C12—C11	0.34 (19)
C2—C3—C4—C5	0.51 (19)	C4—N1—C12—C13	178.70 (11)
C7—C3—C4—C5	179.94 (11)	C7—C11—C12—N1	1.7 (2)
N1—C4—C5—C6	178.92 (11)	C10—C11—C12—N1	179.63 (12)
C3—C4—C5—C6	−0.05 (19)	C7—C11—C12—C13	−176.59 (12)
C4—C5—C6—C1	−0.8 (2)	C10—C11—C12—C13	1.4 (2)
O3—C1—C6—C5	−178.21 (11)	N1—C12—C13—C14	89.79 (14)
C2—C1—C6—C5	1.3 (2)	C11—C12—C13—C14	−91.87 (15)

C4—C3—C7—C11	1.01 (19)	C12—C13—C14—C15	−176.62 (11)
C2—C3—C7—C11	−179.59 (12)	C13—C14—C15—C16	177.09 (10)
C4—C3—C7—C8	−177.84 (12)	O2—O1—C16—C15	178.71 (9)
C2—C3—C7—C8	1.6 (2)	C14—C15—C16—O1	−170.23 (10)
C11—C7—C8—C9	−10.82 (15)	C1—O3—C17—C18	−168.40 (11)

Hydrogen-bond geometry (Å, °)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
O2—H2···N1^{i}	0.84	1.93	2.7466 (14)	165

Symmetry codes: (i) −*x*+1, −*y*+1, −*z*+2.

Fig. 1

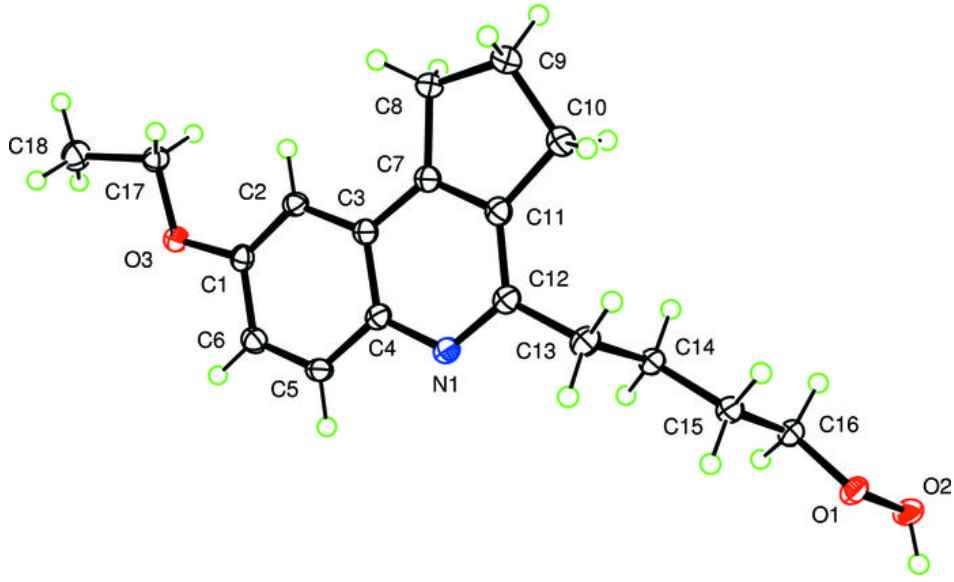
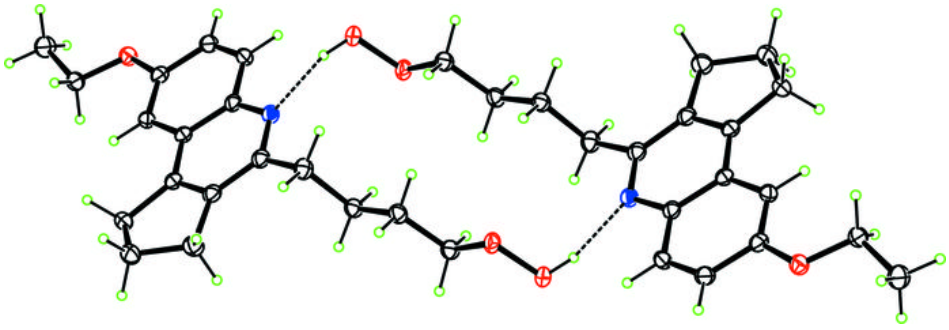

C9
C8
C10
C18
C7
C17
C2
C3
C11
O3
C1
C12
C6
C4
C13
C14
C5
N1
C15
C16
O2
O1

Fig. 2



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(3*E*)-3-[4-(Dimethylamino)phenyl]-1-(4-hydroxyphenyl)prop-2-en-1-one

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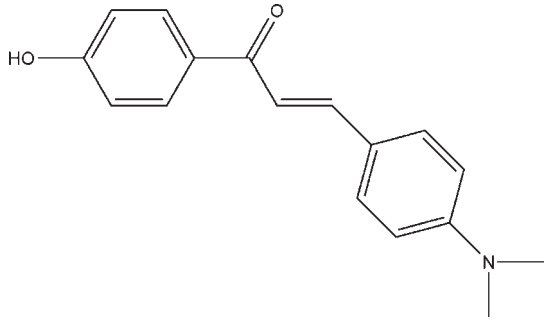
Key indicators: single-crystal X-ray study; T = 100 K; mean σ(C–C) = 0.003 Å; R factor = 0.032; wR factor = 0.078; data-to-parameter ratio = 7.5.

The asymmetric unit of the title compound, $C_{17}H_{17}NO_2$, contains two crystallographically independent molecules. Both molecules adopt a *trans* configuration about the C=C bond, with the C—C=C—C fragments in the two molecules twisted in opposite directions [torsion angles of 174.2 (2) and −175.8 (2)°]. The two benzene rings in each of the molecules make dihedral angles of 20.21 (6) and 48.64 (4)°. In the crystal, adjacent molecules are linked by O—H···O hydrogen bonds into infinite polymeric chains.

Related literature

For the biological activity of chalcones, see: Sortino *et al.* (2007); Katsori & Hadjipavlou-Litina (2009). For the use of chalcones as precursors in the preparation flavonoids, see: Avila *et al.* (2008). For the crystal structures of related chalcone derivatives, see: Liu *et al.* (2002); Fronczek *et al.* (1987).



Experimental

Crystal data

$C_{17}H_{17}NO_2$
M_r = 267.32
Monoclinic, $P2_1$
a = 6.3070 (1) Å
b = 29.5285 (6) Å
c = 7.3880 (2) Å
β = 95.056 (1)°
V = 1370.56 (5) Å^3
Z = 4
Mo $K\alpha$ radiation
μ = 0.09 mm^{-1}
T = 100 K
0.48 × 0.24 × 0.16 mm

Data collection

Bruker APEXII CCD area-detector diffractometer
Absorption correction: multi-scan (*SADABS*; Sheldrick, 2008*a*)
T_{min} = 0.960, T_{max} = 0.987
8837 measured reflections
2756 independent reflections
2646 reflections with $I > 2\sigma(I)$
R_{int} = 0.020

Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.032
$wR(F^2)$ = 0.078
S = 1.13
2756 reflections
367 parameters
1 restraint
H-atom parameters constrained
$\Delta\rho_{max}$ = 0.17 e Å^{-3}
$\Delta\rho_{min}$ = −0.26 e Å^{-3}

Table 1
Hydrogen-bond geometry (Å, °).

D—H···A	D—H	H···A	D···A	D—H···A
O4—H4*O*···O1^{i}	0.82	1.85	2.670 (2)	173
O2—H2*O*···O3^{ii}	0.82	1.85	2.659 (2)	169

Symmetry codes: (i) $x-1, y, z$; (ii) $x-1, y, z-1$.

Data collection: *APEX2* (Bruker, 2008); cell refinement: *SAINT* (Bruker, 2008); data reduction: *SAINT*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008*b*); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008*b*); molecular graphics: *X-SEED* (Barbour, 2001); software used to prepare material for publication: *publCIF* (Westrip, 2010).

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Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: FJ2315).

References

Avila, H. P., Smania, E. F., Monache, F. D. & Smania, A. Jr (2008). *Bioorg. Med. Chem.* **16**, 9790–9794.
Barbour, L. J. (2001). *J. Supramol. Chem.* **1**, 189–191.
Bruker (2008). *APEX2* and *SAINT*. Bruker AXS Inc., Madison, Wisconsin, USA.
Fronczek, F. R., Tanrisever, N. & Fischer, N. H. (1987). *Acta Cryst.* C**43**, 158–160.
Katsori, A. M. & Hadjipavlou-Litina, D. (2009). *Curr. Med. Chem.* **16**, 1062–1081.
Liu, Z.-Q., Fang, Q., Yu, W.-T., Xue, G., Cao, D.-X. & Jiang, M.-H. (2002). *Acta Cryst.* C**58**, o445–o446.
Sheldrick, G. M. (2008*a*). *SADABS*. University of Göttingen, Germany.
Sheldrick, G. M. (2008*b*). *Acta Cryst.* A**64**, 112–122.
Sortino, M., Delgado, P., Juarez, S., Quiroga, J., Abonia, R., Insuasty, B., Nogueras, M., Rodero, L., Garibotto, F. M., Enriz, R. D. & Zacchino, S. A. (2007). *Bioorg. Med. Chem.* **15**, 484–494.
Westrip, S. P. (2010). *J. Appl. Cryst.* **43**. Submitted.

supplementary materials

Acta Cryst. (2010). E**66**, o1808 [**doi:10.1107/S1600536810024050**]

(3*E*)-3-[4-(Dimethylamino)phenyl]-1-(4-hydroxyphenyl)prop-2-en-1-one

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Comment

Chalcone is a unique template that is associated with several biological activities. The radical quenching properties of the phenolic groups present in many chalcones have raised interest in using the compounds or chalcone rich plant extracts as drugs or food preservatives [Sortino, *et al.* (2007); Katsori, *et al.* (2009)]. Chalcones constitute an important group of natural product and serve as precursors for the synthesis of different classes of flavonoids, which are common substances in plants [Avila, *et al.* (2008)]. We report here a substituted chalcone derivative which is prepared from the condensation reaction of *p*-hydroxylacetophenone with 4-(*N,N*-dimethylamino)benzaldehyde. The crystal structure of this compound (common chemical name: 4-hydroxy-4'-dimethylaminochalcone) consists of two independent molecules which form polymeric chains as a result of intermolecular hydrogen bonding between the hydroxyl groups and carbonyl oxygen atoms of adjacent molecules (Fig. 2). In contrast, the related compounds, 2-hydroxy-4'-dimethylaminochalcone [Liu, *et al.* (2002)] and 2,4-dihydroxychalcone [Fronczek, *et al.* (1987)] are discrete molecules. In the title compound, the two asymmetric molecules adopt the *trans* configuration about the olefinic double bond with torsional angles of 174.2 (2)° and -175.8 (2)^{o} . In addition, the two benzene rings in both molecules are not co-planar, but makes a dihedral angle of 20.21 (6)° and 48.64 (4)°, respectively.

Experimental

To a stirred solution of KOH (2.0 g, 45.6 mmol) in distilled water (2 ml) cooled in an ice bath, was added 10 ml of methanoic solution containing *p*-hydroxyacetophenone (g, 1 mmol) and 4-(*N,N*-dimethylamino)benzaldehyde (g, 1 mmol). The reaction mixture was stirred at room temperature for 24 h. The mixture was poured into ice-water (10 ml), adjusted to pH 5 - 6 with 1*M* HCl, and then extracted with ethyl acetate. The organic layer was successively washed with distilled water and saturated brine, dried over anhydrous sodium sulfate. The resulting filtrate was evaporated slowly at room temperature to obtain the yellow crystals.

Refinement

Hydrogen atoms were placed at calculated positions (C–H 0.93 Å; O–H 0.82 Å) and were treated as riding on their parent atoms, with *U*(H) set to 1.2–1.5 times *U*~eq~(C). The absolute structure could not be determined from the X-ray analysis. 2266 Friedel pairs were therefore merged before the final refinement.

Figures

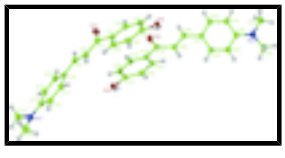

Fig. 1. The molecular structure of 3*E*-(4-dimethylaminophenyl)-1-(4'-hydroxyphenyl)-prop-2-en-1-one showing 70% probability displacement ellipsoids and the atom numbering. Hydrogen atoms are drawn as spheres of arbitrary radius.

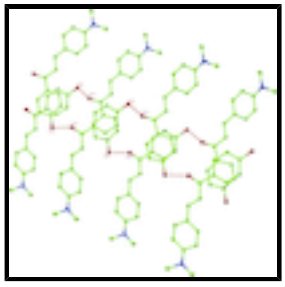

Fig. 2. Crystal packing showing the hydrogen bonding interactions in the molecules.

(3*E*)-3-[4-(Dimethylamino)phenyl]-1-(4-hydroxyphenyl)prop-2-en-1-one

Crystal data

$C_{17}H_{17}NO_2$	$F(000) = 568$
$M_r = 267.32$	$D_x = 1.295$ Mg m^{-3}
Monoclinic, $P2_1$	Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å
Hall symbol: P 2yb	Cell parameters from 4618 reflections
$a = 6.3070$ (1) Å	$\theta = 2.8–29.5°$
$b = 29.5285$ (6) Å	$\mu = 0.09$ mm^{-1}
$c = 7.3880$ (2) Å	$T = 100$ K
$\beta = 95.056$ (1)°	Block, yellow
$V = 1370.56$ (5) Å^3	0.48 × 0.24 × 0.16 mm
$Z = 4$	

Data collection

Bruker APEXII CCD area-detector diffractometer	2756 independent reflections
Radiation source: fine-focus sealed tube	2646 reflections with $I > 2\sigma(I)$
graphite	$R_{int} = 0.020$
ω scans	$\theta_{max} = 26.0°$, $\theta_{min} = 1.4°$
Absorption correction: multi-scan (*SADABS*; Sheldrick, 2008a)	$h = -7\rightarrow7$
$T_{min} = 0.960$, $T_{max} = 0.987$	$k = -35\rightarrow36$
8837 measured reflections	$l = -9\rightarrow8$

Refinement

Refinement on F^2	Primary atom site location: structure-invariant direct methods
Least-squares matrix: full	Secondary atom site location: difference Fourier map
$R[F^2 > 2\sigma(F^2)] = 0.032$	Hydrogen site location: inferred from neighbouring sites
$wR(F^2) = 0.078$	H-atom parameters constrained
$S = 1.13$	$w = 1/[\sigma^2(F_o^2) + (0.0389P)^2 + 0.282P]$ where $P = (F_o^2 + 2F_c^2)/3$
2756 reflections	$(\Delta/\sigma)_{max} = 0.044$

367 parameters	$\Delta\rho_{max} = 0.17$ e Å^{-3}
1 restraint	$\Delta\rho_{min} = -0.26$ e Å^{-3}

Special details

Geometry. All e.s.d.'s (except the e.s.d. in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell e.s.d.'s are taken into account individually in the estimation of e.s.d.'s in distances, angles and torsion angles; correlations between e.s.d.'s in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell e.s.d.'s is used for estimating e.s.d.'s involving l.s. planes.

Refinement. Refinement of F^2 against ALL reflections. The weighted *R*-factor *wR* and goodness of fit *S* are based on F^2, conventional *R*-factors *R* are based on *F*, with *F* set to zero for negative F^2. The threshold expression of $F^2 > \sigma(F^2)$ is used only for calculating *R*-factors(gt) *etc*. and is not relevant to the choice of reflections for refinement. *R*-factors based on F^2 are statistically about twice as large as those based on *F*, and *R*- factors based on ALL data will be even larger.

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å^2)

	x	*y*	*z*	U_{iso}*/U_{eq}
O2	−0.0711 (2)	0.31769 (5)	0.0870 (2)	0.0206 (3)
H2O	−0.1727	0.3108	0.0154	0.031*
O1	0.6270 (2)	0.17288 (6)	0.3369 (2)	0.0228 (4)
O4	−0.0471 (2)	0.14648 (5)	0.5680 (2)	0.0210 (3)
H4O	−0.1537	0.1540	0.5035	0.031*
O3	0.6359 (2)	0.29454 (6)	0.8222 (2)	0.0217 (4)
C22	−0.0250 (3)	0.22737 (8)	0.6122 (3)	0.0178 (5)
H22	−0.1639	0.2313	0.5614	0.021*
C18	0.3052 (3)	0.25932 (7)	0.7460 (3)	0.0159 (4)
C4	0.0430 (3)	0.27980 (8)	0.1369 (3)	0.0167 (4)
C5	−0.0379 (3)	0.23644 (8)	0.1061 (3)	0.0176 (5)
H5	−0.1749	0.2323	0.0510	0.021*
C21	0.0628 (3)	0.18403 (7)	0.6272 (3)	0.0166 (4)
C30	0.1868 (3)	0.50908 (7)	1.0211 (3)	0.0165 (4)
C7	0.4345 (3)	0.16614 (8)	0.2975 (3)	0.0178 (5)
C27	0.3502 (3)	0.42371 (8)	0.9189 (3)	0.0161 (4)
C24	0.4395 (3)	0.29859 (8)	0.8066 (3)	0.0161 (4)
C20	0.2715 (3)	0.17818 (8)	0.7049 (3)	0.0182 (5)
H20	0.3292	0.1493	0.7188	0.022*
C1	0.2959 (3)	0.20472 (8)	0.2383 (3)	0.0162 (4)
C26	0.4387 (3)	0.38086 (8)	0.8657 (3)	0.0166 (4)
H26	0.5806	0.3809	0.8407	0.020*
C6	0.0875 (3)	0.19938 (8)	0.1583 (3)	0.0178 (5)
H6	0.0324	0.1704	0.1399	0.021*
C8	0.3399 (3)	0.12117 (8)	0.3178 (3)	0.0179 (5)
H8	0.1998	0.1160	0.2723	0.021*
C3	0.2483 (3)	0.28595 (7)	0.2200 (3)	0.0179 (5)
H3	0.3007	0.3150	0.2428	0.021*
C25	0.3352 (3)	0.34110 (7)	0.8492 (3)	0.0164 (4)
H25	0.1907	0.3405	0.8656	0.020*

C23	0.0940 (3)	0.26418 (8)	0.6726 (3)	0.0164 (4)
H23	0.0332	0.2929	0.6646	0.020*
C29	0.0770 (3)	0.46832 (8)	1.0495 (3)	0.0183 (4)
H29	−0.0513	0.4693	1.1026	0.022*
C10	0.3791 (3)	0.04249 (7)	0.4464 (3)	0.0165 (4)
C32	0.4583 (3)	0.46418 (8)	0.8915 (3)	0.0183 (4)
H32	0.5873	0.4631	0.8397	0.022*
C19	0.3911 (3)	0.21555 (8)	0.7608 (3)	0.0175 (5)
H19	0.5311	0.2116	0.8090	0.021*
C28	0.1567 (3)	0.42723 (7)	1.0000 (3)	0.0164 (4)
H28	0.0808	0.4010	1.0206	0.020*
C2	0.3732 (3)	0.24881 (8)	0.2682 (3)	0.0178 (5)
H2	0.5110	0.2531	0.3213	0.021*
C9	0.4533 (3)	0.08742 (8)	0.4012 (3)	0.0176 (5)
H9	0.5963	0.0935	0.4339	0.021*
C13	0.2550 (3)	−0.04651 (7)	0.5389 (3)	0.0174 (5)
C11	0.1743 (3)	0.02584 (8)	0.3928 (3)	0.0179 (4)
H11	0.0777	0.0444	0.3259	0.021*
C34	0.2379 (4)	0.59098 (8)	1.0528 (4)	0.0260 (5)
H34A	0.3797	0.5867	1.1087	0.039*
H34B	0.1724	0.6160	1.1095	0.039*
H34C	0.2434	0.5972	0.9257	0.039*
C12	0.1129 (3)	−0.01720 (7)	0.4367 (3)	0.0180 (5)
H12	−0.0237	−0.0272	0.3987	0.022*
C14	0.4592 (3)	−0.02979 (8)	0.5949 (3)	0.0189 (4)
H14	0.5556	−0.0480	0.6641	0.023*
C31	0.3797 (3)	0.50556 (8)	0.9388 (3)	0.0183 (4)
H31	0.4552	0.5317	0.9162	0.022*
C15	0.5175 (3)	0.01333 (7)	0.5481 (3)	0.0182 (5)
H15	0.6541	0.0234	0.5857	0.022*
C17	0.3609 (4)	−0.12290 (8)	0.6381 (3)	0.0230 (5)
H17A	0.4533	−0.1263	0.5425	0.035*
H17B	0.2955	−0.1515	0.6607	0.035*
H17C	0.4421	−0.1128	0.7466	0.035*
C16	−0.0076 (4)	−0.10756 (8)	0.5120 (4)	0.0268 (5)
H16A	−0.1188	−0.0874	0.5420	0.040*
H16B	−0.0294	−0.1368	0.5637	0.040*
H16C	−0.0101	−0.1102	0.3823	0.040*
C33	−0.0982 (4)	0.55599 (8)	1.1320 (4)	0.0258 (5)
H33A	−0.2015	0.5508	1.0308	0.039*
H33B	−0.1138	0.5862	1.1766	0.039*
H33C	−0.1200	0.5347	1.2269	0.039*
N2	0.1144 (3)	0.55029 (7)	1.0744 (3)	0.0235 (4)
N1	0.1970 (3)	−0.08973 (6)	0.5844 (3)	0.0206 (4)

Atomic displacement parameters (Å^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}

O2	0.0188 (8)	0.0162 (8)	0.0260 (9)	0.0006 (6)	−0.0025 (6)	−0.0001 (7)
O1	0.0165 (7)	0.0225 (8)	0.0289 (9)	−0.0018 (6)	−0.0013 (6)	0.0043 (7)
O4	0.0201 (8)	0.0171 (8)	0.0248 (9)	−0.0012 (6)	−0.0036 (7)	0.0010 (7)
O3	0.0156 (7)	0.0207 (8)	0.0282 (9)	0.0017 (6)	−0.0018 (6)	−0.0032 (7)
C22	0.0146 (10)	0.0223 (12)	0.0160 (11)	0.0010 (9)	−0.0016 (8)	0.0000 (9)
C18	0.0157 (10)	0.0183 (11)	0.0136 (11)	0.0007 (9)	0.0011 (8)	0.0000 (9)
C4	0.0175 (10)	0.0184 (11)	0.0143 (10)	0.0009 (9)	0.0029 (8)	0.0013 (9)
C5	0.0153 (10)	0.0192 (11)	0.0180 (11)	−0.0032 (8)	−0.0005 (8)	0.0018 (9)
C21	0.0195 (10)	0.0166 (11)	0.0139 (11)	−0.0027 (8)	0.0035 (8)	−0.0004 (9)
C30	0.0179 (10)	0.0152 (11)	0.0156 (10)	0.0017 (8)	−0.0033 (8)	−0.0015 (9)
C7	0.0189 (10)	0.0219 (12)	0.0126 (11)	−0.0020 (9)	0.0015 (8)	−0.0025 (9)
C27	0.0165 (10)	0.0171 (11)	0.0141 (10)	−0.0011 (8)	−0.0018 (8)	−0.0001 (9)
C24	0.0173 (10)	0.0174 (11)	0.0132 (11)	0.0001 (9)	−0.0003 (8)	0.0006 (9)
C20	0.0206 (10)	0.0163 (11)	0.0174 (11)	0.0048 (9)	0.0004 (8)	0.0002 (9)
C1	0.0186 (10)	0.0170 (11)	0.0132 (11)	−0.0002 (8)	0.0020 (8)	0.0014 (9)
C26	0.0167 (9)	0.0192 (11)	0.0136 (11)	0.0028 (9)	−0.0008 (8)	0.0011 (9)
C6	0.0198 (10)	0.0167 (11)	0.0168 (11)	−0.0040 (9)	0.0003 (8)	0.0007 (9)
C8	0.0167 (10)	0.0169 (11)	0.0199 (12)	−0.0015 (8)	0.0000 (9)	−0.0020 (9)
C3	0.0199 (10)	0.0155 (11)	0.0183 (11)	−0.0046 (8)	0.0020 (8)	−0.0015 (9)
C25	0.0155 (10)	0.0176 (12)	0.0158 (10)	0.0013 (8)	−0.0003 (8)	0.0006 (9)
C23	0.0179 (10)	0.0143 (10)	0.0170 (10)	0.0029 (8)	0.0023 (8)	0.0002 (9)
C29	0.0151 (9)	0.0227 (11)	0.0170 (10)	0.0006 (9)	0.0005 (8)	0.0004 (9)
C10	0.0179 (10)	0.0163 (11)	0.0153 (11)	−0.0007 (8)	0.0010 (8)	−0.0028 (8)
C32	0.0168 (9)	0.0208 (11)	0.0174 (11)	−0.0008 (9)	0.0019 (8)	−0.0010 (9)
C19	0.0149 (10)	0.0209 (12)	0.0165 (11)	0.0024 (8)	−0.0005 (8)	0.0007 (9)
C28	0.0170 (10)	0.0149 (10)	0.0172 (11)	−0.0033 (8)	0.0004 (8)	−0.0001 (9)
C2	0.0157 (10)	0.0226 (12)	0.0149 (11)	−0.0020 (8)	−0.0006 (8)	0.0010 (9)
C9	0.0153 (9)	0.0198 (11)	0.0175 (11)	−0.0021 (8)	0.0007 (8)	−0.0043 (9)
C13	0.0198 (10)	0.0176 (11)	0.0151 (11)	−0.0005 (8)	0.0031 (8)	−0.0015 (8)
C11	0.0166 (10)	0.0190 (11)	0.0178 (11)	0.0034 (9)	−0.0001 (8)	0.0004 (9)
C34	0.0308 (12)	0.0149 (11)	0.0330 (14)	0.0005 (10)	0.0069 (10)	−0.0025 (10)
C12	0.0144 (10)	0.0196 (11)	0.0196 (11)	−0.0009 (8)	−0.0007 (8)	−0.0019 (9)
C14	0.0201 (10)	0.0198 (11)	0.0164 (11)	0.0039 (9)	−0.0015 (8)	0.0012 (9)
C31	0.0189 (10)	0.0172 (11)	0.0186 (11)	−0.0027 (9)	−0.0005 (8)	0.0000 (9)
C15	0.0169 (10)	0.0199 (11)	0.0174 (11)	−0.0010 (8)	−0.0006 (8)	−0.0025 (9)
C17	0.0265 (11)	0.0183 (11)	0.0237 (12)	0.0008 (9)	−0.0007 (10)	0.0043 (9)
C16	0.0235 (11)	0.0207 (12)	0.0352 (14)	−0.0044 (9)	−0.0025 (10)	0.0053 (10)
C33	0.0250 (12)	0.0219 (12)	0.0310 (13)	0.0032 (10)	0.0053 (10)	−0.0032 (10)
N2	0.0196 (9)	0.0182 (10)	0.0333 (11)	−0.0004 (8)	0.0048 (8)	−0.0041 (8)
N1	0.0178 (9)	0.0173 (9)	0.0262 (10)	−0.0007 (8)	−0.0011 (8)	0.0037 (8)

Geometric parameters (Å, °)

O2—C4	1.363 (3)	C23—H23	0.9300
O2—H2O	0.8200	C29—C28	1.376 (3)
O1—C7	1.239 (3)	C29—H29	0.9300
O4—C21	1.359 (3)	C10—C15	1.398 (3)
O4—H4O	0.8200	C10—C11	1.406 (3)
O3—C24	1.239 (3)	C10—C9	1.456 (3)

C22—C23	1.373 (3)	C32—C31	1.375 (3)
C22—C21	1.395 (3)	C32—H32	0.9300
C22—H22	0.9300	C19—H19	0.9300
C18—C23	1.401 (3)	C28—H28	0.9300
C18—C19	1.402 (3)	C2—H2	0.9300
C18—C24	1.481 (3)	C9—H9	0.9300
C4—C5	1.389 (3)	C13—N1	1.378 (3)
C4—C3	1.395 (3)	C13—C14	1.407 (3)
C5—C6	1.385 (3)	C13—C12	1.415 (3)
C5—H5	0.9300	C11—C12	1.376 (3)
C21—C20	1.400 (3)	C11—H11	0.9300
C30—N2	1.370 (3)	C34—N2	1.448 (3)
C30—C31	1.411 (3)	C34—H34A	0.9600
C30—C29	1.413 (3)	C34—H34B	0.9600
C7—C8	1.469 (3)	C34—H34C	0.9600
C7—C1	1.478 (3)	C12—H12	0.9300
C27—C32	1.399 (3)	C14—C15	1.378 (3)
C27—C28	1.410 (3)	C14—H14	0.9300
C27—C26	1.451 (3)	C31—H31	0.9300
C24—C25	1.464 (3)	C15—H15	0.9300
C20—C19	1.379 (3)	C17—N1	1.454 (3)
C20—H20	0.9300	C17—H17A	0.9600
C1—C2	1.401 (3)	C17—H17B	0.9600
C1—C6	1.402 (3)	C17—H17C	0.9600
C26—C25	1.344 (3)	C16—N1	1.452 (3)
C26—H26	0.9300	C16—H16A	0.9600
C6—H6	0.9300	C16—H16B	0.9600
C8—C9	1.344 (3)	C16—H16C	0.9600
C8—H8	0.9300	C33—N2	1.452 (3)
C3—C2	1.379 (3)	C33—H33A	0.9600
C3—H3	0.9300	C33—H33B	0.9600
C25—H25	0.9300	C33—H33C	0.9600
C4—O2—H2O	109.5	C27—C32—H32	119.0
C21—O4—H4O	109.5	C20—C19—C18	121.1 (2)
C23—C22—C21	119.95 (19)	C20—C19—H19	119.4
C23—C22—H22	120.0	C18—C19—H19	119.4
C21—C22—H22	120.0	C29—C28—C27	121.9 (2)
C23—C18—C19	118.2 (2)	C29—C28—H28	119.1
C23—C18—C24	122.4 (2)	C27—C28—H28	119.1
C19—C18—C24	119.43 (19)	C3—C2—C1	121.03 (19)
O2—C4—C5	122.33 (18)	C3—C2—H2	119.5
O2—C4—C3	117.3 (2)	C1—C2—H2	119.5
C5—C4—C3	120.3 (2)	C8—C9—C10	127.8 (2)
C6—C5—C4	119.37 (19)	C8—C9—H9	116.1
C6—C5—H5	120.3	C10—C9—H9	116.1
C4—C5—H5	120.3	N1—C13—C14	120.6 (2)
O4—C21—C22	122.38 (19)	N1—C13—C12	121.82 (19)
O4—C21—C20	117.75 (19)	C14—C13—C12	117.56 (19)
C22—C21—C20	119.9 (2)	C12—C11—C10	121.8 (2)

N2—C30—C31	120.7 (2)	C12—C11—H11	119.1
N2—C30—C29	122.25 (19)	C10—C11—H11	119.1
C31—C30—C29	116.99 (19)	N2—C34—H34A	109.5
O1—C7—C8	121.3 (2)	N2—C34—H34B	109.5
O1—C7—C1	119.2 (2)	H34A—C34—H34B	109.5
C8—C7—C1	119.46 (18)	N2—C34—H34C	109.5
C32—C27—C28	116.7 (2)	H34A—C34—H34C	109.5
C32—C27—C26	120.11 (18)	H34B—C34—H34C	109.5
C28—C27—C26	123.17 (19)	C11—C12—C13	120.82 (19)
O3—C24—C25	121.8 (2)	C11—C12—H12	119.6
O3—C24—C18	119.52 (19)	C13—C12—H12	119.6
C25—C24—C18	118.70 (18)	C15—C14—C13	120.5 (2)
C19—C20—C21	119.6 (2)	C15—C14—H14	119.7
C19—C20—H20	120.2	C13—C14—H14	119.7
C21—C20—H20	120.2	C32—C31—C30	121.2 (2)
C2—C1—C6	118.1 (2)	C32—C31—H31	119.4
C2—C1—C7	118.76 (19)	C30—C31—H31	119.4
C6—C1—C7	123.1 (2)	C14—C15—C10	122.4 (2)
C25—C26—C27	126.26 (19)	C14—C15—H15	118.8
C25—C26—H26	116.9	C10—C15—H15	118.8
C27—C26—H26	116.9	N1—C17—H17A	109.5
C5—C6—C1	121.3 (2)	N1—C17—H17B	109.5
C5—C6—H6	119.3	H17A—C17—H17B	109.5
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C9—C8—C7	120.84 (19)	H17A—C17—H17C	109.5
C9—C8—H8	119.6	H17B—C17—H17C	109.5
C7—C8—H8	119.6	N1—C16—H16A	109.5
C2—C3—C4	119.8 (2)	N1—C16—H16B	109.5
C2—C3—H3	120.1	H16A—C16—H16B	109.5
C4—C3—H3	120.1	N1—C16—H16C	109.5
C26—C25—C24	123.03 (19)	H16A—C16—H16C	109.5
C26—C25—H25	118.5	H16B—C16—H16C	109.5
C24—C25—H25	118.5	N2—C33—H33A	109.5
C22—C23—C18	121.2 (2)	N2—C33—H33B	109.5
C22—C23—H23	119.4	H33A—C33—H33B	109.5
C18—C23—H23	119.4	N2—C33—H33C	109.5
C28—C29—C30	121.08 (19)	H33A—C33—H33C	109.5
C28—C29—H29	119.5	H33B—C33—H33C	109.5
C30—C29—H29	119.5	C30—N2—C34	120.61 (18)
C15—C10—C11	116.80 (19)	C30—N2—C33	121.81 (19)
C15—C10—C9	119.14 (19)	C34—N2—C33	117.11 (19)
C11—C10—C9	124.1 (2)	C13—N1—C16	119.52 (19)
C31—C32—C27	122.06 (19)	C13—N1—C17	119.53 (18)
C31—C32—H32	119.0	C16—N1—C17	116.36 (19)
O2—C4—C5—C6	179.2 (2)	C21—C20—C19—C18	1.9 (3)
C3—C4—C5—C6	−0.2 (3)	C23—C18—C19—C20	−0.1 (3)
C23—C22—C21—O4	−179.3 (2)	C24—C18—C19—C20	−179.62 (19)
C23—C22—C21—C20	0.4 (3)	C30—C29—C28—C27	−0.1 (3)
C23—C18—C24—O3	−160.0 (2)	C32—C27—C28—C29	0.2 (3)

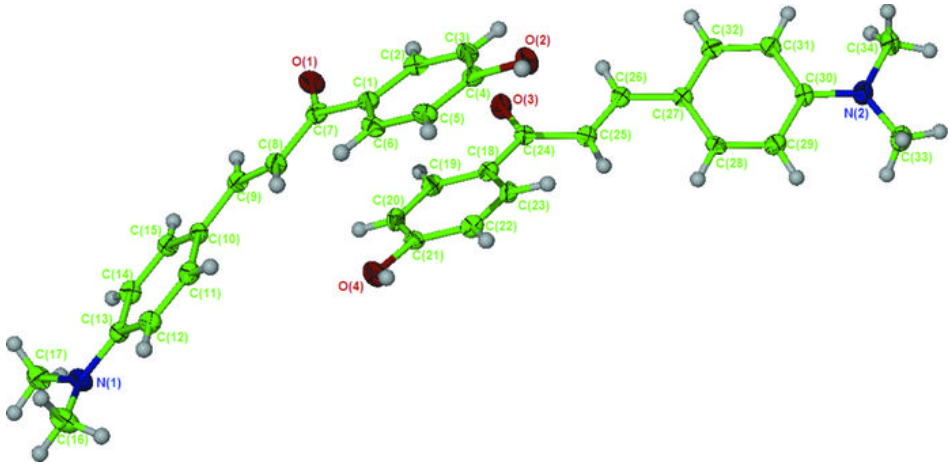
C19—C18—C24—O3	19.5 (3)	C26—C27—C28—C29	179.8 (2)
C23—C18—C24—C25	21.0 (3)	C4—C3—C2—C1	−1.3 (3)
C19—C18—C24—C25	−159.5 (2)	C6—C1—C2—C3	−0.1 (3)
O4—C21—C20—C19	177.69 (19)	C7—C1—C2—C3	−178.3 (2)
C22—C21—C20—C19	−2.1 (3)	C7—C8—C9—C10	174.2 (2)
O1—C7—C1—C2	−14.6 (3)	C15—C10—C9—C8	−174.3 (2)
C8—C7—C1—C2	162.1 (2)	C11—C10—C9—C8	6.1 (4)
O1—C7—C1—C6	167.3 (2)	C15—C10—C11—C12	−0.6 (3)
C8—C7—C1—C6	−16.0 (3)	C9—C10—C11—C12	179.0 (2)
C32—C27—C26—C25	−165.5 (2)	C10—C11—C12—C13	0.2 (3)
C28—C27—C26—C25	14.9 (4)	N1—C13—C12—C11	180.0 (2)
C4—C5—C6—C1	−1.3 (3)	C14—C13—C12—C11	0.7 (3)
C2—C1—C6—C5	1.4 (3)	N1—C13—C14—C15	179.5 (2)
C7—C1—C6—C5	179.5 (2)	C12—C13—C14—C15	−1.1 (3)
O1—C7—C8—C9	8.5 (3)	C27—C32—C31—C30	1.2 (3)
C1—C7—C8—C9	−168.1 (2)	N2—C30—C31—C32	177.3 (2)
O2—C4—C3—C2	−178.01 (19)	C29—C30—C31—C32	−1.0 (3)
C5—C4—C3—C2	1.4 (3)	C13—C14—C15—C10	0.8 (3)
C27—C26—C25—C24	−175.8 (2)	C11—C10—C15—C14	0.1 (3)
O3—C24—C25—C26	16.2 (4)	C9—C10—C15—C14	−179.5 (2)
C18—C24—C25—C26	−164.8 (2)	C31—C30—N2—C34	−2.0 (3)
C21—C22—C23—C18	1.4 (3)	C29—C30—N2—C34	176.3 (2)
C19—C18—C23—C22	−1.6 (3)	C31—C30—N2—C33	169.9 (2)
C24—C18—C23—C22	177.9 (2)	C29—C30—N2—C33	−11.8 (3)
N2—C30—C29—C28	−177.9 (2)	C14—C13—N1—C16	−174.7 (2)
C31—C30—C29—C28	0.5 (3)	C12—C13—N1—C16	6.0 (3)
C28—C27—C32—C31	−0.8 (3)	C14—C13—N1—C17	−19.6 (3)
C26—C27—C32—C31	179.6 (2)	C12—C13—N1—C17	161.1 (2)

Hydrogen-bond geometry (Å, °)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
O4—H4O···O1^{i}	0.82	1.85	2.670 (2)	173
O2—H2O···O3^{ii}	0.82	1.85	2.659 (2)	169

Symmetry codes: (i) *x*−1, *y*, *z*; (ii) *x*−1, *y*, *z*−1.

Fig. 1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O(3)
O(4)
N(1)
N(2)
C(1)
C(2)
C(3)
C(4)
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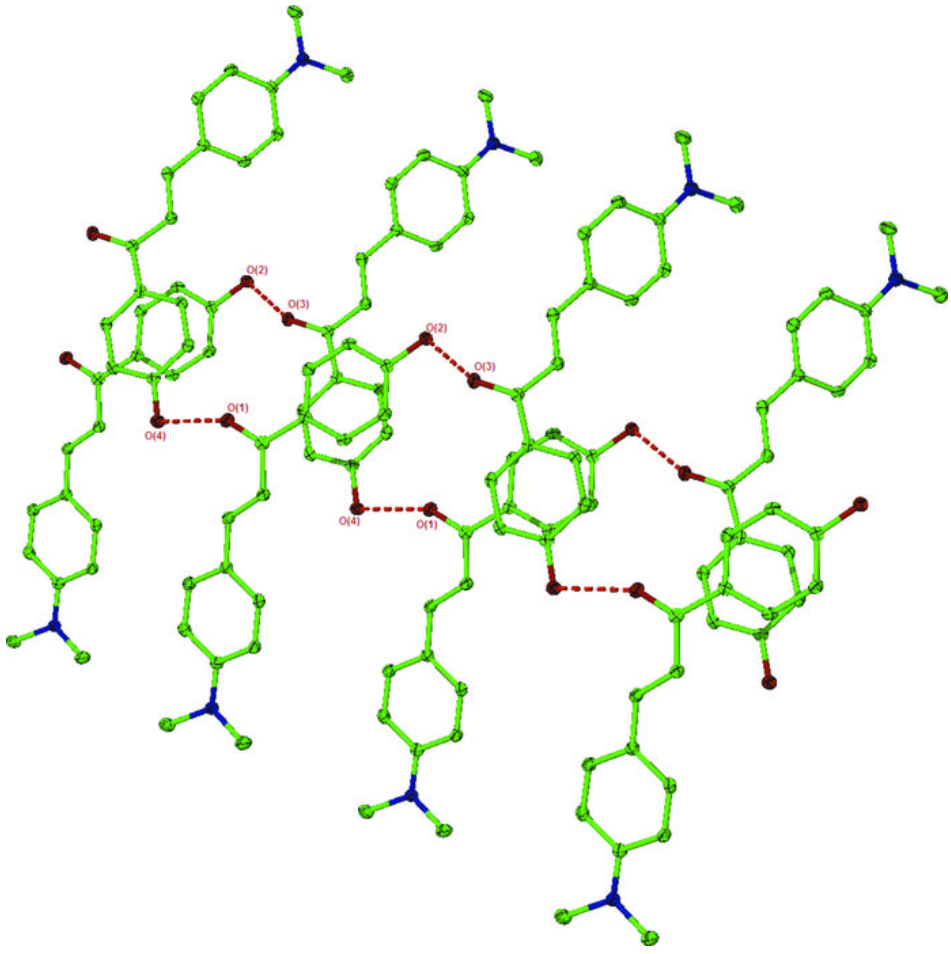
C(34)

Fig. 2



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Neoirietriol

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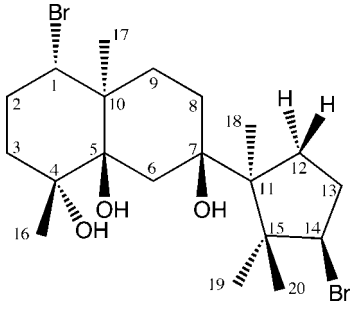
Key indicators: single-crystal X-ray study; T = 296 K; mean σ(C–C) = 0.007 Å; R factor = 0.062; wR factor = 0.151; data-to-parameter ratio = 27.0.

The title compound {systematic name: (1*R*,4*S*,4a*S*,7*R*,8a*R*)-4-bromo-7-[(1*S*,3*R*)-3-bromo-1,2,2-trimethylcyclopentyl]-1,4a-dimethyldecahydronaphthalene-1,7,8a-triol}, $C_{20}H_{34}Br_2O_3$, is a neoirieane-type bromoditerpenoid isolated from *Laurencia yonaguniensis* Masuda et Abe, species inedita. The absolute stereochemistry was established as (1*S*,4*R*,5*R*,7*R*,10*S*,11*S*,14*R*). The structure displays inter- and intramolecular O—H···O hydrogen bonding.

Related literature

For background to neoirieane-type structures, see: Suzuki *et al.* (2002); Takahashi *et al.* (2002). For the related absolute configuration, see: Takahashi *et al.* (2007).



Experimental

Crystal data

$C_{20}H_{34}Br_2O_3$
M_r = 482.29
Monoclinic, $P2_1$
a = 7.5026 (2) Å
b = 11.3985 (3) Å
c = 12.1498 (5) Å
β = 94.9780 (3)°
V = 1035.11 (6) Å^3
Z = 2
Mo $K\alpha$ radiation
μ = 3.94 mm^{-1}
T = 296 K
0.30 × 0.20 × 0.20 mm

Data collection

Nonius KappaCCD diffractometer
Absorption correction: multi-scan (*DENZO-SMN*; Otwinowski & Minor, 1997)
T_{min} = 0.402, T_{max} = 0.454
43586 measured reflections
6129 independent reflections
4774 reflections with $F^2 > 2\sigma(F^2)$
R_{int} = 0.110

Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.062
$wR(F^2)$ = 0.151
S = 1.14
6129 reflections
227 parameters
All H-atom parameters refined
$\Delta\rho_{max}$ = 0.66 e Å^{-3}
$\Delta\rho_{min}$ = −0.44 e Å^{-3}
Absolute structure: Flack (1983)
Flack parameter: −0.014 (12)

Table 1
Hydrogen-bond geometry (Å, °).

D—H···A	D—H	H···A	D···A	D—H···A
O1—H32···O3^{i}	0.82	2.02	2.797 (4)	158
O3—H34···O2	0.82	1.96	2.691 (4)	148

Symmetry code: (i) $x+1, y, z$.

Data collection: *KappaCCD Server Software* (Nonius, 1998); cell refinement: *DENZO-SMN* (Otwinowski & Minor, 1997); data reduction: *CrystalStructure* (Rigaku, 2007); program(s) used to solve structure: *SIR97* (Altomare *et al.*, 1999); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *ORTEP-3* (Farrugia, 1997); software used to prepare material for publication: *publCIF* (Westrip, 2010).

Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: FJ2316).

References

Altomare, A., Burla, M. C., Camalli, M., Cascarano, G. L., Giacovazzo, C., Guagliardi, A., Moliterni, A. G. G., Polidori, G. & Spagna, R. (1999). *J. Appl. Cryst.* **32**, 115–119.
Farrugia, L. J. (1997). *J. Appl. Cryst.* **30**, 565.
Flack, H. D. (1983). *Acta Cryst.* A**39**, 876–881.
Nonius (1998). *KappaCCD Server Software*. Windows 3.11 Version. Nonius BV, Delft, The Netherlands.
Otwinowski, Z. & Minor, W. (1997). *Methods in Enzymology*, Vol. 276, *Macromolecular Crystallography*, Part A, edited by C. W. Carter Jr & R. M. Sweet, pp. 307–326. New York: Academic Press.
Rigaku (2007). *CrystalStructure*. Rigaku Americas, The Woodlands, Texas, USA, and Rigaku Corporation, Tokyo, Japan.
Sheldrick, G. M. (2008). *Acta Cryst.* A**64**, 112–122.
Suzuki, M., Nakano, S., Takahashi, Y., Abe, T., Masuda, M., Takahashi, H. & Kobayashi, K. (2002). *J. Nat. Prod.* **65**, 801–804.
Takahashi, Y., Daitoh, M., Suzuki, M., Abe, T. & Masuda, M. (2002). *J. Nat. Prod.* **65**, 395–398.
Takahashi, H., Takahashi, Y., Suzuki, M., Abe, T. & Masuda, M. (2007). *Anal. Sci.* **23**, x103–x1044.
Westrip, S. P. (2010). *J. Appl. Cryst.* **43**. Submitted.

supplementary materials

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Neoirietriol

H. Takahashi, Y. Takahashi, M. Suzuki, T. Abe and M. Masuda

Comment

As part of our continuing chemotaxonomical studies on Japanese species of the red algal genus *Laurencia* (Rhodomelaceae, Ceramiales), we reported previously the structure of neoirietetraol (Takahashi *et al.*, 2002, Takahashi *et al.*, 2007), including the relative configuration and X-ray crystal structure, isolated from *Laurencia yonaguniensis* Masuda et Abe, species inedita (Masuda, *M.*; unpublished results), which was collected at Yonaguni Island, Okinawa, Japan. Further investigation of the related metabolites from this alga has led to the isolation of a new bromoditerpene, named neoirietriol, having a molecular formula of $C_{20}H_{34}Br_2O_3$, which was established by FD-LRMS (m/*z* 466, 464, 462 (1:2:1); M–H_2O) and FAB-HRMS (m/*z* 479.0813; calcd for $C_{20}H_{33}{}^{79}Br_2O_3$, 479.0796; M–H).

During the course of refinement of the structure, the Flack parameter converged to a value of -0.014 (12) within the derived limits as required for the correct enantiomorph of the structure. The absolute configuration of the title compound was established as (1*S*, 4*R*, 5*R*, 7*S*, 10*R*, 11*S*, 14*R*) (Fig. 1).

In the crystal, an intramolecular hydrogen bond was observed between O3···O2[distance 2.691 (4) Å] and an intermolecular hydrogen bond between O1···O3 (*x* + 1, *y*, *z*; distance 2.797 (4) Å) forming an infinite chain structure along the *a* axis (Fig. 2).

Experimental

Isolation

The partially dried alga (40 g) was soaked in MeOH for 3 days. The MeOH solution was concentrated in *vacuo* and partitioned between Et_2O and H_2O. The Et_2O solution was washed with water, dried over anhydrous Na_2SO_4, and evaporated to leave a dark-green oil (523 mg). The extract was fractionated by column chromatography on Si gel with a step gradient (hexane and ethyl acetate). The fraction (144 mg) eluted with hexane-EtOAc (3:1) was further subjected to preparative TLC with toluene-EtOAc (4:1) gave neoiretriol (40.8 mg, 7.8% based on the weight of MeOH extract).

Neoirietriol: mp 132–133 ^{o}C (from CH_2Cl_2/hexane (2:1)); $[a]_D{}^{28}$ -61^{-} (c 0.53; $CHCl_3$); ^{1}H NMR (400 MHz; C_6D_6), d 0.28 (1*H*, br s, OH: D_2O exchangeable), 0.50 (3*H*, s, H_3-18), 0.54 (1*H*, m, Ha-8), 0.60 (1*H*, ddd, *J* = 13.2, 10.3, 5.4 Hz, Ha-12), 0.75 (1*H*, d, *J* = 2.4 Hz, OH: D_2O exchangeable), 0.93 (1*H*, ddd, *J* = 13.7, 4.9, 2.4 Hz, Ha-3), 0.97 (3*H*, s, H_3-20), 1.20 (3*H*, s, H_3-19), 1.38 (3*H*, s, H_3-17), 1.21 (1*H*, ddd, *J* = 13.2, 13.2, 4.4 Hz, Hb-12), 1.56 (1*H*, m, Ha-9), 1.67 (1*H*, ddd, *J* = 13.2, 13.2, 3.9 Hz, Hb-8), 1.76 (1*H*, dd, *J* = 14.2, 2.4 Hz, Ha-6), 1.83 (1*H*, m, Hb-9), 1.86 (1*H*, m, Ha-13), 1.95 (1*H*, ddd, ddd, *J* = 13.7, 9.3, 4.9 Hz, Hb-13), 2.03 (1*H*, m, Ha-2), 2.13 (1*H*, ddd, *J* = 13.7, 13.7, 4.9 Hz, Hb-3), 2.07 (1*H*, dd, *J* = 14.2, 2.4 Hz, Hb-6), 2.48 (1*H*, dddd, *J* = 13.8, 13.2, 12.7, 4.4 Hz, Hb-2), 4.01 (1*H*, dd, *J* = 10.3, 8.8 Hz, H14), 4.88 (1*H*, dd, *J* = 12.7, 4.4 Hz, H-1), 5.20 (1*H*, s, OH: D_2O exchangeable); ^{13}C NMR (100 MHz, DEPT; C_6D_6) d 18.8 (C, C17), 23.4 (CH_3, C18), 23.5 (CH_3, C19), 23.7 (CH_3, C20), 26.7 (CH_3, C16), 30.3 (CH_2 *x* 2, C8 and C12), 31.4 (CH_2, C2), 32.2 (C,

C9), 31.6 (CH_2, C13), 31.7 (CH_2, C6), 32.2 (CH_2, C2), 38.3 (CH_2, C3), 43.7 (C, C10), 48.5 (C, C15), 51.8 (C, C11), 65.2 (CH, C14), 65.7 (CH, C1), 75.3 (C, C4), 78.5 (C, C5), 81.7 (C, C7).

Refinement

Refinement was performed using all reflections. The weighted *R*-factor (*wR*) and goodness of fit (*S*) are based on F^2. *R*-factor (gt) are based on *F*. The threshold expression of $F^2 > 2.0\ \sigma(F^2)$ is used only for calculating *R*-factor (gt). Non-H atoms were refined anisotropically. H atoms were treated as riding models.

Figures

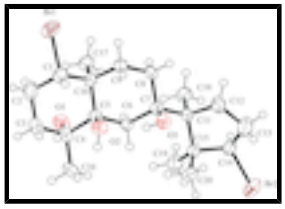


Fig. 1. The structure of the title compound with ellipsoids at the 50% probability level and the atom numbering scheme.

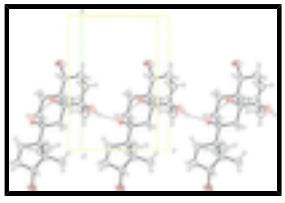


Fig. 2. The packing diagram of the title compound. Inter and intramolecular hydrogen bonds are shown as dashed line.

(1*R*,4*S*,4a*S*,7*R*,8a*R*)-4-bromo-7- [(1*S*,3*R*)-3-bromo-1,2,2-trimethylcyclopentyl]-1,4a- dimethyldecahydronaphthalene-1,7,8a-triol

Crystal data

$C_{20}H_{34}Br_2O_3$	$F(000) = 496.00$
$M_r = 482.29$	$D_x = 1.547$ Mg m^{-3}
Monoclinic, $P2_1$	Mo $K\alpha$ radiation, $\lambda = 0.71069$ Å
Hall symbol: P 2yb	Cell parameters from 1225 reflections
$a = 7.5026\ (2)$ Å	$\theta = 1.8–28.1°$
$b = 11.3985\ (3)$ Å	$\mu = 3.94$ mm^{-1}
$c = 12.1498\ (5)$ Å	$T = 296$ K
$\beta = 94.9780\ (3)°$	Prism, colorless
$V = 1035.11\ (6)$ Å^3	0.30 × 0.20 × 0.20 mm
$Z = 2$	

Data collection

Nonius KappaCCD diffractometer	6129 independent reflections
Radiation source: Mo Kα	4774 reflections with $F^2 > 2\sigma(F^2)$
horizonally mounted graphite crystal	$R_{int} = 0.110$

Detector resolution: 9 pixels mm^{-1}
ω scans
Absorption correction: multi-scan (*DENZO-SMN*; Otwinowski & Minor, 1997)
T_{min} = 0.402, T_{max} = 0.454
43586 measured reflections

θ_{max} = 30.5°
h = −10→10
k = −16→16
l = −17→17

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)]$ = 0.062
$wR(F^2)$ = 0.151
S = 1.14
6129 reflections
227 parameters
All H-atom parameters refined

$w = 1/[\sigma^2(F_o^2) + (0.0612P)^2 + 1.0272P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max}$ = 0.66 e $Å^{-3}$
$\Delta\rho_{min}$ = −0.44 e $Å^{-3}$
Absolute structure: Flack (1983)
Flack parameter: −0.014 (12)

Special details

Refinement. Refinement was performed using all reflections. The weighted *R*-factor (*wR*) and goodness of fit (*S*) are based on F^2. *R*-factor (gt) are based on *F*. The threshold expression of $F^2 > 2.0\ \sigma\ (F^2)$ is used only for calculating *R*-factor (gt).

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters ($Å^2$)

	x	*y*	*z*	U_{iso}*/U_{eq}
Br1	0.82169 (9)	0.64485 (5)	0.41310 (5)	0.05902 (18)
Br2	0.45713 (9)	−0.27536 (5)	0.13400 (6)	0.05993 (18)
O1	1.1510 (4)	0.3045 (3)	0.2533 (3)	0.0471 (8)
O2	0.7088 (4)	0.3800 (3)	0.1271 (2)	0.0381 (7)
O3	0.4700 (3)	0.2183 (3)	0.1812 (2)	0.0357 (6)
C1	0.8500 (7)	0.5365 (4)	0.2880 (4)	0.0421 (10)
C2	1.0332 (8)	0.5566 (5)	0.2479 (5)	0.0552 (14)
C3	1.0585 (8)	0.4788 (5)	0.1477 (5)	0.0522 (13)
C4	1.0244 (6)	0.3474 (4)	0.1691 (4)	0.0378 (9)
C5	0.8363 (5)	0.3340 (3)	0.2131 (3)	0.0299 (8)
C6	0.7899 (5)	0.2032 (3)	0.2322 (3)	0.0286 (8)
C7	0.6015 (5)	0.1830 (3)	0.2705 (3)	0.0298 (8)
C8	0.5726 (6)	0.2635 (4)	0.3683 (4)	0.0381 (10)
C9	0.6148 (6)	0.3931 (4)	0.3459 (4)	0.0355 (9)
C10	0.8119 (6)	0.4086 (3)	0.3189 (3)	0.0316 (8)
C11	0.5662 (6)	0.0505 (3)	0.2964 (3)	0.0310 (8)
C12	0.3623 (7)	0.0296 (4)	0.3094 (5)	0.0463 (11)
C13	0.3165 (9)	−0.0954 (5)	0.2707 (7)	0.0631 (17)
C14	0.4932 (7)	−0.1454 (4)	0.2415 (4)	0.0395 (10)
C15	0.6091 (6)	−0.0428 (4)	0.2044 (4)	0.0338 (9)
C16	1.0421 (8)	0.2773 (6)	0.0629 (4)	0.0538 (14)

C17	0.9349 (6)	0.3707 (4)	0.4209 (4)	0.0404 (10)
C18	0.6753 (8)	0.0176 (4)	0.4068 (4)	0.0445 (11)
C19	0.8045 (7)	−0.0813 (4)	0.2069 (5)	0.0460 (11)
C20	0.5443 (7)	−0.0058 (4)	0.0862 (4)	0.0419 (11)
H1	0.7610	0.5588	0.2279	0.051*
H2	1.1248	0.5387	0.3068	0.066*
H3	1.0455	0.6384	0.2278	0.066*
H4	1.1797	0.4883	0.1271	0.063*
H5	0.9775	0.5048	0.0860	0.063*
H6	0.7994	0.1604	0.1639	0.034*
H7	0.8777	0.1708	0.2872	0.034*
H8	0.6481	0.2370	0.4324	0.046*
H9	0.4491	0.2571	0.3856	0.046*
H10	0.5939	0.4397	0.4103	0.043*
H11	0.5354	0.4213	0.2843	0.043*
H12	0.3382	0.0392	0.3860	0.056*
H13	0.2903	0.0857	0.2651	0.056*
H14	0.2689	−0.1406	0.3291	0.076*
H15	0.2296	−0.0948	0.2068	0.076*
H16	0.5541	−0.1780	0.3094	0.047*
H17	1.1539	0.2958	0.0341	0.065*
H18	0.9453	0.2971	0.0092	0.065*
H19	1.0381	0.1949	0.0789	0.065*
H20	1.0525	0.4023	0.4159	0.048*
H21	0.9414	0.2866	0.4236	0.048*
H22	0.8874	0.3994	0.4866	0.048*
H23	0.7981	0.0396	0.4033	0.053*
H24	0.6679	−0.0655	0.4186	0.053*
H25	0.6272	0.0583	0.4668	0.053*
H26	0.8741	−0.0195	0.1783	0.055*
H27	0.8129	−0.1503	0.1623	0.055*
H28	0.8493	−0.0983	0.2816	0.055*
H29	0.4186	0.0112	0.0822	0.050*
H30	0.5654	−0.0684	0.0360	0.050*
H31	0.6084	0.0629	0.0664	0.050*
H32	1.2265	0.2650	0.2253	0.057*
H33	0.7350	0.3567	0.0667	0.046*
H34	0.5132	0.2691	0.1438	0.043*

Atomic displacement parameters (Å^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Br1	0.0831 (4)	0.0325 (2)	0.0605 (3)	−0.0029 (2)	0.0009 (2)	−0.0086 (2)
Br2	0.0686 (3)	0.0386 (2)	0.0705 (3)	−0.0076 (2)	−0.0061 (2)	−0.0147 (2)
O1	0.0255 (16)	0.063 (2)	0.053 (2)	0.0083 (15)	0.0065 (14)	0.0017 (18)
O2	0.0400 (17)	0.0439 (18)	0.0292 (14)	0.0058 (14)	−0.0033 (12)	0.0043 (13)
O3	0.0261 (13)	0.0377 (15)	0.0425 (15)	0.0037 (13)	−0.0013 (11)	0.0025 (15)
C1	0.050 (2)	0.032 (2)	0.044 (2)	0.000 (2)	0.000 (2)	0.0004 (19)

C2	0.058 (3)	0.036 (2)	0.073 (3)	−0.013 (2)	0.012 (2)	0.001 (2)
C3	0.050 (3)	0.052 (3)	0.056 (3)	−0.012 (2)	0.017 (2)	0.014 (2)
C4	0.032 (2)	0.041 (2)	0.041 (2)	−0.0017 (18)	0.0067 (18)	0.0063 (19)
C5	0.0233 (19)	0.034 (2)	0.032 (2)	0.0022 (16)	−0.0020 (15)	0.0026 (16)
C6	0.0237 (18)	0.029 (2)	0.0336 (19)	0.0022 (14)	0.0040 (14)	−0.0009 (15)
C7	0.027 (2)	0.0292 (17)	0.0326 (19)	0.0031 (16)	0.0006 (17)	−0.0006 (15)
C8	0.035 (2)	0.040 (2)	0.042 (2)	−0.0044 (18)	0.0175 (19)	−0.0039 (19)
C9	0.036 (2)	0.031 (2)	0.041 (2)	0.0022 (18)	0.0081 (19)	−0.0057 (18)
C10	0.031 (2)	0.0289 (19)	0.034 (2)	−0.0022 (16)	−0.0024 (16)	−0.0005 (16)
C11	0.033 (2)	0.031 (2)	0.0299 (19)	−0.0013 (17)	0.0071 (16)	−0.0020 (16)
C12	0.041 (2)	0.038 (2)	0.062 (3)	−0.001 (2)	0.017 (2)	−0.001 (2)
C13	0.047 (3)	0.048 (3)	0.097 (5)	−0.008 (2)	0.018 (3)	−0.014 (3)
C14	0.044 (2)	0.032 (2)	0.042 (2)	−0.0083 (19)	0.001 (2)	−0.0053 (18)
C15	0.030 (2)	0.030 (2)	0.041 (2)	−0.0017 (17)	0.0012 (18)	−0.0043 (17)
C16	0.047 (3)	0.072 (3)	0.046 (2)	−0.004 (2)	0.023 (2)	−0.005 (2)
C17	0.042 (2)	0.043 (2)	0.035 (2)	−0.002 (2)	−0.0061 (18)	−0.0006 (19)
C18	0.065 (3)	0.037 (2)	0.031 (2)	−0.008 (2)	0.000 (2)	0.0044 (19)
C19	0.044 (2)	0.036 (2)	0.058 (3)	0.006 (2)	0.009 (2)	−0.003 (2)
C20	0.052 (3)	0.037 (2)	0.036 (2)	0.001 (2)	0.000 (2)	−0.0084 (19)

Geometric parameters (Å, °)

Br1—C1	1.984 (5)	C2—H3	0.970
Br2—C14	1.978 (4)	C3—H4	0.970
O1—C4	1.421 (6)	C3—H5	0.970
O2—C5	1.452 (5)	C6—H6	0.970
O3—C7	1.458 (5)	C6—H7	0.970
C1—C2	1.515 (9)	C8—H8	0.970
C1—C10	1.539 (6)	C8—H9	0.970
C2—C3	1.531 (9)	C9—H10	0.970
C3—C4	1.545 (8)	C9—H11	0.970
C4—C5	1.559 (6)	C12—H12	0.970
C4—C16	1.533 (8)	C12—H13	0.970
C5—C6	1.553 (5)	C13—H14	0.970
C5—C10	1.565 (6)	C13—H15	0.970
C6—C7	1.543 (6)	C14—H16	0.980
C7—C8	1.532 (6)	C16—H17	0.960
C7—C11	1.570 (6)	C16—H18	0.960
C8—C9	1.541 (6)	C16—H19	0.960
C9—C10	1.552 (6)	C17—H20	0.960
C10—C17	1.541 (6)	C17—H21	0.960
C11—C12	1.569 (7)	C17—H22	0.960
C11—C15	1.597 (6)	C18—H23	0.960
C11—C18	1.556 (6)	C18—H24	0.960
C12—C13	1.530 (8)	C18—H25	0.960
C13—C14	1.513 (8)	C19—H26	0.960
C14—C15	1.547 (6)	C19—H27	0.960
C15—C19	1.528 (7)	C19—H28	0.960
C15—C20	1.534 (6)	C20—H29	0.960

O1—H32	0.820	C20—H30	0.960
C1—H1	0.980	C20—H31	0.960
C2—H2	0.970		
O1···O3^{i}	2.797 (4)	H15···H27^{iii}	3.189
O1···C8^{i}	3.378 (5)	H15···H28^{iii}	3.069
O1···C12^{i}	3.551 (6)	H15···H33^{iv}	3.401
O2···C20^{ii}	3.341 (5)	H16···Br1^{viii}	3.043
O3···O1^{iii}	2.797 (4)	H16···H1^{viii}	3.558
O3···C16^{iii}	3.468 (6)	H17···O3^{i}	2.977
C8···O1^{iii}	3.378 (5)	H17···C19^{xii}	3.285
C12···O1^{iii}	3.551 (6)	H17···C20^{xii}	3.599
C16···O3^{i}	3.468 (6)	H17···H26^{xii}	3.323
C20···O2^{iv}	3.341 (6)	H17···H27^{xii}	2.498
Br1···H9^{v}	3.551	H17···H30^{xii}	2.805
Br1···H12^{v}	3.058	H17···H33	3.276
Br1···H16^{vi}	3.043	H17···H34^{i}	2.917
Br1···H21^{vii}	3.015	H18)···Br2^{ii}	3.452
Br1···H24^{vi}	3.500	H18)···H3^{xi}	3.407
Br1···H28^{vi}	3.350	H18···H5^{xi}	3.591
Br2···H1^{viii}	3.101	H18···H15^{ii}	3.087
Br2···H3^{ix}	3.523	H18···H26^{xii}	3.454
Br2···H4^{ix}	3.401	H18···H27^{xii}	2.941
Br2···H18^{iv}	3.452	H18···H33	1.905
Br2···H31^{iv}	3.060	H19···O3^{i}	3.379
Br2···H33^{iv}	3.111	H19···H5^{xi}	2.946
Br2···H34^{iv}	3.439	H19···H13^{i}	3.083
O1···H9)^{i}	2.694	H19···H29^{i}	3.538
O1···H11^{i}	3.169	H19···H33	2.922
O1···H13^{i}	2.703	H20···C18^{vii}	3.126
O1···H34^{i}	3.153	H20···H9^{i}	3.453
O2···H29^{ii}	3.032	H20···H23^{vii}	2.847
O2···H30^{ii}	2.792	H20···H24^{vii}	2.802
O2···H33	0.820	H20···H25^{vii}	3.221
O2···H34	1.960	H21···Br1^{xiii}	3.015
O3···H17^{iii}	2.977	H22···C12^{v}	3.558
O3···H19^{iii}	3.379	H22···C13^{v}	3.438
O3···H30^{ii}	3.581	H22···H12^{v}	2.873
O3···H32^{iii}	2.020	H22···H14^{v}	2.656
O3···H33	2.976	H22···H23^{vii}	3.060
O3···H34	0.820	H22···H24^{vii}	3.458
C1···H33	3.432	H22···H28^{vii}	3.297

C3···H33	2.895	H23···C17^{xiii}	3.398
C4···H33	2.410	H23···H2^{xiii}	3.520
C5···H33	1.891	H23···H20^{xiii}	2.847
C5···H34	2.604	H23···H22^{xiii}	3.060
C6···H33	2.671	H24···Br1^{viii}	3.500
C6···H34	2.376	H24···C17^{xiii}	3.494
C7···H32^{iii}	2.970	H24···H9^{x}	3.299
C7···H33	3.389	H24···H10^{x}	2.982
C7···H34	1.896	H24···H20^{xiii}	2.802
C8···H32^{iii}	2.996	H24···H22^{xiii}	3.458
C8···H34	2.727	H25···C9^{x}	3.569
C9···H25^{v}	3.569	H25···H2^{xiii}	3.193
C9···H32^{iii}	3.468	H25···H10^{x}	2.690
C9···H34	2.878	H25···H20^{xiii}	3.221
C10···H33	3.125	H26···C13^{i}	3.518
C10···H34	3.354	H26···H5^{xi}	3.500
C11···H32^{iii}	3.582	H26···H13^{i}	3.424
C11···H34	3.111	H26···H15^{i}	2.794
C12···H10^{x}	3.544	H26···H17^{xi}	3.323
C12···H22^{x}	3.558	H26···H18^{xi}	3.454
C12···H32^{iii}	3.017	H27···C16^{xi}	3.142
C13···H22^{x}	3.438	H27···H1^{viii}	3.440
C13···H26^{iii}	3.518	H27···H3^{viii}	3.039
C13···H28^{iii}	3.519	H27···H15^{i}	3.189
C16···H5^{xi}	3.591	H27···H17^{xi}	2.498
C16···H27^{xii}	3.142	H27···H18^{xi}	2.941
C16···H33	2.480	H28···Br1^{viii}	3.350
C16···H34^{i}	3.587	H28···C13^{i}	3.519
C17···H14^{v}	3.520	H28···H3^{viii}	3.431
C17···H23^{vii}	3.398	H28···H14^{i}	3.188
C17···H24^{vii}	3.494	H28···H15^{i}	3.069
C18···H10^{x}	3.253	H28···H22^{xiii}	3.297
C18···H20^{xiii}	3.126	H29···O2^{iv}	3.032
C19···H15^{i}	3.193	H29···H5^{iv}	3.458
C19···H17^{xi}	3.285	H29···H19^{iii}	3.538
C20···H4^{xi}	3.455	H29···H33^{iv}	2.709
C20···H17^{xi}	3.599	H29···H34	3.101
C20···H33^{iv}	3.101	H30···O2^{iv}	2.792
C20···H34	3.224	H30···O3^{iv}	3.581
H1···Br2^{vi}	3.101	H30···H4^{xi}	2.943
H1···H16^{vi}	3.558	H30···H17^{xi}	2.805

H1···H27^{vi}	3.440	H30···H33^{iv}	2.622
H1···H33	3.019	H30···H34^{iv}	2.886
H2···H11^{i}	3.391	H31···Br2^{ii}	3.060
H2···H23^{vii}	3.520	H31···H4^{xi}	3.070
H2···H25^{vii}	3.193	H31···H33	3.482
H3···Br2^{xiv}	3.523	H31···H34	2.653
H3···H14^{xiv}	3.212	H32···O3^{i}	2.020
H3···H15^{xiv}	3.359	H32···C7^{i}	2.970
H3···H18^{xii}	3.407	H32···C8^{i}	2.996
H3···H27^{vi}	3.039	H32···C9^{i}	3.468
H3···H28^{vi}	3.431	H32···C11^{i}	3.582
H4···Br2^{xiv}	3.401	H32···C12^{i}	3.017
H4···C20^{xii}	3.455	H32···H9^{i}	2.454
H4···H11^{i}	3.235	H32···H11^{i}	2.961
H4···H30^{xii}	2.943	H32···H12^{i}	3.295
H4···H31^{xii}	3.070	H32···H13^{i}	2.145
H4···H34^{i}	3.528	H32···H34^{i}	2.445
H5···C16^{xii}	3.591	H33···Br2^{ii}	3.111
H5···H18^{xii}	3.591	H33···O2	0.820
H5···H19^{xii}	2.946	H33···O3	2.976
H5···H26^{xii}	3.500	H33···C1	3.432
H5···H29^{ii}	3.458	H33···C3	2.895
H5···H33	2.478	H33···C4	2.410
H6···H33	2.557	H33···C5	1.891
H6···H34	2.473	H33···C6	2.671
H7···H13^{i}	3.277	H33···C7	3.389
H7···H33	3.510	H33···C10	3.125
H7···H34	3.309	H33···C16	2.480
H8···H14^{v}	3.227	H33···C20^{ii}	3.101
H8···H34	3.583	H33···H1	3.019
H9···Br1^{x}	3.551	H33···H5	2.478
H9···O1^{iii}	2.694	H33···H6	2.557
H9···H20^{iii}	3.453	H33···H7	3.510
H9···H24^{v}	3.299	H33···H11	3.235
H9···H32^{iii}	2.454	H33···H15^{ii}	3.401
H9···H34	3.021	H33···H17	3.276
H10···C12^{v}	3.544	H33···H18	1.905
H10···C18^{v}	3.253	H33···H19	2.922
H10···H12^{v}	2.729	H33···H29^{ii}	2.709
H10···H14^{v}	3.370	H33···H30^{ii}	2.622
H10···H24^{v}	2.982	H33···H31	3.482
H10···H25^{v}	2.690	H33···H34	2.217

H11···O1^{iii}	3.169	H34···Br2^{ii}	3.439
H11···H2^{iii}	3.391	H34···O1^{iii}	3.153
H11···H4^{iii}	3.235	H34···O2	1.960
H11···H32^{iii}	2.961	H34···O3	0.820
H11···H33	3.235	H34···C5	2.604
H11···H34	2.430	H34···C6	2.376
H12···Br1^{x}	3.058	H34···C7	1.896
H12···H10^{x}	2.729	H34···C8	2.727
H12···H22^{x}	2.873	H34···C9	2.878
H12···H32^{iii}	3.295	H34···C10	3.354
H13···O1^{iii}	2.703	H34···C11	3.111
H13···H7^{iii}	3.277	H34···C16^{iii}	3.587
H13···H19^{iii}	3.083	H34···C20	3.224
H13···H26^{iii}	3.424	H34···H4^{iii}	3.528
H13···H32^{iii}	2.145	H34···H6	2.473
H13···H34	3.125	H34···H7	3.309
H14···C17^{x}	3.520	H34···H8	3.583
H14···H3^{ix}	3.212	H34···H9	3.021
H14···H8^{x}	3.227	H34···H11	2.430
H14···H10^{x}	3.370	H34···H13	3.125
H14···H22^{x}	2.656	H34···H17^{iii}	2.917
H14···H28^{iii}	3.188	H34···H29	3.101
H15···C19^{iii}	3.193	H34···H30^{ii}	2.886
H15···H3^{ix}	3.359	H34···H31	2.653
H15···H18^{iv}	3.087	H34···H32^{iii}	2.445
H15···H26^{iii}	2.794	H34···H33	2.217
Br1—C1—C2	108.2 (3)	C4—C3—H4	108.9
Br1—C1—C10	111.7 (3)	C4—C3—H5	108.9
C2—C1—C10	114.5 (4)	H4—C3—H5	107.8
C1—C2—C3	110.3 (4)	C5—C6—H6	108.7
C2—C3—C4	113.2 (5)	C5—C6—H7	108.7
O1—C4—C3	110.2 (4)	C7—C6—H6	108.7
O1—C4—C5	106.7 (3)	C7—C6—H7	108.7
O1—C4—C16	109.0 (4)	H6—C6—H7	107.6
C3—C4—C5	108.7 (4)	C7—C8—H8	109.0
C3—C4—C16	109.7 (4)	C7—C8—H9	109.0
C5—C4—C16	112.6 (4)	C9—C8—H8	109.0
O2—C5—C4	106.1 (3)	C9—C8—H9	109.0
O2—C5—C6	108.2 (3)	H8—C8—H9	107.8
O2—C5—C10	106.2 (3)	C8—C9—H10	109.4
C4—C5—C6	111.5 (3)	C8—C9—H11	109.4
C4—C5—C10	113.7 (3)	C10—C9—H10	109.4
C6—C5—C10	110.8 (3)	C10—C9—H11	109.4
C5—C6—C7	114.3 (3)	H10—C9—H11	108.0

O3—C7—C6	108.2 (3)	C11—C12—H12	110.1
O3—C7—C8	106.3 (3)	C11—C12—H13	110.1
O3—C7—C11	107.4 (3)	C13—C12—H12	110.1
C6—C7—C8	109.9 (3)	C13—C12—H13	110.1
C6—C7—C11	112.3 (3)	H12—C12—H13	108.5
C8—C7—C11	112.5 (3)	C12—C13—H14	110.9
C7—C8—C9	113.0 (4)	C12—C13—H15	110.9
C8—C9—C10	111.1 (3)	C14—C13—H14	110.9
C1—C10—C5	106.1 (3)	C14—C13—H15	110.9
C1—C10—C9	111.1 (3)	H14—C13—H15	108.9
C1—C10—C17	110.5 (3)	Br2—C14—H16	107.4
C5—C10—C9	107.1 (3)	C13—C14—H16	107.4
C5—C10—C17	113.8 (3)	C15—C14—H16	107.4
C9—C10—C17	108.3 (3)	C4—C16—H17	109.5
C7—C11—C12	110.5 (3)	C4—C16—H18	109.5
C7—C11—C15	116.9 (3)	C4—C16—H19	109.5
C7—C11—C18	108.6 (3)	H17—C16—H18	109.5
C12—C11—C15	103.1 (3)	H17—C16—H19	109.5
C12—C11—C18	108.7 (4)	H18—C16—H19	109.5
C15—C11—C18	108.7 (3)	C10—C17—H20	109.5
C11—C12—C13	107.8 (4)	C10—C17—H21	109.5
C12—C13—C14	104.2 (4)	C10—C17—H22	109.5
Br2—C14—C13	111.4 (3)	H20—C17—H21	109.5
Br2—C14—C15	114.9 (3)	H20—C17—H22	109.5
C13—C14—C15	108.0 (4)	H21—C17—H22	109.5
C11—C15—C14	98.4 (3)	C11—C18—H23	109.5
C11—C15—C19	115.4 (3)	C11—C18—H24	109.5
C11—C15—C20	113.9 (3)	C11—C18—H25	109.5
C14—C15—C19	109.9 (4)	H23—C18—H24	109.5
C14—C15—C20	109.9 (3)	H23—C18—H25	109.5
C19—C15—C20	108.9 (4)	H24—C18—H25	109.5
C4—O1—H32	109.5	C15—C19—H26	109.5
C5—O2—H33	109.5	C15—C19—H27	109.5
C7—O3—H34	109.5	C15—C19—H28	109.5
Br1—C1—H1	107.4	H26—C19—H27	109.5
C2—C1—H1	107.4	H26—C19—H28	109.5
C10—C1—H1	107.4	H27—C19—H28	109.5
C1—C2—H2	109.6	C15—C20—H29	109.5
C1—C2—H3	109.6	C15—C20—H30	109.5
C3—C2—H2	109.6	C15—C20—H31	109.5
C3—C2—H3	109.6	H29—C20—H30	109.5
H2—C2—H3	108.1	H29—C20—H31	109.5
C2—C3—H4	108.9	H30—C20—H31	109.5
C2—C3—H5	108.9		

Symmetry codes: (i) *x*+1, *y*, *z*; (ii) −*x*+1, *y*+1/2, −*z*; (iii) *x*−1, *y*, *z*; (iv) −*x*+1, *y*−1/2, −*z*; (v) −*x*+1, *y*+1/2, −*z*+1; (vi) *x*, *y*+1, *z*; (vii) −*x*+2, *y*+1/2, −*z*+1; (viii) *x*, *y*−1, *z*; (ix) *x*−1, *y*−1, *z*; (x) −*x*+1, *y*−1/2, −*z*+1; (xi) −*x*+2, *y*−1/2, −*z*; (xii) −*x*+2, *y*+1/2, −*z*; (xiii) −*x*+2, *y*−1/2, −*z*+1; (xiv) *x*+1, *y*+1, *z*.

Hydrogen-bond geometry (Å, °)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
O1—H32···O3^{i}	0.82	2.02	2.797 (4)	158
O3—H34···O2	0.82	1.96	2.691 (4)	148

Symmetry codes: (i) *x*+1, *y*, *z*.

Fig. 1

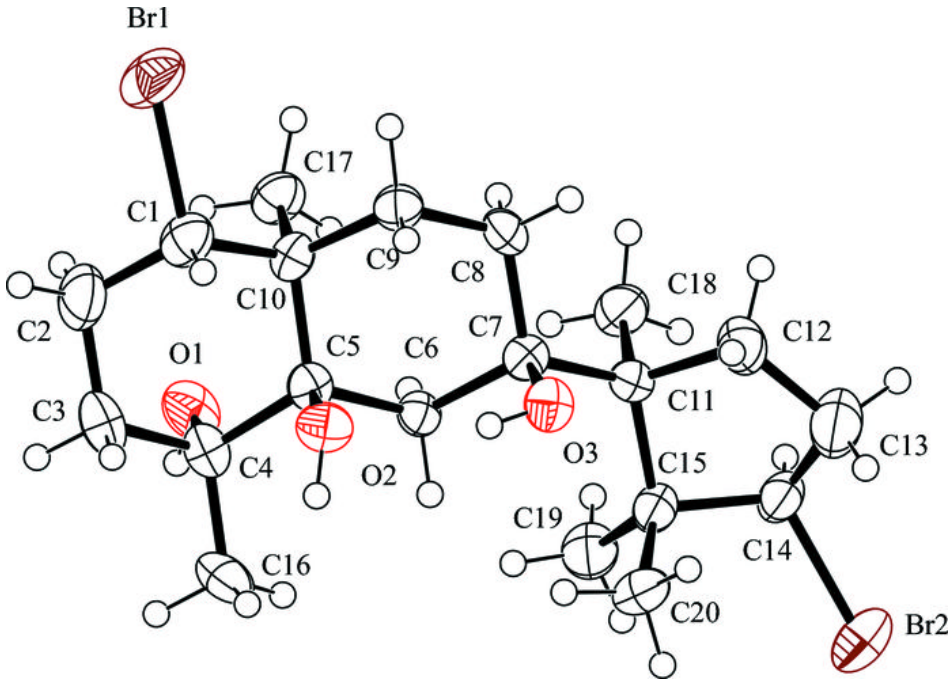
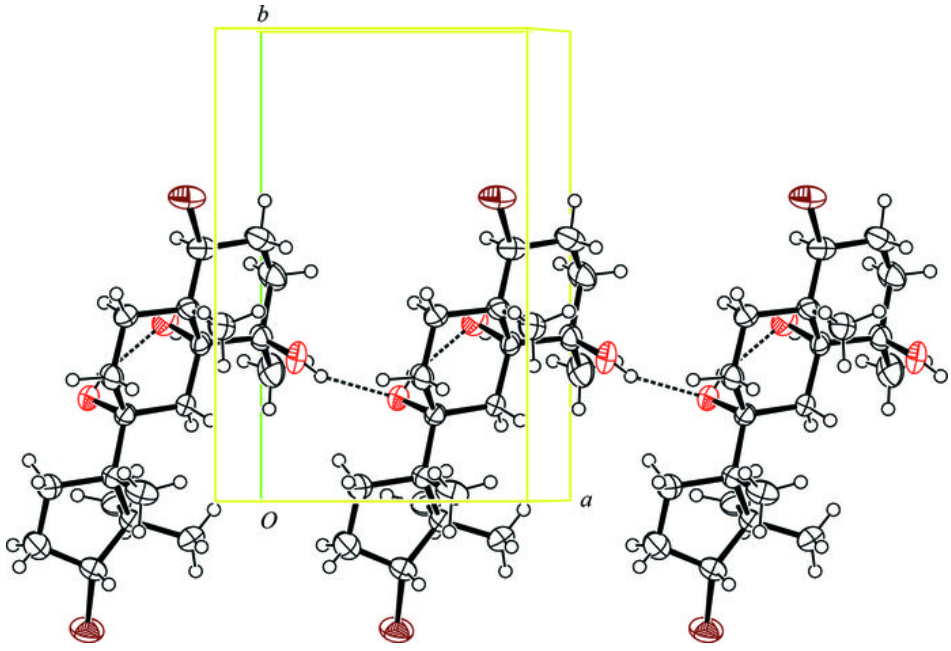

Br1
C17
C1
C9
C8
C18
C10
C2
C7
C12
O1
C5
C6
C3
C11
C13
O3
C4
O2
C15
C19
C14
C16
C20
Br2

Fig. 2



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(2*E*)-1-(2-Bromophenyl)-3-(3,4,5-trimethoxyphenyl)prop-2-en-1-one

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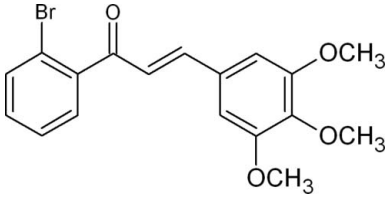
Key indicators: single-crystal X-ray study; T = 110 K; mean σ(C–C) = 0.003 Å; R factor = 0.039; wR factor = 0.112; data-to-parameter ratio = 15.6.

In the chalcone title compound, $C_{18}H_{17}BrO_4$, the dihedral angle between the mean planes of the 2-bromo- and 3,4,5-trimethoxy-substituted benzene rings is 89.3 (1)°. The angles between the mean plane of the prop-2-en-1-one group and the 2-bromophenyl and 3,4,5-trimethoxyphenyl ring planes are 59.7 (1) and 40.5 (8)°, respectively. While no classical hydrogen bonds are present, three weak intermolecular C—H···O interactions and weak C—H···Br and C—H···*Cg* π-ring stacking interactions [C—H···*Cg* distance = 3.377 (2) Å] are observed, which contribute to the stability of crystal packing.

Related literature

For the radical quenching properties of included phenol groups, see: Dhar (1981). For the anticancer activity of chalcones, see: Dimmock *et al.* (1999). For related structures, see: Chantrapromma *et al.* (2009); Patil *et al.* (2006); Suwunwong *et al.* (2009). For bond distances and angles, see: Allen (2002).



Experimental

Crystal data

$C_{18}H_{17}BrO_4$
M_r = 377.23
Orthorhombic, *Pbca*
a = 9.9616 (4) Å
b = 13.6020 (13) Å
c = 24.4162 (17) Å
V = 3308.4 (4) Å^3
Z = 8
Mo $K\alpha$ radiation
μ = 2.50 mm^{-1}
T = 110 K
0.47 × 0.42 × 0.31 mm

Data collection

Oxford Diffraction Xcalibur diffractometer with a Ruby (Gemini Cu) detector
Absorption correction: multi-scan (*CrysAlis RED*; Oxford Diffraction, 2007)
T_{min} = 0.499, T_{max} = 1.000
8122 measured reflections
3296 independent reflections
2940 reflections with $I > 2\sigma(I)$
R_{int} = 0.022

Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.039
$wR(F^2)$ = 0.112
S = 1.04
3296 reflections
211 parameters
H-atom parameters constrained
$\Delta\rho_{max}$ = 0.46 e Å^{-3}
$\Delta\rho_{min}$ = −0.67 e Å^{-3}

Table 1
Hydrogen-bond geometry (Å, °).

*Cg*2 is the centroid of the C10–C15 ring.

D—H···A	D—H	H···A	D···A	D—H···A
C6—H6*A*···O1^{i}	0.95	2.44	3.233 (3)	140
C9—H9*A*···O2^{ii}	0.95	2.51	3.308 (3)	141
C15—H15*A*···O2^{ii}	0.95	2.53	3.202 (2)	128
C17—H17*C*···Br1^{iii}	0.98	2.99	3.746 (2)	135
C17—H17*A*···*Cg*2^{iv}	0.98	2.83	3.379 (2)	125

Symmetry codes: (i) $x-\frac{1}{2}, y, -z+\frac{3}{2}$; (ii) $-x+\frac{1}{2}, y+\frac{1}{2}, z$; (iii) $-x+\frac{1}{2}, y-\frac{1}{2}, z$; (iv) $x-\frac{1}{2}, -y+\frac{1}{2}, -z+1$.

Data collection: *CrysAlis PRO* (Oxford Diffraction, 2007); cell refinement: *CrysAlis PRO*; data reduction: *CrysAlis RED* (Oxford Diffraction, 2007); program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *SHELXTL* (Sheldrick, 2008); software used to prepare material for publication: *SHELXTL*.

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Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: FJ2317).

References

Allen, F. H. (2002). *Acta Cryst.* B**58**, 380–388.
Chantrapromma, S., Suwunwong, T., Karalai, C. & Fun, H.-K. (2009). *Acta Cryst.* E**65**, o893–o894.
Dhar, D. N. (1981). *The Chemistry of Chalcones and Related Compounds*. New York: John Wiley.
Dimmock, J. R., Elias, D. W., Beazely, M. A. & Kandepu, N. M. (1999). *Curr. Med. Chem.* **6**, 1125–1149.
Oxford Diffraction (2007). *CrysAlis PRO* and *CrysAlis RED*. Oxford Diffraction Ltd, Abingdon, Oxfordshire, England.
Patil, P. S., Rosli, M. M., Fun, H.-K., Razak, I. A. & Dharmaprakash, S. M. (2006). *Acta Cryst.* E**62**, o4644–o4645.
Sheldrick, G. M. (2008). *Acta Cryst.* A**64**, 112–122.
Suwunwong, T., Chantrapromma, S. & Fun, H.-K. (2009). *Acta Cryst.* E**65**, o120.

supplementary materials

Acta Cryst. (2010). E**66**, o1676 [**doi:10.1107/S160053681002235X**]

(2*E*)-1-(2-Bromophenyl)-3-(3,4,5-trimethoxyphenyl)prop-2-en-1-one

J. P. Jasinski, R. J. Butcher, K. Veena, B. Narayana and H. S. Yathirajan

Comment

Chalcones, or 1,3-diaryl-2-propen-1-ones, belong to the flavonoid family. Chemically they consist of open-chain flavonoids in which the two aromatic rings are joined by a three-carbon α,β-unsaturated carbonyl system. A vast number of naturally occurring chalcones are polyhydroxylated in the aryl rings. The radical quenching properties of the phenol groups present in many chalcones have raised interest in using the compounds or chalcone rich plant extracts as drugs or food preservatives (Dhar, 1981). Chalcones have been reported to possess many useful biological properties, including anti-inflammatory,antimicrobial, antifungal, antioxidant, cytotoxic, anticancer activities (Dimmock *et al.*, 1999). The crystal structures of some closely related chalcones, *viz*., (*E*)-1-(4-bromophenyl)-3-(3,4,5-trimethoxy-phenyl)prop-2-en-1-one (Suwunwong *et al.*, 2009), (*E*)-1-(4-bromophenyl)-3-(2,4,6-trimethoxyphenyl)prop-2-en-1-one (Chantrapromma *et al.*, 2009) and 1-(4-bromophenyl)-3-(2,4,5-trimethoxyphenyl)prop-2-en-1-one (Patil *et al.*, 2006) have been reported. Hence in continuation with the synthesis and crystal structure determination and also owing to the importance of these flavanoid analogs, this new bromo-trimethoxy substituted chalcone, (I), $C_{18}H_{17}BrO_4$, is synthesized and its crystal structure is reported.

The title compound, (I), $C_{18}H_{17}BrO_4$,is a chalcone with 2-bromophenyl and 3,4,5-trimethoxyphenyl rings bonded at opposite sides of a propene group (Fig. 2). The dihedral angle between mean planes of the benzene rings in the *ortho*-bromo and *meta*- *para*-trimethoxy substituted rings is 89.3 (1)°. The angles between the mean plane of the prop-2-ene-1-one group (C1/C7/O1/C8) and the mean planes of the benzene rings in the 2-bromophenyl (C1–C6)and 3,4,5-trimethoxyphenyl rings (C10—C15) are 59.7 (1)° and 40.5 (8)°, respectively. Bond distances and angles are in normal ranges (Allen, 2002). While no classical hydrogen bonds are present, three weak intermolecular C—H···O interactions (Fig. 3) and weak C—H···Br (Table 1) and C17—H17A···*Cg*2 π-ring stacking interactions (H17A···*Cg*2 = 2.83 Å; H17A–Perp = 2.82 Å; C17—H17A···*Cg*2 = 125°; C17···*Cg*2—H17A = 3.379 (2) Å; *Cg*2 = C10–C15) are observed which contribute to the stability of crystal packing.

Experimental

A 50% KOH solution was added to a mixture of 2-bromo acetophenone (0.01 mol, 1.99 g) and 3,4,5-trimethoxy benzaldehyde (0.01 mol, 1.96 g) in 25 ml of ethanol (Fig. 1). The mixture was stirred for an hour at room temperature and the precipitate was collected by filtration and purified by recrystallization from ethanol. The single-crystal was grown from ethyl acetate by slow evaporation method and yield of the compound was 45% (m.p.325–327 K). Analytical data: Found (Calculated) for $C_{18}H_{17}BrO_4$: C %: 57.26 (57.31%); H%: 4.49 (4.54%).

Refinement

The H atoms were placed in geometrically idealized positions and constrained to ride on their parent atoms with C–H distances = 0.95–0.96Å and with U_{iso}(H) = 1.18–1.50 U_{eq}(C).

Figures

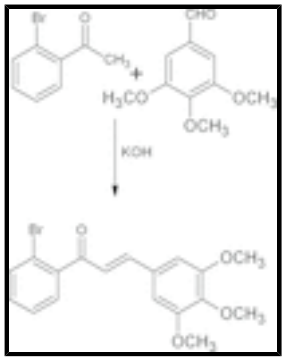


Fig. 1. Reaction Scheme for the title compound.

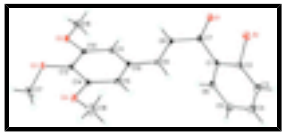


Fig. 2. Molecular structure of (I), $C_{18}H_{17}BrO_4$, showing the atom labeling scheme and 50% probability displacement ellipsoids.

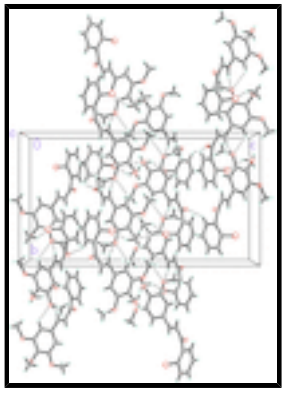


Fig. 3. Packing diagram of the title compound, $C_{18}H_{17}BrO_4$, viewed down the *a* axis. Dashed lines indicate weak C—H···O intermolecular hydrogen bond interactions linking the molecules into chains along the (011).

(2*E*)-1-(2-Bromophenyl)-3-(3,4,5-trimethoxyphenyl)prop-2-en-1-one

Crystal data

$C_{18}H_{17}BrO_4$	$F(000) = 1536$
$M_r = 377.23$	$D_x = 1.515$ Mg m^{-3}
Orthorhombic, *Pbca*	Mo *K*α radiation, λ = 0.71073 Å
Hall symbol: -P 2ac 2ab	Cell parameters from 4251 reflections
$a = 9.9616$ (4) Å	θ = 4.4–74.1°
$b = 13.6020$ (13) Å	μ = 2.50 mm^{-1}
$c = 24.4162$ (17) Å	$T = 110$ K
$V = 3308.4$ (4) Å^3	Chunk, colorless
$Z = 8$	0.47 × 0.42 × 0.31 mm

Data collection

Oxford Diffraction Xcalibur diffractometer with a Ruby (Gemini Cu) detector	3296 independent reflections
Radiation source: Enhance (Cu) X-ray Source	2940 reflections with $I > 2\sigma(I)$

graphite

Detector resolution: 10.5081 pixels mm^{-1}

ω scans

Absorption correction: multi-scan (*CrysAlis RED*; Oxford Diffraction, 2007)

T_{min} = 0.499, T_{max} = 1.000

8122 measured reflections

R_{int} = 0.022

θ_{max} = 26.3°, θ_{min} = 2.6°

h = −12→7

k = −16→15

l = −30→28

Refinement

Refinement on F^2

Least-squares matrix: full

$R[F^2 > 2\sigma(F^2)]$ = 0.039

$wR(F^2)$ = 0.112

S = 1.04

3296 reflections

211 parameters

0 restraints

Primary atom site location: structure-invariant direct methods

Secondary atom site location: difference Fourier map

Hydrogen site location: inferred from neighbouring sites

H-atom parameters constrained

$w = 1/[\sigma^2(F_o^2) + (0.0769P)^2 + 1.9413P]$ where $P = (F_o^2 + 2F_c^2)/3$

$(\Delta/\sigma)_{max}$ = 0.003

$\Delta\rho_{max}$ = 0.46 e $Å^{-3}$

$\Delta\rho_{min}$ = −0.67 e $Å^{-3}$

Special details

Experimental. IR data (KBr) \v cm^{-1}: 2998 cm^{-1}, 2937 cm^{-1}, 2839 cm^{-1} (C—H al. str), 3058 cm^{-1} (C—H ar.str) 1646 cm^{-1} (C=O), 1580 cm^{-1} (C=C); 1245 cm^{-1} (C—O—C).

Geometry. All e.s.d.'s (except the e.s.d. in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell e.s.d.'s are taken into account individually in the estimation of e.s.d.'s in distances, angles and torsion angles; correlations between e.s.d.'s in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell e.s.d.'s is used for estimating e.s.d.'s involving l.s. planes.

Refinement. Refinement of F^2 against ALL reflections. The weighted *R*-factor *wR* and goodness of fit *S* are based on F^2, conventional *R*-factors *R* are based on *F*, with *F* set to zero for negative F^2. The threshold expression of $F^2 > \sigma(F^2)$ is used only for calculating *R*-factors(gt) *etc*. and is not relevant to the choice of reflections for refinement. *R*-factors based on F^2 are statistically about twice as large as those based on *F*, and *R*- factors based on ALL data will be even larger.

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters ($Å^2$)

	x	*y*	*z*	U_{iso}*/U_{eq}
Br1	0.74430 (2)	0.76760 (2)	0.612337 (10)	0.02659 (13)
O1	0.74217 (17)	0.57654 (14)	0.69518 (10)	0.0340 (5)
O2	0.31902 (16)	0.16171 (11)	0.60595 (6)	0.0191 (3)
O3	0.17918 (15)	0.20383 (11)	0.51830 (6)	0.0180 (3)
O4	0.14169 (16)	0.39311 (11)	0.48455 (6)	0.0203 (3)
C1	0.5557 (2)	0.68349 (15)	0.68770 (8)	0.0159 (4)
C2	0.6035 (2)	0.77077 (15)	0.66443 (8)	0.0169 (4)
C3	0.5453 (2)	0.86108 (16)	0.67668 (9)	0.0219 (4)

H3A	0.5798	0.9198	0.6610	0.026*
C4	0.4364 (2)	0.86455 (17)	0.71200 (9)	0.0255 (5)
H4A	0.3966	0.9260	0.7208	0.031*
C5	0.3854 (2)	0.77852 (17)	0.73449 (9)	0.0254 (5)
H5A	0.3101	0.7811	0.7584	0.031*
C6	0.4441 (2)	0.68889 (16)	0.72215 (9)	0.0203 (4)
H6A	0.4079	0.6303	0.7373	0.024*
C7	0.6256 (2)	0.58607 (16)	0.68075 (9)	0.0196 (4)
C8	0.5507 (2)	0.50263 (15)	0.65798 (9)	0.0183 (4)
H8A	0.5862	0.4384	0.6630	0.022*
C9	0.4355 (2)	0.51190 (14)	0.63061 (9)	0.0157 (4)
H9A	0.3975	0.5758	0.6282	0.019*
C10	0.3627 (2)	0.43154 (15)	0.60391 (8)	0.0149 (4)
C11	0.3777 (2)	0.33362 (15)	0.62149 (8)	0.0157 (4)
H11A	0.4324	0.3185	0.6522	0.019*
C12	0.3114 (2)	0.25927 (15)	0.59324 (9)	0.0151 (4)
C13	0.2319 (2)	0.28097 (16)	0.54734 (9)	0.0144 (4)
C14	0.2176 (2)	0.37893 (15)	0.53031 (9)	0.0158 (4)
C15	0.2808 (2)	0.45419 (15)	0.55925 (9)	0.0157 (4)
H15A	0.2681	0.5207	0.5486	0.019*
C16	0.3980 (2)	0.13512 (16)	0.65246 (10)	0.0242 (5)
H16A	0.3929	0.0639	0.6581	0.036*
H16B	0.3637	0.1690	0.6850	0.036*
H16C	0.4916	0.1542	0.6462	0.036*
C17	0.0357 (2)	0.19852 (18)	0.51743 (10)	0.0249 (5)
H17A	0.0077	0.1400	0.4970	0.037*
H17B	−0.0005	0.2574	0.4997	0.037*
H17C	0.0018	0.1945	0.5550	0.037*
C18	0.1511 (3)	0.48850 (18)	0.45889 (11)	0.0319 (6)
H18A	0.0980	0.4887	0.4251	0.048*
H18B	0.2452	0.5027	0.4502	0.048*
H18C	0.1165	0.5388	0.4839	0.048*

Atomic displacement parameters (Å^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Br1	0.02410 (18)	0.0327 (2)	0.02294 (19)	−0.00535 (9)	0.00684 (8)	−0.00220 (9)
O1	0.0244 (9)	0.0223 (9)	0.0552 (13)	0.0010 (6)	−0.0201 (8)	−0.0062 (9)
O2	0.0224 (8)	0.0124 (7)	0.0226 (8)	−0.0033 (6)	−0.0055 (6)	0.0007 (6)
O3	0.0159 (7)	0.0188 (7)	0.0194 (7)	−0.0023 (6)	−0.0009 (6)	−0.0073 (6)
O4	0.0254 (8)	0.0187 (7)	0.0169 (7)	−0.0003 (6)	−0.0078 (6)	0.0006 (6)
C1	0.0177 (9)	0.0161 (10)	0.0138 (9)	−0.0046 (8)	−0.0051 (8)	−0.0020 (7)
C2	0.0177 (10)	0.0213 (11)	0.0117 (9)	−0.0025 (8)	0.0008 (8)	−0.0023 (7)
C3	0.0317 (12)	0.0159 (10)	0.0180 (10)	−0.0011 (9)	−0.0002 (9)	0.0020 (8)
C4	0.0342 (13)	0.0220 (11)	0.0204 (10)	0.0057 (10)	0.0026 (10)	−0.0045 (8)
C5	0.0251 (11)	0.0334 (13)	0.0178 (10)	−0.0009 (10)	0.0052 (9)	−0.0040 (9)
C6	0.0247 (10)	0.0207 (10)	0.0157 (10)	−0.0063 (9)	−0.0027 (8)	0.0007 (8)
C7	0.0208 (10)	0.0183 (10)	0.0197 (10)	−0.0017 (8)	−0.0051 (8)	0.0001 (8)

C8	0.0204 (10)	0.0117 (8)	0.0229 (11)	−0.0009 (8)	−0.0033 (9)	−0.0015 (8)
C9	0.0184 (10)	0.0126 (9)	0.0160 (10)	0.0005 (8)	0.0010 (8)	−0.0011 (7)
C10	0.0142 (9)	0.0141 (9)	0.0164 (9)	−0.0010 (8)	0.0018 (8)	−0.0034 (7)
C11	0.0152 (9)	0.0154 (9)	0.0163 (9)	0.0005 (8)	−0.0024 (8)	−0.0015 (8)
C12	0.0122 (9)	0.0150 (9)	0.0180 (10)	0.0000 (7)	0.0021 (8)	0.0008 (8)
C13	0.0116 (9)	0.0171 (10)	0.0144 (10)	−0.0023 (7)	0.0020 (7)	−0.0038 (8)
C14	0.0134 (8)	0.0194 (10)	0.0145 (9)	0.0019 (8)	0.0010 (8)	−0.0029 (8)
C15	0.0156 (8)	0.0133 (9)	0.0182 (10)	0.0028 (8)	0.0021 (8)	−0.0019 (8)
C16	0.0263 (11)	0.0166 (9)	0.0296 (12)	−0.0004 (9)	−0.0076 (10)	0.0053 (8)
C17	0.0171 (10)	0.0285 (12)	0.0290 (12)	−0.0073 (9)	−0.0057 (9)	0.0013 (9)
C18	0.0448 (15)	0.0260 (12)	0.0251 (12)	−0.0022 (11)	−0.0135 (11)	0.0079 (9)

Geometric parameters (Å, °)

Br1—C2	1.894 (2)	C8—H8A	0.9500
O1—C7	1.221 (3)	C9—C10	1.465 (3)
O2—C12	1.365 (2)	C9—H9A	0.9500
O2—C16	1.428 (3)	C10—C15	1.396 (3)
O3—C13	1.371 (2)	C10—C11	1.407 (3)
O3—C17	1.431 (3)	C11—C12	1.391 (3)
O4—C14	1.363 (3)	C11—H11A	0.9500
O4—C18	1.444 (3)	C12—C13	1.404 (3)
C1—C6	1.396 (3)	C13—C14	1.403 (3)
C1—C2	1.400 (3)	C14—C15	1.394 (3)
C1—C7	1.506 (3)	C15—H15A	0.9500
C2—C3	1.391 (3)	C16—H16A	0.9800
C3—C4	1.386 (3)	C16—H16B	0.9800
C3—H3A	0.9500	C16—H16C	0.9800
C4—C5	1.389 (3)	C17—H17A	0.9800
C4—H4A	0.9500	C17—H17B	0.9800
C5—C6	1.385 (3)	C17—H17C	0.9800
C5—H5A	0.9500	C18—H18A	0.9800
C6—H6A	0.9500	C18—H18B	0.9800
C7—C8	1.468 (3)	C18—H18C	0.9800
C8—C9	1.334 (3)		
C12—O2—C16	117.25 (16)	C12—C11—C10	119.09 (19)
C13—O3—C17	115.38 (17)	C12—C11—H11A	120.5
C14—O4—C18	116.55 (17)	C10—C11—H11A	120.5
C6—C1—C2	118.09 (19)	O2—C12—C11	124.57 (19)
C6—C1—C7	118.82 (18)	O2—C12—C13	114.68 (18)
C2—C1—C7	122.91 (19)	C11—C12—C13	120.74 (19)
C3—C2—C1	121.3 (2)	O3—C13—C14	122.3 (2)
C3—C2—Br1	118.25 (16)	O3—C13—C12	117.91 (19)
C1—C2—Br1	120.35 (15)	C14—C13—C12	119.56 (19)
C4—C3—C2	119.3 (2)	O4—C14—C15	124.20 (19)
C4—C3—H3A	120.3	O4—C14—C13	115.69 (18)
C2—C3—H3A	120.3	C15—C14—C13	120.1 (2)
C3—C4—C5	120.3 (2)	C14—C15—C10	119.83 (19)
C3—C4—H4A	119.9	C14—C15—H15A	120.1

C5—C4—H4A	119.9	C10—C15—H15A	120.1
C6—C5—C4	120.0 (2)	O2—C16—H16A	109.5
C6—C5—H5A	120.0	O2—C16—H16B	109.5
C4—C5—H5A	120.0	H16A—C16—H16B	109.5
C5—C6—C1	120.9 (2)	O2—C16—H16C	109.5
C5—C6—H6A	119.5	H16A—C16—H16C	109.5
C1—C6—H6A	119.5	H16B—C16—H16C	109.5
O1—C7—C8	120.7 (2)	O3—C17—H17A	109.5
O1—C7—C1	120.0 (2)	O3—C17—H17B	109.5
C8—C7—C1	119.23 (18)	H17A—C17—H17B	109.5
C9—C8—C7	123.64 (19)	O3—C17—H17C	109.5
C9—C8—H8A	118.2	H17A—C17—H17C	109.5
C7—C8—H8A	118.2	H17B—C17—H17C	109.5
C8—C9—C10	125.33 (18)	O4—C18—H18A	109.5
C8—C9—H9A	117.3	O4—C18—H18B	109.5
C10—C9—H9A	117.3	H18A—C18—H18B	109.5
C15—C10—C11	120.61 (19)	O4—C18—H18C	109.5
C15—C10—C9	118.17 (18)	H18A—C18—H18C	109.5
C11—C10—C9	121.18 (19)	H18B—C18—H18C	109.5
C6—C1—C2—C3	2.4 (3)	C9—C10—C11—C12	−177.03 (19)
C7—C1—C2—C3	−172.66 (19)	C16—O2—C12—C11	1.8 (3)
C6—C1—C2—Br1	−174.42 (15)	C16—O2—C12—C13	−179.68 (19)
C7—C1—C2—Br1	10.5 (3)	C10—C11—C12—O2	179.33 (19)
C1—C2—C3—C4	−1.0 (3)	C10—C11—C12—C13	0.9 (3)
Br1—C2—C3—C4	175.89 (17)	C17—O3—C13—C14	−68.0 (3)
C2—C3—C4—C5	−0.6 (3)	C17—O3—C13—C12	117.1 (2)
C3—C4—C5—C6	0.7 (4)	O2—C12—C13—O3	−4.5 (3)
C4—C5—C6—C1	0.8 (3)	C11—C12—C13—O3	174.12 (18)
C2—C1—C6—C5	−2.3 (3)	O2—C12—C13—C14	−179.56 (18)
C7—C1—C6—C5	173.0 (2)	C11—C12—C13—C14	−1.0 (3)
C6—C1—C7—O1	−117.3 (3)	C18—O4—C14—C15	13.2 (3)
C2—C1—C7—O1	57.7 (3)	C18—O4—C14—C13	−165.9 (2)
C6—C1—C7—C8	60.9 (3)	O3—C13—C14—O4	3.4 (3)
C2—C1—C7—C8	−124.0 (2)	C12—C13—C14—O4	178.29 (18)
O1—C7—C8—C9	−164.7 (2)	O3—C13—C14—C15	−175.64 (18)
C1—C7—C8—C9	17.1 (3)	C12—C13—C14—C15	−0.8 (3)
C7—C8—C9—C10	175.4 (2)	O4—C14—C15—C10	−176.39 (19)
C8—C9—C10—C15	−153.2 (2)	C13—C14—C15—C10	2.6 (3)
C8—C9—C10—C11	24.9 (3)	C11—C10—C15—C14	−2.7 (3)
C15—C10—C11—C12	1.0 (3)	C9—C10—C15—C14	175.34 (19)

Hydrogen-bond geometry (Å, °)

Cg2 is the centroid of the C10–C15 ring.

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
C6—H6A···O1^{i}	0.95	2.44	3.233 (3)	140
C9—H9A···O2^{ii}	0.95	2.51	3.308 (3)	141
C15—H15A···O2^{ii}	0.95	2.53	3.202 (2)	128

C17—H17C···Br1^{iii}	0.98	2.99	3.746 (2)	135
C17—H17A···Cg2^{iv}	0.98	2.83	3.379 (2)	125

Symmetry codes: (i) *x*−1/2, *y*, −*z*+3/2; (ii) −*x*+1/2, *y*+1/2, *z*; (iii) −*x*+1/2, *y*−1/2, *z*; (iv) *x*−1/2, −*y*+1/2, −*z*+1.

Fig. 1

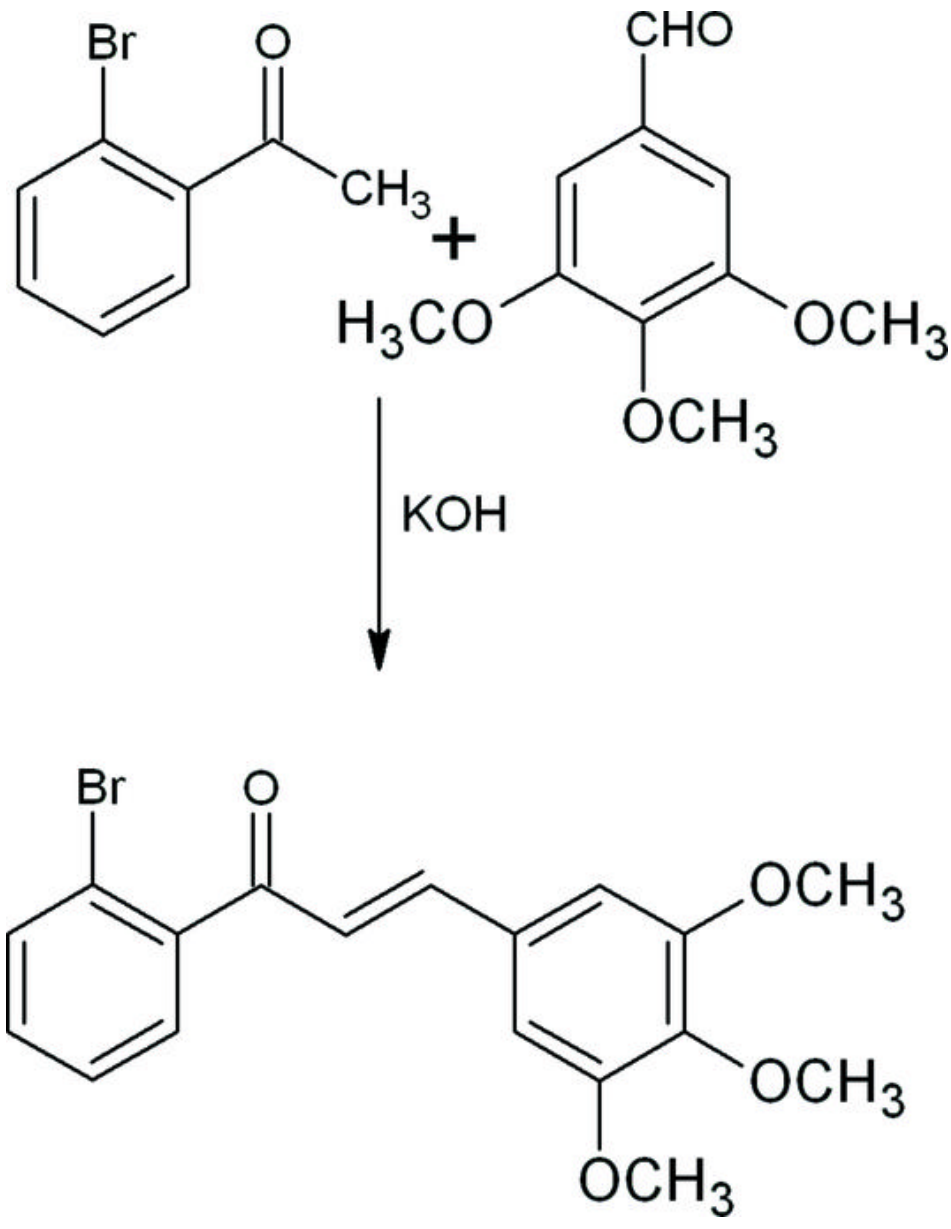


Fig. 2

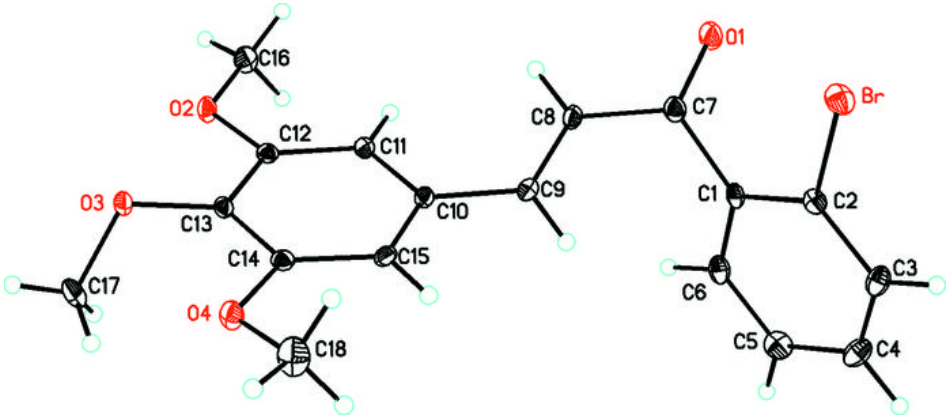
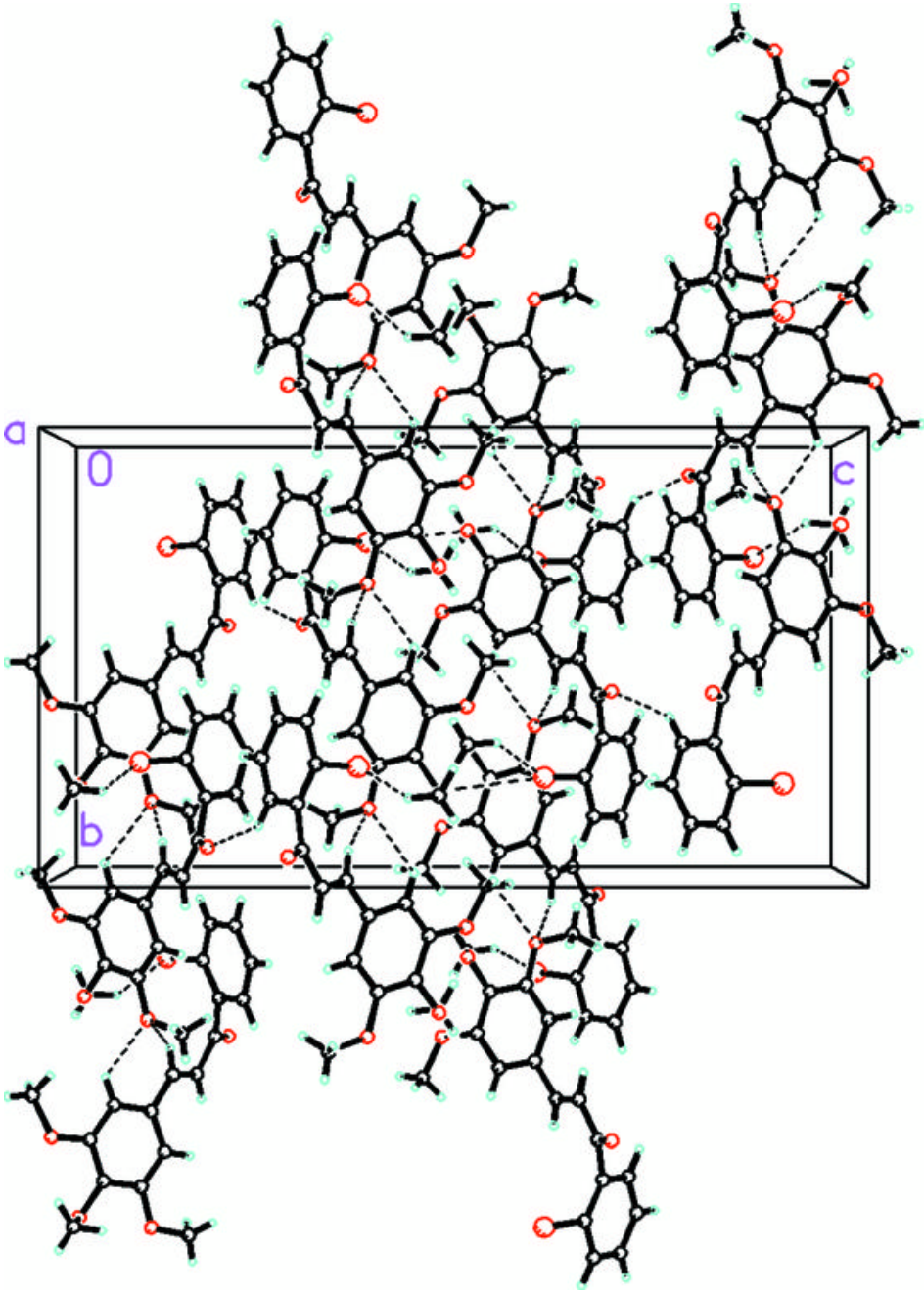

O1
C16
O2
C12
C11
C8
C7
Br
O3
C13
C10
C9
C1
C2
C14
C15
C3
C17
C6
O4
C18
C5
C4

Fig. 3



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(*E*)-7-(Pyren-1-yl)hept-6-enoic acid

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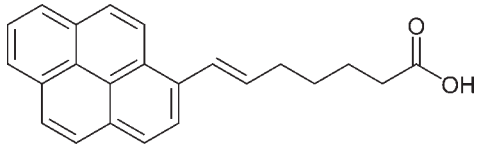
Key indicators: single-crystal X-ray study; T = 123 K; mean σ(C–C) = 0.004 Å; R factor = 0.064; wR factor = 0.164; data-to-parameter ratio = 13.0.

The title compound, $C_{23}H_{20}O_2$, is a precursor of a pyrene-based supramolecular element for non-covalent attachment to a carbon nanotube. The asymmetric unit contains three independent molecules. The carboxylic acid group in each of these molecules serves as an intermolecular hydrogen-bond donor and acceptor, generating the commonly observed double O—H···O hydrogen-bond motif in an eight-membered ring. Weaker C—H···O, π–π [centroid–centroid distance = 3.968 (4) Å] and C—H···π interactions are also found in the crystal structure.

Related literature

Pyrene functionalized with an aliphatic spacer can be used to functionalize molecular skeletons and the resulting mono- or multipyrene derivative bound non-covalently to a π-surface, see: Kavakka *et al.* (2007); Tomonari *et al.* (2006). For related structures, see: Bariamis *et al.* (2009). For hydrogen-bond motifs, see: Bernstein *et al.* (1995). The title compound was synthesized by a Wittig reaction, see: Wittig & Haag (1955); Wittig & Schöllkopf (1954).



Experimental

Crystal data

$C_{23}H_{20}O_2$
M_r = 328.39
Triclinic, $P\overline{1}$
a = 10.7785 (3) Å
b = 13.3315 (4) Å
c = 18.9574 (6) Å
α = 103.287 (2)°
β = 103.064 (2)°
γ = 98.391 (2)°
V = 2525.64 (13) Å^3
Z = 6
Mo $K\alpha$ radiation
μ = 0.08 mm^{-1}
T = 123 K
0.32 × 0.14 × 0.06 mm

Data collection

Bruker–Nonius Kappa CCD diffractometer with an APEXII detector
15113 measured reflections
8885 independent reflections
5729 reflections with $I > 2\sigma(I)$
R_{int} = 0.038

Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.064
$wR(F^2)$ = 0.164
S = 1.06
8885 reflections
685 parameters
9 restraints
H atoms treated by a mixture of independent and constrained refinement
$\Delta\rho_{max}$ = 0.32 e Å^{-3}
$\Delta\rho_{min}$ = −0.39 e Å^{-3}

Table 1
Hydrogen-bond geometry (Å, °).

*Cg*1 and *Cg*2 are the centroids of the C1*A*–C4*A*,C15*A*,C14*A* and C7*C*–C11*C*,C16*C* rings, respectively.

D—H···A	D—H	H···A	D···A	D—H···A
O2*A*—H2*O*···O1*C*^{i}	0.88 (2)	1.79 (2)	2.661 (3)	177 (3)
O2*B*—H2*P*···O1*B*^{ii}	0.87 (2)	1.78 (2)	2.642 (3)	173 (3)
O2*C*—H2*Q*···O1*A*^{iii}	0.86 (2)	1.78 (2)	2.636 (3)	172 (3)
C10*C*—H10*C*···O1*A*^{iv}	0.95	2.46	3.336 (3)	154
C10*B*—H10*B*···O1*B*^{v}	0.95	2.51	3.354 (3)	148
C10*A*—H10*A*···O1*C*^{vi}	0.95	2.51	3.360 (3)	150
C22*C*—H22*E*···*Cg*2^{vii}	0.99	2.63	3.500 (4)	147
C19*A*—H19*A*···*Cg*1^{viii}	0.99	2.72	3.511 (4)	137

Symmetry codes: (i) $x, y+1, z+1$; (ii) $-x+2, -y+2, -z+2$; (iii) $x, y-1, z-1$; (iv) $x, y-1, z$; (v) $-x+2, -y+2, -z+1$; (vi) $x, y+1, z$; (vii) $-x+1, -y+1, -z+1$; (viii) $-x+1, -y+2, -z+1$.

Data collection: *COLLECT* (Bruker, 2008); cell refinement: *DENZO-SMN* (Otwinowski & Minor, 1997); data reduction: *DENZO-SMN*; program(s) used to solve structure: *SIR2004* (Burla *et al.*, 2005); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *ORTEP-3* (Farrugia, 1997) and *Mercury* (Macrae *et al.*, 2008); software used to prepare material for publication: *SHELXL97*.

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Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: FJ2323).

References

Bariamis, S. E., Magoulas, G. E., Athanassopoulos, C. M., Papaioannou, D., Manos, M. J. & Nastopoulos, V. (2009). *Acta Cryst.* E**65**, o2580.
Bernstein, J., Davis, R. E., Shimoni, L. & Chang, N. L. (1995). *Angew. Chem. Int. Ed. Engl.* **34**, 1555–1573.
Bruker (2008). *COLLECT*. Bruker AXS, Delft, The Netherlands.
Burla, M. C., Caliandro, R., Camalli, M., Carrozzini, B., Cascarano, G. L., De Caro, L., Giacovazzo, C., Polidori, G. & Spagna, R. (2005). *J. Appl. Cryst.* **38**, 381–388.
Farrugia, L. J. (1997). *J. Appl. Cryst.* **30**, 565.
Kavakka, J. S., Heikkinen, S., Kilpeläinen, I., Mattila, M., Lipsanen, H. & Helaja, J. (2007). *Chem. Commun.* pp. 519–521.
Macrae, C. F., Bruno, I. J., Chisholm, J. A., Edgington, P. R., McCabe, P., Pidcock, E., Rodriguez-Monge, L., Taylor, R., van de Streek, J. & Wood, P. A. (2008). *J. Appl. Cryst.* **41**, 466–470.

Otwinowski, Z. & Minor, W. (1997). *Methods in Enzymology*, Vol. 276, *Macromolecular Crystallography*, Part A, edited by C. W. Carter & R. M. Sweet, pp. 307–326. New York: Academic Press.
Sheldrick, G. M. (2008). *Acta Cryst.* A**64**, 112–122.
Tomonari, Y., Murakami, H. & Nakashima, N. (2006). *Chem. Eur. J.* **12**, 4027–4034.
Wittig, G. & Haag, W. (1955). *Chem. Ber.* **88**, 1654–1666.
Wittig, G. & Schöllkopf, U. (1954). *Chem. Ber.* **87**, 1318–1330.

supplementary materials

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(*E*)-7-(Pyren-1-yl)hept-6-enoic acid

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Comment

Pyrene functionalized with an aliphatic spacer can be used to functionalize molecular skeletons and the resulting mono- or multipyrene derivative bound non-covalently to a pi-surface. Such a non-covalent functionalization has recently been reported by Kavakka *et al.* (Kavakka, *et al.*, 2007) and Tomonari *et al.* (Tomonari, *et al.*, 2006).

The title compound is synthesized by a Wittig reaction (Wittig & Schöllkopf, 1954; Wittig & Haag, 1955). In the molecule (Fig. 1) the planar pyrene ring is bonded to olefinic end carbon of hepten-6-oic acid chain and the pyrene is not coplanar with the conjugated double bond. In three independent molecules in asymmetric unit (labelled *A*, *B* and *C*) the hepten-6-oic acid side chains are almost straight and the dihedral angles between the pyrene rings and the double bonds are 34.8 (3), 14.5 (5) and 33.7 (2) °, respectively. Similar phenomenon was observed with (2*E*,4*E*,6*E*)-3-Methyl-7-(pyren-1-yl)octa-2,4,6-trienoic acid (Bariamis, *et al.*, 2009), the trienoic acid derivative with two additional methyl groups in the positions of 3 and 7 in the side chain. Similar to that trienoic acid (Bariamis, *et al.*, 2009) the carboxyl groups of three molecules of the title compound are connected to carboxyl group of another molecule with double hydrogen bonding interactions (Table 1), generating the $R^2_2(8)$ graph-set motif (Bernstein *et al.*, 1995). With this motif one centrosymmetric *BB* pair and two non-centrosymmetric *AC* pairs were formed (Fig. 2). Mercury -program (Macrae *et al.*, 2008) also finds some short intermolecular C—H···O, π–π [centroid-centroid distance 3.968 (4) Å] and weak C—H···π contacts (Table 1), which connect these pairs to each other and define the overall structure in the crystal.

Experimental

Bis(trimethylsilyl)amine (HMDS) (526 mg, 3.28 mmol) was dissolved in dry THF under inert atmosphere. 1.6-*M* n-BuLi (6.15 ml) was added at -10 °C temperature and the resulting solution was placed into dropping funnel and kept under inert atmosphere. (5-Carboxypentyl)triphenylphosphonium bromide (1.5 g, 3.28 mmol) was dissolved in dry THF under inert atmosphere. The solution was cooled to -10 °C and LiHMDS was added dropwise to the reaction flask. After addition the reaction mixture was stirred at room temperature for 20 minutes. Then the reaction mixture was cooled again (ice salt bath) and 1-pyrene carboxaldehyde (755 mg, 3.28 mmol), dissolved in dry THF, was added dropwise into reaction mixture under inert atmosphere. After addition the reaction mixture was stirred at room temperature for 1 h. The reaction was quenched with aq. 5% citric acid, extracted with DCM and obtained extract was evaporated to yield brown oil. Brown plates were crystallized out from this oil within two weeks. These plates were directly used in single-crystal analysis.

Refinement

All H atoms were visible in electron density maps, but those bonded to C were calculated at their idealized positions and allowed to ride on their parent atoms at C—H distances of 0.95 Å (aromatic, olefinic) and 0.99 Å (methylene), with U_{iso}(H) of 1.2 times U_{eq}(C). The O—H protons were found in the electron density map and were fixed in place by *DFIX* restraint (s = 0.02) at distances of 0.91 Å from N atoms, and U_{iso}(H) values of 1.5 times U_{eq}(O) were used.

Figures

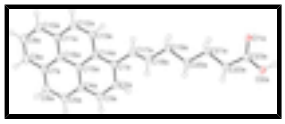


Fig. 1. View of the molecule *A* of title compound showing the atom-labeling scheme. Displacement ellipsoids are drawn at the 50% probability level. H atoms are represented by circles of arbitrary size.

Fig. 2. Packing diagram of the title compound showing the *AC* and *BB* pairs formed by O—H···O interactions between carboxyl groups.

(*E*)-7-(Pyren-1-yl)hept-6-enoic acid

Crystal data

$C_{23}H_{20}O_2$	$Z = 6$
$M_r = 328.39$	$F(000) = 1044$
Triclinic, $P\overline{1}$	$D_x = 1.295$ Mg m^{-3}
Hall symbol: -P 1	Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å
$a = 10.7785$ (3) Å	Cell parameters from 10136 reflections
$b = 13.3315$ (4) Å	$\theta = 0.4$–$28.3°$
$c = 18.9574$ (6) Å	$\mu = 0.08$ mm^{-1}
$\alpha = 103.287$ (2)°	$T = 123$ K
$\beta = 103.064$ (2)°	Plate, brown
$\gamma = 98.391$ (2)°	0.32 × 0.14 × 0.06 mm
$V = 2525.64$ (13) Å^3	

Data collection

Bruker–Nonius Kappa CCD diffractometer with an APEXII detector	5729 reflections with $I > 2\sigma(I)$
Radiation source: fine-focus sealed tube	$R_{int} = 0.038$
graphite	$\theta_{max} = 25.0°$, $\theta_{min} = 2.0°$
Detector resolution: 9 pixels mm^{-1}	$h = -12 \rightarrow 12$
φ and ω scans	$k = -15 \rightarrow 14$
15113 measured reflections	$l = -22 \rightarrow 22$
8885 independent reflections	

Refinement

Refinement on F^2	Primary atom site location: structure-invariant direct methods
Least-squares matrix: full	Secondary atom site location: difference Fourier map
$R[F^2 > 2\sigma(F^2)] = 0.064$	Hydrogen site location: inferred from neighbouring sites
$wR(F^2) = 0.164$	H atoms treated by a mixture of independent and constrained refinement
$S = 1.06$	$w = 1/[\sigma^2(F_o^2) + (0.051P)^2 + 2.3851P]$ where $P = (F_o^2 + 2F_c^2)/3$
8885 reflections	$(\Delta/\sigma)_{max} < 0.001$

685 parameters

9 restraints

$\Delta\rho_{max} = 0.32$ e Å^{-3}

$\Delta\rho_{min} = -0.39$ e Å^{-3}

Special details

Geometry. All s.u.'s (except the s.u. in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell s.u.'s are taken into account individually in the estimation of s.u.'s in distances, angles and torsion angles; correlations between s.u.'s in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell s.u.'s is used for estimating s.u.'s involving l.s. planes.

Refinement. Refinement of F^2 against ALL reflections. The weighted *R*-factor *wR* and goodness of fit *S* are based on F^2, conventional *R*-factors *R* are based on *F*, with *F* set to zero for negative F^2. The threshold expression of $F^2 > 2\sigma(F^2)$ is used only for calculating *R*-factors(gt) *etc*. and is not relevant to the choice of reflections for refinement. *R*-factors based on F^2 are statistically about twice as large as those based on *F*, and *R*- factors based on ALL data will be even larger.

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å^2)

	x	*y*	*z*	U_{iso}*/U_{eq}
O1A	0.7011 (2)	1.28351 (14)	0.93924 (11)	0.0334 (5)
O2A	0.7089 (2)	1.14559 (15)	0.98730 (11)	0.0325 (5)
H2O	0.700 (3)	1.190 (2)	1.0269 (14)	0.049*
C1A	0.6787 (3)	0.9784 (2)	0.45311 (15)	0.0231 (6)
C2A	0.6764 (3)	0.8741 (2)	0.45537 (15)	0.0270 (6)
H2A	0.6868	0.8584	0.5025	0.032*
C3A	0.6597 (3)	0.7931 (2)	0.39162 (15)	0.0273 (6)
H3A	0.6569	0.7231	0.3956	0.033*
C4A	0.6467 (2)	0.8129 (2)	0.32122 (15)	0.0217 (6)
C5A	0.6330 (3)	0.7317 (2)	0.25410 (15)	0.0262 (6)
H5A	0.6293	0.6610	0.2567	0.031*
C6A	0.6252 (3)	0.7529 (2)	0.18704 (16)	0.0285 (6)
H6A	0.6174	0.6973	0.1437	0.034*
C7A	0.6286 (2)	0.8582 (2)	0.18038 (15)	0.0227 (6)
C8A	0.6204 (3)	0.8833 (2)	0.11204 (16)	0.0307 (7)
H8A	0.6140	0.8292	0.0681	0.037*
C9A	0.6215 (3)	0.9859 (2)	0.10714 (16)	0.0327 (7)
H9A	0.6178	1.0014	0.0603	0.039*
C10A	0.6281 (3)	1.0657 (2)	0.17000 (16)	0.0290 (7)
H10A	0.6262	1.1352	0.1658	0.035*
C11A	0.6375 (2)	1.0444 (2)	0.23970 (15)	0.0228 (6)
C12A	0.6431 (3)	1.1248 (2)	0.30620 (15)	0.0259 (6)
H12A	0.6378	1.1940	0.3025	0.031*
C13A	0.6556 (3)	1.1044 (2)	0.37389 (15)	0.0235 (6)
H13A	0.6598	1.1598	0.4166	0.028*
C14A	0.6628 (2)	1.0011 (2)	0.38260 (14)	0.0199 (6)
C15A	0.6496 (2)	0.91896 (19)	0.31704 (14)	0.0190 (6)
C16A	0.6386 (2)	0.9403 (2)	0.24570 (14)	0.0203 (6)
C17A	0.6997 (3)	1.0615 (2)	0.52346 (16)	0.0299 (7)
H17A	0.7488	1.1286	0.5272	0.036*

C18A	0.6569 (3)	1.0513 (2)	0.58107 (15)	0.0292 (7)
H18A	0.6067	0.9841	0.5762	0.035*
C19A	0.6775 (3)	1.1329 (2)	0.65390 (15)	0.0256 (6)
H19A	0.6015	1.1670	0.6512	0.031*
H19B	0.7553	1.1878	0.6613	0.031*
C20A	0.6958 (3)	1.08693 (19)	0.72159 (14)	0.0214 (6)
H20A	0.6226	1.0268	0.7117	0.026*
H20B	0.7772	1.0597	0.7276	0.026*
C21A	0.7024 (3)	1.1674 (2)	0.79478 (14)	0.0219 (6)
H21A	0.6236	1.1980	0.7880	0.026*
H21B	0.7792	1.2252	0.8068	0.026*
C22A	0.7118 (3)	1.1178 (2)	0.86038 (14)	0.0237 (6)
H22A	0.6393	1.0559	0.8460	0.028*
H22B	0.7943	1.0923	0.8693	0.028*
C23A	0.7074 (3)	1.1910 (2)	0.93228 (15)	0.0248 (6)
O1B	1.0145 (2)	1.00042 (15)	0.91661 (11)	0.0400 (5)
O2B	0.9862 (2)	0.85927 (15)	0.95987 (11)	0.0336 (5)
H2P	0.980 (3)	0.906 (2)	0.9987 (14)	0.050*
C1B	1.0025 (2)	0.7018 (2)	0.43238 (15)	0.0218 (6)
C2B	1.0249 (2)	0.6030 (2)	0.43784 (15)	0.0237 (6)
H2B	1.0365	0.5880	0.4853	0.028*
C3B	1.0308 (2)	0.5264 (2)	0.37656 (15)	0.0236 (6)
H3B	1.0465	0.4602	0.3826	0.028*
C4B	1.0140 (2)	0.5448 (2)	0.30571 (15)	0.0215 (6)
C5B	1.0173 (3)	0.4662 (2)	0.24065 (15)	0.0256 (6)
H5B	1.0297	0.3987	0.2454	0.031*
C6B	1.0032 (3)	0.4859 (2)	0.17310 (16)	0.0274 (6)
H6B	1.0057	0.4320	0.1311	0.033*
C7B	0.9844 (2)	0.5867 (2)	0.16315 (15)	0.0235 (6)
C8B	0.9707 (3)	0.6100 (2)	0.09403 (16)	0.0311 (7)
H8B	0.9738	0.5575	0.0514	0.037*
C9B	0.9528 (3)	0.7079 (2)	0.08623 (16)	0.0310 (7)
H9B	0.9438	0.7219	0.0386	0.037*
C10B	0.9478 (3)	0.7860 (2)	0.14783 (15)	0.0269 (6)
H10B	0.9352	0.8530	0.1419	0.032*
C11B	0.9612 (2)	0.7668 (2)	0.21823 (15)	0.0226 (6)
C12B	0.9575 (3)	0.8450 (2)	0.28320 (15)	0.0245 (6)
H12B	0.9458	0.9127	0.2785	0.029*
C13B	0.9702 (2)	0.8255 (2)	0.35100 (15)	0.0234 (6)
H13B	0.9671	0.8797	0.3926	0.028*
C14B	0.9885 (2)	0.7246 (2)	0.36191 (15)	0.0203 (6)
C15B	0.9934 (2)	0.6457 (2)	0.29844 (14)	0.0193 (6)
C16B	0.9798 (2)	0.6661 (2)	0.22665 (14)	0.0198 (6)
C17B	0.9926 (3)	0.7791 (2)	0.49945 (16)	0.0309 (7)
H17B	0.9586	0.8381	0.4901	0.037*
C18B	1.0226 (4)	0.7777 (3)	0.56672 (18)	0.0535 (10)
H18B	1.0583	0.7193	0.5758	0.064*
C19B	1.0111 (3)	0.8540 (2)	0.63549 (16)	0.0334 (7)
H19C	0.9291	0.8792	0.6229	0.040*

H19D	1.0843	0.9157	0.6513	0.040*
C20B	1.0123 (3)	0.8049 (2)	0.70078 (15)	0.0267 (6)
H20C	0.9357	0.7460	0.6859	0.032*
H20D	1.0914	0.7752	0.7109	0.032*
C21B	1.0097 (3)	0.8827 (2)	0.77258 (14)	0.0251 (6)
H21C	0.9310	0.9129	0.7626	0.030*
H21D	1.0868	0.9412	0.7880	0.030*
C22B	1.0095 (3)	0.8319 (2)	0.83661 (15)	0.0259 (6)
H22C	0.9338	0.7721	0.8204	0.031*
H22D	1.0894	0.8032	0.8471	0.031*
C23B	1.0035 (3)	0.9059 (2)	0.90779 (15)	0.0260 (6)
O1C	0.6907 (2)	0.28109 (14)	0.10986 (11)	0.0331 (5)
O2C	0.6698 (2)	0.41463 (15)	0.05805 (11)	0.0333 (5)
H2Q	0.686 (3)	0.371 (2)	0.0220 (15)	0.050*
C1C	0.6603 (2)	0.5787 (2)	0.58619 (15)	0.0215 (6)
C2C	0.6594 (3)	0.6831 (2)	0.58354 (15)	0.0244 (6)
H2C	0.6584	0.7003	0.5375	0.029*
C3C	0.6598 (3)	0.7614 (2)	0.64555 (15)	0.0253 (6)
H3C	0.6584	0.8309	0.6414	0.030*
C4C	0.6622 (2)	0.7396 (2)	0.71438 (15)	0.0221 (6)
C5C	0.6637 (3)	0.8190 (2)	0.78027 (15)	0.0249 (6)
H5C	0.6615	0.8887	0.7770	0.030*
C6C	0.6683 (3)	0.7973 (2)	0.84681 (15)	0.0252 (6)
H6C	0.6701	0.8520	0.8894	0.030*
C7C	0.6705 (3)	0.6923 (2)	0.85436 (15)	0.0241 (6)
C8C	0.6765 (3)	0.6669 (2)	0.92237 (15)	0.0283 (6)
H8C	0.6799	0.7206	0.9659	0.034*
C9C	0.6775 (3)	0.5650 (2)	0.92765 (16)	0.0300 (7)
H9C	0.6822	0.5497	0.9746	0.036*
C10C	0.6719 (3)	0.4855 (2)	0.86485 (15)	0.0276 (6)
H10C	0.6722	0.4158	0.8689	0.033*
C11C	0.6658 (2)	0.5068 (2)	0.79512 (15)	0.0224 (6)
C12C	0.6606 (3)	0.4266 (2)	0.72900 (15)	0.0232 (6)
H12C	0.6585	0.3562	0.7319	0.028*
C13C	0.6589 (2)	0.4486 (2)	0.66270 (15)	0.0226 (6)
H13C	0.6563	0.3933	0.6203	0.027*
C14C	0.6607 (2)	0.5538 (2)	0.65459 (14)	0.0194 (6)
C15C	0.6627 (2)	0.63459 (19)	0.71920 (14)	0.0185 (5)
C16C	0.6667 (2)	0.6115 (2)	0.78970 (14)	0.0205 (6)
C17C	0.6560 (3)	0.4983 (2)	0.51713 (15)	0.0234 (6)
H17C	0.6112	0.4286	0.5108	0.028*
C18C	0.7091 (3)	0.5148 (2)	0.46341 (15)	0.0239 (6)
H18C	0.7573	0.5836	0.4707	0.029*
C19C	0.6997 (3)	0.4343 (2)	0.39215 (14)	0.0237 (6)
H19E	0.6261	0.3750	0.3836	0.028*
H19F	0.7805	0.4062	0.3977	0.028*
C20C	0.6798 (2)	0.47802 (19)	0.32339 (14)	0.0210 (6)
H20E	0.5960	0.5017	0.3158	0.025*
H20F	0.7502	0.5403	0.3333	0.025*

C21C	0.6791 (3)	0.3979 (2)	0.25162 (14)	0.0214 (6)
H21E	0.7603	0.3708	0.2600	0.026*
H21F	0.6050	0.3377	0.2396	0.026*
C22C	0.6679 (3)	0.4450 (2)	0.18521 (14)	0.0223 (6)
H22E	0.5835	0.4673	0.1748	0.027*
H22F	0.7379	0.5088	0.1993	0.027*
C23C	0.6770 (3)	0.3718 (2)	0.11480 (15)	0.0237 (6)

Atomic displacement parameters (Å^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
O1A	0.0587 (14)	0.0231 (11)	0.0227 (11)	0.0115 (9)	0.0163 (10)	0.0075 (9)
O2A	0.0563 (14)	0.0268 (11)	0.0182 (11)	0.0132 (10)	0.0130 (10)	0.0076 (9)
C1A	0.0248 (14)	0.0241 (14)	0.0190 (14)	0.0040 (11)	0.0060 (11)	0.0038 (12)
C2A	0.0362 (16)	0.0286 (15)	0.0199 (15)	0.0088 (12)	0.0081 (12)	0.0120 (13)
C3A	0.0353 (16)	0.0219 (14)	0.0268 (16)	0.0095 (12)	0.0078 (13)	0.0091 (13)
C4A	0.0212 (14)	0.0228 (14)	0.0225 (15)	0.0073 (11)	0.0063 (11)	0.0066 (12)
C5A	0.0285 (15)	0.0217 (14)	0.0281 (16)	0.0078 (11)	0.0081 (12)	0.0045 (12)
C6A	0.0286 (15)	0.0276 (15)	0.0268 (16)	0.0064 (12)	0.0084 (12)	0.0014 (13)
C7A	0.0197 (13)	0.0297 (15)	0.0185 (14)	0.0050 (11)	0.0065 (11)	0.0048 (12)
C8A	0.0337 (16)	0.0374 (17)	0.0203 (15)	0.0076 (13)	0.0103 (12)	0.0032 (13)
C9A	0.0357 (17)	0.0419 (18)	0.0247 (16)	0.0059 (13)	0.0103 (13)	0.0163 (14)
C10A	0.0328 (16)	0.0297 (15)	0.0262 (16)	0.0032 (12)	0.0102 (13)	0.0107 (13)
C11A	0.0241 (14)	0.0246 (14)	0.0193 (14)	0.0027 (11)	0.0067 (11)	0.0062 (12)
C12A	0.0290 (15)	0.0220 (14)	0.0282 (16)	0.0050 (11)	0.0078 (12)	0.0102 (13)
C13A	0.0277 (15)	0.0216 (14)	0.0213 (15)	0.0061 (11)	0.0079 (12)	0.0043 (12)
C14A	0.0192 (13)	0.0222 (13)	0.0184 (14)	0.0053 (10)	0.0055 (11)	0.0047 (11)
C15A	0.0156 (13)	0.0214 (13)	0.0203 (14)	0.0043 (10)	0.0058 (10)	0.0052 (11)
C16A	0.0169 (13)	0.0256 (14)	0.0192 (14)	0.0058 (10)	0.0064 (11)	0.0055 (12)
C17A	0.0389 (17)	0.0257 (15)	0.0235 (16)	0.0039 (12)	0.0071 (13)	0.0066 (13)
C18A	0.0396 (17)	0.0254 (15)	0.0233 (16)	0.0059 (12)	0.0091 (13)	0.0080 (13)
C19A	0.0310 (15)	0.0249 (14)	0.0211 (15)	0.0063 (12)	0.0093 (12)	0.0043 (12)
C20A	0.0252 (14)	0.0190 (13)	0.0202 (14)	0.0050 (10)	0.0072 (11)	0.0040 (11)
C21A	0.0250 (14)	0.0225 (13)	0.0192 (14)	0.0062 (11)	0.0072 (11)	0.0057 (12)
C22A	0.0305 (15)	0.0216 (13)	0.0196 (14)	0.0068 (11)	0.0072 (12)	0.0059 (12)
C23A	0.0270 (15)	0.0269 (15)	0.0217 (15)	0.0050 (11)	0.0067 (12)	0.0089 (12)
O1B	0.0757 (16)	0.0215 (11)	0.0268 (12)	0.0097 (10)	0.0225 (11)	0.0060 (9)
O2B	0.0565 (14)	0.0276 (11)	0.0198 (11)	0.0080 (10)	0.0149 (10)	0.0086 (9)
C1B	0.0195 (13)	0.0273 (14)	0.0180 (14)	0.0038 (11)	0.0049 (11)	0.0056 (12)
C2B	0.0238 (14)	0.0286 (15)	0.0204 (15)	0.0080 (11)	0.0053 (11)	0.0091 (12)
C3B	0.0214 (14)	0.0228 (14)	0.0275 (16)	0.0052 (11)	0.0058 (12)	0.0088 (12)
C4B	0.0162 (13)	0.0240 (14)	0.0229 (15)	0.0026 (10)	0.0048 (11)	0.0049 (12)
C5B	0.0274 (15)	0.0218 (14)	0.0274 (16)	0.0067 (11)	0.0087 (12)	0.0039 (12)
C6B	0.0287 (15)	0.0261 (15)	0.0235 (16)	0.0047 (12)	0.0091 (12)	−0.0021 (12)
C7B	0.0200 (14)	0.0271 (15)	0.0206 (15)	0.0010 (11)	0.0068 (11)	0.0024 (12)
C8B	0.0336 (16)	0.0350 (16)	0.0206 (15)	0.0020 (13)	0.0081 (13)	0.0021 (13)
C9B	0.0345 (16)	0.0401 (17)	0.0199 (15)	0.0040 (13)	0.0072 (12)	0.0134 (14)
C10B	0.0280 (15)	0.0291 (15)	0.0253 (16)	0.0038 (12)	0.0070 (12)	0.0126 (13)

C11B	0.0212 (14)	0.0235 (14)	0.0234 (15)	0.0022 (11)	0.0056 (11)	0.0087 (12)
C12B	0.0276 (15)	0.0212 (14)	0.0267 (16)	0.0064 (11)	0.0081 (12)	0.0089 (12)
C13B	0.0235 (14)	0.0233 (14)	0.0230 (15)	0.0059 (11)	0.0069 (11)	0.0042 (12)
C14B	0.0168 (13)	0.0228 (14)	0.0194 (14)	0.0038 (10)	0.0030 (11)	0.0041 (12)
C15B	0.0141 (12)	0.0227 (14)	0.0202 (14)	0.0025 (10)	0.0050 (10)	0.0048 (12)
C16B	0.0175 (13)	0.0242 (14)	0.0165 (14)	0.0014 (10)	0.0054 (10)	0.0040 (11)
C17B	0.0482 (19)	0.0283 (15)	0.0240 (17)	0.0186 (13)	0.0136 (14)	0.0117 (13)
C18B	0.117 (3)	0.0291 (17)	0.0253 (19)	0.0310 (19)	0.0275 (19)	0.0113 (15)
C19B	0.054 (2)	0.0273 (15)	0.0196 (15)	0.0114 (14)	0.0116 (14)	0.0049 (13)
C20B	0.0342 (16)	0.0261 (14)	0.0199 (15)	0.0077 (12)	0.0054 (12)	0.0076 (12)
C21B	0.0305 (15)	0.0245 (14)	0.0193 (15)	0.0050 (12)	0.0069 (12)	0.0042 (12)
C22B	0.0310 (15)	0.0261 (15)	0.0221 (15)	0.0084 (12)	0.0074 (12)	0.0075 (12)
C23B	0.0307 (15)	0.0267 (15)	0.0207 (15)	0.0039 (12)	0.0072 (12)	0.0074 (12)
O1C	0.0585 (14)	0.0228 (11)	0.0225 (11)	0.0117 (9)	0.0162 (10)	0.0077 (9)
O2C	0.0568 (14)	0.0284 (11)	0.0212 (11)	0.0152 (10)	0.0163 (10)	0.0098 (9)
C1C	0.0195 (13)	0.0235 (14)	0.0207 (15)	0.0039 (11)	0.0054 (11)	0.0049 (12)
C2C	0.0293 (15)	0.0260 (14)	0.0201 (15)	0.0060 (11)	0.0073 (12)	0.0094 (12)
C3C	0.0311 (15)	0.0202 (14)	0.0262 (16)	0.0068 (11)	0.0092 (12)	0.0070 (12)
C4C	0.0242 (14)	0.0202 (13)	0.0231 (15)	0.0062 (11)	0.0068 (11)	0.0069 (12)
C5C	0.0278 (15)	0.0199 (14)	0.0269 (16)	0.0073 (11)	0.0082 (12)	0.0040 (12)
C6C	0.0275 (15)	0.0231 (14)	0.0235 (15)	0.0067 (11)	0.0085 (12)	0.0008 (12)
C7C	0.0240 (14)	0.0264 (14)	0.0215 (15)	0.0048 (11)	0.0069 (11)	0.0054 (12)
C8C	0.0334 (16)	0.0340 (16)	0.0160 (14)	0.0065 (12)	0.0078 (12)	0.0032 (12)
C9C	0.0331 (16)	0.0394 (17)	0.0178 (15)	0.0062 (13)	0.0050 (12)	0.0114 (13)
C10C	0.0330 (16)	0.0300 (15)	0.0236 (16)	0.0083 (12)	0.0095 (12)	0.0120 (13)
C11C	0.0212 (14)	0.0252 (14)	0.0228 (15)	0.0054 (11)	0.0070 (11)	0.0093 (12)
C12C	0.0274 (15)	0.0203 (13)	0.0234 (15)	0.0062 (11)	0.0085 (12)	0.0067 (12)
C13C	0.0268 (14)	0.0183 (13)	0.0217 (15)	0.0052 (11)	0.0088 (12)	0.0009 (11)
C14C	0.0175 (13)	0.0239 (13)	0.0175 (14)	0.0033 (10)	0.0062 (11)	0.0063 (11)
C15C	0.0168 (13)	0.0206 (13)	0.0171 (14)	0.0026 (10)	0.0043 (10)	0.0043 (11)
C16C	0.0176 (13)	0.0242 (14)	0.0193 (14)	0.0039 (11)	0.0049 (11)	0.0054 (12)
C17C	0.0265 (15)	0.0229 (14)	0.0201 (15)	0.0055 (11)	0.0049 (11)	0.0057 (12)
C18C	0.0277 (15)	0.0216 (13)	0.0208 (15)	0.0044 (11)	0.0056 (12)	0.0040 (11)
C19C	0.0298 (15)	0.0239 (14)	0.0194 (14)	0.0081 (11)	0.0085 (12)	0.0062 (12)
C20C	0.0234 (14)	0.0218 (13)	0.0188 (14)	0.0054 (11)	0.0070 (11)	0.0057 (11)
C21C	0.0230 (14)	0.0229 (13)	0.0179 (14)	0.0059 (11)	0.0048 (11)	0.0050 (11)
C22C	0.0264 (14)	0.0231 (14)	0.0177 (14)	0.0050 (11)	0.0071 (11)	0.0050 (12)
C23C	0.0264 (14)	0.0255 (15)	0.0183 (14)	0.0030 (11)	0.0054 (11)	0.0063 (12)

Geometric parameters (Å, °)

O1A—C23A	1.224 (3)	C11B—C16B	1.425 (4)
O2A—C23A	1.319 (3)	C11B—C12B	1.432 (4)
O2A—H2O	0.875 (18)	C12B—C13B	1.350 (4)
C1A—C2A	1.398 (4)	C12B—H12B	0.9500
C1A—C14A	1.416 (4)	C13B—C14B	1.441 (3)
C1A—C17A	1.472 (4)	C13B—H13B	0.9500
C2A—C3A	1.380 (4)	C14B—C15B	1.422 (4)
C2A—H2A	0.9500	C15B—C16B	1.428 (3)

C3A—C4A	1.399 (4)	C17B—C18B	1.248 (4)
C3A—H3A	0.9500	C17B—H17B	0.9500
C4A—C5A	1.431 (4)	C18B—C19B	1.500 (4)
C4A—C15A	1.431 (3)	C18B—H18B	0.9500
C5A—C6A	1.352 (4)	C19B—C20B	1.526 (4)
C5A—H5A	0.9500	C19B—H19C	0.9900
C6A—C7A	1.434 (4)	C19B—H19D	0.9900
C6A—H6A	0.9500	C20B—C21B	1.519 (4)
C7A—C8A	1.398 (4)	C20B—H20C	0.9900
C7A—C16A	1.423 (4)	C20B—H20D	0.9900
C8A—C9A	1.391 (4)	C21B—C22B	1.520 (3)
C8A—H8A	0.9500	C21B—H21C	0.9900
C9A—C10A	1.383 (4)	C21B—H21D	0.9900
C9A—H9A	0.9500	C22B—C23B	1.498 (4)
C10A—C11A	1.399 (4)	C22B—H22C	0.9900
C10A—H10A	0.9500	C22B—H22D	0.9900
C11A—C16A	1.420 (3)	O1C—C23C	1.224 (3)
C11A—C12A	1.437 (4)	O2C—C23C	1.322 (3)
C12A—C13A	1.353 (4)	O2C—H2Q	0.859 (18)
C12A—H12A	0.9500	C1C—C2C	1.405 (4)
C13A—C14A	1.435 (3)	C1C—C14C	1.410 (3)
C13A—H13A	0.9500	C1C—C17C	1.476 (4)
C14A—C15A	1.419 (4)	C2C—C3C	1.380 (4)
C15A—C16A	1.428 (4)	C2C—H2C	0.9500
C17A—C18A	1.304 (4)	C3C—C4C	1.396 (4)
C17A—H17A	0.9500	C3C—H3C	0.9500
C18A—C19A	1.497 (4)	C4C—C15C	1.424 (3)
C18A—H18A	0.9500	C4C—C5C	1.435 (4)
C19A—C20A	1.531 (3)	C5C—C6C	1.350 (4)
C19A—H19A	0.9900	C5C—H5C	0.9500
C19A—H19B	0.9900	C6C—C7C	1.442 (4)
C20A—C21A	1.526 (4)	C6C—H6C	0.9500
C20A—H20A	0.9900	C7C—C8C	1.397 (4)
C20A—H20B	0.9900	C7C—C16C	1.423 (4)
C21A—C22A	1.527 (3)	C8C—C9C	1.387 (4)
C21A—H21A	0.9900	C8C—H8C	0.9500
C21A—H21B	0.9900	C9C—C10C	1.383 (4)
C22A—C23A	1.498 (4)	C9C—H9C	0.9500
C22A—H22A	0.9900	C10C—C11C	1.404 (4)
C22A—H22B	0.9900	C10C—H10C	0.9500
O1B—C23B	1.217 (3)	C11C—C16C	1.421 (3)
O2B—C23B	1.314 (3)	C11C—C12C	1.433 (4)
O2B—H2P	0.872 (18)	C12C—C13C	1.351 (4)
C1B—C2B	1.396 (4)	C12C—H12C	0.9500
C1B—C14B	1.417 (4)	C13C—C14C	1.444 (3)
C1B—C17B	1.477 (4)	C13C—H13C	0.9500
C2B—C3B	1.379 (4)	C14C—C15C	1.427 (4)
C2B—H2B	0.9500	C15C—C16C	1.432 (3)
C3B—C4B	1.397 (4)	C17C—C18C	1.320 (4)

C3B—H3B	0.9500	C17C—H17C	0.9500
C4B—C15B	1.426 (4)	C18C—C19C	1.492 (4)
C4B—C5B	1.434 (4)	C18C—H18C	0.9500
C5B—C6B	1.345 (4)	C19C—C20C	1.531 (3)
C5B—H5B	0.9500	C19C—H19E	0.9900
C6B—C7B	1.435 (4)	C19C—H19F	0.9900
C6B—H6B	0.9500	C20C—C21C	1.522 (4)
C7B—C8B	1.396 (4)	C20C—H20E	0.9900
C7B—C16B	1.424 (4)	C20C—H20F	0.9900
C8B—C9B	1.383 (4)	C21C—C22C	1.520 (3)
C8B—H8B	0.9500	C21C—H21E	0.9900
C9B—C10B	1.391 (4)	C21C—H21F	0.9900
C9B—H9B	0.9500	C22C—C23C	1.494 (4)
C10B—C11B	1.396 (4)	C22C—H22E	0.9900
C10B—H10B	0.9500	C22C—H22F	0.9900
C23A—O2A—H2O	110 (2)	C1B—C14B—C13B	123.1 (2)
C2A—C1A—C14A	118.5 (2)	C15B—C14B—C13B	117.5 (2)
C2A—C1A—C17A	119.6 (2)	C14B—C15B—C4B	120.4 (2)
C14A—C1A—C17A	121.9 (2)	C14B—C15B—C16B	120.8 (2)
C3A—C2A—C1A	122.4 (2)	C4B—C15B—C16B	118.8 (2)
C3A—C2A—H2A	118.8	C7B—C16B—C11B	119.5 (2)
C1A—C2A—H2A	118.8	C7B—C16B—C15B	120.6 (2)
C2A—C3A—C4A	120.8 (2)	C11B—C16B—C15B	119.8 (2)
C2A—C3A—H3A	119.6	C18B—C17B—C1B	129.0 (3)
C4A—C3A—H3A	119.6	C18B—C17B—H17B	115.5
C3A—C4A—C5A	122.6 (2)	C1B—C17B—H17B	115.5
C3A—C4A—C15A	118.2 (2)	C17B—C18B—C19B	130.0 (3)
C5A—C4A—C15A	119.2 (2)	C17B—C18B—H18B	115.0
C6A—C5A—C4A	121.7 (2)	C19B—C18B—H18B	115.0
C6A—C5A—H5A	119.1	C18B—C19B—C20B	112.4 (2)
C4A—C5A—H5A	119.1	C18B—C19B—H19C	109.1
C5A—C6A—C7A	120.9 (3)	C20B—C19B—H19C	109.1
C5A—C6A—H6A	119.5	C18B—C19B—H19D	109.1
C7A—C6A—H6A	119.5	C20B—C19B—H19D	109.1
C8A—C7A—C16A	118.6 (2)	H19C—C19B—H19D	107.9
C8A—C7A—C6A	122.7 (3)	C21B—C20B—C19B	113.2 (2)
C16A—C7A—C6A	118.7 (2)	C21B—C20B—H20C	108.9
C9A—C8A—C7A	121.3 (3)	C19B—C20B—H20C	108.9
C9A—C8A—H8A	119.3	C21B—C20B—H20D	108.9
C7A—C8A—H8A	119.3	C19B—C20B—H20D	108.9
C10A—C9A—C8A	120.5 (3)	H20C—C20B—H20D	107.7
C10A—C9A—H9A	119.8	C20B—C21B—C22B	112.3 (2)
C8A—C9A—H9A	119.8	C20B—C21B—H21C	109.1
C9A—C10A—C11A	120.2 (3)	C22B—C21B—H21C	109.1
C9A—C10A—H10A	119.9	C20B—C21B—H21D	109.1
C11A—C10A—H10A	119.9	C22B—C21B—H21D	109.1
C10A—C11A—C16A	119.9 (2)	H21C—C21B—H21D	107.9
C10A—C11A—C12A	122.0 (2)	C23B—C22B—C21B	113.8 (2)
C16A—C11A—C12A	118.1 (2)	C23B—C22B—H22C	108.8

C13A—C12A—C11A	121.8 (2)	C21B—C22B—H22C	108.8
C13A—C12A—H12A	119.1	C23B—C22B—H22D	108.8
C11A—C12A—H12A	119.1	C21B—C22B—H22D	108.8
C12A—C13A—C14A	121.5 (2)	H22C—C22B—H22D	107.7
C12A—C13A—H13A	119.2	O1B—C23B—O2B	123.2 (3)
C14A—C13A—H13A	119.2	O1B—C23B—C22B	123.0 (2)
C1A—C14A—C15A	119.6 (2)	O2B—C23B—C22B	113.8 (2)
C1A—C14A—C13A	122.6 (2)	C23C—O2C—H2Q	107 (2)
C15A—C14A—C13A	117.8 (2)	C2C—C1C—C14C	118.4 (2)
C14A—C15A—C16A	120.8 (2)	C2C—C1C—C17C	119.3 (2)
C14A—C15A—C4A	120.5 (2)	C14C—C1C—C17C	122.2 (2)
C16A—C15A—C4A	118.7 (2)	C3C—C2C—C1C	122.2 (2)
C11A—C16A—C7A	119.6 (2)	C3C—C2C—H2C	118.9
C11A—C16A—C15A	119.8 (2)	C1C—C2C—H2C	118.9
C7A—C16A—C15A	120.7 (2)	C2C—C3C—C4C	120.7 (2)
C18A—C17A—C1A	126.0 (3)	C2C—C3C—H3C	119.7
C18A—C17A—H17A	117.0	C4C—C3C—H3C	119.7
C1A—C17A—H17A	117.0	C3C—C4C—C15C	118.7 (2)
C17A—C18A—C19A	127.7 (3)	C3C—C4C—C5C	122.4 (2)
C17A—C18A—H18A	116.1	C15C—C4C—C5C	118.9 (2)
C19A—C18A—H18A	116.1	C6C—C5C—C4C	121.8 (2)
C18A—C19A—C20A	112.7 (2)	C6C—C5C—H5C	119.1
C18A—C19A—H19A	109.0	C4C—C5C—H5C	119.1
C20A—C19A—H19A	109.0	C5C—C6C—C7C	121.1 (2)
C18A—C19A—H19B	109.0	C5C—C6C—H6C	119.5
C20A—C19A—H19B	109.0	C7C—C6C—H6C	119.5
H19A—C19A—H19B	107.8	C8C—C7C—C16C	118.7 (2)
C21A—C20A—C19A	112.9 (2)	C8C—C7C—C6C	122.8 (2)
C21A—C20A—H20A	109.0	C16C—C7C—C6C	118.4 (2)
C19A—C20A—H20A	109.0	C9C—C8C—C7C	121.4 (3)
C21A—C20A—H20B	109.0	C9C—C8C—H8C	119.3
C19A—C20A—H20B	109.0	C7C—C8C—H8C	119.3
H20A—C20A—H20B	107.8	C10C—C9C—C8C	120.3 (3)
C20A—C21A—C22A	111.9 (2)	C10C—C9C—H9C	119.9
C20A—C21A—H21A	109.2	C8C—C9C—H9C	119.9
C22A—C21A—H21A	109.2	C9C—C10C—C11C	120.6 (3)
C20A—C21A—H21B	109.2	C9C—C10C—H10C	119.7
C22A—C21A—H21B	109.2	C11C—C10C—H10C	119.7
H21A—C21A—H21B	107.9	C10C—C11C—C16C	119.3 (2)
C23A—C22A—C21A	114.2 (2)	C10C—C11C—C12C	122.1 (2)
C23A—C22A—H22A	108.7	C16C—C11C—C12C	118.5 (2)
C21A—C22A—H22A	108.7	C13C—C12C—C11C	121.7 (2)
C23A—C22A—H22B	108.7	C13C—C12C—H12C	119.2
C21A—C22A—H22B	108.7	C11C—C12C—H12C	119.2
H22A—C22A—H22B	107.6	C12C—C13C—C14C	121.8 (2)
O1A—C23A—O2A	123.1 (3)	C12C—C13C—H13C	119.1
O1A—C23A—C22A	123.5 (2)	C14C—C13C—H13C	119.1
O2A—C23A—C22A	113.5 (2)	C1C—C14C—C15C	119.7 (2)
C23B—O2B—H2P	109 (2)	C1C—C14C—C13C	122.7 (2)

C2B—C1B—C14B	118.7 (2)	C15C—C14C—C13C	117.6 (2)
C2B—C1B—C17B	119.5 (2)	C4C—C15C—C14C	120.2 (2)
C14B—C1B—C17B	121.8 (2)	C4C—C15C—C16C	119.3 (2)
C3B—C2B—C1B	122.1 (2)	C14C—C15C—C16C	120.5 (2)
C3B—C2B—H2B	119.0	C11C—C16C—C7C	119.6 (2)
C1B—C2B—H2B	119.0	C11C—C16C—C15C	119.9 (2)
C2B—C3B—C4B	121.0 (2)	C7C—C16C—C15C	120.5 (2)
C2B—C3B—H3B	119.5	C18C—C17C—C1C	125.7 (2)
C4B—C3B—H3B	119.5	C18C—C17C—H17C	117.2
C3B—C4B—C15B	118.4 (2)	C1C—C17C—H17C	117.2
C3B—C4B—C5B	122.3 (2)	C17C—C18C—C19C	125.5 (2)
C15B—C4B—C5B	119.3 (2)	C17C—C18C—H18C	117.2
C6B—C5B—C4B	121.5 (2)	C19C—C18C—H18C	117.2
C6B—C5B—H5B	119.2	C18C—C19C—C20C	113.1 (2)
C4B—C5B—H5B	119.2	C18C—C19C—H19E	109.0
C5B—C6B—C7B	121.3 (3)	C20C—C19C—H19E	109.0
C5B—C6B—H6B	119.3	C18C—C19C—H19F	109.0
C7B—C6B—H6B	119.3	C20C—C19C—H19F	109.0
C8B—C7B—C16B	118.8 (2)	H19E—C19C—H19F	107.8
C8B—C7B—C6B	122.8 (3)	C21C—C20C—C19C	113.1 (2)
C16B—C7B—C6B	118.4 (2)	C21C—C20C—H20E	109.0
C9B—C8B—C7B	121.4 (3)	C19C—C20C—H20E	109.0
C9B—C8B—H8B	119.3	C21C—C20C—H20F	109.0
C7B—C8B—H8B	119.3	C19C—C20C—H20F	109.0
C8B—C9B—C10B	120.3 (3)	H20E—C20C—H20F	107.8
C8B—C9B—H9B	119.9	C22C—C21C—C20C	112.2 (2)
C10B—C9B—H9B	119.9	C22C—C21C—H21E	109.2
C9B—C10B—C11B	120.6 (3)	C20C—C21C—H21E	109.2
C9B—C10B—H10B	119.7	C22C—C21C—H21F	109.2
C11B—C10B—H10B	119.7	C20C—C21C—H21F	109.2
C10B—C11B—C16B	119.4 (2)	H21E—C21C—H21F	107.9
C10B—C11B—C12B	122.4 (2)	C23C—C22C—C21C	114.2 (2)
C16B—C11B—C12B	118.2 (2)	C23C—C22C—H22E	108.7
C13B—C12B—C11B	121.9 (2)	C21C—C22C—H22E	108.7
C13B—C12B—H12B	119.0	C23C—C22C—H22F	108.7
C11B—C12B—H12B	119.0	C21C—C22C—H22F	108.7
C12B—C13B—C14B	121.7 (2)	H22E—C22C—H22F	107.6
C12B—C13B—H13B	119.1	O1C—C23C—O2C	122.9 (2)
C14B—C13B—H13B	119.1	O1C—C23C—C22C	123.6 (2)
C1B—C14B—C15B	119.4 (2)	O2C—C23C—C22C	113.5 (2)
C14A—C1A—C2A—C3A	0.2 (4)	C1B—C14B—C15B—C16B	−179.9 (2)
C17A—C1A—C2A—C3A	−178.7 (3)	C13B—C14B—C15B—C16B	−0.4 (3)
C1A—C2A—C3A—C4A	1.3 (4)	C3B—C4B—C15B—C14B	−0.8 (4)
C2A—C3A—C4A—C5A	178.1 (3)	C5B—C4B—C15B—C14B	179.4 (2)
C2A—C3A—C4A—C15A	−0.8 (4)	C3B—C4B—C15B—C16B	178.3 (2)
C3A—C4A—C5A—C6A	−177.6 (3)	C5B—C4B—C15B—C16B	−1.5 (3)
C15A—C4A—C5A—C6A	1.2 (4)	C8B—C7B—C16B—C11B	0.2 (4)
C4A—C5A—C6A—C7A	−0.9 (4)	C6B—C7B—C16B—C11B	−180.0 (2)
C5A—C6A—C7A—C8A	−179.8 (3)	C8B—C7B—C16B—C15B	−180.0 (2)

C5A—C6A—C7A—C16A	−0.8 (4)	C6B—C7B—C16B—C15B	−0.1 (4)
C16A—C7A—C8A—C9A	−0.2 (4)	C10B—C11B—C16B—C7B	0.0 (4)
C6A—C7A—C8A—C9A	178.8 (3)	C12B—C11B—C16B—C7B	−179.8 (2)
C7A—C8A—C9A—C10A	−1.3 (4)	C10B—C11B—C16B—C15B	−179.9 (2)
C8A—C9A—C10A—C11A	1.9 (4)	C12B—C11B—C16B—C15B	0.4 (3)
C9A—C10A—C11A—C16A	−0.8 (4)	C14B—C15B—C16B—C7B	−179.8 (2)
C9A—C10A—C11A—C12A	−179.3 (3)	C4B—C15B—C16B—C7B	1.1 (3)
C10A—C11A—C12A—C13A	−178.2 (3)	C14B—C15B—C16B—C11B	0.1 (3)
C16A—C11A—C12A—C13A	3.3 (4)	C4B—C15B—C16B—C11B	−179.0 (2)
C11A—C12A—C13A—C14A	−0.6 (4)	C2B—C1B—C17B—C18B	13.3 (5)
C2A—C1A—C14A—C15A	−2.1 (4)	C14B—C1B—C17B—C18B	−167.4 (4)
C17A—C1A—C14A—C15A	176.8 (2)	C1B—C17B—C18B—C19B	−178.6 (3)
C2A—C1A—C14A—C13A	176.0 (2)	C17B—C18B—C19B—C20B	159.4 (4)
C17A—C1A—C14A—C13A	−5.1 (4)	C18B—C19B—C20B—C21B	176.2 (3)
C12A—C13A—C14A—C1A	178.7 (3)	C19B—C20B—C21B—C22B	179.4 (2)
C12A—C13A—C14A—C15A	−3.2 (4)	C20B—C21B—C22B—C23B	−178.5 (2)
C1A—C14A—C15A—C16A	−177.5 (2)	C21B—C22B—C23B—O1B	−8.9 (4)
C13A—C14A—C15A—C16A	4.2 (4)	C21B—C22B—C23B—O2B	171.5 (2)
C1A—C14A—C15A—C4A	2.7 (4)	C14C—C1C—C2C—C3C	0.5 (4)
C13A—C14A—C15A—C4A	−175.6 (2)	C17C—C1C—C2C—C3C	178.3 (2)
C3A—C4A—C15A—C14A	−1.2 (4)	C1C—C2C—C3C—C4C	0.5 (4)
C5A—C4A—C15A—C14A	179.9 (2)	C2C—C3C—C4C—C15C	−0.7 (4)
C3A—C4A—C15A—C16A	179.0 (2)	C2C—C3C—C4C—C5C	179.5 (2)
C5A—C4A—C15A—C16A	0.1 (4)	C3C—C4C—C5C—C6C	−178.8 (3)
C10A—C11A—C16A—C7A	−0.8 (4)	C15C—C4C—C5C—C6C	1.4 (4)
C12A—C11A—C16A—C7A	177.8 (2)	C4C—C5C—C6C—C7C	−0.6 (4)
C10A—C11A—C16A—C15A	179.3 (2)	C5C—C6C—C7C—C8C	179.3 (3)
C12A—C11A—C16A—C15A	−2.1 (4)	C5C—C6C—C7C—C16C	−0.5 (4)
C8A—C7A—C16A—C11A	1.3 (4)	C16C—C7C—C8C—C9C	−0.6 (4)
C6A—C7A—C16A—C11A	−177.8 (2)	C6C—C7C—C8C—C9C	179.6 (3)
C8A—C7A—C16A—C15A	−178.8 (2)	C7C—C8C—C9C—C10C	−0.3 (4)
C6A—C7A—C16A—C15A	2.1 (4)	C8C—C9C—C10C—C11C	0.4 (4)
C14A—C15A—C16A—C11A	−1.6 (4)	C9C—C10C—C11C—C16C	0.6 (4)
C4A—C15A—C16A—C11A	178.2 (2)	C9C—C10C—C11C—C12C	179.6 (3)
C14A—C15A—C16A—C7A	178.5 (2)	C10C—C11C—C12C—C13C	−177.9 (3)
C4A—C15A—C16A—C7A	−1.7 (4)	C16C—C11C—C12C—C13C	1.1 (4)
C2A—C1A—C17A—C18A	−35.6 (4)	C11C—C12C—C13C—C14C	−0.6 (4)
C14A—C1A—C17A—C18A	145.6 (3)	C2C—C1C—C14C—C15C	−1.2 (4)
C1A—C17A—C18A—C19A	179.0 (3)	C17C—C1C—C14C—C15C	−178.9 (2)
C17A—C18A—C19A—C20A	−143.0 (3)	C2C—C1C—C14C—C13C	178.7 (2)
C18A—C19A—C20A—C21A	−173.9 (2)	C17C—C1C—C14C—C13C	0.9 (4)
C19A—C20A—C21A—C22A	176.3 (2)	C12C—C13C—C14C—C1C	179.3 (2)
C20A—C21A—C22A—C23A	−175.2 (2)	C12C—C13C—C14C—C15C	−0.8 (4)
C21A—C22A—C23A—O1A	−2.3 (4)	C3C—C4C—C15C—C14C	0.0 (4)
C21A—C22A—C23A—O2A	176.7 (2)	C5C—C4C—C15C—C14C	179.8 (2)
C14B—C1B—C2B—C3B	−1.5 (4)	C3C—C4C—C15C—C16C	179.3 (2)
C17B—C1B—C2B—C3B	177.8 (2)	C5C—C4C—C15C—C16C	−0.9 (4)
C1B—C2B—C3B—C4B	−0.2 (4)	C1C—C14C—C15C—C4C	1.0 (4)
C2B—C3B—C4B—C15B	1.4 (4)	C13C—C14C—C15C—C4C	−178.9 (2)

C2B—C3B—C4B—C5B	−178.9 (2)	C1C—C14C—C15C—C16C	−178.3 (2)
C3B—C4B—C5B—C6B	−178.8 (3)	C13C—C14C—C15C—C16C	1.8 (3)
C15B—C4B—C5B—C6B	0.9 (4)	C10C—C11C—C16C—C7C	−1.6 (4)
C4B—C5B—C6B—C7B	0.1 (4)	C12C—C11C—C16C—C7C	179.4 (2)
C5B—C6B—C7B—C8B	179.3 (3)	C10C—C11C—C16C—C15C	178.9 (2)
C5B—C6B—C7B—C16B	−0.5 (4)	C12C—C11C—C16C—C15C	−0.1 (4)
C16B—C7B—C8B—C9B	−0.1 (4)	C8C—C7C—C16C—C11C	1.6 (4)
C6B—C7B—C8B—C9B	−180.0 (3)	C6C—C7C—C16C—C11C	−178.6 (2)
C7B—C8B—C9B—C10B	−0.1 (4)	C8C—C7C—C16C—C15C	−178.9 (2)
C8B—C9B—C10B—C11B	0.2 (4)	C6C—C7C—C16C—C15C	0.9 (4)
C9B—C10B—C11B—C16B	−0.1 (4)	C4C—C15C—C16C—C11C	179.3 (2)
C9B—C10B—C11B—C12B	179.6 (3)	C14C—C15C—C16C—C11C	−1.4 (4)
C10B—C11B—C12B—C13B	179.8 (3)	C4C—C15C—C16C—C7C	−0.2 (4)
C16B—C11B—C12B—C13B	−0.5 (4)	C14C—C15C—C16C—C7C	179.1 (2)
C11B—C12B—C13B—C14B	0.1 (4)	C2C—C1C—C17C—C18C	33.4 (4)
C2B—C1B—C14B—C15B	2.0 (4)	C14C—C1C—C17C—C18C	−148.9 (3)
C17B—C1B—C14B—C15B	−177.4 (2)	C1C—C17C—C18C—C19C	−177.2 (2)
C2B—C1B—C14B—C13B	−177.5 (2)	C17C—C18C—C19C—C20C	139.5 (3)
C17B—C1B—C14B—C13B	3.2 (4)	C18C—C19C—C20C—C21C	176.3 (2)
C12B—C13B—C14B—C1B	179.8 (2)	C19C—C20C—C21C—C22C	−176.3 (2)
C12B—C13B—C14B—C15B	0.3 (4)	C20C—C21C—C22C—C23C	175.6 (2)
C1B—C14B—C15B—C4B	−0.8 (4)	C21C—C22C—C23C—O1C	0.8 (4)
C13B—C14B—C15B—C4B	178.7 (2)	C21C—C22C—C23C—O2C	−178.7 (2)

Hydrogen-bond geometry (Å, °)

Cg1 and Cg2 are the centroids of the C1A–C4A,C15A,C14A and C7C–C11C,C16C rings, respectively.

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
O2A—H2O···O1C^{i}	0.88 (2)	1.79 (2)	2.661 (3)	177 (3)
O2B—H2P···O1B^{ii}	0.87 (2)	1.78 (2)	2.642 (3)	173 (3)
O2C—H2Q···O1A^{iii}	0.86 (2)	1.78 (2)	2.636 (3)	172 (3)
C10C—H10C···O1A^{iv}	0.95	2.46	3.336 (3)	154
C10B—H10B···O1B^{v}	0.95	2.51	3.354 (3)	148
C10A—H10A···O1C^{vi}	0.95	2.51	3.360 (3)	150
C22C—H22E···Cg2^{vii}	0.99	2.63	3.500 (4)	147
C19A—H19A···Cg1^{viii}	0.99	2.72	3.511 (4)	137

Symmetry codes: (i) *x*, *y*+1, *z*+1; (ii) −*x*+2, −*y*+2, −*z*+2; (iii) *x*, *y*−1, *z*−1; (iv) *x*, *y*−1, *z*; (v) −*x*+2, −*y*+2, −*z*+1; (vi) *x*, *y*+1, *z*; (vii) −*x*+1, −*y*+1, −*z*+1; (viii) −*x*+1, −*y*+2, −*z*+1.

Fig. 1

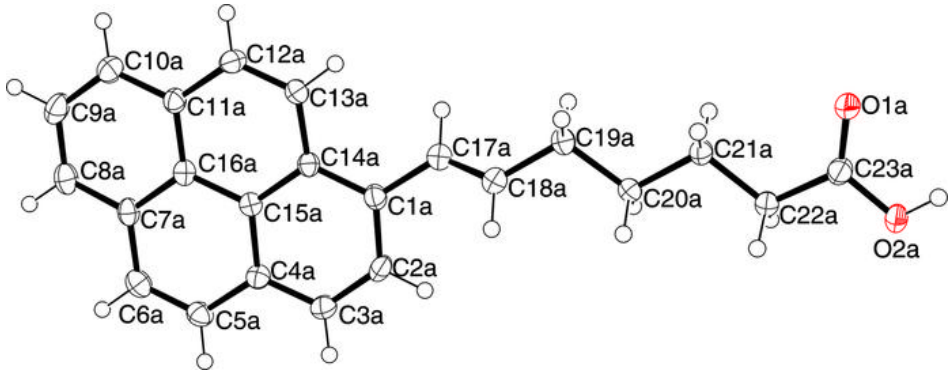
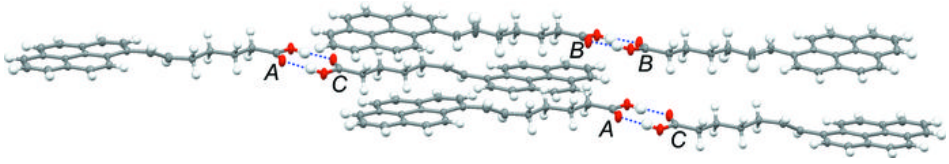

C10a
C12a
C13a
C9a
C11a
C8a
C16a
C14a
C17a
C19a
C21a
O1a
C23a
C18a
C20a
C22a
C1a
C7a
C15a
O2a
C4a
C2a
C6a
C5a
C3a

Fig. 2



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2,3,6,7-Tetrakis(bromomethyl)-naphthalene

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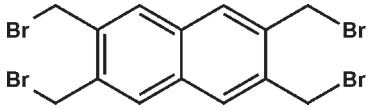
Key indicators: single-crystal X-ray study; T = 100 K; mean σ(C–C) = 0.003 Å; R factor = 0.016; wR factor = 0.034; data-to-parameter ratio = 25.9.

The title compound, $C_{14}H_{12}Br_4$, crystallizes with imposed inversion symmetry. In the crystal, the molecules pack in layers parallel to (10$\bar{1}$). The layers involve two Br···Br and one H···Br contact. Between the layers, one contact each of types Br···Br, H···Br and Br···π is observed.

Related literature

For the use of 2,3,6,7-tetrakis(bromomethyl)naphthalene in the preparation of cyclophanes, see: Otsubo *et al.* (1983, 1989); Yano *et al.* (1999); Skibiński *et al.* (2009). For its applications in the synthesis of hydrogen-bonded molecular capsules, see: Valdes *et al.* (1995); Rivera *et al.* (2001). For reviews on halogen–halogen contacts and 'weak' hydrogen bonding, see: Desiraju & Steiner (1999); Metrangolo & Resnati (2001); Metrangolo *et al.* (2008); Rissanen (2008). For the X-ray structures of the full series of ten isomeric bis(bromomethyl)naphthalenes, see: Jones & Kuś (2010). For the X-ray structures of two isomeric tetrakis(bromomethyl)benzene derivatives, see: Jones & Kuś (2007).



Experimental

Crystal data

$C_{14}H_{12}Br_4$
M_r = 499.88
Triclinic, $P\bar{1}$
a = 6.6144 (2) Å
b = 7.1770 (2) Å
c = 8.7761 (3) Å
α = 84.744 (3)°
β = 78.251 (3)°
γ = 64.555 (3)°
V = 368.32 (2) Å^3
Z = 1
Mo $K\alpha$ radiation
μ = 10.91 mm^{-1}
T = 100 K
0.20 × 0.06 × 0.04 mm

Data collection

Oxford Diffraction Xcalibur Eos diffractometer
Absorption correction: multi-scan (*CrysAlis PRO*; Oxford Diffraction, 2009)
T_{min} = 0.356, T_{max} = 1.000
17701 measured reflections
2122 independent reflections
1716 reflections with $I > 2\sigma(I)$
R_{int} = 0.031

Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.016
$wR(F^2)$ = 0.034
S = 0.92
2122 reflections
82 parameters
H-atom parameters constrained
$\Delta\rho_{max}$ = 0.50 e Å^{-3}
$\Delta\rho_{min}$ = −0.49 e Å^{-3}

Table 1
Hydrogen-bond geometry (Å, °).

D—H···A	D—H	H···A	D···A	D—H···A
C6—H6A···Br2^{i}	0.99	2.96	3.7967 (17)	143
C6—H6A···Br2^{ii}	0.99	2.98	3.7359 (16)	134
C5—H5···Br1^{iii}	0.95	3.11	3.9399 (16)	147

Symmetry codes: (i) $x, y-1, z$; (ii) $-x, -y+1, -z+1$; (iii) $-x+1, -y+1, -z$.

Table 2
Bromine–bromine and related contacts and angles (Å, °).

Cg is the centroid of the C1–C5,C1($-x$, 1 − y, $-z$) ring.

System C—Br···Br—C or C—Br···Cg	Br···Br or Br···Cg	C—Br···Br (or C—Br···Cg), Br···Br—C	Operator
C6—Br1···Br2—C7	3.8972 (3)	76.45 (5), 134.79 (5)	$1-x, 1-y, 1-z$
C7—Br2···Br2—C7	3.8873 (4)	134.93 (5) × 2	$-x, 2-y, 1-z$
C7—Br2···Br2—C7	3.8913 (4)	76.72 (5) × 2	$1-x, 1-y, 1-z$
C6—Br1···Cg	3.89	158	$1+x, -1+y, z$

Data collection: *CrysAlis PRO* (Oxford Diffraction, 2009); cell refinement: *CrysAlis PRO*; data reduction: *CrysAlis PRO*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *XP* (Siemens, 1994); software used to prepare material for publication: *SHELXL97*.

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Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: FK2020).

References

Desiraju, G. R. & Steiner, T. (1999). *The Weak Hydrogen Bond in Structural Chemistry and Biology*. Oxford University Press.
Jones, P. G. & Kuś, P. (2007). *Z. Naturforsch. Teil B*, **62**, 725–731.
Jones, P. G. & Kuś, P. (2010). *Z. Naturforsch. Teil B*, **65**, 433–444.
Metrangolo, P., Meyer, F., Pilati, T., Resnati, G. & Terraneo, G. (2008). *Angew. Chem. Int. Ed.* **47**, 6114–6127.
Metrangolo, P. & Resnati, G. (2001). *Chem. Eur. J.* **7**, 2511–2519.
Otsubo, T., Aso, Y., Ogura, F., Misumi, S., Kawamoto, A. & Tanaka, J. (1989). *Bull. Chem. Soc. Jpn*, **62**, 164–170.
Otsubo, T., Ogura, F. & Misumi, S. (1983). *Tetrahedron Lett.* **24**, 4851–4854.
Oxford Diffraction (2009). *CrysAlis PRO*. Oxford Diffraction Ltd, Yarnton, England.

Rissanen, K. (2008). *CrystEngComm*, **10**, 1107–1113.
Rivera, J. M., Martin, T. & Rebek, J. Jr (2001). *J. Am. Chem. Soc.* **123**, 5213–5220.
Sheldrick, G. M. (2008). *Acta Cryst.* A**64**, 112–122.
Siemens (1994). *XP*. Siemens Analytical X-ray Instruments Inc., Madison, Wisconsin, USA.
Skibiński, M., Gómez, R., Lork, E. & Azov, V. A. (2009). *Tetrahedron*, **65**, 10348–10354.
Valdes, C., Spitz, U. P., Toledo, L. M., Kubik, S. W. & Rebek, J. Jr (1995). *J. Am. Chem. Soc.* **117**, 12733–12745.
Yano, K., Matsuda, S., Tani, K., Yamamoto, K. & Matsubara, H. (1999). *Bull. Chem. Soc. Jpn*, **72**, 2111–2114.

supplementary materials

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2,3,6,7-Tetrakis(bromomethyl)naphthalene

M. Skibinski, V. A. Azov and P. G. Jones

Comment

The title compound is a symmetric rigid molecule with four bromomethyl groups. The bromine atoms can be easily substituted by other nucleophiles, which offers the opportunity of employing the compound as a building block for construction of various functional architectures. The title compound was prepared to serve as a spacer between two tetrathiafulvalene (TTF) groups in TTF-containing molecular tweezers (Skibiński *et al.*, 2009). It was first employed as an intermediate in the preparation of triple-layered [2.2]naphthalenophane (Otsubo *et al.*, 1983), and several other triple-layered cyclophanes (Otsubo *et al.*, 1983; Yano *et al.*, 1999). It was also used as an intermediate in the synthesis of H-bonded molecular capsules (Valdes *et al.*, 1995; Rivera *et al.*, 2001).

The molecule of the title compound is shown in Fig. 1. It displays crystallographic inversion symmetry (operator #1 - *x*, 1 - *y*, 1 - *z*); for this reason, the crystallographic numbering does not correspond to the IUPAC numbering scheme. Bond lengths and angles may be considered normal; the bromine atoms are directed to opposite sides of the ring system, with C(2)—C(3)—C(6)—Br(1) 92.22 (16), C(3)—C(4)—C(7)—Br2 - 79.86 (17)°, which leads to a +/-/-/+ pattern of Br atoms about the ring plane for the IUPAC-numbered C2,3,6,7; this contrasts with the -/-/+/+ pattern in 1,2,4,5-tetrakis(bromomethyl)benzene (Jones & Kuś, 2007), which is also inversion-symmetric.

Details of the packing interactions are given in the Tables. The molecules pack in layers parallel to (10$\bar{1}$). Within the layers, the contacts Br1···Br2, the longer Br2···Br2 and the shorter H6A···Br2 are observed. These combine to form columns of interactions parallel to the *b* axis; chains of molecules parallel to [101] (horizontal in Fig. 2) are also formed. The contacts Br2···Br2 (the shorter), H6A···Br2 (the longer) and Br1···*Cg* (*Cg* = centre of gravity of the ring C1–5 and C1#1) link the layers (Fig. 3). H5···Br1 3.11 Å between the layers is a borderline interaction. The Br···*Cg* interaction could alternatively be interpreted as Br···C5, which at 3.450 (2) Å is by far the shortest of the six Br···C contacts; it is often unclear which is the better interpretation in such systems (Jones & Kuś, 2010). Despite the presence of the naphthalene ring systems, there are no significant *Cg*···*Cg* interactions. The shortest H···*Cg* contact is H7A···*Cg* (1 - *x*,1 - *y*,-*z*) 3.10 Å between layers, but this is both long and has a narrow angle (124°). We can conclude that the crystal packing of the title compound is dominated by the contacts involving bromomethylene groups.

Experimental

The title compound was prepared as described by Rivera *et al.* (2001) by treatment of a solution of 2,3-bis[{[(1,1-dimethylethyl)dimethylsilyl]oxy}methyl]- 6,7-bis[(phenylmethoxy)methyl]-naphthalene in chloroform with gaseous HBr. The compound was obtained as a colourless microcrystalline solid. Yield: 87%. Crystals suitable for X-ray diffraction were grown by slow evaporation of a solution in EtOH/hexane/CH_2Cl_2. *M*.p. (decomp.) 230–231° C (lit. 230° C). ^{1}H NMR ($CDCl_3$): δ = 7.83 (s, 4H), 4.84 (s, 8H) p.p.m..

The title compound is poorly soluble (< 1 g/*L*) in most organic solvents at room temperature, but is much more soluble in aromatic solvents, such as toluene or chlorobenzene, upon reflux.

Refinement

Hydrogen atoms were included at calculated positions using a riding model with aromatic C—H 0.95, methylene C—H 0.99 Å. The U(H) values were fixed at 1.2 × U_{eq}(C) of the parent C atom.

Figures

Fig. 1. Structure of the title compound in the crystal. Ellipsoids represent 50% probability levels. Only the asymmetric unit is numbered.

Fig. 2. Molecular packing of the title compound as a layer parallel to (10$\bar{1}$). Br···Br and H···Br contacts are shown as thick dashed bonds.

Fig. 3. Linking between the layers of the title compound. Br···Br and H···Br contacts are shown as thick dashed bonds. One representative Br···*Cg* contact is shown as a thin dashed bond (top left).

2,3,6,7-Tetrakis(bromomethyl)naphthalene

Crystal data

$C_{14}H_{12}Br_4$	$Z = 1$
$M_r = 499.88$	$F(000) = 236$
Triclinic, $P\bar{1}$	$D_x = 2.254$ Mg m^{-3}
Hall symbol: -P 1	Melting point: 503 K
$a = 6.6144$ (2) Å	Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å
$b = 7.1770$ (2) Å	Cell parameters from 9533 reflections
$c = 8.7761$ (3) Å	$\theta = 2.4$–$30.7°$
$\alpha = 84.744$ (3)°	$\mu = 10.91$ mm^{-1}
$\beta = 78.251$ (3)°	$T = 100$ K
$\gamma = 64.555$ (3)°	Prism, colourless
$V = 368.32$ (2) Å^3	0.20 × 0.06 × 0.04 mm

Data collection

Oxford Diffraction Xcalibur Eos diffractometer	2122 independent reflections
Radiation source: Enhance (Mo) X-ray Source	1716 reflections with $I > 2\sigma(I)$
graphite	$R_{int} = 0.031$
Detector resolution: 16.1419 pixels mm^{-1}	$\theta_{max} = 30.0°$, $\theta_{min} = 2.4°$
ω–scan	$h = -9 \rightarrow 9$
Absorption correction: multi-scan (*CrysAlis PRO*; Oxford Diffraction, 2009)	$k = -10 \rightarrow 10$

T_{min} = 0.356, T_{max} = 1.000
17701 measured reflections

l = −11→12

Refinement

Refinement on F^2
Least-squares matrix: full
$R[F^2 > 2\sigma(F^2)]$ = 0.016
$wR(F^2)$ = 0.034
S = 0.92
2122 reflections
82 parameters
0 restraints

Primary atom site location: structure-invariant direct methods
Secondary atom site location: difference Fourier map
Hydrogen site location: inferred from neighbouring sites
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.0181P)^2]$
where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max}$ = 0.001
$\Delta\rho_{max}$ = 0.50 e Å^{-3}
$\Delta\rho_{min}$ = −0.49 e Å^{-3}

Special details

Geometry. All e.s.d.'s (except the e.s.d. in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell e.s.d.'s are taken into account individually in the estimation of e.s.d.'s in distances, angles and torsion angles; correlations between e.s.d.'s in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell e.s.d.'s is used for estimating e.s.d.'s involving l.s. planes.

Refinement. Refinement of F^2 against ALL reflections. The weighted *R*-factor *wR* and goodness of fit *S* are based on F^2, conventional *R*-factors *R* are based on *F*, with *F* set to zero for negative F^2. The threshold expression of $F^2 > \sigma(F^2)$ is used only for calculating *R*-factors(gt) *etc*. and is not relevant to the choice of reflections for refinement. *R*-factors based on F^2 are statistically about twice as large as those based on *F*, and *R*- factors based on ALL data will be even larger.

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å^2)

	x	*y*	*z*	U_{iso}*/U_{eq}
Br1	0.64988 (3)	−0.00387 (3)	0.24985 (2)	0.01628 (5)
Br2	0.23208 (3)	0.72525 (3)	0.44061 (2)	0.01672 (5)
C1	−0.0170 (3)	0.4100 (3)	0.02483 (19)	0.0108 (3)
C2	0.0922 (3)	0.2877 (3)	0.14549 (19)	0.0122 (3)
H2	0.0699	0.1672	0.1791	0.015*
C3	0.2297 (3)	0.3393 (3)	0.21518 (19)	0.0111 (3)
C4	0.2621 (3)	0.5223 (3)	0.16547 (19)	0.0110 (3)
C5	0.1575 (3)	0.6419 (3)	0.04994 (19)	0.0112 (3)
H5	0.1791	0.7633	0.0185	0.013*
C6	0.3431 (3)	0.2029 (3)	0.34014 (19)	0.0136 (3)
H6A	0.2495	0.1316	0.3945	0.016*
H6B	0.3563	0.2876	0.4173	0.016*
C7	0.4062 (3)	0.5854 (3)	0.24055 (18)	0.0135 (3)
H7A	0.4559	0.6799	0.1704	0.016*
H7B	0.5437	0.4620	0.2592	0.016*

Atomic displacement parameters (Å^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Br1	0.01360 (10)	0.01494 (10)	0.01724 (10)	−0.00349 (8)	−0.00312 (7)	0.00232 (7)
Br2	0.01615 (10)	0.01865 (11)	0.01468 (9)	−0.00544 (8)	−0.00321 (7)	−0.00581 (7)
C1	0.0099 (8)	0.0112 (9)	0.0093 (8)	−0.0031 (7)	0.0001 (6)	−0.0012 (6)
C2	0.0130 (8)	0.0120 (9)	0.0105 (8)	−0.0053 (7)	0.0000 (7)	−0.0003 (6)
C3	0.0085 (8)	0.0127 (9)	0.0087 (8)	−0.0016 (7)	−0.0006 (6)	−0.0008 (6)
C4	0.0092 (8)	0.0139 (9)	0.0097 (8)	−0.0050 (7)	0.0011 (6)	−0.0040 (6)
C5	0.0111 (8)	0.0104 (8)	0.0120 (8)	−0.0055 (7)	0.0012 (6)	−0.0020 (6)
C6	0.0111 (8)	0.0156 (9)	0.0115 (8)	−0.0033 (7)	−0.0017 (7)	0.0003 (7)
C7	0.0128 (8)	0.0177 (9)	0.0101 (8)	−0.0064 (7)	−0.0017 (7)	−0.0023 (7)

Geometric parameters (Å, °)

Br1—C6	1.9801 (16)	C4—C7	1.493 (2)
Br2—C7	1.9806 (16)	C5—C1^{i}	1.422 (2)
C1—C2	1.418 (2)	C2—H2	0.9500
C1—C1^{i}	1.420 (3)	C5—H5	0.9500
C1—C5^{i}	1.422 (2)	C6—H6A	0.9900
C2—C3	1.377 (2)	C6—H6B	0.9900
C3—C4	1.436 (2)	C7—H7A	0.9900
C3—C6	1.494 (2)	C7—H7B	0.9900
C4—C5	1.363 (2)		
C2—C1—C1^{i}	118.85 (18)	C1—C2—H2	119.2
C2—C1—C5^{i}	122.57 (15)	C4—C5—H5	119.0
C1^{i}—C1—C5^{i}	118.58 (19)	C1^{i}—C5—H5	119.0
C3—C2—C1	121.68 (15)	C3—C6—H6A	109.6
C2—C3—C4	119.29 (15)	Br1—C6—H6A	109.6
C2—C3—C6	119.30 (15)	C3—C6—H6B	109.6
C4—C3—C6	121.41 (15)	Br1—C6—H6B	109.6
C5—C4—C3	119.70 (15)	H6A—C6—H6B	108.1
C5—C4—C7	119.52 (15)	C4—C7—H7A	109.6
C3—C4—C7	120.77 (15)	Br2—C7—H7A	109.6
C4—C5—C1^{i}	121.90 (15)	C4—C7—H7B	109.6
C3—C6—Br1	110.35 (11)	Br2—C7—H7B	109.6
C4—C7—Br2	110.18 (11)	H7A—C7—H7B	108.1
C3—C2—H2	119.2		
C1^{i}—C1—C2—C3	0.0 (3)	C6—C3—C4—C7	−1.7 (2)
C5^{i}—C1—C2—C3	179.24 (16)	C3—C4—C5—C1^{i}	−0.5 (2)
C1—C2—C3—C4	0.5 (2)	C7—C4—C5—C1^{i}	−179.53 (15)
C1—C2—C3—C6	−179.09 (15)	C2—C3—C6—Br1	92.22 (16)
C2—C3—C4—C5	−0.2 (2)	C4—C3—C6—Br1	−87.36 (16)
C6—C3—C4—C5	179.34 (15)	C5—C4—C7—Br2	99.15 (16)
C2—C3—C4—C7	178.76 (15)	C3—C4—C7—Br2	−79.86 (17)

Symmetry codes: (i) −*x*, −*y*+1, −*z*.

Hydrogen-bond geometry (Å, °)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
C6—H6A···Br2^{ii}	0.99	2.96	3.7967 (17)	143
C6—H6A···Br2^{iii}	0.99	2.98	3.7359 (16)	134
C5—H5···Br1^{iv}	0.95	3.11	3.9399 (16)	147

Symmetry codes: (ii) *x*, *y*−1, *z*; (iii) −*x*, −*y*+1, −*z*+1; (iv) −*x*+1, −*y*+1, −*z*.

Table 2
Bromine–bromine and related contacts and angles (Å, °)

Cg is the centroid of the C1–C5,C1(-x, 1-y, -z) ring.

System C—Br···Br—C or C—Br···*Cg*	Br···Br or Br···*Cg*	C—Br···Br (or C—Br···*Cg*), Br···Br—C	Operator
C6—Br1···Br2—C7	3.8972 (3)	76.45 (5), 134.79 (5)	1-x, 1-y, 1-z
C7—Br2···Br2—C7	3.8873 (4)	134.93 (5) × 2	-x, 2-y, 1-z
C7—Br2···Br2—C7	3.8913 (4)	76.72 (5) × 2	1-x, 1-y, 1-z
C6—Br1···*Cg*	3.89	158	1+x, -1+y, z

Fig. 1

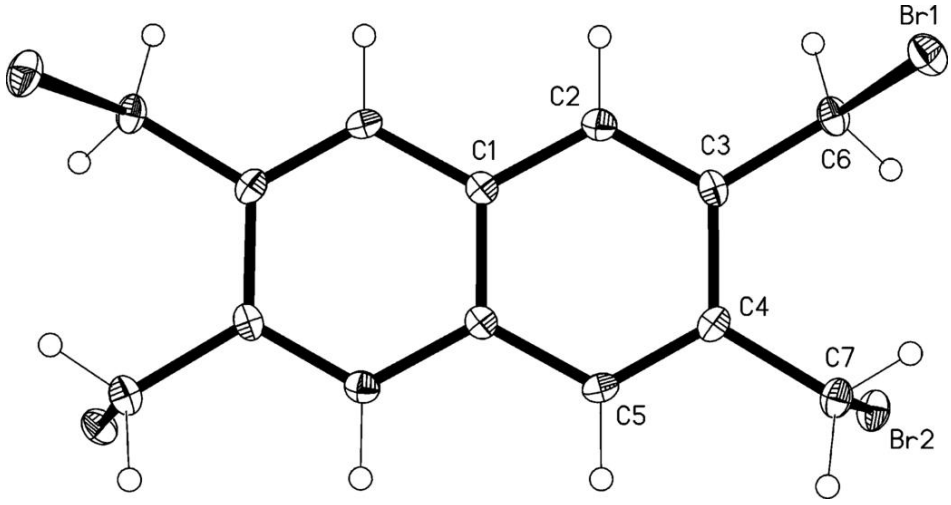


Fig. 2

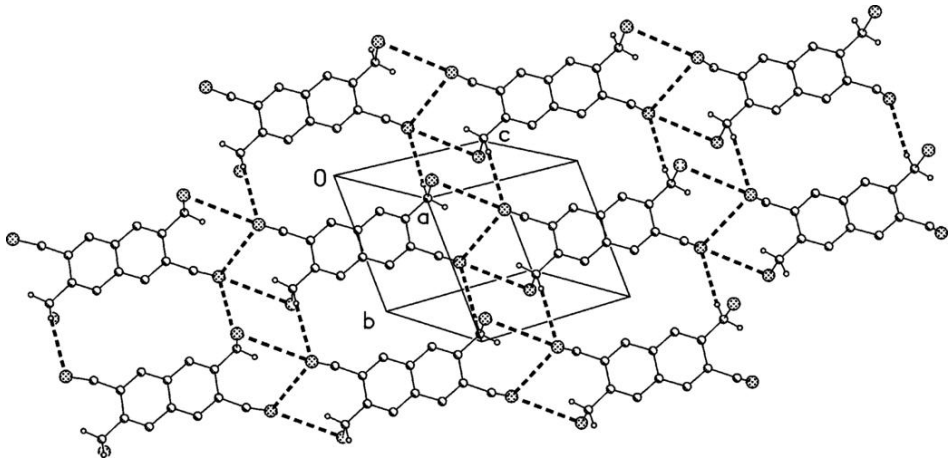
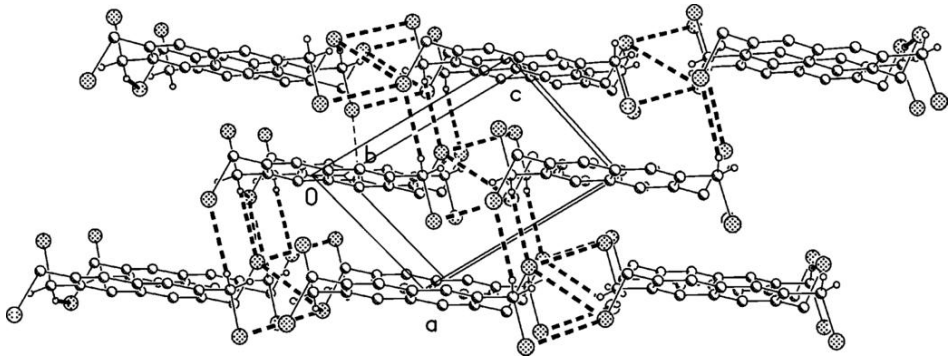


Fig. 3



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5-Methoxy-1-(3,4,5-trimethoxyphenyl)-1*H*-indole

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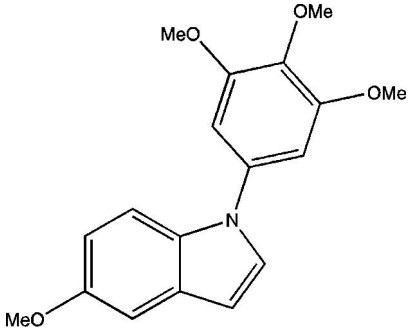
Key indicators: single-crystal X-ray study; T = 295 K; mean σ(C–C) = 0.002 Å; R factor = 0.037; wR factor = 0.110; data-to-parameter ratio = 14.1.

The title compound, $C_{18}H_{19}NO_4$, was prepared as an indole derivative with possible antimitotic properties. The planes of the indole and trimethoxyphenyl rings make a dihedral angle of 45.35 (5)° with one another. In the crystal, molecules related by a twofold screw axis exhibit arene C—H···arene-π interactions which are 3.035 (1) Å in length.

Related literature

For a related structure, see: Suthar *et al.* (2005). For pharmaceutical applications of indoles, see: Fuwa & Sasaki (2009); Li & Martins (2003).



Experimental

Crystal data

$C_{18}H_{19}NO_4$
M_r = 313.34
Monoclinic, $C2/c$
a = 19.0036 (16) Å
b = 7.3179 (14) Å
c = 23.672 (4) Å
β = 96.802 (10)°
V = 3268.8 (9) Å^3
Z = 8
Cu $K\alpha$ radiation
μ = 0.74 mm^{-1}
T = 295 K
0.32 × 0.27 × 0.26 mm

Data collection

Enraf–Nonius CAD-4 diffractometer
6084 measured reflections
2951 independent reflections
2074 reflections with $I > 2\sigma(I)$
R_{int} = 0.026
3 standard reflections every 190 reflections
intensity decay: 4%

Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.037
$wR(F^2)$ = 0.110
S = 1.00
2951 reflections
209 parameters
H-atom parameters constrained
$\Delta\rho_{max}$ = 0.16 e Å^{-3}
$\Delta\rho_{min}$ = −0.16 e Å^{-3}

Data collection: *CAD-4 EXPRESS* (Enraf–Nonius, 1994); cell refinement: *CAD-4 EXPRESS*; data reduction: *XCAD4* (Harms & Wocadlo, 1995); program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *ORTEP-3 for Windows* (Farrugia, 1997), *Mercury* (Macrae *et al.*, 2006); software used to prepare material for publication: *WinGX* (Farrugia, 1999).

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Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: FL2291).

References

Enraf–Nonius (1994). *CAD-4 EXPRESS*. Enraf–Nonius, Delft, The Netherlands.
Farrugia, L. J. (1997). *J. Appl. Cryst.* **30**, 565.
Farrugia, L. J. (1999). *J. Appl. Cryst.* **32**, 837–838.
Fuwa, H. & Sasaki, M. (2009). *J. Org. Chem.* **74**, 212–221.
Harms, K. & Wocadlo, S. (1995). *XCAD4*. University of Marburg, Germany.
Li, L. & Martins, A. (2003). *Tetrahedron Lett.* **44**, 5987–5990.
Macrae, C. F., Edgington, P. R., McCabe, P., Pidcock, E., Shields, G. P., Taylor, R., Towler, M. & van de Streek, J. (2006). *J. Appl. Cryst.* **39**, 453–457.
Sheldrick, G. M. (2008). *Acta Cryst.* A**64**, 112–122.
Suthar, B., Fowler, A., Jones, D. S. & Ogle, C. A. (2005). *Acta Cryst.* E**61**, o607–o608.

supplementary materials

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5-Methoxy-1-(3,4,5-trimethoxyphenyl)-1*H*-indole

T. B. Monroe, C. Rimland, Y. Moazami, D. S. Jones and C. A. Ogle

Comment

The indole core is a common structure observed in a wide variety of biologically active compounds and pharmaceutical products (Li & Martins, 2003). Indole structures are considered as privileged structure motifs, due to their ability to bind many receptors within the body (Fuwa & Sasaki, 2009). As a result, there has been a great deal of research dedicated to incorporating the indole functionality in the design and synthesis of novel anti-mitotic compounds for the treatment of cancer. The title compound was prepared as an indole derivative with possible anti-mitotic properties.

The structure of the title compound is shown in Fig. 1. The plane of the indole ring and the plane of the trimethoxyphenyl ring make a 45.35 (5)° angle with one another. The deviation of methoxy carbon C19 from the indole mean plane is 0.050 (3) Å. The deviations of methoxy carbons C16, C17, and C18 from the plane of the phenyl ring are 0.065 (3) Å, 1.157 (3) Å, and 0.138 (3) Å, respectively. Molecules related by a two-fold screw axis exhibit arene C—H··· arene π interactions, as shown in Fig. 2. The interaction is between C4—H of one molecule and the six membered (C4 through C9) aromatic ring of the screw-related molecule. The H··· ring-centroid distance is 3.035 (1) Å, and the H··· ring-centroid line makes an angle of 5.6 (3)° with the normal to the plane of the ring.

In a comparable structure, 1-(3,4,5-Trimethoxyphenyl)naphthalene (Suthar *et al.*, 2005), the angle between the planes of the napthylene ring and the trimethoxyphenyl ring is 68.19 (10)°.

Experimental

Preparation of the title compound (III) (See Synthesis scheme): To a Schlenk flask equipped with a magnetic stir bar, 1.47 g (10 mmol) of 5-methoxyindole (II), 6.36 g (30 mmol) of K_3PO_4, and 0.190 g (10 mol %) of CuI were added. The reaction flask was then purged with nitrogen gas and charged with 2.94 g (10 mmol) of 5-iodo-1,2,3-trimethoxybenzene (I), 0.22 ml (20 mol %) of *N*,*N*'-dimethylethylenediamine, and 25.0 ml of dry degassed toluene. The reaction mixture was heated to reflux for 24 hours. Upon completion, the crude reaction mixture was filtered through a celite plug, and concentrated on a rotary evaporator to yield an off-white solid. The solid was recrystallized from ethanol to obtain the x-ray quality crystals. Pure product was obtained in 86 % yield (2.70 g). Melting point: 99-101°C. MS(E1): M+ 313 m/z, 298 m/z. 1H NMR (300 MHz, DMSO-d) δ7.62 (d, 1H), 7.56 (d,1*H*), 7.14 (d,1*H*), 6.84(d,1*H*), 6.82 (s, 2H), 6.58 (d, 1H), 3.85 (s,6*H*), 3.78 (s, 3H), 3.71 (s,3*H*)

Refinement

All H atoms were constrained using a riding model. The aromatic C—H bond lengths were fixed at 0.93 Å, with U_{iso}(H) = 1.2 U_{eq}(C). The methyl C—H bond lengths were fixed at 0.96 Å, with U_{iso}(H) = 1.5 U_{eq}(C). An idealized tetrahedral geometry was used for the methyl groups, and the torsion angles around the O—C bonds were refined.

Figures

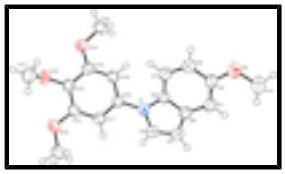


Fig. 1. View of the title compound (50% probability displacement ellipsoids)

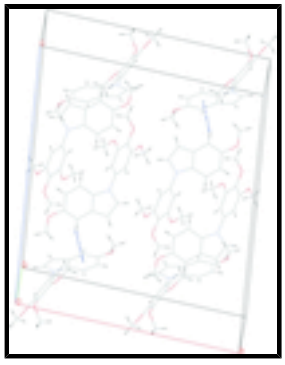


Fig. 2. Packing diagram showing the arene C—H···π interactions between molecules related by a two-fold screw axis

Fig. 3. Synthesis scheme

5-Methoxy-1-(3,4,5-trimethoxyphenyl)-1*H*-indole

Crystal data

$C_{18}H_{19}NO_4$	$F(000) = 1328$
$M_r = 313.34$	$D_x = 1.273$ Mg m^{-3}
Monoclinic, *C*2/*c*	Cu *K*α radiation, λ = 1.54184 Å
Hall symbol: -C 2yc	Cell parameters from 24 reflections
a = 19.0036 (16) Å	θ = 6.4–20.8°
b = 7.3179 (14) Å	μ = 0.74 mm^{-1}
c = 23.672 (4) Å	*T* = 295 K
β = 96.802 (10)°	Prism, colorless
V = 3268.8 (9) Å^3	0.32 × 0.27 × 0.26 mm
Z = 8	

Data collection

Enraf–Nonius CAD-4 diffractometer	$\theta_{max} = 67.4°$, $\theta_{min} = 3.8°$
non–profiled ω/2θ scans	*h* = −22→22
6084 measured reflections	*k* = −8→0
2951 independent reflections	*l* = −28→28
2074 reflections with $I > 2\sigma(I)$	3 standard reflections every 190 reflections
$R_{int} = 0.026$	intensity decay: 4%

Refinement

Refinement on F^2

Least-squares matrix: full

$R[F^2 > 2\sigma(F^2)] = 0.037$

$wR(F^2) = 0.110$

$S = 1.00$

2951 reflections

209 parameters

0 restraints

H-atom parameters constrained

$w = 1/[\sigma^2(F_o^2) + (0.0613P)^2 + 0.605P]$
where $P = (F_o^2 + 2F_c^2)/3$

$(\Delta/\sigma)_{max} < 0.001$

$\Delta\rho_{max} = 0.16$ e Å^{-3}

$\Delta\rho_{min} = -0.16$ e Å^{-3}

Extinction correction: *SHELXL97* (Sheldrick, 2008),
$Fc^* = kFc[1+0.001xFc^2\lambda^3/\sin(2\theta)]^{-1/4}$

Extinction coefficient: 0.00188 (13)

Special details

Geometry. All esds (except the esd in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell esds are taken into account individually in the estimation of esds in distances, angles and torsion angles; correlations between esds in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell esds is used for estimating esds involving l.s. planes.

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å^2)

	x	*y*	*z*	U_{iso}*/U_{eq}
O14	0.15356 (6)	0.12928 (15)	0.49143 (5)	0.0511 (3)
O13	0.07247 (7)	0.29172 (17)	0.40657 (5)	0.0575 (3)
O5	0.40130 (7)	0.77324 (19)	0.74372 (5)	0.0647 (4)
N	0.14855 (7)	0.67340 (19)	0.60827 (5)	0.0451 (3)
O12	0.02905 (7)	0.64188 (17)	0.41594 (5)	0.0562 (4)
C11	0.08846 (8)	0.6630 (2)	0.51210 (7)	0.0459 (4)
H15	0.0741	0.7834	0.5159	0.055*
C15	0.15105 (8)	0.3970 (2)	0.55189 (6)	0.0429 (4)
H11	0.1773	0.3391	0.5824	0.051*
C14	0.13334 (8)	0.3050 (2)	0.50087 (7)	0.0414 (4)
C8	0.21611 (9)	0.6831 (2)	0.63793 (6)	0.0428 (4)
C7	0.27934 (9)	0.6005 (2)	0.62755 (7)	0.0488 (4)
H4	0.2813	0.5235	0.5965	0.059*
C13	0.09214 (8)	0.3894 (2)	0.45562 (6)	0.0430 (4)
C12	0.06941 (8)	0.5691 (2)	0.46185 (7)	0.0435 (4)
C10	0.12910 (8)	0.5758 (2)	0.55666 (6)	0.0427 (4)
C6	0.33859 (10)	0.6368 (3)	0.66472 (7)	0.0519 (4)
H3	0.3813	0.5823	0.6589	0.062*
C5	0.33640 (10)	0.7540 (2)	0.71127 (7)	0.0496 (4)
C3	0.14176 (10)	0.8679 (2)	0.68041 (7)	0.0539 (5)
H9	0.124	0.95	0.7052	0.065*
C18	0.20053 (9)	0.0443 (2)	0.53514 (7)	0.0532 (4)
H18A	0.2109	−0.0777	0.5237	0.08*

H18B	0.1786	0.04	0.5696	0.08*
H18C	0.2437	0.1134	0.5415	0.08*
C4	0.27495 (10)	0.8393 (2)	0.72137 (7)	0.0520 (4)
H7	0.274	0.9179	0.7521	0.062*
C2	0.10450 (10)	0.7872 (2)	0.63464 (7)	0.0512 (4)
H8	0.0566	0.8057	0.6228	0.061*
C9	0.21305 (9)	0.8044 (2)	0.68373 (7)	0.0466 (4)
C16	0.00926 (10)	0.8294 (3)	0.41920 (8)	0.0597 (5)
H16A	−0.0187	0.8644	0.3844	0.09*
H16B	0.0511	0.9038	0.4248	0.09*
H16C	−0.0179	0.8461	0.4505	0.09*
C17	0.10615 (13)	0.3480 (3)	0.35877 (8)	0.0751 (6)
H17A	0.0895	0.2739	0.3265	0.113*
H17B	0.1565	0.3342	0.3673	0.113*
H17C	0.0951	0.4738	0.3504	0.113*
C19	0.40555 (13)	0.8959 (3)	0.78968 (9)	0.0857 (7)
H1A	0.4531	0.8973	0.8086	0.129*
H1B	0.3736	0.858	0.8159	0.129*
H1C	0.3929	1.0162	0.7759	0.129*

Atomic displacement parameters (Å^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
O14	0.0641 (7)	0.0342 (6)	0.0528 (7)	0.0029 (5)	−0.0026 (6)	−0.0024 (5)
O13	0.0760 (8)	0.0458 (7)	0.0466 (6)	−0.0098 (6)	−0.0091 (6)	−0.0038 (5)
O5	0.0659 (8)	0.0628 (9)	0.0605 (8)	−0.0043 (7)	−0.0125 (6)	−0.0102 (7)
N	0.0516 (8)	0.0402 (8)	0.0423 (7)	0.0020 (6)	0.0006 (6)	−0.0044 (6)
O12	0.0620 (8)	0.0452 (7)	0.0560 (7)	0.0041 (6)	−0.0155 (6)	0.0022 (6)
C11	0.0497 (9)	0.0362 (9)	0.0503 (9)	0.0013 (7)	0.0003 (7)	−0.0013 (7)
C15	0.0465 (9)	0.0387 (9)	0.0420 (8)	−0.0023 (7)	−0.0006 (7)	0.0026 (7)
C14	0.0443 (8)	0.0322 (8)	0.0475 (8)	−0.0049 (7)	0.0050 (7)	0.0006 (7)
C8	0.0522 (9)	0.0359 (9)	0.0394 (8)	−0.0001 (7)	0.0009 (7)	−0.0006 (7)
C7	0.0568 (10)	0.0445 (10)	0.0446 (8)	0.0004 (8)	0.0043 (7)	−0.0065 (7)
C13	0.0468 (9)	0.0386 (9)	0.0421 (8)	−0.0093 (7)	−0.0016 (7)	−0.0018 (7)
C12	0.0409 (8)	0.0398 (9)	0.0480 (9)	−0.0034 (7)	−0.0027 (7)	0.0044 (7)
C10	0.0458 (8)	0.0383 (9)	0.0431 (8)	−0.0040 (7)	0.0021 (7)	−0.0025 (7)
C6	0.0531 (10)	0.0494 (10)	0.0528 (10)	0.0010 (8)	0.0044 (8)	−0.0033 (8)
C5	0.0589 (10)	0.0424 (10)	0.0452 (9)	−0.0040 (8)	−0.0040 (8)	0.0020 (7)
C3	0.0648 (11)	0.0459 (10)	0.0505 (9)	0.0095 (8)	0.0050 (8)	−0.0088 (8)
C18	0.0551 (10)	0.0418 (10)	0.0619 (10)	0.0023 (8)	0.0034 (8)	0.0063 (8)
C4	0.0704 (12)	0.0417 (10)	0.0423 (8)	−0.0013 (9)	−0.0001 (8)	−0.0072 (7)
C2	0.0560 (10)	0.0448 (9)	0.0523 (9)	0.0092 (8)	0.0044 (8)	−0.0017 (8)
C9	0.0608 (10)	0.0371 (9)	0.0409 (8)	0.0014 (8)	0.0022 (7)	−0.0016 (7)
C16	0.0653 (12)	0.0456 (11)	0.0654 (12)	0.0073 (9)	−0.0046 (9)	0.0097 (9)
C17	0.1107 (18)	0.0663 (14)	0.0487 (10)	0.0058 (13)	0.0109 (11)	−0.0032 (10)
C19	0.0995 (17)	0.0828 (17)	0.0663 (13)	0.0018 (14)	−0.0254 (12)	−0.0217 (12)

Geometric parameters (Å, °)

O14—C14	1.368 (2)	C13—C12	1.397 (2)
O14—C18	1.427 (2)	C6—C5	1.401 (2)
O13—C13	1.3769 (18)	C6—H3	0.93
O13—C17	1.425 (2)	C5—C4	1.370 (2)
O5—C5	1.381 (2)	C3—C2	1.357 (2)
O5—C19	1.405 (2)	C3—C9	1.426 (2)
N—C2	1.381 (2)	C3—H9	0.93
N—C8	1.390 (2)	C18—H18A	0.96
N—C10	1.4255 (19)	C18—H18B	0.96
O12—C12	1.3622 (18)	C18—H18C	0.96
O12—C16	1.427 (2)	C4—C9	1.412 (2)
C11—C12	1.384 (2)	C4—H7	0.93
C11—C10	1.387 (2)	C2—H8	0.93
C11—H15	0.93	C16—H16A	0.96
C15—C10	1.382 (2)	C16—H16B	0.96
C15—C14	1.389 (2)	C16—H16C	0.96
C15—H11	0.93	C17—H17A	0.96
C14—C13	1.394 (2)	C17—H17B	0.96
C8—C7	1.393 (2)	C17—H17C	0.96
C8—C9	1.408 (2)	C19—H1A	0.96
C7—C6	1.371 (2)	C19—H1B	0.96
C7—H4	0.93	C19—H1C	0.96
C14—O14—C18	117.06 (12)	C2—C3—C9	107.72 (15)
C13—O13—C17	114.63 (14)	C2—C3—H9	126.1
C5—O5—C19	117.49 (16)	C9—C3—H9	126.1
C2—N—C8	108.29 (13)	O14—C18—H18A	109.5
C2—N—C10	125.44 (14)	O14—C18—H18B	109.5
C8—N—C10	126.06 (14)	H18A—C18—H18B	109.5
C12—O12—C16	117.38 (13)	O14—C18—H18C	109.5
C12—C11—C10	119.38 (15)	H18A—C18—H18C	109.5
C12—C11—H15	120.3	H18B—C18—H18C	109.5
C10—C11—H15	120.3	C5—C4—C9	118.11 (15)
C10—C15—C14	119.05 (15)	C5—C4—H7	120.9
C10—C15—H11	120.5	C9—C4—H7	120.9
C14—C15—H11	120.5	C3—C2—N	109.65 (16)
O14—C14—C15	123.64 (14)	C3—C2—H8	125.2
O14—C14—C13	115.72 (14)	N—C2—H8	125.2
C15—C14—C13	120.63 (15)	C8—C9—C4	119.51 (16)
N—C8—C7	130.78 (15)	C8—C9—C3	106.80 (15)
N—C8—C9	107.54 (14)	C4—C9—C3	133.69 (16)
C7—C8—C9	121.66 (15)	O12—C16—H16A	109.5
C6—C7—C8	117.58 (16)	O12—C16—H16B	109.5
C6—C7—H4	121.2	H16A—C16—H16B	109.5
C8—C7—H4	121.2	O12—C16—H16C	109.5
O13—C13—C14	119.30 (15)	H16A—C16—H16C	109.5
O13—C13—C12	121.42 (14)	H16B—C16—H16C	109.5

C14—C13—C12	119.23 (14)	O13—C17—H17A	109.5
O12—C12—C11	123.83 (15)	O13—C17—H17B	109.5
O12—C12—C13	115.82 (14)	H17A—C17—H17B	109.5
C11—C12—C13	120.35 (15)	O13—C17—H17C	109.5
C15—C10—C11	121.32 (15)	H17A—C17—H17C	109.5
C15—C10—N	119.60 (14)	H17B—C17—H17C	109.5
C11—C10—N	119.08 (15)	O5—C19—H1A	109.5
C7—C6—C5	121.68 (17)	O5—C19—H1B	109.5
C7—C6—H3	119.2	H1A—C19—H1B	109.5
C5—C6—H3	119.2	O5—C19—H1C	109.5
C4—C5—O5	125.46 (16)	H1A—C19—H1C	109.5
C4—C5—C6	121.44 (16)	H1B—C19—H1C	109.5
O5—C5—C6	113.10 (16)		

Table 1

Arene C—H··· arene π interactions between screw-related molecules

Interaction between C4—H of one molecule and the centroid of the six membered (C4 through C9) aromatic ring of the screw-related molecule

H··· ring-centroid distance	Angle between the H···ring-centroid line and the aromatic ring normal
3.035 (1) Å	5.6 (3) °

Fig. 1

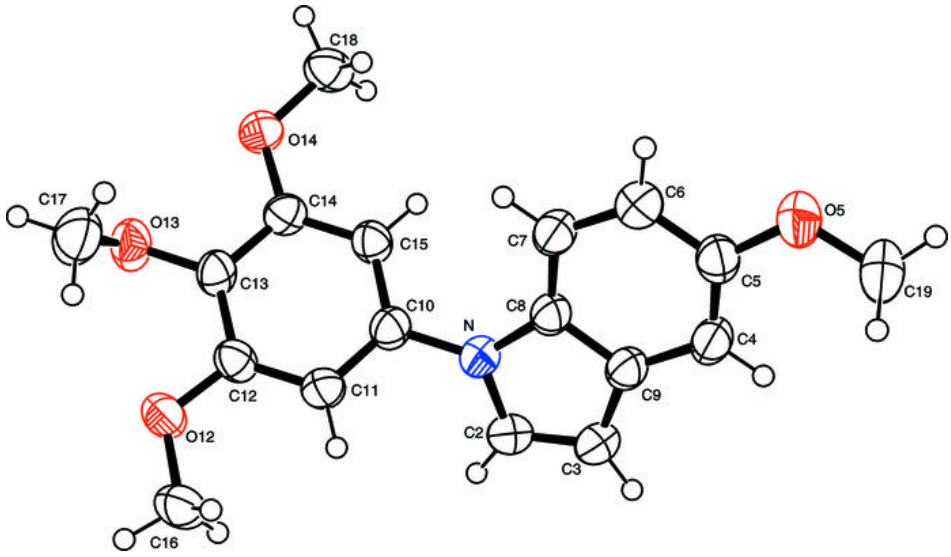

C18
O14
C17
O13
C14
C15
C13
C10
N
C12
C11
O12
C16
C6
C7
O5
C5
C19
C8
C4
C9
C2
C3

Fig. 2

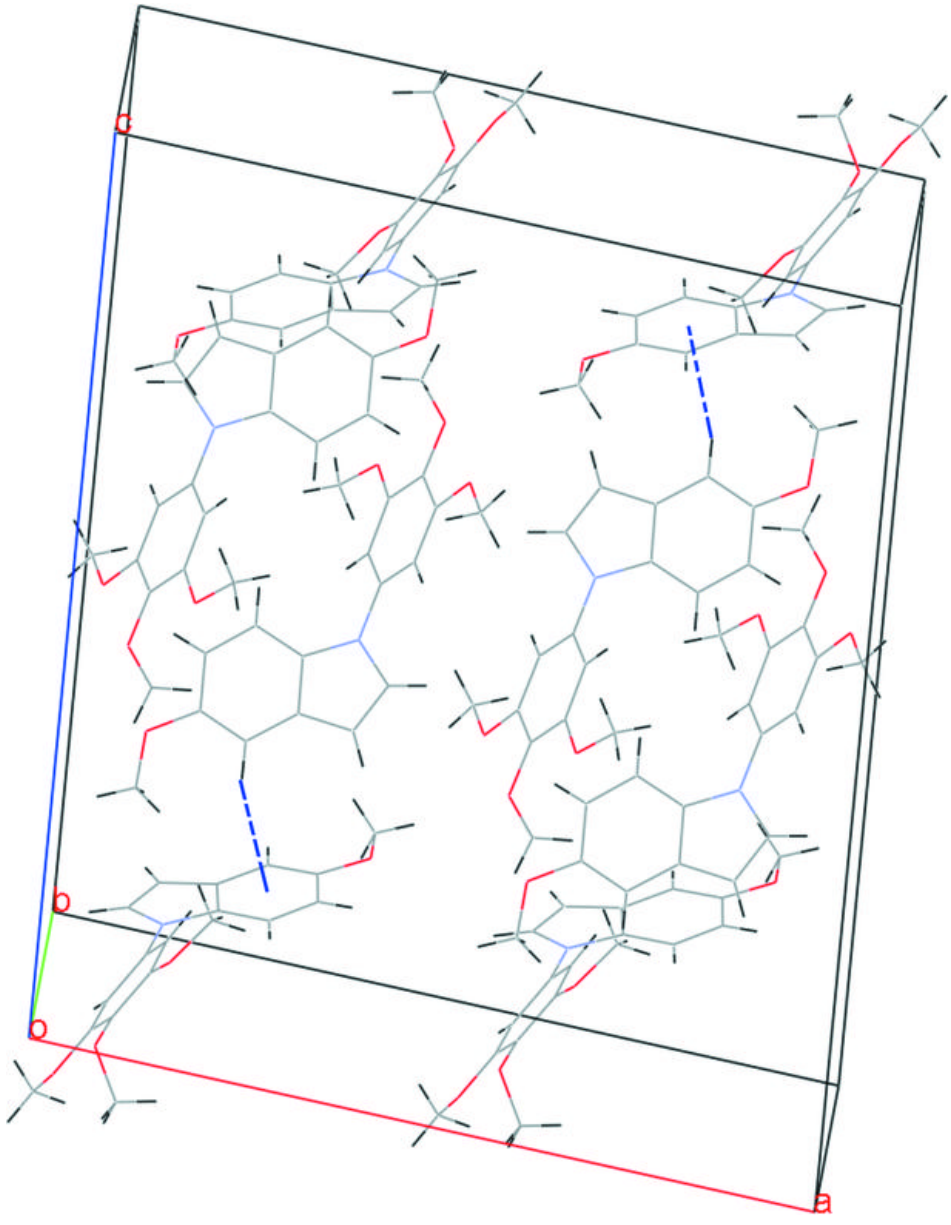
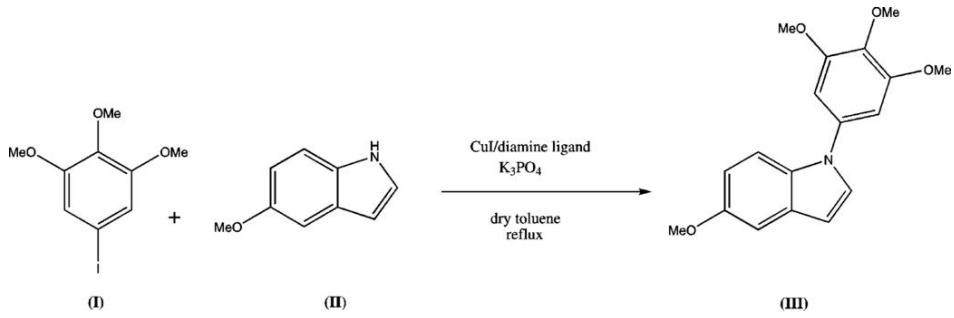


Fig. 3


OMe
MeO
OMe
I
+
H
N
MeO
CuI/diamine ligand
K_3PO_4
dry toluene
reflux
OMe
MeO
OMe
N
MeO

(I) (II) (III)

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3,6,14,17-Tetramethoxy-22,23-diphenyl-1,10,12,21-tetraazahexacyclo-[19.2.1.$0^{2,7}$.$0^{10,23}$.$0^{12,22}$.$0^{13,18}$]tetracosa-2(7),3,5,13(18),14,16-hexaene-11,24-dithione

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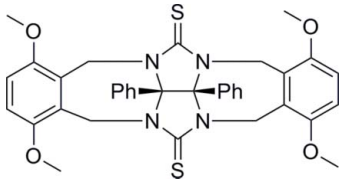
Key indicators: single-crystal X-ray study; T = 298 K; mean σ(C–C) = 0.004 Å; R factor = 0.056; wR factor = 0.162; data-to-parameter ratio = 16.9.

The title compound, $C_{36}H_{34}N_4O_4S_2$, is a thioglycoluril derivative, which bears two phenyl substituents on its convex face and two methoxy substituted *o*-xylylenes as sidewalls of the molecular clip. There is one half-molecule in the asymmetric unit: a crystallographic twofold axis generates the complete molecule. The non-planar seven-membered rings adopt chair conformations, while the two five-membered rings exhibit envelope conformations and make a dihedral angle of 68.46 (12)°. The O atoms of the methoxy groups are coplanar with the six-membered *o*-xylylene sidewalls.

Related literature

For related structures, see: Broan *et al.* (1989); Cao *et al.* (2009); Wang *et al.* (2006); Wang & Xi (2009); Wu & Sun, (2009). For further synthetic details, see: Broan *et al.* (1989); Wu *et al.* (2002). The rigid concave shape of glycoluril makes it a versatile building block in supramolecular chemistry, see: Gao *et al.* (2009); Rowan *et al.* (1999); Hof *et al.* (2002); Kolbel & Menger (2001); Wu *et al.* (2002); Kang *et al.* (2004).



Experimental

Crystal data

$C_{36}H_{34}N_4O_4S_2$
M_r = 650.79
Monoclinic, $C2/c$
a = 17.9993 (15) Å
b = 12.5069 (11) Å
c = 16.0934 (12) Å
β = 115.961 (3)°
V = 3257.3 (5) Å^3
Z = 4
Mo $K\alpha$ radiation
μ = 0.21 mm^{-1}
T = 298 K
0.23 × 0.20 × 0.10 mm

Data collection

Bruker SMART CCD area-detector diffractometer
13570 measured reflections
3546 independent reflections
2279 reflections with $I > 2\sigma(I)$
R_{int} = 0.067

Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.056
$wR(F^2)$ = 0.162
S = 0.98
3546 reflections
210 parameters
H-atom parameters constrained
$\Delta\rho_{max}$ = 0.29 e Å^{-3}
$\Delta\rho_{min}$ = −0.24 e Å^{-3}

Data collection: *SMART* (Bruker, 2001); cell refinement: *SAINT-Plus* (Bruker, 2001); data reduction: *SAINT-Plus*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *PLATON* (Spek, 2009); software used to prepare material for publication: *PLATON*.

The author thanks Professor An-Xin Wu for technical assistance and Dr Meng Xiang-Gao for the data collection.

Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: FL2304).

References

Broan, C. J., Butler, A. R., Reed, D. & Sadler, I. H. (1989). *J. Chem. Soc. Perkin Trans. 2*, pp. 731–740.
Bruker (2001). *SMART* and *SAINT-Plus*. Bruker AXS Inc., Madison, Wisconsin, USA.
Cao, L., Ding, J., Yin, G., Gao, M., Li, Y. & Wu, A. (2009). *Synlett*, pp. 1445–1448.
Gao, M., Cao, L., Wang, Z., Sun, J., She, N. & Wu, A. (2009). *Synlett*, pp. 315–319.
Hof, F., Craig, S. L., Nuckolls, C. & Rebek, J. Jr (2002). *Angew. Chem. Int. Ed.* **41**, 1488–1508.
Kang, J., Jo, J.-H. & In, S. (2004). *Tetrahedron Lett.* **45**, 5225–5228.
Kolbel, M. & Menger, F. M. (2001). *Chem. Commun.* pp. 275–276.
Rowan, A. E., Elemans, J. A. A. W. & Nolte, R. J. M. (1999). *Acc. Chem. Res.* **32**, 995–1006.
Sheldrick, G. M. (2008). *Acta Cryst.* A**64**, 112–122.
Spek, A. L. (2009). *Acta Cryst.* D**65**, 148–155.
Wang, Z. & Xi, H. (2009). *Acta Cryst.* E**65**, o1426.
Wang, Z., Zhou, B., Chen, Y., Yin, G., Li, Y., Wu, A. & Isaacs, L. (2006). *J. Org. Chem.* **71**, 4502–4508.
Wu, A., Chakraborty, A., Witt, D., Lagona, J., Damkaci, F., Ofori, M. A., Chiles, J. K., Fettinger, J. C. & Isaacs, L. (2002). *J. Org. Chem.* **67**, 5817–5830.
Wu, Y. & Sun, Y. (2009). *Acta Cryst.* E**65**, o1715.

supplementary materials

Acta Cryst. (2010). E**66**, o1673 [**doi:10.1107/S160053681002204X**]

3,6,14,17-Tetramethoxy-22,23-diphenyl-1,10,12,21-tetraazahexacyclo[19.2.1.$0^{2,7}$.$0^{10,23}$.$0^{12,22}$.$0^{13,18}$]tetracosa-2(7),3,5,13(18),14,16-hexaene-11,24-dithione

Y. Yang

Comment

The rigid concave shape of glycoluril makes it a versatile building block to construct various supramolecular objects (Gao *et al.*, 2009), including molecular clips and molecular baskets (Rowan *et al.*, 1999), molecular capsules (Hof *et al.*, 2002), xerogels (Kolbel & Menger, 2001), the cucurbit[n]uril family (Wu *et al.*, 2002), and anion-binding receptors (Kang *et al.*, 2004). Based on the previous studies (Broan *et al.*, 1989; Cao *et al.*, 2009; Wang *et al.*, 2006; Wang & Xi, 2009; Wu & Sun, 2009), we report here the structure of the title thioglycoluril derivative (Fig. 1), which is a potential receptor in supramolecular chemistry.

There is one half-molecule in the asymmetric unit. The non-planar seven-membered rings adopt chair conformations, while the two five-membered rings have envelope conformation and the dihedral angle between them is 68.46°. The methoxy groups on sidewalls are coplanar with the six-membered o-xylylene sidewalls. The molecule contains three nonclassical intramolecular C—H···S, C—H···O and C—H···N hydrogen bonds, and its crystal structure is stabilized mostly by intermolecular C—H···π interactions (Table 1).

Experimental

The thioglycoluril was synthesized according to a literature procedure, see : Broan *et al.*, (1989). Preparation of the title compound: A solution of thioglycoluril (326 mg, 1.00 mmol), paraformaldehyde (120 mg, 4.00 mmol) and 1,4-dimethoxybenzene (304 mg, 2.20 mmol) in TFA (5 ml) was stirred and heated at reflux for 6 h. After rotary evaporation the residue was chromatographed to yield the tile compound (521 mg, 0.80 mmol,80%). Crystals of (I) suitable for X-ray diffraction were grown by slow evaporation of a dichloromethane-methanol (1:2) solution of the title compound under 293 K.

Refinement

All H atoms were positioned in geometrically idealized positions and constrained to ride on their parent atoms, with C—H distances in the range 0.93-0.98 Å and Uĩso~(H) = 1.2U~eq~(C) or Uĩso~(H) = 1.5U~eq~(C).

Figures

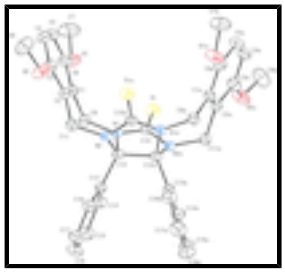


Fig. 1. A view of (I), showing the atom-labelling scheme, with displacement ellipsoids drawn at the 30% probability level.

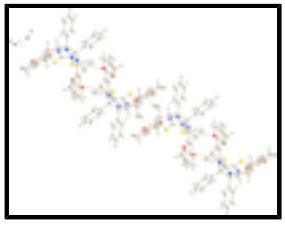


Fig. 2. Packing of (I) with C—H···π interactions drawn as dashed lines showing the formation of a one-dimensional chain.

3,6,14,17-Tetramethoxy-22,23-diphenyl-1,10,12,21-\ tetraazahexacyclo[19.2.1.$0^{2,7}$.$0^{10,23}$.$0^{12,22}$.$0^{13,18}$]tetracosa-\ 2(7),3,5,13 (18),14,16-hexaene-11,24-dithione

Crystal data

$C_{36}H_{34}N_4O_4S_2$	$F(000)$ = 1368
M_r = 650.79	D_x = 1.327 Mg m^{-3}
Monoclinic, $C2/c$	Mo $K\alpha$ radiation, λ = 0.71073 Å
Hall symbol: -C 2yc	Cell parameters from 2697 reflections
a = 17.9993 (15) Å	θ = 2.5–21.3°
b = 12.5069 (11) Å	μ = 0.21 mm^{-1}
c = 16.0934 (12) Å	T = 298 K
β = 115.961 (3)°	Block, colorless
V = 3257.3 (5) Å^3	0.23 × 0.20 × 0.10 mm
Z = 4	

Data collection

Bruker SMART CCD area-detector diffractometer	2279 reflections with $I > 2\sigma(I)$
Radiation source: fine-focus sealed tube	R_{int} = 0.067
graphite	θ_{max} = 27.0°, θ_{min} = 2.1°
phi and ω scans	h = −22→13
13570 measured reflections	k = −15→15
3546 independent reflections	l = −19→20

Refinement

Refinement on F^2	Primary atom site location: structure-invariant direct methods

Least-squares matrix: full	Secondary atom site location: difference Fourier map
$R[F^2 > 2\sigma(F^2)] = 0.056$	Hydrogen site location: inferred from neighbouring sites
$wR(F^2) = 0.162$	H-atom parameters constrained
$S = 0.98$	$w = 1/[\sigma^2(F_o^2) + (0.0878P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
3546 reflections	$(\Delta/\sigma)_{max} = 0.001$
210 parameters	$\Delta\rho_{max} = 0.29$ e Å^{-3}
0 restraints	$\Delta\rho_{min} = -0.24$ e Å^{-3}

Special details

Geometry. All esds (except the esd in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell esds are taken into account individually in the estimation of esds in distances, angles and torsion angles; correlations between esds in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell esds is used for estimating esds involving l.s. planes.

Refinement. Refinement of F^2 against ALL reflections. The weighted *R*-factor wR and goodness of fit *S* are based on F^2, conventional *R*-factors *R* are based on *F*, with *F* set to zero for negative F^2. The threshold expression of $F^2 > \sigma(F^2)$ is used only for calculating *R*-factors(gt) etc. and is not relevant to the choice of reflections for refinement. *R*-factors based on F^2 are statistically about twice as large as those based on *F*, and *R*- factors based on ALL data will be even larger.

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å^2)

	x	*y*	*z*	U_{iso}*/U_{eq}
S1	0.11451 (4)	0.22118 (5)	0.14339 (5)	0.0528 (3)
N1	0.09215 (11)	0.31734 (13)	0.27979 (13)	0.0335 (5)
N2	−0.00738 (11)	0.34780 (13)	0.14082 (13)	0.0325 (4)
C13	0.07957 (13)	0.50126 (16)	0.32973 (15)	0.0343 (5)
C9	0.16813 (14)	0.27755 (17)	0.35521 (17)	0.0388 (6)
H9A	0.1970	0.3371	0.3949	0.047*
H9B	0.2036	0.2489	0.3294	0.047*
C12	0.03855 (13)	0.39284 (16)	0.29759 (15)	0.0306 (5)
C10	0.06573 (14)	0.29489 (16)	0.18917 (16)	0.0326 (5)
O2	0.06197 (14)	0.16264 (16)	0.57355 (15)	0.0713 (6)
O1	0.24132 (13)	0.08009 (14)	0.37734 (15)	0.0683 (6)
C1	0.15415 (14)	0.19204 (17)	0.41322 (17)	0.0393 (6)
C2	0.10798 (15)	0.21274 (17)	0.46227 (17)	0.0406 (6)
C6	0.19350 (16)	0.09225 (18)	0.42349 (19)	0.0477 (7)
C18	0.13789 (15)	0.53676 (19)	0.30210 (19)	0.0497 (7)
H18	0.1560	0.4916	0.2688	0.060*
C11	−0.06462 (15)	0.31850 (18)	0.04628 (16)	0.0392 (6)
H11A	−0.0343	0.3157	0.0092	0.047*
H11B	−0.1060	0.3742	0.0209	0.047*
C3	0.10368 (17)	0.1344 (2)	0.52320 (19)	0.0512 (7)
C14	0.05429 (16)	0.56979 (18)	0.37978 (18)	0.0463 (7)
H14	0.0150	0.5469	0.3988	0.056*
C4	0.14195 (17)	0.0364 (2)	0.5309 (2)	0.0578 (8)

H4	0.1379	−0.0156	0.5701	0.069*
C17	0.16966 (18)	0.6394 (2)	0.3237 (2)	0.0655 (9)
H17	0.2086	0.6631	0.3045	0.079*
C5	0.18588 (18)	0.0156 (2)	0.4811 (2)	0.0564 (8)
H5	0.2108	−0.0508	0.4863	0.068*
C15	0.0865 (2)	0.6717 (2)	0.4019 (2)	0.0638 (9)
H15	0.0693	0.7170	0.4360	0.077*
C16	0.1438 (2)	0.7055 (2)	0.3733 (2)	0.0731 (10)
H16	0.1654	0.7742	0.3878	0.088*
C7	0.2729 (2)	−0.0224 (2)	0.3750 (3)	0.0859 (11)
H7A	0.2924	−0.0550	0.4348	0.129*
H7B	0.3178	−0.0162	0.3583	0.129*
H7C	0.2301	−0.0658	0.3302	0.129*
C8	0.0599 (2)	0.0907 (3)	0.6401 (2)	0.0865 (11)
H8A	0.0241	0.0319	0.6094	0.130*
H8B	0.0396	0.1269	0.6787	0.130*
H8C	0.1146	0.0643	0.6775	0.130*

Atomic displacement parameters (Å^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
S1	0.0520 (5)	0.0520 (4)	0.0612 (5)	0.0130 (3)	0.0311 (4)	−0.0081 (3)
N1	0.0300 (11)	0.0293 (9)	0.0435 (12)	0.0043 (7)	0.0181 (9)	0.0014 (8)
N2	0.0341 (11)	0.0273 (9)	0.0390 (11)	0.0020 (8)	0.0189 (9)	−0.0016 (8)
C13	0.0316 (13)	0.0300 (11)	0.0397 (13)	−0.0029 (9)	0.0141 (10)	0.0006 (9)
C9	0.0268 (13)	0.0385 (13)	0.0466 (14)	0.0035 (10)	0.0118 (11)	0.0042 (10)
C12	0.0317 (12)	0.0264 (10)	0.0391 (12)	0.0013 (9)	0.0205 (10)	0.0006 (9)
C10	0.0327 (13)	0.0270 (11)	0.0395 (14)	−0.0012 (9)	0.0170 (11)	0.0011 (9)
O2	0.0922 (16)	0.0662 (13)	0.0746 (14)	0.0174 (11)	0.0543 (13)	0.0311 (11)
O1	0.0756 (15)	0.0481 (11)	0.0968 (17)	0.0248 (10)	0.0521 (13)	0.0162 (10)
C1	0.0328 (14)	0.0343 (12)	0.0433 (14)	0.0000 (10)	0.0097 (11)	0.0030 (10)
C2	0.0390 (14)	0.0331 (12)	0.0430 (14)	−0.0015 (10)	0.0118 (12)	0.0037 (10)
C6	0.0452 (16)	0.0364 (13)	0.0582 (17)	0.0053 (11)	0.0197 (13)	0.0014 (11)
C18	0.0428 (16)	0.0428 (14)	0.0692 (19)	−0.0048 (11)	0.0300 (14)	0.0017 (12)
C11	0.0397 (14)	0.0408 (13)	0.0357 (13)	0.0020 (10)	0.0153 (11)	−0.0017 (10)
C3	0.0549 (18)	0.0474 (15)	0.0536 (17)	−0.0009 (13)	0.0259 (14)	0.0083 (12)
C14	0.0582 (17)	0.0334 (13)	0.0518 (16)	−0.0035 (11)	0.0284 (14)	−0.0037 (11)
C4	0.063 (2)	0.0437 (15)	0.0596 (18)	0.0013 (13)	0.0207 (16)	0.0190 (13)
C17	0.0486 (18)	0.0531 (17)	0.091 (2)	−0.0183 (14)	0.0267 (17)	0.0117 (16)
C5	0.065 (2)	0.0345 (14)	0.0639 (19)	0.0073 (12)	0.0226 (16)	0.0073 (13)
C15	0.090 (2)	0.0359 (14)	0.0624 (19)	−0.0065 (15)	0.0304 (17)	−0.0115 (13)
C16	0.084 (3)	0.0387 (16)	0.080 (2)	−0.0232 (16)	0.021 (2)	−0.0042 (15)
C7	0.112 (3)	0.055 (2)	0.113 (3)	0.0199 (19)	0.070 (3)	−0.0035 (18)
C8	0.099 (3)	0.095 (3)	0.076 (2)	0.009 (2)	0.048 (2)	0.036 (2)

Geometric parameters (Å, °)

S1—C10	1.652 (2)	C6—C5	1.381 (4)
N1—C10	1.351 (3)	C18—C17	1.386 (4)

N1—C9	1.462 (3)	C18—H18	0.9300
N1—C12	1.465 (3)	C11—C2^{i}	1.511 (3)
N2—C10	1.371 (3)	C11—H11A	0.9700
N2—C12^{i}	1.450 (3)	C11—H11B	0.9700
N2—C11	1.462 (3)	C3—C4	1.384 (4)
C13—C18	1.381 (3)	C14—C15	1.381 (3)
C13—C14	1.382 (3)	C14—H14	0.9300
C13—C12	1.522 (3)	C4—C5	1.375 (4)
C9—C1	1.511 (3)	C4—H4	0.9300
C9—H9A	0.9700	C17—C16	1.364 (4)
C9—H9B	0.9700	C17—H17	0.9300
C12—N2^{i}	1.450 (3)	C5—H5	0.9300
C12—C12^{i}	1.553 (4)	C15—C16	1.369 (4)
O2—C3	1.370 (3)	C15—H15	0.9300
O2—C8	1.412 (3)	C16—H16	0.9300
O1—C6	1.369 (3)	C7—H7A	0.9600
O1—C7	1.410 (3)	C7—H7B	0.9600
C1—C2	1.398 (3)	C7—H7C	0.9600
C1—C6	1.409 (3)	C8—H8A	0.9600
C2—C3	1.412 (3)	C8—H8B	0.9600
C2—C11^{i}	1.511 (3)	C8—H8C	0.9600
C10—N1—C9	125.79 (19)	N2—C11—H11A	108.6
C10—N1—C12	113.23 (17)	C2^{i}—C11—H11A	108.6
C9—N1—C12	120.91 (18)	N2—C11—H11B	108.6
C10—N2—C12^{i}	111.24 (18)	C2^{i}—C11—H11B	108.6
C10—N2—C11	122.26 (18)	H11A—C11—H11B	107.6
C12^{i}—N2—C11	120.09 (18)	O2—C3—C4	123.7 (2)
C18—C13—C14	118.6 (2)	O2—C3—C2	116.3 (2)
C18—C13—C12	120.1 (2)	C4—C3—C2	120.0 (3)
C14—C13—C12	121.1 (2)	C15—C14—C13	121.0 (3)
N1—C9—C1	113.92 (19)	C15—C14—H14	119.5
N1—C9—H9A	108.8	C13—C14—H14	119.5
C1—C9—H9A	108.8	C5—C4—C3	120.4 (2)
N1—C9—H9B	108.8	C5—C4—H4	119.8
C1—C9—H9B	108.8	C3—C4—H4	119.8
H9A—C9—H9B	107.7	C16—C17—C18	120.0 (3)
N2^{i}—C12—N1	111.61 (16)	C16—C17—H17	120.0
N2^{i}—C12—C13	112.90 (18)	C18—C17—H17	120.0
N1—C12—C13	112.20 (18)	C4—C5—C6	120.8 (2)
N2^{i}—C12—C12^{i}	103.2 (2)	C4—C5—H5	119.6
N1—C12—C12^{i}	100.82 (17)	C6—C5—H5	119.6
C13—C12—C12^{i}	115.23 (12)	C16—C15—C14	119.4 (3)
N1—C10—N2	108.02 (18)	C16—C15—H15	120.3
N1—C10—S1	126.35 (17)	C14—C15—H15	120.3
N2—C10—S1	125.57 (17)	C17—C16—C15	120.7 (3)
C3—O2—C8	119.2 (2)	C17—C16—H16	119.7

C6—O1—C7	118.2 (2)	C15—C16—H16	119.7
C2—C1—C6	119.4 (2)	O1—C7—H7A	109.5
C2—C1—C9	121.2 (2)	O1—C7—H7B	109.5
C6—C1—C9	119.2 (2)	H7A—C7—H7B	109.5
C1—C2—C3	119.4 (2)	O1—C7—H7C	109.5
C1—C2—C11^{i}	121.4 (2)	H7A—C7—H7C	109.5
C3—C2—C11^{i}	119.2 (2)	H7B—C7—H7C	109.5
O1—C6—C5	123.9 (2)	O2—C8—H8A	109.5
O1—C6—C1	116.0 (2)	O2—C8—H8B	109.5
C5—C6—C1	120.0 (3)	H8A—C8—H8B	109.5
C13—C18—C17	120.3 (3)	O2—C8—H8C	109.5
C13—C18—H18	119.8	H8A—C8—H8C	109.5
C17—C18—H18	119.8	H8B—C8—H8C	109.5
N2—C11—C2^{i}	114.50 (19)		
C10—N1—C9—C1	−106.3 (3)	C7—O1—C6—C5	11.7 (4)
C12—N1—C9—C1	77.1 (3)	C7—O1—C6—C1	−171.6 (3)
C10—N1—C12—N2^{i}	122.1 (2)	C2—C1—C6—O1	−176.5 (2)
C9—N1—C12—N2^{i}	−60.9 (2)	C9—C1—C6—O1	−1.2 (3)
C10—N1—C12—C13	−110.1 (2)	C2—C1—C6—C5	0.4 (4)
C9—N1—C12—C13	66.9 (2)	C9—C1—C6—C5	175.7 (2)
C10—N1—C12—C12^{i}	13.1 (2)	C14—C13—C18—C17	−0.5 (4)
C9—N1—C12—C12^{i}	−169.92 (18)	C12—C13—C18—C17	173.8 (2)
C18—C13—C12—N2^{i}	155.7 (2)	C10—N2—C11—C2^{i}	70.0 (3)
C14—C13—C12—N2^{i}	−30.1 (3)	C12^{i}—N2—C11—C2^{i}	−79.4 (2)
C18—C13—C12—N1	28.6 (3)	C8—O2—C3—C4	2.6 (4)
C14—C13—C12—N1	−157.3 (2)	C8—O2—C3—C2	−175.9 (3)
C18—C13—C12—C12^{i}	−86.0 (3)	C1—C2—C3—O2	175.8 (2)
C14—C13—C12—C12^{i}	88.1 (3)	C11^{i}—C2—C3—O2	−2.3 (4)
C9—N1—C10—N2	−179.57 (19)	C1—C2—C3—C4	−2.8 (4)
C12—N1—C10—N2	−2.7 (2)	C11^{i}—C2—C3—C4	179.0 (2)
C9—N1—C10—S1	−2.1 (3)	C18—C13—C14—C15	0.0 (4)
C12—N1—C10—S1	174.75 (16)	C12—C13—C14—C15	−174.3 (2)
C12^{i}—N2—C10—N1	−10.2 (2)	O2—C3—C4—C5	−177.0 (3)
C11—N2—C10—N1	−162.05 (19)	C2—C3—C4—C5	1.5 (4)
C12^{i}—N2—C10—S1	172.29 (15)	C13—C18—C17—C16	0.6 (4)
C11—N2—C10—S1	20.5 (3)	C3—C4—C5—C6	0.8 (4)
N1—C9—C1—C2	−61.3 (3)	O1—C6—C5—C4	174.9 (2)
N1—C9—C1—C6	123.5 (2)	C1—C6—C5—C4	−1.8 (4)
C6—C1—C2—C3	1.8 (4)	C13—C14—C15—C16	0.5 (4)
C9—C1—C2—C3	−173.4 (2)	C18—C17—C16—C15	−0.2 (5)
C6—C1—C2—C11^{i}	180.0 (2)	C14—C15—C16—C17	−0.4 (5)
C9—C1—C2—C11^{i}	4.8 (3)		

Symmetry codes: (i) −*x*, *y*, −*z*+1/2.

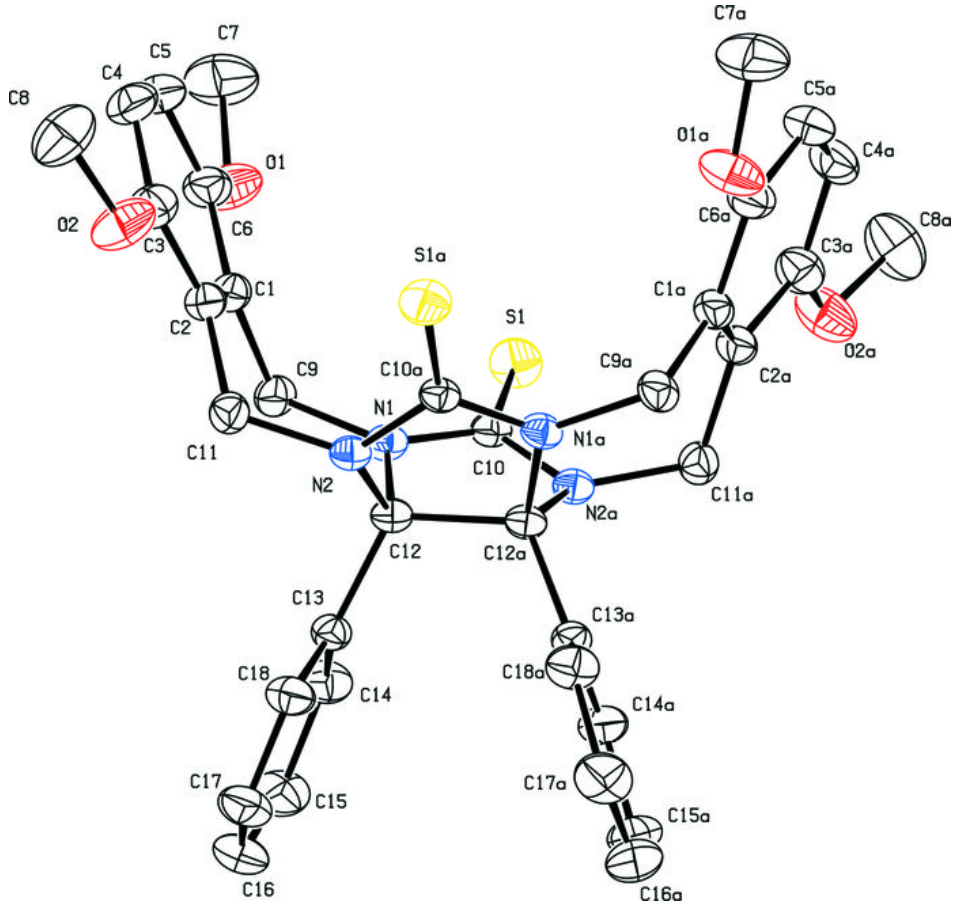
Hydrogen-bond geometry (Å, °)

Cg1 is the centroid of the C1–C6 ring.

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
C9—H9A···Cg1^{ii}	0.97	2.70	3.540	145.
C11—H11A···O2^{ii}	0.97	2.26	2.757 (3)	111
C14—H14···N2^{ii}	0.93	2.56	2.879 (3)	101
C18—H18···N1	0.93	2.51	2.842 (3)	102
C9—H9B···S1	0.97	2.73	3.189 (3)	110
C9—H9B···O1	0.97	2.25	2.748 (3)	111

Symmetry codes: (ii) −*x*, *y*, −*z*+1/2.

Fig. 1


C7a
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C4a
O1a
C6a
C8a
C3a
O2a
C1a
C2a
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N2a
C12a
C13a
C18a
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N1
N2
C12
C13
C18
C14
C17
C15
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C1
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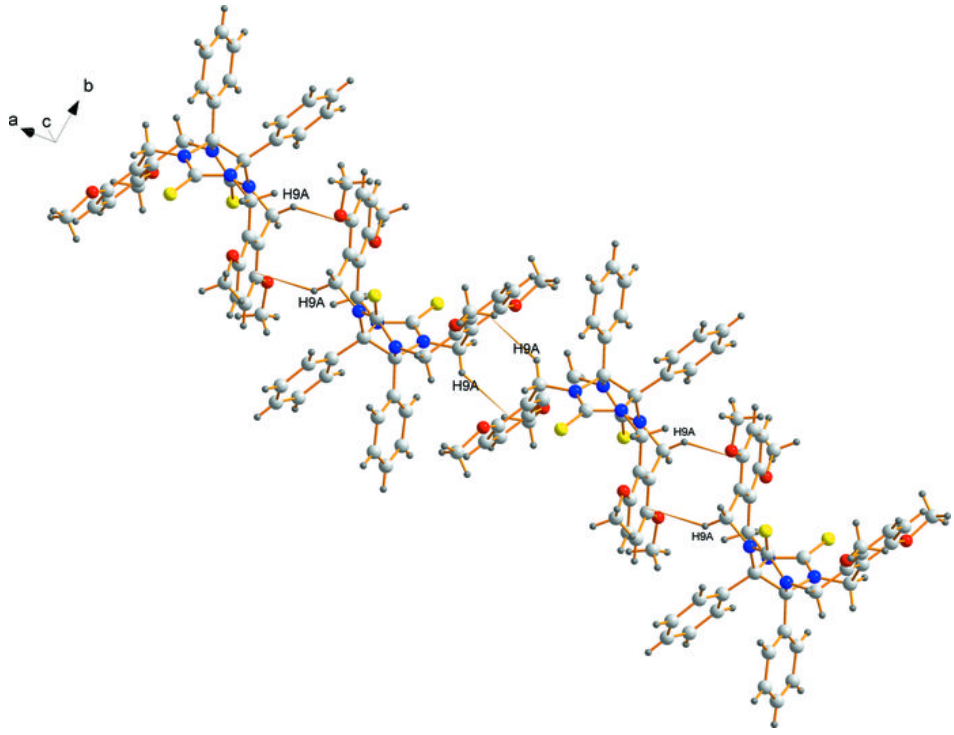
C3
O2
C8
C4
C5
C7
O1
C6

Fig. 2



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(2*E*)-2-[2-(4-Chlorophenyl)hydrazin-1-ylidene]-4,4,4-trifluoro-3-oxobutanal

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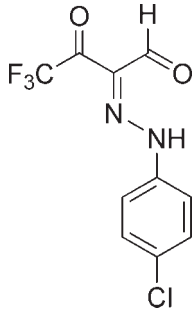
Key indicators: single-crystal X-ray study; T = 173 K; mean σ(C–C) = 0.003 Å; R factor = 0.033; wR factor = 0.111; data-to-parameter ratio = 13.5.

The title compound, $C_{10}H_6ClF_3N_2O_2$, was synthesized by coupling 4-dimethylamino-1,1,1-trifluorobut-3-en-2-one with 4-chlorobenzenediazonium chloride. It crystallizes with two molecules in the asymmetric unit, which form two similar centrosymmetric dimers *via* hydrogen bonds. Extensive electron delocalization and intramolecular N—H···O hydrogen bonds are responsible for a planar conformation of the molecules (maximum deviations = 0.010 and −0.015 Å for the two molecules). In addition to hydrogen bonds, π–π stacking interactions with centroid–centroid distances of 3.604 (2) and 3.583 (2) Å contribute to the stability of the crystal structure.

Related literature

For the crystal structure of the isostructural iodo derivative, see: Jiang & Zhu (2008).



Experimental

Crystal data

$C_{10}H_6ClF_3N_2O_2$
M_r = 278.62
Triclinic, $P\overline{1}$
a = 7.6440 (4) Å
b = 7.7139 (4) Å
c = 19.4221 (10) Å
α = 86.134 (1)°
β = 81.706 (1)°
γ = 88.999 (1)°
V = 1130.63 (10) Å^3
Z = 4
Mo $K\alpha$ radiation
μ = 0.37 mm^{-1}
T = 173 K
0.44 × 0.38 × 0.35 mm

Data collection

Bruker SMART 1000 CCD diffractometer
Absorption correction: multi-scan (*SADABS*; Bruker, 2001)
T_{min} = 0.853, T_{max} = 0.880
8820 measured reflections
4387 independent reflections
3577 reflections with $I > 2\sigma(I)$
R_{int} = 0.017

Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.033
$wR(F^2)$ = 0.111
S = 1.05
4387 reflections
325 parameters
H-atom parameters constrained
$\Delta\rho_{max}$ = 0.29 e Å^{-3}
$\Delta\rho_{min}$ = −0.23 e Å^{-3}

Table 1
Hydrogen-bond geometry (Å, °).

D—H···A	D—H	H···A	D···A	D—H···A
N11—H11···O8	0.88	2.01	2.6746 (18)	131
N29—H29···O26	0.88	2.03	2.679 (2)	130
N29—H29···O26^{i}	0.88	2.42	3.2159 (19)	150
C27—H27···O6^{ii}	0.95	2.59	3.491 (2)	158
C36—H36···O26^{i}	0.95	2.52	3.323 (3)	143

Symmetry codes: (i) $-x, -y, -z+2$; (ii) $x-1, y, z$.

Data collection: *SMART* (Bruker, 2001); cell refinement: *SAINT-Plus* (Bruker, 2003); data reduction: *SAINT-Plus*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *ORTEP-3 for Windows* (Farrugia, 1997); software used to prepare material for publication: *SHELXL97*.

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Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: GK2268).

References

Bruker (2001). *SAINT-Plus* and *SADABS*. Bruker AXS Inc., Madison, Wisconsin, USA.
Bruker (2003). *SMART*. Bruker AXS Inc., Madison, Wisconsin, USA.
Farrugia, L. J. (1997). *J. Appl. Cryst.* **30**, 565.
Jiang, H. & Zhu, S. (2008). *J. Fluorine Chem.* **129**, 40–44.
Sheldrick, G. M. (2008). *Acta Cryst.* A**64**, 112–122.

supplementary materials

Acta Cryst. (2010). E**66**, o1654 [**doi:10.1107/S1600536810021835**]

(2*E*)-2-[2-(4-Chlorophenyl)hydrazin-1-ylidene]-4,4,4-trifluoro-3-oxobutanal

Y.-P. Huo and L.-H. Zhou

Comment

Herein, we report the crystal structure of (2*E*)-2-[2-(4-chlorophenyl)]hydrazinylidene]-4,4,4-trifluoro-3-oxobutanal, which was prepared *via* a reaction of 4-(dimethylamino)-1,1,1-trifluorobut-3-en-2-one with diazonium salt according to the procedure reported by Zhu *et al.* (2008). The title compound, **3**, has been characterized by ESI-MS, NMR, FTIR spectroscopy and elemental analysis. Here we report the crystal structure of **3**. It crystallizes with two almost identical molecules in the asymmetric unit. The molecule is almost planar except for the $–CF_3$ group F atoms. There are some supramolecular interactions in the compound **3**. The intramolecular N—H···O hydrogen bonds are N11—H11···O8 and N29—H29···O26 (Table 1) together with strong π-π stacking interactions [centroid-to-centroid distance = 3.604 (2) Å; 3.583 (2) Å] that contribute to the stability of the structure.

Experimental

The title compound was prepared *via* the reaction of 4-(dimethylamino)-1,1,1-trifluorobut-3-en-2-one with diazonium salt according to the procedure reported by Zhu *et al.* (2008). A solution of the *p*-chloroaniline **2** (1.28 g, 10 mmol) in a solution of 3 *M* HCl (5 ml) was diazotized at 0 °C by slow addition of a solution of $NaNO_2$ (0.7 g, 10 mmol) in 5 ml H_2O. The solution of aniline diazonium salt was added dropwise to a mixture of compound **1** (see scheme) (1.67 g, 10 mmol) with NaOH (1.6 g, 40 mmol) and ethanol (50 ml) in ice-salt bath. The reaction mixture was stirred for 1 h at the same temperature, then TLC analysis showed that the reaction had finished. The resulting precipitate was filtered off. Purification by column chromatography on silica gel (hexane:AcOEt = 30:1) gave red solid **3** in 75% yield. mp 418-420 K. ^{1}H NMR ($CDCl_3$, 300 MHz) δ14.87 (1*H*, s, NH), 10.03 (1*H*, s, CHO), 7.45 (4*H*, s, Ph), ^{19}F NMR ($CDCl_3$): -71.50 (3 F, s, CF_3). IR (KBr, cm^{-1}): 2924, 1699, 1526, 1308, 1187, 1157, 897; ESI-MS *m*/*z*: 279.9 ($[M+H]^+$); Elemental analysis: found C: 43.13, H: 2.29, N: 10.07; calculated for ($C_{10}H_6ClF_3N_2O_2$) C: 43.11 H: 2.17 N: 10.05 (%). 20 mg of compound **3** was dissolved in 10 ml (EtOAc:pPetroleum ether = 1:8) and the solution was kept at room temperature for 6 d, natural evaporation gave red single crystals of compound **3** suitable for X-ray analysis.

Refinement

All H atoms were positioned geometrically and refined using a riding model, with all C—H = 0.95 Å, N—H = 0.88 Å and with U_{iso}(H) = 1.2U_{eq}(C), U_{iso}(H) = 1.2U_{eq}(N).

Figures

Fig. 1. The synthesis of (*E*)-2-(2-(4-Chlophenyl)hydrazono)-4,4,4-trifluoro-3-oxobutanal

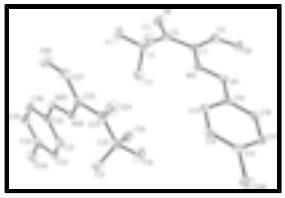


Fig. 2. View of the asymmetric unit in the title compound.

(2*E*)-2-[2-(4-Chlorophenyl)hydrazin-1-ylidene]-4,4,4-trifluoro- 3-oxobutanal

Crystal data

$C_{10}H_6ClF_3N_2O_2$	$Z = 4$
$M_r = 278.62$	$F(000) = 560$
Triclinic, $P\overline{1}$	$D_x = 1.637$ Mg m^{-3}
Hall symbol: -P 1	Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å
$a = 7.6440$ (4) Å	Cell parameters from 8820 reflections
$b = 7.7139$ (4) Å	$\theta = 1.1$–$26.0°$
$c = 19.4221$ (10) Å	$\mu = 0.37$ mm^{-1}
$\alpha = 86.134$ (1)°	$T = 173$ K
$\beta = 81.706$ (1)°	Block, yellow
$\gamma = 88.999$ (1)°	0.44 × 0.38 × 0.35 mm
$V = 1130.63$ (10) Å^3	

Data collection

Bruker SMART 1000 CCD diffractometer	4387 independent reflections
Radiation source: fine-focus sealed tube	3577 reflections with $I > 2\sigma(I)$
graphite	$R_{int} = 0.017$
ω scans	$\theta_{max} = 26.0°$, $\theta_{min} = 1.1°$
Absorption correction: multi-scan (*SADABS*; Bruker, 2001)	$h = -9 \rightarrow 9$
$T_{min} = 0.853$, $T_{max} = 0.880$	$k = -9 \rightarrow 9$
8820 measured reflections	$l = -23 \rightarrow 23$

Refinement

Refinement on F^2	Primary atom site location: structure-invariant direct methods
Least-squares matrix: full	Secondary atom site location: difference Fourier map
$R[F^2 > 2\sigma(F^2)] = 0.033$	Hydrogen site location: inferred from neighbouring sites
$wR(F^2) = 0.111$	H-atom parameters constrained
$S = 1.05$	$w = 1/[\sigma^2(F_o^2) + (0.0688P)^2 + 0.2643P]$ where $P = (F_o^2 + 2F_c^2)/3$
4387 reflections	$(\Delta/\sigma)_{max} = 0.001$
325 parameters	$\Delta\rho_{max} = 0.29$ e Å^{-3}
0 restraints	$\Delta\rho_{min} = -0.23$ e Å^{-3}

Special details

Geometry. All esds (except the esd in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell esds are taken into account individually in the estimation of esds in distances, angles and torsion angles; correlations between esds in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell esds is used for estimating esds involving l.s. planes.

Refinement. Refinement of F^2 against ALL reflections. The weighted R-factor wR and goodness of fit S are based on F^2, conventional R-factors R are based on F, with F set to zero for negative F^2. The threshold expression of $F^2 > 2\text{sigma}(F^2)$ is used only for calculating R-factors(gt) etc. and is not relevant to the choice of reflections for refinement. R-factors based on F^2 are statistically about twice as large as those based on F, and R- factors based on ALL data will be even larger.

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters ($Å^2$)

	x	*y*	*z*	U_{iso}*/U_{eq}
F1	0.41928 (17)	−0.14617 (18)	0.81983 (6)	0.0571 (4)
F2	0.43024 (15)	0.08932 (15)	0.75482 (6)	0.0461 (3)
F3	0.36230 (15)	−0.15031 (16)	0.71485 (6)	0.0464 (3)
C4	0.4666 (3)	−0.0800 (3)	0.75480 (10)	0.0373 (4)
C5	0.6660 (2)	−0.1153 (2)	0.73104 (9)	0.0312 (4)
O6	0.7481 (2)	−0.19276 (19)	0.77259 (7)	0.0478 (4)
C7	0.7407 (2)	−0.0528 (2)	0.66091 (9)	0.0271 (4)
O8	0.99555 (16)	−0.04137 (17)	0.57727 (7)	0.0362 (3)
C9	0.9266 (2)	−0.0873 (2)	0.63594 (10)	0.0315 (4)
H9	0.9963	−0.1478	0.6666	0.038*
N10	0.62895 (18)	0.03374 (17)	0.62508 (7)	0.0258 (3)
N11	0.67864 (18)	0.09586 (17)	0.56194 (7)	0.0255 (3)
H11	0.7879	0.0804	0.5417	0.031*
C12	0.5552 (2)	0.18901 (19)	0.52582 (8)	0.0244 (3)
C13	0.3785 (2)	0.2002 (2)	0.55450 (9)	0.0287 (4)
H13	0.3384	0.1459	0.5992	0.034*
C14	0.2614 (2)	0.2914 (2)	0.51727 (10)	0.0316 (4)
H14	0.1398	0.2989	0.5359	0.038*
C15	0.3231 (2)	0.3710 (2)	0.45304 (9)	0.0290 (4)
Cl16	0.17686 (7)	0.48727 (6)	0.40584 (3)	0.04196 (15)
C17	0.4984 (2)	0.3604 (2)	0.42417 (9)	0.0296 (4)
H17	0.5382	0.4158	0.3796	0.036*
C18	0.6156 (2)	0.2678 (2)	0.46094 (9)	0.0287 (4)
H18	0.7367	0.2585	0.4417	0.034*
F19	0.14628 (17)	0.47780 (18)	0.67586 (6)	0.0541 (3)
F20	0.32094 (14)	0.45871 (15)	0.75272 (6)	0.0422 (3)
F21	0.06433 (17)	0.57720 (15)	0.77605 (7)	0.0525 (3)
C22	0.1519 (2)	0.4478 (3)	0.74380 (10)	0.0368 (4)
C23	0.0728 (2)	0.2668 (2)	0.76964 (10)	0.0344 (4)
O24	0.0173 (2)	0.1827 (2)	0.72714 (8)	0.0522 (4)
C25	0.0720 (2)	0.2110 (2)	0.84266 (9)	0.0302 (4)
O26	0.0099 (2)	−0.01845 (17)	0.92755 (7)	0.0438 (3)
C27	0.0109 (2)	0.0371 (2)	0.86723 (10)	0.0367 (4)

H27	−0.0294	−0.0355	0.8353	0.044*
N28	0.13267 (18)	0.32559 (19)	0.88092 (7)	0.0287 (3)
N29	0.13874 (19)	0.29289 (19)	0.94648 (7)	0.0295 (3)
H29	0.1023	0.1924	0.9673	0.035*
C30	0.2050 (2)	0.4213 (2)	0.98458 (9)	0.0287 (4)
C31	0.2464 (2)	0.5856 (2)	0.95348 (10)	0.0346 (4)
H31	0.2305	0.6132	0.9064	0.042*
C32	0.3108 (3)	0.7084 (3)	0.99149 (11)	0.0391 (4)
H32	0.3400	0.8212	0.9707	0.047*
C33	0.3327 (2)	0.6661 (3)	1.06009 (10)	0.0367 (4)
Cl34	0.41607 (7)	0.82172 (8)	1.10737 (3)	0.05462 (18)
C35	0.2909 (3)	0.5042 (3)	1.09141 (10)	0.0397 (4)
H35	0.3058	0.4773	1.1387	0.048*
C36	0.2265 (2)	0.3804 (3)	1.05305 (10)	0.0355 (4)
H36	0.1974	0.2677	1.0739	0.043*

Atomic displacement parameters (Å^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
F1	0.0558 (8)	0.0763 (9)	0.0332 (7)	−0.0031 (7)	0.0083 (6)	0.0094 (6)
F2	0.0472 (7)	0.0443 (7)	0.0457 (7)	0.0121 (5)	−0.0005 (5)	−0.0122 (5)
F3	0.0399 (6)	0.0555 (7)	0.0441 (7)	−0.0124 (5)	−0.0044 (5)	−0.0055 (5)
C4	0.0405 (11)	0.0413 (10)	0.0281 (9)	−0.0002 (8)	0.0008 (8)	−0.0012 (8)
C5	0.0361 (9)	0.0271 (8)	0.0306 (9)	0.0005 (7)	−0.0056 (8)	−0.0019 (7)
O6	0.0513 (9)	0.0526 (9)	0.0378 (8)	0.0088 (7)	−0.0084 (7)	0.0115 (7)
C7	0.0293 (8)	0.0254 (8)	0.0274 (9)	0.0005 (7)	−0.0058 (7)	−0.0031 (6)
O8	0.0294 (7)	0.0437 (7)	0.0344 (7)	0.0009 (6)	−0.0017 (5)	−0.0011 (6)
C9	0.0299 (9)	0.0311 (9)	0.0344 (10)	0.0017 (7)	−0.0068 (8)	−0.0031 (7)
N10	0.0293 (7)	0.0225 (7)	0.0262 (7)	−0.0011 (6)	−0.0056 (6)	−0.0028 (5)
N11	0.0238 (7)	0.0257 (7)	0.0267 (7)	−0.0001 (5)	−0.0031 (6)	−0.0007 (6)
C12	0.0289 (8)	0.0188 (7)	0.0266 (8)	0.0002 (6)	−0.0071 (7)	−0.0035 (6)
C13	0.0307 (9)	0.0256 (8)	0.0290 (9)	−0.0008 (7)	−0.0018 (7)	−0.0008 (7)
C14	0.0269 (9)	0.0285 (9)	0.0398 (10)	0.0013 (7)	−0.0044 (7)	−0.0050 (7)
C15	0.0344 (9)	0.0235 (8)	0.0318 (9)	0.0047 (7)	−0.0129 (7)	−0.0052 (7)
Cl16	0.0452 (3)	0.0363 (3)	0.0482 (3)	0.0099 (2)	−0.0215 (2)	−0.0017 (2)
C17	0.0369 (9)	0.0266 (8)	0.0255 (9)	0.0000 (7)	−0.0056 (7)	−0.0012 (7)
C18	0.0282 (8)	0.0281 (8)	0.0294 (9)	0.0005 (7)	−0.0020 (7)	−0.0028 (7)
F19	0.0567 (8)	0.0720 (9)	0.0322 (6)	−0.0073 (6)	−0.0087 (5)	0.0149 (6)
F20	0.0355 (6)	0.0476 (6)	0.0424 (6)	−0.0043 (5)	−0.0058 (5)	0.0071 (5)
F21	0.0563 (8)	0.0395 (6)	0.0557 (8)	0.0145 (6)	0.0049 (6)	0.0082 (6)
C22	0.0339 (10)	0.0426 (11)	0.0326 (10)	0.0036 (8)	−0.0030 (8)	0.0024 (8)
C23	0.0291 (9)	0.0417 (10)	0.0321 (10)	0.0027 (8)	−0.0039 (7)	−0.0026 (8)
O24	0.0641 (10)	0.0588 (9)	0.0367 (8)	−0.0119 (8)	−0.0154 (7)	−0.0049 (7)
C25	0.0281 (9)	0.0313 (9)	0.0302 (9)	0.0021 (7)	−0.0015 (7)	−0.0020 (7)
O26	0.0559 (9)	0.0368 (7)	0.0379 (8)	−0.0070 (6)	−0.0066 (6)	0.0050 (6)
C27	0.0389 (10)	0.0337 (10)	0.0374 (11)	−0.0014 (8)	−0.0037 (8)	−0.0041 (8)
N28	0.0245 (7)	0.0328 (8)	0.0277 (8)	0.0039 (6)	−0.0008 (6)	−0.0002 (6)
N29	0.0295 (7)	0.0310 (8)	0.0268 (8)	−0.0002 (6)	−0.0011 (6)	0.0006 (6)

C30	0.0215 (8)	0.0346 (9)	0.0291 (9)	0.0017 (7)	−0.0002 (7)	−0.0030 (7)
C31	0.0340 (9)	0.0383 (10)	0.0303 (9)	−0.0017 (8)	−0.0014 (8)	0.0003 (8)
C32	0.0363 (10)	0.0373 (10)	0.0424 (11)	−0.0042 (8)	−0.0012 (8)	−0.0028 (8)
C33	0.0253 (9)	0.0460 (11)	0.0396 (11)	−0.0003 (8)	−0.0028 (8)	−0.0137 (8)
Cl34	0.0433 (3)	0.0645 (4)	0.0607 (4)	−0.0052 (3)	−0.0112 (3)	−0.0283 (3)
C35	0.0346 (10)	0.0545 (12)	0.0308 (10)	0.0021 (9)	−0.0076 (8)	−0.0049 (9)
C36	0.0354 (10)	0.0397 (10)	0.0307 (10)	0.0005 (8)	−0.0051 (8)	0.0023 (8)

Geometric parameters (Å, °)

F1—C4	1.332 (2)	F19—C22	1.331 (2)
F2—C4	1.331 (2)	F20—C22	1.333 (2)
F3—C4	1.335 (2)	F21—C22	1.333 (2)
C4—C5	1.553 (3)	C22—C23	1.553 (3)
C5—O6	1.213 (2)	C23—O24	1.210 (2)
C5—C7	1.453 (2)	C23—C25	1.453 (3)
C7—N10	1.322 (2)	C25—N28	1.324 (2)
C7—C9	1.459 (2)	C25—C27	1.455 (2)
O8—C9	1.217 (2)	O26—C27	1.219 (2)
C9—H9	0.9500	C27—H27	0.9500
N10—N11	1.2924 (19)	N28—N29	1.289 (2)
N11—C12	1.414 (2)	N29—C30	1.418 (2)
N11—H11	0.8800	N29—H29	0.8800
C12—C18	1.382 (2)	C30—C36	1.378 (3)
C12—C13	1.388 (2)	C30—C31	1.388 (3)
C13—C14	1.384 (2)	C31—C32	1.378 (3)
C13—H13	0.9500	C31—H31	0.9500
C14—C15	1.376 (3)	C32—C33	1.383 (3)
C14—H14	0.9500	C32—H32	0.9500
C15—C17	1.380 (3)	C33—C35	1.374 (3)
C15—Cl16	1.7444 (17)	C33—Cl34	1.7418 (19)
C17—C18	1.384 (2)	C35—C36	1.388 (3)
C17—H17	0.9500	C35—H35	0.9500
C18—H18	0.9500	C36—H36	0.9500
F2—C4—F1	106.75 (15)	F19—C22—F20	106.75 (15)
F2—C4—F3	107.72 (16)	F19—C22—F21	107.22 (15)
F1—C4—F3	107.31 (15)	F20—C22—F21	107.53 (16)
F2—C4—C5	111.72 (15)	F19—C22—C23	110.29 (16)
F1—C4—C5	110.14 (16)	F20—C22—C23	112.13 (15)
F3—C4—C5	112.91 (15)	F21—C22—C23	112.62 (15)
O6—C5—C7	124.78 (17)	O24—C23—C25	124.99 (18)
O6—C5—C4	117.46 (17)	O24—C23—C22	117.30 (17)
C7—C5—C4	117.76 (15)	C25—C23—C22	117.70 (16)
N10—C7—C5	114.86 (15)	N28—C25—C23	115.36 (16)
N10—C7—C9	125.69 (16)	N28—C25—C27	125.67 (17)
C5—C7—C9	119.46 (15)	C23—C25—C27	118.95 (16)
O8—C9—C7	122.43 (16)	O26—C27—C25	122.08 (18)
O8—C9—H9	118.8	O26—C27—H27	119.0
C7—C9—H9	118.8	C25—C27—H27	119.0

N11—N10—C7	121.04 (14)	N29—N28—C25	121.73 (15)
N10—N11—C12	119.13 (14)	N28—N29—C30	118.97 (14)
N10—N11—H11	120.4	N28—N29—H29	120.5
C12—N11—H11	120.4	C30—N29—H29	120.5
C18—C12—C13	121.04 (15)	C36—C30—C31	120.69 (17)
C18—C12—N11	117.95 (15)	C36—C30—N29	118.84 (16)
C13—C12—N11	121.01 (15)	C31—C30—N29	120.47 (16)
C14—C13—C12	119.29 (16)	C32—C31—C30	119.47 (18)
C14—C13—H13	120.4	C32—C31—H31	120.3
C12—C13—H13	120.4	C30—C31—H31	120.3
C15—C14—C13	119.29 (16)	C31—C32—C33	119.50 (18)
C15—C14—H14	120.4	C31—C32—H32	120.2
C13—C14—H14	120.4	C33—C32—H32	120.2
C14—C15—C17	121.74 (16)	C35—C33—C32	121.38 (18)
C14—C15—Cl16	119.69 (14)	C35—C33—Cl34	119.53 (16)
C17—C15—Cl16	118.57 (14)	C32—C33—Cl34	119.09 (16)
C15—C17—C18	119.14 (16)	C33—C35—C36	119.10 (18)
C15—C17—H17	120.4	C33—C35—H35	120.4
C18—C17—H17	120.4	C36—C35—H35	120.4
C12—C18—C17	119.49 (16)	C30—C36—C35	119.85 (18)
C12—C18—H18	120.3	C30—C36—H36	120.1
C17—C18—H18	120.3	C35—C36—H36	120.1
F2—C4—C5—O6	117.94 (19)	F19—C22—C23—O24	−0.9 (2)
F1—C4—C5—O6	−0.5 (2)	F20—C22—C23—O24	−119.74 (19)
F3—C4—C5—O6	−120.46 (19)	F21—C22—C23—O24	118.8 (2)
F2—C4—C5—C7	−61.9 (2)	F19—C22—C23—C25	178.66 (15)
F1—C4—C5—C7	179.66 (15)	F20—C22—C23—C25	59.8 (2)
F3—C4—C5—C7	59.7 (2)	F21—C22—C23—C25	−61.6 (2)
O6—C5—C7—N10	−177.83 (17)	O24—C23—C25—N28	−177.47 (18)
C4—C5—C7—N10	2.0 (2)	C22—C23—C25—N28	3.0 (2)
O6—C5—C7—C9	1.8 (3)	O24—C23—C25—C27	4.1 (3)
C4—C5—C7—C9	−178.39 (15)	C22—C23—C25—C27	−175.47 (16)
N10—C7—C9—O8	−2.0 (3)	N28—C25—C27—O26	0.5 (3)
C5—C7—C9—O8	178.45 (16)	C23—C25—C27—O26	178.74 (17)
C5—C7—N10—N11	−179.81 (14)	C23—C25—N28—N29	179.78 (15)
C9—C7—N10—N11	0.6 (2)	C27—C25—N28—N29	−1.9 (3)
C7—N10—N11—C12	−179.37 (14)	C25—N28—N29—C30	−179.92 (14)
N10—N11—C12—C18	174.08 (14)	N28—N29—C30—C36	−174.13 (15)
N10—N11—C12—C13	−6.2 (2)	N28—N29—C30—C31	6.3 (2)
C18—C12—C13—C14	0.2 (2)	C36—C30—C31—C32	0.5 (3)
N11—C12—C13—C14	−179.47 (15)	N29—C30—C31—C32	−179.94 (16)
C12—C13—C14—C15	−0.9 (2)	C30—C31—C32—C33	−0.2 (3)
C13—C14—C15—C17	1.0 (3)	C31—C32—C33—C35	−0.3 (3)
C13—C14—C15—Cl16	−179.66 (13)	C31—C32—C33—Cl34	179.43 (14)
C14—C15—C17—C18	−0.3 (3)	C32—C33—C35—C36	0.5 (3)
Cl16—C15—C17—C18	−179.69 (13)	Cl34—C33—C35—C36	−179.23 (14)
C13—C12—C18—C17	0.4 (2)	C31—C30—C36—C35	−0.3 (3)
N11—C12—C18—C17	−179.87 (14)	N29—C30—C36—C35	−179.87 (15)
C15—C17—C18—C12	−0.4 (2)	C33—C35—C36—C30	−0.2 (3)

Hydrogen-bond geometry (Å, °)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
N11—H11···O8	0.88	2.01	2.6746 (18)	131
N29—H29···O26	0.88	2.03	2.679 (2)	130
N29—H29···O26^{i}	0.88	2.42	3.2159 (19)	150
C27—H27···O6^{ii}	0.95	2.59	3.491 (2)	158
C36—H36···O26^{i}	0.95	2.52	3.323 (3)	143

Symmetry codes: (i) −*x*, −*y*, −*z*+2; (ii) *x*−1, *y*, *z*.

Fig. 1

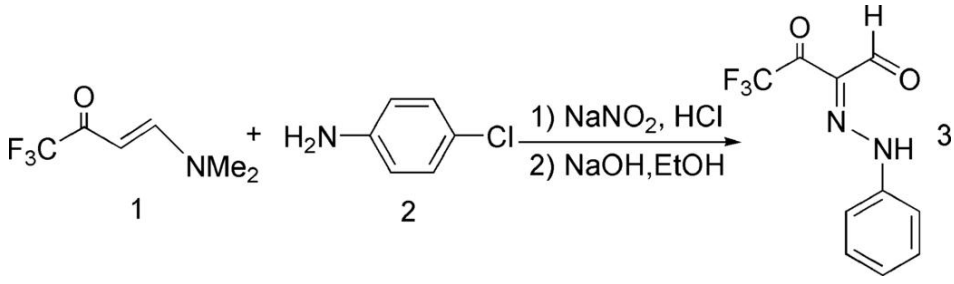
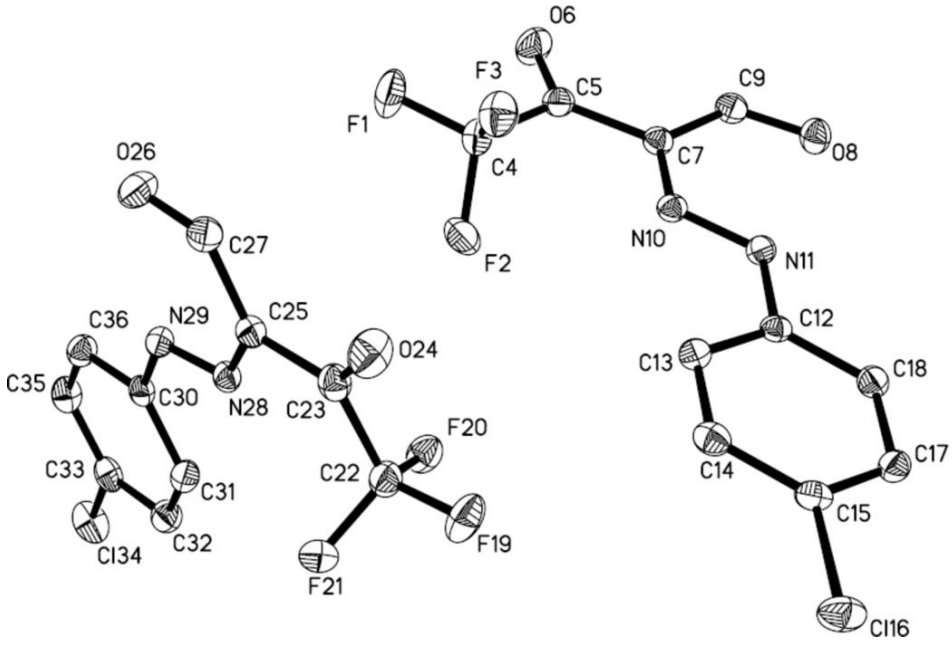


Fig. 2


O6
F3
C5
C9
F1
C4
C7
O8
O26
C27
F2
N10
N11
C36
N29
C25
C12
O24
C13
C18
C35
C30
N28
C23
F20
C33
C22
C14
C17
C31
C15
C32
Cl34
F19
F21
Cl16

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3-[(2-Chloro-6-methylquinolin-3-yl)-methyl]quinazolin-4(3*H*)-one

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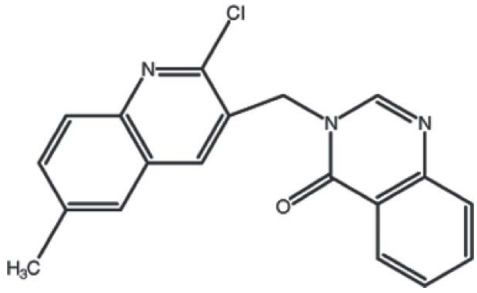
Key indicators: single-crystal X-ray study; T = 295 K; mean σ(C–C) = 0.002 Å; R factor = 0.034; wR factor = 0.096; data-to-parameter ratio = 13.9.

In the title molecule, $C_{19}H_{14}ClN_3O$, the quinoline and quinazoline ring systems form a dihedral angle of 80.75 (4)°. In the crystal, the molecules are linked by pairs of C—H···N hydrogen bonds into centrosymmetric dimers, generating $R_2^2(6)$ ring motifs. The structure is further stabilized by C—H···π interactions and π–π stacking interactions [centroid–centroid distances = 3.7869 (8) and 3.8490 (8) Å].

Related literature

For quinoline analogues, see: Roopan *et al.* (2009); Khan *et al.* (2009, 2010*a*,*b*). For quinazolinone analogues, see: Roopan *et al.* (2008*a*,*b*). For the properties and applications of related compounds, see: Abdel-Hamide *et al.* (1996); Bekhit & Khalil (1998); Chapman *et al.* (1963); Honda *et al.* (1979).



Experimental

Crystal data

$C_{19}H_{14}ClN_3O$
M_r = 335.78
Monoclinic, $P2_1/c$
a = 7.86728 (14) Å
b = 14.7098 (3) Å
c = 13.7055 (3) Å
β = 102.1500 (17)°
V = 1550.56 (5) Å^3
Z = 4
Mo $K\alpha$ radiation
μ = 0.26 mm^{-1}
T = 295 K
0.25 × 0.21 × 0.16 mm

Data collection

Oxford Diffraction Xcalibur E CCD diffractometer
Absorption correction: multi-scan (*CrysAlis PRO*; Oxford Diffraction, 2009)
T_{min} = 0.938, T_{max} = 0.960
15755 measured reflections
3048 independent reflections
2417 reflections with $I > 2\sigma(I)$
R_{int} = 0.026

Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.034
$wR(F^2)$ = 0.096
S = 1.14
3048 reflections
219 parameters
H-atom parameters constrained
$\Delta\rho_{max}$ = 0.18 e Å^{-3}
$\Delta\rho_{min}$ = −0.19 e Å^{-3}

Table 1
Hydrogen-bond geometry (Å, °).

*Cg*1 and *Cg*2 are the centroids of the N1/C1–C4/C9 and N2/N3/C12/C13/C18/C19 rings, respectively.

D—H···A	D—H	H···A	D···A	D—H···A
C19—H19···N3^{i}	0.93	2.51	3.271 (2)	139
C8—H8···*Cg*2^{ii}	0.93	2.89	3.6598 (16)	142
C10—H10*A*···*Cg*1^{iii}	0.96	2.68	3.5189 (17)	146

Symmetry codes: (i) $-x+2, -y+1, -z+2$; (ii) $x, -y+\frac{1}{2}, z+\frac{1}{2}$; (iii) $-x+1, -y, -z+2$.

Data collection: *CrysAlis PRO* (Oxford Diffraction, 2009); cell refinement: *CrysAlis PRO*; data reduction: *CrysAlis PRO*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *ORTEP-3* (Farrugia, 1997); software used to prepare material for publication: *WinGX* (Farrugia, 1999).

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Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: GK2276).

References

Abdel-Hamide, S. G., El-Hakim, A. E. & El-Helby, A. A. (1996). *Az. J. Pharm. Sci.* **17**, 35–40.
Bekhit, A. A. & Khalil, M. A. (1998). *Pharmazie*, **53**, 539–543.
Chapman, N. B., Clarke, K. & Wilson, K. (1963). *J. Chem. Soc.* pp. 2256–2266.
Farrugia, L. J. (1997). *J. Appl. Cryst.* **30**, 565.
Farrugia, L. J. (1999). *J. Appl. Cryst.* **32**, 837–838.
Honda, G., Tabata, M. & Tsuda, M. (1979). *Planta Med.* **37**, 172–174.
Khan, F. N., Mohana Roopan, S., Hathwar, V. R. & Ng, S. W. (2010*a*). *Acta Cryst.* E**66**, o200.
Khan, F. N., Mohana Roopan, S., Hathwar, V. R. & Ng, S. W. (2010*b*). *Acta Cryst.* E**66**, o201.
Khan, F. N., Subashini, R., Roopan, S. M., Hathwar, V. R. & Ng, S. W. (2009). *Acta Cryst.* E**65**, o2686.
Oxford Diffraction (2009). *CrysAlis PRO*. Oxford Diffraction Ltd, Yarnton, England.
Roopan, S. M. & Khan, F. N. (2008*b*). *Indian J. Heterocycl. Chem.* **18**, 183–184.
Roopan, S. M. & Khan, F. N. (2009). *ARKIVOC*, **xiii**, 161–169.
Roopan, S. M., Khan, F. N. & Maiyalagan, T. (2008*a*). *Can. J. Chem.* **86** , 1019–1025.
Sheldrick, G. M. (2008). *Acta Cryst.* A**64**, 112–122.

supplementary materials

Acta Cryst. (2010). E**66**, o1545 [**doi:10.1107/S1600536810020830**]

3-[(2-Chloro-6-methylquinolin-3-yl)methyl]quinazolin-4(3*H*)-one

S. M. Roopan, F. N. Khan, S. Kone, V. R. Hathwar and M. Akkurt

Comment

Heterocyclic chemistry comprises at least half of all organic chemistry research worldwide (Roopan *et al.*, 2008*a*,b). In particular, heterocyclic structures form the basis of many pharmaceutical, agrochemical and veterinary products. 4(3*H*)-quinazolinones and quinolines (Roopan *et al.*, 2009) are classes of fused heterocycles that are of considerable interest because of their biological properties. Some are endowed with antimicrobial, aniconvulsant, antihistamine and anti-inflammatory properties (Abdel-Hamide *et al.*, 1996, Chapman *et al.*, 1963, Bekhit *et al.*, 1998). On the other hand, some quinoline derivatives also have various biological properties like antioxidant, hemolytic and cytotoxicity. These observations prompted us to synthesized heterocyclic compounds containing a quinolinyl-quinazolinone moiety.

As shown in Fig. 1, the quinoline (N1/C1–C9) and quinazoline (N2/N3/C12–C19) ring systems of the title molecule (I) are almost planar with maximum deviations of -0.016 (1) Å for C2 and 0.065 (1) Å for N2, respectively, and there is a dihedral angle of 80.75 (4)° between them.

Two neighbouring molecules are linked by a pair of C—H···N hydrogen bonds into a pseudo-centrosymmetric dimer, generating an $R^2_2(6)$ ring motif (Table 1, Fig. 2). In addition, the structure is stabilized by C—H···π interactions (Table 1) and π-π stacking interactions [*Cg*1···*Cg*3(2 - *x*,-*y*, 2 - *z*) = 3.7869 (8) Å and *Cg*3···*Cg*3(1 - *x*, -*y*, 2 - *z*) = 3.8490 (8) Å; where *Cg*1 and *Cg*3 are centroids of the N1/C1–C4/C9 and C4–C9 rings, respectively].

Experimental

To a solution of 4(3*H*)-quinazolinone (146 mg, 1 mmol) in 2 ml of DMF were added KOtBu (112 mg, 1 mmol) in 10 ml of THF and 2-chloro-3-(chloromethyl)-6-methylquinoline (225 mg, 1 mmol) and the resulting mixture was refluxed at 343 K for 1 h. After the completion, the reaction was cooled and the excess of solvent removed under reduced pressure. Crushed ice was mixed with the residue. White solid was formed which was purified by column chromatography using hexane and ethylacetate as the eluant. Crystals of suitable quality were grown by solvent evaporation from a solution of the compound in diethyl ether.

Refinement

The H atoms were positioned geometrically with C—H = 0.93, 0.97 and 0.96 Å, for aromatic, methylene and methyl H, respectively, and constrained to ride on their parent atoms, with U_{iso}(H) = xU$_{eq}$(C), where x = 1.5 for methyl H, and x = 1.2 for others H atoms.

Figures

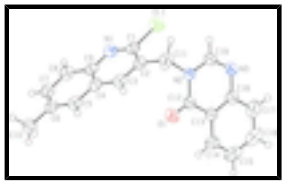


Fig. 1. The molecular structure of the title compound, showing the atom-numbering scheme and displacement ellipsoids drawn at the 50% probability level.

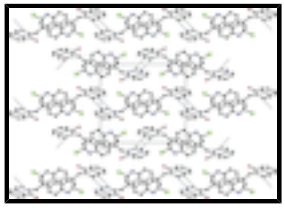


Fig. 2. Crystal packing viewed down *a* axis. H atoms not involved in the intermolecular interactions (dashed lines) have been omitted for clarity.

3-[(2-Chloro-6-methylquinolin-3-yl)methyl]quinazolin-4(3*H*)-one

Crystal data

$C_{19}H_{14}ClN_3O$	$F(000) = 696$
$M_r = 335.78$	$D_x = 1.438$ Mg m^{-3}
Monoclinic, $P2_1/c$	Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å
Hall symbol: -P 2ybc	Cell parameters from 1326 reflections
$a = 7.86728$ (14) Å	$\theta = 2.0$–$20.7°$
$b = 14.7098$ (3) Å	$\mu = 0.26$ mm^{-1}
$c = 13.7055$ (3) Å	$T = 295$ K
$\beta = 102.1500$ (17)°	Needle, colourless
$V = 1550.56$ (5) Å^3	0.25 × 0.21 × 0.16 mm
$Z = 4$	

Data collection

Oxford Diffraction Xcalibur E CCD diffractometer	3048 independent reflections
Radiation source: Enhance (Mo) X-ray Source	2417 reflections with $I > 2\sigma(I)$
graphite	$R_{int} = 0.026$
ω scans	$\theta_{max} = 26.0°$, $\theta_{min} = 2.7°$
Absorption correction: multi-scan (*CrysAlis PRO*; Oxford Diffraction, 2009)	$h = -9 \rightarrow 9$
$T_{min} = 0.938$, $T_{max} = 0.960$	$k = -18 \rightarrow 18$
15755 measured reflections	$l = -16 \rightarrow 16$

Refinement

Refinement on F^2	Secondary atom site location: difference Fourier map
Least-squares matrix: full	Hydrogen site location: inferred from neighbouring sites
$R[F^2 > 2\sigma(F^2)] = 0.034$	H-atom parameters constrained

$wR(F^2) = 0.096$	$w = 1/[\sigma^2(F_o^2) + (0.0511P)^2 + 0.0739P]$ where $P = (F_o^2 + 2F_c^2)/3$
$S = 1.14$	$(\Delta/\sigma)_{max} = 0.001$
3048 reflections	$\Delta\rho_{max} = 0.18$ e Å^{-3}
219 parameters	$\Delta\rho_{min} = -0.19$ e Å^{-3}
0 restraints	Extinction correction: *SHELXL97* (Sheldrick, 2008), $FC^*=KFC[1+0.001XFC^2\Lambda^3/SIN(2\Theta)]^{-1/4}$
Primary atom site location: structure-invariant direct methods	Extinction coefficient: 0.0123 (15)

Special details

Geometry. Bond distances, angles *etc*. have been calculated using the rounded fractional coordinates. All su's are estimated from the variances of the (full) variance-covariance matrix. The cell e.s.d.'s are taken into account in the estimation of distances, angles and torsion angles

Refinement. Refinement on F^2 for ALL reflections except those flagged by the user for potential systematic errors. Weighted *R*-factors *wR* and all goodnesses of fit *S* are based on F^2, conventional *R*-factors *R* are based on *F*, with *F* set to zero for negative F^2. The observed criterion of $F^2 > \sigma(F^2)$ is used only for calculating -*R*-factor-obs *etc*. and is not relevant to the choice of reflections for refinement. *R*-factors based on F^2 are statistically about twice as large as those based on *F*, and *R*-factors based on ALL data will be even larger.

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å^2)

	x	*y*	*z*	U_{iso}*/U_{eq}
Cl1	1.05099 (5)	0.28142 (3)	1.12633 (3)	0.0552 (2)
O1	0.60460 (15)	0.24457 (8)	0.79970 (8)	0.0550 (4)
N1	0.90795 (14)	0.12379 (9)	1.13506 (8)	0.0409 (4)
N2	0.82439 (14)	0.32871 (8)	0.89095 (8)	0.0368 (4)
N3	0.79403 (17)	0.48498 (9)	0.92418 (9)	0.0453 (4)
C1	0.94294 (18)	0.18353 (10)	1.07237 (11)	0.0389 (5)
C2	0.90272 (18)	0.17726 (10)	0.96669 (10)	0.0374 (5)
C3	0.82067 (18)	0.09933 (10)	0.92894 (10)	0.0395 (5)
C4	0.77799 (17)	0.03094 (10)	0.99195 (10)	0.0366 (4)
C5	0.69103 (18)	−0.05001 (10)	0.95563 (11)	0.0413 (5)
C6	0.64859 (18)	−0.11435 (10)	1.01883 (11)	0.0403 (5)
C7	0.6946 (2)	−0.09747 (11)	1.12254 (11)	0.0461 (5)
C8	0.77957 (19)	−0.02054 (11)	1.16013 (11)	0.0444 (5)
C9	0.82367 (17)	0.04583 (10)	1.09569 (10)	0.0373 (5)
C10	0.5554 (2)	−0.20015 (11)	0.97943 (13)	0.0519 (6)
C11	0.9436 (2)	0.25093 (11)	0.89857 (12)	0.0442 (5)
C12	0.65169 (19)	0.31653 (10)	0.84072 (10)	0.0383 (4)
C13	0.54199 (18)	0.39518 (10)	0.84513 (10)	0.0376 (5)
C14	0.3617 (2)	0.38997 (12)	0.80976 (11)	0.0497 (6)
C15	0.2604 (2)	0.46424 (15)	0.81376 (12)	0.0613 (7)
C16	0.3351 (3)	0.54611 (15)	0.85043 (13)	0.0658 (7)
C17	0.5113 (2)	0.55297 (12)	0.88491 (12)	0.0571 (6)
C18	0.61654 (19)	0.47690 (10)	0.88456 (10)	0.0406 (5)

C19	0.88460 (19)	0.41208 (11)	0.92637 (11)	0.0415 (5)
H3	0.79220	0.09100	0.86020	0.0470*
H5	0.66180	−0.06000	0.88710	0.0500*
H7	0.66590	−0.14020	1.16640	0.0550*
H8	0.80880	−0.01170	1.22880	0.0530*
H10A	0.44010	−0.19950	0.99230	0.0780*
H10B	0.61780	−0.25170	1.01190	0.0780*
H10C	0.54880	−0.20420	0.90880	0.0780*
H11A	1.06170	0.27200	0.92330	0.0530*
H11B	0.93730	0.22560	0.83250	0.0530*
H14	0.31130	0.33570	0.78350	0.0600*
H15	0.14040	0.46010	0.79180	0.0740*
H16	0.26500	0.59680	0.85160	0.0790*
H17	0.56050	0.60830	0.90850	0.0690*
H19	1.00250	0.41650	0.95480	0.0500*

Atomic displacement parameters (Å^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Cl1	0.0554 (3)	0.0545 (3)	0.0522 (3)	−0.0078 (2)	0.0032 (2)	−0.0056 (2)
O1	0.0623 (7)	0.0417 (7)	0.0540 (7)	−0.0106 (5)	−0.0034 (5)	−0.0054 (5)
N1	0.0375 (7)	0.0482 (8)	0.0363 (7)	0.0036 (6)	0.0060 (5)	−0.0013 (6)
N2	0.0353 (6)	0.0375 (7)	0.0368 (6)	−0.0034 (5)	0.0059 (5)	0.0015 (5)
N3	0.0483 (8)	0.0392 (8)	0.0451 (7)	−0.0082 (6)	0.0021 (6)	0.0015 (6)
C1	0.0316 (7)	0.0426 (9)	0.0422 (8)	0.0051 (6)	0.0068 (6)	−0.0016 (7)
C2	0.0347 (8)	0.0412 (9)	0.0377 (8)	0.0094 (6)	0.0110 (6)	0.0016 (6)
C3	0.0442 (8)	0.0435 (9)	0.0320 (7)	0.0103 (7)	0.0109 (6)	−0.0005 (6)
C4	0.0365 (8)	0.0397 (8)	0.0347 (7)	0.0109 (6)	0.0100 (6)	0.0001 (6)
C5	0.0440 (8)	0.0446 (9)	0.0361 (8)	0.0083 (7)	0.0105 (6)	−0.0042 (7)
C6	0.0358 (8)	0.0401 (9)	0.0468 (9)	0.0088 (6)	0.0128 (6)	0.0002 (7)
C7	0.0449 (9)	0.0495 (10)	0.0467 (9)	0.0038 (7)	0.0158 (7)	0.0083 (7)
C8	0.0439 (8)	0.0557 (10)	0.0341 (8)	0.0024 (7)	0.0096 (6)	0.0028 (7)
C9	0.0326 (7)	0.0436 (9)	0.0369 (8)	0.0087 (6)	0.0099 (6)	0.0007 (6)
C10	0.0519 (10)	0.0455 (10)	0.0604 (10)	0.0026 (8)	0.0169 (8)	−0.0015 (8)
C11	0.0436 (9)	0.0479 (9)	0.0436 (8)	0.0035 (7)	0.0152 (7)	0.0017 (7)
C12	0.0430 (8)	0.0383 (8)	0.0317 (7)	−0.0078 (7)	0.0038 (6)	0.0041 (6)
C13	0.0392 (8)	0.0436 (9)	0.0293 (7)	−0.0041 (7)	0.0054 (6)	0.0083 (6)
C14	0.0414 (9)	0.0646 (11)	0.0400 (9)	−0.0059 (8)	0.0015 (7)	0.0123 (8)
C15	0.0433 (10)	0.0941 (15)	0.0460 (10)	0.0117 (10)	0.0084 (7)	0.0210 (10)
C16	0.0701 (13)	0.0799 (14)	0.0482 (10)	0.0341 (11)	0.0143 (9)	0.0114 (10)
C17	0.0739 (12)	0.0484 (10)	0.0478 (10)	0.0125 (9)	0.0101 (8)	0.0022 (8)
C18	0.0475 (9)	0.0425 (9)	0.0318 (7)	−0.0007 (7)	0.0083 (6)	0.0046 (6)
C19	0.0386 (8)	0.0432 (9)	0.0402 (8)	−0.0114 (7)	0.0028 (6)	0.0039 (7)

Geometric parameters (Å, °)

Cl1—C1	1.7545 (15)	C13—C14	1.401 (2)
O1—C12	1.2191 (19)	C13—C18	1.396 (2)
N1—C1	1.2984 (19)	C14—C15	1.360 (3)

N1—C9	1.3767 (19)	C15—C16	1.387 (3)
N2—C11	1.469 (2)	C16—C17	1.371 (3)
N2—C12	1.3994 (19)	C17—C18	1.393 (2)
N2—C19	1.367 (2)	C3—H3	0.9300
N3—C18	1.393 (2)	C5—H5	0.9300
N3—C19	1.284 (2)	C7—H7	0.9300
C1—C2	1.419 (2)	C8—H8	0.9300
C2—C3	1.363 (2)	C10—H10A	0.9600
C2—C11	1.509 (2)	C10—H10B	0.9600
C3—C4	1.412 (2)	C10—H10C	0.9600
C4—C5	1.411 (2)	C11—H11A	0.9700
C4—C9	1.4084 (19)	C11—H11B	0.9700
C5—C6	1.371 (2)	C14—H14	0.9300
C6—C7	1.413 (2)	C15—H15	0.9300
C6—C10	1.502 (2)	C16—H16	0.9300
C7—C8	1.359 (2)	C17—H17	0.9300
C8—C9	1.408 (2)	C19—H19	0.9300
C12—C13	1.452 (2)		
Cl1···N2	3.4130 (12)	C15···H3^{ix}	2.9900
Cl1···C19	3.3776 (16)	C16···H3^{ix}	2.9200
Cl1···H11A	2.8000	C18···H8^{vi}	2.9100
Cl1···H19	3.0400	C19···H15^{x}	3.0800
Cl1···H16^{i}	3.1300	C19···H19^{iv}	3.0300
Cl1···H11B^{ii}	3.1400	C19···H8^{vi}	3.0300
O1···C2	3.0757 (18)	H3···O1	2.7300
O1···C3	3.0535 (18)	H3···H5	2.5100
O1···H3	2.7300	H3···H11B	2.3600
O1···H11B	2.5800	H3···C15^{xi}	2.9900
O1···H14	2.6400	H3···C16^{xi}	2.9200
O1···H7^{iii}	2.7400	H5···H3	2.5100
N2···Cl1	3.4130 (12)	H5···H10C	2.3400
N3···C19^{iv}	3.271 (2)	H5···C14^{xi}	2.7700
N1···H15^{v}	2.8000	H5···C15^{xi}	2.9600
N3···H19^{iv}	2.5100	H7···O1^{iii}	2.7400
N3···H8^{vi}	2.7300	H8···N3^{ii}	2.7300
C1···C5^{vii}	3.573 (2)	H8···C18^{ii}	2.9100
C2···O1	3.0757 (18)	H8···C19^{ii}	3.0300
C3···O1	3.0535 (18)	H10A···C1^{iii}	2.9700
C3···C9^{vii}	3.592 (2)	H10A···C2^{iii}	2.8900
C3···C12	3.572 (2)	H10A···C3^{iii}	2.9100
C4···C4^{vii}	3.5715 (19)	H10A···C4^{iii}	3.0500
C4···C6^{iii}	3.547 (2)	H10A···C12^{iii}	3.0700
C5···C1^{vii}	3.572 (2)	H10B···H17^{viii}	2.4900
C6···C4^{iii}	3.547 (2)	H10B···H11A^{vii}	2.5100

C9···C3^{vii}	3.592 (2)	H10C···H5	2.3400
C12···C3	3.572 (2)	H11A···Cl1	2.8000
C16···C18^{i}	3.587 (2)	H11A···H19	2.2400
C17···C18^{i}	3.539 (2)	H11A···H10B^{vii}	2.5100
C17···C17^{i}	3.557 (2)	H11B···O1	2.5800
C18···C17^{i}	3.539 (2)	H11B···H3	2.3600
C18···C16^{i}	3.587 (2)	H11B···Cl1^{vi}	3.1400
C19···N3^{iv}	3.271 (2)	H14···O1	2.6400
C19···Cl1	3.3776 (16)	H15···C19^{xii}	3.0800
C19···C19^{iv}	3.538 (2)	H15···N1^{xiii}	2.8000
C1···H10A^{iii}	2.9700	H16···Cl1^{i}	3.1300
C2···H10A^{iii}	2.8900	H17···C10^{xiv}	2.9800
C3···H10A^{iii}	2.9100	H17···H10B^{xiv}	2.4900
C4···H10A^{iii}	3.0500	H19···Cl1	3.0400
C10···H17^{viii}	2.9800	H19···H11A	2.2400
C12···H10A^{iii}	3.0700	H19···N3^{iv}	2.5100
C14···H5^{ix}	2.7700	H19···C19^{iv}	3.0300
C15···H5^{ix}	2.9600		
C1—N1—C9	117.14 (12)	C16—C17—C18	119.90 (17)
C11—N2—C12	118.32 (12)	N3—C18—C13	121.98 (13)
C11—N2—C19	120.35 (12)	N3—C18—C17	118.56 (14)
C12—N2—C19	121.18 (12)	C13—C18—C17	119.46 (14)
C18—N3—C19	116.34 (13)	N2—C19—N3	126.29 (14)
Cl1—C1—N1	115.34 (11)	C2—C3—H3	119.00
Cl1—C1—C2	117.89 (11)	C4—C3—H3	119.00
N1—C1—C2	126.78 (14)	C4—C5—H5	119.00
C1—C2—C3	115.35 (13)	C6—C5—H5	119.00
C1—C2—C11	123.66 (13)	C6—C7—H7	119.00
C3—C2—C11	120.99 (13)	C8—C7—H7	119.00
C2—C3—C4	121.45 (13)	C7—C8—H8	120.00
C3—C4—C5	123.08 (13)	C9—C8—H8	120.00
C3—C4—C9	117.63 (13)	C6—C10—H10A	110.00
C5—C4—C9	119.29 (13)	C6—C10—H10B	109.00
C4—C5—C6	121.62 (13)	C6—C10—H10C	109.00
C5—C6—C7	118.00 (14)	H10A—C10—H10B	109.00
C5—C6—C10	121.23 (14)	H10A—C10—H10C	109.00
C7—C6—C10	120.78 (14)	H10B—C10—H10C	109.00
C6—C7—C8	121.94 (14)	N2—C11—H11A	109.00
C7—C8—C9	120.39 (14)	N2—C11—H11B	109.00
N1—C9—C4	121.65 (13)	C2—C11—H11A	109.00
N1—C9—C8	119.58 (12)	C2—C11—H11B	109.00
C4—C9—C8	118.76 (13)	H11A—C11—H11B	108.00
N2—C11—C2	112.79 (12)	C13—C14—H14	120.00
O1—C12—N2	120.49 (14)	C15—C14—H14	120.00
O1—C12—C13	125.83 (14)	C14—C15—H15	120.00

N2—C12—C13	113.67 (12)	C16—C15—H15	120.00
C12—C13—C14	120.61 (14)	C15—C16—H16	120.00
C12—C13—C18	119.82 (13)	C17—C16—H16	120.00
C14—C13—C18	119.57 (14)	C16—C17—H17	120.00
C13—C14—C15	120.08 (16)	C18—C17—H17	120.00
C14—C15—C16	120.32 (17)	N2—C19—H19	117.00
C15—C16—C17	120.62 (19)	N3—C19—H19	117.00
C9—N1—C1—Cl1	−179.80 (10)	C3—C4—C9—N1	−0.4 (2)
C9—N1—C1—C2	0.3 (2)	C3—C4—C9—C8	178.79 (13)
C1—N1—C9—C4	0.4 (2)	C5—C4—C9—N1	−179.72 (13)
C1—N1—C9—C8	−178.82 (13)	C5—C4—C9—C8	−0.5 (2)
C12—N2—C11—C2	−69.62 (16)	C4—C5—C6—C7	0.0 (2)
C19—N2—C11—C2	114.68 (14)	C4—C5—C6—C10	179.76 (14)
C11—N2—C12—O1	−4.0 (2)	C5—C6—C7—C8	−0.5 (2)
C11—N2—C12—C13	174.94 (12)	C10—C6—C7—C8	179.74 (15)
C19—N2—C12—O1	171.64 (13)	C6—C7—C8—C9	0.5 (2)
C19—N2—C12—C13	−9.40 (18)	C7—C8—C9—N1	179.26 (14)
C11—N2—C19—N3	−179.97 (14)	C7—C8—C9—C4	0.1 (2)
C12—N2—C19—N3	4.5 (2)	O1—C12—C13—C14	7.1 (2)
C19—N3—C18—C13	−2.9 (2)	O1—C12—C13—C18	−172.61 (14)
C19—N3—C18—C17	176.95 (14)	N2—C12—C13—C14	−171.76 (13)
C18—N3—C19—N2	2.1 (2)	N2—C12—C13—C18	8.50 (19)
Cl1—C1—C2—C3	179.26 (11)	C12—C13—C14—C15	−179.62 (14)
Cl1—C1—C2—C11	−1.6 (2)	C18—C13—C14—C15	0.1 (2)
N1—C1—C2—C3	−0.8 (2)	C12—C13—C18—N3	−2.7 (2)
N1—C1—C2—C11	178.31 (14)	C12—C13—C18—C17	177.48 (13)
C1—C2—C3—C4	0.7 (2)	C14—C13—C18—N3	177.54 (13)
C11—C2—C3—C4	−178.43 (14)	C14—C13—C18—C17	−2.3 (2)
C1—C2—C11—N2	−75.60 (18)	C13—C14—C15—C16	1.7 (2)
C3—C2—C11—N2	103.49 (16)	C14—C15—C16—C17	−1.3 (3)
C2—C3—C4—C5	179.10 (14)	C15—C16—C17—C18	−0.9 (3)
C2—C3—C4—C9	−0.2 (2)	C16—C17—C18—N3	−177.16 (15)
C3—C4—C5—C6	−178.76 (14)	C16—C17—C18—C13	2.7 (2)
C9—C4—C5—C6	0.5 (2)		

Symmetry codes: (i) −*x*+1, −*y*+1, −*z*+2; (ii) *x*, −*y*+1/2, *z*+1/2; (iii) −*x*+1, −*y*, −*z*+2; (iv) −*x*+2, −*y*+1, −*z*+2; (v) *x*+1, −*y*+1/2, *z*+1/2; (vi) *x*, −*y*+1/2, *z*−1/2; (vii) −*x*+2, −*y*, −*z*+2; (viii) *x*, *y*−1, *z*; (ix) −*x*+1, *y*+1/2, −*z*+3/2; (x) *x*+1, *y*, *z*; (xi) −*x*+1, *y*−1/2, −*z*+3/2; (xii) *x*−1, *y*, *z*; (xiii) *x*−1, −*y*+1/2, *z*−1/2; (xiv) *x*, *y*+1, *z*.

Hydrogen-bond geometry (Å, °)

Cg1 and Cg2 are the centroids of the N1/C1–C4/C9 and N2/N3/C12/C13/C18/C19 rings, respectively.

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
C19—H19···N3^{iv}	0.93	2.51	3.271 (2)	139
C8—H8···Cg2^{ii}	0.93	2.89	3.6598 (16)	142
C10—H10A···Cg1^{iii}	0.96	2.68	3.5189 (17)	146

Symmetry codes: (iv) −*x*+2, −*y*+1, −*z*+2; (ii) *x*, −*y*+1/2, *z*+1/2; (iii) −*x*+1, −*y*, −*z*+2.

Fig. 1

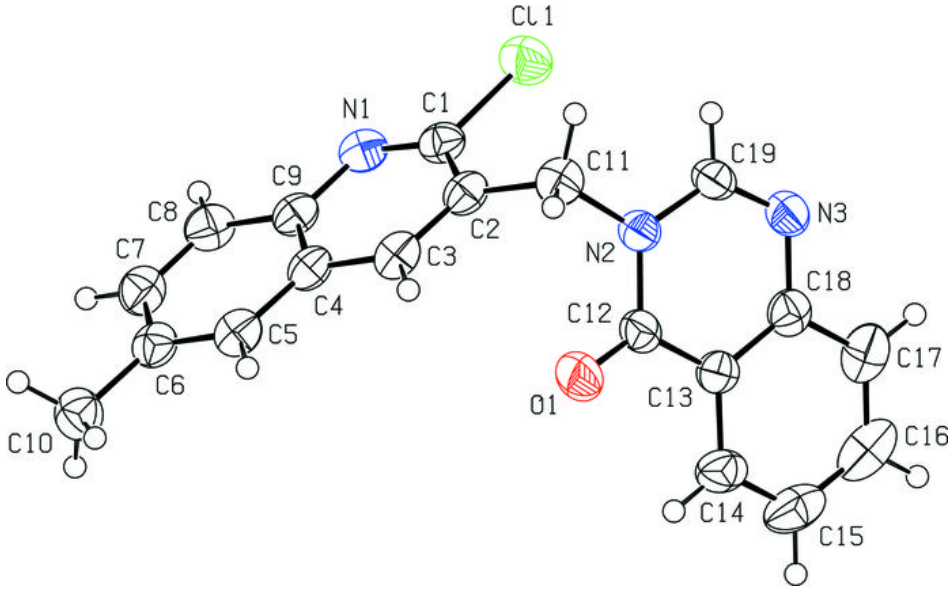
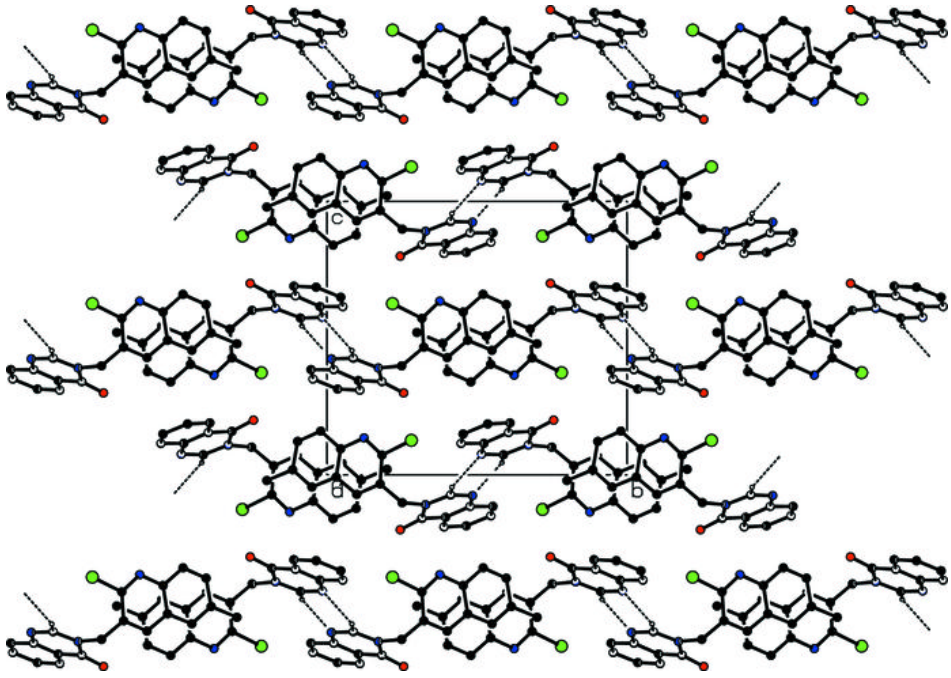

Cl1
N1
C1
C11
C19
C9
C8
C2
N3
C7
C3
N2
C18
C4
C12
C5
C17
C6
O1
C13
C16
C10
C14
C15

Fig. 2



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p-Tolyl 2-*O*-benzoyl-3-*O*-benzyl-4,6-*O*-benzylidene-1-thio-α-L-idopyranoside

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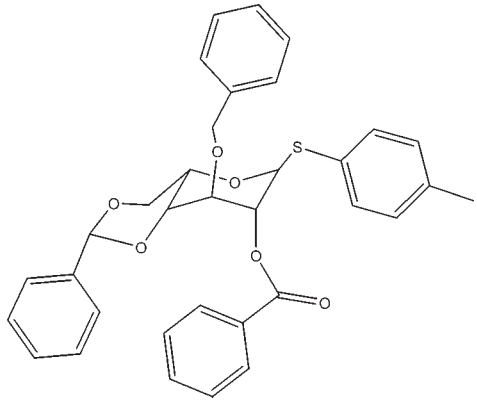
Key indicators: single-crystal X-ray study; T = 123 K; mean σ(C–C) = 0.009 Å; disorder in main residue; R factor = 0.068; wR factor = 0.201; data-to-parameter ratio = 14.2.

The title compound, $C_{34}H_{32}O_6S$, is an *ido*-configured thioglycoside building block for heparan sulfate fragments. It contains disordered tolyl and O-benzyl groups with occupancy ratios of 0.539 (13):0.461 (13) and 0.613 (13):0.387 (13), respectively, as determined from a weakly diffracting crystal. The fused rings adopt chair conformations with the molecules packing into a three-dimensional network *via* C—H···O and three C—H···π interactions. The former interactions, occuring between molecules related by a twofold axis, define an $R_2^2(26)$ motif.

Related literature

For the synthesis, see: Barroca & Jacquinet (2000); Polat & Wong (2007). For a related structure, see: Zhou *et al.* (2006). For ring conformations, see: Cremer & Pople (1975) and for hydrogen-bond motifs, see: Bernstein *et al.* (1995).



Experimental

Crystal data

$C_{34}H_{32}O_6S$
M_r = 568.66
Monoclinic, $C2$
a = 19.296 (4) Å
b = 8.2060 (16) Å
c = 19.045 (4) Å
β = 101.27 (3)°
V = 2957.5 (10) Å^3
Z = 4
Cu $K\alpha$ radiation
μ = 1.34 mm^{-1}
T = 123 K
0.60 × 0.11 × 0.11 mm

Data collection

Rigaku Spider diffractometer
Absorption correction: multi-scan (*ABSCOR*; Higashi, 1995)
T_{min} = 0.754, T_{max} = 1.0
10947 measured reflections
4882 independent reflections
2352 reflections with $I > 2\sigma(I)$
R_{int} = 0.052

Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.068
$wR(F^2)$ = 0.201
S = 1.03
4882 reflections
343 parameters
1 restraint
H-atom parameters constrained
$\Delta\rho_{max}$ = 0.28 e Å^{-3}
$\Delta\rho_{min}$ = −0.31 e Å^{-3}
Absolute structure: Flack (1983), 1939 Friedel pairs
Flack parameter: 0.01 (4)

Table 1
Hydrogen-bond geometry (Å, °).

*Cg*1, *Cg*2 and *Cg*3 are the centroids of the C2,C9–C13, C14*A*–C19*A* and C22–C27 phenyl rings, respectively.

D—H···A	D—H	H···A	D···A	D—H···A
C11—H11···O4^{i}	0.95	2.50	3.359 (8)	150
C1—H1···O2^{ii}	1.00	2.62	3.592 (7)	164
C3—H3*A*···*Cg*1^{ii}	0.99	2.60	3.506 (7)	152
C28*A*—H28*B*···*Cg*3^{iii}	0.99	2.60	3.572 (11)	165
C31*A*—H31*A*···*Cg*2^{iii}	0.95	2.87	3.526 (13)	127
C31*B*—H31*B*···*Cg*2^{iii}	0.93	2.81	3.68 (2)	157

Symmetry codes: (i) $-x+1, y, -z$; (ii) $-x+\frac{1}{2}, y-\frac{1}{2}, -z$; (iii) $x, y-1, z$.

Data collection: *CrystalClear* (Rigaku, 2005); cell refinement: *FSProcess* (Rigaku, 1998); data reduction: *FSProcess*; program(s) used to solve structure: *SIR92* (Altomare *et al.*, 1993); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *ORTEP* in *WinGX* (Farrugia, 1999) and Mercury (Macrae *et al.*, 2006); software used to prepare material for publication: *SHELXL97* and *PLATON* (Spek, 2009).

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Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: GK2277).

References

Altomare, A., Cascarano, G., Giacovazzo, C. & Guagliardi, A. (1993). *J. Appl. Cryst.* **26**, 343–350.
Barroca, N. & Jacquinet, J.-C. (2000). *Carbohydr. Res.* **329**, 667–679.
Bernstein, J., Davis, R. E., Shimoni, L. & Chang, N.-L. (1995). *Angew. Chem. Int. Ed. Engl.* **34**, 1555–1573.

Cremer, D. & Pople, J. A. (1975). *J. Am. Chem. Soc.* **97**, 1354–1358.
Farrugia, L. J. (1999). *J. Appl. Cryst.* **32**, 837–838.
Flack, H. D. (1983). *Acta Cryst.* A**39**, 876–881.
Higashi, T. (1995). *ABSCOR*. Rigaku Corporation, Tokyo, Japan.
Macrae, C. F., Edgington, P. R., McCabe, P., Pidcock, E., Shields, G. P., Taylor, R., Towler, M. & van de Streek, J. (2006). *J. Appl. Cryst.* **39**, 453–457.
Polat, T. & Wong, C.-H. (2007). *J. Am. Chem. Soc.* **129**, 12795–12800.
Rigaku (1998). *FSProcess*. Rigaku Corporation, Tokyo, Japan.
Rigaku (2005). *CrystalClear*. Rigaku Americas Corporation, The Woodlands, Texas, USA.
Sheldrick, G. M. (2008). *Acta Cryst.* A**64**, 112–122.
Spek, A. L. (2009). *Acta Cryst.* D**65**, 148–155.
Zhou, F.-Y., Zhou, F.-Y. & Zhong, J.-H. (2006). *Acta Cryst.* E**62**, o266–o267.

supplementary materials

Acta Cryst. (2010). E**66**, o1598-o1599 [**doi:10.1107/S1600536810020970**]

p-Tolyl 2-*O*-benzoyl-3-*O*-benzyl-4,6-*O*-benzylidene-1-thio-*α*-L-idopyranoside

G. J. Gainsford, P. C. Tyler and O. V. Zubkova

Comment

Heparan sulfates (HSs), highly sulfated glycosaminoglycans, have emerged as a novel and exciting class of molecules with a huge variety of critical functions in cell signalling and development. HSs are made up of repeating 1,4-linked disaccharide units. These are composed of a hexuronic acid (*ido*- and *gluco*-configured) and an *N*-acetyl or *N*-sulfoglucosamine which bear one or several *O*-sulfate substituents. *Ido*-configured thioglycoside building blocks **2** and **3** (Figure 1) were prepared to be used in our synthesis of defined fragments of HS.

The title compound (**4**, Figure 1), $C_{34}H_{32}O_6S$, crystallizes with one independent molecule in the asymmetric unit (Figure 2). For information, its systematic name is benzoic acid 8-benzyloxy-2-phenyl-6-*p*-tolylsulfanyl -hexahydro-pyrano[3,2-*d*][1,3]dioxin-7-yl ester. The phenyl rings (C14–C19 & C29–C34 plus linked atoms C20, O6 & C25) are disordered between two conformations which are labelled a & b respectively (Figure 3) with the final refined occupancies a:b being 0.539 (13):0.461 (13) and 0.613 (10):0.387 (10) respectively. Note that it was not possible to refine two positions at the C15 & C16 sites so these atoms were given unit occupancies.

The determined absolute configuration with C1(*R*), C4(S), C5(*R*), C6(S), C7(*R*) & C8(*R*) confirms the expected stereochemistry and is different from the diacetate derivative (XAZLUG) with configurations *R*,*R*,*S*,*S*,*R*,*S* respectively (Zhou *et al.*, 2006). The fused rings adopt chair configurations: for O1,C1–C5 the puckering amplitude Q is 0.559 (6) Å, θ 166.6 (6)° and φ 243 (3)° while for O5, C4–C8 the corresponding values are 0.525 (6) Å, 13.9 (7)° and 333 (3)° (Cremer & Pople, 1975).

The molecules pack into a three dimensional network using C—H···O and C–H···π interactions (Table 1) with phenyl, tertiary & methylene carbon donor atoms (Figure 2). The C—H···O interactions form a dimeric $R^2_2(26)$ motif (Bernstein *et al.*, 1995) through O4, between molecules related by the 2-fold rotation axis, and a weaker C(3) link through O1, respectively (Figure 4). The *Cg*1, *Cg*2 & *Cg*3 atom designations in Table 1 are the centroids of phenyl rings (C2,C9–C13), (C14A–C19A) and (C22–C27) respectively. The related diacetate (XUGLAG) packing was reported as two dimensional sheets *via* C–H···O interactions, but these sheets are interconnected *via* at least one C–H···π interaction.

Experimental

(see Figure 1) *p*-Tolyl 2-*O*-benzoyl-3-*O*-benzyl-4,6-*O*-benzyl idene-1-thio-a-L-idopyranoside (**4**) was prepared in 4 steps from the known 1,2,4,6-Tetra-*O*-benzoyl-3-*O*-benzyl-β-L-idopyranoside (Barroca & Jacquinet, 2000). The starting tetrabenzoate (7.45 g, 10.85 mmol) was dissolved in (CH_2Cl_2, hereafter DCM)(50 ml) and treated with thiocresol (2 g, 16.27 mmol) in the presence of boron trifluoride etherate (0.534 ml, 4.34 mmol) at room temperature for 4 h. The solution was diluted with DCM, washed with water and sat. $NaHCO_3$ solution, dried and concentrated. Chromatography (EtOAc: hexanes, 1: 5) furnished the *p*-tolyl-derivative (**1**, 6.1 g, 8.86 mmol) in 82% yield as a clear syrup. Then Zemplen deacetylation (Polat & Wong, 2007) of the tri-benzoate (**1**, 6 g, 8.71 mmol) at room temperature afforded a triol (**2**, 3.1 g, 8.23 mmol) in 95% yield as a syrup. Triol (**2**, 1 g, 2.66 mmol) was dissolved in dry DMF (15 ml) and treated with benzaldehyde dimethylacetal

(1 ml, 6.66 mmol, 2.5 eq.) followed by a catalytic amount (40 mg) of *p*-toluenesulfonic acid. After 1 h at 60°C the solvents were removed *in vacuo* and the residue was purified by flash chromatography on silica gel to give the benzylidene-derivative (**3**)(1.1 g, 2.37 mmol) in 89% yield as a white foam. The benzylidene-derivative (**3**, 1 g, 2.15 mmol) was dissolved in a mixture of dry DCM (10 ml) and dry pyridine (10 ml) and cooled to 0°C. Treatment with benzoyl chloride (0.625 ml, 5.38 mmol) at 0°C rising to room temperature for 12 h was followed by an aqueous work-up. The solution was diluted with DCM, washed with water and sat. $NaHCO_3$ solution, dried and concentrated. Chromatography (EtOAc: hexanes 1: 4) furnished the benzoate (**4**, 1.2 g, 2.11 mmol) in 98% yield as a white foam. Compound **4 (**100 mg) was dissolved in a hot mixture of EtOAc: hexanes (1:10), and the solution was allowed to cool down slowly. Single crystals were collected and dried *in vacuo*.

^{1}H NMR (300 MHz, $CDCl_3$) δ 2.29 (s, 3H), 3.91 (ddd, 1H, $J_{3,4}$ 2.6 Hz, $J_{2,3}$ 2.5 Hz, H-3); 4.12 (dd, 1H, $J_{4,5}$ 1.6 Hz, H-4), 4.34 (dd, 1H, $J_{6a,6\,b}$ 12.3 Hz, H-6a), 4.19 (dd, 1H, H–6 b), 4.51 (ddd, 1H, $J_{5,6a}$ 1.5 Hz, $J_{5,6\,b}$ 2.0 Hz, H-5), 4.71 and 4.95 (2 d, 2H, *J* 11.7 Hz, $PhCH_2$), 5.52 (dd, 1H, $J_{2,4}$ 1.0 Hz, H-2), 5.56 (s, 1H, PhCH), 5.74 (d, 1H, $J_{1,2}$ 1.3 Hz, H-1), 7.07–8.06 (m, 19H, aromatic). ^{13}C NMR (300 MHz, $CDCl_3$) δ 21.4, 51.7, 60.9, 68.3, 70.3, 71.5, 72.8, 73.6, 73.7, 77.0, 77.5, 77.9, 86.7, 101.4, 126.8, 127.6, 128.3, 128.4, 128.6, 128.9, 129.2, 129.9, 130.1, 130.6, 130.9, 131.1, 131.4, 133.2, 133.4, 133.9, 137.5, 137.7, 138.3, 166.1. HRMS calcd for $C_{34}H_{32}O_6S$ $(M+Na)^+$ 591.1817, found 591.1824.

The benzoate (**4**) was converted to the known compound *p*-tolyl 2-*O*-benzoyl-3-*O*-benzyl-1-thio-α-L-idopyranoside (Polat & Wong, 2007). Benzoate (**4**, 200 mg, 352 µmol) was dissolved in 80% AcOH (10 ml) and stirred at 80°C for 16 h. Concentration and chromatography (EtOAc, hexanes 1: 2) afforded the *p*-tolyl 2-*O*-benzoyl-3-*O*-benzyl-1-thio-α-L-idopyranoside (169 mg, 352 µmol) as a white foam. The ^{1}H and ^{13}C spectra and mass spectral analyses of this were in accord with literature data (Polat & Wong, 2007).

Refinement

The methyl H atoms were constrained to an ideal geometry (C—H = 0.98 Å) with U_{iso}(H) = 1.5U_{eq}(C), but were allowed to rotate freely about the adjacent C—C bonds. Hydrogen H31B was fixed in a calculated position in the last cycles of refinement. All other H atoms were placed in geometrically idealized positions and constrained to ride on their parent atoms with C—H distances of 0.95 (aromatic), 1.00 (tertiary) or 0.99 (methylene) Å with U_{iso}(H) = 1.2U_{eq}(C,*N*). A total of 116 reflections at high theta with negative intensities were clearly outliers (Delta/sigw > 3.5) and were removed from the refinement. One low angle reflection (10,0,0) was also removed as an outlier. A total of 82 reflections out of the 2878 expected within θ 67.7° are therefore not reported. The crystals were poor diffractors but sufficient data was obtained to solve the structure, confirming the absolute configuration.

Figures

Fig. 1. Chemical synthesis steps to the title compound (see text).

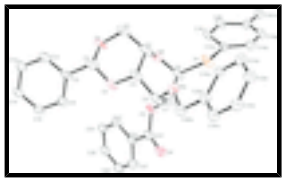


Fig. 2. An *ORTEP* (Farrugia, 1999) view showing the asymmetric unit with 40% probabilility ellipsoids. Only one set (A) of the disordered atoms are shown for clarity.

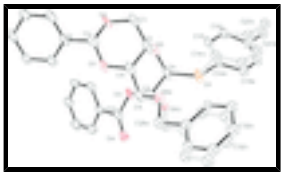


Fig. 3. An *ORTEP* (Farrugia, 1999) view showing the conformational disorder using 40% probabilility ellipsoids. Dotted bonds indicate the minor set (B) atoms; only representattive atoms labels are shown for clarity.

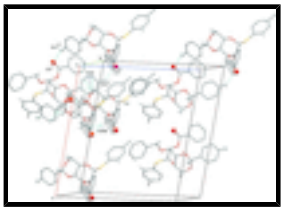


Fig. 4. Mercury cell packing view (Macrae *et al.*, 2006) showing most of the C–H···O and C–H···π interactions (dotted lines, Table 1). All contact atoms are in ball mode with other H atoms omitted for clarity. Symmetry operations: (i) 1/2 - *x*, *y* - 1/2, -*z* (ii) *x* - 1/2, *y* - 1/2, -*z*

p-Tolyl 2-*O*-benzoyl-3-*O*-benzyl- 4,6-*O*-benzylidene-1-thio-α-L-idopyranoside

Crystal data

$C_{34}H_{32}O_6S$	$F(000) = 1200$
$M_r = 568.66$	$D_x = 1.277$ Mg m^{-3}
Monoclinic, *C*2	Cu *K*α radiation, λ = 1.54178 Å
Hall symbol: C 2y	Cell parameters from 1721 reflections
$a = 19.296$ (4) Å	θ = 6.5–66.9°
$b = 8.2060$ (16) Å	μ = 1.34 mm^{-1}
$c = 19.045$ (4) Å	$T = 123$ K
β = 101.27 (3)°	Needle, colourless
$V = 2957.5$ (10) Å^3	0.60 × 0.11 × 0.11 mm
$Z = 4$	

Data collection

Rigaku Spider diffractometer	4882 independent reflections
Radiation source: Rigaku MM007 rotating anode	2352 reflections with $I > 2\sigma(I)$
Rigaku VariMax-HF Confocal Optical System	$R_{int} = 0.052$
Detector resolution: 10 pixels mm^{-1}	$\theta_{max} = 72.2°$, $\theta_{min} = 6.5°$
ω–scans	$h = -22 \rightarrow 23$
Absorption correction: multi-scan (*ABSCOR*; Higashi, 1995)	$k = -9 \rightarrow 8$
$T_{min} = 0.754$, $T_{max} = 1.0$	$l = -17 \rightarrow 23$
10947 measured reflections	

Refinement

Refinement on F^2	Hydrogen site location: inferred from neighbouring sites
Least-squares matrix: full	H-atom parameters constrained
$R[F^2 > 2\sigma(F^2)] = 0.068$	$w = 1/[\sigma^2(F_o^2) + (0.0855P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$

$wR(F^2) = 0.201$	$(\Delta/\sigma)_{max} = 0.002$
$S = 1.03$	$\Delta\rho_{max} = 0.28$ e Å^{-3}
4882 reflections	$\Delta\rho_{min} = -0.31$ e Å^{-3}
343 parameters	Extinction correction: *SHELXL97* (Sheldrick, 2008), $Fc^*=kFc[1+0.001xFc^2\lambda^3/\sin(2\theta)]^{-1/4}$
1 restraint	Extinction coefficient: 0.0019 (2)
Primary atom site location: structure-invariant direct methods	Absolute structure: Flack (1983), 1939 Friedel pairs
Secondary atom site location: difference Fourier map	Flack parameter: 0.01 (4)

Special details

Geometry. All e.s.d.'s (except the e.s.d. in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell e.s.d.'s are taken into account individually in the estimation of e.s.d.'s in distances, angles and torsion angles; correlations between e.s.d.'s in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell e.s.d.'s is used for estimating e.s.d.'s involving l.s. planes.

Refinement. Refinement of F^2 against ALL reflections. The weighted *R*-factor *wR* and goodness of fit *S* are based on F^2, conventional *R*-factors *R* are based on *F*, with *F* set to zero for negative F^2. The threshold expression of $F^2 > \sigma(F^2)$ is used only for calculating *R*-factors(gt) *etc*. and is not relevant to the choice of reflections for refinement. *R*-factors based on F^2 are statistically about twice as large as those based on *F*, and *R*- factors based on ALL data will be even larger.

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å^2)

	x	*y*	*z*	U_{iso}*/U_{eq}	Occ. (<1)
S1	0.26771 (9)	0.5118 (2)	0.32352 (10)	0.0904 (6)	
O1	0.3489 (2)	0.4758 (5)	0.0899 (2)	0.0674 (11)	
O2	0.23586 (18)	0.5312 (5)	0.0294 (2)	0.0685 (11)	
O3	0.3923 (2)	0.7274 (5)	0.2062 (2)	0.0671 (11)	
O4	0.5075 (2)	0.7017 (6)	0.2613 (2)	0.0898 (15)	
O5	0.2527 (2)	0.6221 (5)	0.1852 (3)	0.0702 (12)	
C1	0.2993 (3)	0.4463 (7)	0.0262 (4)	0.0712 (18)	
H1	0.2893	0.3269	0.0214	0.085*	
C2	0.3277 (3)	0.5043 (7)	−0.0372 (4)	0.0635 (16)	
C3	0.2032 (3)	0.4603 (8)	0.0837 (4)	0.0777 (19)	
H3A	0.1890	0.3471	0.0698	0.093*	
H3B	0.1599	0.5225	0.0867	0.093*	
C4	0.2516 (3)	0.4592 (7)	0.1565 (4)	0.0746 (19)	
H4	0.2321	0.3829	0.1887	0.090*	
C5	0.3255 (3)	0.4017 (8)	0.1499 (4)	0.0713 (18)	
H5	0.3233	0.2813	0.1417	0.086*	
C6	0.2959 (3)	0.6339 (8)	0.2545 (3)	0.0718 (18)	
H6	0.2945	0.7504	0.2697	0.086*	
C7	0.3720 (3)	0.5973 (7)	0.2490 (3)	0.0703 (18)	
H7	0.4023	0.6025	0.2980	0.084*	
C9	0.3943 (3)	0.5753 (7)	−0.0304 (3)	0.0655 (17)	
H9	0.4232	0.5885	0.0157	0.085*	
C8	0.3821 (3)	0.4344 (7)	0.2166 (4)	0.0738 (19)	

H8	0.4306	0.4243	0.2058	0.089*	
C10	0.4185 (3)	0.6267 (8)	−0.0907 (4)	0.0767 (19)	
H10	0.4640	0.6747	−0.0860	0.092*	
C11	0.3760 (3)	0.6076 (8)	−0.1576 (4)	0.0763 (19)	
H11	0.3926	0.6419	−0.1991	0.092*	
C12	0.3099 (3)	0.5392 (8)	−0.1645 (4)	0.0781 (19)	
H12	0.2807	0.5284	−0.2106	0.094*	
C13	0.2858 (3)	0.4864 (8)	−0.1051 (4)	0.0791 (19)	
H13	0.2404	0.4374	−0.1104	0.095*	
O6A	0.3646 (5)	0.2944 (12)	0.2544 (6)	0.064 (3)*	0.59 (2)
C14A	0.2117 (6)	0.6505 (15)	0.3596 (6)	0.050 (3)*	0.539 (13)
C15	0.1681 (3)	0.7644 (8)	0.3084 (3)	0.0723 (17)	
H15	0.1718	0.7678	0.2594	0.087*	
C16	0.1223 (3)	0.8646 (9)	0.3351 (3)	0.0769 (19)	
H16	0.0924	0.9363	0.3036	0.092*	
C17A	0.1189 (7)	0.8623 (17)	0.4122 (8)	0.0657 (13)*	0.539 (13)
C18A	0.1578 (7)	0.7442 (16)	0.4544 (7)	0.0657 (13)*	0.539 (13)
H18A	0.1529	0.7357	0.5029	0.079*	0.539 (13)
C19A	0.2027 (7)	0.6396 (17)	0.4305 (7)	0.0657 (13)*	0.539 (13)
H19A	0.2277	0.5598	0.4617	0.079*	0.539 (13)
C20A	0.0731 (7)	0.9795 (17)	0.4412 (6)	0.0657 (13)*	0.539 (13)
H20A	0.0361	0.9199	0.4590	0.099*	0.539 (13)
H20B	0.0514	1.0546	0.4032	0.099*	0.539 (13)
H20C	0.1017	1.0414	0.4805	0.099*	0.539 (13)
C21	0.4617 (3)	0.7713 (8)	0.2173 (4)	0.0713 (18)	
C22	0.4727 (3)	0.9110 (7)	0.1729 (3)	0.0613 (16)	
C23	0.4227 (3)	0.9586 (7)	0.1144 (3)	0.0620 (16)	
H23	0.3804	0.8976	0.1009	0.074*	
C24	0.4339 (3)	1.0941 (8)	0.0755 (3)	0.0680 (17)	
H24	0.3990	1.1262	0.0356	0.082*	
C25	0.4956 (3)	1.1845 (9)	0.0941 (3)	0.0729 (17)	
H25	0.5029	1.2786	0.0674	0.088*	
C26	0.5459 (4)	1.1357 (8)	0.1516 (4)	0.081 (2)	
H26	0.5883	1.1966	0.1646	0.097*	
C27	0.5357 (3)	1.0011 (9)	0.1903 (3)	0.0754 (17)	
H27	0.5715	0.9678	0.2294	0.091*	
C28A	0.4234 (5)	0.1966 (16)	0.2865 (6)	0.0727 (11)*	0.613 (10)
H28A	0.4617	0.2669	0.3125	0.087*	0.613 (10)
H28B	0.4418	0.1362	0.2490	0.087*	0.613 (10)
C29A	0.3993 (8)	0.0763 (16)	0.3388 (7)	0.0727 (11)*	0.613 (10)
C30A	0.3302 (5)	0.0774 (15)	0.3568 (6)	0.053 (3)*	0.613 (10)
H30	0.2982	0.1623	0.3386	0.064*	0.613 (10)
C31A	0.3088 (6)	−0.0416 (15)	0.4000 (6)	0.0727 (11)*	0.613 (10)
H31A	0.2633	−0.0393	0.4120	0.087*	0.613 (10)
C32A	0.3585 (6)	−0.1674 (15)	0.4255 (6)	0.0727 (11)*	0.613 (10)
H32A	0.3447	−0.2552	0.4523	0.087*	0.613 (10)
C33A	0.4261 (7)	−0.1638 (16)	0.4120 (6)	0.0727 (11)*	0.613 (10)
H33A	0.4596	−0.2430	0.4332	0.087*	0.613 (10)
C34A	0.4455 (6)	−0.0452 (15)	0.3676 (6)	0.0727 (11)*	0.613 (10)

H34A	0.4916	−0.0478	0.3568	0.087*	0.613 (10)
O6B	0.3821 (6)	0.3383 (16)	0.2850 (8)	0.054 (5)*	0.41 (2)
C14B	0.1955 (9)	0.628 (2)	0.3382 (9)	0.0657 (13)*	0.461 (13)
C17B	0.1005 (8)	0.829 (2)	0.3942 (9)	0.0657 (13)*	0.461 (13)
C18B	0.1331 (8)	0.7014 (19)	0.4340 (8)	0.0657 (13)*	0.461 (13)
H18B	0.1217	0.6782	0.4793	0.079*	0.461 (13)
C19B	0.1832 (8)	0.6041 (19)	0.4088 (8)	0.0657 (13)*	0.461 (13)
H19B	0.2088	0.5229	0.4388	0.079*	0.461 (13)
C20B	0.0442 (8)	0.9276 (19)	0.4240 (7)	0.0657 (13)*	0.461 (13)
H20D	−0.0010	0.8696	0.4136	0.099*	0.461 (13)
H20E	0.0387	1.0353	0.4013	0.099*	0.461 (13)
H20F	0.0594	0.9404	0.4759	0.099*	0.461 (13)
C28B	0.4256 (9)	0.274 (2)	0.3140 (10)	0.0727 (11)*	0.387 (10)
H28C	0.4506	0.3485	0.3515	0.087*	0.387 (10)
H28D	0.4582	0.2522	0.2809	0.087*	0.387 (10)
C29B	0.4141 (11)	0.121 (3)	0.3485 (12)	0.0727 (11)*	0.387 (10)
C30B	0.3541 (13)	0.079 (3)	0.3547 (12)	0.0727 (11)*	0.387 (10)
H30B	0.3156	0.1366	0.3269	0.087*	0.387 (10)
C31B	0.3372 (9)	−0.049 (3)	0.4002 (10)	0.0727 (11)*	0.387 (10)
H31B	0.2946	−0.0856	0.4095	0.087*	0.387 (10)
C32B	0.3913 (10)	−0.137 (2)	0.4345 (10)	0.0727 (11)*	0.387 (10)
H32B	0.3831	−0.2210	0.4664	0.087*	0.387 (10)
C33B	0.4565 (10)	−0.109 (2)	0.4248 (9)	0.0727 (11)*	0.387 (10)
H33B	0.4936	−0.1797	0.4468	0.087*	0.387 (10)
C34B	0.4724 (9)	0.024 (2)	0.3821 (8)	0.0727 (11)*	0.387 (10)
H34B	0.5193	0.0462	0.3765	0.087*	0.387 (10)

Atomic displacement parameters (Å^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
S1	0.0924 (13)	0.0693 (11)	0.1261 (14)	0.0217 (10)	0.0622 (11)	0.0350 (11)
O1	0.061 (2)	0.055 (3)	0.098 (3)	0.001 (2)	0.045 (2)	0.006 (2)
O2	0.050 (2)	0.058 (3)	0.109 (3)	0.006 (2)	0.044 (2)	0.004 (2)
O3	0.059 (3)	0.064 (3)	0.087 (3)	0.003 (2)	0.035 (2)	0.022 (2)
O4	0.069 (3)	0.105 (4)	0.100 (3)	0.020 (3)	0.030 (2)	0.036 (3)
O5	0.069 (3)	0.041 (2)	0.112 (3)	0.009 (2)	0.045 (3)	0.014 (2)
C1	0.063 (4)	0.040 (3)	0.117 (5)	−0.004 (3)	0.033 (4)	−0.007 (3)
C2	0.044 (3)	0.046 (3)	0.109 (5)	0.002 (3)	0.038 (3)	0.009 (4)
C3	0.065 (4)	0.061 (4)	0.120 (6)	−0.004 (3)	0.049 (4)	0.011 (4)
C4	0.069 (4)	0.043 (4)	0.125 (5)	0.003 (3)	0.050 (4)	0.016 (4)
C5	0.064 (4)	0.047 (4)	0.115 (5)	0.008 (3)	0.049 (4)	0.005 (4)
C6	0.076 (4)	0.053 (4)	0.099 (5)	0.010 (3)	0.049 (4)	0.025 (3)
C7	0.067 (4)	0.059 (4)	0.093 (5)	0.010 (3)	0.034 (4)	0.021 (4)
C9	0.051 (4)	0.067 (4)	0.082 (4)	0.010 (3)	0.021 (3)	0.007 (3)
C8	0.075 (4)	0.052 (4)	0.108 (5)	0.017 (3)	0.050 (4)	0.029 (3)
C10	0.054 (4)	0.093 (5)	0.089 (5)	0.000 (4)	0.028 (4)	0.002 (4)
C11	0.065 (4)	0.075 (5)	0.102 (5)	0.002 (3)	0.048 (4)	−0.020 (4)
C12	0.068 (4)	0.078 (5)	0.095 (5)	0.002 (4)	0.031 (4)	−0.031 (4)

C13	0.066 (4)	0.065 (4)	0.114 (6)	−0.001 (3)	0.037 (4)	−0.032 (4)
C15	0.068 (4)	0.076 (5)	0.084 (4)	0.009 (4)	0.040 (3)	0.007 (4)
C16	0.070 (4)	0.086 (5)	0.084 (5)	0.013 (4)	0.039 (4)	0.020 (4)
C21	0.054 (4)	0.071 (4)	0.097 (5)	0.007 (3)	0.034 (4)	0.008 (4)
C22	0.053 (4)	0.058 (4)	0.079 (4)	0.006 (3)	0.027 (3)	0.018 (3)
C23	0.052 (3)	0.051 (4)	0.086 (4)	0.003 (3)	0.022 (3)	0.009 (3)
C24	0.053 (4)	0.066 (4)	0.087 (4)	0.012 (3)	0.016 (3)	0.014 (4)
C25	0.067 (4)	0.074 (5)	0.086 (5)	0.000 (4)	0.036 (4)	0.010 (4)
C26	0.071 (4)	0.070 (5)	0.103 (5)	−0.021 (4)	0.021 (4)	0.006 (4)
C27	0.049 (4)	0.083 (5)	0.094 (5)	−0.005 (4)	0.015 (3)	0.008 (4)

Geometric parameters (Å, °)

S1—C14B	1.755 (17)	C20A—H20B	0.9800
S1—C14A	1.796 (13)	C20A—H20C	0.9800
S1—C6	1.818 (6)	C21—C22	1.465 (8)
O1—C1	1.412 (6)	C22—C23	1.379 (7)
O1—C5	1.442 (6)	C22—C27	1.406 (7)
O2—C1	1.420 (6)	C23—C24	1.376 (7)
O2—C3	1.435 (6)	C23—H23	0.9500
O3—C21	1.362 (7)	C24—C25	1.388 (8)
O3—C7	1.443 (6)	C24—H24	0.9500
O4—C21	1.232 (7)	C25—C26	1.375 (8)
O5—C6	1.421 (6)	C25—H25	0.9500
O5—C4	1.443 (7)	C26—C27	1.363 (8)
C1—C2	1.498 (8)	C26—H26	0.9500
C1—H1	1.0000	C27—H27	0.9500
C2—C13	1.392 (7)	C28A—C29A	1.537 (17)
C2—C9	1.394 (7)	C28A—H28A	0.9900
C3—C4	1.513 (8)	C28A—H28B	0.9900
C3—H3A	0.9900	C29A—C34A	1.378 (15)
C3—H3B	0.9900	C29A—C30A	1.441 (17)
C4—C5	1.530 (7)	C30A—C31A	1.391 (15)
C4—H4	1.0000	C30A—H30	0.9500
C5—C8	1.529 (8)	C31A—C32A	1.428 (16)
C5—H5	1.0000	C31A—H31A	0.9500
C6—C7	1.523 (7)	C32A—C33A	1.378 (14)
C6—H6	1.0000	C32A—H32A	0.9500
C7—C8	1.501 (8)	C33A—C34A	1.388 (15)
C7—H7	1.0000	C33A—H33A	0.9500
C9—C10	1.387 (7)	C34A—H34A	0.9500
C9—H9	0.9500	O6B—C28B	1.050 (19)
C8—O6A	1.430 (8)	C14B—C19B	1.42 (2)
C8—O6B	1.522 (12)	C17B—C18B	1.371 (19)
C8—H8	1.0000	C17B—C20B	1.547 (19)
C10—C11	1.384 (8)	C18B—C19B	1.409 (19)
C10—H10	0.9500	C18B—H18B	0.9500
C11—C12	1.377 (8)	C19B—H19B	0.9500
C11—H11	0.9500	C20B—H20D	0.9800

C12—C13	1.374 (8)	C20B—H20E	0.9800
C12—H12	0.9500	C20B—H20F	0.9800
C13—H13	0.9500	C28B—C29B	1.46 (3)
O6A—C28A	1.426 (12)	C28B—H28C	0.9900
C14A—C19A	1.397 (16)	C28B—H28D	0.9900
C14A—C15	1.488 (13)	C29B—C30B	1.24 (3)
C15—C16	1.375 (7)	C29B—C34B	1.43 (2)
C15—H15	0.9500	C30B—C31B	1.44 (3)
C16—C17A	1.484 (15)	C30B—H30B	0.9500
C16—H16	0.9500	C31B—C32B	1.33 (2)
C17A—C18A	1.383 (16)	C31B—H31B	0.922 (19)
C17A—C20A	1.483 (17)	C32B—C33B	1.33 (2)
C18A—C19A	1.359 (15)	C32B—H32B	0.9500
C18A—H18A	0.9500	C33B—C34B	1.43 (2)
C19A—H19A	0.9500	C33B—H33B	0.9500
C20A—H20A	0.9800	C34B—H34B	0.9500
C14B—S1—C6	100.0 (6)	C18A—C19A—H19A	120.3
C14A—S1—C6	102.4 (4)	C14A—C19A—H19A	120.3
C1—O1—C5	110.1 (5)	O4—C21—O3	122.4 (6)
C1—O2—C3	109.6 (4)	O4—C21—C22	126.1 (6)
C21—O3—C7	118.3 (5)	O3—C21—C22	111.4 (6)
C6—O5—C4	112.2 (5)	C23—C22—C27	118.5 (6)
O1—C1—O2	109.0 (5)	C23—C22—C21	122.1 (6)
O1—C1—C2	110.2 (5)	C27—C22—C21	119.4 (6)
O2—C1—C2	109.4 (5)	C24—C23—C22	120.3 (6)
O1—C1—H1	109.4	C24—C23—H23	119.8
O2—C1—H1	109.4	C22—C23—H23	119.8
C2—C1—H1	109.4	C23—C24—C25	120.8 (6)
C13—C2—C9	119.2 (6)	C23—C24—H24	119.6
C13—C2—C1	118.6 (6)	C25—C24—H24	119.6
C9—C2—C1	122.2 (6)	C26—C25—C24	118.9 (6)
O2—C3—C4	112.5 (5)	C26—C25—H25	120.5
O2—C3—H3A	109.1	C24—C25—H25	120.5
C4—C3—H3A	109.1	C27—C26—C25	120.9 (6)
O2—C3—H3B	109.1	C27—C26—H26	119.6
C4—C3—H3B	109.1	C25—C26—H26	119.6
H3A—C3—H3B	107.8	C26—C27—C22	120.5 (6)
O5—C4—C3	107.6 (5)	C26—C27—H27	119.8
O5—C4—C5	111.8 (5)	C22—C27—H27	119.8
C3—C4—C5	110.2 (6)	O6A—C28A—C29A	108.9 (9)
O5—C4—H4	109.1	O6A—C28A—H28A	109.9
C3—C4—H4	109.1	C29A—C28A—H28A	109.9
C5—C4—H4	109.1	O6A—C28A—H28B	109.9
O1—C5—C8	107.6 (5)	C29A—C28A—H28B	109.9
O1—C5—C4	112.1 (5)	H28A—C28A—H28B	108.3
C8—C5—C4	113.7 (6)	C34A—C29A—C30A	117.8 (12)
O1—C5—H5	107.7	C34A—C29A—C28A	118.0 (12)
C8—C5—H5	107.7	C30A—C29A—C28A	124.1 (11)
C4—C5—H5	107.7	C31A—C30A—C29A	122.2 (10)

O5—C6—C7	108.7 (5)	C31A—C30A—H30	118.9
O5—C6—S1	115.5 (4)	C29A—C30A—H30	118.9
C7—C6—S1	111.7 (4)	C30A—C31A—C32A	116.8 (10)
O5—C6—H6	106.8	C30A—C31A—H31A	121.6
C7—C6—H6	106.8	C32A—C31A—H31A	121.6
S1—C6—H6	106.8	C33A—C32A—C31A	121.2 (12)
O3—C7—C8	110.9 (5)	C33A—C32A—H32A	119.4
O3—C7—C6	105.4 (4)	C31A—C32A—H32A	119.4
C8—C7—C6	114.1 (6)	C32A—C33A—C34A	120.5 (11)
O3—C7—H7	108.8	C32A—C33A—H33A	119.8
C8—C7—H7	108.8	C34A—C33A—H33A	119.8
C6—C7—H7	108.8	C29A—C34A—C33A	121.3 (12)
C10—C9—C2	120.2 (6)	C29A—C34A—H34A	119.4
C10—C9—H9	119.9	C33A—C34A—H34A	119.4
C2—C9—H9	119.9	C28B—O6B—C8	125.0 (13)
O6A—C8—C7	116.6 (7)	C19B—C14B—S1	111.1 (12)
C7—C8—O6B	95.1 (7)	C18B—C17B—C20B	118.4 (14)
O6A—C8—C5	94.4 (7)	C17B—C18B—C19B	121.1 (15)
C7—C8—C5	111.7 (5)	C17B—C18B—H18B	119.5
O6B—C8—C5	120.1 (8)	C19B—C18B—H18B	119.5
O6A—C8—H8	111.0	C18B—C19B—C14B	119.7 (14)
C7—C8—H8	111.0	C18B—C19B—H19B	120.1
O6B—C8—H8	106.8	C14B—C19B—H19B	120.1
C5—C8—H8	111.0	C17B—C20B—H20D	109.5
C11—C10—C9	119.6 (6)	C17B—C20B—H20E	109.5
C11—C10—H10	120.2	H20D—C20B—H20E	109.5
C9—C10—H10	120.2	C17B—C20B—H20F	109.5
C12—C11—C10	120.3 (6)	H20D—C20B—H20F	109.5
C12—C11—H11	119.8	H20E—C20B—H20F	109.5
C10—C11—H11	119.8	O6B—C28B—C29B	119.4 (18)
C13—C12—C11	120.4 (6)	O6B—C28B—H28C	107.5
C13—C12—H12	119.8	C29B—C28B—H28C	107.5
C11—C12—H12	119.8	O6B—C28B—H28D	107.5
C12—C13—C2	120.2 (6)	C29B—C28B—H28D	107.5
C12—C13—H13	119.9	H28C—C28B—H28D	107.0
C2—C13—H13	119.9	C30B—C29B—C34B	118 (2)
C28A—O6A—C8	114.9 (8)	C30B—C29B—C28B	121 (2)
C19A—C14A—C15	120.8 (10)	C34B—C29B—C28B	120.6 (18)
C19A—C14A—S1	121.8 (9)	C29B—C30B—C31B	126 (2)
C15—C14A—S1	116.9 (8)	C29B—C30B—H30B	117.0
C16—C15—C14A	117.1 (7)	C31B—C30B—H30B	117.0
C16—C15—H15	121.5	C32B—C31B—C30B	116.3 (19)
C14A—C15—H15	121.5	C32B—C31B—H31B	112 (2)
C15—C16—C17A	121.0 (7)	C30B—C31B—H31B	132 (2)
C15—C16—H16	119.5	C33B—C32B—C31B	121 (2)
C17A—C16—H16	119.5	C33B—C32B—H32B	119.6
C18A—C17A—C20A	122.2 (12)	C31B—C32B—H32B	119.6
C18A—C17A—C16	117.4 (11)	C32B—C33B—C34B	121.7 (17)
C20A—C17A—C16	120.4 (11)	C32B—C33B—H33B	119.1

C19A—C18A—C17A	123.9 (12)	C34B—C33B—H33B	119.1
C19A—C18A—H18A	118.1	C29B—C34B—C33B	116.4 (17)
C17A—C18A—H18A	118.1	C29B—C34B—H34B	121.8
C18A—C19A—C14A	119.4 (12)	C33B—C34B—H34B	121.8
C5—O1—C1—O2	67.1 (5)	C14B—S1—C14A—C15	−47 (3)
C5—O1—C1—C2	−172.8 (5)	C6—S1—C14A—C15	35.7 (9)
C3—O2—C1—O1	−67.6 (5)	C19A—C14A—C15—C16	4.0 (13)
C3—O2—C1—C2	171.8 (5)	S1—C14A—C15—C16	176.5 (6)
O1—C1—C2—C13	−179.6 (5)	C14A—C15—C16—C17A	2.2 (11)
O2—C1—C2—C13	−59.8 (7)	C15—C16—C17A—C18A	−6.7 (14)
O1—C1—C2—C9	0.3 (7)	C15—C16—C17A—C20A	175.5 (8)
O2—C1—C2—C9	120.1 (6)	C20A—C17A—C18A—C19A	−176.9 (11)
C1—O2—C3—C4	56.9 (6)	C16—C17A—C18A—C19A	5.3 (17)
C6—O5—C4—C3	178.9 (4)	C17A—C18A—C19A—C14A	0.8 (18)
C6—O5—C4—C5	−60.0 (6)	C15—C14A—C19A—C18A	−5.6 (16)
O2—C3—C4—O5	77.3 (6)	S1—C14A—C19A—C18A	−177.8 (9)
O2—C3—C4—C5	−44.9 (6)	C7—O3—C21—O4	1.6 (9)
C1—O1—C5—C8	178.7 (4)	C7—O3—C21—C22	−176.5 (5)
C1—O1—C5—C4	−55.5 (6)	O4—C21—C22—C23	165.3 (6)
O5—C4—C5—O1	−75.6 (7)	O3—C21—C22—C23	−16.6 (8)
C3—C4—C5—O1	44.0 (7)	O4—C21—C22—C27	−15.3 (10)
O5—C4—C5—C8	46.8 (7)	O3—C21—C22—C27	162.7 (5)
C3—C4—C5—C8	166.3 (5)	C27—C22—C23—C24	−1.8 (8)
C4—O5—C6—C7	63.8 (6)	C21—C22—C23—C24	177.6 (5)
C4—O5—C6—S1	−62.7 (5)	C22—C23—C24—C25	0.4 (9)
C14B—S1—C6—O5	−75.0 (7)	C23—C24—C25—C26	0.6 (9)
C14A—S1—C6—O5	−91.3 (6)	C24—C25—C26—C27	−0.2 (10)
C14B—S1—C6—C7	160.1 (7)	C25—C26—C27—C22	−1.2 (10)
C14A—S1—C6—C7	143.8 (6)	C23—C22—C27—C26	2.2 (9)
C21—O3—C7—C8	−85.0 (7)	C21—C22—C27—C26	−177.2 (6)
C21—O3—C7—C6	151.1 (5)	C8—O6A—C28A—C29A	167.0 (10)
O5—C6—C7—O3	65.1 (6)	O6A—C28A—C29A—C34A	170.7 (10)
S1—C6—C7—O3	−166.4 (4)	O6A—C28A—C29A—C30A	−6.1 (15)
O5—C6—C7—C8	−56.8 (6)	C34A—C29A—C30A—C31A	−1.9 (15)
S1—C6—C7—C8	71.8 (6)	C28A—C29A—C30A—C31A	174.8 (11)
C13—C2—C9—C10	−0.3 (9)	C29A—C30A—C31A—C32A	−0.6 (16)
C1—C2—C9—C10	179.8 (6)	C30A—C31A—C32A—C33A	4.5 (16)
O3—C7—C8—O6A	179.3 (7)	C31A—C32A—C33A—C34A	−5.9 (17)
C6—C7—C8—O6A	−61.9 (9)	C30A—C29A—C34A—C33A	0.7 (15)
O3—C7—C8—O6B	161.0 (6)	C28A—C29A—C34A—C33A	−176.3 (10)
C6—C7—C8—O6B	−80.2 (7)	C32A—C33A—C34A—C29A	3.2 (17)
O3—C7—C8—C5	−73.7 (7)	O6A—C8—O6B—C28B	103 (3)
C6—C7—C8—C5	45.1 (7)	C7—C8—O6B—C28B	−114 (2)
O1—C5—C8—O6A	−154.0 (5)	C5—C8—O6B—C28B	127 (2)
C4—C5—C8—O6A	81.2 (6)	C14A—S1—C14B—C19B	−54 (3)
O1—C5—C8—C7	85.1 (6)	C6—S1—C14B—C19B	−153.7 (11)
C4—C5—C8—C7	−39.8 (7)	C20B—C17B—C18B—C19B	178.1 (11)
O1—C5—C8—O6B	−165.0 (6)	C17B—C18B—C19B—C14B	−6(2)
C4—C5—C8—O6B	70.2 (9)	S1—C14B—C19B—C18B	172.3 (10)

C2—C9—C10—C11	0.2 (9)	C8—O6B—C28B—C29B	−144.0 (16)
C9—C10—C11—C12	0.5 (9)	O6B—C28B—C29B—C30B	−12 (4)
C10—C11—C12—C13	−1.2 (10)	O6B—C28B—C29B—C34B	174 (2)
C11—C12—C13—C2	1.2 (10)	C34B—C29B—C30B—C31B	8(4)
C9—C2—C13—C12	−0.4 (9)	C28B—C29B—C30B—C31B	−165.9 (19)
C1—C2—C13—C12	179.5 (6)	C29B—C30B—C31B—C32B	−5(4)
C7—C8—O6A—C28A	−111.1 (10)	C30B—C31B—C32B—C33B	−2(3)
O6B—C8—O6A—C28A	−68.8 (14)	C31B—C32B—C33B—C34B	5(3)
C5—C8—O6A—C28A	131.9 (11)	C30B—C29B—C34B—C33B	−4(3)
C14B—S1—C14A—C19A	125 (4)	C28B—C29B—C34B—C33B	169.7 (17)
C6—S1—C14A—C19A	−151.8 (9)	C32B—C33B—C34B—C29B	−2(3)

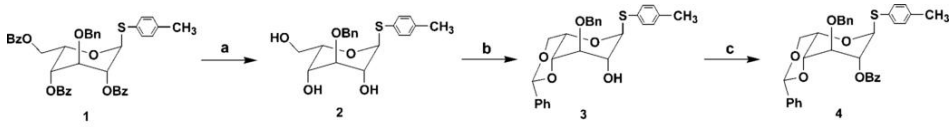
Hydrogen-bond geometry (Å, °)

*Cg*1, *Cg*2 and *Cg*3 are the centroids of the C2,C9–C13, C14A–C19A and C22-C27 phenyl rings, respectively.

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
C11—H11···O4^{i}	0.95	2.50	3.359 (8)	150
C1—H1···O2^{ii}	1.00	2.62	3.592 (7)	164
C3—H3A···Cg1^{ii}	0.99	2.60	3.506 (7)	152
C28A—H28B···Cg3^{iii}	0.99	2.60	3.572 (11)	165
C31A—H31A···Cg2^{iii}	0.95	2.87	3.526 (13)	127
C31B—H31B···Cg2^{iii}	0.93	2.81	3.68 (2)	157

Symmetry codes: (i) −*x*+1, *y*, −*z*; (ii) −*x*+1/2, *y*−1/2, −*z*; (iii) *x*, *y*−1, *z*.

Fig. 1



Reagents and conditions: (a) NaOMe, MeOH, 95%; (b) Benzaldehyde dimethylacetal, TosOH, 89%; (c) BzCl, Py, 98%.

Fig. 2

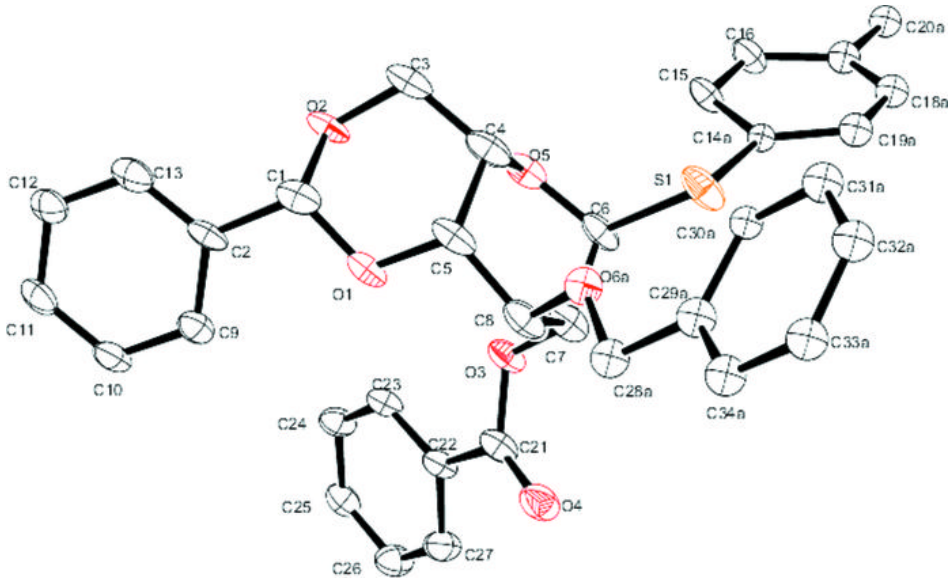

C20a
C16
C15
C18a
C3
O2
C4
C14a
C19a
C12
C13
C1
O5
S1
C31a
C6
C30a
C32a
C2
O1
C5
O6a
C29a
C11
C9
C8
C7
C33a
O3
C28a
C10
C34a
C23
C24
C22
C21
C25
O4
C27
C26

Fig. 3

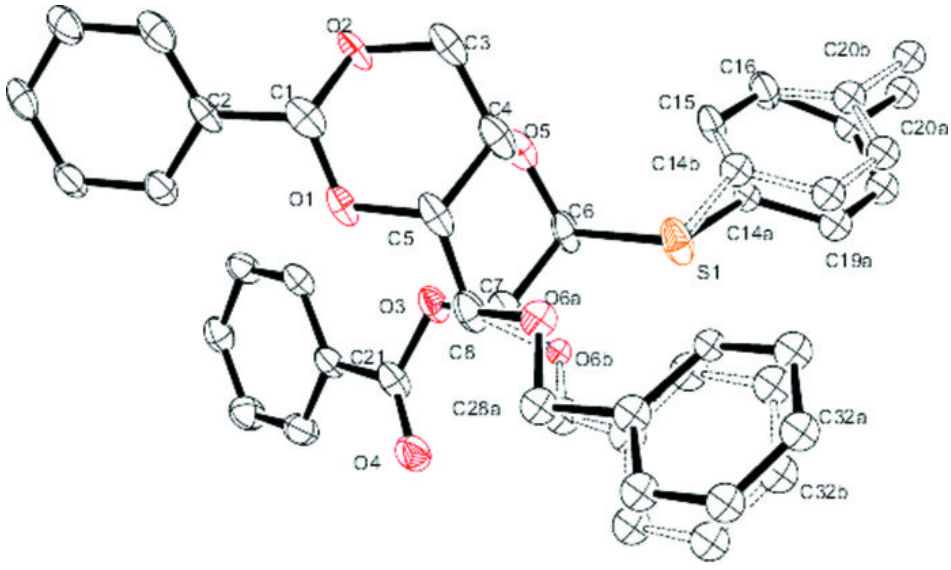
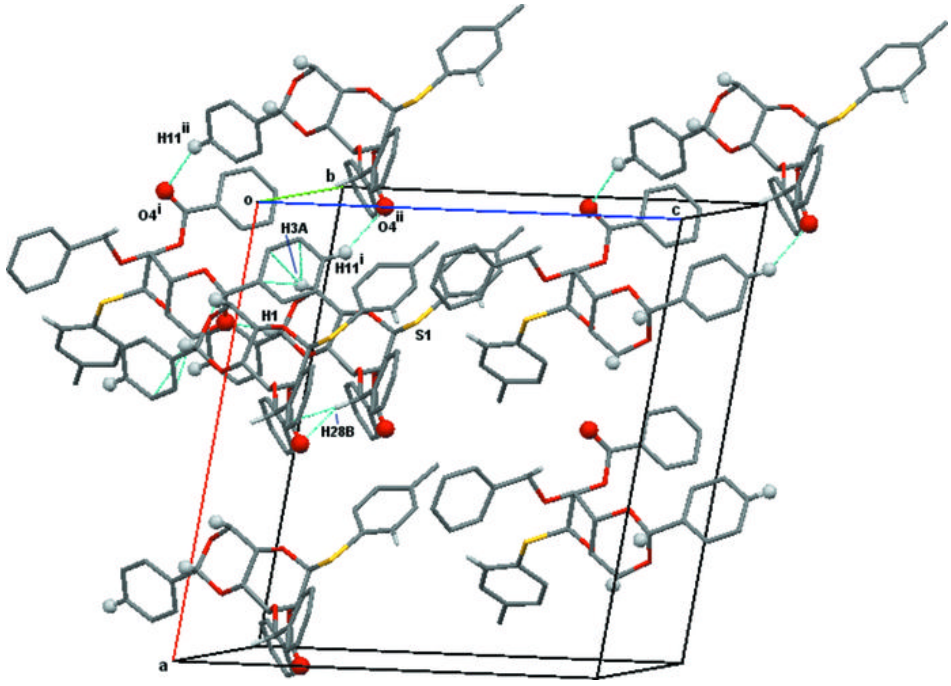

O2
C3
C20b
C16
C15
C20a
C2
C1
C4
O5
C14b
O1
C6
C14a
C19a
C5
S1
C7
O6a
O3
C8
O6b
C21
C28a
C32a
O4
C32b

Fig. 4



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Dispiro[cyclopropane-1,5′-*endo*-tricyclo-[5.2.1.0^{2,6}]deca-3,8-diene-10′,1″-cyclopropane]

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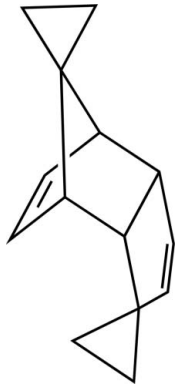
Key indicators: single-crystal X-ray study; T = 293 K; mean σ(C–C) = 0.003 Å; R factor = 0.060; wR factor = 0.168; data-to-parameter ratio = 17.9.

The title compound, $C_{14}H_{16}$, is built up from three five-membered rings. Two of the five-membered rings display an envelope conformation and the third one is almost planar (r.m.s. deviation = 0.014 Å).

Related literature

For the synthesis, see: Khusnutdinov *et al.* (1988); Wilcox *et al.* (1961). For related structures, see: Caira *et al.* (1995); Haumann *et al.* (1997); Brookings *et al.* (2001).



Experimental

Crystal data

$C_{14}H_{16}$
M_r = 184.27
Triclinic, $P\overline{1}$
a = 6.4079 (5) Å
b = 8.6355 (8) Å
c = 10.7216 (10) Å
α = 68.488 (9)°
β = 81.625 (7)°
γ = 73.351 (8)°
V = 528.27 (8) Å^3
Z = 2
Mo $K\alpha$ radiation
μ = 0.07 mm^{-1}
T = 293 K
0.23 × 0.22 × 0.21 mm

Data collection

Oxford Diffraction Xcalibur S diffractometer
Absorption correction: multi-scan (*CrysAlis PRO*; Oxford Diffraction, 2009)
T_{min} = 0.775, T_{max} = 1
3444 measured reflections
2269 independent reflections
1348 reflections with $I > 2\sigma(I)$
R_{int} = 0.024

Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.060
$wR(F^2)$ = 0.168
S = 0.99
2269 reflections
127 parameters
H-atom parameters constrained
$\Delta\rho_{max}$ = 0.22 e Å^{-3}
$\Delta\rho_{min}$ = −0.15 e Å^{-3}

Data collection: *CrysAlis PRO* (Oxford Diffraction, 2009); cell refinement: *CrysAlis PRO*; data reduction: *CrysAlis PRO*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *ORTEP-3 for Windows* (Farrugia, 1997); software used to prepare material for publication: *WinGX* (Farrugia, 1999).

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Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: GK2280).

References

Brookings, D. C., Harrison, S. A., Whitby, R. J., Crombie, B. & Jones, R. V. H. (2001). *Organometallics*, **20**, 4574–4583.
Caira, M. R., Bedekar, A. V. & Singh, V. (1995). *J. Chem. Crystallogr.* **25**, 583–587.
Farrugia, L. J. (1997). *J. Appl. Cryst.* **30**, 565.
Farrugia, L. J. (1999). *J. Appl. Cryst.* **32**, 837–838.
Haumann, T., Boese, R., Kozhushkov, S. I., Rauch, K. & de Meijere, A. (1997). *Liebigs Ann. Chem.* **10**, 2047–2053.
Khusnutdinov, R. I., Dokichev, V. A., Galeev, D. K., Asylguzhina, N. F., Sultanov, S. Z. & Dzhemilev, U. M. (1988). *Russ. Chem. Bull.* **37**, 1932–1935.
Oxford Diffraction (2009). *CrysAlis PRO*. Oxford Diffraction Ltd, Yarnton, England.
Sheldrick, G. M. (2008). *Acta Cryst.* A**64**, 112–122.
Wilcox, C. F. & Craig, R. R. (1961). *J. Am. Chem. Soc.* **83**, 3866–3871.

supplementary materials

Acta Cryst. (2010). E**66**, o1648 [**doi:10.1107/S1600536810021951**]

Dispiro[cyclopropane-1,5'-*endo*-tricyclo[5.2.1.0^{2,6}]deca-3,8-diene-10',1''-cyclopropane]

R. Grubba, L. Ponikiewski and J. Pikies

Comment

The title compound (I) is a product of cyclodimerization of spiro[2.4]hepta-4,6-diene. After few weeks of storing of the starting diene at room temperature big crystals of (I) were isolated with relatively high yield. In contrast to previously reported method of synthesis of (I) (Khusnutdinov *et al.* 1988), we did not use the additional heating and the catalyst.

The X-ray crystallographic analysis confirms this proposed molecular structure (Fig. 1). The $C_{14}H_{16}$ is built up from three five-membered rings and two three-membered rings. The one of the five-membered rings (C2—C3—C4—C5—C6) is almost planar. The mean deviation of the five atoms C2, C3, C4, C5, C6 from their least-squares plane is 0.0136 Å. Additionally, the C5 atom is a junction between the five-membered ring and a cyclopropane ring. The dihedral angle between the central ring planes is 89.89 (2)°.

The second and third five-membered rings (C1—C2—C6—C7—C10 and C7—C8—C9—C1—C10) have an envelope conformation.The C10 atom is a junction with the second cyclopropane ring.

The typical C2=C3 and C6=C7 double bonds lengths 1.312 (3) Å, 1.309 (3) Å respectively suggest that the C2, C3, C6, C7 atoms are sp^2 hybridized. The bond lengths and angles are within normal ranges (Brookings *et al.* 2001; Caira *et al.* 1995; Haumann *et al.* 1997).

Experimental

Spiro[2.4]hepta-4,6-diene was obtained according to the literature procedure (Wilcox *et al.*, 1961). First fraction from the final distillation of spiro[2.4]hepta-4,6-diene (2.05 g) was stored at room temperature for few weeks. After this time large, colorless crystals of the title compound deposited with 54% (1.10 g) yield.

Refinement

All H atoms were positioned geometrically and refined using a riding model, with C–H = 0.93–0.98 Å, U_{iso}(H) = 1.2 U_{eq}(C).

Figures

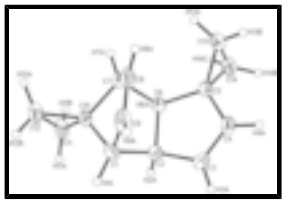


Fig. 1. The molecular structure of the title compound showing the atom-labelling scheme and displacement ellipsoids at the 25% probability level.

Dispiro[cyclopropane-1,5'-*endo*-tricyclo[5.2.1.0^{2,6}]deca-3,8-diene- 10',1''-cyclopropane]

Crystal data

$C_{14}H_{16}$	$Z = 2$
$M_r = 184.27$	$F(000) = 200$
Triclinic, $P\overline{1}$	$D_x = 1.158$ Mg m^{-3}
Hall symbol: -P 1	Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å
$a = 6.4079$ (5) Å	Cell parameters from 1384 reflections
$b = 8.6355$ (8) Å	$\theta = 2.6$–$28.5°$
$c = 10.7216$ (10) Å	$\mu = 0.07$ mm^{-1}
$\alpha = 68.488$ (9)°	$T = 293$ K
$\beta = 81.625$ (7)°	Block, colourless
$\gamma = 73.351$ (8)°	0.23 × 0.22 × 0.21 mm
$V = 528.27$ (8) Å^3	

Data collection

Oxford Diffraction Xcalibur S diffractometer	2269 independent reflections
graphite	1348 reflections with $I > 2\sigma(I)$
Detector resolution: 8.1883 pixels mm^{-1}	$R_{int} = 0.024$
ω scans	$\theta_{max} = 27.0°$, $\theta_{min} = 2.6°$
Absorption correction: multi-scan (*CrysAlis PRO*; Oxford Diffraction, 2009)	$h = -8 \rightarrow 8$
$T_{min} = 0.775$, $T_{max} = 1$	$k = -10 \rightarrow 10$
3444 measured reflections	$l = -8 \rightarrow 13$

Refinement

Refinement on F^2	Primary atom site location: structure-invariant direct methods
Least-squares matrix: full	Secondary atom site location: difference Fourier map
$R[F^2 > 2\sigma(F^2)] = 0.060$	Hydrogen site location: inferred from neighbouring sites
$wR(F^2) = 0.168$	H-atom parameters constrained
$S = 0.99$	$w = 1/[\sigma^2(F_o^2) + (0.095P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
2269 reflections	$(\Delta/\sigma)_{max} < 0.001$
127 parameters	$\Delta\rho_{max} = 0.22$ e Å^{-3}
0 restraints	$\Delta\rho_{min} = -0.15$ e Å^{-3}

Special details

Geometry. All e.s.d.'s (except the e.s.d. in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell e.s.d.'s are taken into account individually in the estimation of e.s.d.'s in distances, angles and torsion angles; correlations

between e.s.d.'s in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell e.s.d.'s is used for estimating e.s.d.'s involving l.s. planes.

Refinement. Refinement of F^2 against ALL reflections. The weighted *R*-factor *wR* and goodness of fit *S* are based on F^2, conventional *R*-factors *R* are based on *F*, with *F* set to zero for negative F^2. The threshold expression of $F^2 > \sigma(F^2)$ is used only for calculating *R*-factors(gt) *etc*. and is not relevant to the choice of reflections for refinement. *R*-factors based on F^2 are statistically about twice as large as those based on *F*, and *R*- factors based on ALL data will be even larger.

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å^2)

	x	*y*	*z*	U_{iso}*/U_{eq}
C1	0.7397 (3)	0.6967 (3)	0.2398 (2)	0.0523 (6)
H1A	0.7789	0.7846	0.2623	0.063*
C2	0.7772 (3)	0.5136 (3)	0.35036 (19)	0.0469 (5)
H2A	0.7291	0.522	0.4392	0.056*
C3	0.9992 (3)	0.3926 (3)	0.3543 (2)	0.0577 (6)
H3A	1.1234	0.4104	0.3763	0.069*
C4	0.9994 (3)	0.2591 (3)	0.3232 (2)	0.0539 (6)
H4A	1.1241	0.1731	0.3191	0.065*
C5	0.7809 (3)	0.2602 (2)	0.29543 (19)	0.0441 (5)
C6	0.6293 (3)	0.4281 (2)	0.30671 (18)	0.0398 (5)
H6A	0.5122	0.4035	0.3749	0.048*
C7	0.5333 (3)	0.5718 (2)	0.17594 (18)	0.0451 (5)
H7A	0.4042	0.5598	0.145	0.054*
C8	0.7187 (4)	0.5983 (3)	0.0741 (2)	0.0559 (6)
H8A	0.7437	0.5677	−0.0024	0.067*
C9	0.8395 (3)	0.6717 (3)	0.1112 (2)	0.0594 (6)
H9A	0.9646	0.7027	0.0658	0.071*
C10	0.5010 (3)	0.7287 (2)	0.21729 (19)	0.0455 (5)
C11	0.3131 (4)	0.7909 (3)	0.3016 (2)	0.0631 (6)
H11A	0.3434	0.8275	0.371	0.076*
H11B	0.1933	0.7363	0.3235	0.076*
C12	0.3480 (4)	0.8997 (3)	0.1568 (2)	0.0646 (6)
H12A	0.2489	0.9102	0.0921	0.078*
H12B	0.399	1.0014	0.1396	0.078*
C13	0.7460 (4)	0.1787 (3)	0.2006 (2)	0.0620 (6)
H13A	0.6199	0.2352	0.1456	0.074*
H13B	0.874	0.1232	0.1577	0.074*
C14	0.7068 (4)	0.0959 (3)	0.3469 (2)	0.0644 (6)
H14B	0.8112	−0.0099	0.393	0.077*
H14C	0.5569	0.1022	0.3809	0.077*

Atomic displacement parameters (Å^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
C1	0.0501 (12)	0.0406 (12)	0.0711 (14)	−0.0082 (9)	−0.0029 (10)	−0.0272 (11)
C2	0.0463 (11)	0.0487 (13)	0.0494 (11)	−0.0028 (9)	−0.0071 (9)	−0.0260 (10)
C3	0.0425 (12)	0.0604 (15)	0.0706 (14)	−0.0029 (10)	−0.0187 (10)	−0.0245 (12)

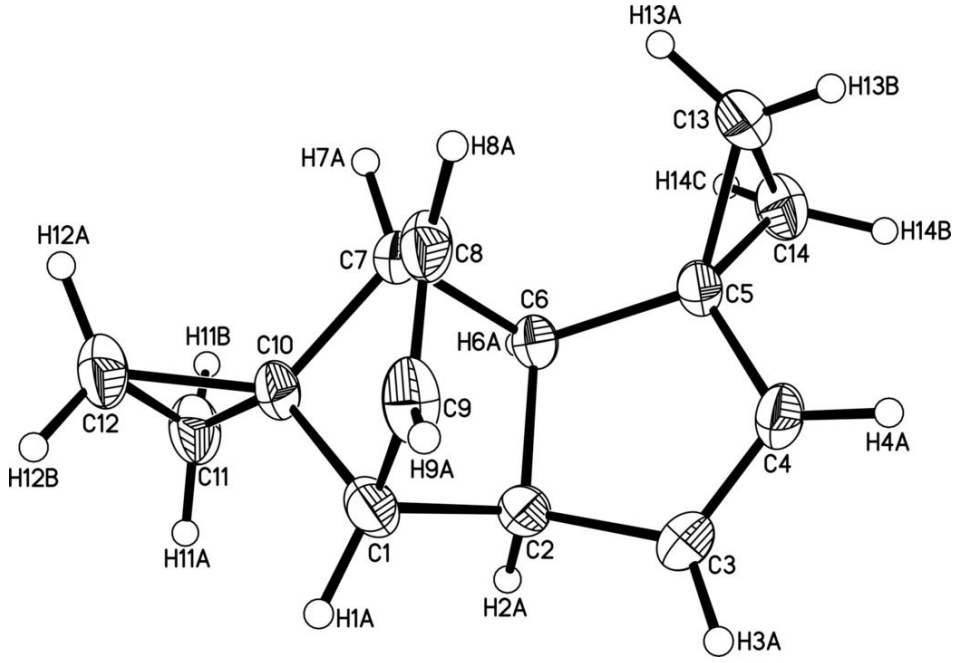
C4	0.0396 (11)	0.0502 (14)	0.0637 (13)	0.0054 (10)	−0.0080 (9)	−0.0207 (11)
C5	0.0454 (11)	0.0349 (11)	0.0479 (11)	−0.0001 (9)	−0.0058 (9)	−0.0156 (9)
C6	0.0368 (10)	0.0360 (11)	0.0435 (10)	−0.0049 (8)	0.0011 (8)	−0.0143 (8)
C7	0.0419 (10)	0.0398 (12)	0.0527 (12)	0.0024 (9)	−0.0124 (9)	−0.0205 (9)
C8	0.0647 (14)	0.0459 (13)	0.0417 (11)	0.0098 (11)	−0.0027 (10)	−0.0156 (10)
C9	0.0503 (13)	0.0419 (13)	0.0681 (14)	−0.0068 (10)	0.0119 (11)	−0.0077 (11)
C10	0.0434 (11)	0.0351 (12)	0.0542 (12)	0.0013 (9)	−0.0025 (9)	−0.0193 (9)
C11	0.0592 (14)	0.0509 (15)	0.0694 (15)	0.0054 (11)	0.0040 (11)	−0.0267 (12)
C12	0.0638 (14)	0.0429 (14)	0.0744 (16)	0.0062 (11)	−0.0035 (12)	−0.0204 (12)
C13	0.0758 (15)	0.0457 (14)	0.0672 (15)	−0.0036 (12)	−0.0123 (12)	−0.0279 (12)
C14	0.0731 (15)	0.0398 (13)	0.0736 (16)	−0.0078 (11)	−0.0065 (12)	−0.0158 (11)

Geometric parameters (Å, °)

C1—C9	1.496 (3)	C7—C10	1.525 (2)
C1—C10	1.513 (3)	C7—H7A	0.98
C1—C2	1.566 (3)	C8—C9	1.309 (3)
C1—H1A	0.98	C8—H8A	0.93
C2—C3	1.500 (3)	C9—H9A	0.93
C2—C6	1.564 (2)	C10—C12	1.489 (3)
C2—H2A	0.98	C10—C11	1.491 (3)
C3—C4	1.312 (3)	C11—C12	1.514 (3)
C3—H3A	0.93	C11—H11A	0.97
C4—C5	1.470 (3)	C11—H11B	0.97
C4—H4A	0.93	C12—H12A	0.97
C5—C13	1.503 (3)	C12—H12B	0.97
C5—C14	1.509 (3)	C13—C14	1.483 (3)
C5—C6	1.532 (3)	C13—H13A	0.97
C6—C7	1.556 (3)	C13—H13B	0.97
C6—H6A	0.98	C14—H14B	0.97
C7—C8	1.500 (3)	C14—H14C	0.97
C9—C1—C10	100.07 (16)	C9—C8—C7	108.46 (17)
C9—C1—C2	106.78 (17)	C9—C8—H8A	125.8
C10—C1—C2	99.49 (14)	C7—C8—H8A	125.8
C9—C1—H1A	116	C8—C9—C1	107.59 (16)
C10—C1—H1A	116	C8—C9—H9A	126.2
C2—C1—H1A	116	C1—C9—H9A	126.2
C3—C2—C6	103.53 (15)	C12—C10—C11	61.07 (14)
C3—C2—C1	117.77 (17)	C12—C10—C1	125.94 (18)
C6—C2—C1	102.59 (14)	C11—C10—C1	126.01 (17)
C3—C2—H2A	110.8	C12—C10—C7	125.59 (17)
C6—C2—H2A	110.8	C11—C10—C7	125.14 (17)
C1—C2—H2A	110.8	C1—C10—C7	94.78 (15)
C4—C3—C2	112.80 (18)	C10—C11—C12	59.39 (13)
C4—C3—H3A	123.6	C10—C11—H11A	117.8
C2—C3—H3A	123.6	C12—C11—H11A	117.8
C3—C4—C5	112.61 (19)	C10—C11—H11B	117.8
C3—C4—H4A	123.7	C12—C11—H11B	117.8
C5—C4—H4A	123.7	H11A—C11—H11B	115

C4—C5—C13	122.29 (18)	C10—C12—C11	59.55 (14)
C4—C5—C14	120.29 (18)	C10—C12—H12A	117.8
C13—C5—C14	58.99 (13)	C11—C12—H12A	117.8
C4—C5—C6	105.79 (15)	C10—C12—H12B	117.8
C13—C5—C6	123.02 (17)	C11—C12—H12B	117.8
C14—C5—C6	120.92 (17)	H12A—C12—H12B	115
C5—C6—C7	118.11 (15)	C14—C13—C5	60.73 (13)
C5—C6—C2	105.17 (14)	C14—C13—H13A	117.7
C7—C6—C2	102.28 (14)	C5—C13—H13A	117.7
C5—C6—H6A	110.2	C14—C13—H13B	117.7
C7—C6—H6A	110.2	C5—C13—H13B	117.7
C2—C6—H6A	110.2	H13A—C13—H13B	114.8
C8—C7—C10	99.26 (15)	C13—C14—C5	60.28 (13)
C8—C7—C6	107.61 (16)	C13—C14—H14B	117.7
C10—C7—C6	99.27 (14)	C5—C14—H14B	117.7
C8—C7—H7A	116.1	C13—C14—H14C	117.7
C10—C7—H7A	116.1	C5—C14—H14C	117.7
C6—C7—H7A	116.1	H14B—C14—H14C	114.9
C9—C1—C2—C3	45.1 (2)	C6—C7—C8—C9	−70.4 (2)
C10—C1—C2—C3	148.69 (16)	C7—C8—C9—C1	0.2 (2)
C9—C1—C2—C6	−67.80 (18)	C10—C1—C9—C8	−33.2 (2)
C10—C1—C2—C6	35.83 (17)	C2—C1—C9—C8	70.0 (2)
C6—C2—C3—C4	−0.8 (2)	C9—C1—C10—C12	−91.6 (2)
C1—C2—C3—C4	−113.1 (2)	C2—C1—C10—C12	159.29 (19)
C2—C3—C4—C5	−1.3 (3)	C9—C1—C10—C11	−169.39 (19)
C3—C4—C5—C13	150.9 (2)	C2—C1—C10—C11	81.5 (2)
C3—C4—C5—C14	−138.8 (2)	C9—C1—C10—C7	49.82 (17)
C3—C4—C5—C6	2.8 (2)	C2—C1—C10—C7	−59.27 (16)
C4—C5—C6—C7	110.17 (18)	C8—C7—C10—C12	92.4 (2)
C13—C5—C6—C7	−37.6 (3)	C6—C7—C10—C12	−157.93 (19)
C14—C5—C6—C7	−108.5 (2)	C8—C7—C10—C11	169.4 (2)
C4—C5—C6—C2	−3.09 (19)	C6—C7—C10—C11	−80.9 (2)
C13—C5—C6—C2	−150.86 (18)	C8—C7—C10—C1	−49.28 (17)
C14—C5—C6—C2	138.22 (18)	C6—C7—C10—C1	60.43 (16)
C3—C2—C6—C5	2.37 (18)	C1—C10—C11—C12	115.3 (2)
C1—C2—C6—C5	125.38 (16)	C7—C10—C11—C12	−115.1 (2)
C3—C2—C6—C7	−121.60 (17)	C1—C10—C12—C11	−115.4 (2)
C1—C2—C6—C7	1.41 (17)	C7—C10—C12—C11	114.4 (2)
C5—C6—C7—C8	−49.8 (2)	C4—C5—C13—C14	108.4 (2)
C2—C6—C7—C8	65.04 (17)	C6—C5—C13—C14	−108.9 (2)
C5—C6—C7—C10	−152.68 (15)	C4—C5—C14—C13	−111.8 (2)
C2—C6—C7—C10	−37.84 (17)	C6—C5—C14—C13	112.4 (2)
C10—C7—C8—C9	32.5 (2)		

Fig. 1


H13A
H13B
C13
H7A
H8A
H14C
H12A
C7
C8
C14
H14B
C6
C5
H11B
C10
H6A
C9
C12
C4
H4A
H12B
C11
H9A
C1
C2
C3
H11A
H1A
H2A
H3A

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4-(3-Iodophenyl)-1-(2-oxoindolin-3-ylidene)thiosemicarbazide

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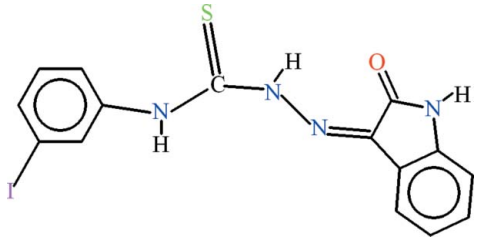
Key indicators: single-crystal X-ray study; T = 296 K; mean σ(C–C) = 0.013 Å; R factor = 0.055; wR factor = 0.157; data-to-parameter ratio = 14.0.

In the title compound, $C_{15}H_{11}IN_4OS$, intramolecular N—H···N, N—H···O and C—H···S interactions generate one $S(5)$ and two $S(6)$ ring motifs. In the crystal, molecules form centrosymmetric dimers *via* pairs of N—H···O interactions, generating $R_2^2(8)$ ring motifs. In addition a short intermolecular I···S contact of 3.352 (3) Å is observed.

Related literature

For the preparation of biologically important N^4-aryl-substituted isatin-3-thiosemicarbazones, see: Pervez *et al.* (2007, 2008, 2010*a*). For a related structure, see: Pervez *et al.* (2010*b*). For graph-set notation, see: Bernstein *et al.* (1995).



Experimental

Crystal data

$C_{15}H_{11}IN_4OS$
M_r = 422.24
Monoclinic, $P2_1/c$
a = 5.7620 (3) Å
b = 16.7989 (11) Å
c = 16.152 (1) Å
β = 100.153 (4)°
V = 1538.96 (16) Å^3
Z = 4
Mo $K\alpha$ radiation
μ = 2.22 mm^{-1}
T = 296 K
0.32 × 0.14 × 0.12 mm

Data collection

Bruker Kappa APEXII CCD diffractometer
Absorption correction: multi-scan (*SADABS*; Bruker, 2005)
T_{min} = 0.742, T_{max} = 0.752
11310 measured reflections
2778 independent reflections
1677 reflections with $I > 2\sigma(I)$
R_{int} = 0.022

Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.055
$wR(F^2)$ = 0.157
S = 1.01
2778 reflections
199 parameters
H-atom parameters constrained
$\Delta\rho_{max}$ = 2.76 e Å^{-3}
$\Delta\rho_{min}$ = −0.48 e Å^{-3}

Table 1
Hydrogen-bond geometry (Å, °).

D—H···A	D—H	H···A	D···A	D—H···A
N1—H1···O1^{i}	0.86	2.09	2.939 (9)	169
N3—H3A···O1	0.86	2.07	2.761 (9)	137
N4—H4A···N2	0.86	2.18	2.618 (9)	111
C15—H15···S1	0.93	2.51	3.183 (10)	129

Symmetry code: (i) $-x-1, -y, -z+1$.

Data collection: *APEX2* (Bruker, 2007); cell refinement: *SAINT* (Bruker, 2007); data reduction: *SAINT*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *ORTEP-3 for Windows* (Farrugia, 1997) and *PLATON* (Spek, 2009); software used to prepare material for publication: *WinGX* (Farrugia, 1999) and *PLATON*.

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Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: GK2281).

References

Bernstein, J., Davis, R. E., Shimoni, L. & Chang, N.-L. (1995). *Angew. Chem. Int. Ed. Engl.* **34**, 1555–1573.
Bruker (2005). *SADABS*. Bruker AXS Inc., Madison, Wisconsin, USA.
Bruker (2007). *APEX2* and *SAINT*. Bruker AXS Inc., Madison, Wisconsin, USA.
Farrugia, L. J. (1997). *J. Appl. Cryst.* **30**, 565.
Farrugia, L. J. (1999). *J. Appl. Cryst.* **32**, 837–838.
Pervez, H., Iqbal, M. S., Saira, N., Yaqub, M. & Tahir, M. N. (2010*b*). *Acta Cryst.* E**66**, o1404.
Pervez, H., Iqbal, M. S., Tahir, M. Y., Choudhary, M. I. & Khan, K. M. (2007). *Nat. Prod. Res.* **21**, 1178–1186.
Pervez, H., Iqbal, M. S., Tahir, M. Y., Nasim, F. H., Choudhary, M. I. & Khan, K. M. (2008). *J. Enz. Inhib. Med. Chem.* **23**, 848–854.
Pervez, H., Manzoor, N., Yaqub, M., Khan, A., Khan, K. M., Nasim, F. H. & Choudhary, M. I. (2010*a*). *Lett. Drug Des. Discov.* **7**, 102–108.
Sheldrick, G. M. (2008). *Acta Cryst.* A**64**, 112–122.
Spek, A. L. (2009). *Acta Cryst.* D**65**, 148–155.

supplementary materials

Acta Cryst. (2010). E**66**, o1629 [**doi:10.1107/S1600536810021938**]

4-(3-Iodophenyl)-1-(2-oxoindolin-3-ylidene)thiosemicarbazide

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Comment

As a part of our drug discovery program, we very recently reported the synthesis and biological evaluation of a number of N^4-aryl substituted isatins-thiosemicarbazones (Pervez *et al.*, 2007, 2008, 2010*a*). In continuation of the same, we report herein the structure and synthesis of the title compound (I, Fig. 1).

The crystal structure of (II) *i.e.* 4-(3-methoxyphenyl)-1-(2-oxoindolin-3-ylidene)thiosemicarbazides has been published (Pervez *et al.*, 2010*b*). The title compound differs from (II) due to the presence of iodo instead of methoxy function at position-3 of the phenyl ring substituted at N^4 of the thiosemicarbazone moiety.

In (I) the 2-oxoindolin A (C1–C8/N1/O1), thiosemicarbazide B (N2/N3/C9/S1/N4) and phenyl ring of 2-ethylphenyl C (C10—C16) are planar with r. m. s. deviations of 0.0086, 0.0029 and 0.0414 Å, respectively. The dihedral angle between A/B, A/C and B/C is 4.65 (41)°, 11.89 (41)° and 13.37 (37)°, respectively. Due to intramolecular H-bondings (Table 1, Fig. 1), one S(5) and two S(6) (Bernstein *et al.*, 1995) ring motifs are formed. The molecules are dimerized (Fig. 2) due to intermolecular H-bonding of N—H···O type with $R_2^2(8)$ ring motifs.

Experimental

To a hot solution of isatin (0.74 g, 5.0 mmol) in ethanol (10 ml) containing a few drops of glacial acetic acid was added 4-(3-iodophenyl)thiosemicarbazide (1.47 g, 5.0 mmol) dissolved in ethanol (10 ml) under stirring. The reaction mixture was then heated under reflux for 2 h. The yellow crystalline solid formed during heating was collected by suction filtration. Thorough washing with hot ethanol followed by ether afforded the target compound (I) in pure form (1.77 g, 84%), m. p. 503 K (*d*). The single crystals of (I) were grown in acetone-ethanol (1:4) by diffusion method at room temperature.

Refinement

All H-atoms were positioned geometrically (N–H = 0.86 Å, C–H = 0.93 Å) and refined as riding with $U_{iso}(H) = xU_{eq}$(C, N), where x = 1.2 for all H-atoms. A residual peak of 2.76 e/Å^3 exists at a distance of 1.48 and 1.95 Å from C14 and C13, respectively.

Figures

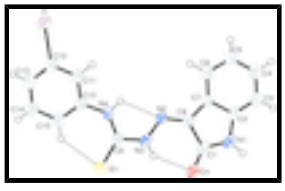


Fig. 1. View of the title molecule with the atom numbering scheme. The displacement ellipsoids are drawn at the 50% probability level. H-atoms are shown by small circles of arbitrary radii. The dotted lines indicate intramolecular hydrogen bonds.

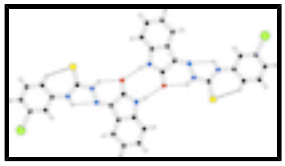


Fig. 2. The partial packing (*PLATON*; Spek, 2009) which shows that molecules form dimers.

4-(3-Iodophenyl)-1-(2-oxoindolin-3-ylidene)thiosemicarbazide

Crystal data

$C_{15}H_{11}IN_4OS$	$F(000) = 824$
$M_r = 422.24$	$D_x = 1.822$ Mg m^{-3}
Monoclinic, $P2_1/c$	Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å
Hall symbol: -P 2ybc	Cell parameters from 1677 reflections
$a = 5.7620$ (3) Å	$\theta = 2.7$–$25.3°$
$b = 16.7989$ (11) Å	$\mu = 2.22$ mm^{-1}
$c = 16.152$ (1) Å	$T = 296$ K
$\beta = 100.153$ (4)°	Needle, yellow
$V = 1538.96$ (16) Å^3	0.32 × 0.14 × 0.12 mm
$Z = 4$	

Data collection

Bruker Kappa APEXII CCD diffractometer	2778 independent reflections
Radiation source: fine-focus sealed tube	1677 reflections with $I > 2\sigma(I)$
graphite	$R_{int} = 0.022$
Detector resolution: 8.10 pixels mm^{-1}	$\theta_{max} = 25.3°$, $\theta_{min} = 2.7°$
ω scans	$h = -6 \rightarrow 6$
Absorption correction: multi-scan (*SADABS*; Bruker, 2005)	$k = -20 \rightarrow 20$
$T_{min} = 0.742$, $T_{max} = 0.752$	$l = -16 \rightarrow 19$
11310 measured reflections	

Refinement

Refinement on F^2	Primary atom site location: structure-invariant direct methods
Least-squares matrix: full	Secondary atom site location: difference Fourier map
$R[F^2 > 2\sigma(F^2)] = 0.055$	Hydrogen site location: inferred from neighbouring sites
$wR(F^2) = 0.157$	H-atom parameters constrained
$S = 1.01$	$w = 1/[\sigma^2(F_o^2) + (0.0776P)^2 + 1.1429P]$ where $P = (F_o^2 + 2F_c^2)/3$
2778 reflections	$(\Delta/\sigma)_{max} < 0.001$
199 parameters	$\Delta\rho_{max} = 2.76$ e Å^{-3}
0 restraints	$\Delta\rho_{min} = -0.48$ e Å^{-3}

Special details

Geometry. Bond distances, angles *etc*. have been calculated using the rounded fractional coordinates. All su's are estimated from the variances of the (full) variance-covariance matrix. The cell e.s.d.'s are taken into account in the estimation of distances, angles and torsion angles

Refinement. Refinement of F^2 against ALL reflections. The weighted *R*-factor *wR* and goodness of fit *S* are based on F^2, conventional *R*-factors *R* are based on *F*, with *F* set to zero for negative F^2. The threshold expression of $F^2 > \sigma(F^2)$ is used only for calculating *R*-factors(gt) *etc*. and is not relevant to the choice of reflections for refinement. *R*-factors based on F^2 are statistically about twice as large as those based on *F*, and *R*- factors based on ALL data will be even larger.

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å^2)

	x	*y*	*z*	U_{iso}*/U_{eq}
I1	1.07185 (10)	0.31162 (4)	0.23986 (4)	0.0483 (3)
S1	0.4332 (4)	0.20616 (18)	0.59942 (16)	0.0586 (10)
O1	−0.2092 (9)	0.0552 (4)	0.5161 (4)	0.045 (2)
N1	−0.4370 (12)	0.0106 (4)	0.3922 (4)	0.040 (3)
N2	0.0812 (11)	0.1226 (4)	0.3935 (4)	0.034 (2)
N3	0.1620 (11)	0.1406 (4)	0.4736 (4)	0.037 (3)
N4	0.4525 (10)	0.2139 (4)	0.4329 (4)	0.034 (2)
C1	−0.2557 (14)	0.0481 (5)	0.4378 (6)	0.039 (3)
C2	−0.4343 (14)	0.0140 (5)	0.3070 (6)	0.038 (3)
C3	−0.5883 (15)	−0.0147 (6)	0.2406 (6)	0.050 (3)
C4	−0.5463 (17)	−0.0022 (6)	0.1609 (7)	0.058 (4)
C5	−0.3504 (17)	0.0387 (6)	0.1472 (6)	0.055 (4)
C6	−0.1928 (16)	0.0702 (6)	0.2141 (6)	0.049 (3)
C7	−0.2329 (13)	0.0575 (5)	0.2942 (5)	0.035 (3)
C8	−0.1107 (13)	0.0803 (5)	0.3755 (5)	0.036 (3)
C9	0.3534 (13)	0.1884 (5)	0.4975 (5)	0.036 (3)
C10	0.6498 (14)	0.2638 (5)	0.4318 (5)	0.035 (3)
C11	0.7303 (13)	0.2695 (5)	0.3565 (6)	0.038 (3)
C12	0.9304 (14)	0.3131 (5)	0.3511 (5)	0.038 (3)
C13	1.0440 (15)	0.3535 (5)	0.4199 (6)	0.044 (3)
C14	0.9691 (16)	0.3505 (6)	0.4947 (6)	0.050 (3)
C15	0.7723 (16)	0.3050 (6)	0.5021 (6)	0.048 (3)
H1	−0.54474	−0.01324	0.41344	0.0478*
H3	−0.72140	−0.04269	0.24913	0.0602*
H3A	0.09085	0.12147	0.51176	0.0443*
H4	−0.65213	−0.02171	0.11525	0.0694*
H4A	0.38484	0.19719	0.38428	0.0404*
H5	−0.32307	0.04539	0.09258	0.0658*
H6	−0.06263	0.09934	0.20473	0.0588*
H11	0.64938	0.24387	0.30899	0.0460*
H13	1.17608	0.38384	0.41514	0.0529*
H14	1.04853	0.37862	0.54072	0.0598*
H15	0.72130	0.30179	0.55351	0.0580*

Atomic displacement parameters (Å^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
I1	0.0373 (4)	0.0617 (5)	0.0487 (4)	0.0009 (3)	0.0153 (3)	0.0093 (3)
S1	0.0525 (15)	0.083 (2)	0.0409 (14)	−0.0148 (14)	0.0096 (11)	0.0018 (14)
O1	0.038 (3)	0.052 (4)	0.050 (4)	−0.003 (3)	0.021 (3)	−0.001 (3)
N1	0.034 (4)	0.039 (4)	0.052 (5)	−0.007 (3)	0.020 (3)	0.000 (4)
N2	0.026 (4)	0.041 (4)	0.038 (4)	−0.002 (3)	0.011 (3)	0.002 (3)
N3	0.032 (4)	0.048 (5)	0.034 (4)	−0.006 (3)	0.012 (3)	0.005 (4)
N4	0.026 (4)	0.037 (4)	0.040 (4)	−0.005 (3)	0.009 (3)	0.001 (3)
C1	0.030 (5)	0.033 (5)	0.058 (7)	0.004 (4)	0.023 (4)	0.005 (5)
C2	0.027 (4)	0.036 (5)	0.054 (6)	−0.002 (4)	0.013 (4)	0.008 (5)
C3	0.039 (5)	0.048 (6)	0.063 (7)	−0.014 (4)	0.010 (5)	0.002 (5)
C4	0.051 (6)	0.063 (7)	0.058 (7)	−0.013 (5)	0.006 (5)	−0.001 (6)
C5	0.063 (6)	0.063 (7)	0.039 (6)	−0.016 (5)	0.011 (5)	0.001 (5)
C6	0.049 (5)	0.049 (6)	0.051 (6)	−0.015 (5)	0.016 (5)	0.000 (5)
C7	0.036 (4)	0.032 (5)	0.040 (5)	−0.005 (4)	0.016 (4)	0.002 (4)
C8	0.027 (4)	0.044 (6)	0.039 (5)	0.006 (4)	0.010 (4)	0.007 (4)
C9	0.026 (4)	0.037 (5)	0.045 (5)	0.001 (4)	0.007 (4)	0.006 (4)
C10	0.035 (5)	0.036 (5)	0.036 (5)	0.005 (4)	0.010 (4)	0.003 (4)
C11	0.027 (4)	0.036 (5)	0.051 (6)	0.005 (4)	0.004 (4)	0.005 (5)
C12	0.029 (4)	0.035 (5)	0.049 (6)	0.009 (4)	0.008 (4)	0.010 (5)
C13	0.032 (5)	0.039 (6)	0.061 (7)	−0.004 (4)	0.005 (4)	0.003 (5)
C14	0.047 (6)	0.048 (6)	0.057 (6)	−0.012 (5)	0.014 (5)	−0.012 (5)
C15	0.040 (5)	0.055 (6)	0.052 (6)	−0.008 (5)	0.014 (4)	−0.005 (5)

Geometric parameters (Å, °)

I1—C12	2.100 (8)	C5—C6	1.388 (14)
S1—C9	1.656 (8)	C6—C7	1.371 (12)
O1—C1	1.251 (11)	C7—C8	1.429 (11)
N1—C1	1.326 (11)	C10—C15	1.409 (13)
N1—C2	1.380 (11)	C10—C11	1.379 (12)
N2—N3	1.330 (9)	C11—C12	1.382 (11)
N2—C8	1.303 (10)	C12—C13	1.367 (12)
N3—C9	1.364 (10)	C13—C14	1.354 (13)
N4—C9	1.345 (10)	C14—C15	1.390 (14)
N4—C10	1.415 (10)	C3—H3	0.9300
N1—H1	0.8600	C4—H4	0.9300
N3—H3A	0.8600	C5—H5	0.9300
N4—H4A	0.8600	C6—H6	0.9300
C1—C8	1.517 (12)	C11—H11	0.9300
C2—C3	1.355 (13)	C13—H13	0.9300
C2—C7	1.417 (11)	C14—H14	0.9300
C3—C4	1.367 (14)	C15—H15	0.9300
C4—C5	1.372 (14)		
I1···S1^{i}	3.352 (3)	C9···O1^{iv}	3.344 (10)

I1···S1^{ii}	3.979 (3)	C10···C8^{iv}	3.560 (12)
I1···H3^{iii}	3.2000	C11···C8^{iv}	3.307 (12)
I1···H4A^{iv}	3.3000	C11···N2^{iv}	3.180 (11)
S1···C15	3.183 (10)	C12···N2^{iv}	3.355 (11)
S1···I1^{v}	3.352 (3)	C13···N4^{iv}	3.303 (11)
S1···I1^{vi}	3.979 (3)	C13···C9^{iv}	3.414 (12)
S1···H15	2.5100	C14···C9^{iv}	3.505 (13)
O1···N2	3.028 (9)	C15···S1	3.183 (10)
O1···N3	2.761 (9)	C1···H3A	2.4700
O1···C9^{vii}	3.344 (10)	C1···H1^{ix}	2.9000
O1···C1^{viii}	3.168 (10)	C1···H3A^{viii}	3.0700
O1···O1^{viii}	3.157 (8)	C5···H13^{x}	3.0200
O1···N1^{ix}	2.939 (9)	C9···H15	2.8700
O1···C8^{viii}	3.241 (10)	C12···H3^{iii}	3.0400
O1···H3A	2.0700	C13···H4^{iii}	3.0600
O1···H1^{ix}	2.0900	C14···H5^{xi}	3.0500
N1···O1^{ix}	2.939 (9)	C15···H5^{xi}	3.0100
N2···O1	3.028 (9)	H1···O1^{ix}	2.0900
N2···N4	2.618 (9)	H1···C1^{ix}	2.9000
N2···C11^{vii}	3.180 (11)	H3···I1^{xii}	3.2000
N2···C12^{vii}	3.355 (11)	H3···C12^{xii}	3.0400
N3···O1	2.761 (9)	H3A···O1	2.0700
N4···C1^{iv}	3.247 (11)	H3A···C1	2.4700
N4···N2	2.618 (9)	H3A···C1^{viii}	3.0700
N4···C13^{vii}	3.303 (11)	H4···C13^{xii}	3.0600
N2···H4A	2.1800	H4A···I1^{vii}	3.3000
C1···N4^{vii}	3.247 (11)	H4A···N2	2.1800
C1···C9^{vii}	3.511 (12)	H4A···H11	2.2500
C1···O1^{viii}	3.168 (10)	H5···C14^{xiii}	3.0500
C8···O1^{viii}	3.241 (10)	H5···C15^{xiii}	3.0100
C8···C10^{vii}	3.560 (12)	H11···H4A	2.2500
C8···C11^{vii}	3.307 (12)	H13···C5^{xiv}	3.0200
C9···C14^{vii}	3.505 (13)	H15···S1	2.5100
C9···C1^{iv}	3.511 (12)	H15···C9	2.8700
C9···C13^{vii}	3.414 (12)		
C1—N1—C2	112.8 (7)	S1—C9—N4	129.2 (6)
N3—N2—C8	118.6 (7)	C11—C10—C15	118.6 (8)
N2—N3—C9	122.4 (6)	N4—C10—C15	124.8 (7)
C9—N4—C10	130.6 (7)	N4—C10—C11	116.6 (7)
C2—N1—H1	124.00	C10—C11—C12	120.4 (8)
C1—N1—H1	124.00	I1—C12—C13	119.9 (6)
N2—N3—H3A	119.00	I1—C12—C11	120.1 (6)

C9—N3—H3A	119.00	C11—C12—C13	119.8 (8)
C10—N4—H4A	115.00	C12—C13—C14	121.7 (8)
C9—N4—H4A	115.00	C13—C14—C15	119.4 (9)
O1—C1—N1	127.9 (8)	C10—C15—C14	120.1 (8)
N1—C1—C8	105.9 (7)	C2—C3—H3	120.00
O1—C1—C8	126.3 (7)	C4—C3—H3	120.00
C3—C2—C7	120.5 (8)	C3—C4—H4	119.00
N1—C2—C3	130.8 (8)	C5—C4—H4	119.00
N1—C2—C7	108.7 (7)	C4—C5—H5	120.00
C2—C3—C4	119.4 (9)	C6—C5—H5	120.00
C3—C4—C5	121.1 (10)	C5—C6—H6	121.00
C4—C5—C6	120.6 (9)	C7—C6—H6	121.00
C5—C6—C7	118.7 (9)	C10—C11—H11	120.00
C6—C7—C8	133.5 (8)	C12—C11—H11	120.00
C2—C7—C6	119.8 (8)	C12—C13—H13	119.00
C2—C7—C8	106.7 (7)	C14—C13—H13	119.00
N2—C8—C1	126.3 (7)	C13—C14—H14	120.00
C1—C8—C7	105.9 (7)	C15—C14—H14	120.00
N2—C8—C7	127.8 (7)	C10—C15—H15	120.00
S1—C9—N3	117.2 (6)	C14—C15—H15	120.00
N3—C9—N4	113.6 (7)		
C1—N1—C2—C3	−178.2 (9)	C3—C2—C7—C6	−0.4 (13)
C2—N1—C1—O1	−179.7 (8)	C3—C2—C7—C8	179.0 (8)
C2—N1—C1—C8	−0.6 (9)	C2—C3—C4—C5	0.2 (15)
C1—N1—C2—C7	0.2 (10)	C3—C4—C5—C6	−1.7 (16)
N3—N2—C8—C7	176.9 (8)	C4—C5—C6—C7	2.0 (15)
C8—N2—N3—C9	−176.1 (7)	C5—C6—C7—C8	179.8 (9)
N3—N2—C8—C1	−0.3 (12)	C5—C6—C7—C2	−1.0 (13)
N2—N3—C9—S1	179.6 (6)	C2—C7—C8—N2	−178.4 (8)
N2—N3—C9—N4	−1.0 (11)	C6—C7—C8—N2	0.9 (16)
C10—N4—C9—S1	−1.0 (13)	C6—C7—C8—C1	178.6 (10)
C9—N4—C10—C15	−7.2 (14)	C2—C7—C8—C1	−0.7 (9)
C10—N4—C9—N3	179.7 (7)	N4—C10—C11—C12	−176.1 (7)
C9—N4—C10—C11	170.5 (8)	C15—C10—C11—C12	1.6 (13)
O1—C1—C8—N2	−2.3 (14)	N4—C10—C15—C14	177.9 (8)
O1—C1—C8—C7	180.0 (8)	C11—C10—C15—C14	0.3 (14)
N1—C1—C8—N2	178.5 (8)	C10—C11—C12—I1	173.5 (6)
N1—C1—C8—C7	0.8 (9)	C10—C11—C12—C13	−2.7 (13)
N1—C2—C3—C4	179.0 (9)	I1—C12—C13—C14	−174.5 (7)
C7—C2—C3—C4	0.8 (14)	C11—C12—C13—C14	1.7 (13)
N1—C2—C7—C6	−179.0 (8)	C12—C13—C14—C15	0.3 (14)
N1—C2—C7—C8	0.4 (9)	C13—C14—C15—C10	−1.3 (14)

Symmetry codes: (i) *x*+1, −*y*+1/2, *z*−1/2; (ii) *x*, −*y*+1/2, *z*−1/2; (iii) −*x*, *y*+1/2, −*z*+1/2; (iv) *x*+1, *y*, *z*; (v) *x*−1, −*y*+1/2, *z*+1/2; (vi) *x*, −*y*+1/2, *z*+1/2; (vii) *x*−1, *y*, *z*; (viii) −*x*, −*y*, −*z*+1; (ix) −*x*−1, −*y*, −*z*+1; (x) −*x*+1, *y*−1/2, −*z*+1/2; (xi) *x*+1, −*y*+1/2, *z*+1/2; (xii) −*x*, *y*−1/2, −*z*+1/2; (xiii) *x*−1, −*y*+1/2, *z*−1/2; (xiv) −*x*+1, *y*+1/2, −*z*+1/2.

Hydrogen-bond geometry (Å, °)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*

N1—H1···O1^{ix}	0.86	2.09	2.939 (9)	169
N3—H3A···O1	0.86	2.07	2.761 (9)	137
N4—H4A···N2	0.86	2.18	2.618 (9)	111
C15—H15···S1	0.93	2.51	3.183 (10)	129

Symmetry codes: (ix) −*x*−1, −*y*, −*z*+1.

Fig. 1

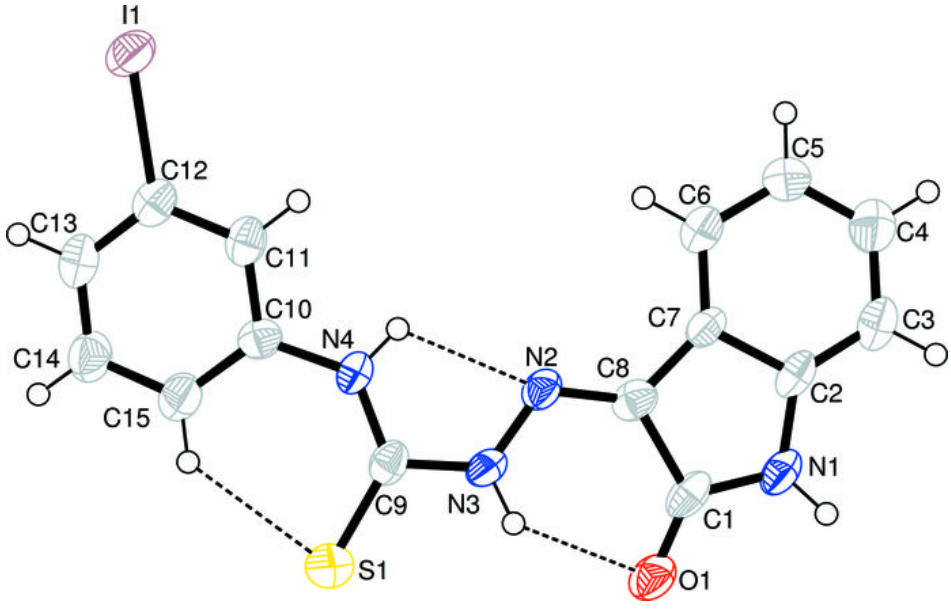
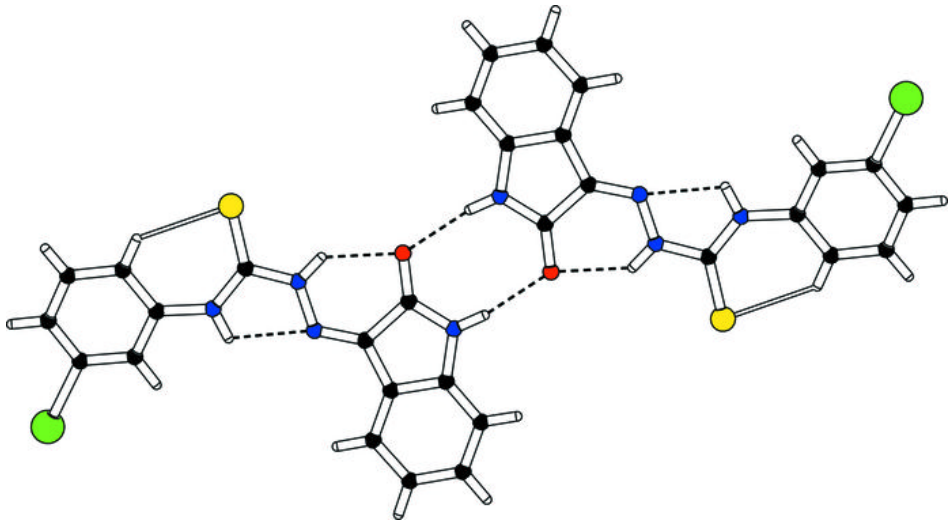

I1
C12
C13
C11
C10
N4
C14
C15
C9
S1
N2
N3
C8
C7
C6
C5
C4
C3
C2
N1
C1
O1

Fig. 2



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8-[(1*E*)-1-(2-Aminophenyliminio)ethyl]-2-oxo-2*H*-chromen-7-olate

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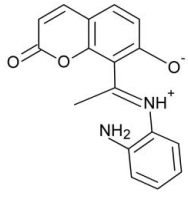
Key indicators: single-crystal X-ray study; T = 296 K; mean σ(C–C) = 0.002 Å; R factor = 0.038; wR factor = 0.095; data-to-parameter ratio = 13.5.

The title Schiff base, $C_{17}H_{14}N_2O_3$, exists as an NH tautomer with the H atom of the phenol group transferred to the imine N atom. The iminium H atom is involved in a strong intramolecular N^+—H···O^- hydrogen bond to the phenolate O atom, forming an $S(6)$ motif. In the crystal structure, N—H···O hydrogen bonds form a $C(9)$ chain parallel to [100] and a $C(11)$ chain parallel to [010], while C—H···O hydrogen bonds form a $C(11)$ chain parallel to [010]. The combination of N—H···O and C—H···O hydrogen bonds generates $R_4^3(30)$ rings parallel to the *ab* plane

Related literature

For related structures, see: Patil *et al.* (2010); Aazam *et al.* (2006); Filarowski (2005); El Husseiny *et al.* (2008); Aazam *et al.* (2008); Karabıyık *et al.* (2008). For the graph-set analysis of hydrogen-bond patterns, see: Bernstein *et al.* (1995).



Experimental

Crystal data

$C_{17}H_{14}N_2O_3$
M_r = 294.30
Orthorhombic, *Pbca*
a = 7.5462 (3) Å
b = 18.9324 (11) Å
c = 20.0445 (9) Å
V = 2863.7 (2) Å^3
Z = 8
Mo $K\alpha$ radiation
μ = 0.10 mm^{-1}
T = 296 K
0.44 × 0.29 × 0.20 mm

Data collection

Stoe IPDS 2 diffractometer
Absorption correction: integration (*X-RED32*; Stoe & Cie, 2002)
T_{min} = 0.962, T_{max} = 0.984
25561 measured reflections
2868 independent reflections
1972 reflections with $I > 2\sigma(I)$
R_{int} = 0.039

Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.038
$wR(F^2)$ = 0.095
S = 1.00
2868 reflections
212 parameters
1 restraint
H atoms treated by a mixture of independent and constrained refinement
$\Delta\rho_{max}$ = 0.11 e Å^{-3}
$\Delta\rho_{min}$ = −0.15 e Å^{-3}

Table 1
Hydrogen-bond geometry (Å, °).

D—H···A	D—H	H···A	D···A	D—H···A
N1—H1···O1	0.95 (2)	1.56 (2)	2.4534 (17)	155 (2)
N2—H2A···O1^{i}	0.92 (2)	2.13 (2)	2.9933 (19)	154.7 (15)
N2—H2B···O2^{ii}	0.91 (2)	2.37 (2)	3.1203 (19)	138.7 (17)
C5—H5···O2^{iii}	0.93	2.48	3.242 (2)	139

Symmetry codes: (i) $x+\frac{1}{2}, y, -z+\frac{1}{2}$; (ii) $-x+\frac{3}{2}, y+\frac{1}{2}, z$; (iii) $-x+\frac{1}{2}, y+\frac{1}{2}, z$.

Data collection: *X-AREA* (Stoe & Cie, 2002); cell refinement: *X-AREA*; data reduction: *X-RED32* (Stoe & Cie, 2002); program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *ORTEP-3 for Windows* (Farrugia, 1997); software used to prepare material for publication: *WinGX* (Farrugia, 1999).

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Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: GK2282).

References

Aazam, E. S., Fawazy, A. & Hitchcock, P. B. (2006). *Acta Cryst.* E**62**, o4285–o4287.
Aazam, E. S., El Husseiny, A. F., Hitchcock, P. B. & Al Shehary, J. (2008). *Centr. Eur. J. Chem.* **6**, 319–323.
Bernstein, J., Davis, R. E., Shimoni, L. & Chang, N.-L. (1995). *Angew. Chem. Int. Ed. Engl.* **34**, 1555–1573.
El Husseiny, A. F., Aazam, E. S. & Al Shehary, J. (2008). *ICAIJ*, **3**, 64–68.
Farrugia, L. J. (1997). *J. Appl. Cryst.* **30**, 565.
Farrugia, L. J. (1999). *J. Appl. Cryst.* **32**, 837–838.
Filarowski, A. (2005). *J. Phys. Org. Chem.* **18**, 686–698.
Karabıyık, H., Ocak Iskeleli, N., Petek, H., Albayrak, Ç. & Agar, E. (2008). *J. Mol. Struct.* **873**, 130–136.
Patil, S. A., Naik, V. H., Kulkarni, A. D. & Badami, P. S. (2010). *Spectrochimica Acta Part A*, **75**, 347-354.
Sheldrick, G. M. (2008). *Acta Cryst.* A**64**, 112–122.
Stoe & Cie (2002). *X-AREA* and *X-RED32*. Stoe & Cie, Darmstadt, Germany.

supplementary materials

Acta Cryst. (2010). E**66**, o1796 [**doi:10.1107/S1600536810023093**]

8-[(1*E*)-1-(2-Aminophenyliminio)ethyl]-2-oxo-2*H*-chromen-7-olate

E. S. Aazam, A. F. El Husseiny, H. M. Al-Amri and O. Büyükgüngör

Comment

Coumarin and its derivatives have been a subject of numerous investigations due to their diverse biological activities, interesting photophysical, photochemical and metal binding properties. Schiff base complexes play an important role in coordination chemistry (Patil *et al.*, 2010). We have recently reported synthesis, single-crystal X-ray diffraction studies, characterization and antibacterial activity of a Schiff-base ligand incorporating coumarin moiety and their metal complexes (Aazam *et al.*, 2006; El Husseiny, *et al.*, 2008; Aazam *et al.*, 2008). In this work, we would like to present an X-ray investigation of a newly synthesized coumarin Schiff base derived from 8-acetyl-7-hydroxycoumarin and *o*-phenylenediamine. We report here the crystal structure of (I) (Figure 1).

Schiff bases exhibit two well known tautomeric forms *viz*. OH and NH tautomers. NH tautomers can be regarded as a resonance hybrid of two canonical structures the non-charged quinoid and ionic zwitterionic forms. Our investigations show that compound (I) formula can be given as a combination of two canonical forms: phenolate with negative charge predominantly at the phenolate O atom or as chromen-8-ide with negative charge at the C atom. Compound I is a hyprid of two zwitterionic canonical forms (Fig. 2) having N^{+}—H bond (0.952 Å) longer than standared interatomic separations observed in neutral N—H bonds (0.878 Å)(Karabıyık *et al.*, 2008). Compound (I) crystallizes in the orthorhombic space group Pbca (No. 61) with one molecule per asymmetric unit. The iminium H atom is almost coplanar with the coumarin ring (deviation from the coumarin plane 0.0444 Å) and on the same side of the molecule as the phenolic O atom, allowing the formation of an intramolecular N—H···O hydrogen bond. A summary of bond lengths and angles of the ketoimine system is presented in Table 1.

In order to compare the bond lengths found in (I) with other molecules containing similar functional groups, a comparison with a previous search in the Cambridge Structural Database (CSD) was performed (Filarowski, 2005). The comparison with the mean bond lengths of similar molecules clearly tends to confirm that (I) is *cis*-ketoimine tauutomer and that the C7—N1 in agreement with double-bond character, the C10—O1 is 1.3040 Å, this bond is not double (keto group) and is one of the longest among similar iminium derivatives, also C7—C9 bond length is not a typical single-bond. Moreover C9—C14 ring is in agreement with the cyclohexadienide bond character. The intramolecular hydrogen bond produces S(6) motif (Bernstein *et al.*, 1995). The amino atom N2 in the molecule at (*x*, *y*, *z*) acts as a hydrogen-bond donor (Table 1) to atom $O1^{i}$ so forming a C(9) chain running parallel to the [100] direction. Amino atom N2 in the molecule at (*x*, *y*, *z*) acts as a hydrogen-bond donor to atom $O2^{ii}$ so forming a C(11) chain running parallel to the [010] direction. Similarly, atom C5 in the molecule at (*x*, *y*, *z*) acts as a hydrogen-bond donor to atom $O2^{iii}$ so forming a C(11) chain running parallel to the [010] direction. The combination of N—H···O and C—H···O hydrogen bonds generates $R_4^3(30)$ rings parallel to the *ab* plane (Fig. 3).

Experimental

A clear solution of *o*-phenylenediamine (0.26 g, 2.5 mmol) in 10 ml of ethanol was added to a warm solution of 8-acetyl-7-hydroxy coumarin (0.5 g, 2.5 mmol) in the same solvent (30 ml). The resulting mixture was refluxed for 2–3 h. The yellow

product was precipitated, filtered off and washed with ethanol followed by diethyl ether, dried in a vacuum desiccator and crystallized from chloroform/ethanol (2:1). Single crystals were obtained by slow evaporation of dichloromethane solution of I at room temperature; Yield (75%), m.p. 480 K. Purity of the ligand was checked using TLC; (methanol: benzene, 1:4).

Refinement

All H atoms bound to C atoms were refined using a riding model, with C—H = 0.93Å and U_{iso}(H) = 1.2U_{eq}(C) for aromatic C atoms and C—H = 0.96Å and U_{iso}(H) = 1.5U_{eq}(C) for methyl C atoms. Amino H atoms bound to N atom were located in difference maps and refined freely. Other H atom bound to N atom was located in difference maps and refined subject to a *DFIX* restraint of N—H = 0.86 (2) Å.

Figures

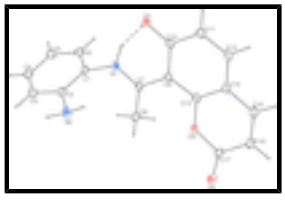


Fig. 1. A view of one molecule of (I), showing the atom-numbering scheme. Displacement ellipsoids are drawn at the 30% probability level. Hydrogen bonds are indicated by dashed lines.

Fig. 2. Zwitterionic canonical forms of I.

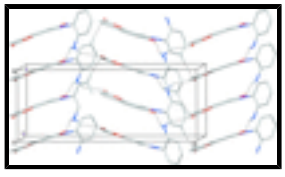


Fig. 3. Part of the crystal structure of (I), showing the formation of a hydrogen-bonded sheet built from C(9) and C(11) chains. For the sake of clarity, H atoms not involved in the motif shown have been omitted.

8-[(1*E*)-1-(2-Aminophenyliminio)ethyl]-2-oxo-2*H*-chromen-7-olate

Crystal data

$C_{17}H_{14}N_2O_3$	$F(000)$ = 1232
M_r = 294.30	D_x = 1.365 Mg m^{-3}
Orthorhombic, *Pbca*	Mo *K*α radiation, λ = 0.71073 Å
Hall symbol: -P 2ac 2ab	Cell parameters from 25561 reflections
a = 7.5462 (3) Å	θ = 2.0–26.7°
b = 18.9324 (11) Å	μ = 0.10 mm^{-1}
c = 20.0445 (9) Å	*T* = 296 K
V = 2863.7 (2) Å^3	Prism, yellow
Z = 8	0.44 × 0.29 × 0.20 mm

Data collection

Stoe IPDS 2 diffractometer	2868 independent reflections

Radiation source: fine-focus sealed tube	1972 reflections with $I > 2\sigma(I)$
graphite	$R_{int} = 0.039$
rotation method scans	$\theta_{max} = 26.2°$, $\theta_{min} = 2.0°$
Absorption correction: integration (*X-RED32*; Stoe & Cie, 2002)	$h = -9 \rightarrow 9$
$T_{min} = 0.962$, $T_{max} = 0.984$	$k = -23 \rightarrow 23$
25561 measured reflections	$l = -24 \rightarrow 24$

Refinement

Refinement on F^2	Primary atom site location: structure-invariant direct methods
Least-squares matrix: full	Secondary atom site location: difference Fourier map
$R[F^2 > 2\sigma(F^2)] = 0.038$	Hydrogen site location: inferred from neighbouring sites
$wR(F^2) = 0.095$	H atoms treated by a mixture of independent and constrained refinement
$S = 1.00$	$w = 1/[\sigma^2(F_o^2) + (0.0515P)^2 +]$ where $P = (F_o^2 + 2F_c^2)/3$
2868 reflections	$(\Delta/\sigma)_{max} < 0.001$
212 parameters	$\Delta\rho_{max} = 0.11$ e Å^{-3}
1 restraint	$\Delta\rho_{min} = -0.15$ e Å^{-3}

Special details

Geometry. All e.s.d.'s (except the e.s.d. in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell e.s.d.'s are taken into account individually in the estimation of e.s.d.'s in distances, angles and torsion angles; correlations between e.s.d.'s in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell e.s.d.'s is used for estimating e.s.d.'s involving l.s. planes.

Refinement. Refinement of F^2 against ALL reflections. The weighted *R*-factor *wR* and goodness of fit *S* are based on F^2, conventional *R*-factors *R* are based on *F*, with *F* set to zero for negative F^2. The threshold expression of $F^2 > \sigma(F^2)$ is used only for calculating *R*-factors(gt) *etc*. and is not relevant to the choice of reflections for refinement. *R*-factors based on F^2 are statistically about twice as large as those based on *F*, and *R*- factors based on ALL data will be even larger.

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å^2)

	x	*y*	*z*	U_{iso}*/U_{eq}
C1	0.3733 (2)	0.81253 (7)	0.38471 (7)	0.0462 (4)
C2	0.5193 (2)	0.83854 (7)	0.41971 (8)	0.0487 (4)
C3	0.4876 (2)	0.89106 (8)	0.46724 (8)	0.0584 (4)
H3	0.5822	0.9095	0.4914	0.070*
C4	0.3197 (3)	0.91605 (8)	0.47909 (9)	0.0632 (5)
H4	0.3019	0.9507	0.5113	0.076*
C5	0.1777 (3)	0.89021 (9)	0.44379 (9)	0.0646 (5)
H5	0.0642	0.9073	0.4519	0.077*
C6	0.2051 (2)	0.83870 (8)	0.39613 (9)	0.0581 (4)
H6	0.1098	0.8215	0.3716	0.070*

C7	0.44310 (18)	0.69702 (7)	0.33766 (7)	0.0446 (3)
C8	0.4588 (2)	0.66606 (8)	0.40572 (8)	0.0602 (4)
H8A	0.4121	0.6987	0.4379	0.072*
H8B	0.5813	0.6569	0.4154	0.072*
H8C	0.3932	0.6227	0.4077	0.072*
C9	0.47034 (19)	0.65822 (7)	0.27529 (7)	0.0442 (3)
C10	0.4368 (2)	0.69219 (7)	0.21251 (8)	0.0491 (4)
C11	0.4623 (2)	0.65452 (8)	0.15220 (8)	0.0584 (4)
H11	0.4402	0.6767	0.1117	0.070*
C12	0.5186 (2)	0.58675 (8)	0.15284 (9)	0.0587 (4)
H12	0.5332	0.5630	0.1126	0.070*
C13	0.5555 (2)	0.55134 (7)	0.21273 (8)	0.0525 (4)
C14	0.53174 (19)	0.58766 (7)	0.27212 (8)	0.0455 (4)
C15	0.6172 (2)	0.48034 (8)	0.21610 (10)	0.0641 (5)
H15	0.6307	0.4548	0.1768	0.077*
C16	0.6561 (2)	0.44943 (8)	0.27412 (10)	0.0671 (5)
H16	0.6943	0.4027	0.2746	0.081*
C17	0.6397 (2)	0.48719 (7)	0.33552 (10)	0.0588 (4)
N1	0.39971 (17)	0.76316 (6)	0.33146 (7)	0.0488 (3)
N2	0.68956 (19)	0.81302 (8)	0.41013 (8)	0.0631 (4)
O1	0.38245 (16)	0.75749 (5)	0.20935 (6)	0.0603 (3)
O2	0.67878 (17)	0.46798 (5)	0.39135 (7)	0.0735 (4)
O3	0.57044 (14)	0.55503 (5)	0.33133 (5)	0.0541 (3)
H1	0.390 (3)	0.7742 (10)	0.2853 (8)	0.087 (6)*
H2A	0.715 (2)	0.7907 (9)	0.3703 (10)	0.071 (5)*
H2B	0.772 (3)	0.8469 (11)	0.4178 (11)	0.099 (7)*

Atomic displacement parameters (Å^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
C1	0.0615 (9)	0.0363 (7)	0.0409 (9)	−0.0009 (6)	0.0025 (7)	0.0007 (6)
C2	0.0586 (9)	0.0435 (7)	0.0439 (9)	−0.0018 (7)	0.0053 (7)	−0.0002 (6)
C3	0.0700 (11)	0.0557 (8)	0.0494 (10)	−0.0061 (8)	0.0042 (8)	−0.0116 (7)
C4	0.0844 (13)	0.0537 (9)	0.0515 (10)	0.0048 (8)	0.0143 (9)	−0.0090 (7)
C5	0.0651 (10)	0.0662 (10)	0.0623 (12)	0.0133 (8)	0.0086 (9)	−0.0029 (9)
C6	0.0586 (10)	0.0577 (9)	0.0579 (11)	0.0039 (7)	−0.0008 (8)	−0.0007 (8)
C7	0.0490 (8)	0.0393 (7)	0.0454 (9)	−0.0045 (6)	−0.0014 (7)	0.0024 (6)
C8	0.0889 (12)	0.0459 (8)	0.0459 (10)	0.0056 (8)	0.0010 (9)	0.0037 (7)
C9	0.0483 (8)	0.0397 (7)	0.0446 (9)	−0.0056 (6)	−0.0026 (6)	−0.0011 (6)
C10	0.0563 (9)	0.0455 (7)	0.0454 (9)	−0.0067 (6)	−0.0048 (7)	0.0001 (6)
C11	0.0734 (11)	0.0588 (9)	0.0431 (10)	−0.0053 (8)	−0.0043 (8)	−0.0011 (7)
C12	0.0681 (10)	0.0594 (9)	0.0486 (11)	−0.0077 (8)	0.0003 (8)	−0.0134 (7)
C13	0.0544 (9)	0.0465 (8)	0.0565 (11)	−0.0054 (6)	−0.0008 (7)	−0.0097 (7)
C14	0.0474 (8)	0.0411 (7)	0.0480 (10)	−0.0076 (6)	−0.0040 (7)	0.0001 (6)
C15	0.0686 (11)	0.0489 (8)	0.0749 (13)	−0.0011 (8)	−0.0002 (10)	−0.0181 (8)
C16	0.0724 (11)	0.0416 (8)	0.0874 (15)	0.0047 (7)	−0.0082 (10)	−0.0091 (9)
C17	0.0586 (10)	0.0384 (7)	0.0795 (14)	−0.0011 (7)	−0.0101 (9)	0.0018 (8)
N1	0.0667 (8)	0.0393 (6)	0.0403 (8)	0.0007 (5)	−0.0026 (6)	−0.0012 (5)

N2	0.0562 (8)	0.0674 (9)	0.0659 (10)	−0.0034 (7)	0.0055 (8)	−0.0179 (8)
O1	0.0862 (8)	0.0476 (6)	0.0472 (7)	0.0064 (5)	−0.0074 (6)	0.0060 (5)
O2	0.0904 (9)	0.0482 (6)	0.0820 (10)	0.0054 (6)	−0.0181 (8)	0.0106 (6)
O3	0.0671 (7)	0.0391 (5)	0.0560 (7)	0.0035 (5)	−0.0068 (5)	0.0008 (5)

Geometric parameters (Å, °)

C1—C6	1.381 (2)	C9—C10	1.436 (2)
C1—C2	1.396 (2)	C10—O1	1.3040 (17)
C1—N1	1.4327 (18)	C10—C11	1.417 (2)
C2—N2	1.386 (2)	C11—C12	1.351 (2)
C2—C3	1.398 (2)	C11—H11	0.9300
C3—C4	1.373 (2)	C12—C13	1.403 (2)
C3—H3	0.9300	C12—H12	0.9300
C4—C5	1.374 (3)	C13—C14	1.386 (2)
C4—H4	0.9300	C13—C15	1.424 (2)
C5—C6	1.381 (2)	C14—O3	1.3695 (17)
C5—H5	0.9300	C15—C16	1.334 (2)
C6—H6	0.9300	C15—H15	0.9300
C7—N1	1.3004 (17)	C16—C17	1.429 (3)
C7—C9	1.464 (2)	C16—H16	0.9300
C7—C8	1.490 (2)	C17—O2	1.213 (2)
C8—H8A	0.9600	C17—O3	1.3893 (17)
C8—H8B	0.9600	N1—H1	0.952 (15)
C8—H8C	0.9600	N2—H2A	0.92 (2)
C9—C14	1.4153 (19)	N2—H2B	0.91 (2)
C6—C1—C2	121.01 (14)	O1—C10—C9	121.51 (13)
C6—C1—N1	119.04 (14)	C11—C10—C9	119.89 (13)
C2—C1—N1	119.65 (13)	C12—C11—C10	120.84 (16)
N2—C2—C1	122.62 (14)	C12—C11—H11	119.6
N2—C2—C3	120.05 (15)	C10—C11—H11	119.6
C1—C2—C3	117.31 (14)	C11—C12—C13	121.61 (15)
C4—C3—C2	121.38 (16)	C11—C12—H12	119.2
C4—C3—H3	119.3	C13—C12—H12	119.2
C2—C3—H3	119.3	C14—C13—C12	118.17 (13)
C3—C4—C5	120.51 (15)	C14—C13—C15	118.01 (16)
C3—C4—H4	119.7	C12—C13—C15	123.82 (16)
C5—C4—H4	119.7	O3—C14—C13	119.53 (13)
C4—C5—C6	119.43 (16)	O3—C14—C9	117.17 (13)
C4—C5—H5	120.3	C13—C14—C9	123.30 (14)
C6—C5—H5	120.3	C16—C15—C13	121.81 (16)
C5—C6—C1	120.36 (16)	C16—C15—H15	119.1
C5—C6—H6	119.8	C13—C15—H15	119.1
C1—C6—H6	119.8	C15—C16—C17	120.82 (15)
N1—C7—C9	115.89 (13)	C15—C16—H16	119.6
N1—C7—C8	119.11 (13)	C17—C16—H16	119.6
C9—C7—C8	124.99 (12)	O2—C17—O3	115.12 (15)
C7—C8—H8A	109.5	O2—C17—C16	128.58 (15)
C7—C8—H8B	109.5	O3—C17—C16	116.29 (16)

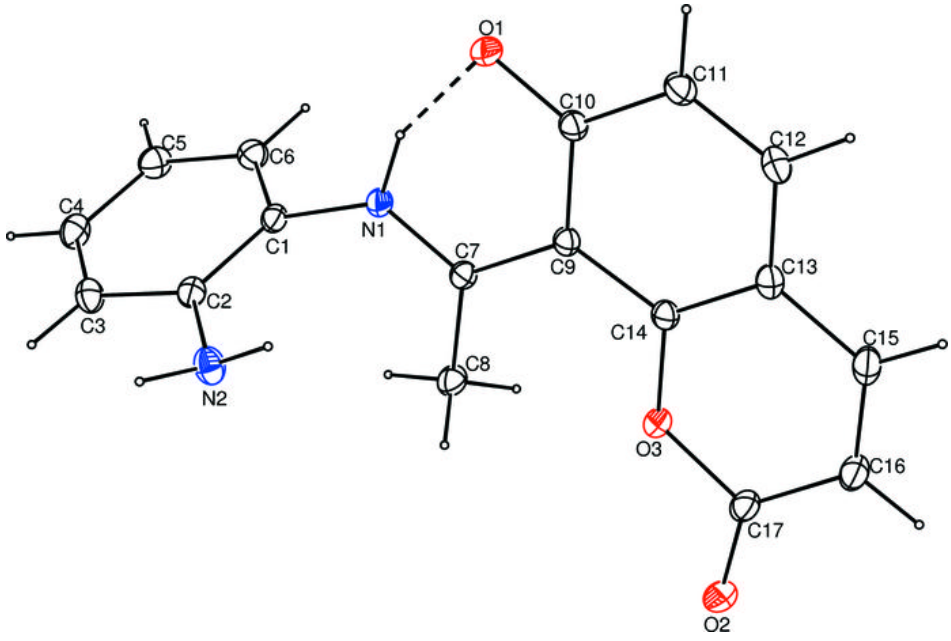
H8A—C8—H8B	109.5	C7—N1—C1	126.31 (13)
C7—C8—H8C	109.5	C7—N1—H1	108.9 (11)
H8A—C8—H8C	109.5	C1—N1—H1	124.8 (11)
H8B—C8—H8C	109.5	C2—N2—H2A	118.0 (11)
C14—C9—C10	116.18 (13)	C2—N2—H2B	111.5 (13)
C14—C9—C7	123.89 (13)	H2A—N2—H2B	109.3 (17)
C10—C9—C7	119.92 (12)	C14—O3—C17	123.35 (13)
O1—C10—C11	118.60 (14)		
C6—C1—C2—N2	179.24 (15)	C11—C12—C13—C15	−179.15 (16)
N1—C1—C2—N2	−7.1 (2)	C12—C13—C14—O3	−178.55 (13)
C6—C1—C2—C3	1.0 (2)	C15—C13—C14—O3	1.0 (2)
N1—C1—C2—C3	174.61 (13)	C12—C13—C14—C9	0.8 (2)
N2—C2—C3—C4	−178.25 (16)	C15—C13—C14—C9	−179.68 (14)
C1—C2—C3—C4	0.0 (2)	C10—C9—C14—O3	177.82 (12)
C2—C3—C4—C5	−0.5 (3)	C7—C9—C14—O3	−1.3 (2)
C3—C4—C5—C6	0.0 (3)	C10—C9—C14—C13	−1.5 (2)
C4—C5—C6—C1	1.0 (3)	C7—C9—C14—C13	179.41 (14)
C2—C1—C6—C5	−1.5 (2)	C14—C13—C15—C16	−1.7 (2)
N1—C1—C6—C5	−175.19 (14)	C12—C13—C15—C16	177.81 (17)
N1—C7—C9—C14	174.71 (14)	C13—C15—C16—C17	−1.0 (3)
C8—C7—C9—C14	−6.3 (2)	C15—C16—C17—O2	−175.59 (18)
N1—C7—C9—C10	−4.4 (2)	C15—C16—C17—O3	4.2 (3)
C8—C7—C9—C10	174.68 (14)	C9—C7—N1—C1	−177.28 (14)
C14—C9—C10—O1	−178.93 (14)	C8—C7—N1—C1	3.6 (2)
C7—C9—C10—O1	0.2 (2)	C6—C1—N1—C7	−112.84 (17)
C14—C9—C10—C11	1.2 (2)	C2—C1—N1—C7	73.42 (19)
C7—C9—C10—C11	−179.71 (14)	C13—C14—O3—C17	2.5 (2)
O1—C10—C11—C12	179.96 (15)	C9—C14—O3—C17	−176.83 (13)
C9—C10—C11—C12	−0.1 (2)	O2—C17—O3—C14	174.78 (14)
C10—C11—C12—C13	−0.7 (3)	C16—C17—O3—C14	−5.1 (2)
C11—C12—C13—C14	0.4 (2)		

Hydrogen-bond geometry (Å, °)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
N1—H1···O1	0.95 (2)	1.56 (2)	2.4534 (17)	155.(2)
N2—H2A···O1^{i}	0.92 (2)	2.13 (2)	2.9933 (19)	154.7 (15)
N2—H2B···O2^{ii}	0.91 (2)	2.37 (2)	3.1203 (19)	138.7 (17)
C5—H5···O2^{iii}	0.93	2.48	3.242 (2)	139

Symmetry codes: (i) *x*+1/2, *y*, −*z*+1/2; (ii) −*x*+3/2, *y*+1/2, *z*; (iii) −*x*+1/2, *y*+1/2, *z*.

Fig. 1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C10
C12
C5
C6
C4
N1
C1
C7
C9
C13
C2
C3
C14
C15
C8
N2
O3
C16
C17
O2

Fig. 2

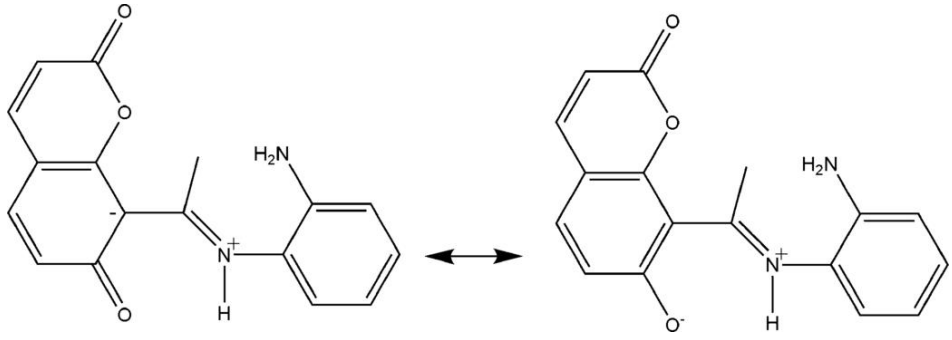
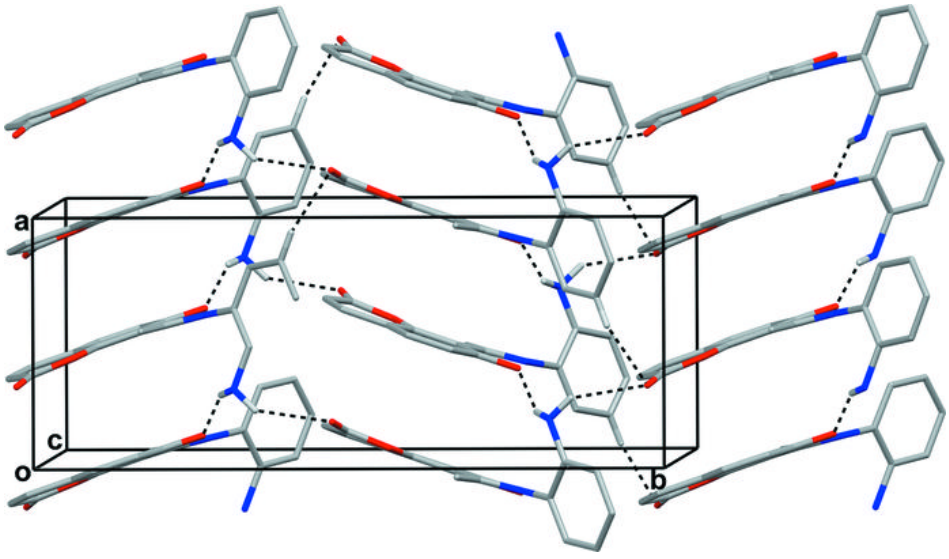


Fig. 3



Acta Crystallographica Section E
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N-{2-[*N*-(4-Methylphenyl)oxamoyl]-phenyl}propanamide

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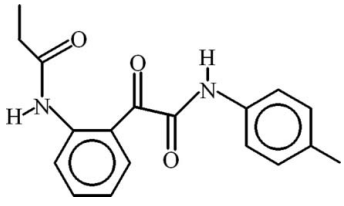
Key indicators: single-crystal X-ray study; T = 296 K; mean σ(C–C) = 0.003 Å; R factor = 0.039; wR factor = 0.111; data-to-parameter ratio = 14.0.

The title compound, $C_{18}H_{18}N_2O_3$, is the product of the heterocyclic ring cleavage at position 2 of 1-propionylisatin. Two centrosymmetric cyclic motifs, *viz.* $R_2^2(14)$ and $R_2^2(18)$, are formed by N—H···O hydrogen bonds with the propanamide and aminophenyl units, respectively, as the N—H donors. These motifs combine into two $C_2^2(8)$ chain motifs parallel to the b axis. The chain structure is stabilized by C—H···π interactions between the benzene rings, where C—H is from the phenyl ring of the cleaved part of 1-propionylisatin.

Related literature

For related structures, see: Hohne & Seidel (1979); Boryczka *et al.* (1998); Zukerman-Schpector *et al.* (1994). For synthetic background, see: Pervez *et al.* (2009, 2010*a*,*b*). For graph-set notation, see: Bernstein *et al.* (1995).



Experimental

Crystal data

$C_{18}H_{18}N_2O_3$
M_r = 310.34
Triclinic, $P\overline{1}$
a = 9.2048 (4) Å
b = 9.7717 (3) Å
c = 10.4404 (4) Å
α = 72.962 (2)°
β = 72.920 (1)°
γ = 69.285 (2)°
V = 820.63 (6) Å^3
Z = 2
Mo $K\alpha$ radiation
μ = 0.09 mm^{-1}
T = 296 K
0.32 × 0.24 × 0.22 mm

Data collection

Bruker Kappa APEXII CCD diffractometer
Absorption correction: multi-scan (*SADABS*; Bruker, 2005)
T_{min} = 0.942, T_{max} = 0.952
11476 measured reflections
2933 independent reflections
2402 reflections with $I > 2\sigma(I)$
R_{int} = 0.023

Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.039
$wR(F^2)$ = 0.111
S = 1.03
2933 reflections
210 parameters
H-atom parameters constrained
$\Delta\rho_{max}$ = 0.18 e Å^{-3}
$\Delta\rho_{min}$ = −0.21 e Å^{-3}

Table 1
Hydrogen-bond geometry (Å, °).

*Cg*1 is the centroid of C1–C6 benzene ring.

D—H···A	D—H	H···A	D···A	D—H···A
N1—H1···O2	0.86	2.46	2.7678 (17)	102
N1—H1···O3^{i}	0.86	2.14	2.9247 (18)	152
N2—H2*A*···O1^{ii}	0.86	2.07	2.8821 (16)	157
C2—H2···O2^{i}	0.93	2.58	3.506 (2)	175
C14—H14···*Cg*1^{ii}	0.93	2.89	3.6693 (18)	142

Symmetry codes: (i) $-x+1, -y, -z+1$; (ii) $-x+1, -y+1, -z+1$.

Data collection: *APEX2* (Bruker, 2007); cell refinement: *SAINT* (Bruker, 2007); data reduction: *SAINT*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *ORTEP-3 for Windows* (Farrugia, 1997) and *PLATON* (Spek, 2009); software used to prepare material for publication: *WinGX* (Farrugia, 1999) and *PLATON*.

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Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: GK2285).

References

Bernstein, J., Davis, R. E., Shimoni, L. & Chang, N.-L. (1995). *Angew. Chem. Int. Ed. Engl.* **34**, 1555–1573.
Boryczka, S., Suwinska, K., Guillanton, G., Do Le, T. Q. & Elothmani, D. (1998). *J. Chem. Crystallogr.* **28**, 555–560.
Bruker (2005). *SADABS*. Bruker AXS Inc., Madison, Wisconsin, USA.
Bruker (2007). *APEX2* and *SAINT*. Bruker AXS Inc., Madison, Wisconsin, USA.
Farrugia, L. J. (1997). *J. Appl. Cryst.* **30**, 565.
Farrugia, L. J. (1999). *J. Appl. Cryst.* **32**, 837–838.
Hohne, E. & Seidel, I. (1979). *Krist. Tech.* **14**, 1097–1101.
Pervez, H., Yaqub, M., Manzoor, N., Tahir, M. N. & Iqbal, M. S. (2009). *Acta Cryst.* E**65**, o2858.
Pervez, H., Yaqub, M., Ramzan, M., Tahir, M. N. & Iqbal, M. S. (2010*a*). *Acta Cryst.* E**66**, o1609.
Pervez, H., Iqbal, M. S., Saira, N., Yaqub, M. & Tahir, M. N. (2010*b*). *Acta Cryst.* E**66**, o1169–o1170.
Sheldrick, G. M. (2008). *Acta Cryst.* A**64**, 112–122.
Spek, A. L. (2009). *Acta Cryst.* D**65**, 148–155.
Zukerman-Schpector, J., Pinto, A. DaC., Da Silva, J. F. M. & Da Silva, R. B. (1994). *Acta Cryst.* C**50**, 87–88.

supplementary materials

Acta Cryst. (2010). E**66**, o1729 [**doi:10.1107/S1600536810023263**]

N-{2-[*N*-(4-Methylphenyl)oxamoyl]phenyl}propanamide

H. Pervez, M. Ahmad, M. Yaqub, M. N. Tahir and N. Saira

Comment

We recently have reported the synthesis and crystal structures of certain isatin derivatives (Pervez *et al.*, 2009, 2010*a*, 2010*b*). The title compound (I), (Fig. 1) is the side product obtained in low yield due to the heterocyclic ring cleavage at position-2 of 1-propionylisatin when reacted with *p*-toluidine.

The crystal structures of (II) *i.e.* 2-oxo-*N*,2-diphenylacetamide (Boryczka *et al.*, 1998) and (III) *i.e. p*-tolyl-glyoxylic acid *p*-chloroanilide (Hohne & Seidel, 1979) have been published. The crystal structure of (I) differs from (II) and (III) due to substituants at the phenyl rings. The crystal structure of (IV) *i.e.* 2'-(*N*-isopropyloxamoyl)acetanilide (Zukerman-Schpector *et al.*, 1994) has been published, which has isopropyl instead of tolyl and methyl instead of ethyl when compared to (I).

In the crystal structure of (I), the tolylamino group A (C1—C7/N1) and B(C9–C15/N2) of the cleaved part of 1-propionylisatin are planar with r. m. s. deviation of 0.0364 and 0.0456 Å, respectively. The dihedral angle between A/B is 80.25 (5) °. There exist an S(5) ring motif (Bernstein *et al.*, 1995) due to N—H···O interactions (Table 1). In the central part short intramolecular C═O···C═O contact replaces a hydrogen-bond plausible S(6). The central part of (I) has twisting flexibility to set the orientation of substituated phenyl rings. The intermolecular interactions of N—H···O and C—H···O types complete $R_2^2(12)$ and $R_2^2(18)$ ring motifs setting the two molecules in dimeric way. These dimers are interlinked through N—H···O interactions with $R_2^2(14)$ ring motif (Table 1, Fig. 2). The polymeric chain extends along the crystallographic *b* axis. The C—H···π interaction (Table 1) also play role in stabilizing the molecules.

Experimental

To a refluxing solution of 1-propionylisatin (1.02 g, 5 mmol) in ethanol (15 ml) containing 2–3 drops of concentrated sulfuric acid was added the solution of *p*-toluidine (0.54 g, 5 mmol) made in ethanol (5 ml). The reaction mixture was then refluxed for 2 h, after which it was left at room temperature overnight. The reddish yellow solid formed was collected by suction filtration, washing of which with ethanol to get rid of the soluble impurities, however, gave a dirty white solid. Recrystallization of the same from ethanol furnished the title heterocyclic ring cleavage product (I) in pure form (0.33 g, 21%) m.p. 423 K. The single crystals of (I) for *x*-ray analysis were grown in ethyl acetate-petroleum ether (1:4) by diffusion method at room temperature.

Refinement

The H-atoms were positioned geometrically (N–H = 0.86 Å, C–H = 0.93–0.97 Å) and refined as riding with $U_{iso}(H) = xU_{eq}(C, N)$, where $x = 1.5$ for methyl and $x = 1.2$ for all other H-atoms. !5

Figures

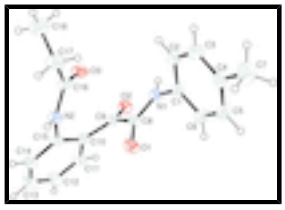


Fig. 1. View of the title compound with the atom numbering scheme. The displacement ellipsoids are drawn at the 30% probability level. H-atoms are shown by small circles of arbitrary radii.

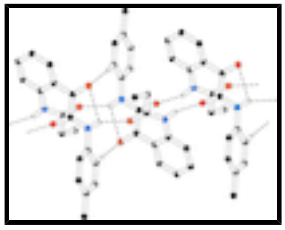


Fig. 2. The partial packing (*PLATON*; Spek, 2009) which shows that molecules arranged *via* hydrogen bonds into one-dimensional polymeric chains extending along the *b* axis.

N-{2-[*N*-(4-Methylphenyl)oxamoyl]phenyl}propanamide

Crystal data

$C_{18}H_{18}N_2O_3$	$Z = 2$
$M_r = 310.34$	$F(000) = 328$
Triclinic, $P\overline{1}$	$D_x = 1.254$ Mg m^{-3}
Hall symbol: -P 1	Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å
$a = 9.2048$ (4) Å	Cell parameters from 2402 reflections
$b = 9.7717$ (3) Å	$\theta = 2.8$–$25.3°$
$c = 10.4404$ (4) Å	$\mu = 0.09$ mm^{-1}
$\alpha = 72.962$ (2)°	$T = 296$ K
$\beta = 72.920$ (1)°	Prism, yellow
$\gamma = 69.285$ (2)°	0.32 × 0.24 × 0.22 mm
$V = 820.63$ (6) Å^3	

Data collection

Bruker Kappa APEXII CCD diffractometer	2933 independent reflections
Radiation source: fine-focus sealed tube	2402 reflections with $I > 2\sigma(I)$
graphite	$R_{int} = 0.023$
Detector resolution: 8.2 pixels mm^{-1}	$\theta_{max} = 25.3°$, $\theta_{min} = 2.8°$
ω scans	$h = -11 \rightarrow 10$
Absorption correction: multi-scan (*SADABS*; Bruker, 2005)	$k = -11 \rightarrow 11$
$T_{min} = 0.942$, $T_{max} = 0.952$	$l = -12 \rightarrow 12$
11476 measured reflections	

Refinement

Refinement on F^2	Primary atom site location: structure-invariant direct methods
Least-squares matrix: full	Secondary atom site location: difference Fourier map
$R[F^2 > 2\sigma(F^2)] = 0.039$	Hydrogen site location: inferred from neighbouring sites
$wR(F^2) = 0.111$	H-atom parameters constrained
$S = 1.03$	$w = 1/[\sigma^2(F_o^2) + (0.0538P)^2 + 0.1939P]$ where $P = (F_o^2 + 2F_c^2)/3$
2933 reflections	$(\Delta/\sigma)_{max} < 0.001$
210 parameters	$\Delta\rho_{max} = 0.18$ e Å^{-3}
0 restraints	$\Delta\rho_{min} = -0.21$ e Å^{-3}

Special details

Geometry. Bond distances, angles *etc*. have been calculated using the rounded fractional coordinates. All su's are estimated from the variances of the (full) variance-covariance matrix. The cell e.s.d.'s are taken into account in the estimation of distances, angles and torsion angles

Refinement. Refinement of F^2 against ALL reflections. The weighted *R*-factor *wR* and goodness of fit *S* are based on F^2, conventional *R*-factors *R* are based on *F*, with *F* set to zero for negative F^2. The threshold expression of $F^2 > \sigma(F^2)$ is used only for calculating *R*-factors(gt) *etc*. and is not relevant to the choice of reflections for refinement. *R*-factors based on F^2 are statistically about twice as large as those based on *F*, and *R*- factors based on ALL data will be even larger.

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å^2)

	x	*y*	*z*	U_{iso}*/U_{eq}
O1	0.73296 (14)	0.26832 (11)	0.51591 (11)	0.0532 (4)
O2	0.60422 (14)	−0.02427 (11)	0.72653 (12)	0.0527 (4)
O3	0.36026 (15)	0.18977 (12)	0.55159 (12)	0.0572 (4)
N1	0.73440 (15)	0.06472 (13)	0.45212 (13)	0.0454 (4)
N2	0.36473 (15)	0.41064 (13)	0.57412 (12)	0.0434 (4)
C1	0.81861 (17)	0.09987 (16)	0.31438 (16)	0.0423 (5)
C2	0.7508 (2)	0.11442 (19)	0.20806 (17)	0.0533 (6)
C3	0.8280 (2)	0.1562 (2)	0.07434 (18)	0.0584 (6)
C4	0.9720 (2)	0.18504 (18)	0.04359 (18)	0.0541 (6)
C5	1.0394 (2)	0.1665 (2)	0.15214 (19)	0.0585 (6)
C6	0.96495 (19)	0.12374 (19)	0.28597 (18)	0.0533 (6)
C7	1.0503 (3)	0.2377 (3)	−0.1028 (2)	0.0789 (8)
C8	0.69138 (17)	0.15593 (15)	0.53889 (15)	0.0396 (5)
C9	0.58882 (17)	0.10771 (15)	0.67838 (15)	0.0404 (5)
C10	0.49283 (17)	0.22541 (16)	0.75877 (14)	0.0394 (4)
C11	0.5065 (2)	0.19194 (19)	0.89436 (16)	0.0503 (5)
C12	0.4344 (2)	0.2961 (2)	0.97574 (17)	0.0606 (6)
C13	0.3468 (2)	0.4365 (2)	0.92194 (18)	0.0619 (6)
C14	0.3263 (2)	0.47161 (18)	0.78955 (17)	0.0513 (5)

C15	0.39731 (17)	0.36707 (15)	0.70660 (14)	0.0390 (4)
C16	0.33857 (18)	0.32494 (17)	0.50734 (16)	0.0444 (5)
C17	0.2851 (3)	0.4048 (2)	0.3751 (2)	0.0701 (7)
C18	0.1504 (3)	0.3664 (3)	0.3605 (3)	0.0991 (10)
H1	0.71043	−0.01814	0.48038	0.0544*
H2	0.65336	0.09623	0.22615	0.0639*
H2A	0.36115	0.50119	0.53138	0.0521*
H3	0.78158	0.16501	0.00316	0.0701*
H5	1.13748	0.18326	0.13421	0.0702*
H6	1.01320	0.11098	0.35712	0.0640*
H7A	1.16236	0.18772	−0.11688	0.1184*
H7B	1.03271	0.34386	−0.12098	0.1184*
H7C	1.00549	0.21520	−0.16359	0.1184*
H11	0.56593	0.09679	0.93107	0.0604*
H12	0.44498	0.27149	1.06627	0.0727*
H13	0.30103	0.50856	0.97527	0.0744*
H14	0.26406	0.56636	0.75514	0.0616*
H17A	0.25468	0.51191	0.36884	0.0841*
H17B	0.37380	0.38080	0.29937	0.0841*
H18A	0.06159	0.39040	0.43466	0.1487*
H18B	0.18084	0.26134	0.36232	0.1487*
H18C	0.12098	0.42260	0.27493	0.1487*

Atomic displacement parameters (Å^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
O1	0.0656 (7)	0.0375 (6)	0.0605 (7)	−0.0269 (5)	−0.0023 (5)	−0.0126 (5)
O2	0.0635 (7)	0.0321 (5)	0.0596 (7)	−0.0167 (5)	−0.0155 (5)	0.0002 (5)
O3	0.0757 (8)	0.0411 (6)	0.0698 (8)	−0.0238 (5)	−0.0319 (6)	−0.0087 (5)
N1	0.0516 (8)	0.0360 (6)	0.0531 (8)	−0.0213 (6)	−0.0045 (6)	−0.0122 (5)
N2	0.0566 (8)	0.0321 (6)	0.0465 (7)	−0.0200 (5)	−0.0182 (6)	0.0002 (5)
C1	0.0417 (8)	0.0338 (7)	0.0522 (9)	−0.0120 (6)	−0.0048 (7)	−0.0143 (6)
C2	0.0465 (9)	0.0610 (10)	0.0617 (11)	−0.0255 (8)	−0.0069 (8)	−0.0191 (8)
C3	0.0581 (11)	0.0693 (11)	0.0555 (10)	−0.0246 (9)	−0.0114 (8)	−0.0176 (8)
C4	0.0508 (10)	0.0466 (9)	0.0596 (10)	−0.0144 (7)	−0.0001 (8)	−0.0152 (7)
C5	0.0408 (9)	0.0644 (11)	0.0714 (12)	−0.0227 (8)	−0.0031 (8)	−0.0159 (9)
C6	0.0442 (9)	0.0586 (10)	0.0622 (11)	−0.0185 (8)	−0.0124 (8)	−0.0147 (8)
C7	0.0777 (14)	0.0777 (14)	0.0698 (13)	−0.0306 (11)	0.0063 (11)	−0.0111 (10)
C8	0.0420 (8)	0.0293 (7)	0.0491 (9)	−0.0116 (6)	−0.0126 (7)	−0.0061 (6)
C9	0.0439 (8)	0.0325 (7)	0.0494 (9)	−0.0153 (6)	−0.0170 (7)	−0.0032 (6)
C10	0.0423 (8)	0.0368 (7)	0.0419 (8)	−0.0184 (6)	−0.0089 (6)	−0.0040 (6)
C11	0.0582 (10)	0.0475 (9)	0.0462 (9)	−0.0181 (7)	−0.0179 (8)	−0.0013 (7)
C12	0.0765 (12)	0.0680 (12)	0.0415 (9)	−0.0242 (10)	−0.0147 (8)	−0.0118 (8)
C13	0.0784 (13)	0.0568 (10)	0.0527 (10)	−0.0194 (9)	−0.0076 (9)	−0.0215 (8)
C14	0.0591 (10)	0.0386 (8)	0.0556 (10)	−0.0141 (7)	−0.0101 (8)	−0.0115 (7)
C15	0.0436 (8)	0.0345 (7)	0.0428 (8)	−0.0189 (6)	−0.0098 (6)	−0.0039 (6)
C16	0.0481 (9)	0.0417 (8)	0.0497 (9)	−0.0199 (7)	−0.0148 (7)	−0.0063 (7)
C17	0.0917 (14)	0.0686 (12)	0.0623 (12)	−0.0303 (11)	−0.0355 (11)	−0.0043 (9)

C18	0.1088 (19)	0.0778 (15)	0.133 (2)	−0.0164 (13)	−0.0782 (18)	−0.0158 (14)

Geometric parameters (Å, °)

O1—C8	1.2244 (19)	C12—C13	1.371 (3)
O2—C9	1.2119 (18)	C13—C14	1.376 (2)
O3—C16	1.228 (2)	C14—C15	1.391 (2)
N1—C1	1.425 (2)	C16—C17	1.501 (3)
N1—C8	1.3359 (19)	C17—C18	1.475 (4)
N2—C15	1.4116 (19)	C2—H2	0.9300
N2—C16	1.352 (2)	C3—H3	0.9300
N1—H1	0.8600	C5—H5	0.9300
N2—H2A	0.8600	C6—H6	0.9300
C1—C6	1.380 (3)	C7—H7A	0.9600
C1—C2	1.376 (2)	C7—H7B	0.9600
C2—C3	1.382 (2)	C7—H7C	0.9600
C3—C4	1.379 (3)	C11—H11	0.9300
C4—C7	1.508 (3)	C12—H12	0.9300
C4—C5	1.384 (3)	C13—H13	0.9300
C5—C6	1.376 (3)	C14—H14	0.9300
C8—C9	1.529 (2)	C17—H17A	0.9700
C9—C10	1.490 (2)	C17—H17B	0.9700
C10—C11	1.390 (2)	C18—H18A	0.9600
C10—C15	1.402 (2)	C18—H18B	0.9600
C11—C12	1.377 (2)	C18—H18C	0.9600
O1···N2	3.1213 (19)	C3···H13^{i}	3.0000
O1···C6	3.027 (2)	C6···H14^{i}	3.0100
O1···C15	3.138 (2)	C8···H6	2.9700
O1···N2^{i}	2.8821 (16)	C10···H7A^{vi}	3.0400
O2···N1	2.7678 (17)	C11···H11^{iii}	3.0500
O2···O3	3.0986 (18)	C11···H3^{vii}	2.9700
O3···C8	2.914 (2)	C12···H3^{vii}	3.0600
O3···N1^{ii}	2.9247 (18)	C15···H7A^{vi}	3.1000
O3···C10	2.930 (2)	H1···O2	2.4600
O3···C9	2.577 (2)	H1···O3^{ii}	2.1400
O3···N1	3.178 (2)	H1···H18B^{ii}	2.5200
O3···O2	3.0986 (18)	H2···O2^{ii}	2.5800
O1···H6	2.8200	H2A···H14	2.4300
O1···H14^{i}	2.8200	H2A···H17A	2.1600
O1···H17A^{i}	2.8000	H2A···O1^{i}	2.0700
O1···H2A^{i}	2.0700	H2A···N2^{i}	2.7700
O2···H12^{iii}	2.8000	H2A···H2A^{i}	2.4400
O2···H1	2.4600	H3···C11^{viii}	2.9700
O2···H11	2.6100	H3···C12^{viii}	3.0600
O2···H2^{ii}	2.5800	H3···H7C	2.3700

O2···H5^{iv}	2.8800	H5···H7A	2.5500
O2···H18B^{ii}	2.6600	H5···O2^{iv}	2.8800
O3···H18B	2.7200	H6···O1	2.8200
O3···H1^{ii}	2.1400	H6···C8	2.9700
N1···O2	2.7678 (17)	H6···H18B^{ix}	2.5000
N1···O3	3.178 (2)	H7A···C10^{x}	3.0400
N1···O3^{ii}	2.9247 (18)	H7A···C15^{x}	3.1000
N2···O1	3.1213 (19)	H7A···H5	2.5500
N2···C8	3.157 (2)	H7B···H18C^{xi}	2.5900
N2···O1^{i}	2.8821 (16)	H7C···H3	2.3700
N2···N2^{i}	3.298 (2)	H11···O2	2.6100
N2···H2A^{i}	2.7700	H11···C11^{iii}	3.0500
C3···C4^{v}	3.572 (3)	H11···H11^{iii}	2.4700
C3···C7^{v}	3.554 (3)	H12···O2^{iii}	2.8000
C4···C3^{v}	3.572 (3)	H13···C3^{i}	3.0000
C6···O1	3.027 (2)	H14···H2A	2.4300
C7···C3^{v}	3.554 (3)	H14···O1^{i}	2.8200
C8···C16	3.146 (2)	H14···C1^{i}	2.9900
C8···N2	3.157 (2)	H14···C6^{i}	3.0100
C8···O3	2.914 (2)	H17A···H2A	2.1600
C9···C16	3.120 (2)	H17A···O1^{i}	2.8000
C9···O3	2.577 (2)	H18B···O3	2.7200
C10···O3	2.930 (2)	H18B···H6^{xii}	2.5000
C15···O1	3.138 (2)	H18B···O2^{ii}	2.6600
C16···C8	3.146 (2)	H18B···H1^{ii}	2.5200
C16···C9	3.120 (2)	H18C···H7B^{xi}	2.5900
C1···H14^{i}	2.9900		
C1—N1—C8	122.33 (13)	C16—C17—C18	113.78 (19)
C15—N2—C16	126.83 (13)	C1—C2—H2	120.00
C8—N1—H1	119.00	C3—C2—H2	120.00
C1—N1—H1	119.00	C2—C3—H3	119.00
C16—N2—H2A	117.00	C4—C3—H3	119.00
C15—N2—H2A	117.00	C4—C5—H5	119.00
C2—C1—C6	119.50 (16)	C6—C5—H5	119.00
N1—C1—C6	121.04 (15)	C1—C6—H6	120.00
N1—C1—C2	119.43 (16)	C5—C6—H6	120.00
C1—C2—C3	119.74 (18)	C4—C7—H7A	109.00
C2—C3—C4	121.78 (18)	C4—C7—H7B	109.00
C3—C4—C7	120.86 (19)	C4—C7—H7C	109.00
C5—C4—C7	121.7 (2)	H7A—C7—H7B	109.00
C3—C4—C5	117.39 (17)	H7A—C7—H7C	110.00
C4—C5—C6	121.66 (19)	H7B—C7—H7C	109.00
C1—C6—C5	119.89 (17)	C10—C11—H11	119.00
O1—C8—N1	124.88 (14)	C12—C11—H11	119.00

N1—C8—C9	115.40 (13)	C11—C12—H12	120.00
O1—C8—C9	119.66 (13)	C13—C12—H12	120.00
O2—C9—C8	119.57 (13)	C12—C13—H13	120.00
O2—C9—C10	122.47 (14)	C14—C13—H13	120.00
C8—C9—C10	117.22 (12)	C13—C14—H14	120.00
C11—C10—C15	118.54 (14)	C15—C14—H14	120.00
C9—C10—C11	116.22 (14)	C16—C17—H17A	109.00
C9—C10—C15	125.18 (13)	C16—C17—H17B	109.00
C10—C11—C12	121.67 (16)	C18—C17—H17A	109.00
C11—C12—C13	119.31 (16)	C18—C17—H17B	109.00
C12—C13—C14	120.45 (17)	H17A—C17—H17B	108.00
C13—C14—C15	120.80 (16)	C17—C18—H18A	109.00
N2—C15—C10	123.90 (13)	C17—C18—H18B	109.00
N2—C15—C14	116.97 (13)	C17—C18—H18C	109.00
C10—C15—C14	119.12 (14)	H18A—C18—H18B	109.00
O3—C16—C17	122.47 (16)	H18A—C18—H18C	109.00
N2—C16—C17	115.84 (14)	H18B—C18—H18C	109.00
O3—C16—N2	121.68 (15)		
C8—N1—C1—C2	−118.93 (18)	N1—C8—C9—C10	−159.46 (15)
C8—N1—C1—C6	59.2 (2)	O1—C8—C9—O2	−147.04 (17)
C1—N1—C8—O1	−8.3 (3)	C8—C9—C10—C15	47.4 (2)
C1—N1—C8—C9	174.65 (14)	O2—C9—C10—C11	40.4 (2)
C15—N2—C16—O3	−9.2 (3)	O2—C9—C10—C15	−142.61 (18)
C16—N2—C15—C10	38.2 (3)	C8—C9—C10—C11	−129.66 (17)
C16—N2—C15—C14	−140.31 (18)	C15—C10—C11—C12	−2.8 (3)
C15—N2—C16—C17	172.10 (17)	C9—C10—C15—N2	7.8 (3)
C2—C1—C6—C5	2.1 (3)	C9—C10—C15—C14	−173.71 (16)
N1—C1—C2—C3	176.60 (15)	C9—C10—C11—C12	174.46 (17)
C6—C1—C2—C3	−1.6 (3)	C11—C10—C15—N2	−175.24 (16)
N1—C1—C6—C5	−176.03 (15)	C11—C10—C15—C14	3.3 (3)
C1—C2—C3—C4	−0.4 (3)	C10—C11—C12—C13	0.0 (3)
C2—C3—C4—C7	−177.02 (19)	C11—C12—C13—C14	2.3 (3)
C2—C3—C4—C5	1.8 (3)	C12—C13—C14—C15	−1.8 (3)
C3—C4—C5—C6	−1.2 (3)	C13—C14—C15—N2	177.53 (17)
C7—C4—C5—C6	177.57 (19)	C13—C14—C15—C10	−1.1 (3)
C4—C5—C6—C1	−0.7 (3)	O3—C16—C17—C18	47.0 (3)
O1—C8—C9—C10	23.3 (2)	N2—C16—C17—C18	−134.27 (19)
N1—C8—C9—O2	30.2 (2)		

Symmetry codes: (i) −*x*+1, −*y*+1, −*z*+1; (ii) −*x*+1, −*y*, −*z*+1; (iii) −*x*+1, −*y*, −*z*+2; (iv) −*x*+2, −*y*, −*z*+1; (v) −*x*+2, −*y*, −*z*; (vi) *x*−1, *y*, *z*+1; (vii) *x*, *y*, *z*+1; (viii) *x*, *y*, *z*−1; (ix) *x*+1, *y*, *z*; (x) *x*+1, *y*, *z*−1; (xi) −*x*+1, −*y*+1, −*z*; (xii) *x*−1, *y*, *z*.

Hydrogen-bond geometry (Å, °)

Cg1 is the centroid of C1–C6 benzene ring.

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
N1—H1···O2	0.86	2.46	2.7678 (17)	102
N1—H1···O3^{ii}	0.86	2.14	2.9247 (18)	152
N2—H2A···O1^{i}	0.86	2.07	2.8821 (16)	157

C2—H2···O2^{ii}	0.93	2.58	3.506 (2)	175
C14—H14···Cg1^{i}	0.93	2.89	3.6693 (18)	142

Symmetry codes: (ii) −*x*+1, −*y*, −*z*+1; (i) −*x*+1, −*y*+1, −*z*+1.

Fig. 1

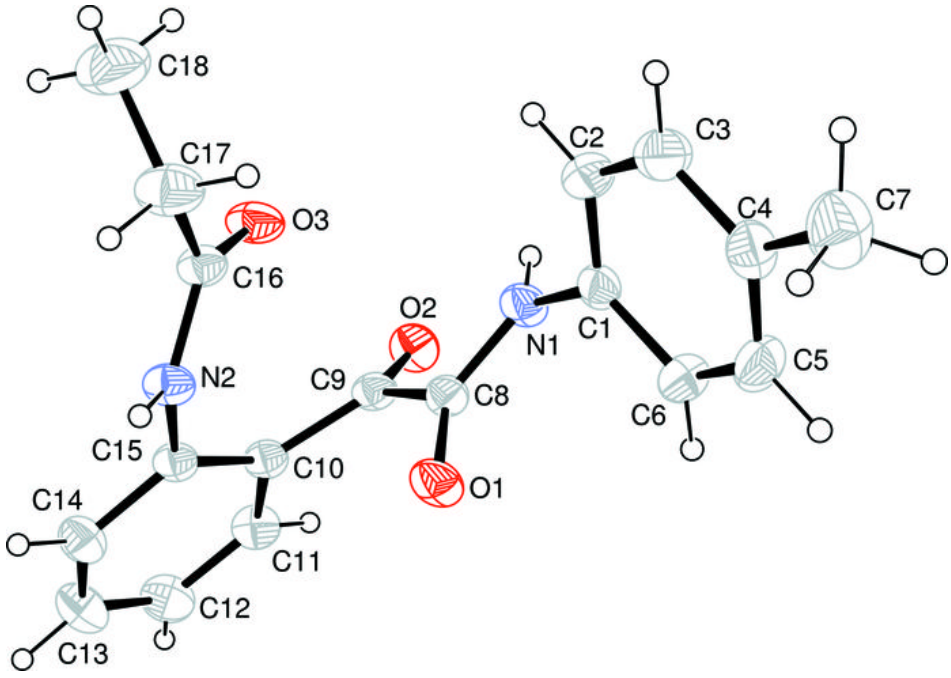
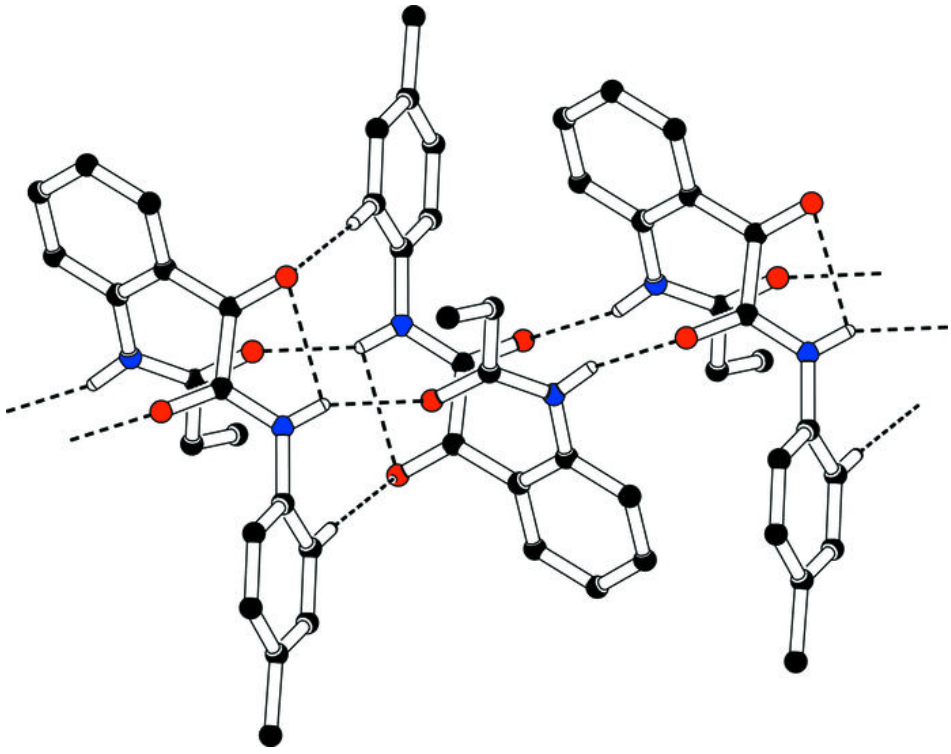

C18
C17
O3
C16
N2
C15
C14
C13
C12
C11
C10
C9
O2
C8
O1
N1
C1
C2
C3
C4
C5
C6
C7

Fig. 2



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2-Hydroxy-5-nitro-*N*-phenylbenzamide

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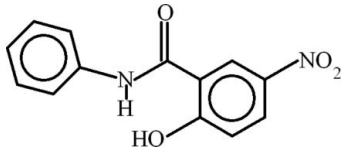
Key indicators: single-crystal X-ray study; T = 296 K; mean σ(C–C) = 0.003 Å; R factor = 0.029; wR factor = 0.071; data-to-parameter ratio = 6.0.

The molecule of the title compound, $C_{13}H_{10}N_2O_4$, is almost planar with a dihedral angle between the benzene rings of 1.99 (13)°. The nitro group and its parent benzene ring are oriented at a dihedral angle of 7.6 (3)°. Intramolecular C—H···O and N—H···O hydrogen bonds form two planar S(6) motifs. Intermolecular O—H···O=C hydrogen bonds join molecules into chains extending along the c axis.

Related literature

For similar structures, see: Raza *et al.* (2009*a*,*b*). For graph-set notation of hydrogen-bond motifs, see: Bernstein *et al.* (1995).



Experimental

Crystal data

$C_{13}H_{10}N_2O_4$
M_r = 258.23
Monoclinic, *Pc*
a = 9.9012 (2) Å
b = 4.7821 (1) Å
c = 12.3369 (4) Å
β = 97.919 (1)°
V = 578.56 (3) Å^3
Z = 2
Mo $K\alpha$ radiation
μ = 0.11 mm^{-1}
T = 296 K
0.34 × 0.12 × 0.10 mm

Data collection

Bruker Kappa APEXII CCD diffractometer
Absorption correction: multi-scan (*SADABS*; Bruker, 2009)
T_{min} = 0.979, T_{max} = 0.988
4381 measured reflections
1042 independent reflections
966 reflections with $I > 2\sigma(I)$
R_{int} = 0.022

Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.029
$wR(F^2)$ = 0.071
S = 1.06
1042 reflections
173 parameters
2 restraints
H-atom parameters constrained
$\Delta\rho_{max}$ = 0.13 e Å^{-3}
$\Delta\rho_{min}$ = −0.13 e Å^{-3}

Table 1
Hydrogen-bond geometry (Å, °).

D—H···A	D—H	H···A	D···A	D—H···A
O1—H1···O4^{i}	0.82	1.79	2.609 (2)	176
N2—H2A···O1	0.86	1.95	2.675 (2)	141
C2—H2···O4^{i}	0.93	2.54	3.212 (3)	130
C9—H9···O4	0.93	2.26	2.853 (3)	121
C11—H11···O2^{ii}	0.93	2.59	3.335 (4)	137

Symmetry codes: (i) $x, -y+2, z-\frac{1}{2}$; (ii) $x-1, y-2, z$.

Data collection: *APEX2* (Bruker, 2009); cell refinement: *SAINT* (Bruker, 2009); data reduction: *SAINT*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *ORTEP-3 for Windows* (Farrugia, 1997) and *PLATON* (Spek, 2009); software used to prepare material for publication: *WinGX* (Farrugia, 1999) and *PLATON*.

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Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: GK2288).

References

Bernstein, J., Davis, R. E., Shimoni, L. & Chang, N.-L. (1995). *Angew. Chem. Int. Ed. Engl.* **34**, 1555-1573.
Bruker (2009). *APEX2*, *SAINT* and *SADABS*. Bruker AXS Inc. Madison, Wisconsin, USA.
Farrugia, L. J. (1997). *J. Appl. Cryst.* **30**, 565.
Farrugia, L. J. (1999). *J. Appl. Cryst.* **32**, 837–838.
Raza, A. R., Danish, M., Tahir, M. N., Nisar, B. & Park, G. (2009*a*). *Acta Cryst.* E**65**, o1042.
Raza, A. R., Tahir, M. N., Nisar, B., Danish, M. & Iqbal, M. S. (2009*b*). *Acta Cryst.* E**65**, o3260.
Sheldrick, G. M. (2008). *Acta Cryst.* A**64**, 112–122.
Spek, A. L. (2009). *Acta Cryst.* D**65**, 148–155.

supplementary materials

Acta Cryst. (2010). E**66**, o1852 [**doi:10.1107/S1600536810024621**]

2-Hydroxy-5-nitro-*N*-phenylbenzamide

A. R. Raza, B. Nisar and M. N. Tahir

Comment

The title compound (I), (Fig. 1) has been synthesized as a precursor for benzoxazepines.

Previously, we have reported the crystal structures of N-phenyl-2-hydroxy-3-nitrobenzamide (Raza *et al.*, 2009a). The title compound differs from it due to the attachement of nitro group at position-5 instead of position-3. We, also have reported the crystal structure of 2-hydroxy-5-nitrobenzamide (Raza *et al.*, 2009b) which is related to (I).

In (I), the phenyl rings, A (C1–C6) of 2-hydroxy-5-nitrobenzamide and B (C8–C13) attached with 2-hydroxy-5-nitrobenzamide are planar with r. m. s. deviation of 0.0027 Å and 0.0031 Å, respectively. The O-atom of hydroxy group is at a distance of 0.014 (3) Å from the mean square plane of parent ring A. Nitro group C (O2/N1/O3) is of course planar. The dihedral angle between A/B, A/C and B/C is 1.99 (13)°, 7.63 (33)° and 6.20 (34)°, respectively. There exist a weak intramolecular H-bonding of C—H···O type forming an S(5) and a S(6) ring motif (Bernstein *et al.*, 1995), whereas H-bonding of N—H···O type complete an S(6) ring motif. The intermolecular H-bonding of C—H···O and O—H···O types complete $R_2^1(6)$ ring motif (Table 1, Fig. 2). The molecules are essentially stabilized in the form of one dimensional chains extending along the c-axis. However, weak interactions of C—H···O type form 2-dimensional polymeric sheets (Fig. 2).

Experimental

A solution of *N*-pheny-2-hydroxybenzamide (5.3 g, 0.025 mol) in ethyl acetate (EtOAc) (25 mL) was added dropwise to a nitrating mixture of HNO_3 (2.25 mL, 3.15 g , 0.05 mol) and H_2SO_4 (1.33 mL, 2.45 g, 0.025 mol) with constant stirring while the temperature was kept below 278 K. The reaction mixture was refluxed for 5 h, cooled to room temperature, neutralized with aqueous $NaHCO_3$ (10%) and extracted with EtOAc (3 × 25 mL). The organic extract was combined, dried over anhydrous Na_2SO_4, filtered and concentrated under reduced pressure to afford reddish brown solid. The column chromatographic purification with 0, 2.5, and 5 % EtOAc in n-hexane (0.5 L each) over a silica gel packed column (25.5 cm) afforded the title compound I in 5th-34th fraction of 50 mL each upon leaving at room temperature.

Refinement

In the absence of significant anomalous scattering effects, all Friedal pairs were merged. All H atoms were found in difference Fourier maps however for the refinement they were positioned geometrically with O–H = 0.82, N–H= 0.86 and C–H = 0.93 Å and refined as riding with U_{iso}(H) = 1.2U_{eq}(C, N) and U_{iso}(H) = 1.5U_{eq}(O).

Figures

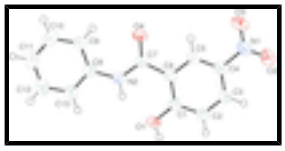


Fig. 1. View of the title compound with the atom numbering scheme. The displacement ellipsoids are drawn at the 50% probability level. H-atoms are shown by small circles of arbitrary radii.

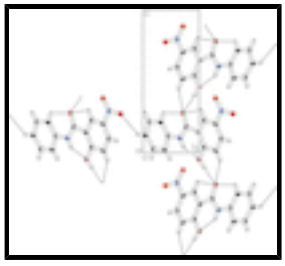


Fig. 2. The partial packing (*PLATON*; Spek, 2009) which shows that molecules form polymeric chains extending along the *c*-axis. Hydrogen bonds are shown by dashed lines.

2-Hydroxy-5-nitro-*N*-phenylbenzamide

Crystal data

$C_{13}H_{10}N_2O_4$	$F(000) = 268$
$M_r = 258.23$	$D_x = 1.482$ Mg m^{-3}
Monoclinic, *Pc*	Mo *K*α radiation, λ = 0.71073 Å
Hall symbol: P -2yc	Cell parameters from 931 reflections
$a = 9.9012$ (2) Å	θ = 2.8–26.0°
$b = 4.7821$ (1) Å	μ = 0.11 mm^{-1}
$c = 12.3369$ (4) Å	$T = 296$ K
β = 97.919 (1)°	Needle, colorless
$V = 578.56$ (3) Å^3	0.34 × 0.12 × 0.10 mm
$Z = 2$	

Data collection

Bruker Kappa APEXII CCD diffractometer	1042 independent reflections
Radiation source: fine-focus sealed tube	966 reflections with $I > 2\sigma(I)$
graphite	$R_{int} = 0.022$
Detector resolution: 8.20 pixels mm^{-1}	$\theta_{max} = 25.3°$, $\theta_{min} = 3.7°$
ω scans	$h = -11 \rightarrow 11$
Absorption correction: multi-scan (*SADABS*; Bruker, 2009)	$k = -5 \rightarrow 5$
$T_{min} = 0.979$, $T_{max} = 0.988$	$l = -14 \rightarrow 14$
4381 measured reflections	

Refinement

Refinement on F^2	Primary atom site location: structure-invariant direct methods
Least-squares matrix: full	Secondary atom site location: difference Fourier map

$R[F^2 > 2\sigma(F^2)] = 0.029$	Hydrogen site location: inferred from neighbouring sites
$wR(F^2) = 0.071$	H-atom parameters constrained
$S = 1.06$	$w = 1/[\sigma^2(F_o^2) + (0.0447P)^2 + 0.0284P]$ where $P = (F_o^2 + 2F_c^2)/3$
1042 reflections	$(\Delta/\sigma)_{max} < 0.001$
173 parameters	$\Delta\rho_{max} = 0.13$ e Å^{-3}
2 restraints	$\Delta\rho_{min} = -0.13$ e Å^{-3}

Special details

Geometry. Bond distances, angles etc. have been calculated using the rounded fractional coordinates. All su's are estimated from the variances of the (full) variance-covariance matrix. The cell esds are taken into account in the estimation of distances, angles and torsion angles

Refinement. Refinement of F^2 against ALL reflections. The weighted *R*-factor *wR* and goodness of fit *S* are based on F^2, conventional *R*-factors *R* are based on *F*, with *F* set to zero for negative F^2. The threshold expression of $F^2 > \sigma(F^2)$ is used only for calculating *R*-factors(gt) *etc*. and is not relevant to the choice of reflections for refinement. *R*-factors based on F^2 are statistically about twice as large as those based on *F*, and *R*- factors based on ALL data will be even larger.

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å^2)

	x	*y*	*z*	U_{iso}*/U_{eq}
O1	0.87642 (17)	0.9971 (4)	−0.04316 (13)	0.0503 (6)
O2	1.3304 (2)	1.6021 (5)	0.27212 (18)	0.0782 (8)
O3	1.2680 (2)	1.2889 (5)	0.38093 (16)	0.0688 (8)
O4	0.88497 (17)	0.7133 (3)	0.27868 (13)	0.0484 (5)
N1	1.25998 (19)	1.4015 (5)	0.29149 (17)	0.0502 (7)
N2	0.78477 (17)	0.6615 (4)	0.10417 (14)	0.0398 (6)
C1	0.9697 (2)	1.0963 (5)	0.03785 (17)	0.0374 (7)
C2	1.0633 (2)	1.2998 (5)	0.01674 (19)	0.0452 (8)
C3	1.1591 (2)	1.4007 (5)	0.09772 (19)	0.0440 (8)
C4	1.1606 (2)	1.2957 (5)	0.20283 (19)	0.0395 (7)
C5	1.0696 (2)	1.0964 (5)	0.22608 (17)	0.0382 (7)
C6	0.9712 (2)	0.9923 (4)	0.14475 (17)	0.0353 (7)
C7	0.8756 (2)	0.7790 (4)	0.18042 (17)	0.0356 (6)
C8	0.6844 (2)	0.4564 (4)	0.11679 (19)	0.0378 (7)
C9	0.6723 (3)	0.3201 (5)	0.2141 (2)	0.0467 (8)
C10	0.5716 (3)	0.1191 (5)	0.2159 (2)	0.0562 (9)
C11	0.4843 (3)	0.0530 (5)	0.1231 (3)	0.0565 (9)
C12	0.4959 (2)	0.1904 (5)	0.0268 (2)	0.0563 (9)
C13	0.5957 (3)	0.3893 (5)	0.0230 (2)	0.0494 (8)
H1	0.88228	1.08314	−0.09982	0.0754*
H2	1.06061	1.36856	−0.05404	0.0542*
H2A	0.78731	0.71755	0.03824	0.0477*
H3	1.22149	1.53593	0.08284	0.0528*
H5	1.07351	1.02973	0.29727	0.0459*
H9	0.73090	0.36301	0.27744	0.0561*

H10	0.56322	0.02735	0.28111	0.0674*
H11	0.41778	−0.08347	0.12537	0.0677*
H12	0.43598	0.14877	−0.03597	0.0675*
H13	0.60379	0.47916	−0.04261	0.0592*

Atomic displacement parameters (Å^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
O1	0.0561 (9)	0.0674 (11)	0.0251 (9)	−0.0152 (8)	−0.0027 (7)	0.0045 (8)
O2	0.0822 (13)	0.0874 (15)	0.0612 (13)	−0.0397 (13)	−0.0041 (10)	−0.0068 (11)
O3	0.0754 (13)	0.0863 (14)	0.0391 (12)	−0.0147 (11)	−0.0117 (9)	0.0010 (10)
O4	0.0645 (10)	0.0525 (9)	0.0267 (9)	−0.0075 (8)	0.0014 (7)	0.0006 (7)
N1	0.0480 (11)	0.0581 (13)	0.0424 (13)	−0.0011 (10)	−0.0009 (9)	−0.0086 (10)
N2	0.0470 (11)	0.0462 (11)	0.0258 (10)	−0.0058 (8)	0.0041 (8)	0.0007 (8)
C1	0.0381 (11)	0.0458 (12)	0.0275 (12)	0.0011 (10)	0.0016 (8)	−0.0024 (9)
C2	0.0503 (14)	0.0554 (14)	0.0301 (13)	−0.0010 (11)	0.0060 (10)	0.0036 (10)
C3	0.0416 (12)	0.0488 (14)	0.0419 (14)	−0.0062 (10)	0.0067 (10)	−0.0030 (11)
C4	0.0372 (11)	0.0447 (12)	0.0356 (13)	0.0026 (10)	0.0014 (9)	−0.0067 (10)
C5	0.0429 (12)	0.0432 (12)	0.0279 (12)	0.0038 (10)	0.0026 (9)	−0.0006 (9)
C6	0.0386 (11)	0.0378 (12)	0.0288 (12)	0.0050 (9)	0.0026 (8)	−0.0015 (8)
C7	0.0427 (11)	0.0380 (11)	0.0258 (11)	0.0029 (10)	0.0032 (8)	−0.0015 (9)
C8	0.0392 (11)	0.0380 (12)	0.0364 (12)	0.0033 (9)	0.0063 (9)	−0.0007 (9)
C9	0.0515 (13)	0.0488 (14)	0.0396 (14)	−0.0017 (11)	0.0056 (10)	0.0038 (11)
C10	0.0593 (15)	0.0536 (15)	0.0581 (18)	−0.0024 (12)	0.0169 (13)	0.0125 (12)
C11	0.0476 (13)	0.0478 (14)	0.075 (2)	−0.0085 (11)	0.0117 (13)	0.0008 (13)
C12	0.0479 (14)	0.0542 (15)	0.0637 (18)	−0.0065 (12)	−0.0030 (12)	−0.0065 (13)
C13	0.0534 (14)	0.0517 (15)	0.0412 (14)	−0.0063 (12)	0.0002 (11)	0.0012 (11)

Geometric parameters (Å, °)

O1—C1	1.350 (3)	C6—C7	1.498 (3)
O2—N1	1.229 (3)	C8—C13	1.390 (3)
O3—N1	1.221 (3)	C8—C9	1.386 (3)
O4—C7	1.243 (3)	C9—C10	1.387 (4)
O1—H1	0.8200	C10—C11	1.373 (4)
N1—C4	1.457 (3)	C11—C12	1.376 (4)
N2—C8	1.420 (3)	C12—C13	1.377 (3)
N2—C7	1.333 (3)	C2—H2	0.9300
N2—H2A	0.8600	C3—H3	0.9300
C1—C6	1.408 (3)	C5—H5	0.9300
C1—C2	1.393 (3)	C9—H9	0.9300
C2—C3	1.367 (3)	C10—H10	0.9300
C3—C4	1.389 (3)	C11—H11	0.9300
C4—C5	1.369 (3)	C12—H12	0.9300
C5—C6	1.391 (3)	C13—H13	0.9300
O1···N2	2.675 (2)	C8···C11^{viii}	3.480 (3)
O1···O4^{i}	2.609 (2)	C8···C6^{vii}	3.583 (3)
O2···C11^{ii}	3.335 (4)	C8···C1^{vii}	3.557 (3)

O3···C3^{iii}	3.364 (3)	C9···C7^{vii}	3.339 (3)
O4···C2^{iv}	3.212 (3)	C9···O4	2.853 (3)
O4···C9	2.853 (3)	C9···C6^{vii}	3.556 (3)
O4···O1^{iv}	2.609 (2)	C10···C7^{vii}	3.501 (3)
O4···C1^{iv}	3.319 (3)	C11···C8^{vii}	3.480 (3)
O1···H2A	1.9500	C11···C3^{xi}	3.599 (4)
O2···H3	2.4500	C11···O2^{xii}	3.335 (4)
O2···H12^{v}	2.7300	C1···H2A	2.5600
O2···H11^{ii}	2.5900	C7···H9	2.8100
O3···H5	2.4000	C7···H1^{iv}	2.7800
O3···H12^{vi}	2.7800	H1···H2	2.2400
O3···H2^{iii}	2.8300	H1···O4^{i}	1.7900
O3···H3^{iii}	2.7300	H1···C7^{i}	2.7800
O4···H5	2.3900	H1···H5^{i}	2.4800
O4···H9	2.2600	H2···H1	2.2400
O4···H1^{iv}	1.7900	H2···O3^{x}	2.8300
O4···H2^{iv}	2.5400	H2···O4^{i}	2.5400
N2···O1	2.675 (2)	H2A···O1	1.9500
N2···C1^{vii}	3.426 (3)	H2A···C1	2.5600
C1···N2^{viii}	3.426 (3)	H2A···H13	2.2600
C1···C8^{viii}	3.557 (3)	H3···O2	2.4500
C1···O4^{i}	3.319 (3)	H3···O3^{x}	2.7300
C2···O4^{i}	3.212 (3)	H5···O3	2.4000
C3···C6^{viii}	3.478 (3)	H5···O4	2.3900
C3···C11^{ix}	3.599 (4)	H5···H1^{iv}	2.4800
C3···O3^{x}	3.364 (3)	H9···O4	2.2600
C6···C8^{viii}	3.583 (3)	H9···C7	2.8100
C6···C3^{vii}	3.478 (3)	H11···O2^{xii}	2.5900
C6···C9^{viii}	3.556 (3)	H12···O2^{xiii}	2.7300
C7···C10^{viii}	3.501 (3)	H12···O3^{xiv}	2.7800
C7···C9^{viii}	3.339 (3)	H13···H2A	2.2600
C1—O1—H1	109.00	N2—C8—C13	116.1 (2)
O2—N1—O3	123.5 (2)	C9—C8—C13	119.5 (2)
O2—N1—C4	117.9 (2)	C8—C9—C10	119.2 (2)
O3—N1—C4	118.6 (2)	C9—C10—C11	121.2 (2)
C7—N2—C8	128.92 (18)	C10—C11—C12	119.5 (2)
C8—N2—H2A	116.00	C11—C12—C13	120.3 (2)
C7—N2—H2A	116.00	C8—C13—C12	120.3 (2)
O1—C1—C2	120.8 (2)	C1—C2—H2	119.00
O1—C1—C6	119.16 (19)	C3—C2—H2	119.00
C2—C1—C6	120.04 (19)	C2—C3—H3	121.00
C1—C2—C3	121.5 (2)	C4—C3—H3	121.00
C2—C3—C4	118.2 (2)	C4—C5—H5	120.00

N1—C4—C3	119.6 (2)	C6—C5—H5	119.00
N1—C4—C5	118.7 (2)	C8—C9—H9	120.00
C3—C4—C5	121.7 (2)	C10—C9—H9	120.00
C4—C5—C6	120.9 (2)	C9—C10—H10	119.00
C5—C6—C7	116.10 (18)	C11—C10—H10	119.00
C1—C6—C7	126.17 (19)	C10—C11—H11	120.00
C1—C6—C5	117.73 (19)	C12—C11—H11	120.00
O4—C7—N2	122.28 (19)	C11—C12—H12	120.00
O4—C7—C6	119.55 (18)	C13—C12—H12	120.00
N2—C7—C6	118.16 (18)	C8—C13—H13	120.00
N2—C8—C9	124.4 (2)	C12—C13—H13	120.00
O3—N1—C4—C3	−173.4 (2)	N1—C4—C5—C6	178.9 (2)
O2—N1—C4—C5	−171.8 (2)	C3—C4—C5—C6	−0.4 (3)
O2—N1—C4—C3	7.4 (3)	C4—C5—C6—C1	0.8 (3)
O3—N1—C4—C5	7.4 (3)	C4—C5—C6—C7	−178.9 (2)
C8—N2—C7—C6	179.93 (17)	C1—C6—C7—N2	4.2 (3)
C7—N2—C8—C9	−6.5 (3)	C5—C6—C7—O4	2.4 (3)
C8—N2—C7—O4	1.4 (3)	C5—C6—C7—N2	−176.16 (19)
C7—N2—C8—C13	174.8 (2)	C1—C6—C7—O4	−177.2 (2)
C6—C1—C2—C3	0.8 (3)	N2—C8—C9—C10	−178.7 (2)
O1—C1—C6—C5	179.3 (2)	C13—C8—C9—C10	0.0 (4)
O1—C1—C2—C3	−179.5 (2)	N2—C8—C13—C12	179.3 (2)
C2—C1—C6—C5	−1.0 (3)	C9—C8—C13—C12	0.5 (4)
C2—C1—C6—C7	178.6 (2)	C8—C9—C10—C11	0.1 (4)
O1—C1—C6—C7	−1.2 (3)	C9—C10—C11—C12	−0.7 (4)
C1—C2—C3—C4	−0.3 (3)	C10—C11—C12—C13	1.1 (4)
C2—C3—C4—C5	0.1 (3)	C11—C12—C13—C8	−1.0 (4)
C2—C3—C4—N1	−179.1 (2)		

Symmetry codes: (i) *x*, −*y*+2, *z*−1/2; (ii) *x*+1, *y*+2, *z*; (iii) *x*, −*y*+3, *z*+1/2; (iv) *x*, −*y*+2, *z*+1/2; (v) *x*+1, −*y*+2, *z*+1/2; (vi) *x*+1, −*y*+1, *z*+1/2; (vii) *x*, *y*−1, *z*; (viii) *x*, *y*+1, *z*; (ix) *x*+1, *y*+1, *z*; (x) *x*, −*y*+3, *z*−1/2; (xi) *x*−1, *y*−1, *z*; (xii) *x*−1, *y*−2, *z*; (xiii) *x*−1, −*y*+2, *z*−1/2; (xiv) *x*−1, −*y*+1, *z*−1/2.

Hydrogen-bond geometry (Å, °)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
O1—H1···O4^{i}	0.82	1.79	2.609 (2)	176
N2—H2A···O1	0.86	1.95	2.675 (2)	141
C2—H2···O4^{i}	0.93	2.54	3.212 (3)	130
C5—H5···O4	0.93	2.39	2.729 (3)	101
C9—H9···O4	0.93	2.26	2.853 (3)	121
C11—H11···O2^{xii}	0.93	2.59	3.335 (4)	137

Symmetry codes: (i) *x*, −*y*+2, *z*−1/2; (xii) *x*−1, *y*−2, *z*.

Fig. 1

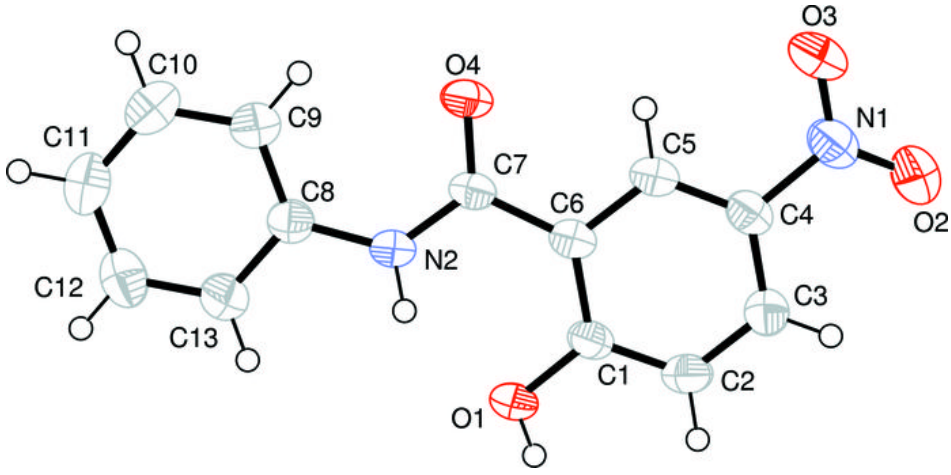
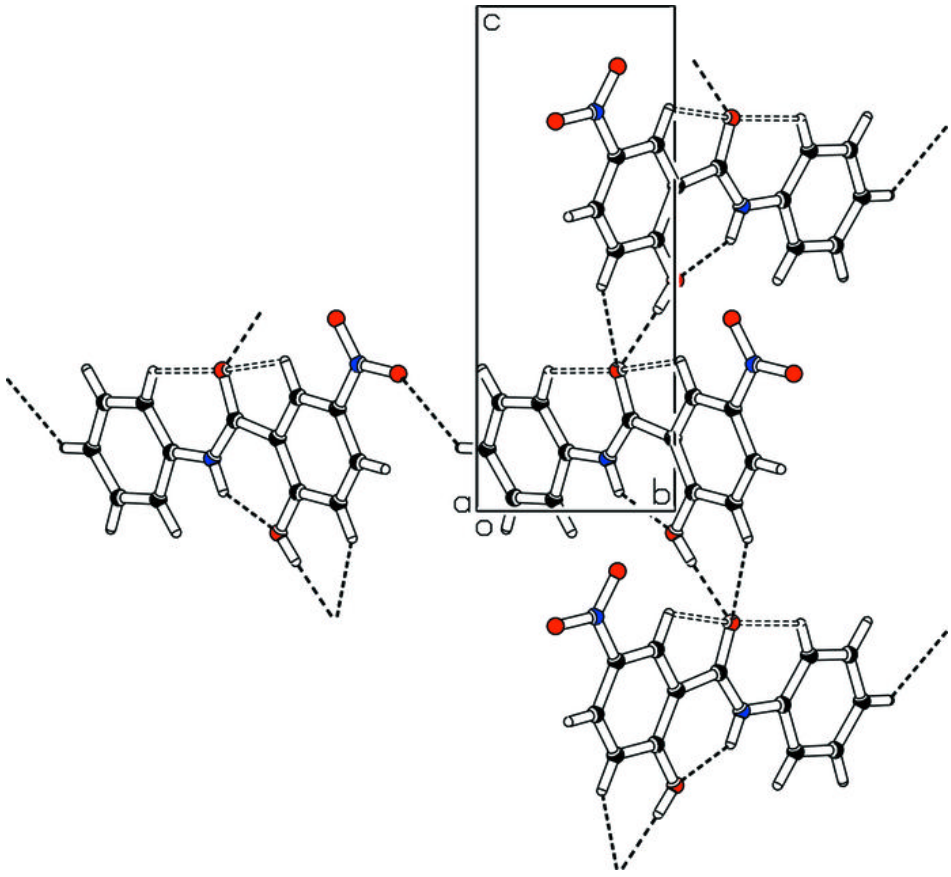


Fig. 2



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Ethyl 3,4-dimethyl-5-[(*E*)-(phenylimino)-methyl]-1*H*-pyrrole-2-carboxylate

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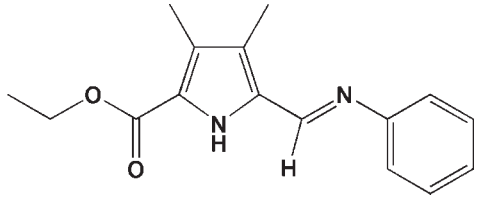
Key indicators: single-crystal X-ray study; T = 296 K; mean σ(C–C) = 0.003 Å; R factor = 0.044; wR factor = 0.144; data-to-parameter ratio = 18.5.

In the title compound, $C_{16}H_{18}N_2O_2$, the molecule adopts an E conformation about the C=N double bond. The dihedral angle between the pyrrole and phenyl rings is 41.55 (8)°. In the crystal structure, pairs of intermolecular N—H···O hydrogen bonds link the molecules into centrosymmetric dimers. In the dimer, the two pyrrole rings are almost coplanar and the two phenyl rings are parallel to each other.

Related literature

For the structure of 5-formyl-3,4-dimethyl-1*H*-pyrrole-2-carboxylate, see Wu *et al.* (2009). For the similar structure of ethyl 5-[(2,3-dimethyl-5-oxo-1-phenyl-2,5-dihydro-1*H*-pyrazol-4-yl)iminomethyl]-3,4-dimethyl-1*H*-pyrrole-2-carboxylate, see Wang *et al.* (2009). For the coordination abilities for metal ions of pyrrol-2-ylmethyleneamine ligands, see: Wang *et al.* (2010); Yang *et al.* (2003).



Experimental

Crystal data

$C_{16}H_{18}N_2O_2$
M_r = 270.32
Monoclinic, $P2_1/c$
a = 12.5463 (7) Å
b = 14.6525 (9) Å
c = 8.4490 (5) Å
β = 105.042 (3)°
V = 1500.00 (15) Å^3
Z = 4
Mo $K\alpha$ radiation
μ = 0.08 mm^{-1}
T = 296 K
0.35 × 0.26 × 0.18 mm

Data collection

Bruker SMART CCD diffractometer
Absorption correction: multi-scan (*SADABS*; Sheldrick, 1996)
T_{min} = 0.975, T_{max} = 0.986
12405 measured reflections
3413 independent reflections
2078 reflections with $I > 2\sigma(I)$
R_{int} = 0.030

Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.044
$wR(F^2)$ = 0.144
S = 1.01
3413 reflections
184 parameters
H-atom parameters constrained
$\Delta\rho_{max}$ = 0.20 e Å^{-3}
$\Delta\rho_{min}$ = −0.16 e Å^{-3}

Table 1
Hydrogen-bond geometry (Å, °).

D—H···A	D—H	H···A	D···A	D—H···A
N2—H2A···O3^{i}	0.86	2.06	2.8883 (18)	162

Symmetry code: (i) $-x, -y, -z$.

Data collection: *SMART* (Bruker, 1997); cell refinement: *SAINT* (Bruker, 1997); data reduction: *SAINT*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *SHELXTL* (Sheldrick, 2008); software used to prepare material for publication: *SHELXTL*.

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Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: GW2080).

References

Bruker (1997). *SMART*, *SAINT* and *SADABS*. Bruker AXS Inc., Madison, Wisconsin, USA.
Sheldrick, G. M. (1996). *SADABS*. University of Göttingen, Germany.
Sheldrick, G. M. (2008). *Acta Cryst.* A**64**, 112–122.
Wang, Y., Wu, W.-N. & Wang, Q.-F. (2009). *Acta Cryst.* E**65**, o1933.
Wang, Y., Wu, W.-N., Wang, Q. & Yang, Z.-Y. (2010). *J. Coord. Chem.* **63**, 147–155.
Wu, W.-N., Wang, Y. & Wang, Q.-F. (2009). *Acta Cryst.* E**65**, o1661.
Yang, L. Y., Chen, Q. Q., Yang, G. Q. & Ma, J. S. (2003). *Tetrahedron*, **59**, 10037–10041.

supplementary materials

Acta Cryst. (2010). E**66**, o1655 [**doi:10.1107/S1600536810022051**]

Ethyl 3,4-dimethyl-5-[(*E*)-(phenylimino)methyl]-1*H*-pyrrole-2-carboxylate

W.-N. Wu, L. Yang, X.-X. Li, B.-F. Qin and Q.-F. Wang

Comment

Pyrrol-2-ylmethyleneamine ligands have attracted much recent attention due to their excellent coordination abilities for metal ions (Yang *et al.*, 2006 & Wang *et al.*, 2010). As part of our ongoing search for a biologically active material, the title compound was synthesized and characterized by X-ray diffraction.

In the title compound, all the bond lengths are comparable with those observed in the other similar compound (Wang *et al.*, 2009). The molecule adopts an E configuration at the C=N double bond. The dihedral angle between pyrrole ring (N2/C8–C11, r.m.s. deviation 0.0035 Å) and phenyl ring (C1–C6, r.m.s. deviation 0.0036 Å) is 41.55 (8)°. In the crystal, the molecules are linked into a centrosymmetric dimer by two intermolecular N—H···O hydrogen bonds, forming a $R_2^2(10)$ ring motif (Table1, Fig. 2). In the dimer, the two pyrrole rings are almost coplanar (r.m.s. deviation 0.028 Å) and the two phenyl rings are parallel with each other. The crystal packing is further stabilized by the stacking between the C=N with the adjacent pyrrole ring, with centroid–centroid distances of 3.642 Å.

Experimental

A quantity of aniline (0.186 g, 2 mmol) was dissolved in ethanol (10 ml), then an ethanol solution (10 ml) containing ethyl 5-formyl-3,4-dimethyl-1*H*-pyrrole-2-carboxylate (0.39 g, 2 mmol) was added dropwise at room temperature. After stirring for 4 h, the mixture was filtered and set aside to crystallize at room temperature for several days, giving yellow block crystals.

Refinement

All H atoms were placed in calculated positions, with C—H = 0.93–0.97 Å and N—H = 0.86 Å, and were thereafter treated as riding, with U_{iso}(H) values of 1.5Ueq(C) for methyl groups and 1.2Ueq(C,*N*) for others.

Figures

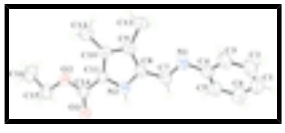


Fig. 1. The molecular structure shown with 50% probability displacement ellipsoids.

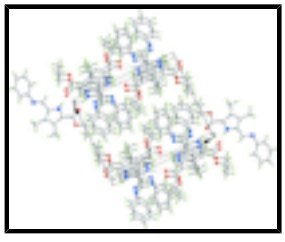


Fig. 2. Crystal packing of the title compound showing the dimers formed by hydrogen bonds (dashed lines).

Ethyl 3,4-dimethyl-5-[(*E*)-(phenylimino)methyl]-1*H*-pyrrole-2-carboxylate

Crystal data

$C_{16}H_{18}N_2O_2$	$F(000) = 576$
$M_r = 270.32$	$D_x = 1.197$ Mg m^{-3}
Monoclinic, $P2_1/c$	Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å
Hall symbol: -P 2ybc	Cell parameters from 5515 reflections
$a = 12.5463$ (7) Å	$\theta = 2.2$–$26.2°$
$b = 14.6525$ (9) Å	$\mu = 0.08$ mm^{-1}
$c = 8.4490$ (5) Å	$T = 296$ K
$\beta = 105.042$ (3)°	Block, yellow
$V = 1500.00$ (15) Å^3	0.35 × 0.26 × 0.18 mm
$Z = 4$	

Data collection

Bruker SMART CCD diffractometer	3413 independent reflections
Radiation source: fine-focus sealed tube	2078 reflections with $I > 2\sigma(I)$
graphite	$R_{int} = 0.030$
phi and ω scans	$\theta_{max} = 27.6°$, $\theta_{min} = 1.7°$
Absorption correction: multi-scan (*SADABS*; Sheldrick, 1996)	$h = -14 \rightarrow 16$
$T_{min} = 0.975$, $T_{max} = 0.986$	$k = -14 \rightarrow 19$
12405 measured reflections	$l = -10 \rightarrow 8$

Refinement

Refinement on F^2	Primary atom site location: structure-invariant direct methods
Least-squares matrix: full	Secondary atom site location: difference Fourier map
$R[F^2 > 2\sigma(F^2)] = 0.044$	Hydrogen site location: inferred from neighbouring sites
$wR(F^2) = 0.144$	H-atom parameters constrained
$S = 1.01$	$w = 1/[\sigma^2(F_o^2) + (0.0645P)^2 + 0.3198P]$ where $P = (F_o^2 + 2F_c^2)/3$
3413 reflections	$(\Delta/\sigma)_{max} = 0.007$
184 parameters	$\Delta\rho_{max} = 0.20$ e Å^{-3}
0 restraints	$\Delta\rho_{min} = -0.16$ e Å^{-3}

Special details

Geometry. All e.s.d.'s (except the e.s.d. in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell e.s.d.'s are taken into account individually in the estimation of e.s.d.'s in distances, angles and torsion angles; correlations

between e.s.d.'s in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell e.s.d.'s is used for estimating e.s.d.'s involving l.s. planes.

Refinement. Refinement of F^2 against ALL reflections. The weighted *R*-factor *wR* and goodness of fit *S* are based on F^2, conventional *R*-factors *R* are based on *F*, with *F* set to zero for negative F^2. The threshold expression of $F^2 > \sigma(F^2)$ is used only for calculating *R*-factors(gt) *etc*. and is not relevant to the choice of reflections for refinement. *R*-factors based on F^2 are statistically about twice as large as those based on *F*, and *R*- factors based on ALL data will be even larger.

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å^2)

	x	*y*	*z*	U_{iso}*/U_{eq}
N2	0.02009 (11)	0.14614 (9)	0.03549 (16)	0.0474 (3)
H2A	−0.0130	0.0983	−0.0125	0.057*
O2	0.24807 (9)	0.06709 (8)	0.35169 (14)	0.0576 (3)
O3	0.12317 (10)	−0.01491 (9)	0.17093 (15)	0.0612 (4)
C14	0.15990 (13)	0.05888 (12)	0.22476 (19)	0.0462 (4)
C11	0.11351 (13)	0.14570 (11)	0.16129 (19)	0.0444 (4)
N1	−0.15004 (12)	0.33049 (10)	−0.16873 (18)	0.0545 (4)
C8	−0.01284 (13)	0.23366 (11)	−0.0027 (2)	0.0466 (4)
C10	0.14228 (13)	0.23604 (11)	0.20337 (19)	0.0458 (4)
C4	−0.25266 (15)	0.33933 (12)	−0.2860 (2)	0.0543 (5)
C7	−0.11212 (14)	0.25067 (12)	−0.1305 (2)	0.0514 (4)
H7	−0.1500	0.2012	−0.1874	0.062*
C9	0.06264 (13)	0.29161 (11)	0.1002 (2)	0.0465 (4)
C12	0.05849 (16)	0.39340 (12)	0.1001 (2)	0.0619 (5)
H12A	0.0308	0.4150	−0.0102	0.093*
H12B	0.1313	0.4172	0.1452	0.093*
H12C	0.0106	0.4135	0.1652	0.093*
C3	−0.26627 (17)	0.41010 (14)	−0.3976 (2)	0.0634 (5)
H3	−0.2072	0.4482	−0.3985	0.076*
C13	0.24063 (14)	0.26959 (13)	0.3311 (2)	0.0606 (5)
H13A	0.2367	0.3347	0.3399	0.091*
H13B	0.3067	0.2533	0.3006	0.091*
H13C	0.2416	0.2422	0.4347	0.091*
C2	−0.3674 (2)	0.42436 (17)	−0.5076 (3)	0.0782 (7)
H2	−0.3756	0.4714	−0.5838	0.094*
C15	0.29547 (16)	−0.01538 (14)	0.4354 (2)	0.0635 (5)
H15A	0.3295	−0.0515	0.3656	0.076*
H15B	0.2388	−0.0519	0.4644	0.076*
C16	0.37962 (17)	0.01386 (17)	0.5854 (3)	0.0793 (6)
H16A	0.4327	0.0528	0.5553	0.119*
H16B	0.4163	−0.0389	0.6416	0.119*
H16C	0.3442	0.0465	0.6562	0.119*
C5	−0.34233 (16)	0.28429 (15)	−0.2859 (3)	0.0727 (6)
H5	−0.3348	0.2364	−0.2116	0.087*
C1	−0.4555 (2)	0.37029 (19)	−0.5058 (3)	0.0869 (7)
H1	−0.5238	0.3809	−0.5789	0.104*
C6	−0.44248 (18)	0.30041 (18)	−0.3958 (3)	0.0893 (7)
H6	−0.5023	0.2631	−0.3950	0.107*

Atomic displacement parameters (Å^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
N2	0.0494 (8)	0.0418 (8)	0.0461 (8)	0.0011 (6)	0.0038 (6)	−0.0006 (6)
O2	0.0557 (7)	0.0545 (8)	0.0523 (7)	0.0022 (6)	−0.0044 (6)	0.0051 (6)
O3	0.0666 (8)	0.0467 (8)	0.0594 (8)	0.0035 (6)	−0.0030 (6)	−0.0027 (6)
C14	0.0456 (9)	0.0511 (11)	0.0405 (9)	0.0002 (8)	0.0086 (7)	−0.0011 (7)
C11	0.0459 (9)	0.0457 (9)	0.0396 (9)	−0.0005 (7)	0.0075 (7)	0.0011 (7)
N1	0.0567 (9)	0.0494 (9)	0.0542 (9)	0.0074 (7)	0.0083 (7)	0.0051 (7)
C8	0.0506 (9)	0.0433 (9)	0.0460 (9)	0.0041 (7)	0.0128 (7)	0.0036 (7)
C10	0.0492 (9)	0.0479 (10)	0.0420 (9)	−0.0043 (7)	0.0149 (7)	−0.0020 (7)
C4	0.0579 (10)	0.0494 (10)	0.0528 (11)	0.0119 (8)	0.0092 (8)	0.0005 (8)
C7	0.0540 (10)	0.0481 (10)	0.0496 (10)	0.0036 (8)	0.0089 (8)	0.0022 (8)
C9	0.0512 (9)	0.0446 (9)	0.0465 (9)	−0.0008 (7)	0.0176 (8)	0.0013 (7)
C12	0.0680 (12)	0.0455 (10)	0.0714 (13)	−0.0028 (9)	0.0164 (10)	−0.0009 (9)
C3	0.0763 (13)	0.0590 (12)	0.0550 (11)	0.0166 (10)	0.0170 (10)	0.0081 (9)
C13	0.0593 (11)	0.0601 (12)	0.0583 (12)	−0.0110 (9)	0.0079 (9)	−0.0053 (9)
C2	0.0990 (17)	0.0783 (15)	0.0530 (12)	0.0344 (14)	0.0118 (12)	0.0095 (11)
C15	0.0636 (11)	0.0639 (12)	0.0568 (11)	0.0111 (9)	0.0046 (9)	0.0116 (9)
C16	0.0634 (12)	0.1025 (18)	0.0616 (13)	0.0050 (12)	−0.0025 (10)	0.0135 (12)
C5	0.0632 (12)	0.0629 (13)	0.0847 (15)	0.0045 (10)	0.0058 (11)	0.0142 (10)
C1	0.0742 (15)	0.0951 (19)	0.0755 (16)	0.0244 (14)	−0.0093 (12)	−0.0066 (13)
C6	0.0633 (13)	0.0848 (17)	0.106 (2)	0.0012 (12)	−0.0026 (13)	−0.0002 (15)

Geometric parameters (Å, °)

N2—C8	1.360 (2)	C12—H12C	0.9600
N2—C11	1.363 (2)	C3—C2	1.381 (3)
N2—H2A	0.8600	C3—H3	0.9300
O2—C14	1.3313 (18)	C13—H13A	0.9600
O2—C15	1.448 (2)	C13—H13B	0.9600
O3—C14	1.216 (2)	C13—H13C	0.9600
C14—C11	1.443 (2)	C2—C1	1.363 (3)
C11—C10	1.394 (2)	C2—H2	0.9300
N1—C7	1.272 (2)	C15—C16	1.487 (3)
N1—C4	1.412 (2)	C15—H15A	0.9700
C8—C9	1.395 (2)	C15—H15B	0.9700
C8—C7	1.443 (2)	C16—H16A	0.9600
C10—C9	1.403 (2)	C16—H16B	0.9600
C10—C13	1.496 (2)	C16—H16C	0.9600
C4—C3	1.382 (2)	C5—C6	1.375 (3)
C4—C5	1.384 (3)	C5—H5	0.9300
C7—H7	0.9300	C1—C6	1.364 (3)
C9—C12	1.492 (2)	C1—H1	0.9300
C12—H12A	0.9600	C6—H6	0.9300
C12—H12B	0.9600		
C8—N2—C11	109.65 (13)	C4—C3—H3	119.9

C8—N2—H2A	125.2	C2—C3—H3	119.9
C11—N2—H2A	125.2	C10—C13—H13A	109.5
C14—O2—C15	117.92 (14)	C10—C13—H13B	109.5
O3—C14—O2	122.44 (15)	H13A—C13—H13B	109.5
O3—C14—C11	124.58 (15)	C10—C13—H13C	109.5
O2—C14—C11	112.98 (14)	H13A—C13—H13C	109.5
N2—C11—C10	107.94 (14)	H13B—C13—H13C	109.5
N2—C11—C14	118.44 (14)	C1—C2—C3	120.7 (2)
C10—C11—C14	133.60 (15)	C1—C2—H2	119.6
C7—N1—C4	118.36 (15)	C3—C2—H2	119.6
N2—C8—C9	108.10 (14)	O2—C15—C16	106.66 (17)
N2—C8—C7	119.37 (15)	O2—C15—H15A	110.4
C9—C8—C7	132.53 (16)	C16—C15—H15A	110.4
C11—C10—C9	107.29 (14)	O2—C15—H15B	110.4
C11—C10—C13	127.36 (15)	C16—C15—H15B	110.4
C9—C10—C13	125.34 (16)	H15A—C15—H15B	108.6
C3—C4—C5	118.75 (18)	C15—C16—H16A	109.5
C3—C4—N1	118.45 (17)	C15—C16—H16B	109.5
C5—C4—N1	122.62 (17)	H16A—C16—H16B	109.5
N1—C7—C8	122.82 (16)	C15—C16—H16C	109.5
N1—C7—H7	118.6	H16A—C16—H16C	109.5
C8—C7—H7	118.6	H16B—C16—H16C	109.5
C8—C9—C10	107.02 (14)	C6—C5—C4	120.0 (2)
C8—C9—C12	126.15 (15)	C6—C5—H5	120.0
C10—C9—C12	126.84 (15)	C4—C5—H5	120.0
C9—C12—H12A	109.5	C2—C1—C6	119.4 (2)
C9—C12—H12B	109.5	C2—C1—H1	120.3
H12A—C12—H12B	109.5	C6—C1—H1	120.3
C9—C12—H12C	109.5	C1—C6—C5	121.0 (2)
H12A—C12—H12C	109.5	C1—C6—H6	119.5
H12B—C12—H12C	109.5	C5—C6—H6	119.5
C4—C3—C2	120.1 (2)		

C15—O2—C14—O3	−5.1 (2)	C9—C8—C7—N1	−1.8 (3)
C15—O2—C14—C11	174.30 (15)	N2—C8—C9—C10	−0.44 (18)
C8—N2—C11—C10	−0.93 (18)	C7—C8—C9—C10	178.79 (17)
C8—N2—C11—C14	177.75 (15)	N2—C8—C9—C12	179.75 (15)
O3—C14—C11—N2	2.1 (3)	C7—C8—C9—C12	−1.0 (3)
O2—C14—C11—N2	−177.28 (13)	C11—C10—C9—C8	−0.12 (18)
O3—C14—C11—C10	−179.64 (17)	C13—C10—C9—C8	178.52 (15)
O2—C14—C11—C10	1.0 (3)	C11—C10—C9—C12	179.69 (16)
C11—N2—C8—C9	0.85 (18)	C13—C10—C9—C12	−1.7 (3)
C11—N2—C8—C7	−178.50 (14)	C5—C4—C3—C2	−0.8 (3)
N2—C11—C10—C9	0.63 (18)	N1—C4—C3—C2	−176.03 (17)
C14—C11—C10—C9	−177.76 (18)	C4—C3—C2—C1	1.3 (3)
N2—C11—C10—C13	−177.97 (15)	C14—O2—C15—C16	−171.10 (15)
C14—C11—C10—C13	3.6 (3)	C3—C4—C5—C6	0.2 (3)
C7—N1—C4—C3	−141.86 (17)	N1—C4—C5—C6	175.21 (19)
C7—N1—C4—C5	43.1 (3)	C3—C2—C1—C6	−1.2 (3)
C4—N1—C7—C8	−174.75 (16)	C2—C1—C6—C5	0.6 (4)

N2—C8—C7—N1	177.38 (16)	C4—C5—C6—C1	−0.1 (4)

Hydrogen-bond geometry (Å, °)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
N2—H2A···O3^{i}	0.86	2.06	2.8883 (18)	162.

Symmetry codes: (i) −*x*, −*y*, −*z*.

Fig. 1

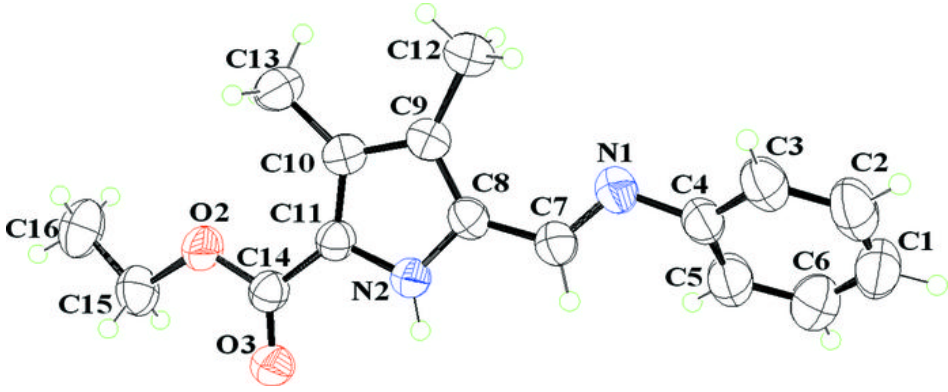
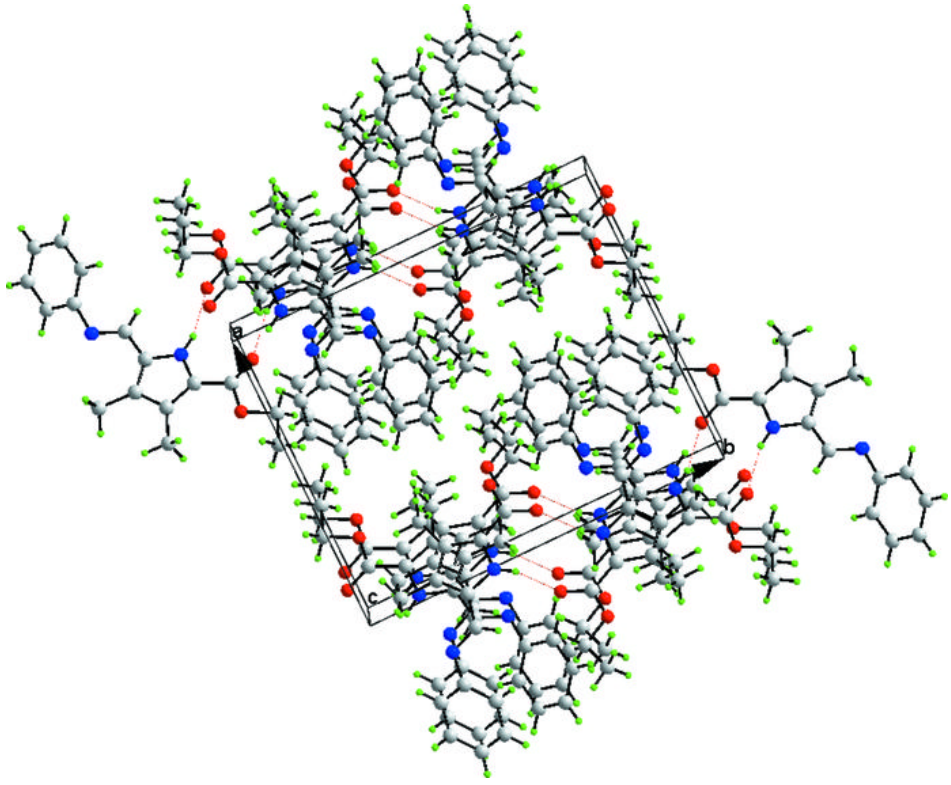


Fig. 2



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Phenyl 2,3,4-tri-*O*-benzyl-1-thio-α-D-mannopyranoside monohydrate

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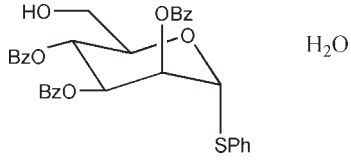
Key indicators: single-crystal X-ray study; T = 150 K; mean σ(C–C) = 0.003 Å; disorder in main residue; R factor = 0.030; wR factor = 0.062; data-to-parameter ratio = 13.0.

In the title compound, $C_{33}H_{34}O_5S\cdot H_2O$, the mannopyranoside ring adopts a chair conformation with the 2-α-thiophenyl group occupying an axial position. One of the pendant benzyl groups is disordered over two sets of sites in a 0.5:0.5 ratio. In the crystal, the water molecule makes two O—H···O hydrogen bonds to an adjacent sugar molecule with the O atoms of the primary alcohol and ether groups acting as acceptors. At the same time, the OH group of the sugar makes a hydrogen bond to a water molecule.

Related literature

For background to the synthesis and properties of mannopyranosides, see: Boons (1991); Szurmai *et al.* (1994); Caravano *et al.* (2003); Grizot *et al.* (2006); Dohi *et al.* (2008). For ring conformation analysis, see: Cremer & Pople (1975).



Experimental

Crystal data

$C_{33}H_{34}O_5S\cdot H_2O$
M_r = 560.69
Monoclinic, $P2_1$
a = 12.628 (1) Å
b = 8.084 (1) Å
c = 14.832 (2) Å
β = 101.380 (5)°
V = 1484.4 (2) Å^3
Z = 2
Mo $K\alpha$ radiation
μ = 0.15 mm^{-1}
T = 150 K
0.35 × 0.30 × 0.17 mm

Data collection

Oxford Diffraction Gemini Ruby CCD diffractometer
Absorption correction: multi-scan (*CrysAlis PRO*; Oxford Diffraction, 2009)
T_{min} = 0.948, T_{max} = 0.974
12650 measured reflections
5205 independent reflections
4333 reflections with $I > 2\sigma(I)$
R_{int} = 0.022

Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.030
$wR(F^2)$ = 0.062
S = 0.97
5205 reflections
400 parameters
17 restraints
H atoms treated by a mixture of independent and constrained refinement
$\Delta\rho_{max}$ = 0.13 e Å^{-3}
$\Delta\rho_{min}$ = −0.17 e Å^{-3}
Absolute structure: Flack (1983), 2381 Friedel pairs
Flack parameter: 0.01 (5)

Table 1
Hydrogen-bond geometry (Å, °).

D—H···A	D—H	H···A	D···A	D—H···A
OW—HW1···O2	0.88 (3)	2.00 (3)	2.861 (2)	166 (2)
OW—HW2···O6	0.78 (2)	2.07 (2)	2.827 (2)	165 (2)
O6—H6···OW^{i}	0.87 (2)	1.89 (2)	2.745 (2)	169 (2)

Symmetry code: (i) $-x+1, y-\frac{1}{2}, -z+2$.

Data collection: *CrysAlis CCD* (Oxford Diffraction, 2009); cell refinement: *CrysAlis RED* (Oxford Diffraction, 2009); data reduction: *CrysAlis RED*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *PLATON* (Spek, 2009); software used to prepare material for publication: *PLATON*.

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Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: HB5424).

References

Boons, G. J. (1991). *J. Carbohydr. Chem.* **10**, 995–1007.
Caravano, A., Mengin-Lecreulx, D., Brondello, J.-M., Vincent, S. & Sinay, P. (2003). *Chem. Eur. J.* **23**, 5888–98.
Cremer, D. & Pople, J. A. (1975). *J. Am. Chem. Soc.* **97**, 1354–1358.
Dohi, H., Perion, R., Durka, M., Bosco, Y., Roue, Y., Moreau, F., Grizot, S., Ducruix, A., Escaich, S. & Vincent, S. (2008). *Chem. Eur. J.* **14**, 9530–9539.
Flack, H. D. (1983). *Acta Cryst.* A**39**, 876–881.
Grizot, S., Salem, M., Vongsouthi, V., Durand, L., Moreau, F., Vincent, S., Dohi, H., Escaich, S. & Ducruix, A. (2006). *J. Mol. Biol.* **363**, 383–394.
Oxford Diffraction (2009). *CrysAlis CCD*, *CrysAlis RED* and *CrysAlis PRO*. Oxford Diffraction Ltd, Yarnton, England.
Sheldrick, G. M. (2008). *Acta Cryst.* A**64**, 112–122.
Spek, A. L. (2009). *Acta Cryst.* D**65**, 148–155.
Szurmai, Z., Baaltoni, L. & Liptak, A. (1994). *Carbohydr. Res.* **254**, 301–309.

supplementary materials

Acta Cryst. (2010). E**66**, o1525 [**doi:10.1107/S1600536810019604**]

Phenyl 2,3,4-tri-*O*-benzyl-1-thio-*α*-D-mannopyranoside monohydrate

M. Durka, B. Norberg, Y. Roué, S. P. Vincent and J. Wouters

Comment

Oligosaccharides are natural ligands of lectins, which are important receptors involved in key biological processes. Efficient strategies for the regioselective transformations of monosaccharides to achieve glycosylation reactions or further functionalizations are of paramount importance. Furthermore, the knowledge of the conformations of carbohydrates alone or bound to protein gives access to key informations that can be exploited to understand biocatalytic processes or stereoelectronic effects (Caravano *et al.*, 2003).

Numerous strategies of protections of mannopyranosides have been described in the litterature (*e.g.* Boons, 1991; Szurmai *et al.*, 1994) in order to derivatise the primary alcohol. The title compound is also a key intermediate for the synthesis of heptosyl transferase inhibitors (Dohi *et al.*, 2008; Grizot *et al.*, 2006).

Crystal structure of the title compound confirms the expected relative stereochemistry : C1 *R*, C2 *S*, C3 *S*, C4 *R*, C5 *R*. The mannopyranoside adopts a chair conformation with puckering amplitude (Q) = 0.522 (3) Å, Theta = 3.6 (3) °, and Phi = 60 (5) ° (Cremer & Pople, 1975).

The 2-alpha-thiophenyl group on C1 and the *O*-benzyl group on C2 occupy an axial position, the two other *O*-benzyl groups (on C3 and C4) and carbon atom C6 occupying an equatorial position.

Thiophenyl-2,3,4-*O*-tri-benzyl-alpha-*D*-mannopyranoside co-crystallized with one water molecule (O_W). This water molecule is part of a H bond network involving the primary alcohol O6 and also secondary alcohol O2 (Table 1). Packing is further reinforced by van der Waals interactions involving the aromatic rings.

Experimental

The title compound was obtained by a six-step synthetic route that will be described in details elsewhere. Overall yield is 70%. Colourless prisms of (I) were obtained by evaporation of a solution in ethyl acetate.

Refinement

Disorder of the benzyl C(21) > C(27) moiety substituting oxygen O(4) was included in the refinement (0.5 occupacy for both parts that were restrained to have similar bond lengths and angles). H atoms on water oxygen atom O_W and on alcohol oxygen atom O(6) were located by Fourier difference maps and allowed to ride on their parent O atoms.

All other H atoms were placed at idealized positions and allowed to ride on their parent atoms, with C—H = 0.97 Å and $U_{iso}(H) = 1.2U_{eq}(C)$ for methylene groups, C—H = 0.93 Å and $U_{iso}(H) = 1.2U_{eq}(C)$ for aromatic carbons, and C—H = 0.96 Å and $U_{iso}(H) = 1.5U_{eq}(C)$ for the methyl group.

Figures

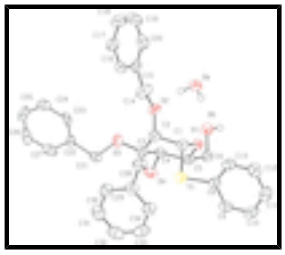


Fig. 1. The molecular structure of (I): C-bound H atoms are omitted and disorder is not presented for clarity. Displacement ellipsoids for non-H atoms are drawn at the 50% probability level.

Phenyl 2,3,4-tri-*O*-benzyl-1-thio-α-D-mannopyranoside monohydrate

Crystal data

$C_{33}H_{34}O_5S·H_2O$	$F(000) = 596.0$
$M_r = 560.69$	$D_x = 1.255$ Mg m^{-3}
Monoclinic, $P2_1$	Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å
Hall symbol: P 2yb	Cell parameters from 7534 reflections
$a = 12.628$ (1) Å	$\theta = 3.0–28.2°$
$b = 8.084$ (1) Å	$\mu = 0.15$ mm^{-1}
$c = 14.832$ (2) Å	$T = 150$ K
$\beta = 101.380$ (5)°	Prism, colourless
$V = 1484.4$ (2) Å^3	0.35 × 0.30 × 0.17 mm
$Z = 2$	

Data collection

Oxford Diffraction Gemini Ruby CCD diffractometer	5205 independent reflections
Radiation source: Enhanced fine-focus sealed tube	4333 reflections with $I > 2\sigma(I)$
graphite	$R_{int} = 0.022$
ω scans	$\theta_{max} = 25.0°$, $\theta_{min} = 3.0°$
Absorption correction: multi-scan (*CrysAlis PRO*; Oxford Diffraction, 2009)	$h = -15\rightarrow14$
$T_{min} = 0.948$, $T_{max} = 0.974$	$k = -9\rightarrow9$
12650 measured reflections	$l = -17\rightarrow17$

Refinement

Refinement on F^2	Secondary atom site location: difference Fourier map
Least-squares matrix: full	Hydrogen site location: inferred from neighbouring sites
$R[F^2 > 2\sigma(F^2)] = 0.030$	H atoms treated by a mixture of independent and constrained refinement
$wR(F^2) = 0.062$	$w = 1/[\sigma^2(F_o^2) + (0.0359P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
$S = 0.97$	$(\Delta/\sigma)_{max} = 0.001$

5205 reflections	$\Delta\rho_{max}$ = 0.13 e Å^{-3}
400 parameters	$\Delta\rho_{min}$ = −0.17 e Å^{-3}
17 restraints	Absolute structure: Flack (1983), 2381 Friedel pairs
Primary atom site location: structure-invariant direct methods	Flack parameter: 0.01 (5)

Special details

Geometry. All esds (except the esd in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell esds are taken into account individually in the estimation of esds in distances, angles and torsion angles; correlations between esds in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell esds is used for estimating esds involving l.s. planes.

Refinement. Refinement of F^2 against ALL reflections. The weighted *R*-factor wR and goodness of fit *S* are based on F^2, conventional *R*-factors *R* are based on *F*, with *F* set to zero for negative F^2. The threshold expression of $F^2 > \sigma(F^2)$ is used only for calculating *R*-factors(gt) etc. and is not relevant to the choice of reflections for refinement. *R*-factors based on F^2 are statistically about twice as large as those based on *F*, and *R*- factors based on ALL data will be even larger.

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å^2)

	x	*y*	*z*	U_{iso}*/U_{eq}	Occ. (<1)
C1	0.28677 (14)	0.7097 (2)	0.89516 (11)	0.0300 (4)	
H1	0.3281	0.7834	0.9416	0.036*	
C2	0.32672 (13)	0.7370 (2)	0.80557 (11)	0.0334 (4)	
H2	0.3072	0.8487	0.7825	0.040*	
C3	0.27664 (14)	0.6105 (2)	0.73342 (11)	0.0337 (4)	
H3	0.1995	0.6349	0.7142	0.040*	
C4	0.28925 (14)	0.4357 (2)	0.77082 (10)	0.0297 (4)	
H4	0.3641	0.3989	0.7759	0.036*	
C5	0.25565 (14)	0.4210 (2)	0.86404 (10)	0.0276 (4)	
H5	0.1771	0.4349	0.8547	0.033*	
C6	0.28498 (13)	0.2565 (2)	0.90995 (11)	0.0323 (4)	
H6A	0.2635	0.2547	0.9692	0.039*	
H6B	0.2466	0.1688	0.8725	0.039*	
C8	0.11808 (13)	0.7620 (2)	0.98996 (11)	0.0308 (4)	
C9	0.02534 (15)	0.6816 (2)	1.00193 (13)	0.0370 (5)	
H9	−0.0181	0.6284	0.9525	0.044*	
C10	−0.00307 (16)	0.6802 (2)	1.08781 (14)	0.0448 (5)	
H10	−0.0665	0.6283	1.0954	0.054*	
C11	0.06208 (17)	0.7552 (3)	1.16149 (13)	0.0489 (5)	
H11	0.0431	0.7537	1.2190	0.059*	
C12	0.15545 (18)	0.8325 (3)	1.14995 (13)	0.0453 (5)	
H12	0.2004	0.8810	1.2002	0.054*	
C13	0.18316 (15)	0.8388 (2)	1.06442 (13)	0.0378 (5)	
H13	0.2453	0.8945	1.0568	0.045*	
C14	0.50097 (18)	0.8655 (2)	0.81855 (16)	0.0507 (6)	
H14A	0.5083	0.9246	0.8764	0.061*	
H14B	0.4635	0.9367	0.7699	0.061*	

C15	0.61013 (15)	0.8228 (2)	0.80096 (11)	0.0322 (4)	
C16	0.62073 (15)	0.7141 (2)	0.73104 (11)	0.0367 (4)	
H16	0.5595	0.6650	0.6961	0.044*	
C17	0.72045 (17)	0.6782 (3)	0.71287 (13)	0.0478 (5)	
H17	0.7264	0.6048	0.6659	0.057*	
C18	0.81128 (17)	0.7497 (3)	0.76340 (17)	0.0603 (6)	
H18	0.8787	0.7253	0.7505	0.072*	
C19	0.80278 (18)	0.8570 (3)	0.83291 (16)	0.0578 (7)	
H19	0.8647	0.9052	0.8673	0.069*	
C20	0.70225 (17)	0.8946 (2)	0.85263 (12)	0.0434 (5)	
H20	0.6968	0.9673	0.9001	0.052*	
O3	0.32582 (10)	0.61829 (18)	0.65476 (8)	0.0464 (4)	
C21	0.2578 (3)	0.6608 (6)	0.5714 (2)	0.0441 (11)	0.50
H21A	0.2135	0.7550	0.5805	0.053*	0.50
H21B	0.2102	0.5689	0.5495	0.053*	0.50
C22	0.3247 (5)	0.7026 (7)	0.5018 (4)	0.0280 (18)	0.50
C23	0.4047 (6)	0.8186 (9)	0.5201 (3)	0.043 (2)	0.50
H23	0.4207	0.8676	0.5779	0.051*	0.50
C24	0.4617 (5)	0.8638 (7)	0.4547 (5)	0.0407 (15)	0.50
H24	0.5178	0.9396	0.4692	0.049*	0.50
C25	0.4364 (5)	0.7974 (10)	0.3673 (5)	0.0456 (16)	0.50
H25	0.4748	0.8301	0.3229	0.055*	0.50
C26	0.3545 (7)	0.6830 (9)	0.3456 (3)	0.0481 (19)	0.50
H26	0.3372	0.6388	0.2866	0.058*	0.50
C27	0.2978 (6)	0.6338 (10)	0.4127 (4)	0.044 (2)	0.50
H27	0.2427	0.5562	0.3988	0.053*	0.50
C21'	0.2980 (4)	0.7526 (6)	0.5997 (2)	0.0413 (7)	0.50
H21C	0.3253	0.8515	0.6334	0.050*	0.50
H21D	0.2199	0.7608	0.5844	0.050*	0.50
C22'	0.3411 (10)	0.7456 (13)	0.5118 (7)	0.0413 (7)	0.50
C23'	0.4273 (9)	0.8369 (12)	0.4994 (6)	0.0413 (7)	0.50
H23'	0.4617	0.9043	0.5471	0.050*	0.50
C24'	0.4653 (6)	0.8333 (8)	0.4192 (7)	0.0413 (7)	0.50
H24'	0.5225	0.9015	0.4122	0.050*	0.50
C25'	0.4206 (7)	0.7315 (9)	0.3503 (6)	0.0413 (7)	0.50
H25'	0.4465	0.7287	0.2958	0.050*	0.50
C26'	0.3361 (8)	0.6316 (8)	0.3617 (6)	0.0413 (7)	0.50
H26'	0.3052	0.5596	0.3149	0.050*	0.50
C27'	0.2970 (8)	0.6377 (14)	0.4420 (8)	0.0413 (7)	0.50
H27'	0.2405	0.5687	0.4494	0.050*	0.50
C28	0.26726 (15)	0.2153 (3)	0.66005 (13)	0.0451 (5)	
H28A	0.3146	0.1422	0.7016	0.054*	
H28B	0.3101	0.2731	0.6224	0.054*	
C29	0.17992 (15)	0.1171 (2)	0.60016 (12)	0.0376 (5)	
C30	0.17758 (17)	0.1035 (3)	0.50676 (13)	0.0445 (5)	
H30	0.2310	0.1538	0.4812	0.053*	
C31	0.09579 (19)	0.0151 (3)	0.45124 (14)	0.0540 (6)	
H31	0.0945	0.0064	0.3885	0.065*	
C32	0.01714 (19)	−0.0592 (3)	0.48815 (15)	0.0570 (6)	

H32	−0.0373	−0.1189	0.4506	0.068*
C33	0.01817 (17)	−0.0461 (3)	0.58167 (15)	0.0516 (6)
H33	−0.0359	−0.0957	0.6067	0.062*
C34	0.09947 (16)	0.0405 (3)	0.63681 (13)	0.0430 (5)
H34	0.1007	0.0480	0.6996	0.052*
O1	0.30602 (9)	0.54559 (13)	0.92705 (7)	0.0281 (3)
O2	0.44079 (9)	0.71853 (15)	0.82204 (8)	0.0383 (3)
O4	0.21835 (9)	0.32927 (16)	0.71031 (8)	0.0385 (3)
O6	0.39918 (10)	0.22905 (16)	0.92224 (9)	0.0376 (3)
OW	0.55620 (12)	0.4829 (2)	0.94836 (10)	0.0379 (3)
S1	0.14464 (4)	0.77358 (5)	0.87681 (3)	0.03636 (13)
HW1	0.528 (2)	0.551 (4)	0.9035 (18)	0.084 (9)*
HW2	0.5117 (18)	0.417 (3)	0.9508 (13)	0.047 (7)*
H6	0.4137 (16)	0.142 (3)	0.9571 (13)	0.050 (6)*

Atomic displacement parameters (Å^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
C1	0.0308 (10)	0.0249 (9)	0.0353 (10)	0.0021 (8)	0.0090 (8)	0.0008 (7)
C2	0.0287 (10)	0.0296 (10)	0.0436 (10)	0.0051 (8)	0.0111 (8)	0.0099 (8)
C3	0.0279 (10)	0.0449 (11)	0.0295 (9)	0.0067 (9)	0.0089 (8)	0.0063 (8)
C4	0.0231 (10)	0.0371 (11)	0.0284 (9)	0.0003 (8)	0.0037 (7)	−0.0026 (8)
C5	0.0255 (10)	0.0274 (10)	0.0303 (9)	−0.0021 (8)	0.0061 (7)	−0.0032 (8)
C6	0.0313 (10)	0.0333 (10)	0.0333 (8)	−0.0040 (9)	0.0088 (7)	−0.0021 (8)
C8	0.0266 (10)	0.0275 (9)	0.0394 (9)	0.0041 (8)	0.0093 (7)	−0.0005 (9)
C9	0.0277 (11)	0.0346 (11)	0.0477 (11)	0.0026 (8)	0.0048 (8)	0.0003 (8)
C10	0.0356 (11)	0.0380 (12)	0.0662 (14)	0.0049 (9)	0.0232 (10)	0.0098 (10)
C11	0.0597 (14)	0.0457 (12)	0.0468 (11)	0.0112 (12)	0.0238 (10)	0.0057 (11)
C12	0.0497 (13)	0.0427 (12)	0.0427 (11)	0.0021 (10)	0.0073 (9)	−0.0073 (9)
C13	0.0318 (11)	0.0327 (10)	0.0501 (12)	0.0001 (8)	0.0105 (9)	−0.0028 (9)
C14	0.0534 (14)	0.0313 (12)	0.0750 (14)	−0.0061 (10)	0.0314 (11)	−0.0078 (10)
C15	0.0386 (11)	0.0282 (10)	0.0313 (9)	−0.0064 (8)	0.0103 (8)	0.0023 (8)
C16	0.0331 (11)	0.0442 (11)	0.0312 (9)	−0.0001 (9)	0.0024 (8)	0.0017 (8)
C17	0.0458 (13)	0.0565 (14)	0.0441 (11)	0.0070 (11)	0.0165 (10)	0.0045 (10)
C18	0.0344 (13)	0.0552 (15)	0.0942 (17)	0.0017 (12)	0.0198 (12)	0.0163 (14)
C19	0.0390 (14)	0.0482 (14)	0.0751 (16)	−0.0134 (11)	−0.0160 (12)	0.0203 (12)
C20	0.0600 (15)	0.0312 (10)	0.0345 (10)	−0.0123 (10)	−0.0011 (10)	0.0050 (8)
O3	0.0426 (8)	0.0664 (9)	0.0334 (7)	0.0167 (7)	0.0157 (6)	0.0184 (7)
C21	0.031 (2)	0.065 (3)	0.032 (2)	−0.020 (2)	−0.0058 (17)	0.002 (2)
C22	0.036 (3)	0.022 (4)	0.025 (3)	0.011 (3)	0.007 (3)	0.010 (3)
C23	0.049 (5)	0.065 (4)	0.011 (2)	0.006 (4)	0.001 (2)	−0.004 (2)
C24	0.033 (3)	0.046 (3)	0.041 (4)	−0.012 (2)	0.000 (3)	−0.004 (3)
C25	0.052 (4)	0.052 (4)	0.041 (4)	0.009 (3)	0.030 (3)	0.010 (3)
C26	0.080 (5)	0.047 (4)	0.017 (2)	0.012 (4)	0.008 (3)	−0.002 (2)
C27	0.038 (3)	0.036 (3)	0.052 (6)	−0.011 (2)	−0.007 (4)	−0.002 (4)
C21'	0.0536 (15)	0.0354 (13)	0.0370 (14)	0.0045 (11)	0.0144 (11)	0.0001 (11)
C22'	0.0536 (15)	0.0354 (13)	0.0370 (14)	0.0045 (11)	0.0144 (11)	0.0001 (11)
C23'	0.0536 (15)	0.0354 (13)	0.0370 (14)	0.0045 (11)	0.0144 (11)	0.0001 (11)

C24'	0.0536 (15)	0.0354 (13)	0.0370 (14)	0.0045 (11)	0.0144 (11)	0.0001 (11)
C25'	0.0536 (15)	0.0354 (13)	0.0370 (14)	0.0045 (11)	0.0144 (11)	0.0001 (11)
C26'	0.0536 (15)	0.0354 (13)	0.0370 (14)	0.0045 (11)	0.0144 (11)	0.0001 (11)
C27'	0.0536 (15)	0.0354 (13)	0.0370 (14)	0.0045 (11)	0.0144 (11)	0.0001 (11)
C28	0.0364 (11)	0.0497 (13)	0.0494 (11)	0.0013 (10)	0.0092 (9)	−0.0137 (10)
C29	0.0362 (11)	0.0329 (10)	0.0443 (12)	0.0027 (9)	0.0097 (9)	−0.0077 (9)
C30	0.0488 (13)	0.0425 (12)	0.0447 (12)	−0.0036 (10)	0.0152 (10)	−0.0046 (9)
C31	0.0657 (15)	0.0514 (14)	0.0423 (12)	−0.0035 (12)	0.0040 (11)	−0.0069 (10)
C32	0.0486 (15)	0.0532 (15)	0.0629 (14)	−0.0103 (11)	−0.0046 (12)	−0.0147 (11)
C33	0.0439 (14)	0.0417 (13)	0.0709 (15)	−0.0084 (10)	0.0157 (11)	−0.0053 (11)
C34	0.0427 (12)	0.0416 (11)	0.0464 (11)	0.0025 (10)	0.0124 (9)	−0.0043 (9)
O1	0.0309 (7)	0.0244 (6)	0.0286 (6)	−0.0002 (5)	0.0054 (5)	0.0000 (5)
O2	0.0307 (7)	0.0340 (7)	0.0521 (7)	−0.0014 (6)	0.0127 (6)	0.0108 (6)
O4	0.0283 (7)	0.0484 (8)	0.0378 (7)	0.0024 (6)	0.0042 (5)	−0.0151 (6)
O6	0.0350 (8)	0.0285 (8)	0.0494 (7)	0.0019 (6)	0.0082 (6)	0.0079 (6)
OW	0.0299 (8)	0.0340 (8)	0.0469 (8)	−0.0020 (7)	0.0005 (6)	0.0019 (6)
S1	0.0316 (3)	0.0396 (3)	0.0383 (2)	0.0082 (2)	0.00785 (19)	0.0010 (2)

Geometric parameters (Å, °)

C1—O1	1.414 (2)	O3—C21	1.403 (3)
C1—C2	1.528 (2)	C21—C22	1.496 (6)
C1—S1	1.8355 (17)	C21—H21A	0.9700
C1—H1	0.9800	C21—H21B	0.9700
C2—O2	1.421 (2)	C22—C23	1.366 (8)
C2—C3	1.524 (2)	C22—C27	1.412 (7)
C2—H2	0.9800	C23—C24	1.366 (7)
C3—O3	1.427 (2)	C23—H23	0.9300
C3—C4	1.515 (3)	C24—C25	1.382 (7)
C3—H3	0.9800	C24—H24	0.9300
C4—O4	1.425 (2)	C25—C26	1.377 (8)
C4—C5	1.529 (2)	C25—H25	0.9300
C4—H4	0.9800	C26—C27	1.393 (8)
C5—O1	1.4347 (18)	C26—H26	0.9300
C5—C6	1.506 (2)	C27—H27	0.9300
C5—H5	0.9800	C21'—C22'	1.510 (8)
C6—O6	1.435 (2)	C21'—H21C	0.9700
C6—H6A	0.9700	C21'—H21D	0.9700
C6—H6B	0.9700	C22'—C23'	1.356 (10)
C8—C9	1.381 (2)	C22'—C27'	1.384 (10)
C8—C13	1.386 (2)	C23'—C24'	1.370 (9)
C8—S1	1.7777 (17)	C23'—H23'	0.9300
C9—C10	1.390 (3)	C24'—C25'	1.346 (9)
C9—H9	0.9300	C24'—H24'	0.9300
C10—C11	1.372 (3)	C25'—C26'	1.375 (9)
C10—H10	0.9300	C25'—H25'	0.9300
C11—C12	1.375 (3)	C26'—C27'	1.377 (9)
C11—H11	0.9300	C26'—H26'	0.9300
C12—C13	1.382 (3)	C27'—H27'	0.9300

C12—H12	0.9300	C28—O4	1.403 (2)
C13—H13	0.9300	C28—C29	1.500 (3)
C14—O2	1.417 (2)	C28—H28A	0.9700
C14—C15	1.493 (3)	C28—H28B	0.9700
C14—H14A	0.9700	C29—C30	1.384 (3)
C14—H14B	0.9700	C29—C34	1.389 (3)
C15—C16	1.386 (2)	C30—C31	1.386 (3)
C15—C20	1.388 (3)	C30—H30	0.9300
C16—C17	1.370 (3)	C31—C32	1.365 (3)
C16—H16	0.9300	C31—H31	0.9300
C17—C18	1.368 (3)	C32—C33	1.389 (3)
C17—H17	0.9300	C32—H32	0.9300
C18—C19	1.368 (3)	C33—C34	1.372 (3)
C18—H18	0.9300	C33—H33	0.9300
C19—C20	1.392 (3)	C34—H34	0.9300
C19—H19	0.9300	O6—H6	0.87 (2)
C20—H20	0.9300	OW—HW1	0.88 (3)
O3—C21'	1.362 (4)	OW—HW2	0.78 (2)
O1—C1—C2	111.21 (14)	C21—O3—C3	116.2 (2)
O1—C1—S1	114.34 (12)	O3—C21—C22	109.4 (4)
C2—C1—S1	108.15 (11)	O3—C21—H21A	109.8
O1—C1—H1	107.6	C22—C21—H21A	109.8
C2—C1—H1	107.6	O3—C21—H21B	109.8
S1—C1—H1	107.6	C22—C21—H21B	109.8
O2—C2—C3	108.46 (14)	H21A—C21—H21B	108.2
O2—C2—C1	109.45 (13)	C23—C22—C27	119.2 (6)
C3—C2—C1	110.59 (14)	C23—C22—C21	120.9 (5)
O2—C2—H2	109.4	C27—C22—C21	119.5 (5)
C3—C2—H2	109.4	C22—C23—C24	121.0 (5)
C1—C2—H2	109.4	C22—C23—H23	119.5
O3—C3—C4	108.00 (14)	C24—C23—H23	119.5
O3—C3—C2	110.94 (15)	C23—C24—C25	120.4 (4)
C4—C3—C2	111.68 (13)	C23—C24—H24	119.8
O3—C3—H3	108.7	C25—C24—H24	119.8
C4—C3—H3	108.7	C26—C25—C24	120.3 (5)
C2—C3—H3	108.7	C26—C25—H25	119.9
O4—C4—C3	108.98 (12)	C24—C25—H25	119.9
O4—C4—C5	105.68 (14)	C25—C26—C27	119.5 (5)
C3—C4—C5	112.09 (14)	C25—C26—H26	120.2
O4—C4—H4	110.0	C27—C26—H26	120.2
C3—C4—H4	110.0	C26—C27—C22	119.6 (6)
C5—C4—H4	110.0	C26—C27—H27	120.2
O1—C5—C6	106.70 (11)	C22—C27—H27	120.2
O1—C5—C4	111.58 (13)	O3—C21'—C22'	113.2 (5)
C6—C5—C4	112.98 (14)	O3—C21'—H21C	108.9
O1—C5—H5	108.5	C22'—C21'—H21C	108.9
C6—C5—H5	108.5	O3—C21'—H21D	108.9
C4—C5—H5	108.5	C22'—C21'—H21D	108.9
O6—C6—C5	110.21 (14)	H21C—C21'—H21D	107.8

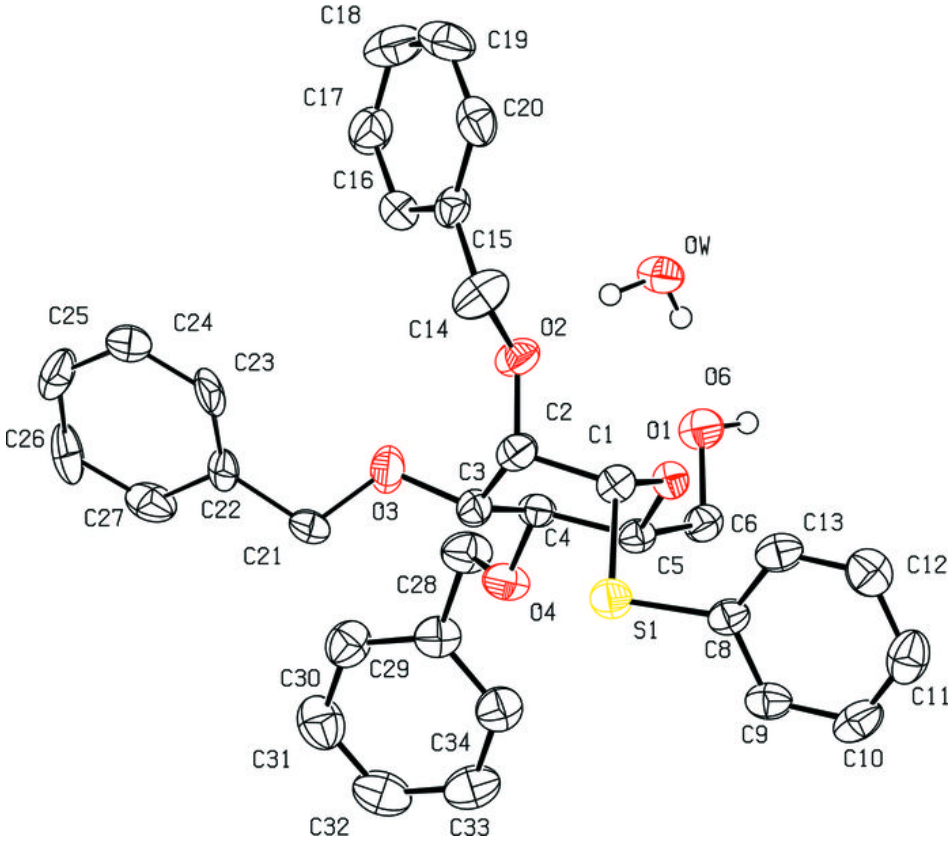
O6—C6—H6A	109.6	C23'—C22'—C27'	117.2 (8)
C5—C6—H6A	109.6	C23'—C22'—C21'	122.1 (10)
O6—C6—H6B	109.6	C27'—C22'—C21'	120.6 (9)
C5—C6—H6B	109.6	C22'—C23'—C24'	122.3 (7)
H6A—C6—H6B	108.1	C22'—C23'—H23'	118.9
C9—C8—C13	119.53 (16)	C24'—C23'—H23'	118.9
C9—C8—S1	117.95 (13)	C25'—C24'—C23'	120.4 (7)
C13—C8—S1	122.40 (14)	C25'—C24'—H24'	119.8
C8—C9—C10	120.02 (17)	C23'—C24'—H24'	119.8
C8—C9—H9	120.0	C24'—C25'—C26'	119.0 (7)
C10—C9—H9	120.0	C24'—C25'—H25'	120.5
C11—C10—C9	120.23 (19)	C26'—C25'—H25'	120.5
C11—C10—H10	119.9	C25'—C26'—C27'	120.3 (8)
C9—C10—H10	119.9	C25'—C26'—H26'	119.9
C10—C11—C12	119.72 (18)	C27'—C26'—H26'	119.9
C10—C11—H11	120.1	C26'—C27'—C22'	120.7 (9)
C12—C11—H11	120.1	C26'—C27'—H27'	119.7
C11—C12—C13	120.66 (17)	C22'—C27'—H27'	119.7
C11—C12—H12	119.7	O4—C28—C29	108.24 (15)
C13—C12—H12	119.7	O4—C28—H28A	110.0
C12—C13—C8	119.79 (18)	C29—C28—H28A	110.0
C12—C13—H13	120.1	O4—C28—H28B	110.0
C8—C13—H13	120.1	C29—C28—H28B	110.0
O2—C14—C15	109.44 (16)	H28A—C28—H28B	108.4
O2—C14—H14A	109.8	C30—C29—C34	118.92 (17)
C15—C14—H14A	109.8	C30—C29—C28	120.18 (18)
O2—C14—H14B	109.8	C34—C29—C28	120.90 (17)
C15—C14—H14B	109.8	C29—C30—C31	120.1 (2)
H14A—C14—H14B	108.2	C29—C30—H30	119.9
C16—C15—C20	118.96 (19)	C31—C30—H30	119.9
C16—C15—C14	120.41 (16)	C32—C31—C30	120.32 (19)
C20—C15—C14	120.61 (18)	C32—C31—H31	119.8
C17—C16—C15	120.65 (18)	C30—C31—H31	119.8
C17—C16—H16	119.7	C31—C32—C33	120.20 (19)
C15—C16—H16	119.7	C31—C32—H32	119.9
C18—C17—C16	120.4 (2)	C33—C32—H32	119.9
C18—C17—H17	119.8	C34—C33—C32	119.5 (2)
C16—C17—H17	119.8	C34—C33—H33	120.2
C19—C18—C17	119.9 (2)	C32—C33—H33	120.2
C19—C18—H18	120.0	C33—C34—C29	120.89 (18)
C17—C18—H18	120.0	C33—C34—H34	119.6
C18—C19—C20	120.51 (19)	C29—C34—H34	119.6
C18—C19—H19	119.7	C1—O1—C5	114.61 (11)
C20—C19—H19	119.7	C14—O2—C2	116.02 (14)
C15—C20—C19	119.52 (19)	C28—O4—C4	116.34 (13)
C15—C20—H20	120.2	C6—O6—H6	106.8 (14)
C19—C20—H20	120.2	HW1—OW—HW2	106 (2)
C21'—O3—C21	40.1 (2)	C8—S1—C1	101.91 (8)
C21'—O3—C3	115.02 (19)		

Hydrogen-bond geometry (Å, °)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
OW—HW1···O2	0.88 (3)	2.00 (3)	2.861 (2)	166 (2)
OW—HW2···O6	0.78 (2)	2.07 (2)	2.827 (2)	165 (2)
O6—H6···OW^{i}	0.87 (2)	1.89 (2)	2.745 (2)	169 (2)

Symmetry codes: (i) −*x*+1, *y*−1/2, −*z*+2.

Fig. 1


C18
C19
C17
C20
C16
C15
OW
C14
O2
C25
C24
C23
O6
C2
C26
C1
O1
C3
C27
C22
O3
C6
C13
C4
C21
C5
C12
C28
O4
S1
C8
C29
C30
C11
C34
C9
C31
C10
C32
C33

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Tetrabutylammonium bis[4,4′-dimethyl-2,2′-(3,7-dimethyl-1*H*-4,2,1-benzothiazasiline-1,1-diyl)dibenzenethiolato]-vanadium(III) acetonitrile tetrasolvate

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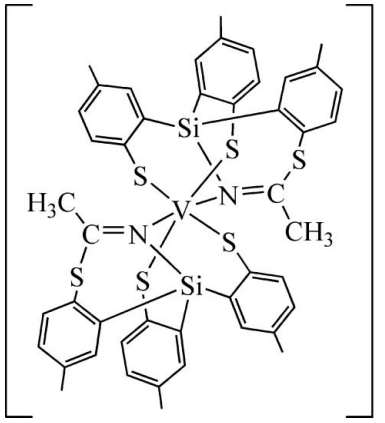
Key indicators: single-crystal X-ray study; T = 200 K; mean σ(C–C) = 0.005 Å; R factor = 0.053; wR factor = 0.144; data-to-parameter ratio = 22.3.

In the title compound, $[N(C_4H_9)_4][V(C_{23}H_{21}NS_3Si)_2]\cdot 4CH_3CN$, the V^{III} atom (site symmetry $\overline{1}$) is coordinated by two *N*,*S*,*S*′-tridentate 4,4′-dimethyl-2,2′-(3,7-dimethyl-1*H*-4,2,1-benzothiazasiline-1,1-diyl)dibenzenethiolate ligands in a distorted *trans*-VN_2S_4 octahedral geometry. The complete cation is generated by crystallographic twofold symmetry, with the V atom lying on the rotation axis. The unusual ligand arose from nucleophilic attack on the coordinated nitrile by the thiolate precursor and reduction of nitrile to the imidate.

Related literature

For background to vanadium thiolate chemistry, see: Rehder (2008); Crans *et al.* (2004); Eady (2003); Janas & Sobota (2005); Ye *et al.* (2010); Tsai *et al.* (2007). For further mechanistic information, see: Block *et al.* (1989). For related structures, see: Zhu *et al.* (1997, 2002).



$(C_4H_9)_4N^+$
4 CH_3CN

Experimental

Crystal data

$(C_{16}H_{36}N)[V(C_{23}H_{21}NS_3Si)_2]\cdot 4C_2H_3N$
M_r = 1328.97
Monoclinic, $C2/c$
a = 27.0867 (16) Å
b = 14.6525 (9) Å
c = 22.0590 (13) Å
β = 126.359 (1)°
V = 7050.5 (7) Å^3
Z = 4
Mo $K\alpha$ radiation
μ = 0.40 mm^{-1}
T = 200 K
0.50 × 0.50 × 0.40 mm

Data collection

Bruker APEXII CCD area-detector diffractometer
Absorption correction: multi-scan (*SADABS*; Bruker, 2004)
T_{min} = 0.490, T_{max} = 1.000
26980 measured reflections
8840 independent reflections
5635 reflections with $I > 2\sigma(I)$
R_{int} = 0.063

Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.053
$wR(F^2)$ = 0.144
S = 1.05
8840 reflections
396 parameters
H-atom parameters constrained
$\Delta\rho_{max}$ = 0.66 e Å^{-3}
$\Delta\rho_{min}$ = −0.44 e Å^{-3}

Table 1
Selected geometric parameters (Å).

V1—N1	2.188 (2)	V1—S2	2.4617 (7)
V1—S1	2.4161 (6)		

Data collection: *APEX2* (Bruker, 2004); cell refinement: *SAINT* (Bruker, 2004); data reduction: *SAINT*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *SHELXTL* (Sheldrick, 2008); software used to prepare material for publication: *SHELXTL*.

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Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: HB5425).

References

Block, E., Kang, H., Ofori-Okai, G. & Zubieta, J. (1989). *Inorg. Chim. Acta*, **156**, 27–28.
Bruker (2004). *APEX2*, *SAINT* and *SADABS*. Bruker AXS Inc., Madison, Wisconsin, USA.
Crans, D. C., Smee, J. J., Gaidamauskas, E. & Yang, L. (2004). *Chem. Rev.* **104**, 849–902.
Eady, R. R. (2003). *Coord. Chem. Rev.* **237**, 23–30.
Janas, Z. & Sobota, P. (2005). *Coord. Chem. Rev.* **249**, 2144–2155.
Rehder, D. (2008). *Bioinorganic Vanadium Chemistry*. New York: John Wiley & Sons.
Sheldrick, G. M. (2008). *Acta Cryst.* A**64**, 112–122.
Tsai, Y.-F., Huang, G.-S., Yang, C.-I., Tsai, H.-L., Liu, Y.-H., Kuo, T.-S. & Hsu, H.-F. (2007). *Inorg. Chem.* **46**, 10467–10469.
Ye, S., Neese, F., Ozarowski, A., Smirnov, D., Krzystek, J., Telser, J., Liao, J.-H., Hung, C.-H., Chu, W.-C., Tsai, Y.-F., Wang, R.-C., Chen, K.-Y. & Hsu, H.-F. (2010). *Inorg. Chem.* **49**, 977–988.
Zhu, H., Chen, C., Zhang, X., Liu, Q., Liao, D. & Li, L. (2002). *Inorg. Chim. Acta*, **328**, 96–104.
Zhu, H.-P., Deng, Y.-H., Huang, X.-Y., Chen, C.-N. & Liu, Q.-T. (1997). *Acta Cryst.* C**53**, 692–693.

supplementary materials

Acta Cryst. (2010). E**66**, m844 [**doi:10.1107/S1600536810022014**]

Tetrabutylammonium bis[4,4'-dimethyl-2,2'-(3,7-dimethyl-1*H*-4,2,1-benzothiazasiline-1,1-diyl)dibenzenethiolato]vanadium(III) acetonitrile tetrasolvate

Y.-F. Tsai, H.-F. Hsu, K.-F. Hsu and J.-C. Wang

Comment

Vanadium thiolate chemistry has been drawing much attention due to its biological relevance as well as its medical application (Rehder, 2008; Crans *et al.*, 2004). For example, alternative nitrogenase is proposed to contain a [Fe_7VS_9] cofactor, where V site likely binds to three sulfides, His442 and homocitrate (Eady, 2003). To elucidate the role of vanadium in the enzyme, it is essential to understand fundamental chemistry of vanadium, particularly in a S-rich ligation environment (Janas & Sobota, 2005). Thus, we have been exploring the reactions of vanadium ion with thiolato containing ligands (Ye *et al.*, 2010; Tsai *et al.*, 2007). At this work, the reaction of [VCl_3THF_3] with H_3L1 [H_3L1 = HSi(5-Me–C_6H_4-2-SH)$_3$] and three equivalents of nBu-Li in CH_3CN generated a deep purple solution. The addition of the cation, [$N(C_4H_9)_4$]Br, to the reaction mixture yielded a crystalline solid of the title compound (**I**).

The molecular structure of the anion in (**I**) is shown in Fig 1. It consists a V^{III} ion coordinated to two L2 ligands [L2 = Si{CH_3(5-Me– C_6H_4-2-S)CN} (5-Me–C_6H_4-2-S)$_2$]. L2 ligand has a S2N donor set that contains two benzenethiolates and one thioimidate group. The formation of a thioimidate group in L2 ligand upon the reaction is likely a consequence of nucleophilic attack on the coordinated nitrile by thiolate and reduction of nitrile to the imidate. Similar chemistry was demonstrated in a rhenium complex with thiolate ligands (Block *et al* ., 1989). The V^{III} ion lies on the inversion centre and forms a normal octahedral geometry with a S4N2 ligation environment, four S atoms from thiolate groups and two N atoms from thioimidate groups. Two N donor atoms of thioimidate groups are in *trans* positions.

The bond lengths and bond angles in compound (**I**) are shown in Table 1. The V—S distances of 2.416 (1) Å and 2.462 (1) Å are close to those of reported six-coordinate V^{III} thiolate complexes (Ye *et al.*, 2010; Zhu *et al.*, 2002; Zhu *et al.*, 1997).

The packing diagrams of compound (**I**) are shown in Fig 2. There is no interaction observed between molecules. The methyl groups on the phenyl rings of the ligands probably prevent the occurrence of inter-molecular π-π stacking interactions. The shortest distance between centers of two phenyl rings is 5.181 (2) Å.

Experimental

A THF solution of $VCl_3(THF)_3$ (0.094 g, 0.25 mmol) was added to a acetonitrile solution (10 ml) of HSi(5-Me–C_6H_4-2-SH)$_3$ (0.202 g, 0.51 mmol) and n-BuLi (0.098 g, 1.53 mmol) to generate a deep purple solution. The solution was concentrated and layered with [$N(C_4H_9)_4$]Br (0.080 g, 0.25 mmol) in acetonitrile solution (5 ml). After one week, deep purple blocks of (I) were obtained.

Refinement

H atoms were generated geometrically, with *C*—H_{methyl} = 0.96 Å; *C*—H_{aryl} = 0.93 Å; $U_{iso}H_{methyl}$ = 1.5U_{eq}(C_{methyl}); $U_{iso}H_{aryl}$ = 1.2U_{eq}(C_{aryl}). In case of the CH_3 group, the positional parameters of the hydrogens were constrained by the SHELXL-97 command to the idealized tetrahedral geometry by the command AFIX 137 (Sheldrick, 2008).

Figures

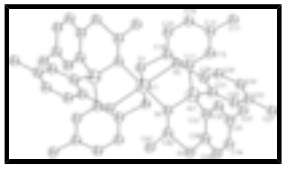


Fig. 1. The anion in (I) with displacement ellipsoids drawn at the 35 % probability level. Unlabelled atoms are generated by the symmetry operation (1–x, –y, 1–z).

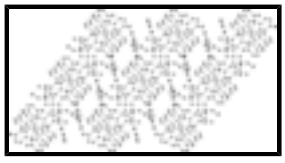


Fig. 2. The packing diagram of (I): A view of the sheet parallel to the ac plane, H atoms have been omitted for clarity.

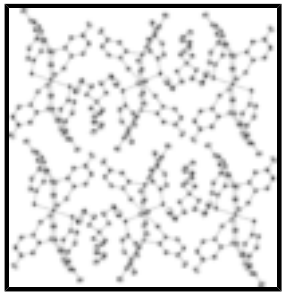


Fig. 3. View of the packing in (I) approximately down the a axis, acetonitrile molecules and H atoms have been omitted for clarity.

Tetrabutylammonium bis[4,4'-dimethyl-2,2'-(3,7-dimethyl-1*H*- 4,2,1-benzothiazasiline-1,1-diyl)dibenzenethiolato]vanadium(III) acetonitrile tetrasolvate

Crystal data

$(C_{16}H_{36}N)[V(C_{23}H_{21}NS_3Si)_2]\cdot 4C_2H_3N$	$F(000)$ = 2824
M_r = 1328.97	D_x = 1.252 Mg m^{-3}
Monoclinic, *C*2/*c*	Mo *K*α radiation, λ = 0.71073 Å
Hall symbol: -C 2yc	Cell parameters from 5232 reflections
a = 27.0867 (16) Å	θ = 2.3–28.1°
b = 14.6525 (9) Å	μ = 0.40 mm^{-1}
c = 22.0590 (13) Å	*T* = 200 K
β = 126.359 (1)°	Block, deep purple
V = 7050.5 (7) Å^3	0.50 × 0.50 × 0.40 mm
Z = 4	

Data collection

Bruker APEXII CCD area-detector	8840 independent reflections

diffractometer

Radiation source: fine-focus sealed tube

graphite

φ and ω scans

Absorption correction: multi-scan (*SADABS*; Bruker, 2004)

T_{min} = 0.490, T_{max} = 1.000

26980 measured reflections

5635 reflections with $I > 2\sigma(I)$

R_{int} = 0.063

θ_{max} = 28.4°, θ_{min} = 1.7°

$h = -33 \rightarrow 36$

$k = -19 \rightarrow 19$

$l = -28 \rightarrow 29$

Refinement

Refinement on F^2

Least-squares matrix: full

$R[F^2 > 2\sigma(F^2)]$ = 0.053

$wR(F^2)$ = 0.144

S = 1.05

8840 reflections

396 parameters

0 restraints

0 constraints

Primary atom site location: structure-invariant direct methods

Secondary atom site location: difference Fourier map

Hydrogen site location: inferred from neighbouring sites

H-atom parameters constrained

$w = 1/[\sigma^2(F_o^2) + (0.0702P)^2 + 1.1431P]$ where $P = (F_o^2 + 2F_c^2)/3$

$(\Delta/\sigma)_{max}$ = 0.001

$\Delta\rho_{max}$ = 0.66 e Å^{-3}

$\Delta\rho_{min}$ = −0.44 e Å^{-3}

Special details

Geometry. All esds (except the esd in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell esds are taken into account individually in the estimation of esds in distances, angles and torsion angles; correlations between esds in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell esds is used for estimating esds involving l.s. planes.

Refinement. Refinement of F^2 against ALL reflections. The weighted *R*-factor wR and goodness of fit *S* are based on F^2, conventional *R*-factors *R* are based on *F*, with *F* set to zero for negative F^2. The threshold expression of $F^2 > \sigma(F^2)$ is used only for calculating *R*-factors(gt) etc. and is not relevant to the choice of reflections for refinement. *R*-factors based on F^2 are statistically about twice as large as those based on *F*, and *R*- factors based on ALL data will be even larger.

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å^2)

	x	*y*	*z*	U_{iso}*/U_{eq}
V1	0.5000	0.0000	0.5000	0.02112 (15)
Si1	0.47274 (3)	0.21699 (5)	0.46284 (4)	0.02117 (16)
S1	0.57178 (3)	0.05741 (5)	0.47806 (4)	0.02504 (16)
S2	0.53127 (3)	0.09662 (5)	0.60866 (4)	0.02710 (16)
S3	0.32852 (3)	0.19171 (5)	0.31598 (4)	0.03403 (18)
N1	0.43811 (10)	0.10819 (14)	0.42448 (12)	0.0222 (5)
N2	0.5000	0.1548 (2)	0.2500	0.0255 (7)
N3	0.2424 (3)	0.3201 (5)	0.3810 (3)	0.182 (4)
N4	0.2660 (2)	0.5583 (4)	0.1270 (3)	0.125 (2)

C11	0.55730 (12)	0.23091 (18)	0.51487 (14)	0.0237 (5)
C12	0.58127 (12)	0.31516 (19)	0.55119 (15)	0.0271 (6)
H12A	0.5547	0.3575	0.5489	0.033*
C13	0.64280 (13)	0.3384 (2)	0.59036 (16)	0.0294 (6)
C14	0.68221 (13)	0.2732 (2)	0.59387 (16)	0.0316 (6)
H14A	0.7236	0.2868	0.6193	0.038*
C15	0.66030 (13)	0.1887 (2)	0.55997 (16)	0.0298 (6)
H15A	0.6874	0.1460	0.5637	0.036*
C16	0.59806 (12)	0.16615 (18)	0.52012 (14)	0.0242 (5)
C17	0.66594 (14)	0.4308 (2)	0.62743 (18)	0.0395 (7)
H17A	0.6356	0.4595	0.6304	0.059*
H17B	0.6737	0.4681	0.5982	0.059*
H17C	0.7032	0.4232	0.6772	0.059*
C21	0.45354 (12)	0.24289 (18)	0.52897 (15)	0.0232 (5)
C22	0.41580 (12)	0.31461 (19)	0.52041 (16)	0.0274 (6)
H22A	0.3971	0.3513	0.4778	0.033*
C23	0.40540 (13)	0.3326 (2)	0.57407 (17)	0.0320 (7)
C24	0.43478 (14)	0.2781 (2)	0.63787 (17)	0.0346 (7)
H24A	0.4294	0.2902	0.6750	0.042*
C25	0.47203 (14)	0.20590 (19)	0.64746 (16)	0.0308 (6)
H25A	0.4908	0.1699	0.6905	0.037*
C26	0.48153 (13)	0.18693 (18)	0.59321 (15)	0.0253 (6)
C27	0.36400 (16)	0.4096 (2)	0.5628 (2)	0.0491 (9)
H27A	0.3652	0.4161	0.6070	0.074*
H27B	0.3228	0.3966	0.5202	0.074*
H27C	0.3776	0.4653	0.5541	0.074*
C31	0.43356 (12)	0.29874 (18)	0.38172 (15)	0.0235 (5)
C32	0.46213 (13)	0.37586 (18)	0.37750 (16)	0.0276 (6)
H32A	0.5037	0.3847	0.4153	0.033*
C33	0.43175 (14)	0.43956 (19)	0.31998 (17)	0.0322 (6)
C34	0.36973 (15)	0.4254 (2)	0.26367 (17)	0.0359 (7)
H34A	0.3481	0.4678	0.2250	0.043*
C35	0.33984 (14)	0.3497 (2)	0.26423 (16)	0.0336 (7)
H35A	0.2985	0.3406	0.2256	0.040*
C36	0.37176 (13)	0.28682 (19)	0.32289 (15)	0.0278 (6)
C37	0.46425 (16)	0.5222 (2)	0.3187 (2)	0.0464 (8)
H37A	0.5077	0.5119	0.3508	0.070*
H37B	0.4547	0.5745	0.3362	0.070*
H37C	0.4510	0.5329	0.2682	0.070*
C41	0.34431 (13)	0.01434 (19)	0.34091 (16)	0.0304 (6)
H41A	0.3674	−0.0339	0.3763	0.046*
H41B	0.3359	−0.0011	0.2933	0.046*
H41C	0.3064	0.0224	0.3348	0.046*
C42	0.38056 (12)	0.10112 (18)	0.36956 (15)	0.0256 (6)
C51	0.68030 (15)	0.3592 (2)	0.43581 (19)	0.0455 (8)
H51A	0.6921	0.4068	0.4720	0.068*
H51B	0.6849	0.3804	0.3983	0.068*
H51C	0.7059	0.3068	0.4607	0.068*
C52	0.61384 (14)	0.3336 (2)	0.39858 (17)	0.0337 (7)

H52A	0.6092	0.3133	0.4368	0.040*
H52B	0.5883	0.3871	0.3745	0.040*
C53	0.59212 (15)	0.2588 (2)	0.34048 (17)	0.0363 (7)
H53A	0.6235	0.2122	0.3602	0.044*
H53B	0.5855	0.2840	0.2956	0.044*
C54	0.53288 (13)	0.21578 (19)	0.31999 (15)	0.0289 (6)
H54A	0.5051	0.2642	0.3119	0.035*
H54B	0.5420	0.1797	0.3624	0.035*
C55	0.31405 (18)	0.0422 (3)	0.1459 (2)	0.0661 (11)
H55A	0.2820	0.0107	0.1438	0.099*
H55B	0.3003	0.0574	0.0958	0.099*
H55C	0.3243	0.0972	0.1748	0.099*
C56	0.36886 (16)	−0.0172 (2)	0.18187 (19)	0.0450 (8)
H56A	0.3578	−0.0732	0.1531	0.054*
H56B	0.3819	−0.0332	0.2320	0.054*
C57	0.42201 (15)	0.0271 (2)	0.18751 (18)	0.0384 (7)
H57A	0.4069	0.0578	0.1405	0.046*
H57B	0.4507	−0.0197	0.1956	0.046*
C58	0.45487 (14)	0.09565 (19)	0.25166 (16)	0.0302 (6)
H58A	0.4247	0.1346	0.2490	0.036*
H58B	0.4766	0.0630	0.2991	0.036*
C61	0.1622 (2)	0.2502 (4)	0.2518 (2)	0.0830 (15)
H61A	0.1721	0.2621	0.2173	0.124*
H61B	0.1229	0.2761	0.2324	0.124*
H61C	0.1611	0.1855	0.2577	0.124*
C62	0.2073 (3)	0.2900 (4)	0.3223 (3)	0.106 (2)
C63	0.18371 (17)	0.6328 (3)	0.0028 (2)	0.0598 (10)
H63A	0.1721	0.6895	0.0129	0.090*
H63B	0.1487	0.5934	−0.0250	0.090*
H63C	0.1990	0.6443	−0.0261	0.090*
C64	0.22959 (19)	0.5909 (3)	0.0711 (3)	0.0625 (11)

Atomic displacement parameters (Å^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
V1	0.0260 (3)	0.0229 (3)	0.0141 (3)	0.0032 (3)	0.0117 (3)	0.0016 (2)
Si1	0.0233 (4)	0.0242 (4)	0.0162 (3)	0.0026 (3)	0.0117 (3)	0.0012 (3)
S1	0.0306 (4)	0.0265 (3)	0.0223 (3)	0.0039 (3)	0.0181 (3)	0.0017 (3)
S2	0.0351 (4)	0.0260 (4)	0.0160 (3)	0.0032 (3)	0.0129 (3)	0.0003 (3)
S3	0.0243 (4)	0.0312 (4)	0.0345 (4)	0.0040 (3)	0.0108 (3)	0.0033 (3)
N1	0.0252 (12)	0.0269 (12)	0.0144 (10)	0.0021 (9)	0.0116 (10)	0.0003 (9)
N2	0.0369 (19)	0.0229 (16)	0.0215 (16)	0.000	0.0198 (15)	0.000
N3	0.119 (5)	0.178 (6)	0.110 (4)	0.088 (4)	−0.009 (4)	−0.069 (4)
N4	0.099 (3)	0.198 (6)	0.102 (4)	0.087 (4)	0.073 (3)	0.093 (4)
C11	0.0256 (14)	0.0292 (14)	0.0162 (13)	0.0025 (11)	0.0124 (11)	0.0034 (11)
C12	0.0289 (15)	0.0309 (15)	0.0209 (13)	0.0012 (11)	0.0144 (12)	0.0000 (11)
C13	0.0311 (15)	0.0346 (16)	0.0215 (14)	−0.0039 (12)	0.0151 (13)	−0.0008 (12)
C14	0.0260 (15)	0.0408 (17)	0.0239 (14)	−0.0023 (12)	0.0126 (13)	0.0037 (13)

C15	0.0288 (15)	0.0338 (16)	0.0263 (15)	0.0077 (12)	0.0160 (13)	0.0083 (12)
C16	0.0266 (14)	0.0298 (14)	0.0160 (13)	0.0022 (11)	0.0126 (12)	0.0041 (11)
C17	0.0369 (18)	0.0411 (18)	0.0369 (18)	−0.0092 (14)	0.0199 (15)	−0.0101 (15)
C21	0.0239 (14)	0.0263 (14)	0.0209 (13)	−0.0046 (10)	0.0141 (12)	−0.0034 (11)
C22	0.0271 (14)	0.0278 (14)	0.0275 (15)	−0.0012 (11)	0.0162 (13)	−0.0039 (12)
C23	0.0341 (16)	0.0327 (16)	0.0370 (17)	−0.0072 (12)	0.0253 (15)	−0.0137 (13)
C24	0.0466 (19)	0.0355 (16)	0.0354 (17)	−0.0084 (13)	0.0319 (16)	−0.0125 (13)
C25	0.0436 (17)	0.0271 (15)	0.0258 (15)	−0.0093 (12)	0.0229 (14)	−0.0054 (12)
C26	0.0322 (15)	0.0238 (14)	0.0238 (14)	−0.0052 (11)	0.0186 (13)	−0.0060 (11)
C27	0.050 (2)	0.050 (2)	0.056 (2)	0.0040 (16)	0.036 (2)	−0.0153 (18)
C31	0.0277 (14)	0.0261 (14)	0.0188 (13)	0.0050 (11)	0.0149 (12)	0.0001 (11)
C32	0.0318 (15)	0.0284 (15)	0.0248 (14)	0.0047 (11)	0.0179 (13)	0.0002 (11)
C33	0.0439 (18)	0.0263 (15)	0.0272 (15)	0.0069 (13)	0.0215 (14)	0.0028 (12)
C34	0.0473 (19)	0.0285 (16)	0.0236 (15)	0.0116 (13)	0.0164 (15)	0.0064 (12)
C35	0.0324 (16)	0.0293 (16)	0.0239 (15)	0.0079 (12)	0.0084 (13)	0.0001 (12)
C36	0.0319 (15)	0.0270 (14)	0.0232 (14)	0.0052 (11)	0.0156 (13)	0.0004 (11)
C37	0.052 (2)	0.0323 (17)	0.051 (2)	0.0036 (15)	0.0284 (18)	0.0137 (16)
C41	0.0319 (16)	0.0314 (16)	0.0246 (15)	−0.0008 (12)	0.0149 (13)	−0.0018 (12)
C42	0.0286 (15)	0.0304 (15)	0.0192 (13)	0.0030 (11)	0.0149 (12)	−0.0006 (11)
C51	0.047 (2)	0.0407 (19)	0.0371 (18)	0.0006 (15)	0.0188 (17)	0.0009 (15)
C52	0.0411 (18)	0.0249 (15)	0.0301 (16)	−0.0016 (12)	0.0184 (15)	−0.0026 (12)
C53	0.0438 (18)	0.0357 (17)	0.0312 (16)	−0.0070 (13)	0.0233 (15)	−0.0050 (13)
C54	0.0394 (17)	0.0278 (15)	0.0221 (14)	0.0005 (12)	0.0196 (13)	−0.0033 (11)
C55	0.049 (2)	0.084 (3)	0.060 (3)	−0.003 (2)	0.030 (2)	0.006 (2)
C56	0.052 (2)	0.051 (2)	0.0305 (17)	−0.0151 (16)	0.0235 (17)	−0.0018 (15)
C57	0.053 (2)	0.0337 (16)	0.0347 (17)	−0.0107 (14)	0.0294 (17)	−0.0064 (14)
C58	0.0423 (17)	0.0268 (14)	0.0285 (15)	−0.0020 (12)	0.0248 (14)	0.0015 (12)
C61	0.064 (3)	0.118 (4)	0.039 (2)	0.026 (3)	0.015 (2)	−0.011 (3)
C62	0.080 (4)	0.124 (5)	0.062 (3)	0.056 (3)	0.014 (3)	−0.027 (3)
C63	0.049 (2)	0.065 (3)	0.057 (2)	0.0072 (19)	0.027 (2)	0.011 (2)
C64	0.058 (3)	0.081 (3)	0.061 (3)	0.027 (2)	0.042 (2)	0.027 (2)

Geometric parameters (Å, °)

V1—N1^{i}	2.188 (2)	C31—C32	1.404 (4)
V1—N1	2.188 (2)	C32—C33	1.386 (4)
V1—S1^{i}	2.4161 (6)	C32—H32A	0.9300
V1—S1	2.4161 (6)	C33—C34	1.391 (4)
V1—S2	2.4617 (7)	C33—C37	1.508 (4)
V1—S2^{i}	2.4617 (7)	C34—C35	1.378 (4)
Si1—N1	1.788 (2)	C34—H34A	0.9300
Si1—C21	1.855 (3)	C35—C36	1.395 (4)
Si1—C11	1.868 (3)	C35—H35A	0.9300
Si1—C31	1.874 (3)	C37—H37A	0.9600
S1—C16	1.767 (3)	C37—H37B	0.9600
S2—C26	1.771 (3)	C37—H37C	0.9600
S3—C36	1.768 (3)	C41—C42	1.498 (4)
S3—C42	1.781 (3)	C41—H41A	0.9600

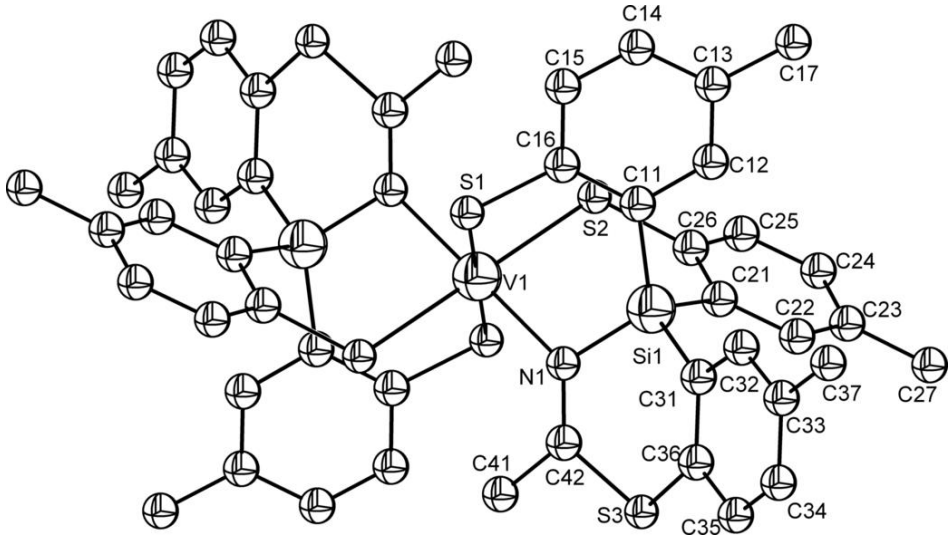
N1—C42	1.292 (3)	C41—H41B	0.9600
N2—C58	1.516 (3)	C41—H41C	0.9600
N2—C58^{ii}	1.516 (3)	C51—C52	1.518 (4)
N2—C54	1.532 (3)	C51—H51A	0.9600
N2—C54^{ii}	1.532 (3)	C51—H51B	0.9600
N3—C62	1.148 (6)	C51—H51C	0.9600
N4—C64	1.131 (5)	C52—C53	1.515 (4)
C11—C12	1.404 (4)	C52—H52A	0.9700
C11—C16	1.407 (4)	C52—H52B	0.9700
C12—C13	1.390 (4)	C53—C54	1.522 (4)
C12—H12A	0.9300	C53—H53A	0.9700
C13—C14	1.400 (4)	C53—H53B	0.9700
C13—C17	1.511 (4)	C54—H54A	0.9700
C14—C15	1.386 (4)	C54—H54B	0.9700
C14—H14A	0.9300	C55—C56	1.482 (5)
C15—C16	1.402 (4)	C55—H55A	0.9600
C15—H15A	0.9300	C55—H55B	0.9600
C17—H17A	0.9600	C55—H55C	0.9600
C17—H17B	0.9600	C56—C57	1.515 (4)
C17—H17C	0.9600	C56—H56A	0.9700
C21—C22	1.399 (4)	C56—H56B	0.9700
C21—C26	1.407 (4)	C57—C58	1.520 (4)
C22—C23	1.395 (4)	C57—H57A	0.9700
C22—H22A	0.9300	C57—H57B	0.9700
C23—C24	1.387 (4)	C58—H58A	0.9700
C23—C27	1.504 (4)	C58—H58B	0.9700
C24—C25	1.389 (4)	C61—C62	1.413 (7)
C24—H24A	0.9300	C61—H61A	0.9600
C25—C26	1.393 (4)	C61—H61B	0.9600
C25—H25A	0.9300	C61—H61C	0.9600
C27—H27A	0.9600	C63—C64	1.404 (5)
C27—H27B	0.9600	C63—H63A	0.9600
C27—H27C	0.9600	C63—H63B	0.9600
C31—C36	1.393 (4)	C63—H63C	0.9600
N1^{i}—V1—N1	180.0	C32—C33—C37	121.5 (3)
N1^{i}—V1—S1^{i}	86.54 (6)	C34—C33—C37	120.8 (3)
N1—V1—S1^{i}	93.46 (6)	C35—C34—C33	121.1 (3)
N1^{i}—V1—S1	93.46 (6)	C35—C34—H34A	119.4
N1—V1—S1	86.54 (6)	C33—C34—H34A	119.4
S1^{i}—V1—S1	180.0	C34—C35—C36	119.7 (3)
N1^{i}—V1—S2	90.53 (6)	C34—C35—H35A	120.1
N1—V1—S2	89.47 (6)	C36—C35—H35A	120.1
S1^{i}—V1—S2	81.86 (2)	C31—C36—C35	121.5 (3)
S1—V1—S2	98.14 (2)	C31—C36—S3	123.2 (2)
N1^{i}—V1—S2^{i}	89.47 (6)	C35—C36—S3	115.2 (2)
N1—V1—S2^{i}	90.53 (6)	C33—C37—H37A	109.5

S1^{i}—V1—S2^{i}	98.14 (2)	C33—C37—H37B	109.5
S1—V1—S2^{i}	81.86 (2)	H37A—C37—H37B	109.5
S2—V1—S2^{i}	180.0	C33—C37—H37C	109.5
N1—Si1—C21	103.98 (11)	H37A—C37—H37C	109.5
N1—Si1—C11	119.77 (11)	H37B—C37—H37C	109.5
C21—Si1—C11	107.92 (12)	C42—C41—H41A	109.5
N1—Si1—C31	106.07 (11)	C42—C41—H41B	109.5
C21—Si1—C31	110.86 (12)	H41A—C41—H41B	109.5
C11—Si1—C31	108.12 (12)	C42—C41—H41C	109.5
C16—S1—V1	109.28 (8)	H41A—C41—H41C	109.5
C26—S2—V1	117.31 (9)	H41B—C41—H41C	109.5
C36—S3—C42	107.89 (13)	N1—C42—C41	126.0 (2)
C42—N1—Si1	121.20 (19)	N1—C42—S3	127.1 (2)
C42—N1—V1	127.58 (18)	C41—C42—S3	106.85 (19)
Si1—N1—V1	109.60 (11)	C52—C51—H51A	109.5
C58—N2—C58^{ii}	110.3 (3)	C52—C51—H51B	109.5
C58—N2—C54	107.73 (15)	H51A—C51—H51B	109.5
C58^{ii}—N2—C54	111.25 (15)	C52—C51—H51C	109.5
C58—N2—C54^{ii}	111.25 (15)	H51A—C51—H51C	109.5
C58^{ii}—N2—C54^{ii}	107.73 (15)	H51B—C51—H51C	109.5
C54—N2—C54^{ii}	108.6 (3)	C53—C52—C51	112.2 (3)
C12—C11—C16	118.1 (2)	C53—C52—H52A	109.2
C12—C11—Si1	115.51 (19)	C51—C52—H52A	109.2
C16—C11—Si1	126.4 (2)	C53—C52—H52B	109.2
C13—C12—C11	123.3 (3)	C51—C52—H52B	109.2
C13—C12—H12A	118.4	H52A—C52—H52B	107.9
C11—C12—H12A	118.4	C52—C53—C54	111.3 (2)
C12—C13—C14	117.4 (3)	C52—C53—H53A	109.4
C12—C13—C17	121.0 (3)	C54—C53—H53A	109.4
C14—C13—C17	121.5 (3)	C52—C53—H53B	109.4
C15—C14—C13	120.8 (3)	C54—C53—H53B	109.4
C15—C14—H14A	119.6	H53A—C53—H53B	108.0
C13—C14—H14A	119.6	C53—C54—N2	114.9 (2)
C14—C15—C16	121.3 (3)	C53—C54—H54A	108.5
C14—C15—H15A	119.3	N2—C54—H54A	108.5
C16—C15—H15A	119.3	C53—C54—H54B	108.5
C15—C16—C11	119.1 (3)	N2—C54—H54B	108.5
C15—C16—S1	120.1 (2)	H54A—C54—H54B	107.5
C11—C16—S1	120.8 (2)	C56—C55—H55A	109.5
C13—C17—H17A	109.5	C56—C55—H55B	109.5
C13—C17—H17B	109.5	H55A—C55—H55B	109.5
H17A—C17—H17B	109.5	C56—C55—H55C	109.5
C13—C17—H17C	109.5	H55A—C55—H55C	109.5
H17A—C17—H17C	109.5	H55B—C55—H55C	109.5
H17B—C17—H17C	109.5	C55—C56—C57	113.2 (3)
C22—C21—C26	119.2 (2)	C55—C56—H56A	108.9
C22—C21—Si1	124.8 (2)	C57—C56—H56A	108.9

C26—C21—Si1	115.95 (19)	C55—C56—H56B	108.9
C23—C22—C21	121.8 (3)	C57—C56—H56B	108.9
C23—C22—H22A	119.1	H56A—C56—H56B	107.7
C21—C22—H22A	119.1	C56—C57—C58	111.3 (3)
C24—C23—C22	118.0 (3)	C56—C57—H57A	109.4
C24—C23—C27	121.5 (3)	C58—C57—H57A	109.4
C22—C23—C27	120.5 (3)	C56—C57—H57B	109.4
C23—C24—C25	121.4 (3)	C58—C57—H57B	109.4
C23—C24—H24A	119.3	H57A—C57—H57B	108.0
C25—C24—H24A	119.3	N2—C58—C57	113.0 (2)
C24—C25—C26	120.6 (3)	N2—C58—H58A	109.0
C24—C25—H25A	119.7	C57—C58—H58A	109.0
C26—C25—H25A	119.7	N2—C58—H58B	109.0
C25—C26—C21	119.0 (2)	C57—C58—H58B	109.0
C25—C26—S2	119.4 (2)	H58A—C58—H58B	107.8
C21—C26—S2	121.55 (19)	C62—C61—H61A	109.5
C23—C27—H27A	109.5	C62—C61—H61B	109.5
C23—C27—H27B	109.5	H61A—C61—H61B	109.5
H27A—C27—H27B	109.5	C62—C61—H61C	109.5
C23—C27—H27C	109.5	H61A—C61—H61C	109.5
H27A—C27—H27C	109.5	H61B—C61—H61C	109.5
H27B—C27—H27C	109.5	N3—C62—C61	176.4 (9)
C36—C31—C32	116.4 (2)	C64—C63—H63A	109.5
C36—C31—Si1	119.8 (2)	C64—C63—H63B	109.5
C32—C31—Si1	123.7 (2)	H63A—C63—H63B	109.5
C33—C32—C31	123.5 (3)	C64—C63—H63C	109.5
C33—C32—H32A	118.3	H63A—C63—H63C	109.5
C31—C32—H32A	118.3	H63B—C63—H63C	109.5
C32—C33—C34	117.7 (3)	N4—C64—C63	178.3 (5)

Symmetry codes: (i) −*x*+1, −*y*, −*z*+1; (ii) −*x*+1, *y*, −*z*+1/2.

Fig. 1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C41
C42
S3
C35
C34

Fig. 2

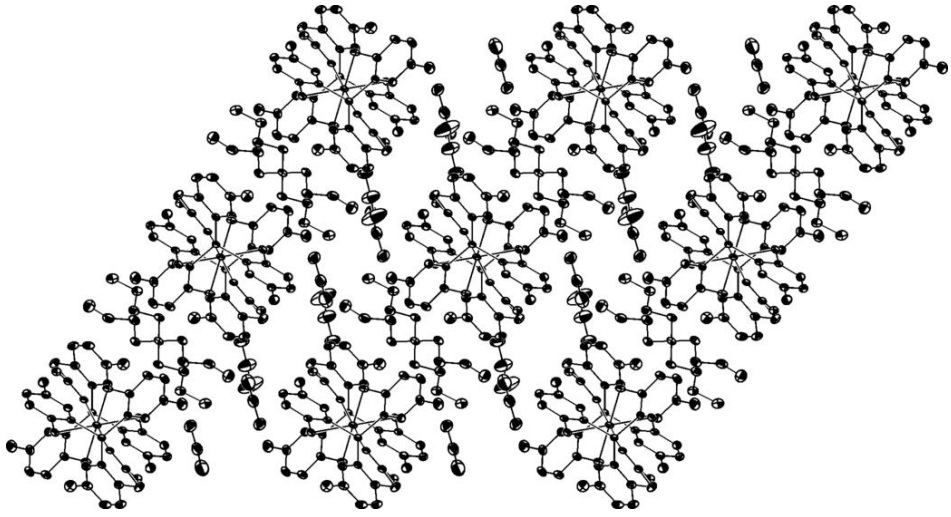
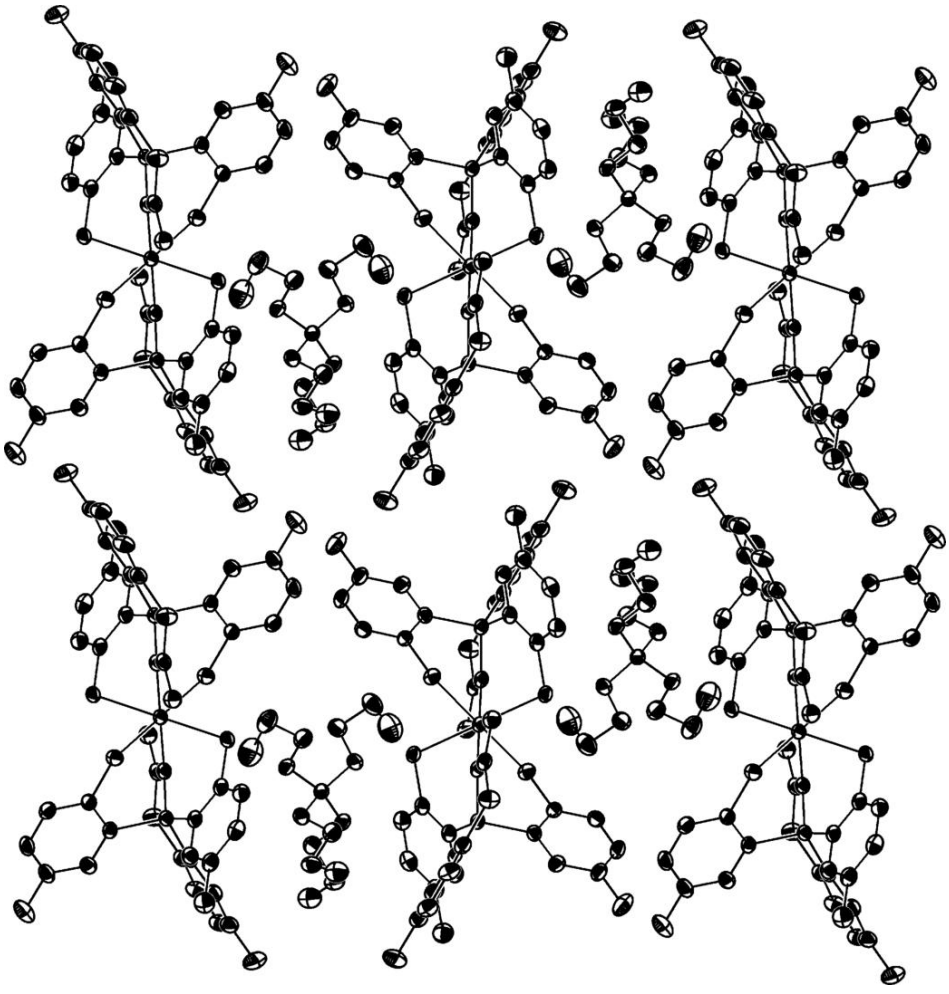


Fig. 3



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(1*R**,2*R**)-1-(4-Chlorophenyl)-4-dimethylamino-1-(3-methoxy-2-naphthyl)-2-(1-naphthyl)butan-2-ol

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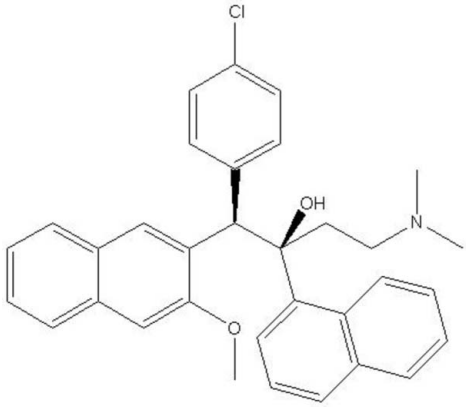
Key indicators: single-crystal X-ray study; T = 116 K; mean σ(C–C) = 0.002 Å; R factor = 0.036; wR factor = 0.099; data-to-parameter ratio = 13.5.

In the title compound, $C_{33}H_{32}ClNO_2$, the benzene ring is oriented at dihedral angles of 6.23 (5) and 66.44 (5)° with respect to the two naphthalene ring systems. An intramolecular O—H···N hydrogen bond between the hydroxy H atom and the amine N atom generates an S(6) ring.

Related literature

For general background and the synthesis of diarylquinoline anti-tuberculosis drugs, see: Cohen (2004), Andries *et al.* (2005); Guillemont *et al.* (2004).



Experimental

Crystal data

$C_{33}H_{32}ClNO_2$
M_r = 510.05
Monoclinic, $P2_1/c$
a = 18.712 (5) Å
b = 9.135 (2) Å
c = 16.369 (4) Å
β = 111.991 (4)°
V = 2594.2 (11) Å^3
Z = 4
Mo $K\alpha$ radiation
μ = 0.18 mm^{-1}
T = 116 K
0.20 × 0.16 × 0.12 mm

Data collection

Rigaku Saturn CCD diffractometer
Absorption correction: multi-scan (*CrystalClear*; Rigaku/MSC, 2005)
T_{min} = 0.965, T_{max} = 0.979
18901 measured reflections
4573 independent reflections
3918 reflections with $I > 2\sigma(I)$
R_{int} = 0.032

Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.036
$wR(F^2)$ = 0.099
S = 1.09
4573 reflections
338 parameters
H-atom parameters constrained
$\Delta\rho_{max}$ = 0.18 e Å^{-3}
$\Delta\rho_{min}$ = −0.31 e Å^{-3}

Table 1
Hydrogen-bond geometry (Å, °).

D—H···A	D—H	H···A	D···A	D—H···A
O2—H2···N1	0.82	1.93	2.6995 (17)	157

Data collection: *CrystalClear* (Rigaku/MSC, 2005); cell refinement: *CrystalClear*; data reduction: *CrystalClear*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *SHELXTL* (Sheldrick, 2008); software used to prepare material for publication: *CrystalStructure* (Rigaku/MSC, 2005).

This work was supported by the 863 Program (2006 A A020601)

Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: HB5430).

References

Andries, K., Verhasselt, P. & Guillemont, J. (2005). *Science*, **307**, 223–227.
Cohen, J. (2004). *Science*, **306**, 1872.
Guillemont, J., Van Gestel, J., Venet, M., Poignet, H., Decrane, L. & Vernier, D. (2004). WO Patent WO2004011436.
Rigaku/MSC (2005). *CrystalClear*. Rigaku/MSC, The Woodlands, Texas, USA.
Sheldrick, G. M. (2008). *Acta Cryst.* A**64**, 112–122.

supplementary materials

Acta Cryst. (2010). E**66**, o1571 [**doi:10.1107/S160053681001891X**]

(1*R**,2*R**)-1-(4-Chlorophenyl)-4-dimethylamino-1-(3-methoxy-2-naphthyl)-2-(1-naphthyl)butan-2-ol

P. Liu, J. Xiao, W. Zhong, S. Li and X. Yang

Comment

The compound (1*R*,2S)-1-(6-bromo-2-methoxyquinolin-3-yl)-4-(dimethylamino)-2-(naphthalene- 1-yl)-1-phenylbutan-2-ol, is a promising drug against tuberculosis (Andries *et al.*, 2005; Cohen, 2004 and Guillemont *et al.* 2004). We modified this compound in order to get some more efficient antituberculosis drugs. To characterize our product its single crystal structure was determined.

In the molecule of the title compound (Fig.1), the dihedral angle between the naphthalene ring (C20—C29) and the benzene ring (C13—C18) amount to 6.232 (46)° whereas the other naphthalene ring (C2—C10) is oriented with respect to the benzene ring at a dihedral angle of 66.438 (51)°. In the structure an intramolecular O—H···N hydrogen bond is found (Tab. 1).

Experimental

n-BuLi (2.5M in hexanes, 4 ml, 10 mmol) was added slowly at 233 K under N_2 to a solution of diisopropylamine (1.4 ml, 10 mmol) in THF (15 ml). The mixture was stirred at 233k for 30 min, then cooled to 195 K. Afterwards a solution of 2-(4-chlorobenzyl)-3-methoxynaphthalene (2.59 g, 9.2 mmol) in THF (20 ml) was added slowly. The mixture was stirred at 195 K for about 40 min and then a solution of 3-(dimethylamino)-1-(naphthalen-1-yl)propan-1-one (2.9 g, 12.8 mmol) in THF (20 ml) was added slowly. The mixture was stirred at 195 K for 8 h, hydrolyzed with ice water at 233 K and extracted with ethyl acetate. The organic layer was separated, dried over $MgSO_4$, filtered and the solvent was evaporated. The residue was purified by column chromatography over silica gel (eluent: petroleum ether/ethyl acetate, 50/1). Two fractions were collected (Guillemont *et al.*, 2004). On evaporation of the solvent (petroleum ether/ethyl acetate, 50/1) from fraction at room temperature in air colourless prisms of (I) were obtained.

Refinement

All H atoms were positioned with ideal geometry (O—H H atoms allowed to rotate but not to tip) and with d(C—H)=0.93 Å for aromatic, 0.98 Å for CH, 0.97 Å for CH_2 and 0.96 Å for CH_3 atoms and were refined with Uiso(H) = 1.2 Ueq(C) for CH and CH_2 H atoms and Uiso(H) = 1.5 Ueq(C) for CH_3 and O—H H atoms.

Figures

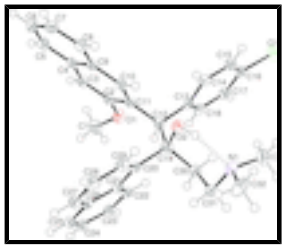


Fig. 1. Ellipsoid plot

(1*R,2*R**)-1-(4-Chlorophenyl)-4-dimethylamino- 1-(3-methoxy-2-naphthyl)-2-(1-naphthyl)butan-2-ol**

Crystal data

$C_{33}H_{32}ClNO_2$	$F(000) = 1080$
$M_r = 510.05$	$D_x = 1.306$ Mg m^{-3}
Monoclinic, $P2_1/c$	Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å
Hall symbol: -P 2ybc	Cell parameters from 8940 reflections
$a = 18.712$ (5) Å	$\theta = 2.2$–$27.9°$
$b = 9.135$ (2) Å	$\mu = 0.18$ mm^{-1}
$c = 16.369$ (4) Å	$T = 116$ K
$\beta = 111.991$ (4)°	Prism, colorless
$V = 2594.2$ (11) Å^3	0.20 × 0.16 × 0.12 mm
$Z = 4$	

Data collection

Rigaku Saturn CCD diffractometer	4573 independent reflections
Radiation source: rotating anode	3918 reflections with $I > 2\sigma(I)$
multilayer	$R_{int} = 0.032$
Detector resolution: 14.63 pixels mm^{-1}	$\theta_{max} = 25.0°$, $\theta_{min} = 2.4°$
ω and φ scans	$h = -19 \rightarrow 22$
Absorption correction: multi-scan (*CrystalClear*; Rigaku/MSC, 2005)	$k = -10 \rightarrow 10$
$T_{min} = 0.965$, $T_{max} = 0.979$	$l = -19 \rightarrow 19$
18901 measured reflections	

Refinement

Refinement on F^2	Primary atom site location: structure-invariant direct methods
Least-squares matrix: full	Secondary atom site location: difference Fourier map
$R[F^2 > 2\sigma(F^2)] = 0.036$	Hydrogen site location: inferred from neighbouring sites
$wR(F^2) = 0.099$	H-atom parameters constrained
$S = 1.09$	$w = 1/[\sigma^2(F_o^2) + (0.0587P)^2 + 0.0772P]$

	where $P = (F_o^2 + 2F_c^2)/3$
4573 reflections	$(\Delta/\sigma)_{max} = 0.001$
338 parameters	$\Delta\rho_{max} = 0.18$ e Å^{-3}
0 restraints	$\Delta\rho_{min} = -0.31$ e Å^{-3}

Special details

Geometry. All esds (except the esd in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell esds are taken into account individually in the estimation of esds in distances, angles and torsion angles; correlations between esds in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell esds is used for estimating esds involving l.s. planes.

Refinement. Refinement of F^2 against ALL reflections. The weighted *R*-factor wR and goodness of fit *S* are based on F^2, conventional *R*-factors *R* are based on *F*, with *F* set to zero for negative F^2. The threshold expression of $F^2 > \sigma(F^2)$ is used only for calculating *R*-factors(gt) etc. and is not relevant to the choice of reflections for refinement. *R*-factors based on F^2 are statistically about twice as large as those based on *F*, and *R*- factors based on ALL data will be even larger.

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å^2)

	x	*y*	*z*	U_{iso}*/U_{eq}
Cl1	0.08594 (2)	−0.07359 (5)	0.46621 (2)	0.03327 (14)
O1	0.37601 (6)	0.47214 (13)	0.67039 (6)	0.0280 (3)
O2	0.15042 (6)	0.45626 (11)	0.76790 (6)	0.0224 (2)
H2	0.1037	0.4674	0.7520	0.034*
N1	0.00317 (7)	0.54248 (15)	0.68199 (8)	0.0262 (3)
C1	0.43816 (10)	0.55500 (19)	0.66354 (11)	0.0350 (4)
H1A	0.4497	0.6357	0.7040	0.053*
H1B	0.4238	0.5914	0.6045	0.053*
H1C	0.4828	0.4936	0.6775	0.053*
C2	0.38276 (8)	0.42853 (16)	0.75343 (9)	0.0213 (3)
C3	0.45183 (8)	0.39820 (17)	0.81939 (9)	0.0234 (3)
H3	0.4971	0.4067	0.8088	0.028*
C4	0.45519 (8)	0.35391 (16)	0.90395 (9)	0.0220 (3)
C5	0.52573 (9)	0.32564 (17)	0.97478 (10)	0.0269 (4)
H5	0.5719	0.3335	0.9660	0.032*
C6	0.52683 (9)	0.28711 (18)	1.05574 (10)	0.0294 (4)
H6	0.5736	0.2686	1.1015	0.035*
C7	0.45778 (9)	0.27531 (17)	1.07038 (10)	0.0287 (4)
H7	0.4590	0.2499	1.1259	0.034*
C8	0.38864 (9)	0.30102 (17)	1.00330 (10)	0.0252 (4)
H8	0.3432	0.2918	1.0136	0.030*
C9	0.38510 (8)	0.34155 (16)	0.91827 (9)	0.0212 (3)
C10	0.31462 (8)	0.37265 (16)	0.84820 (9)	0.0211 (3)
H10	0.2688	0.3636	0.8577	0.025*
C11	0.31159 (8)	0.41579 (15)	0.76655 (9)	0.0192 (3)
C12	0.23748 (8)	0.45229 (16)	0.69006 (9)	0.0191 (3)
H12	0.2530	0.5143	0.6507	0.023*
C13	0.20123 (8)	0.31600 (16)	0.63590 (9)	0.0190 (3)

C14	0.17019 (8)	0.20240 (17)	0.66875 (9)	0.0222 (3)
H14	0.1730	0.2070	0.7266	0.027*
C15	0.13521 (8)	0.08287 (17)	0.61745 (9)	0.0237 (3)
H15	0.1140	0.0087	0.6402	0.028*
C16	0.13221 (8)	0.07529 (17)	0.53164 (9)	0.0227 (3)
C17	0.16557 (9)	0.18162 (17)	0.49810 (9)	0.0250 (4)
H17	0.1655	0.1735	0.4414	0.030*
C18	0.19958 (8)	0.30198 (16)	0.55077 (9)	0.0225 (3)
H18	0.2217	0.3748	0.5282	0.027*
C19	0.17914 (8)	0.54677 (16)	0.71574 (9)	0.0205 (3)
C20	0.21941 (8)	0.68257 (16)	0.76984 (9)	0.0208 (3)
C21	0.26013 (8)	0.79135 (16)	0.73961 (9)	0.0209 (3)
C22	0.26584 (8)	0.79312 (16)	0.65518 (9)	0.0214 (3)
H22	0.2414	0.7199	0.6149	0.026*
C23	0.30608 (8)	0.89908 (17)	0.63137 (10)	0.0247 (4)
H23	0.3079	0.8969	0.5754	0.030*
C24	0.34450 (9)	1.01083 (17)	0.69010 (11)	0.0281 (4)
H24	0.3725	1.0813	0.6738	0.034*
C25	0.34029 (8)	1.01492 (18)	0.77106 (10)	0.0271 (4)
H25	0.3658	1.0891	0.8100	0.033*
C26	0.29797 (8)	0.90910 (17)	0.79797 (9)	0.0218 (3)
C27	0.29246 (9)	0.92087 (17)	0.88158 (10)	0.0278 (4)
H27	0.3165	0.9979	0.9189	0.033*
C28	0.25203 (9)	0.81963 (18)	0.90722 (10)	0.0293 (4)
H28	0.2475	0.8289	0.9617	0.035*
C29	0.21699 (9)	0.70118 (17)	0.85237 (9)	0.0249 (4)
H29	0.1910	0.6321	0.8725	0.030*
C30	0.11066 (8)	0.59297 (17)	0.63159 (9)	0.0227 (3)
H30A	0.1286	0.6659	0.6006	0.027*
H30B	0.0936	0.5085	0.5933	0.027*
C31	0.04188 (9)	0.65525 (17)	0.64869 (10)	0.0265 (4)
H31A	0.0593	0.7339	0.6914	0.032*
H31B	0.0053	0.6959	0.5944	0.032*
C32	−0.04747 (10)	0.6089 (2)	0.72092 (11)	0.0421 (5)
H32A	−0.0868	0.6645	0.6769	0.063*
H32B	−0.0180	0.6725	0.7682	0.063*
H32C	−0.0710	0.5336	0.7433	0.063*
C33	−0.04136 (10)	0.44129 (19)	0.61219 (11)	0.0365 (4)
H33A	−0.0670	0.3714	0.6355	0.055*
H33B	−0.0073	0.3910	0.5900	0.055*
H33C	−0.0789	0.4951	0.5653	0.055*

Atomic displacement parameters (Å^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Cl1	0.0334 (2)	0.0323 (3)	0.0330 (2)	−0.00749 (18)	0.01111 (19)	−0.01273 (17)
O1	0.0230 (6)	0.0368 (7)	0.0278 (6)	−0.0038 (5)	0.0136 (5)	0.0018 (5)
O2	0.0187 (5)	0.0247 (6)	0.0265 (5)	0.0016 (5)	0.0115 (5)	0.0046 (4)

N1	0.0195 (7)	0.0352 (8)	0.0249 (7)	0.0038 (6)	0.0096 (6)	0.0013 (6)
C1	0.0330 (10)	0.0371 (11)	0.0395 (9)	−0.0092 (8)	0.0187 (8)	0.0022 (8)
C2	0.0217 (8)	0.0184 (9)	0.0253 (8)	−0.0019 (6)	0.0105 (7)	−0.0033 (6)
C3	0.0173 (8)	0.0223 (9)	0.0327 (8)	−0.0017 (6)	0.0119 (7)	−0.0057 (7)
C4	0.0217 (8)	0.0162 (8)	0.0275 (8)	0.0002 (6)	0.0085 (7)	−0.0060 (6)
C5	0.0209 (8)	0.0237 (9)	0.0357 (9)	0.0008 (7)	0.0101 (7)	−0.0085 (7)
C6	0.0241 (9)	0.0263 (10)	0.0287 (8)	0.0061 (7)	−0.0006 (7)	−0.0041 (7)
C7	0.0333 (9)	0.0247 (9)	0.0253 (8)	0.0036 (7)	0.0077 (7)	0.0000 (7)
C8	0.0251 (8)	0.0233 (9)	0.0281 (8)	−0.0012 (7)	0.0109 (7)	−0.0013 (7)
C9	0.0215 (8)	0.0157 (8)	0.0254 (8)	−0.0008 (6)	0.0076 (7)	−0.0036 (6)
C10	0.0187 (8)	0.0185 (8)	0.0266 (8)	−0.0007 (6)	0.0092 (7)	−0.0013 (6)
C11	0.0185 (8)	0.0147 (8)	0.0248 (7)	−0.0008 (6)	0.0086 (6)	−0.0036 (6)
C12	0.0183 (8)	0.0189 (8)	0.0219 (7)	−0.0003 (6)	0.0094 (6)	0.0019 (6)
C13	0.0142 (7)	0.0201 (8)	0.0217 (7)	0.0034 (6)	0.0057 (6)	0.0015 (6)
C14	0.0213 (8)	0.0248 (9)	0.0213 (7)	0.0007 (6)	0.0090 (6)	−0.0001 (6)
C15	0.0218 (8)	0.0218 (9)	0.0299 (8)	−0.0020 (6)	0.0127 (7)	0.0004 (6)
C16	0.0167 (8)	0.0240 (9)	0.0238 (7)	0.0025 (6)	0.0034 (6)	−0.0049 (6)
C17	0.0265 (9)	0.0279 (9)	0.0195 (7)	0.0046 (7)	0.0072 (7)	0.0009 (6)
C18	0.0225 (8)	0.0213 (9)	0.0251 (8)	0.0030 (6)	0.0104 (7)	0.0043 (6)
C19	0.0214 (8)	0.0196 (8)	0.0231 (7)	0.0004 (6)	0.0111 (6)	0.0028 (6)
C20	0.0187 (8)	0.0212 (9)	0.0220 (7)	0.0065 (6)	0.0071 (6)	0.0023 (6)
C21	0.0186 (8)	0.0187 (8)	0.0243 (7)	0.0052 (6)	0.0069 (6)	0.0016 (6)
C22	0.0217 (8)	0.0187 (9)	0.0240 (7)	0.0034 (6)	0.0088 (6)	0.0002 (6)
C23	0.0230 (8)	0.0249 (9)	0.0282 (8)	0.0027 (7)	0.0118 (7)	0.0024 (7)
C24	0.0242 (9)	0.0211 (9)	0.0423 (9)	−0.0001 (7)	0.0163 (7)	0.0043 (7)
C25	0.0210 (8)	0.0211 (9)	0.0350 (9)	0.0009 (7)	0.0056 (7)	−0.0028 (7)
C26	0.0177 (8)	0.0197 (9)	0.0248 (7)	0.0056 (6)	0.0044 (6)	0.0010 (6)
C27	0.0298 (9)	0.0235 (9)	0.0263 (8)	0.0047 (7)	0.0062 (7)	−0.0050 (7)
C28	0.0363 (10)	0.0305 (10)	0.0214 (8)	0.0076 (7)	0.0111 (7)	−0.0020 (7)
C29	0.0284 (9)	0.0239 (9)	0.0262 (8)	0.0035 (7)	0.0146 (7)	0.0021 (7)
C30	0.0215 (8)	0.0231 (9)	0.0243 (7)	0.0002 (6)	0.0097 (7)	0.0034 (6)
C31	0.0235 (8)	0.0235 (9)	0.0292 (8)	0.0051 (7)	0.0061 (7)	−0.0004 (7)
C32	0.0301 (10)	0.0687 (14)	0.0294 (9)	0.0167 (9)	0.0133 (8)	0.0060 (9)
C33	0.0287 (9)	0.0394 (11)	0.0402 (10)	−0.0052 (8)	0.0116 (8)	−0.0022 (8)

Geometric parameters (Å, °)

Cl1—C16	1.7469 (15)	C15—H15	0.9300
O1—C2	1.3761 (17)	C16—C17	1.375 (2)
O1—C1	1.4268 (18)	C17—C18	1.395 (2)
O2—C19	1.4299 (17)	C17—H17	0.9300
O2—H2	0.8200	C18—H18	0.9300
N1—C32	1.4576 (19)	C19—C20	1.546 (2)
N1—C33	1.463 (2)	C19—C30	1.548 (2)
N1—C31	1.476 (2)	C20—C29	1.379 (2)
C1—H1A	0.9600	C20—C21	1.447 (2)
C1—H1B	0.9600	C21—C22	1.4256 (19)
C1—H1C	0.9600	C21—C26	1.437 (2)
C2—C3	1.367 (2)	C22—C23	1.369 (2)

C2—C11	1.431 (2)	C22—H22	0.9300
C3—C4	1.421 (2)	C23—C24	1.402 (2)
C3—H3	0.9300	C23—H23	0.9300
C4—C5	1.417 (2)	C24—C25	1.357 (2)
C4—C9	1.421 (2)	C24—H24	0.9300
C5—C6	1.364 (2)	C25—C26	1.420 (2)
C5—H5	0.9300	C25—H25	0.9300
C6—C7	1.404 (2)	C26—C27	1.415 (2)
C6—H6	0.9300	C27—C28	1.357 (2)
C7—C8	1.368 (2)	C27—H27	0.9300
C7—H7	0.9300	C28—C29	1.402 (2)
C8—C9	1.418 (2)	C28—H28	0.9300
C8—H8	0.9300	C29—H29	0.9300
C9—C10	1.415 (2)	C30—C31	1.526 (2)
C10—C11	1.374 (2)	C30—H30A	0.9700
C10—H10	0.9300	C30—H30B	0.9700
C11—C12	1.517 (2)	C31—H31A	0.9700
C12—C13	1.532 (2)	C31—H31B	0.9700
C12—C19	1.567 (2)	C32—H32A	0.9600
C12—H12	0.9800	C32—H32B	0.9600
C13—C18	1.3881 (19)	C32—H32C	0.9600
C13—C14	1.392 (2)	C33—H33A	0.9600
C14—C15	1.383 (2)	C33—H33B	0.9600
C14—H14	0.9300	C33—H33C	0.9600
C15—C16	1.386 (2)		
C2—O1—C1	117.08 (12)	C13—C18—H18	119.1
C19—O2—H2	109.5	C17—C18—H18	119.1
C32—N1—C33	109.34 (13)	O2—C19—C20	109.47 (11)
C32—N1—C31	111.10 (14)	O2—C19—C30	108.55 (12)
C33—N1—C31	111.54 (12)	C20—C19—C30	110.76 (12)
O1—C1—H1A	109.5	O2—C19—C12	107.27 (11)
O1—C1—H1B	109.5	C20—C19—C12	110.87 (12)
H1A—C1—H1B	109.5	C30—C19—C12	109.82 (11)
O1—C1—H1C	109.5	C29—C20—C21	117.70 (14)
H1A—C1—H1C	109.5	C29—C20—C19	118.17 (13)
H1B—C1—H1C	109.5	C21—C20—C19	124.12 (12)
C3—C2—O1	123.29 (13)	C22—C21—C26	116.03 (13)
C3—C2—C11	121.53 (13)	C22—C21—C20	125.40 (13)
O1—C2—C11	115.18 (12)	C26—C21—C20	118.56 (13)
C2—C3—C4	120.75 (13)	C23—C22—C21	122.18 (14)
C2—C3—H3	119.6	C23—C22—H22	118.9
C4—C3—H3	119.6	C21—C22—H22	118.9
C5—C4—C9	119.03 (13)	C22—C23—C24	120.99 (14)
C5—C4—C3	122.48 (14)	C22—C23—H23	119.5
C9—C4—C3	118.46 (13)	C24—C23—H23	119.5
C6—C5—C4	120.84 (14)	C25—C24—C23	119.16 (15)
C6—C5—H5	119.6	C25—C24—H24	120.4
C4—C5—H5	119.6	C23—C24—H24	120.4
C5—C6—C7	120.38 (14)	C24—C25—C26	121.81 (15)

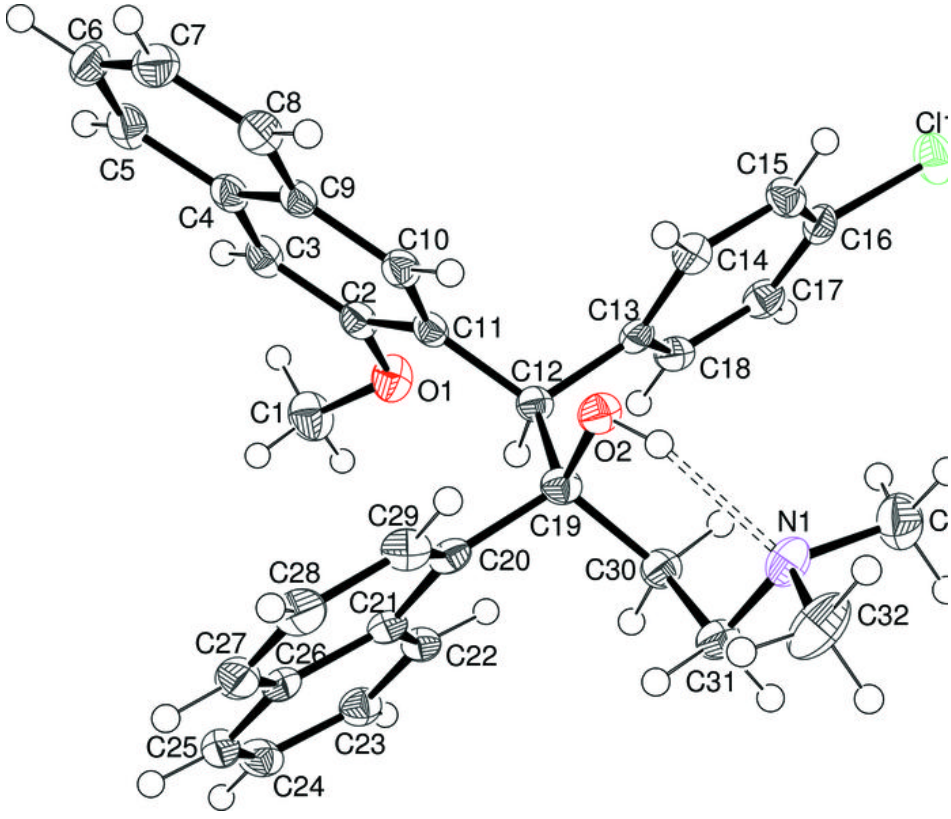
C5—C6—H6	119.8	C24—C25—H25	119.1
C7—C6—H6	119.8	C26—C25—H25	119.1
C8—C7—C6	120.28 (15)	C27—C26—C25	119.96 (14)
C8—C7—H7	119.9	C27—C26—C21	120.26 (14)
C6—C7—H7	119.9	C25—C26—C21	119.78 (13)
C7—C8—C9	121.03 (15)	C28—C27—C26	119.90 (15)
C7—C8—H8	119.5	C28—C27—H27	120.0
C9—C8—H8	119.5	C26—C27—H27	120.0
C10—C9—C8	122.33 (14)	C27—C28—C29	120.60 (14)
C10—C9—C4	119.22 (13)	C27—C28—H28	119.7
C8—C9—C4	118.43 (13)	C29—C28—H28	119.7
C11—C10—C9	122.17 (14)	C20—C29—C28	122.92 (14)
C11—C10—H10	118.9	C20—C29—H29	118.5
C9—C10—H10	118.9	C28—C29—H29	118.5
C10—C11—C2	117.87 (13)	C31—C30—C19	114.37 (12)
C10—C11—C12	123.90 (13)	C31—C30—H30A	108.7
C2—C11—C12	118.22 (12)	C19—C30—H30A	108.7
C11—C12—C13	111.65 (12)	C31—C30—H30B	108.7
C11—C12—C19	114.39 (12)	C19—C30—H30B	108.7
C13—C12—C19	113.64 (11)	H30A—C30—H30B	107.6
C11—C12—H12	105.4	N1—C31—C30	111.82 (13)
C13—C12—H12	105.4	N1—C31—H31A	109.3
C19—C12—H12	105.4	C30—C31—H31A	109.3
C18—C13—C14	117.61 (14)	N1—C31—H31B	109.3
C18—C13—C12	119.65 (13)	C30—C31—H31B	109.3
C14—C13—C12	122.73 (12)	H31A—C31—H31B	107.9
C15—C14—C13	121.66 (13)	N1—C32—H32A	109.5
C15—C14—H14	119.2	N1—C32—H32B	109.5
C13—C14—H14	119.2	H32A—C32—H32B	109.5
C14—C15—C16	119.00 (14)	N1—C32—H32C	109.5
C14—C15—H15	120.5	H32A—C32—H32C	109.5
C16—C15—H15	120.5	H32B—C32—H32C	109.5
C17—C16—C15	121.13 (14)	N1—C33—H33A	109.5
C17—C16—Cl1	119.99 (11)	N1—C33—H33B	109.5
C15—C16—Cl1	118.87 (12)	H33A—C33—H33B	109.5
C16—C17—C18	118.69 (13)	N1—C33—H33C	109.5
C16—C17—H17	120.7	H33A—C33—H33C	109.5
C18—C17—H17	120.7	H33B—C33—H33C	109.5
C13—C18—C17	121.78 (14)		
C1—O1—C2—C3	−31.0 (2)	C12—C13—C18—C17	−178.43 (13)
C1—O1—C2—C11	149.34 (14)	C16—C17—C18—C13	0.7 (2)
O1—C2—C3—C4	179.86 (13)	C11—C12—C19—O2	−69.07 (15)
C11—C2—C3—C4	−0.5 (2)	C13—C12—C19—O2	60.76 (15)
C2—C3—C4—C5	−178.10 (14)	C11—C12—C19—C20	50.41 (16)
C2—C3—C4—C9	0.1 (2)	C13—C12—C19—C20	−179.75 (11)
C9—C4—C5—C6	0.0 (2)	C11—C12—C19—C30	173.14 (12)
C3—C4—C5—C6	178.22 (15)	C13—C12—C19—C30	−57.03 (15)
C4—C5—C6—C7	−0.2 (2)	O2—C19—C20—C29	−4.46 (18)
C5—C6—C7—C8	0.6 (2)	C30—C19—C20—C29	115.19 (14)

C6—C7—C8—C9	−0.7 (2)	C12—C19—C20—C29	−122.62 (14)
C7—C8—C9—C10	−178.28 (15)	O2—C19—C20—C21	175.08 (12)
C7—C8—C9—C4	0.5 (2)	C30—C19—C20—C21	−65.26 (17)
C5—C4—C9—C10	178.70 (14)	C12—C19—C20—C21	56.92 (17)
C3—C4—C9—C10	0.4 (2)	C29—C20—C21—C22	−177.28 (14)
C5—C4—C9—C8	−0.1 (2)	C19—C20—C21—C22	3.2 (2)
C3—C4—C9—C8	−178.39 (14)	C29—C20—C21—C26	2.2 (2)
C8—C9—C10—C11	178.18 (14)	C19—C20—C21—C26	−177.31 (12)
C4—C9—C10—C11	−0.6 (2)	C26—C21—C22—C23	1.1 (2)
C9—C10—C11—C2	0.2 (2)	C20—C21—C22—C23	−179.36 (14)
C9—C10—C11—C12	−179.08 (13)	C21—C22—C23—C24	0.7 (2)
C3—C2—C11—C10	0.4 (2)	C22—C23—C24—C25	−1.3 (2)
O1—C2—C11—C10	−179.99 (13)	C23—C24—C25—C26	0.0 (2)
C3—C2—C11—C12	179.68 (13)	C24—C25—C26—C27	−177.40 (14)
O1—C2—C11—C12	−0.69 (19)	C24—C25—C26—C21	1.9 (2)
C10—C11—C12—C13	−87.94 (17)	C22—C21—C26—C27	176.94 (13)
C2—C11—C12—C13	92.80 (15)	C20—C21—C26—C27	−2.6 (2)
C10—C11—C12—C19	42.9 (2)	C22—C21—C26—C25	−2.3 (2)
C2—C11—C12—C19	−136.39 (13)	C20—C21—C26—C25	178.11 (13)
C11—C12—C13—C18	−111.46 (15)	C25—C26—C27—C28	−179.97 (14)
C19—C12—C13—C18	117.34 (14)	C21—C26—C27—C28	0.8 (2)
C11—C12—C13—C14	67.65 (17)	C26—C27—C28—C29	1.5 (2)
C19—C12—C13—C14	−63.55 (18)	C21—C20—C29—C28	−0.1 (2)
C18—C13—C14—C15	−3.3 (2)	C19—C20—C29—C28	179.50 (13)
C12—C13—C14—C15	177.58 (13)	C27—C28—C29—C20	−1.9 (2)
C13—C14—C15—C16	1.0 (2)	O2—C19—C30—C31	49.88 (17)
C14—C15—C16—C17	2.2 (2)	C20—C19—C30—C31	−70.33 (16)
C14—C15—C16—Cl1	−178.46 (11)	C12—C19—C30—C31	166.88 (13)
C15—C16—C17—C18	−3.1 (2)	C32—N1—C31—C30	164.04 (13)
Cl1—C16—C17—C18	177.63 (11)	C33—N1—C31—C30	−73.70 (16)
C14—C13—C18—C17	2.4 (2)	C19—C30—C31—N1	−68.12 (17)

Hydrogen-bond geometry (Å, °)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
O2—H2···N1	0.82	1.93	2.6995 (17)	157

Fig. 1


C6
C7
C8
C5
C9
C4
C3
C10
C2
C11
O1
C1
C12
O2
C13
C18
C14
C17
C15
C16
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C24
N1
C30
C31
C32

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3-(6-Methoxy-2-naphthyl)-1-(2-pyridyl)-prop-2-en-1-one

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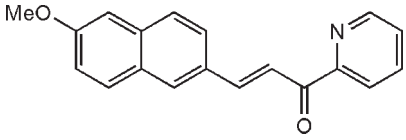
Key indicators: single-crystal X-ray study; T = 293 K; mean σ(C–C) = 0.010 Å; R factor = 0.071; wR factor = 0.080; data-to-parameter ratio = 13.4.

There are two molecules in the asymmetric unit of the title compound, $C_{19}H_{15}NO_2$, in which the dihedral angles between the naphthalene ring system and the pyridine ring are 40.5 (3) and 41.2 (4)°. In the crystal, C—H···O hydrogen bonds link the molecules.

Related literature

For medicinal background, see: Petrov *et al.* (2006).



Experimental

Crystal data

$C_{19}H_{15}NO_2$
M_r = 289.32
Orthorhombic, $Pca2_1$
a = 7.8560 (16) Å
b = 11.542 (2) Å
c = 32.353 (7) Å
V = 2933.6 (10) Å^3
Z = 8
Mo $K\alpha$ radiation
μ = 0.09 mm^{-1}
T = 293 K
0.20 × 0.10 × 0.10 mm

Data collection

Enraf–Nonius CAD-4 diffractometer
5329 measured reflections
5329 independent reflections
2245 reflections with $I > 2\sigma(I)$
R_{int} = 0.067
3 standard reflections every 200 reflections
intensity decay: 1%

Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.071
$wR(F^2)$ = 0.080
S = 1.01
5329 reflections
397 parameters
4 restraints
H-atom parameters constrained
$\Delta\rho_{max}$ = 0.16 e Å^{-3}
$\Delta\rho_{min}$ = −0.18 e Å^{-3}

Table 1
Hydrogen-bond geometry (Å, °).

D—H···A	D—H	H···A	D···A	D—H···A
C38—H38B···O1^{i}	0.96	2.53	3.356 (10)	143

Symmetry code: (i) $x-\frac{1}{2}, -y+1, z$.

Data collection: *CAD-4 Software* (Enraf–Nonius, 1989); cell refinement: *CAD-4 Software*; data reduction: *XCAD4* (Harms & Wocadlo, 1995); program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *ORTEP-3* (Farrugia, 1997); software used to prepare material for publication: *SHELXL97*.

Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: HB5431).

References

Enraf–Nonius (1989). *CAD-4 Software*. Enraf–Nonius, Delft. The Netherlands.
Farrugia, L. J. (1997). *J. Appl. Cryst.* **30**, 565.
Harms, K. & Wocadlo, S. (1995). *XCAD4*. University of Marburg, Germany.
Petrov, K. G., Zhang, Y.-M., Carter, M., Cockerill, G. S., Dickerson, S., Gauthier, C. A., Guo, Y., Mook, R. A., Rusnak, D. W., Walker, A. L., Wood, E. R. & Lackey, K. E. (2006). *Bioorg. Med. Chem. Lett.* **16**, 4686–4691.
Sheldrick, G. M. (2008). *Acta Cryst.* A**64**, 112–122.

supplementary materials

Acta Cryst. (2010). E**66**, o1613 [**doi:10.1107/S1600536810016880**]

3-(6-Methoxy-2-naphthyl)-1-(2-pyridyl)prop-2-en-1-one

X. Li

Experimental

In the presence of sodium hydroxide, 6-methoxy-2-naphthaldehyde and 1-(pyridin-2-yl)ethanone in liquid ammonia were stirred at 313 K for 4 h. Sodium hydroxide was filtered off and the filtrate was duluted with dichlormethane and washed by brine. The organic phase was dried over anhydrous sodium sulfate, filtered, and concentrated to give crude product which was recrystallised from from dichlormethane to give yellow blocks of (I).

Refinement

The absolute structure of the title compound is indeterminate in the present refinement. H atoms were positioned geometrically, with C-H = 0.93, 0.97 and 0.96 Å for aromatic, methylene and methyl H, respectively, and constrained to ride on their parent atoms, with $U_{iso}(H) = xU_{eq}(C)$, where x = 1.5 for methyl H and x = 1.2 for all other H atoms.

Figures

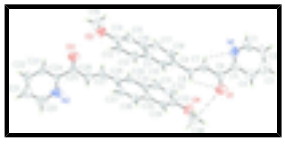


Fig. 1. Ellipsoid plot.

3-(6-Methoxy-2-naphthyl)-1-(2-pyridyl)prop-2-en-1-one

Crystal data

$C_{19}H_{15}NO_2$	$D_x = 1.310$ Mg m^{-3}
$M_r = 289.32$	Melting point: 513 K
Orthorhombic, $Pca2_1$	Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å
Hall symbol: P 2c -2ac	Cell parameters from 25 reflections
$a = 7.8560$ (16) Å	$\theta = 9$–12°
$b = 11.542$ (2) Å	$\mu = 0.09$ mm^{-1}
$c = 32.353$ (7) Å	$T = 293$ K
$V = 2933.6$ (10) Å^3	Needle, yellow
$Z = 8$	0.20 × 0.10 × 0.10 mm
$F(000) = 1216$	

Data collection

Enraf–Nonius CAD-4 diffractometer	$R_{int} = 0.067$

Radiation source: fine-focus sealed tube	$\theta_{max} = 25.3°$, $\theta_{min} = 1.3°$
graphite	$h = 0 \rightarrow 9$
ω/2θ scans	$k = 0 \rightarrow 13$
5329 Please give correct value measured reflections	$l = -38 \rightarrow 38$
5329 independent reflections	3 standard reflections every 200 reflections
2245 reflections with $I > 2\sigma(I)$	intensity decay: 1%

Refinement

Refinement on F^2	Primary atom site location: structure-invariant direct methods
Least-squares matrix: full	Secondary atom site location: difference Fourier map
$R[F^2 > 2\sigma(F^2)] = 0.071$	Hydrogen site location: inferred from neighbouring sites
$wR(F^2) = 0.080$	H-atom parameters constrained
$S = 1.01$	$w = 1/[\sigma^2(F_o^2) + (0.0012P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
5329 reflections	$(\Delta/\sigma)_{max} < 0.001$
397 parameters	$\Delta\rho_{max} = 0.16$ e Å^{-3}
4 restraints	$\Delta\rho_{min} = -0.18$ e Å^{-3}

Special details

Geometry. All esds (except the esd in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell esds are taken into account individually in the estimation of esds in distances, angles and torsion angles; correlations between esds in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell esds is used for estimating esds involving l.s. planes.

Refinement. Refinement of F^2 against ALL reflections. The weighted R-factor wR and goodness of fit S are based on F^2, conventional R-factors R are based on F, with F set to zero for negative F^2. The threshold expression of $F^2 > 2\text{sigma}(F^2)$ is used only for calculating R-factors(gt) etc. and is not relevant to the choice of reflections for refinement. R-factors based on F^2 are statistically about twice as large as those based on F, and R- factors based on ALL data will be even larger.

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å^2)

	x	*y*	*z*	U_{iso}*/U_{eq}
O1	0.7960 (7)	0.2745 (4)	0.4482 (2)	0.0861 (18)
O2	0.3909 (6)	0.1159 (4)	0.14036 (15)	0.0620 (14)
N1	0.8162 (10)	−0.0296 (6)	0.46063 (19)	0.058 (2)
C1	0.8679 (12)	−0.1063 (8)	0.4882 (3)	0.075 (3)
H1B	0.8507	−0.1840	0.4819	0.090*
C2	0.9437 (11)	−0.0822 (9)	0.5249 (3)	0.073 (3)
H2A	0.9850	−0.1410	0.5418	0.088*
C3	0.9574 (13)	0.0347 (9)	0.5365 (3)	0.081 (3)
H3A	0.9990	0.0564	0.5623	0.097*
C4	0.9069 (13)	0.1144 (8)	0.5081 (2)	0.062 (3)
H4A	0.9192	0.1928	0.5141	0.075*
C5	0.8360 (11)	0.0813 (7)	0.4697 (3)	0.059 (2)

C6	0.7680 (9)	0.1729 (6)	0.4408 (2)	0.058 (2)
C7	0.6862 (8)	0.1310 (6)	0.40378 (19)	0.0527 (18)
H7A	0.6472	0.0550	0.4027	0.063*
C8	0.6656 (9)	0.2015 (6)	0.37045 (19)	0.0478 (19)
H8A	0.7015	0.2778	0.3735	0.057*
C9	0.5936 (10)	0.1705 (6)	0.3306 (2)	0.0489 (19)
C10	0.6365 (9)	0.2318 (6)	0.29665 (17)	0.0415 (18)
H10A	0.7065	0.2964	0.2992	0.050*
C11	0.5771 (8)	0.1993 (5)	0.2577 (2)	0.0454 (17)
C12	0.6205 (8)	0.2602 (6)	0.22134 (19)	0.049 (2)
H12A	0.6951	0.3225	0.2232	0.059*
C13	0.5558 (9)	0.2302 (6)	0.18330 (18)	0.054 (2)
H13A	0.5861	0.2725	0.1600	0.065*
C14	0.4439 (9)	0.1356 (6)	0.1796 (2)	0.054 (2)
C15	0.3968 (8)	0.0729 (6)	0.2144 (2)	0.053 (2)
H15A	0.3228	0.0103	0.2120	0.063*
C16	0.4615 (8)	0.1045 (6)	0.2532 (2)	0.0433 (17)
C17	0.4135 (9)	0.0422 (6)	0.2887 (2)	0.0473 (19)
H17A	0.3393	−0.0203	0.2864	0.057*
C18	0.4779 (8)	0.0745 (6)	0.3275 (2)	0.052 (2)
H18A	0.4458	0.0339	0.3511	0.063*
C19	0.2639 (13)	0.0281 (7)	0.1341 (3)	0.073 (3)
H19A	0.2370	0.0230	0.1052	0.110*
H19B	0.1631	0.0478	0.1494	0.110*
H19C	0.3067	−0.0452	0.1435	0.110*
O3	−0.0515 (7)	0.2385 (5)	0.11856 (18)	0.0871 (18)
O4	0.3447 (6)	0.3763 (4)	0.42812 (15)	0.0726 (15)
N2	−0.0607 (10)	0.5392 (7)	0.1072 (2)	0.072 (2)
C20	−0.1230 (14)	0.6188 (8)	0.0806 (3)	0.079 (3)
H20A	−0.1219	0.6963	0.0884	0.094*
C21	−0.1890 (14)	0.5899 (9)	0.0420 (3)	0.090 (4)
H21A	−0.2152	0.6475	0.0230	0.107*
C22	−0.2144 (14)	0.4768 (9)	0.0325 (3)	0.080 (3)
H22A	−0.2674	0.4554	0.0080	0.096*
C23	−0.1595 (11)	0.3954 (9)	0.0602 (3)	0.071 (3)
H23A	−0.1754	0.3169	0.0549	0.085*
C24	−0.0819 (10)	0.4303 (7)	0.0953 (2)	0.0412 (19)
C25	−0.0261 (9)	0.3403 (7)	0.1266 (2)	0.059 (2)
C26	0.0593 (9)	0.3751 (6)	0.16455 (19)	0.060 (2)
H26A	0.1091	0.4481	0.1660	0.073*
C27	0.0680 (9)	0.3057 (6)	0.1972 (2)	0.052 (2)
H27A	0.0192	0.2326	0.1947	0.062*
C28	0.1465 (8)	0.3335 (6)	0.2362 (2)	0.0470 (19)
C29	0.1024 (8)	0.2713 (6)	0.2717 (2)	0.0483 (19)
H29A	0.0288	0.2086	0.2691	0.058*
C30	0.1640 (8)	0.2993 (5)	0.3108 (2)	0.0452 (18)
C31	0.1138 (10)	0.2353 (7)	0.3453 (2)	0.071 (3)
H31A	0.0394	0.1732	0.3423	0.085*
C32	0.1747 (9)	0.2641 (6)	0.3839 (2)	0.061 (2)

H32A	0.1413	0.2220	0.4071	0.074*
C33	0.2896 (8)	0.3591 (6)	0.3880 (2)	0.0485 (19)
C34	0.3415 (8)	0.4223 (6)	0.3555 (2)	0.0496 (19)
H34A	0.4181	0.4829	0.3589	0.059*
C35	0.2762 (8)	0.3942 (6)	0.3156 (2)	0.0474 (18)
C36	0.3226 (10)	0.4554 (6)	0.2796 (2)	0.054 (2)
H36A	0.3981	0.5171	0.2820	0.065*
C37	0.2623 (8)	0.4281 (6)	0.2421 (2)	0.055 (2)
H37A	0.2964	0.4715	0.2193	0.066*
C38	0.4780 (14)	0.4655 (7)	0.4339 (3)	0.094 (3)
H38A	0.5073	0.4705	0.4626	0.141*
H38B	0.4360	0.5391	0.4245	0.141*
H38C	0.5771	0.4447	0.4182	0.141*

Atomic displacement parameters (Å^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
O1	0.114 (5)	0.051 (3)	0.093 (4)	−0.004 (3)	−0.023 (4)	−0.014 (3)
O2	0.068 (4)	0.059 (3)	0.059 (4)	−0.006 (3)	0.001 (3)	−0.004 (3)
N1	0.076 (5)	0.064 (4)	0.036 (4)	−0.009 (5)	−0.003 (4)	0.025 (3)
C1	0.067 (6)	0.076 (6)	0.082 (7)	0.019 (5)	0.005 (6)	0.047 (5)
C2	0.045 (5)	0.108 (8)	0.067 (6)	0.001 (6)	−0.021 (5)	0.042 (6)
C3	0.059 (7)	0.122 (8)	0.062 (7)	−0.018 (7)	0.014 (5)	0.004 (7)
C4	0.078 (7)	0.066 (6)	0.044 (5)	−0.012 (5)	0.032 (5)	0.008 (5)
C5	0.058 (6)	0.055 (5)	0.064 (6)	−0.006 (5)	−0.003 (5)	0.002 (4)
C6	0.052 (5)	0.050 (5)	0.073 (6)	−0.001 (4)	0.004 (4)	0.000 (4)
C7	0.044 (5)	0.064 (5)	0.050 (4)	−0.003 (4)	−0.008 (4)	0.001 (4)
C8	0.054 (5)	0.040 (4)	0.050 (5)	0.013 (4)	0.006 (4)	−0.011 (4)
C9	0.064 (5)	0.040 (4)	0.043 (4)	0.006 (4)	0.003 (4)	−0.005 (3)
C10	0.047 (4)	0.040 (4)	0.038 (4)	−0.004 (3)	0.011 (4)	−0.004 (3)
C11	0.036 (4)	0.036 (4)	0.064 (5)	0.001 (3)	0.015 (4)	−0.012 (4)
C12	0.038 (4)	0.057 (5)	0.052 (5)	−0.013 (4)	−0.003 (4)	−0.001 (4)
C13	0.072 (5)	0.065 (5)	0.025 (4)	−0.008 (5)	−0.007 (4)	0.014 (4)
C14	0.058 (5)	0.045 (5)	0.058 (5)	0.008 (4)	0.005 (4)	−0.010 (4)
C15	0.054 (5)	0.041 (5)	0.064 (5)	−0.001 (4)	0.003 (4)	0.003 (4)
C16	0.044 (4)	0.042 (4)	0.044 (4)	0.006 (3)	0.004 (4)	0.012 (4)
C17	0.039 (4)	0.044 (4)	0.059 (5)	−0.009 (4)	0.011 (4)	0.003 (4)
C18	0.047 (5)	0.050 (5)	0.059 (5)	0.009 (4)	0.012 (4)	0.006 (4)
C19	0.055 (6)	0.095 (7)	0.070 (6)	−0.028 (5)	0.002 (5)	0.004 (5)
O3	0.128 (5)	0.052 (4)	0.081 (4)	−0.005 (4)	−0.005 (4)	−0.007 (3)
O4	0.075 (4)	0.083 (4)	0.059 (4)	−0.003 (3)	−0.006 (3)	−0.007 (3)
N2	0.056 (5)	0.066 (5)	0.094 (6)	0.018 (5)	0.003 (4)	−0.015 (5)
C20	0.095 (8)	0.069 (6)	0.072 (7)	0.006 (6)	0.025 (6)	−0.019 (6)
C21	0.106 (9)	0.094 (8)	0.069 (7)	0.037 (7)	0.021 (7)	0.009 (6)
C22	0.060 (7)	0.114 (8)	0.066 (7)	0.020 (7)	−0.037 (5)	0.003 (7)
C23	0.052 (6)	0.097 (7)	0.062 (6)	0.003 (5)	−0.012 (5)	−0.032 (6)
C24	0.040 (5)	0.053 (5)	0.031 (4)	0.010 (4)	0.015 (4)	0.007 (4)
C25	0.070 (6)	0.048 (5)	0.058 (5)	0.007 (4)	0.018 (4)	−0.007 (4)

C26	0.075 (6)	0.062 (5)	0.044 (4)	−0.010 (5)	−0.005 (4)	−0.001 (4)
C27	0.038 (5)	0.058 (5)	0.060 (5)	0.008 (4)	0.006 (4)	0.007 (4)
C28	0.022 (4)	0.057 (5)	0.061 (5)	0.007 (4)	−0.002 (4)	0.020 (4)
C29	0.042 (4)	0.034 (4)	0.069 (5)	−0.001 (3)	−0.010 (4)	0.004 (4)
C30	0.052 (5)	0.024 (4)	0.059 (5)	0.004 (3)	0.001 (4)	0.017 (3)
C31	0.074 (6)	0.059 (6)	0.080 (6)	−0.005 (5)	0.009 (5)	0.002 (5)
C32	0.049 (5)	0.036 (4)	0.098 (6)	−0.007 (4)	0.034 (5)	0.004 (4)
C33	0.050 (5)	0.055 (5)	0.040 (4)	0.006 (4)	−0.007 (4)	−0.004 (4)
C34	0.048 (5)	0.041 (4)	0.059 (5)	−0.002 (4)	−0.008 (4)	0.005 (4)
C35	0.037 (4)	0.051 (5)	0.055 (4)	0.003 (4)	0.005 (4)	0.002 (4)
C36	0.064 (5)	0.037 (4)	0.060 (5)	−0.003 (4)	−0.002 (4)	0.004 (4)
C37	0.044 (5)	0.056 (5)	0.066 (5)	0.009 (4)	0.014 (4)	0.017 (4)
C38	0.097 (8)	0.101 (7)	0.083 (7)	0.011 (7)	−0.016 (6)	−0.032 (6)

Geometric parameters (Å, °)

O1—C6	1.217 (7)	O3—C25	1.219 (8)
O2—C14	1.355 (8)	O4—C33	1.383 (7)
O2—C19	1.436 (8)	O4—C38	1.480 (9)
N1—C1	1.320 (9)	N2—C24	1.325 (10)
N1—C5	1.323 (10)	N2—C20	1.351 (11)
C1—C2	1.357 (12)	C20—C21	1.393 (13)
C1—H1B	0.9300	C20—H20A	0.9300
C2—C3	1.404 (12)	C21—C22	1.355 (12)
C2—H2A	0.9300	C21—H21A	0.9300
C3—C4	1.359 (12)	C22—C23	1.368 (12)
C3—H3A	0.9300	C22—H22A	0.9300
C4—C5	1.415 (11)	C23—C24	1.352 (10)
C4—H4A	0.9300	C23—H23A	0.9300
C5—C6	1.509 (10)	C24—C25	1.516 (10)
C6—C7	1.443 (8)	C25—C26	1.455 (9)
C7—C8	1.361 (8)	C26—C27	1.328 (8)
C7—H7A	0.9300	C26—H26A	0.9300
C8—C9	1.453 (8)	C27—C28	1.442 (9)
C8—H8A	0.9300	C27—H27A	0.9300
C9—C10	1.349 (8)	C28—C29	1.398 (9)
C9—C18	1.437 (8)	C28—C37	1.433 (9)
C10—C11	1.396 (8)	C29—C30	1.391 (8)
C10—H10A	0.9300	C29—H29A	0.9300
C11—C12	1.411 (9)	C30—C31	1.397 (9)
C11—C16	1.430 (7)	C30—C35	1.414 (8)
C12—C13	1.376 (7)	C31—C32	1.379 (10)
C12—H12A	0.9300	C31—H31A	0.9300
C13—C14	1.407 (8)	C32—C33	1.426 (8)
C13—H13A	0.9300	C32—H32A	0.9300
C14—C15	1.390 (9)	C33—C34	1.342 (9)
C15—C16	1.403 (8)	C34—C35	1.427 (8)
C15—H15A	0.9300	C34—H34A	0.9300
C16—C17	1.405 (8)	C35—C36	1.410 (9)

C17—C18	1.404 (9)	C36—C37	1.340 (9)
C17—H17A	0.9300	C36—H36A	0.9300
C18—H18A	0.9300	C37—H37A	0.9300
C19—H19A	0.9600	C38—H38A	0.9600
C19—H19B	0.9600	C38—H38B	0.9600
C19—H19C	0.9600	C38—H38C	0.9600
C14—O2—C19	117.7 (7)	C33—O4—C38	116.0 (7)
C1—N1—C5	117.6 (8)	C24—N2—C20	114.5 (8)
N1—C1—C2	126.0 (9)	N2—C20—C21	122.9 (9)
N1—C1—H1B	117.0	N2—C20—H20A	118.5
C2—C1—H1B	117.0	C21—C20—H20A	118.5
C1—C2—C3	117.7 (9)	C22—C21—C20	119.3 (10)
C1—C2—H2A	121.2	C22—C21—H21A	120.4
C3—C2—H2A	121.2	C20—C21—H21A	120.4
C4—C3—C2	116.6 (9)	C21—C22—C23	117.9 (9)
C4—C3—H3A	121.7	C21—C22—H22A	121.1
C2—C3—H3A	121.7	C23—C22—H22A	121.1
C3—C4—C5	121.7 (9)	C24—C23—C22	119.1 (9)
C3—C4—H4A	119.2	C24—C23—H23A	120.4
C5—C4—H4A	119.2	C22—C23—H23A	120.4
N1—C5—C4	120.1 (8)	N2—C24—C23	125.8 (8)
N1—C5—C6	120.0 (8)	N2—C24—C25	114.8 (7)
C4—C5—C6	119.6 (8)	C23—C24—C25	119.2 (8)
O1—C6—C7	124.6 (7)	O3—C25—C26	121.5 (7)
O1—C6—C5	119.3 (7)	O3—C25—C24	118.0 (8)
C7—C6—C5	115.9 (7)	C26—C25—C24	120.5 (7)
C8—C7—C6	120.7 (7)	C27—C26—C25	121.9 (7)
C8—C7—H7A	119.7	C27—C26—H26A	119.1
C6—C7—H7A	119.7	C25—C26—H26A	119.1
C7—C8—C9	127.0 (7)	C26—C27—C28	125.8 (7)
C7—C8—H8A	116.5	C26—C27—H27A	117.1
C9—C8—H8A	116.5	C28—C27—H27A	117.1
C10—C9—C18	120.4 (7)	C29—C28—C37	116.1 (7)
C10—C9—C8	119.7 (7)	C29—C28—C27	119.9 (7)
C18—C9—C8	119.9 (6)	C37—C28—C27	123.8 (6)
C9—C10—C11	120.7 (7)	C30—C29—C28	122.7 (7)
C9—C10—H10A	119.6	C30—C29—H29A	118.7
C11—C10—H10A	119.6	C28—C29—H29A	118.7
C10—C11—C12	122.6 (6)	C29—C30—C31	120.4 (7)
C10—C11—C16	120.6 (6)	C29—C30—C35	119.8 (6)
C12—C11—C16	116.8 (7)	C31—C30—C35	119.8 (7)
C13—C12—C11	122.1 (7)	C32—C31—C30	120.0 (8)
C13—C12—H12A	119.0	C32—C31—H31A	120.0
C11—C12—H12A	119.0	C30—C31—H31A	120.0
C12—C13—C14	120.2 (7)	C31—C32—C33	119.2 (7)
C12—C13—H13A	119.9	C31—C32—H32A	120.4
C14—C13—H13A	119.9	C33—C32—H32A	120.4
O2—C14—C15	126.2 (7)	C34—C33—O4	124.2 (7)
O2—C14—C13	113.8 (7)	C34—C33—C32	122.6 (7)

C15—C14—C13	120.1 (7)	O4—C33—C32	113.2 (7)
C14—C15—C16	119.6 (7)	C33—C34—C35	118.4 (7)
C14—C15—H15A	120.2	C33—C34—H34A	120.8
C16—C15—H15A	120.2	C35—C34—H34A	120.8
C15—C16—C17	120.0 (7)	C36—C35—C30	117.3 (7)
C15—C16—C11	121.3 (6)	C36—C35—C34	122.8 (6)
C17—C16—C11	118.7 (7)	C30—C35—C34	120.0 (7)
C18—C17—C16	119.8 (7)	C37—C36—C35	122.6 (8)
C18—C17—H17A	120.1	C37—C36—H36A	118.7
C16—C17—H17A	120.1	C35—C36—H36A	118.7
C17—C18—C9	119.7 (6)	C36—C37—C28	121.5 (7)
C17—C18—H18A	120.2	C36—C37—H37A	119.2
C9—C18—H18A	120.2	C28—C37—H37A	119.2
O2—C19—H19A	109.5	O4—C38—H38A	109.5
O2—C19—H19B	109.5	O4—C38—H38B	109.5
H19A—C19—H19B	109.5	H38A—C38—H38B	109.5
O2—C19—H19C	109.5	O4—C38—H38C	109.5
H19A—C19—H19C	109.5	H38A—C38—H38C	109.5
H19B—C19—H19C	109.5	H38B—C38—H38C	109.5
C5—N1—C1—C2	−1.6 (16)	C24—N2—C20—C21	−6.1 (15)
N1—C1—C2—C3	5.3 (16)	N2—C20—C21—C22	9.5 (18)
C1—C2—C3—C4	−5.7 (14)	C20—C21—C22—C23	−5.7 (18)
C2—C3—C4—C5	3.1 (15)	C21—C22—C23—C24	−0.5 (17)
C1—N1—C5—C4	−1.4 (14)	C20—N2—C24—C23	−0.7 (12)
C1—N1—C5—C6	−175.6 (8)	C20—N2—C24—C25	−175.0 (8)
C3—C4—C5—N1	0.5 (15)	C22—C23—C24—N2	4.0 (14)
C3—C4—C5—C6	174.7 (9)	C22—C23—C24—C25	178.1 (8)
N1—C5—C6—O1	−175.6 (8)	N2—C24—C25—O3	175.7 (7)
C4—C5—C6—O1	10.2 (12)	C23—C24—C25—O3	1.0 (11)
N1—C5—C6—C7	−1.1 (11)	N2—C24—C25—C26	−5.9 (10)
C4—C5—C6—C7	−175.4 (7)	C23—C24—C25—C26	179.4 (7)
O1—C6—C7—C8	13.6 (11)	O3—C25—C26—C27	−20.5 (12)
C5—C6—C7—C8	−160.5 (7)	C24—C25—C26—C27	161.1 (7)
C6—C7—C8—C9	176.9 (7)	C25—C26—C27—C28	−178.6 (6)
C7—C8—C9—C10	−155.4 (7)	C26—C27—C28—C29	159.6 (7)
C7—C8—C9—C18	24.3 (11)	C26—C27—C28—C37	−16.2 (12)
C18—C9—C10—C11	−3.6 (11)	C37—C28—C29—C30	0.9 (10)
C8—C9—C10—C11	176.1 (6)	C27—C28—C29—C30	−175.2 (6)
C9—C10—C11—C12	−179.3 (7)	C28—C29—C30—C31	179.0 (7)
C9—C10—C11—C16	3.7 (10)	C28—C29—C30—C35	0.0 (10)
C10—C11—C12—C13	−177.4 (6)	C29—C30—C31—C32	−179.6 (7)
C16—C11—C12—C13	−0.2 (10)	C35—C30—C31—C32	−0.5 (11)
C11—C12—C13—C14	−0.6 (11)	C30—C31—C32—C33	−0.3 (12)
C19—O2—C14—C15	5.2 (10)	C38—O4—C33—C34	−4.3 (10)
C19—O2—C14—C13	−174.2 (6)	C38—O4—C33—C32	173.8 (6)
C12—C13—C14—O2	−179.8 (6)	C31—C32—C33—C34	0.0 (11)
C12—C13—C14—C15	0.8 (11)	C31—C32—C33—O4	−178.1 (7)
O2—C14—C15—C16	−179.4 (6)	O4—C33—C34—C35	179.1 (6)
C13—C14—C15—C16	−0.1 (10)	C32—C33—C34—C35	1.2 (10)

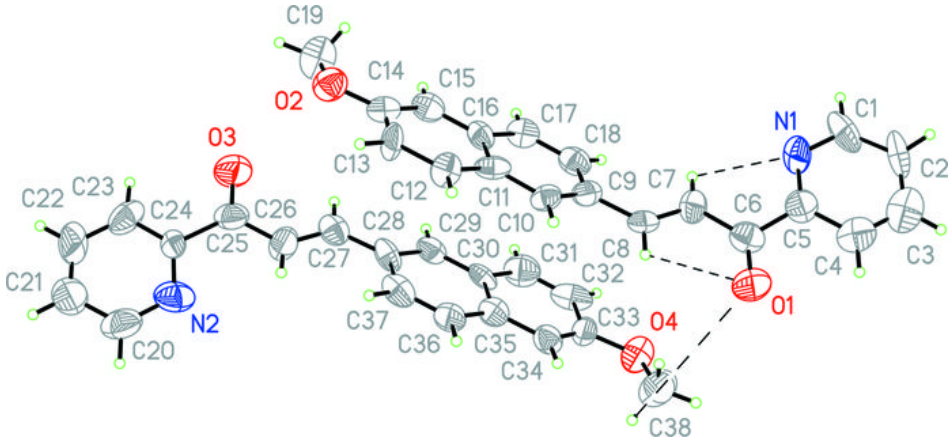
C14—C15—C16—C17	179.5 (7)	C29—C30—C35—C36	−1.1 (9)
C14—C15—C16—C11	−0.8 (10)	C31—C30—C35—C36	179.9 (7)
C10—C11—C16—C15	178.1 (6)	C29—C30—C35—C34	−179.2 (6)
C12—C11—C16—C15	0.9 (9)	C31—C30—C35—C34	1.7 (10)
C10—C11—C16—C17	−2.2 (9)	C33—C34—C35—C36	179.9 (7)
C12—C11—C16—C17	−179.4 (6)	C33—C34—C35—C30	−2.1 (10)
C15—C16—C17—C18	−179.7 (6)	C30—C35—C36—C37	1.3 (11)
C11—C16—C17—C18	0.6 (10)	C34—C35—C36—C37	179.4 (7)
C16—C17—C18—C9	−0.5 (10)	C35—C36—C37—C28	−0.4 (11)
C10—C9—C18—C17	2.0 (11)	C29—C28—C37—C36	−0.7 (10)
C8—C9—C18—C17	−177.7 (6)	C27—C28—C37—C36	175.3 (7)

Hydrogen-bond geometry (Å, °)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
C38—H38B···O1^{i}	0.96	2.53	3.356 (10)	143

Symmetry codes: (i) *x*−1/2, −*y*+1, *z*.

Fig. 1


C19
O2
C14
C15
C16
C17
C18
C13
C12
C11
C9
C7
N1
C1
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C3
C4
C5
C6
O3
C22
C23
C24
C25
C26
C27
C28
C29
C10
C30
C31
C8
C32
C21
N2
C20
C37
C36
C35
C34
C33
O4
O1
C38

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Hexakis(4-acetylpyridinium) octadecachloridotetraantimonate(III)

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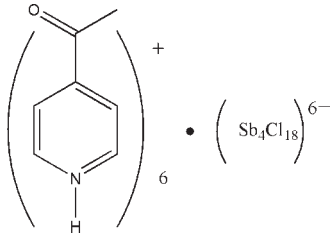
Key indicators: single-crystal X-ray study; T = 298 K; mean σ(C–C) = 0.006 Å; R factor = 0.030; wR factor = 0.070; data-to-parameter ratio = 22.2.

The title compound, $(C_7H_8NO)_6[Sb_4Cl_{18}]$, contains centrosymmetric hexaanions built up from four vertex-sharing alternating $SbCl_5$ square-based pyramids and highly distorted $SbCl_6$ octahedra when long (<3.2 Å) 'secondary' Sb—Cl interactions are taken into account. The inter-polyhedral Sb—Cl bonds define a square-shape. In the crystal, the components are linked by N—H···Cl, C—H···Cl and C—H···O hydrogen bonds, generating a three-dimensional network.

Related literature

For general background to phase transitions in coordination networks, see: Li *et al.* (2008); Zhang *et al.* (2009). For crystal structures containing the 4-acetylpyridinium cation, see: Fu (2009*a*,*b*); Majerz *et al.* (1991); Pang *et al.* (1994); Steffen & Palenik (1977).



Experimental

Crystal data

$(C_7H_8NO)_6[Sb_4Cl_{18}]$
M_r = 1857.96
Triclinic, $P\overline{1}$
a = 9.0589 (18) Å
b = 13.838 (3) Å
c = 15.128 (3) Å
α = 108.29 (3)°
β = 98.00 (3)°
γ = 107.10 (3)°
V = 1664.1 (6) Å^3
Z = 1
Mo $K\alpha$ radiation
μ = 2.37 mm^{-1}
T = 298 K
0.40 × 0.30 × 0.20 mm

Data collection

Rigaku SCXmini diffractometer
Absorption correction: multi-scan (*CrystalClear*; Rigaku, 2005)
T_{min} = 0.430, T_{max} = 0.622
17638 measured reflections
7613 independent reflections
6371 reflections with $I > 2\sigma(I)$
R_{int} = 0.028

Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.030
$wR(F^2)$ = 0.070
S = 1.04
7613 reflections
343 parameters
H-atom parameters constrained
$\Delta\rho_{max}$ = 0.39 e Å^{-3}
$\Delta\rho_{min}$ = −0.38 e Å^{-3}

Table 1
Selected bond lengths (Å).

Sb1—Cl4	2.4036 (9)	Sb2—Cl7	2.3516 (12)
Sb1—Cl3	2.4107 (10)	Sb2—Cl8	2.4459 (10)
Sb1—Cl2	2.4113 (14)	Sb2—Cl9	2.4498 (10)
Sb1—Cl1	2.9359 (12)	Sb2—Cl5	2.8352 (11)
Sb1—Cl5	3.0214 (12)	Sb2—Cl6	2.8937 (11)
Sb1—Cl6^{i}	3.1275 (12)		

Symmetry code: (i) $-x+2, -y+1, -z+1$.

Table 2
Hydrogen-bond geometry (Å, °).

D—H···A	D—H	H···A	D···A	D—H···A
N2—H2A···Cl6	0.86	2.30	3.148 (3)	170
N1—H1D···Cl1^{ii}	0.86	2.20	3.056 (3)	174
N3—H3A···Cl5^{iii}	0.86	2.35	3.198 (3)	168
C1—H1A···O2^{iv}	0.96	2.60	3.506 (5)	158
C5—H5A···Cl8^{v}	0.93	2.78	3.585 (4)	146
C13—H13A···Cl1^{i}	0.93	2.76	3.661 (4)	162
C19—H19A···Cl7^{iii}	0.93	2.67	3.449 (4)	141
C21—H21A···O1^{iii}	0.93	2.42	3.349 (4)	177

Symmetry codes: (i) $-x+2, -y+1, -z+1$; (ii) $x, y, z-1$; (iii) $-x+1, -y+1, -z+1$; (iv) $x, y-1, z$; (v) $x, y-1, z-1$.

Data collection: *CrystalClear* (Rigaku, 2005); cell refinement: *CrystalClear*; data reduction: *CrystalClear*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *SHELXTL* (Sheldrick, 2008); software used to prepare material for publication: *SHELXL97*.

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Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: HB5440).

References

Fu, X. (2009*a*). *Acta Cryst.* E**65**, o1804.
Fu, X. (2009*b*). *Acta Cryst.* E**65**, o2385.
Li, X. Z., Qu, Z. R. & Xiong, R. G. (2008). *Chin. J. Chem.* **11**, 1959–1962.
Majerz, I., Malarski, Z. & Sawka-Dobrowolska, W. (1991). *J. Mol. Struct.* **249**, 109–116.
Pang, L., Whitehead, M. A., Bermardinelli, G. & Lucken, E. A. C. (1994). *J. Chem. Crystallogr.* **24**, 203–211.
Rigaku (2005). *CrystalClear*. Rigaku Corporation, Tokyo, Japan.
Sheldrick, G. M. (2008). *Acta Cryst.* A**64**, 112–122.
Steffen, W. L. & Palenik, G. J. (1977). *Inorg. Chem.* **16**, 1119–1128.
Zhang, W., Chen, L. Z., Xiong, R. G., Nakamura, T. & Huang, S. D. (2009). *J. Am. Chem. Soc.* **131**, 12544–12545.

supplementary materials

Acta Cryst. (2010). E**66**, m736 [**doi:10.1107/S160053681002057X**]

Hexakis(4-acetylpyridinium) octadecachloridotetraantimonate(III)

X. Fu

Comment

As a continuation of our study of phase transition materials, including organic ligands (Li *et al.*, 2008), metal-organic coordination compounds (Zhang *et al.*, 2009), organic-inorganic hybrids, we studied the dielectric properties of the title compound, unfortunately, there was no distinct anomaly observed from 93 K to 400 K, (m.p. 421–423 K), suggesting that this compound should be not a real ferroelectrics or there may be no distinct phase transition occurred within the measured temperature range. In this article, the crystal structure of (I) has been presented.

4-Acetylpyridine may be used as a ligand in coordination compounds *e.g.* with Zn (Steffen & Palenik, 1977) or Ni (Pang *et al.*, 1994). The crystal structures of 4-acetylpyridine together with inorganic acids are also known *e.g.* with sulfuric acid (Fu, 2009b) and perchloric acid (Fu, 2009a).

The cell unit of the title compound is made up of six almost planar protonated 4-acetylpyridinium cations and a $[Sb_4Cl_{18}]^{6-}$ anion (Fig. 1.).In the coordinate anion of $[Sb_4Cl_{18}]^{6-}$, antimony(III) atoms have two kinds of coordination pattern. Sb^{3+}(2) coordinated with five Cl ions construct a distorted tetragonal pyramidal structure, composing two briding and three terminal Cl atoms. There are Cl—Sb secondary bonds by the linkage between the Sb^{3+}(1)···Cl5 and Sb^{3+}(1)···Cl6, with the bond lengths of these secondary bonds 3.0210 (11)Å and 3.1280 (11) Å, respectively, compared to the normal coordination bonds of Sb—Cl 2.3516 (12)Å to 2.8937 (11) Å. Owing to these secondary bonds, the coordination number of the central ion Sb^{3+}(1) increases to six, and it adopts a distorted octahedral geometry.

The tridimensional network arrangement in the crystal structure of (I) is mainly determined by relatively strong and directional hydrogen bonds (Table. 1),

Experimental

2.28 g (10 mmol) $SbCl_3$ was firstly dissolved in 10 ml 1:1 HCl solution, to which 2.42 g (20 mmol) 4-acetylpyridine ethanol solution was then added under stirring. Hydrochloric acid was added until the precipitated substrates disappeared. The acid solution was allowed to slowly evaporate at room temperature until colorless prisms of (I) were grown.

Refinement

Positional parameters of all the H atoms were calculated geometrically and were allowed to ride on the C and N atoms to which they are bonded, with $U_{iso}(H) = 1.2U_{eq}(C)$,

$U_{iso}(H) = 1.2U_{eq}(N)$.

Figures

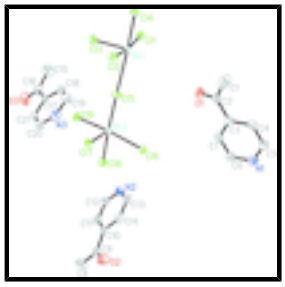


Fig. 1. The molecular structure of (I) with displacement ellipsoids drawn at the 30% probability level (all H atoms have been omitted for clarity). Unlabelled atoms are generated by the symmetry operation (2–x, 1–y, 1–z).

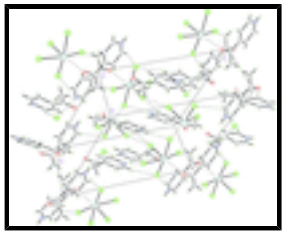


Fig. 2. A view of the packing of (I), stacking along the *a* axis. Dashed lines indicate hydrogen bonds.

Hexakis(4-acetylpyridinium) octadecachloridotetraantimonate(III)

Crystal data

$(C_7H_8NO)_6[Sb_4Cl_{18}]$	$Z = 1$
$M_r = 1857.96$	$F(000) = 900$
Triclinic, $P\overline{1}$	$D_x = 1.854$ Mg m^{-3}
Hall symbol: -P 1	Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å
$a = 9.0589$ (18) Å	Cell parameters from 8056 reflections
$b = 13.838$ (3) Å	$\theta = 3.1$–$27.7°$
$c = 15.128$ (3) Å	$\mu = 2.37$ mm^{-1}
$\alpha = 108.29$ (3)°	$T = 298$ K
$\beta = 98.00$ (3)°	Prism, colourless
$\gamma = 107.10$ (3)°	0.40 × 0.30 × 0.20 mm
$V = 1664.1$ (6) Å^3	

Data collection

Rigaku SCXmini diffractometer	7613 independent reflections
Radiation source: fine-focus sealed tube	6371 reflections with $I > 2\sigma(I)$
graphite	$R_{int} = 0.028$
Detector resolution: 13.6612 pixels mm^{-1}	$\theta_{max} = 27.5°$, $\theta_{min} = 3.1°$
ω scans	$h = -11 \rightarrow 11$
Absorption correction: multi-scan (*CrystalClear*; Rigaku, 2005)	$k = -17 \rightarrow 17$
$T_{min} = 0.430$, $T_{max} = 0.622$	$l = -19 \rightarrow 19$
17638 measured reflections	

Refinement

Refinement on F^2	Primary atom site location: structure-invariant direct methods
Least-squares matrix: full	Secondary atom site location: difference Fourier map
$R[F^2 > 2\sigma(F^2)] = 0.030$	Hydrogen site location: inferred from neighbouring sites
$wR(F^2) = 0.070$	H-atom parameters constrained
$S = 1.04$	$w = 1/[\sigma^2(F_o^2) + (0.0307P)^2 + 0.5066P]$ where $P = (F_o^2 + 2F_c^2)/3$
7613 reflections	$(\Delta/\sigma)_{max} = 0.001$
343 parameters	$\Delta\rho_{max} = 0.39$ e Å^{-3}
0 restraints	$\Delta\rho_{min} = -0.38$ e Å^{-3}

Special details

Geometry. All e.s.d.'s (except the e.s.d. in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell e.s.d.'s are taken into account individually in the estimation of e.s.d.'s in distances, angles and torsion angles; correlations between e.s.d.'s in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell e.s.d.'s is used for estimating e.s.d.'s involving l.s. planes.

Refinement. Refinement of F^2 against ALL reflections. The weighted *R*-factor *wR* and goodness of fit *S* are based on F^2, conventional *R*-factors *R* are based on *F*, with *F* set to zero for negative F^2. The threshold expression of $F^2 > \sigma(F^2)$ is used only for calculating *R*-factors(gt) *etc*. and is not relevant to the choice of reflections for refinement. *R*-factors based on F^2 are statistically about twice as large as those based on *F*, and *R*- factors based on ALL data will be even larger.

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å^2)

	x	*y*	*z*	U_{iso}*/U_{eq}
O1	0.7595 (3)	0.1417 (2)	0.15768 (17)	0.0544 (6)
N1	0.9897 (4)	0.2973 (3)	−0.0627 (2)	0.0573 (8)
H1D	1.0377	0.3389	−0.0898	0.069*
C3	0.8404 (4)	0.1681 (3)	0.0233 (2)	0.0408 (7)
C6	0.9436 (5)	0.3405 (3)	0.0152 (3)	0.0574 (10)
H6A	0.9616	0.4147	0.0386	0.069*
C4	0.8871 (4)	0.1248 (3)	−0.0588 (2)	0.0490 (8)
H4A	0.8660	0.0503	−0.0855	0.059*
C7	0.8713 (4)	0.2783 (3)	0.0610 (3)	0.0525 (9)
H7A	0.8428	0.3094	0.1169	0.063*
C5	0.9634 (5)	0.1912 (3)	−0.0998 (2)	0.0557 (9)
H5A	0.9976	0.1629	−0.1540	0.067*
C2	0.7623 (4)	0.0986 (3)	0.0748 (3)	0.0497 (8)
Sb1	0.86744 (2)	0.350428 (15)	0.674838 (14)	0.03137 (6)
Cl4	0.83619 (12)	0.17158 (6)	0.67419 (6)	0.0519 (2)
Cl3	0.74694 (11)	0.39130 (8)	0.80769 (6)	0.0528 (2)
Cl2	0.61006 (10)	0.27520 (7)	0.56102 (6)	0.0543 (2)
C1	0.6945 (7)	−0.0208 (3)	0.0234 (4)	0.110 (2)

H1A	0.6487	−0.0545	0.0648	0.165*
H1B	0.7775	−0.0467	0.0054	0.165*
H1C	0.6133	−0.0390	−0.0333	0.165*
Cl1	1.15940 (10)	0.43033 (7)	0.82937 (7)	0.0529 (2)
Sb2	0.93951 (2)	0.785682 (15)	0.693125 (14)	0.03208 (6)
Cl7	0.67862 (9)	0.73910 (7)	0.60241 (6)	0.0474 (2)
Cl9	0.83859 (11)	0.82021 (8)	0.83764 (6)	0.0544 (2)
Cl8	0.99930 (12)	0.97530 (7)	0.70831 (7)	0.0595 (2)
Cl5	0.86213 (12)	0.56019 (7)	0.65539 (7)	0.0577 (2)
Cl6	1.00732 (11)	0.73440 (8)	0.50601 (6)	0.0557 (2)
C10	0.6128 (4)	0.9155 (3)	0.3188 (2)	0.0436 (8)
C14	0.6375 (4)	0.8208 (3)	0.2737 (3)	0.0525 (9)
H14A	0.5913	0.7814	0.2082	0.063*
N2	0.7927 (4)	0.8408 (3)	0.4180 (3)	0.0584 (8)
H2A	0.8511	0.8172	0.4493	0.070*
C12	0.7702 (5)	0.9308 (3)	0.4648 (3)	0.0595 (10)
H12A	0.8150	0.9669	0.5308	0.071*
C11	0.6807 (4)	0.9711 (3)	0.4161 (3)	0.0512 (9)
H11A	0.6659	1.0355	0.4484	0.061*
C13	0.7289 (5)	0.7851 (3)	0.3245 (3)	0.0610 (10)
H13A	0.7471	0.7216	0.2939	0.073*
O2	0.4633 (4)	0.9034 (3)	0.1749 (2)	0.0794 (9)
C9	0.5172 (4)	0.9568 (3)	0.2594 (3)	0.0537 (9)
C8	0.4958 (6)	1.0602 (4)	0.3054 (3)	0.0865 (15)
H8A	0.4326	1.0748	0.2582	0.130*
H8B	0.5982	1.1180	0.3327	0.130*
H8C	0.4424	1.0555	0.3553	0.130*
C18	0.4716 (4)	0.5259 (3)	0.7037 (3)	0.0540 (9)
H18A	0.5403	0.4988	0.7313	0.065*
N3	0.3089 (4)	0.5204 (3)	0.5680 (2)	0.0584 (8)
H3A	0.2674	0.4905	0.5069	0.070*
C17	0.4345 (4)	0.6097 (2)	0.7603 (2)	0.0418 (7)
C16	0.4972 (4)	0.6600 (3)	0.8688 (3)	0.0587 (10)
C21	0.3347 (4)	0.6486 (3)	0.7166 (3)	0.0537 (9)
H21A	0.3100	0.7066	0.7534	0.064*
C15	0.5935 (6)	0.6125 (4)	0.9162 (3)	0.0897 (15)
H15A	0.6250	0.6526	0.9845	0.135*
H15B	0.6870	0.6161	0.8924	0.135*
H15C	0.5314	0.5377	0.9027	0.135*
C20	0.2716 (5)	0.6023 (3)	0.6191 (3)	0.0588 (10)
H20A	0.2035	0.6280	0.5892	0.071*
O3	0.4681 (4)	0.7375 (2)	0.9125 (2)	0.0803 (9)
C19	0.4076 (5)	0.4828 (3)	0.6073 (3)	0.0642 (11)
H19A	0.4332	0.4264	0.5686	0.077*

Atomic displacement parameters (Å^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}

O1	0.0600 (16)	0.0584 (15)	0.0478 (14)	0.0245 (12)	0.0219 (12)	0.0173 (12)
N1	0.068 (2)	0.063 (2)	0.0528 (19)	0.0261 (16)	0.0166 (16)	0.0331 (17)
C3	0.0408 (17)	0.0425 (18)	0.0348 (17)	0.0151 (14)	0.0048 (13)	0.0109 (15)
C6	0.075 (3)	0.046 (2)	0.058 (2)	0.0281 (19)	0.023 (2)	0.0205 (19)
C4	0.065 (2)	0.0417 (19)	0.0358 (18)	0.0204 (17)	0.0090 (16)	0.0096 (15)
C7	0.060 (2)	0.049 (2)	0.050 (2)	0.0259 (17)	0.0191 (17)	0.0118 (17)
C5	0.076 (3)	0.060 (2)	0.0344 (18)	0.031 (2)	0.0144 (18)	0.0157 (18)
C2	0.050 (2)	0.047 (2)	0.048 (2)	0.0174 (16)	0.0158 (16)	0.0107 (17)
Sb1	0.03433 (11)	0.03025 (11)	0.03262 (11)	0.01447 (8)	0.00818 (8)	0.01327 (9)
Cl4	0.0760 (6)	0.0343 (4)	0.0502 (5)	0.0230 (4)	0.0131 (4)	0.0206 (4)
Cl3	0.0535 (5)	0.0654 (6)	0.0479 (5)	0.0294 (4)	0.0235 (4)	0.0201 (4)
Cl2	0.0417 (4)	0.0604 (5)	0.0524 (5)	0.0143 (4)	−0.0025 (4)	0.0199 (4)
C1	0.156 (5)	0.050 (3)	0.100 (4)	0.001 (3)	0.076 (4)	0.012 (3)
Cl1	0.0454 (5)	0.0531 (5)	0.0556 (5)	0.0120 (4)	0.0120 (4)	0.0201 (4)
Sb2	0.03311 (11)	0.03102 (11)	0.03265 (11)	0.01310 (8)	0.00899 (8)	0.01088 (9)
Cl7	0.0387 (4)	0.0537 (5)	0.0463 (5)	0.0207 (4)	0.0039 (3)	0.0133 (4)
Cl9	0.0555 (5)	0.0718 (6)	0.0403 (4)	0.0266 (4)	0.0207 (4)	0.0195 (4)
Cl8	0.0743 (6)	0.0327 (4)	0.0724 (6)	0.0173 (4)	0.0249 (5)	0.0198 (4)
Cl5	0.0680 (6)	0.0411 (5)	0.0661 (6)	0.0207 (4)	0.0095 (5)	0.0252 (4)
Cl6	0.0632 (6)	0.0692 (6)	0.0527 (5)	0.0359 (5)	0.0274 (4)	0.0295 (5)
C10	0.0378 (17)	0.0436 (18)	0.050 (2)	0.0115 (14)	0.0189 (15)	0.0174 (16)
C14	0.049 (2)	0.045 (2)	0.054 (2)	0.0113 (16)	0.0148 (17)	0.0098 (17)
N2	0.0512 (18)	0.062 (2)	0.074 (2)	0.0242 (16)	0.0188 (17)	0.0363 (19)
C12	0.060 (2)	0.066 (3)	0.051 (2)	0.021 (2)	0.0104 (19)	0.024 (2)
C11	0.058 (2)	0.0444 (19)	0.048 (2)	0.0174 (17)	0.0160 (17)	0.0134 (17)
C13	0.062 (2)	0.045 (2)	0.084 (3)	0.0245 (19)	0.032 (2)	0.025 (2)
O2	0.086 (2)	0.097 (2)	0.0539 (18)	0.0350 (18)	0.0098 (16)	0.0284 (18)
C9	0.049 (2)	0.064 (2)	0.054 (2)	0.0180 (18)	0.0191 (18)	0.029 (2)
C8	0.115 (4)	0.073 (3)	0.086 (3)	0.058 (3)	0.019 (3)	0.029 (3)
C18	0.052 (2)	0.050 (2)	0.063 (2)	0.0253 (17)	0.0139 (18)	0.0182 (19)
N3	0.0535 (19)	0.059 (2)	0.0435 (17)	0.0063 (15)	0.0064 (14)	0.0091 (15)
C17	0.0345 (16)	0.0369 (17)	0.0491 (19)	0.0089 (13)	0.0141 (14)	0.0118 (15)
C16	0.043 (2)	0.062 (2)	0.054 (2)	0.0087 (18)	0.0123 (17)	0.011 (2)
C21	0.057 (2)	0.056 (2)	0.060 (2)	0.0328 (18)	0.0253 (19)	0.0211 (19)
C15	0.084 (3)	0.105 (4)	0.068 (3)	0.033 (3)	−0.005 (3)	0.028 (3)
C20	0.055 (2)	0.072 (3)	0.062 (3)	0.030 (2)	0.0186 (19)	0.034 (2)
O3	0.082 (2)	0.0704 (19)	0.0608 (18)	0.0244 (16)	0.0179 (15)	−0.0077 (15)
C19	0.081 (3)	0.046 (2)	0.057 (2)	0.026 (2)	0.020 (2)	0.0038 (19)

Geometric parameters (Å, °)

O1—C2	1.215 (4)	C14—C13	1.350 (5)
N1—C6	1.327 (4)	C14—H14A	0.9300
N1—C5	1.329 (5)	N2—C12	1.316 (5)
N1—H1D	0.8600	N2—C13	1.325 (5)
C3—C7	1.374 (4)	N2—H2A	0.8600
C3—C4	1.381 (4)	C12—C11	1.367 (5)
C3—C2	1.502 (5)	C12—H12A	0.9300
C6—C7	1.348 (5)	C11—H11A	0.9300

C6—H6A	0.9300	C13—H13A	0.9300
C4—C5	1.345 (5)	O2—C9	1.200 (4)
C4—H4A	0.9300	C9—C8	1.464 (5)
C7—H7A	0.9300	C8—H8A	0.9600
C5—H5A	0.9300	C8—H8B	0.9600
C2—C1	1.476 (5)	C8—H8C	0.9600
C1—H1A	0.9600	C18—C19	1.354 (5)
C1—H1B	0.9600	C18—C17	1.370 (4)
C1—H1C	0.9600	C18—H18A	0.9300
Sb1—Cl4	2.4036 (9)	N3—C20	1.320 (5)
Sb1—Cl3	2.4107 (10)	N3—C19	1.320 (5)
Sb1—Cl2	2.4113 (14)	N3—H3A	0.8600
Sb1—Cl1	2.9359 (12)	C17—C21	1.374 (5)
Sb1—Cl5	3.0214 (12)	C17—C16	1.514 (5)
Sb1—Cl6^{i}	3.1275 (12)	C16—O3	1.194 (4)
Sb2—Cl7	2.3516 (12)	C16—C15	1.473 (6)
Sb2—Cl8	2.4459 (10)	C21—C20	1.367 (5)
Sb2—Cl9	2.4498 (10)	C21—H21A	0.9300
Sb2—Cl5	2.8352 (11)	C15—H15A	0.9600
Sb2—Cl6	2.8937 (11)	C15—H15B	0.9600
C10—C14	1.373 (4)	C15—H15C	0.9600
C10—C11	1.378 (5)	C20—H20A	0.9300
C10—C9	1.511 (5)	C19—H19A	0.9300
C6—N1—C5	121.5 (3)	C12—N2—H2A	118.7
C6—N1—H1D	119.2	C13—N2—H2A	118.7
C5—N1—H1D	119.2	N2—C12—C11	119.7 (4)
C7—C3—C4	119.3 (3)	N2—C12—H12A	120.1
C7—C3—C2	118.9 (3)	C11—C12—H12A	120.1
C4—C3—C2	121.8 (3)	C12—C11—C10	119.3 (3)
N1—C6—C7	121.0 (3)	C12—C11—H11A	120.3
N1—C6—H6A	119.5	C10—C11—H11A	120.3
C7—C6—H6A	119.5	N2—C13—C14	119.8 (3)
C5—C4—C3	119.5 (3)	N2—C13—H13A	120.1
C5—C4—H4A	120.2	C14—C13—H13A	120.1
C3—C4—H4A	120.2	O2—C9—C8	122.4 (4)
C6—C7—C3	118.6 (3)	O2—C9—C10	117.8 (4)
C6—C7—H7A	120.7	C8—C9—C10	119.7 (3)
C3—C7—H7A	120.7	C9—C8—H8A	109.5
N1—C5—C4	120.0 (3)	C9—C8—H8B	109.5
N1—C5—H5A	120.0	H8A—C8—H8B	109.5
C4—C5—H5A	120.0	C9—C8—H8C	109.5
O1—C2—C1	121.9 (4)	H8A—C8—H8C	109.5
O1—C2—C3	119.5 (3)	H8B—C8—H8C	109.5
C1—C2—C3	118.6 (3)	C19—C18—C17	119.5 (4)
Cl4—Sb1—Cl3	92.15 (4)	C19—C18—H18A	120.2
Cl4—Sb1—Cl2	89.42 (5)	C17—C18—H18A	120.2
Cl3—Sb1—Cl2	90.96 (4)	C20—N3—C19	122.4 (3)
C2—C1—H1A	109.5	C20—N3—H3A	118.8

C2—C1—H1B	109.5	C19—N3—H3A	118.8
H1A—C1—H1B	109.5	C18—C17—C21	118.4 (3)
C2—C1—H1C	109.5	C18—C17—C16	122.7 (3)
H1A—C1—H1C	109.5	C21—C17—C16	118.8 (3)
H1B—C1—H1C	109.5	O3—C16—C15	122.5 (4)
Cl7—Sb2—Cl8	90.05 (5)	O3—C16—C17	118.7 (4)
Cl7—Sb2—Cl9	87.97 (4)	C15—C16—C17	118.8 (4)
Cl8—Sb2—Cl9	90.76 (4)	C20—C21—C17	120.2 (3)
Cl7—Sb2—Cl5	86.83 (5)	C20—C21—H21A	119.9
Cl8—Sb2—Cl5	174.29 (3)	C17—C21—H21A	119.9
Cl9—Sb2—Cl5	93.90 (4)	C16—C15—H15A	109.5
Cl7—Sb2—Cl6	83.07 (4)	C16—C15—H15B	109.5
Cl8—Sb2—Cl6	89.72 (4)	H15A—C15—H15B	109.5
Cl9—Sb2—Cl6	171.03 (3)	C16—C15—H15C	109.5
Cl5—Sb2—Cl6	85.17 (4)	H15A—C15—H15C	109.5
C14—C10—C11	118.7 (3)	H15B—C15—H15C	109.5
C14—C10—C9	118.9 (3)	N3—C20—C21	119.0 (4)
C11—C10—C9	122.4 (3)	N3—C20—H20A	120.5
C13—C14—C10	119.9 (4)	C21—C20—H20A	120.5
C13—C14—H14A	120.0	N3—C19—C18	120.4 (3)
C10—C14—H14A	120.0	N3—C19—H19A	119.8
C12—N2—C13	122.5 (3)	C18—C19—H19A	119.8
C5—N1—C6—C7	1.5 (6)	C12—N2—C13—C14	0.3 (6)
C7—C3—C4—C5	0.7 (5)	C10—C14—C13—N2	0.9 (6)
C2—C3—C4—C5	−176.9 (3)	C14—C10—C9—O2	1.7 (5)
N1—C6—C7—C3	−2.4 (6)	C11—C10—C9—O2	179.5 (3)
C4—C3—C7—C6	1.3 (5)	C14—C10—C9—C8	−177.2 (4)
C2—C3—C7—C6	179.0 (3)	C11—C10—C9—C8	0.6 (5)
C6—N1—C5—C4	0.6 (6)	C19—C18—C17—C21	−1.1 (5)
C3—C4—C5—N1	−1.7 (6)	C19—C18—C17—C16	178.2 (4)
C7—C3—C2—O1	−16.1 (5)	C18—C17—C16—O3	175.1 (4)
C4—C3—C2—O1	161.5 (3)	C21—C17—C16—O3	−5.6 (5)
C7—C3—C2—C1	165.5 (4)	C18—C17—C16—C15	−4.1 (5)
C4—C3—C2—C1	−16.9 (5)	C21—C17—C16—C15	175.1 (4)
C11—C10—C14—C13	−1.0 (5)	C18—C17—C21—C20	1.6 (5)
C9—C10—C14—C13	176.9 (3)	C16—C17—C21—C20	−177.7 (3)
C13—N2—C12—C11	−1.4 (6)	C19—N3—C20—C21	−1.3 (6)
N2—C12—C11—C10	1.2 (6)	C17—C21—C20—N3	−0.4 (6)
C14—C10—C11—C12	0.0 (5)	C20—N3—C19—C18	1.9 (6)
C9—C10—C11—C12	−177.8 (3)	C17—C18—C19—N3	−0.6 (6)

Symmetry codes: (i) −*x*+2, −*y*+1, −*z*+1.

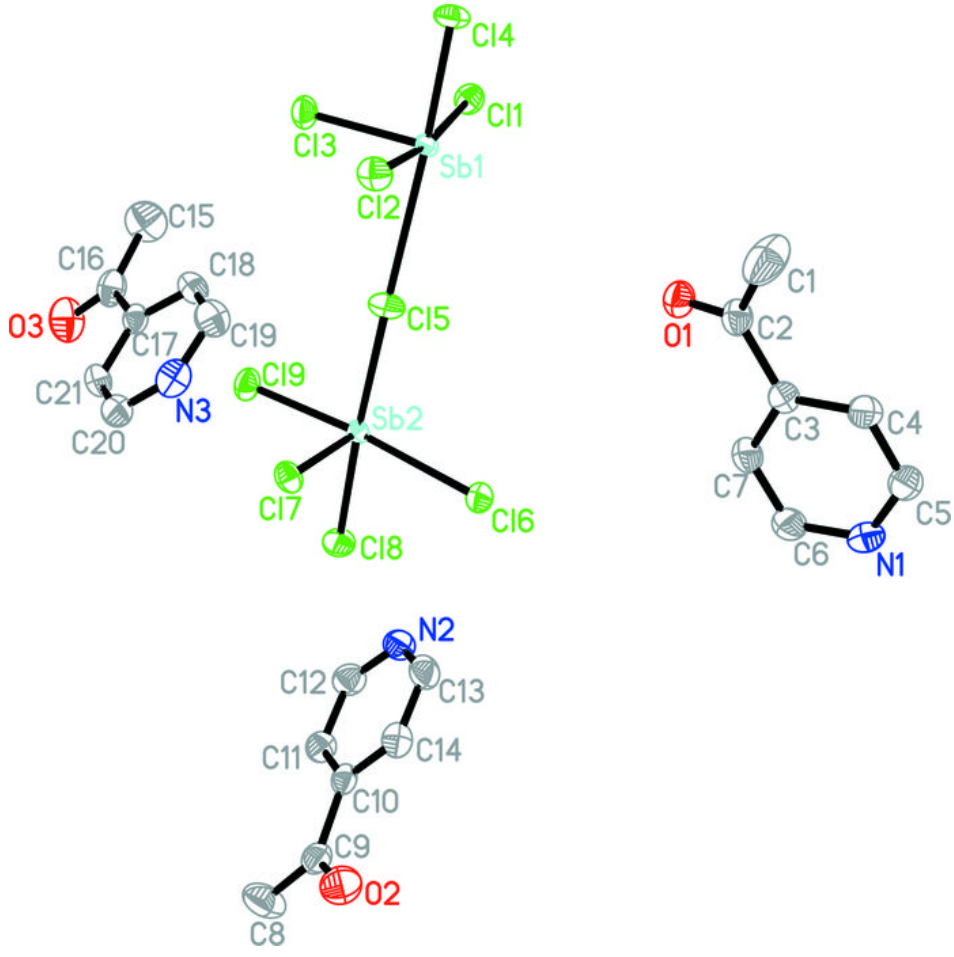
Hydrogen-bond geometry (Å, °)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
N2—H2A···Cl6	0.86	2.30	3.148 (3)	170
N1—H1D···Cl1^{ii}	0.86	2.20	3.056 (3)	174
N3—H3A···Cl5^{iii}	0.86	2.35	3.198 (3)	168

C1—H1A···O2^{iv}	0.96	2.60	3.506 (5)	158
C5—H5A···Cl8^{v}	0.93	2.78	3.585 (4)	146
C13—H13A···Cl1^{i}	0.93	2.76	3.661 (4)	162
C19—H19A···Cl7^{iii}	0.93	2.67	3.449 (4)	141
C21—H21A···O1^{iii}	0.93	2.42	3.349 (4)	177

Symmetry codes: (ii) *x*, *y*, *z*−1; (iii) −*x*+1, −*y*+1, −*z*+1; (iv) *x*, *y*−1, *z*; (v) *x*, *y*−1, *z*−1; (i) −*x*+2, −*y*+1, −*z*+1.

Fig. 1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C2
C3
C4
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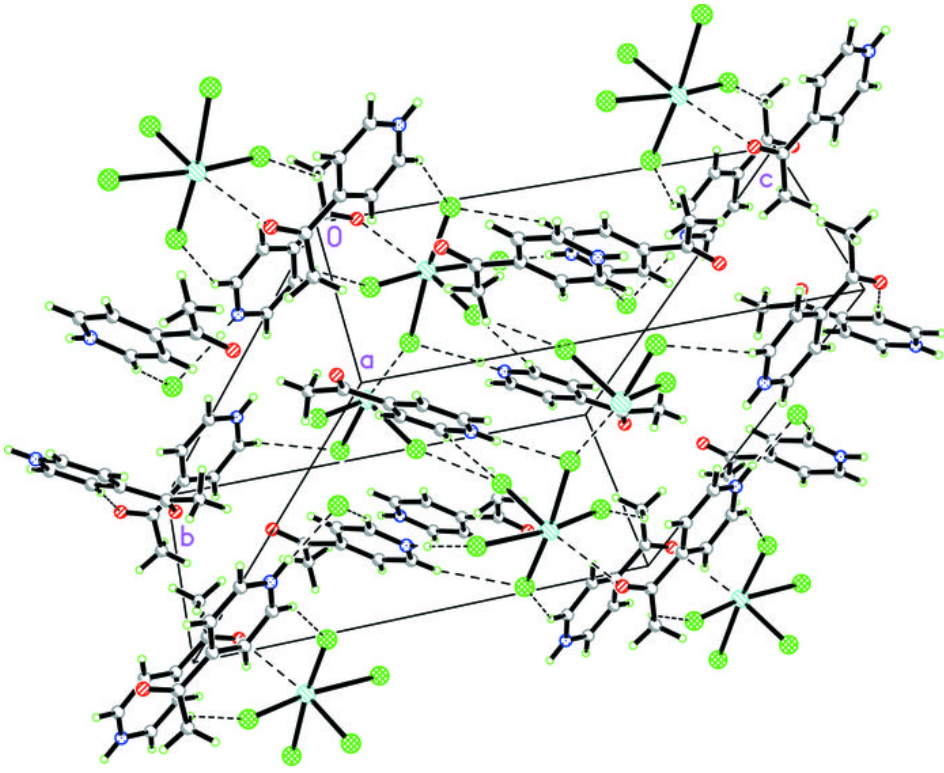
C5
C6
N1
N2
C12
C13
C11
C14
C10
C9
O2
C8

Fig. 2



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2-Oxo-4-trifluoromethyl-2*H*-chromen-7-yl 2-bromo-2-methylpropanoate

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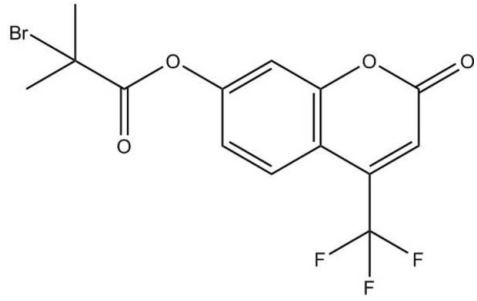
Key indicators: single-crystal X-ray study; T = 298 K; mean σ(C–C) = 0.004 Å; R factor = 0.040; wR factor = 0.109; data-to-parameter ratio = 18.9.

In the title compound, $C_{14}H_{10}BrF_3O_4$, the coumarin ring system is almost plannar (r.m.s. deviation = 0.025 Å) and a short C—H···F contact occurs. The propanoate fragment is orientated almost perpendicular to the ring [dihedral angle = 71.80 (12)°]. In the crystal, molecules are linked by C—H···O hydrogen bonds, generating [100] chains.

Related literature

For the applications of the title compound in polymer chemistry, see: Sinkel *et al.* (2008); Matyjaszewski *et al.* (2008); Stenzel-Rosenbaum *et al.* (2001).



Experimental

Crystal data

$C_{14}H_{10}BrF_3O_4$
M_r = 379.13
Triclinic, $P\overline{1}$
a = 6.1842 (4) Å
b = 11.0297 (6) Å
c = 11.0619 (7) Å
α = 99.982 (2)°
β = 91.797 (2)°
γ = 104.387 (2)°
V = 717.61 (8) Å^3
Z = 2
Mo $K\alpha$ radiation
μ = 2.91 mm^{-1}
T = 298 K
0.40 × 0.26 × 0.24 mm

Data collection

Bruker APEXII CCD diffractometer
Absorption correction: multi-scan (*SADABS*; Bruker, 2004)
T_{min} = 0.389, T_{max} = 0.542
9951 measured reflections
3796 independent reflections
2390 reflections with $I > 2\sigma(I)$
R_{int} = 0.022

Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.040
$wR(F^2)$ = 0.109
S = 1.01
3796 reflections
201 parameters
H-atom parameters constrained
$\Delta\rho_{max}$ = 0.78 e Å^{-3}
$\Delta\rho_{min}$ = −0.85 e Å^{-3}

Table 1
Hydrogen-bond geometry (Å, °).

D—H···A	D—H	H···A	D···A	D—H···A
C5—H5···F2	0.93	2.47	3.019 (3)	118
C6—H6···O4^{i}	0.93	2.52	3.261 (4)	136

Symmetry code: (i) $x+1, y, z$.

Data collection: *APEX2* (Bruker, 2004); cell refinement: *SAINT-Plus* (Bruker, 2004); data reduction: *SAINT-Plus* and *XPREP* (Bruker, 2004); program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *ORTEP-3* (Farrugia, 1997); software used to prepare material for publication: *SHELXL97*.

The authors acknowledge the Department of Chemistry, IIT Madras, for the X-ray data collection.

Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: HB5450).

References

Bruker (2004). *APEX2*, *SAINT-Plus* and *SADABS*. Bruker AXS Inc., Madison, Wisconsin, USA.
Farrugia, L. J. (1997). *J. Appl. Cryst.* **30**, 565.
Matyjaszewski, K. & Mueller, L. (2008). *Macromolecules*, **41**, 1067–1069.
Sheldrick, G. M. (2008). *Acta Cryst.* A**64**, 112–122.
Sinkel, C., Greiner, A. & Agarwal, S. (2008). *Macromolecules*, **41**, 1067–1069.
Stenzel-Rosenbaum, M., Davis, T. P., Chen, V. & Fane, A. G. (2001). *J. Polym. Sci. A Polym. Chem.* **39**, 2777–2783.

supplementary materials

Acta Cryst. (2010). E**66**, o1606 [**doi:10.1107/S1600536810020234**]

2-Oxo-4-trifluoromethyl-2*H*-chromen-7-yl 2-bromo-2-methylpropanoate

N. Haridharan, V. Ramkumar and R. Dhamodharan

Comment

The title compound $C_{14}H_{10}BrF_3O_4$, is a monofunctional coumarin derivative, which is used as an initiator (Sinkel *et al.* 2008) in Atom Transfer Radical Polymerization (ATRP). Being a monofunctional unit it can form end-functionalized linear polymers (Matyjaszewski *et al.* 2008; Stenzel-Rosenbaum *et al.*2001) when used as an initiator. Since most of the synthesized functionalized initiators are characterized by other techniques, their single crystal XRD reports are few.

The title compound is one such successful ATRP initiator which was crystallised from chloroform. It contains coumarin derivative with bromo methyl propanoate. The coumarin moiety is an important oxygen containing heterocyclic compound with diverse bioactivities such as non peptidic HIV protease inhibition and tyrosine kinase inhibition. Owing to such interesting properties, the synthesis of coumarin based initiators and their crystal structures are worth while to study.

In the title compound C_{14} H_{10} Br F_3 O_4, the coumarin ring system is plannar with the 2-bromo-2-methyl propanoate moiety almost perpendicular. The C—F bond lengths of 1.333 (2) Å,1.324 (3)Å and 1.331 (3)Å are normal in this structure. One F atom (F1) lie in plane with the coumarin ring system and the other two F atoms are above and below the plane. The torsion angle of C6—C7—O3—C11 and C8—C7—O3—C11 are -114.21 (3)° and 71.42 (2)° respectively. The crystal is stabilized by intermolecular C—H···O hydrogen bond.

Experimental

7-Hydroxy-4-trifluoromethylcoumarin 5 g (0.02 mole), triethylamine 4.83 g (0.04 mole) and THF (400 ml) were placed in a 3-neck round bottomed flask. Bromoisobutyrl bromide 10.9 g (0.04 mole) was added slowly, using a syringe, with stirring, upon which an white precipitate of triethylammonium bromide was formed. The mixture was left to react for 6 hours, with stirring. Subsequently, triethylammonium bromide, the precipitate was removed by filtration and the THF was removed by rotary evaporation. The resulting crude product was dissolved in ethyl acetate, washed with bicarbonate solution and then with water thrice followed by brine solution and dried over anhydrous sodium sulphate. The resulting solvent was removed by rotary evaporation. The product was purified by column chromatography technique using 15% ethyl acetate in hexane as the eluent to obtain pure initiator as a bright white solid. Recrystallization of the compound from chloroform gave colourless blocks of (I).

Refinement

All hydrogen atoms were fixed geometrically and allowed to ride on the parent carbon atoms, with aromatic C—H = 0.93 Å and methyl C—H = 0.96 Å. The displacement parameters were set for phenyl H atoms at $U_{iso}(H) = 1.2U_{eq}(C)$ and methyl H atoms at $U_{iso}(H) = 1.5U_{eq}(C)$.

Figures

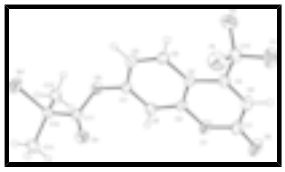


Fig. 1. View of (I) with atoms represented as 30% probability ellipsoids.

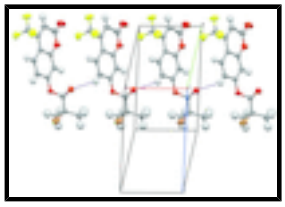


Fig. 2. The packing diagram showing the C—H···O interaction.

2-Oxo-4-trifluoromethyl-2*H*-chromen-7-yl 2-bromo-2-methylpropanoate

Crystal data

$C_{14}H_{10}BrF_3O_4$	$Z = 2$
$M_r = 379.13$	$F(000) = 376$
Triclinic, $P\overline{1}$	$D_x = 1.755$ Mg m^{-3}
Hall symbol: -P 1	Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å
$a = 6.1842$ (4) Å	Cell parameters from 3404 reflections
$b = 11.0297$ (6) Å	$\theta = 2.4$–$25.3°$
$c = 11.0619$ (7) Å	$\mu = 2.91$ mm^{-1}
$\alpha = 99.982$ (2)°	$T = 298$ K
$\beta = 91.797$ (2)°	Rectangular, colourless
$\gamma = 104.387$ (2)°	0.40 × 0.26 × 0.24 mm
$V = 717.61$ (8) Å^3	

Data collection

Bruker APEXII CCD diffractometer	3796 independent reflections
Radiation source: fine-focus sealed tube	2390 reflections with $I > 2\sigma(I)$
graphite	$R_{int} = 0.022$
phi and ω scans	$\theta_{max} = 30.8°$, $\theta_{min} = 1.9°$
Absorption correction: multi-scan (*SADABS*; Bruker, 2004)	$h = -7 \rightarrow 8$
$T_{min} = 0.389$, $T_{max} = 0.542$	$k = -15 \rightarrow 14$
9951 measured reflections	$l = -13 \rightarrow 15$

Refinement

Refinement on F^2	Primary atom site location: structure-invariant direct methods
Least-squares matrix: full	Secondary atom site location: difference Fourier map

$R[F^2 > 2\sigma(F^2)] = 0.040$	Hydrogen site location: inferred from neighbouring sites
$wR(F^2) = 0.109$	H-atom parameters constrained
$S = 1.01$	$w = 1/[\sigma^2(F_o^2) + (0.0464P)^2 + 0.448P]$ where $P = (F_o^2 + 2F_c^2)/3$
3796 reflections	$(\Delta/\sigma)_{max} < 0.001$
201 parameters	$\Delta\rho_{max} = 0.78$ e Å^{-3}
0 restraints	$\Delta\rho_{min} = -0.85$ e Å^{-3}

Special details

Geometry. All esds (except the esd in the dihedral angle between two l.s. planes are estimated using the full covariance matrix. The cell esds are taken into account individually in the estimation of esds in distances, angles and torsion angles; correlations between esds in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell esds is used for estimating esds involving l.s. planes.

Refinement. Refinement of F^2 against ALL reflections. The weighted *R*-factor wR and goodness of fit *S* are based on F^2, conventional *R*-factors *R* are based on *F*, with *F* set to zero for negative F^2. The threshold expression of $F^2 > \sigma(F^2)$ is used only for calculating *R*-factors(gt) etc. and is not relevant to the choice of reflections for refinement. *R*-factors based on F^2 are statistically about twice as large as those based on *F*, and *R*- factors based on ALL data will be even larger.

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å^2)

	x	*y*	*z*	U_{iso}*/U_{eq}
Br1	0.06908 (6)	−0.04175 (3)	0.29516 (4)	0.06662 (16)
C1	0.2614 (5)	0.5339 (3)	−0.2219 (3)	0.0450 (7)
C2	0.4147 (5)	0.4806 (3)	−0.2966 (3)	0.0450 (7)
H2	0.4574	0.5118	−0.3675	0.054*
C3	0.4972 (4)	0.3873 (3)	−0.2666 (2)	0.0363 (6)
C4	0.4377 (4)	0.3379 (2)	−0.1559 (2)	0.0322 (5)
C5	0.5183 (4)	0.2437 (3)	−0.1127 (2)	0.0375 (6)
H5	0.6232	0.2098	−0.1557	0.045*
C6	0.4449 (5)	0.2007 (3)	−0.0080 (3)	0.0408 (6)
H6	0.4995	0.1385	0.0202	0.049*
C7	0.2881 (4)	0.2518 (3)	0.0548 (2)	0.0359 (6)
C8	0.2074 (4)	0.3459 (3)	0.0179 (2)	0.0386 (6)
H8	0.1041	0.3801	0.0622	0.046*
C9	0.2849 (4)	0.3880 (2)	−0.0872 (2)	0.0333 (6)
C10	0.6453 (5)	0.3300 (3)	−0.3523 (3)	0.0464 (7)
C11	0.0108 (4)	0.1442 (3)	0.1690 (3)	0.0361 (6)
C12	−0.0307 (4)	0.1167 (3)	0.2974 (3)	0.0389 (6)
C13	0.1076 (6)	0.2198 (3)	0.4010 (3)	0.0541 (8)

H13A	0.2639	0.2317	0.3887	0.081*
H13B	0.0784	0.1940	0.4787	0.081*
H13C	0.0672	0.2983	0.4005	0.081*
C14	−0.2790 (5)	0.0855 (3)	0.3145 (3)	0.0516 (8)
H14A	−0.3331	0.1596	0.3129	0.077*
H14B	−0.3045	0.0591	0.3923	0.077*
H14C	−0.3569	0.0179	0.2493	0.077*
F1	0.6893 (4)	0.3893 (2)	−0.44723 (18)	0.0775 (6)
F2	0.8423 (3)	0.3353 (2)	−0.29621 (18)	0.0652 (5)
F3	0.5518 (3)	0.20819 (19)	−0.39741 (17)	0.0645 (5)
O1	0.2025 (3)	0.48421 (18)	−0.11926 (17)	0.0429 (5)
O2	0.1777 (4)	0.6161 (2)	−0.2441 (2)	0.0648 (6)
O3	0.2269 (3)	0.2130 (2)	0.16562 (17)	0.0452 (5)
O4	−0.1216 (3)	0.1118 (2)	0.08271 (19)	0.0498 (5)

Atomic displacement parameters (Å^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Br1	0.0781 (3)	0.0645 (3)	0.0835 (3)	0.04411 (19)	0.0312 (2)	0.0426 (2)
C1	0.0603 (18)	0.0383 (16)	0.0422 (16)	0.0201 (13)	0.0037 (14)	0.0123 (13)
C2	0.0613 (18)	0.0436 (17)	0.0361 (15)	0.0170 (13)	0.0083 (13)	0.0174 (13)
C3	0.0408 (14)	0.0373 (15)	0.0311 (13)	0.0087 (11)	0.0039 (11)	0.0083 (11)
C4	0.0354 (13)	0.0320 (13)	0.0301 (13)	0.0100 (10)	0.0012 (11)	0.0066 (11)
C5	0.0398 (14)	0.0386 (15)	0.0398 (15)	0.0179 (11)	0.0082 (12)	0.0103 (12)
C6	0.0420 (15)	0.0426 (16)	0.0436 (16)	0.0157 (12)	0.0015 (13)	0.0166 (13)
C7	0.0355 (13)	0.0419 (15)	0.0314 (13)	0.0071 (11)	0.0006 (11)	0.0141 (12)
C8	0.0399 (14)	0.0448 (16)	0.0359 (14)	0.0165 (12)	0.0090 (12)	0.0114 (12)
C9	0.0371 (13)	0.0322 (13)	0.0343 (14)	0.0136 (11)	−0.0003 (11)	0.0097 (11)
C10	0.0507 (17)	0.055 (2)	0.0388 (16)	0.0182 (14)	0.0111 (13)	0.0158 (14)
C11	0.0355 (13)	0.0387 (15)	0.0409 (15)	0.0163 (11)	0.0076 (12)	0.0150 (12)
C12	0.0410 (14)	0.0400 (15)	0.0434 (16)	0.0164 (12)	0.0110 (12)	0.0184 (13)
C13	0.063 (2)	0.062 (2)	0.0375 (16)	0.0097 (16)	0.0049 (14)	0.0203 (15)
C14	0.0483 (17)	0.0514 (18)	0.060 (2)	0.0164 (14)	0.0240 (15)	0.0162 (16)
F1	0.1027 (17)	0.1013 (16)	0.0556 (12)	0.0515 (13)	0.0434 (12)	0.0444 (12)
F2	0.0437 (10)	0.0907 (15)	0.0663 (12)	0.0224 (10)	0.0112 (9)	0.0201 (11)
F3	0.0773 (13)	0.0584 (12)	0.0548 (11)	0.0235 (10)	0.0128 (10)	−0.0077 (9)
O1	0.0573 (12)	0.0422 (11)	0.0403 (11)	0.0277 (9)	0.0093 (9)	0.0146 (9)
O2	0.0941 (18)	0.0559 (14)	0.0647 (15)	0.0455 (13)	0.0132 (13)	0.0270 (12)
O3	0.0371 (10)	0.0647 (13)	0.0372 (10)	0.0071 (9)	0.0029 (8)	0.0271 (9)
O4	0.0422 (11)	0.0607 (13)	0.0453 (12)	0.0078 (9)	−0.0033 (10)	0.0161 (10)

Geometric parameters (Å, °)

Br1—C12	1.990 (3)	C8—H8	0.9300
C1—O2	1.205 (3)	C9—O1	1.378 (3)
C1—O1	1.366 (3)	C10—F3	1.324 (4)
C1—C2	1.444 (4)	C10—F1	1.332 (3)
C2—C3	1.340 (4)	C10—F2	1.333 (4)
C2—H2	0.9300	C11—O4	1.181 (3)

C3—C4	1.447 (4)	C11—O3	1.368 (3)
C3—C10	1.507 (4)	C11—C12	1.520 (4)
C4—C9	1.391 (4)	C12—C14	1.513 (4)
C4—C5	1.404 (4)	C12—C13	1.529 (4)
C5—C6	1.375 (4)	C13—H13A	0.9600
C5—H5	0.9300	C13—H13B	0.9600
C6—C7	1.385 (4)	C13—H13C	0.9600
C6—H6	0.9300	C14—H14A	0.9600
C7—C8	1.373 (4)	C14—H14B	0.9600
C7—O3	1.400 (3)	C14—H14C	0.9600
C8—C9	1.382 (4)		
O2—C1—O1	117.5 (3)	F3—C10—F2	106.4 (3)
O2—C1—C2	125.6 (3)	F1—C10—F2	106.6 (2)
O1—C1—C2	116.9 (2)	F3—C10—C3	111.5 (2)
C3—C2—C1	121.9 (3)	F1—C10—C3	112.1 (3)
C3—C2—H2	119.1	F2—C10—C3	112.4 (2)
C1—C2—H2	119.1	O4—C11—O3	123.6 (2)
C2—C3—C4	120.6 (3)	O4—C11—C12	126.0 (2)
C2—C3—C10	119.4 (3)	O3—C11—C12	110.4 (2)
C4—C3—C10	119.9 (2)	C14—C12—C11	110.2 (2)
C9—C4—C5	117.5 (2)	C14—C12—C13	112.9 (3)
C9—C4—C3	116.5 (2)	C11—C12—C13	114.2 (2)
C5—C4—C3	126.0 (2)	C14—C12—Br1	107.64 (19)
C6—C5—C4	121.1 (2)	C11—C12—Br1	102.84 (17)
C6—C5—H5	119.4	C13—C12—Br1	108.4 (2)
C4—C5—H5	119.4	C12—C13—H13A	109.5
C5—C6—C7	118.8 (2)	C12—C13—H13B	109.5
C5—C6—H6	120.6	H13A—C13—H13B	109.5
C7—C6—H6	120.6	C12—C13—H13C	109.5
C8—C7—C6	122.4 (2)	H13A—C13—H13C	109.5
C8—C7—O3	119.5 (2)	H13B—C13—H13C	109.5
C6—C7—O3	117.8 (2)	C12—C14—H14A	109.5
C7—C8—C9	117.7 (2)	C12—C14—H14B	109.5
C7—C8—H8	121.2	H14A—C14—H14B	109.5
C9—C8—H8	121.2	C12—C14—H14C	109.5
O1—C9—C8	115.6 (2)	H14A—C14—H14C	109.5
O1—C9—C4	121.9 (2)	H14B—C14—H14C	109.5
C8—C9—C4	122.5 (2)	C1—O1—C9	122.1 (2)
F3—C10—F1	107.5 (2)	C11—O3—C7	117.3 (2)
O2—C1—C2—C3	−178.7 (3)	C2—C3—C10—F3	−115.9 (3)
O1—C1—C2—C3	−0.5 (4)	C4—C3—C10—F3	61.5 (3)
C1—C2—C3—C4	−1.1 (4)	C2—C3—C10—F1	4.7 (4)
C1—C2—C3—C10	176.3 (3)	C4—C3—C10—F1	−177.9 (2)
C2—C3—C4—C9	2.8 (4)	C2—C3—C10—F2	124.8 (3)
C10—C3—C4—C9	−174.5 (2)	C4—C3—C10—F2	−57.8 (3)
C2—C3—C4—C5	−177.8 (3)	O4—C11—C12—C14	−20.7 (4)
C10—C3—C4—C5	4.8 (4)	O3—C11—C12—C14	159.3 (2)
C9—C4—C5—C6	1.5 (4)	O4—C11—C12—C13	−149.0 (3)

C3—C4—C5—C6	−177.9 (3)	O3—C11—C12—C13	31.0 (3)
C4—C5—C6—C7	0.2 (4)	O4—C11—C12—Br1	93.8 (3)
C5—C6—C7—C8	−1.6 (4)	O3—C11—C12—Br1	−86.2 (2)
C5—C6—C7—O3	−175.8 (2)	O2—C1—O1—C9	178.6 (3)
C6—C7—C8—C9	1.2 (4)	C2—C1—O1—C9	0.3 (4)
O3—C7—C8—C9	175.3 (2)	C8—C9—O1—C1	−178.9 (2)
C7—C8—C9—O1	−178.8 (2)	C4—C9—O1—C1	1.6 (4)
C7—C8—C9—C4	0.6 (4)	O4—C11—O3—C7	3.3 (4)
C5—C4—C9—O1	177.5 (2)	C12—C11—O3—C7	−176.7 (2)
C3—C4—C9—O1	−3.1 (4)	C8—C7—O3—C11	71.5 (3)
C5—C4—C9—C8	−1.9 (4)	C6—C7—O3—C11	−114.2 (3)
C3—C4—C9—C8	177.5 (2)		

Hydrogen-bond geometry (Å, °)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
C5—H5···F2	0.93	2.47	3.019 (3)	118
C6—H6···O4^{i}	0.93	2.52	3.261 (4)	136

Symmetry codes: (i) *x*+1, *y*, *z*.

Fig. 1

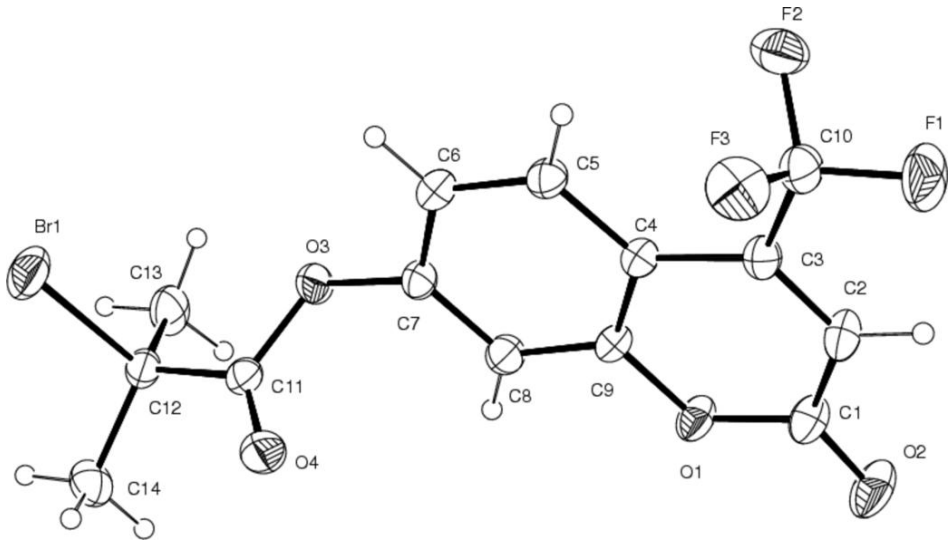
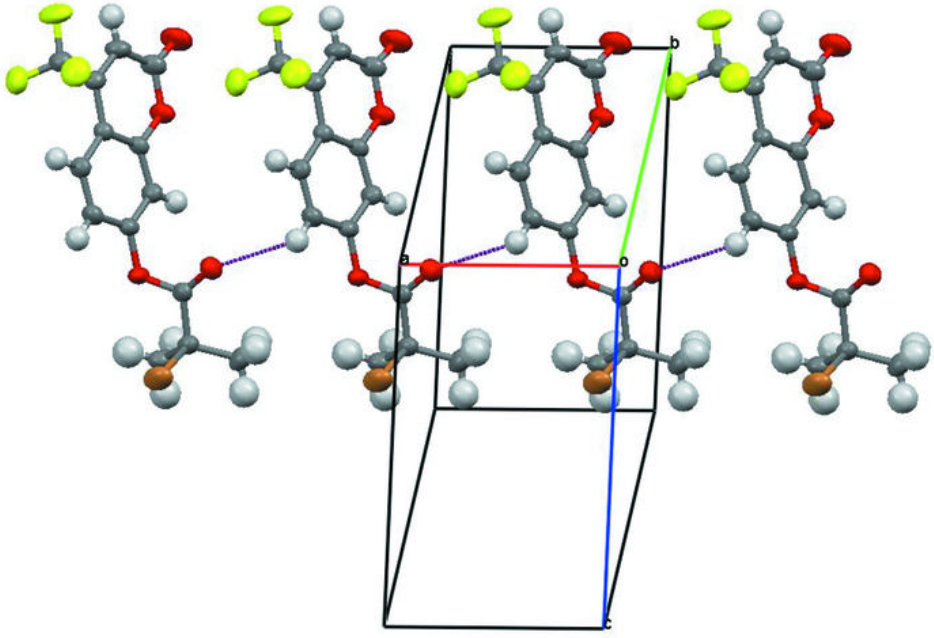

F2
F3
C10
F1
C6
C5
C4
C3
Br1
O3
C13
C2
C7
C11
C12
C8
C9
C1
O4
O1
O2
C14

Fig. 2



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(4-Aminobenzenesulfonato)heptaaquagadolinium(III) 4-aminobenzenesulfonate nitrate 4,4′-bipyridyl tetrasolvate dihydrate

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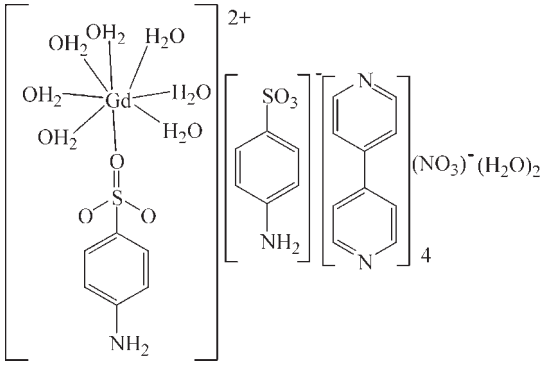
Key indicators: single-crystal X-ray study; T = 296 K; mean σ(C–C) = 0.010 Å; R factor = 0.036; wR factor = 0.088; data-to-parameter ratio = 12.9.

In the title compound, $[Gd(C_6H_6O_3S)(H_2O)_7](C_6H_6O_3S)(NO_3)\cdot 4C_{10}H_8N_2\cdot 2H_2O$, the Gd^{III} ion is octacoordinated by seven water molecules and one O-bonded 4-aminobenzenesulfonate anion in a square-antiprismatic arrangement. In the crystal, the components are linked by N—H···O, O—H···N and O—H···O hydrogen bonds.

Related literature

For background to lanthanide coordination networks, see: Karthikeyan *et al.* (1989).



Experimental

Crystal data

$[Gd(C_6H_6O_3S)(H_2O)_7](C_6H_6O_3S)(NO_3)\cdot 4C_{10}H_8N_2\cdot 2H_2O$
M_r = 1350.50
Orthorhombic, *Aba*2
a = 33.529 (2) Å
b = 23.3375 (10) Å
c = 15.2046 (10) Å
V = 11897.3 (12) Å^3
Z = 8
Mo $K\alpha$ radiation
μ = 1.26 mm^{-1}
T = 296 K
0.12 × 0.10 × 0.08 mm

Data collection

Bruker APEXII CCD diffractometer
Absorption correction: multi-scan (*SADABS*; Bruker, 2001)
T_{min} = 0.863, T_{max} = 0.906
41191 measured reflections
10477 independent reflections
8881 reflections with $I > 2\sigma(I)$
R_{int} = 0.045

Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.036
$wR(F^2)$ = 0.088
S = 1.00
10477 reflections
811 parameters
27 restraints
H atoms treated by a mixture of independent and constrained refinement
$\Delta\rho_{max}$ = 0.35 e Å^{-3}
$\Delta\rho_{min}$ = −0.53 e Å^{-3}
Absolute structure: Flack (1983), 5009 Friedel pairs
Flack parameter: 0.002 (1)

Table 1
Selected bond lengths (Å).

Gd1—O6*W*	2.375 (4)	Gd1—O7*W*	2.391 (4)
Gd1—O2*W*	2.373 (4)	Gd1—O5*W*	2.401 (4)
Gd1—O1*W*	2.389 (4)	Gd1—O1	2.434 (4)
Gd1—O3*W*	2.392 (4)	Gd1—O4*W*	2.440 (4)

Table 2
Hydrogen-bond geometry (Å, °).

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
O1*W*—H1*W*···N6	0.82 (2)	2.12 (2)	2.770 (7)	136 (3)
O1*W*—H2*W*···O5	0.82 (2)	2.13 (1)	2.759 (6)	134 (3)
O2*W*—H3*W*···O8*W*	0.82 (2)	1.93 (1)	2.657 (7)	147 (2)
O3*W*—H6*W*···N8	0.82 (2)	1.99 (1)	2.728 (7)	149 (2)
O4*W*—H8*W*···N9^{i}	0.82 (2)	2.19 (2)	2.807 (7)	133 (1)
O5*W*—H9*W*···N4^{ii}	0.82 (1)	1.86 (1)	2.647 (7)	159 (2)
O5*W*—H10*W*···O3	0.82 (2)	2.51 (2)	3.236 (6)	148 (4)
O5*W*—H10*W*···O1	0.82 (2)	2.50 (3)	2.931 (5)	114 (2)
O6*W*—H11*W*···O3^{iii}	0.82 (3)	1.95 (3)	2.765 (6)	175 (5)
O6*W*—H12*W*···N3	0.82 (1)	1.90 (1)	2.719 (7)	178 (8)
O7*W*—H13*W*···N1^{iv}	0.82 (3)	2.19 (2)	2.902 (7)	145 (3)
O7*W*—H14*W*···N5^{ii}	0.82 (1)	2.37 (4)	2.758 (7)	110 (3)
O7*W*—H14*W*···O3*W*	0.82 (1)	2.29 (1)	2.709 (6)	112 (3)
O8*W*—H16*W*···N11^{v}	0.82 (3)	1.98 (3)	2.798 (9)	176 (6)
O9*W*—H17*W*···O20	0.82 (3)	2.06 (4)	2.873 (7)	169 (6)
O9*W*—H18*W*···O2^{vi}	0.82 (4)	2.24 (5)	3.028 (7)	161 (7)
N1—H1*A*···O6^{vi}	0.86	2.22	2.972 (7)	146
N1—H1*B*···O2^{vi}	0.86	2.14	2.958 (6)	159
N7—H7*B*···O14^{vii}	0.86	2.51	3.289 (12)	151
N7—H7*A*···O15^{viii}	0.86	2.63	3.345 (12)	141
N7—H7*A*···O16^{viii}	0.86	2.46	3.302 (13)	167

Symmetry codes: (i) $-x+\frac{3}{2}, y-\frac{1}{2}, z$; (ii) $x, y, z-1$; (iii) $-x+2, -y+1, z$; (iv) $-x+2, -y+\frac{3}{2}, z-\frac{1}{2}$; (v) $-x+\frac{3}{2}, y, z-\frac{1}{2}$; (vi) $-x+2, -y+\frac{3}{2}, z+\frac{1}{2}$; (vii) $x, y+\frac{1}{2}, z+\frac{1}{2}$; (viii) $-x+\frac{3}{2}, y+\frac{1}{2}, z$.

Data collection: *APEX2* (Bruker, 2004); cell refinement: *SAINT-Plus* (Bruker, 2001); data reduction: *SAINT-Plus*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *SHELXTL* (Sheldrick, 2008); software used to prepare material for publication: *SHELXTL*.

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Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: HB5454).

References

Bruker (2001). *SAINT-Plus* and *SADABS*. Bruker AXS Inc., Madison, Wisconsin, USA.
Bruker (2004). *APEX2*. Bruker AXS Inc., Madison, Wisconsin, USA.
Flack, H. D. (1983). *Acta Cryst.* A**39**, 876–881.
Karthikeyan, S., Ryan, R. R. & Paine, R. T. (1989). *Inorg. Chem.* **28**, 2783–2789.
Sheldrick, G. M. (2008). *Acta Cryst.* A**64**, 112–122.

supplementary materials

Acta Cryst. (2010). E**66**, m740-m741 [**doi:10.1107/S1600536810020520**]

(4-Aminobenzenesulfonato)heptaaquagadolinium(III) 4-aminobenzenesulfonate nitrate 4,4'-bipyridyl tetrasolvate dihydrate

L. Hao, X. Zhang and J. Chen

Comment

The design and synthesis of metal-organic compounds has attracted continuous research interest not only because of their appealing structural and topological novelties, but also due to their interesting optical, electronic, magnetic, and catalytic properties, as well as their potential medical applications (Karthikeyan *et al.*, 1989). Here, we describe the synthesis and structural characterization of the title compound.

As shown in Figure 1, Gd(III) is octacoordinated by senven water molecules and one *p*-amino-benzenesulfonate anion. The Gd—O bond lengths are in the range of 2.370 (4)—2.439 (4) Å. In the molecule, one *p*-amino-benzenesulfonate, one nitrate, and two water molecules disassociate. N—H···O2, N—H···S, O—H···N, O—H···N, O—H···O hydrogen bonding between the cationic and anionic moieties and the uncoordinated water molecules leads to a consolidation of the structure (Fig. 2; Table 2).

Experimental

A mixture of 4-aminobenzene sulfonic acid (1 mmol 0.17 g), gadolinium(III) nitrate hexahydrate (0.5 mmol, 0.17 g), and 4,4-bipyridine (1 mmol, 0.14 g) in 10 ml distilled water was sealed in a 25 ml Teflon-lined stainless steel autoclave and was kept at 433 K for three days. Colourless blocks of (I) were obtained upon cooling. Anal. $C_{52}H_{62}GdN_{11}O_{18}S_2$: C, 46.22; H, 4.59; N, 11.41. Found: C, 46.01; H, 4.48; N, 11.23%.

Refinement

All hydrogen atoms bound to aromatic carbon atoms were refined in calculated positions using a riding model with a C—H distance of 0.93 Å and U_{iso} = 1.2U_{eq}(C). The hydrogen atoms bound to N atoms were refined in calculated positions using a riding model with a N—H distance of 0.86 Å and U_{iso} = 1.2U_{eq}(C). Water molecules are refined by using the '*DFIX*' command with the hydrogen atoms were separated with 1.38 Å, and the lengths of bond H—O were constrained with 0.82 Å with error 0.02 and U_{iso} = 1.5U_{eq} (O). The location of the water H atoms should be regarded as less certain that those of the other H atoms.

Figures

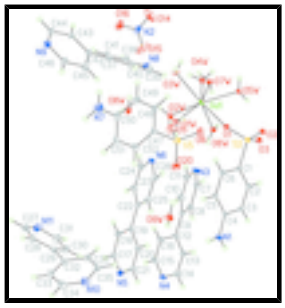

Fig. 1. The building blocks of (I) with displacement ellipsoids drawn at the 30% probability level; H atoms are given as spheres of arbitrary radius.

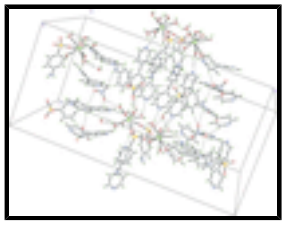

Fig. 2. The crystal packing of (I), displayed with N—H···O and O—H···O hydrogen bonds as dashed lines.

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Crystal data

$[Gd(C_6H_6O_3S)(H_2O)_7](C_6H_6O_3S)(NO_3)\cdot 4C_{10}H_8N_2\cdot 2H_2O$	$F(000) = 5528$
$M_r = 1350.50$	$D_x = 1.508$ Mg m^{-3}
Orthorhombic, *Aba*2	Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å
Hall symbol: A 2 -2ac	Cell parameters from 10477 reflections
$a = 33.529$ (2) Å	$\theta = 2.4$–$25.0°$
$b = 23.3375$ (10) Å	$\mu = 1.26$ mm^{-1}
$c = 15.2046$ (10) Å	$T = 296$ K
$V = 11897.3$ (12) Å^3	Block, colourless
$Z = 8$	0.12 × 0.10 × 0.08 mm

Data collection

Bruker APEXII CCD diffractometer	10477 independent reflections
Radiation source: fine-focus sealed tube	8881 reflections with $I > 2\sigma(I)$
graphite	$R_{int} = 0.045$
phi and ω scans	$\theta_{max} = 25.0°$, $\theta_{min} = 2.4°$
Absorption correction: multi-scan (*SADABS*; Bruker, 2001)	$h = -39 \rightarrow 39$
$T_{min} = 0.863$, $T_{max} = 0.906$	$k = -27 \rightarrow 25$
41191 measured reflections	$l = -18 \rightarrow 18$

Refinement

Refinement on F^2	Secondary atom site location: difference Fourier map
Least-squares matrix: full	Hydrogen site location: inferred from neighbouring sites
$R[F^2 > 2\sigma(F^2)] = 0.036$	H atoms treated by a mixture of independent and constrained refinement
$wR(F^2) = 0.088$	$w = 1/[\sigma^2(F_o^2) + (0.044P)^2 + 12.9607P]$ where $P = (F_o^2 + 2F_c^2)/3$
$S = 1.00$	$(\Delta/\sigma)_{max} = 0.001$
10477 reflections	$\Delta\rho_{max} = 0.35$ e Å^{-3}
811 parameters	$\Delta\rho_{min} = -0.53$ e Å^{-3}
27 restraints	Absolute structure: Flack (1983), 5009 Friedel pairs
Primary atom site location: structure-invariant direct methods	Flack parameter: 0.002 (1)

Special details

Geometry. All e.s.d.'s (except the e.s.d. in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell e.s.d.'s are taken into account individually in the estimation of e.s.d.'s in distances, angles and torsion angles; correlations between e.s.d.'s in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell e.s.d.'s is used for estimating e.s.d.'s involving l.s. planes.

Refinement. Refinement of F^2 against ALL reflections. The weighted *R*-factor *wR* and goodness of fit *S* are based on F^2, conventional *R*-factors *R* are based on *F*, with *F* set to zero for negative F^2. The threshold expression of $F^2 > \sigma(F^2)$ is used only for calculating *R*-factors(gt) *etc*. and is not relevant to the choice of reflections for refinement. *R*-factors based on F^2 are statistically about twice as large as those based on *F*, and *R*- factors based on ALL data will be even larger.

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å^2)

	x	*y*	*z*	U_{iso}*/U_{eq}
C1	1.01881 (15)	0.6735 (2)	0.4126 (3)	0.0317 (11)
C2	1.04516 (16)	0.6502 (2)	0.4716 (3)	0.0373 (12)
H2	1.0613	0.6198	0.4545	0.045*
C3	1.04792 (18)	0.6714 (3)	0.5561 (4)	0.0423 (14)
H3	1.0658	0.6549	0.5955	0.051*
C4	1.02425 (16)	0.7174 (2)	0.5830 (3)	0.0366 (13)
C5	0.99778 (17)	0.7407 (2)	0.5226 (3)	0.0391 (14)
H5	0.9818	0.7714	0.5391	0.047*
C6	0.99492 (16)	0.7190 (2)	0.4389 (4)	0.0392 (13)
H6	0.9768	0.7350	0.3995	0.047*
C7	0.9597 (2)	0.5837 (3)	0.5639 (5)	0.065 (2)
H7	0.9668	0.6149	0.5294	0.078*
C8	0.9629 (2)	0.5891 (3)	0.6540 (5)	0.058 (2)
H8	0.9726	0.6230	0.6781	0.069*
C9	0.9520 (2)	0.5445 (3)	0.7085 (4)	0.0402 (16)
C10	0.9388 (3)	0.4959 (3)	0.6658 (4)	0.069 (2)

H10	0.9316	0.4638	0.6983	0.083*
C11	0.9361 (3)	0.4947 (4)	0.5753 (5)	0.083 (3)
H11	0.9259	0.4618	0.5492	0.099*
C12	0.95518 (19)	0.5476 (3)	0.8045 (4)	0.0364 (15)
C13	0.9811 (2)	0.5832 (3)	0.8464 (5)	0.065 (2)
H13	0.9976	0.6072	0.8139	0.077*
C14	0.9829 (3)	0.5837 (4)	0.9365 (5)	0.077 (3)
H14	1.0010	0.6084	0.9630	0.092*
C15	0.9355 (3)	0.5184 (4)	0.9479 (5)	0.074 (3)
H15	0.9195	0.4950	0.9826	0.089*
C16	0.9307 (2)	0.5152 (3)	0.8572 (5)	0.063 (2)
H16	0.9114	0.4915	0.8327	0.075*
C17	0.8646 (2)	0.6318 (3)	0.9382 (5)	0.056 (2)
H17	0.8504	0.6059	0.9726	0.067*
C18	0.8591 (2)	0.6306 (3)	0.8485 (5)	0.053 (2)
H18	0.8414	0.6042	0.8245	0.064*
C19	0.87929 (19)	0.6675 (3)	0.7936 (4)	0.0357 (16)
C20	0.9046 (2)	0.7060 (3)	0.8358 (5)	0.055 (2)
H20	0.9189	0.7329	0.8036	0.066*
C21	0.9079 (2)	0.7037 (4)	0.9264 (5)	0.063 (2)
H21	0.9250	0.7300	0.9529	0.076*
C22	0.87594 (19)	0.6666 (3)	0.6959 (5)	0.0395 (17)
C23	0.8567 (2)	0.6225 (3)	0.6532 (4)	0.056 (2)
H23	0.8445	0.5933	0.6850	0.067*
C24	0.8556 (3)	0.6222 (4)	0.5622 (6)	0.068 (2)
H24	0.8428	0.5918	0.5345	0.081*
C25	0.8918 (2)	0.7093 (3)	0.6430 (5)	0.0504 (18)
H25	0.9044	0.7407	0.6685	0.060*
C26	0.8890 (2)	0.7054 (3)	0.5529 (5)	0.058 (2)
H26	0.9000	0.7347	0.5191	0.070*
C27	0.7098 (2)	0.7503 (4)	0.9084 (5)	0.077 (2)
H27	0.6825	0.7551	0.9003	0.092*
C28	0.7333 (2)	0.7988 (3)	0.9122 (5)	0.066 (2)
H28	0.7220	0.8349	0.9062	0.079*
C29	0.77372 (19)	0.7930 (3)	0.9250 (4)	0.0522 (16)
C30	0.7882 (2)	0.7383 (3)	0.9354 (5)	0.069 (2)
H30	0.8153	0.7322	0.9454	0.083*
C31	0.7622 (2)	0.6925 (3)	0.9310 (6)	0.083 (3)
H31	0.7725	0.6559	0.9396	0.099*
C32	0.80115 (18)	0.8427 (3)	0.9256 (4)	0.0506 (15)
C33	0.7922 (2)	0.8937 (3)	0.9665 (5)	0.072 (2)
H33	0.7683	0.8983	0.9969	0.087*
C34	0.8197 (3)	0.9385 (3)	0.9614 (6)	0.078 (2)
H34	0.8135	0.9725	0.9903	0.094*
C35	0.8615 (2)	0.8864 (3)	0.8783 (5)	0.0587 (18)
H35	0.8851	0.8836	0.8464	0.070*
C36	0.8371 (2)	0.8394 (3)	0.8811 (5)	0.0566 (18)
H36	0.8446	0.8055	0.8534	0.068*
C37	0.7417 (2)	0.7246 (3)	0.1777 (6)	0.071 (2)

H37	0.7148	0.7151	0.1814	0.086*
C38	0.7696 (2)	0.6819 (3)	0.1772 (6)	0.081 (2)
H38	0.7609	0.6442	0.1805	0.097*
C39	0.8195 (2)	0.7462 (4)	0.1683 (5)	0.072 (2)
H39	0.8466	0.7542	0.1654	0.087*
C40	0.79343 (19)	0.7909 (3)	0.1685 (5)	0.0617 (18)
H40	0.8031	0.8282	0.1655	0.074*
C41	0.75276 (18)	0.7816 (3)	0.1729 (4)	0.0501 (15)
C42	0.72368 (16)	0.8286 (3)	0.1737 (4)	0.0444 (14)
C43	0.68574 (18)	0.8222 (3)	0.1372 (4)	0.0564 (17)
H43	0.6784	0.7881	0.1101	0.068*
C44	0.6595 (2)	0.8671 (4)	0.1419 (5)	0.063 (2)
H44	0.6344	0.8620	0.1170	0.075*
C45	0.73194 (17)	0.8813 (3)	0.2124 (4)	0.0541 (17)
H45	0.7568	0.8881	0.2376	0.065*
C46	0.7029 (2)	0.9237 (3)	0.2131 (5)	0.063 (2)
H46	0.7090	0.9587	0.2389	0.075*
C47	0.87083 (17)	0.8856 (2)	0.3376 (4)	0.0432 (14)
C48	0.86031 (16)	0.9022 (2)	0.2554 (6)	0.0486 (14)
H48	0.8721	0.8845	0.2072	0.058*
C49	0.83240 (17)	0.9449 (3)	0.2418 (7)	0.0632 (16)
H49	0.8256	0.9552	0.1847	0.076*
C50	0.81468 (18)	0.9721 (3)	0.3113 (6)	0.0602 (18)
C51	0.8256 (2)	0.9552 (3)	0.3948 (5)	0.0631 (19)
H51	0.8140	0.9730	0.4432	0.076*
C52	0.8533 (2)	0.9124 (3)	0.4081 (4)	0.0557 (17)
H52	0.8602	0.9016	0.4650	0.067*
Gd1	0.914673 (6)	0.583155 (8)	0.24786 (4)	0.02827 (7)
N1	1.02869 (15)	0.7404 (2)	0.6662 (3)	0.0519 (13)
H1A	1.0461	0.7264	0.7017	0.062*
H1B	1.0140	0.7687	0.6824	0.062*
N2	0.7594 (2)	0.5425 (3)	0.0739 (6)	0.0738 (19)
N3	0.9470 (2)	0.5368 (3)	0.5235 (4)	0.0637 (19)
N4	0.9609 (2)	0.5518 (3)	0.9875 (4)	0.0626 (17)
N5	0.88924 (17)	0.6679 (3)	0.9780 (4)	0.0525 (15)
N6	0.87160 (17)	0.6623 (3)	0.5119 (4)	0.0558 (15)
N7	0.78776 (18)	1.0158 (3)	0.2970 (5)	0.088 (2)
H7A	0.7820	1.0262	0.2442	0.106*
H7B	0.7767	1.0328	0.3409	0.106*
N8	0.80819 (19)	0.6914 (3)	0.1722 (5)	0.0732 (17)
N9	0.66714 (17)	0.9169 (2)	0.1790 (4)	0.0606 (14)
N10	0.8535 (2)	0.9358 (3)	0.9186 (5)	0.0723 (17)
N11	0.72363 (19)	0.6974 (3)	0.9154 (5)	0.0815 (19)
O1	0.97175 (11)	0.64181 (16)	0.2889 (3)	0.0445 (9)
O2	1.03318 (10)	0.68583 (14)	0.2462 (4)	0.0483 (8)
O3	1.03391 (12)	0.59050 (16)	0.3044 (3)	0.0515 (10)
O5	0.88950 (15)	0.77808 (18)	0.3359 (4)	0.0797 (16)
O6	0.93894 (13)	0.84568 (19)	0.2913 (3)	0.0678 (13)
O14	0.7721 (3)	0.5527 (4)	0.0030 (7)	0.185 (5)

O15	0.7793 (2)	0.5406 (3)	0.1387 (7)	0.155 (4)
O16	0.7249 (2)	0.5362 (4)	0.0840 (6)	0.143 (3)
O20	0.92070 (18)	0.8376 (2)	0.4442 (3)	0.0874 (17)
O1W	0.88775 (12)	0.65990 (17)	0.3333 (2)	0.0464 (10)
O2W	0.86855 (12)	0.54534 (19)	0.3511 (3)	0.0533 (11)
O3W	0.85363 (11)	0.59444 (18)	0.1683 (3)	0.0483 (10)
O4W	0.89860 (12)	0.49138 (17)	0.1797 (3)	0.0485 (10)
O5W	0.96918 (11)	0.54819 (17)	0.1606 (2)	0.0418 (9)
O6W	0.95002 (14)	0.52250 (18)	0.3461 (2)	0.0468 (10)
O7W	0.91889 (12)	0.66144 (19)	0.1469 (3)	0.0490 (11)
O8W	0.7948 (2)	0.5832 (3)	0.3771 (5)	0.0923 (19)
O9W	0.94198 (16)	0.8969 (2)	0.6030 (3)	0.0660 (13)
S2	1.01437 (4)	0.64533 (6)	0.30545 (9)	0.0351 (3)
S5	0.90793 (5)	0.83258 (7)	0.35428 (12)	0.0509 (4)
H1W	0.8955 (12)	0.6538 (11)	0.3835 (6)	0.076*
H2W	0.8968 (11)	0.68906 (11)	0.3108 (18)	0.076*
H3W	0.8467 (2)	0.5584 (15)	0.3374 (17)	0.076*
H6W	0.8437 (6)	0.6238 (9)	0.1882 (18)	0.076*
H8W	0.8762 (5)	0.4857 (9)	0.199 (2)	0.076*
H9W	0.9625 (6)	0.5555 (17)	0.1100 (2)	0.076*
H10W	0.9884 (2)	0.5665 (14)	0.178 (2)	0.076*
H11W	0.955 (2)	0.4895 (9)	0.331 (3)	0.076*
H12W	0.950 (2)	0.527 (2)	0.3995 (6)	0.076*
H14W	0.89570 (17)	0.6682 (13)	0.133 (2)	0.076*
H16W	0.789 (2)	0.6161 (9)	0.390 (4)	0.076*
H17W	0.937 (2)	0.884 (2)	0.5539 (16)	0.076*
H18W	0.943 (2)	0.8730 (18)	0.642 (3)	0.076*
H15W	0.793 (2)	0.5599 (18)	0.417 (3)	0.06 (3)*
H5W	0.8410 (5)	0.5651 (7)	0.179 (2)	0.14 (4)*
H4W	0.8703 (9)	0.51038 (19)	0.347 (2)	0.22 (7)*
H7W	0.9160 (8)	0.4709 (4)	0.201 (2)	0.15 (5)*
H13W	0.9299 (13)	0.6871 (7)	0.1746 (11)	0.15 (5)*

Atomic displacement parameters (Å^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
C1	0.031 (3)	0.034 (3)	0.030 (3)	−0.004 (2)	−0.001 (2)	−0.001 (2)
C2	0.038 (3)	0.038 (3)	0.036 (3)	0.010 (2)	−0.001 (2)	0.000 (2)
C3	0.044 (3)	0.049 (4)	0.034 (3)	0.001 (3)	−0.014 (3)	0.003 (3)
C4	0.039 (3)	0.038 (3)	0.033 (3)	−0.006 (3)	0.003 (2)	−0.004 (2)
C5	0.040 (3)	0.036 (3)	0.041 (4)	0.006 (3)	−0.001 (3)	−0.009 (3)
C6	0.038 (3)	0.038 (3)	0.042 (3)	0.005 (2)	−0.005 (2)	0.000 (3)
C7	0.062 (5)	0.076 (6)	0.057 (5)	−0.003 (4)	0.009 (4)	0.022 (4)
C8	0.064 (5)	0.069 (5)	0.040 (4)	−0.021 (4)	−0.001 (4)	−0.001 (4)
C9	0.041 (4)	0.040 (4)	0.039 (3)	−0.002 (3)	0.009 (3)	0.005 (3)
C10	0.124 (7)	0.049 (5)	0.035 (4)	−0.016 (4)	0.002 (4)	0.003 (3)
C11	0.142 (8)	0.058 (5)	0.049 (5)	−0.013 (5)	−0.007 (5)	−0.005 (4)
C12	0.038 (3)	0.045 (4)	0.027 (3)	0.005 (3)	−0.001 (3)	0.001 (3)

C13	0.063 (5)	0.080 (6)	0.051 (4)	−0.030 (4)	0.003 (4)	−0.008 (4)
C14	0.072 (5)	0.108 (7)	0.050 (5)	−0.028 (5)	−0.012 (4)	−0.021 (5)
C15	0.110 (7)	0.078 (7)	0.034 (5)	−0.015 (5)	0.009 (4)	0.001 (4)
C16	0.075 (5)	0.072 (5)	0.041 (4)	−0.029 (4)	0.006 (4)	−0.006 (4)
C17	0.070 (5)	0.057 (5)	0.041 (4)	−0.012 (4)	0.001 (3)	0.017 (4)
C18	0.056 (4)	0.047 (4)	0.057 (5)	−0.019 (4)	−0.011 (4)	0.001 (4)
C19	0.041 (4)	0.038 (4)	0.029 (3)	−0.001 (3)	−0.008 (3)	0.006 (3)
C20	0.058 (4)	0.067 (5)	0.041 (4)	−0.024 (4)	0.000 (3)	0.010 (3)
C21	0.070 (5)	0.073 (5)	0.047 (4)	−0.027 (4)	−0.018 (4)	0.003 (4)
C22	0.036 (4)	0.040 (4)	0.042 (4)	0.011 (3)	−0.003 (3)	0.001 (4)
C23	0.080 (5)	0.060 (5)	0.028 (4)	−0.022 (4)	−0.002 (3)	−0.001 (3)
C24	0.081 (6)	0.071 (6)	0.051 (5)	−0.028 (5)	0.003 (4)	−0.009 (4)
C25	0.066 (5)	0.043 (4)	0.042 (4)	−0.010 (3)	0.000 (3)	0.004 (3)
C26	0.075 (5)	0.055 (5)	0.045 (4)	0.002 (4)	0.006 (4)	0.011 (4)
C27	0.044 (4)	0.108 (7)	0.078 (5)	−0.015 (5)	−0.005 (4)	0.012 (5)
C28	0.048 (4)	0.067 (5)	0.081 (5)	0.006 (4)	0.008 (4)	0.019 (4)
C29	0.051 (4)	0.048 (4)	0.057 (4)	0.003 (3)	0.004 (3)	0.004 (3)
C30	0.050 (4)	0.054 (4)	0.103 (6)	−0.007 (3)	−0.016 (4)	0.012 (4)
C31	0.067 (5)	0.057 (5)	0.123 (8)	−0.014 (4)	−0.013 (5)	0.013 (5)
C32	0.047 (4)	0.047 (4)	0.058 (4)	0.000 (3)	−0.001 (3)	0.018 (3)
C33	0.080 (5)	0.052 (4)	0.085 (6)	0.005 (4)	0.028 (4)	0.007 (4)
C34	0.106 (6)	0.047 (4)	0.081 (5)	−0.002 (4)	0.017 (5)	−0.003 (4)
C35	0.051 (4)	0.059 (5)	0.066 (5)	0.005 (4)	−0.004 (3)	0.013 (4)
C36	0.047 (4)	0.047 (4)	0.075 (5)	0.004 (3)	−0.012 (3)	−0.002 (4)
C37	0.045 (4)	0.060 (5)	0.109 (6)	0.004 (3)	0.004 (4)	−0.007 (4)
C38	0.068 (5)	0.055 (5)	0.119 (7)	0.010 (4)	−0.010 (5)	−0.010 (5)
C39	0.042 (4)	0.086 (6)	0.089 (6)	0.006 (4)	−0.010 (4)	−0.014 (5)
C40	0.046 (4)	0.049 (4)	0.090 (5)	0.006 (3)	−0.017 (4)	−0.001 (4)
C41	0.046 (4)	0.054 (4)	0.050 (4)	0.001 (3)	−0.007 (3)	−0.006 (3)
C42	0.039 (3)	0.053 (4)	0.041 (3)	0.002 (3)	−0.005 (3)	0.003 (3)
C43	0.044 (4)	0.065 (5)	0.061 (4)	0.007 (3)	−0.006 (3)	−0.008 (3)
C44	0.041 (4)	0.078 (6)	0.069 (5)	0.008 (4)	−0.008 (3)	0.008 (4)
C45	0.041 (3)	0.049 (4)	0.073 (4)	−0.005 (3)	−0.002 (3)	0.006 (3)
C46	0.058 (4)	0.045 (4)	0.084 (5)	0.005 (3)	0.001 (3)	0.001 (3)
C47	0.047 (3)	0.036 (3)	0.047 (4)	−0.008 (3)	0.006 (3)	0.000 (3)
C48	0.055 (3)	0.046 (3)	0.045 (3)	−0.005 (2)	−0.001 (4)	0.003 (4)
C49	0.060 (3)	0.057 (4)	0.073 (4)	−0.001 (3)	−0.016 (5)	−0.008 (5)
C50	0.040 (3)	0.041 (4)	0.099 (6)	−0.007 (3)	−0.002 (4)	−0.012 (4)
C51	0.061 (4)	0.058 (5)	0.070 (5)	−0.004 (4)	0.017 (4)	−0.009 (4)
C52	0.059 (4)	0.058 (4)	0.049 (4)	−0.006 (3)	0.012 (3)	0.007 (3)
Gd1	0.03323 (11)	0.02543 (11)	0.02617 (10)	−0.00137 (9)	0.00040 (18)	−0.00023 (17)
N1	0.067 (3)	0.053 (3)	0.036 (3)	0.003 (3)	−0.008 (2)	−0.011 (2)
N2	0.064 (4)	0.056 (4)	0.101 (6)	0.008 (3)	−0.026 (4)	−0.001 (4)
N3	0.093 (5)	0.069 (5)	0.028 (3)	0.011 (4)	0.002 (3)	0.005 (3)
N4	0.069 (4)	0.077 (5)	0.042 (3)	0.011 (3)	−0.006 (3)	−0.008 (3)
N5	0.056 (3)	0.058 (4)	0.043 (3)	−0.007 (3)	−0.009 (3)	0.011 (3)
N6	0.063 (4)	0.070 (4)	0.035 (3)	−0.005 (3)	0.004 (3)	−0.006 (3)
N7	0.078 (4)	0.063 (4)	0.124 (6)	0.023 (4)	−0.013 (4)	−0.020 (4)
N8	0.065 (4)	0.067 (4)	0.087 (5)	0.022 (3)	−0.015 (3)	−0.005 (4)

N9	0.059 (4)	0.056 (4)	0.067 (4)	0.010 (3)	0.003 (3)	0.008 (3)
N10	0.081 (4)	0.055 (4)	0.081 (4)	−0.014 (3)	0.009 (4)	0.010 (3)
N11	0.064 (4)	0.076 (5)	0.104 (5)	−0.019 (4)	−0.007 (4)	0.011 (4)
O1	0.042 (2)	0.044 (2)	0.047 (2)	−0.0058 (18)	−0.0118 (17)	−0.0100 (18)
O2	0.056 (2)	0.052 (2)	0.0373 (17)	−0.0096 (16)	0.003 (3)	0.003 (3)
O3	0.063 (3)	0.041 (2)	0.051 (2)	0.012 (2)	0.000 (2)	−0.0114 (19)
O5	0.081 (3)	0.033 (3)	0.125 (5)	−0.003 (2)	−0.007 (3)	−0.002 (3)
O6	0.054 (3)	0.068 (3)	0.082 (3)	0.004 (2)	0.013 (2)	−0.004 (3)
O14	0.277 (14)	0.140 (7)	0.136 (7)	0.073 (7)	0.105 (9)	0.027 (7)
O15	0.138 (6)	0.094 (5)	0.232 (10)	−0.034 (5)	−0.109 (7)	0.059 (6)
O16	0.073 (5)	0.174 (8)	0.181 (8)	−0.017 (5)	−0.017 (5)	−0.019 (7)
O20	0.109 (5)	0.089 (4)	0.064 (3)	0.024 (3)	−0.029 (3)	−0.009 (3)
O1W	0.069 (3)	0.039 (2)	0.031 (2)	−0.001 (2)	0.010 (2)	−0.0043 (17)
O2W	0.053 (3)	0.041 (3)	0.066 (3)	0.004 (2)	0.020 (2)	0.015 (2)
O3W	0.039 (2)	0.036 (2)	0.070 (3)	0.0021 (19)	−0.010 (2)	0.000 (2)
O4W	0.040 (2)	0.039 (2)	0.066 (3)	−0.002 (2)	0.005 (2)	−0.010 (2)
O5W	0.038 (2)	0.052 (3)	0.036 (2)	−0.0039 (19)	−0.0014 (17)	−0.0115 (19)
O6W	0.066 (3)	0.046 (3)	0.028 (2)	0.010 (2)	−0.002 (2)	0.0045 (18)
O7W	0.055 (3)	0.052 (3)	0.040 (2)	−0.012 (2)	−0.017 (2)	0.016 (2)
O8W	0.078 (4)	0.086 (5)	0.113 (5)	0.030 (4)	0.004 (4)	−0.014 (5)
O9W	0.078 (3)	0.069 (3)	0.052 (3)	0.009 (3)	0.004 (3)	0.004 (2)
S2	0.0392 (7)	0.0337 (7)	0.0324 (7)	−0.0002 (6)	−0.0037 (6)	−0.0052 (6)
S5	0.0543 (9)	0.0388 (9)	0.0594 (10)	−0.0008 (7)	−0.0002 (8)	−0.0030 (7)

Geometric parameters (Å, °)

C1—C2	1.371 (7)	C35—H35	0.9300
C1—C6	1.389 (7)	C36—H36	0.9300
C1—S2	1.763 (5)	C37—C38	1.367 (9)
C2—C3	1.380 (8)	C37—C41	1.384 (9)
C2—H2	0.9300	C37—H37	0.9300
C3—C4	1.396 (8)	C38—N8	1.314 (9)
C3—H3	0.9300	C38—H38	0.9300
C4—N1	1.382 (7)	C39—N8	1.335 (9)
C4—C5	1.388 (8)	C39—C40	1.361 (9)
C5—C6	1.372 (8)	C39—H39	0.9300
C5—H5	0.9300	C40—C41	1.382 (9)
C6—H6	0.9300	C40—H40	0.9300
C7—N3	1.324 (10)	C41—C42	1.468 (8)
C7—C8	1.380 (11)	C42—C43	1.396 (8)
C7—H7	0.9300	C42—C45	1.391 (8)
C8—C9	1.380 (9)	C43—C44	1.369 (9)
C8—H8	0.9300	C43—H43	0.9300
C9—C10	1.380 (10)	C44—N9	1.317 (9)
C9—C12	1.465 (8)	C44—H44	0.9300
C10—C11	1.379 (10)	C45—C46	1.389 (9)
C10—H10	0.9300	C45—H45	0.9300
C11—N3	1.312 (10)	C46—N9	1.316 (9)
C11—H11	0.9300	C46—H46	0.9300

C12—C13	1.361 (9)	C47—C48	1.355 (10)
C12—C16	1.373 (9)	C47—C52	1.372 (8)
C13—C14	1.372 (11)	C47—S5	1.773 (6)
C13—H13	0.9300	C48—C49	1.382 (8)
C14—N4	1.302 (10)	C48—H48	0.9300
C14—H14	0.9300	C49—C50	1.369 (11)
C15—N4	1.302 (10)	C49—H49	0.9300
C15—C16	1.391 (10)	C50—N7	1.381 (8)
C15—H15	0.9300	C50—C51	1.378 (10)
C16—H16	0.9300	C51—C52	1.381 (10)
C17—N5	1.325 (9)	C51—H51	0.9300
C17—C18	1.376 (10)	C52—H52	0.9300
C17—H17	0.9300	Gd1—O6W	2.375 (4)
C18—C19	1.377 (9)	Gd1—O2W	2.373 (4)
C18—H18	0.9300	Gd1—O1W	2.389 (4)
C19—C20	1.392 (9)	Gd1—O3W	2.392 (4)
C19—C22	1.489 (6)	Gd1—O7W	2.391 (4)
C20—C21	1.383 (10)	Gd1—O5W	2.401 (4)
C20—H20	0.9300	Gd1—O1	2.434 (4)
C21—N5	1.307 (9)	Gd1—O4W	2.440 (4)
C21—H21	0.9300	N1—H1A	0.8600
C22—C25	1.388 (9)	N1—H1B	0.8600
C22—C23	1.377 (9)	N2—O16	1.176 (8)
C23—C24	1.384 (10)	N2—O14	1.184 (10)
C23—H23	0.9300	N2—O15	1.190 (9)
C24—N6	1.322 (10)	N7—H7A	0.8600
C24—H24	0.9300	N7—H7B	0.8600
C25—C26	1.376 (9)	O1—S2	1.453 (4)
C25—H25	0.9300	O2—S2	1.450 (4)
C26—N6	1.320 (9)	O3—S2	1.438 (4)
C26—H26	0.9300	O5—S5	1.441 (5)
C27—N11	1.322 (10)	O6—S5	1.446 (5)
C27—C28	1.381 (10)	O20—S5	1.437 (5)
C27—H27	0.9300	O1W—H1W	0.819 (17)
C28—C29	1.375 (9)	O1W—H2W	0.820 (19)
C28—H28	0.9300	O2W—H3W	0.820 (17)
C29—C30	1.376 (9)	O2W—H4W	0.820 (7)
C29—C32	1.481 (9)	O3W—H6W	0.82 (2)
C30—C31	1.380 (10)	O3W—H5W	0.821 (18)
C30—H30	0.9300	O4W—H8W	0.82 (2)
C31—N11	1.321 (9)	O4W—H7W	0.82 (2)
C31—H31	0.9300	O5W—H9W	0.819 (11)
C32—C36	1.385 (9)	O5W—H10W	0.82 (2)
C32—C33	1.377 (10)	O6W—H11W	0.82 (3)
C33—C34	1.395 (10)	O6W—H12W	0.819 (12)
C33—H33	0.9300	O8W—H16W	0.82 (3)
C34—N10	1.310 (10)	O8W—H15W	0.82 (4)
C34—H34	0.9300	O9W—H17W	0.82 (3)
C35—N10	1.335 (9)	O9W—H18W	0.82 (4)

C35—C36	1.369 (9)		
C2—C1—C6	119.1 (5)	C39—C40—C41	120.9 (7)
C2—C1—S2	120.7 (4)	C39—C40—H40	119.5
C6—C1—S2	120.2 (4)	C41—C40—H40	119.5
C1—C2—C3	120.6 (5)	C37—C41—C40	114.7 (6)
C1—C2—H2	119.7	C37—C41—C42	122.7 (6)
C3—C2—H2	119.7	C40—C41—C42	122.6 (6)
C2—C3—C4	120.7 (5)	C43—C42—C45	116.4 (6)
C2—C3—H3	119.6	C43—C42—C41	121.5 (6)
C4—C3—H3	119.6	C45—C42—C41	122.1 (5)
N1—C4—C3	120.4 (5)	C44—C43—C42	118.8 (7)
N1—C4—C5	121.5 (5)	C44—C43—H43	120.6
C3—C4—C5	118.1 (5)	C42—C43—H43	120.6
C6—C5—C4	120.9 (5)	N9—C44—C43	125.0 (7)
C6—C5—H5	119.5	N9—C44—H44	117.5
C4—C5—H5	119.5	C43—C44—H44	117.5
C5—C6—C1	120.5 (5)	C46—C45—C42	119.6 (6)
C5—C6—H6	119.7	C46—C45—H45	120.2
C1—C6—H6	119.7	C42—C45—H45	120.2
N3—C7—C8	124.3 (7)	N9—C46—C45	123.3 (7)
N3—C7—H7	117.9	N9—C46—H46	118.3
C8—C7—H7	117.9	C45—C46—H46	118.3
C7—C8—C9	120.4 (7)	C48—C47—C52	118.6 (6)
C7—C8—H8	119.8	C48—C47—S5	120.9 (5)
C9—C8—H8	119.8	C52—C47—S5	120.4 (5)
C8—C9—C10	115.0 (6)	C47—C48—C49	121.3 (8)
C8—C9—C12	122.8 (7)	C47—C48—H48	119.3
C10—C9—C12	122.2 (7)	C49—C48—H48	119.3
C11—C10—C9	120.5 (7)	C50—C49—C48	120.9 (9)
C11—C10—H10	119.8	C50—C49—H49	119.6
C9—C10—H10	119.8	C48—C49—H49	119.6
N3—C11—C10	124.4 (8)	C49—C50—N7	120.4 (8)
N3—C11—H11	117.8	C49—C50—C51	117.6 (7)
C10—C11—H11	117.8	N7—C50—C51	122.0 (7)
C13—C12—C16	116.4 (6)	C52—C51—C50	121.3 (7)
C13—C12—C9	122.8 (7)	C52—C51—H51	119.3
C16—C12—C9	120.7 (7)	C50—C51—H51	119.3
C12—C13—C14	120.0 (7)	C51—C52—C47	120.2 (6)
C12—C13—H13	120.0	C51—C52—H52	119.9
C14—C13—H13	120.0	C47—C52—H52	119.9
N4—C14—C13	124.5 (7)	O6W—Gd1—O2W	71.80 (15)
N4—C14—H14	117.8	O6W—Gd1—O1W	107.07 (14)
C13—C14—H14	117.8	O2W—Gd1—O1W	70.93 (15)
N4—C15—C16	124.5 (8)	O6W—Gd1—O3W	144.17 (16)
N4—C15—H15	117.7	O2W—Gd1—O3W	79.51 (15)
C16—C15—H15	117.7	O1W—Gd1—O3W	82.48 (14)
C12—C16—C15	118.6 (7)	O6W—Gd1—O7W	146.10 (15)
C12—C16—H16	120.7	O2W—Gd1—O7W	138.36 (14)
C15—C16—H16	120.7	O1W—Gd1—O7W	78.38 (14)

N5—C17—C18	123.2 (7)	O3W—Gd1—O7W	68.99 (14)
N5—C17—H17	118.4	O6W—Gd1—O5W	76.42 (13)
C18—C17—H17	118.4	O2W—Gd1—O5W	137.30 (14)
C17—C18—C19	121.5 (7)	O1W—Gd1—O5W	147.41 (14)
C17—C18—H18	119.2	O3W—Gd1—O5W	114.14 (14)
C19—C18—H18	119.2	O7W—Gd1—O5W	81.94 (14)
C20—C19—C18	115.0 (6)	O6W—Gd1—O1	77.38 (15)
C20—C19—C22	121.0 (7)	O2W—Gd1—O1	123.49 (14)
C18—C19—C22	124.0 (7)	O1W—Gd1—O1	74.70 (13)
C21—C20—C19	118.9 (7)	O3W—Gd1—O1	137.76 (14)
C21—C20—H20	120.5	O7W—Gd1—O1	71.85 (14)
C19—C20—H20	120.5	O5W—Gd1—O1	74.60 (13)
N5—C21—C20	125.7 (7)	O6W—Gd1—O4W	81.63 (15)
N5—C21—H21	117.2	O2W—Gd1—O4W	79.08 (15)
C20—C21—H21	117.1	O1W—Gd1—O4W	143.66 (14)
C25—C22—C23	116.3 (7)	O3W—Gd1—O4W	72.10 (15)
C25—C22—C19	122.6 (7)	O7W—Gd1—O4W	114.26 (15)
C23—C22—C19	121.1 (7)	O5W—Gd1—O4W	68.59 (13)
C24—C23—C22	119.1 (7)	O1—Gd1—O4W	140.92 (13)
C24—C23—H23	120.4	C4—N1—H1A	120.0
C22—C23—H23	120.4	C4—N1—H1B	120.0
N6—C24—C23	124.4 (8)	H1A—N1—H1B	120.0
N6—C24—H24	117.8	O16—N2—O14	119.8 (10)
C23—C24—H24	117.8	O16—N2—O15	116.1 (10)
C22—C25—C26	120.2 (7)	O14—N2—O15	124.0 (10)
C22—C25—H25	119.9	C7—N3—C11	115.4 (7)
C26—C25—H25	119.9	C14—N4—C15	115.8 (7)
N6—C26—C25	123.4 (7)	C21—N5—C17	115.6 (6)
N6—C26—H26	118.3	C26—N6—C24	116.5 (6)
C25—C26—H26	118.3	C50—N7—H7A	120.0
N11—C27—C28	124.1 (7)	C50—N7—H7B	120.0
N11—C27—H27	118.0	H7A—N7—H7B	120.0
C28—C27—H27	118.0	C38—N8—C39	116.3 (6)
C29—C28—C27	119.2 (7)	C38—N8—H14W	158.5 (9)
C29—C28—H28	120.4	C39—N8—H14W	83.6 (7)
C27—C28—H28	120.4	C46—N9—C44	116.9 (6)
C30—C29—C28	117.1 (6)	C34—N10—C35	116.3 (7)
C30—C29—C32	120.5 (6)	C27—N11—C31	116.1 (7)
C28—C29—C32	122.4 (6)	S2—O1—Gd1	148.1 (2)
C31—C30—C29	119.3 (7)	S2—O2—H13W	77.1 (2)
C31—C30—H30	120.4	Gd1—O1W—H1W	105 (2)
C29—C30—H30	120.4	Gd1—O1W—H2W	104.8 (18)
N11—C31—C30	124.1 (8)	H1W—O1W—H2W	115 (3)
N11—C31—H31	118.0	Gd1—O2W—H3W	106.0 (19)
C30—C31—H31	118.0	Gd1—O2W—H4W	106 (2)
C36—C32—C33	117.4 (6)	H3W—O2W—H4W	115 (3)
C36—C32—C29	119.6 (6)	Gd1—O3W—H6W	104.7 (17)
C33—C32—C29	123.0 (6)	Gd1—O3W—H5W	104.4 (16)
C32—C33—C34	118.5 (7)	H6W—O3W—H5W	115 (2)

C32—C33—H33	120.7	Gd1—O4W—H8W	101.1 (17)
C34—C33—H33	120.7	Gd1—O4W—H7W	100.8 (14)
N10—C34—C33	124.4 (8)	H8W—O4W—H7W	115 (3)
N10—C34—H34	117.8	Gd1—O5W—H9W	103.9 (17)
C33—C34—H34	117.8	Gd1—O5W—H10W	104.1 (18)
N10—C35—C36	124.0 (7)	H9W—O5W—H10W	114 (3)
N10—C35—H35	118.0	Gd1—O6W—H11W	118 (4)
C36—C35—H35	118.0	Gd1—O6W—H12W	122 (4)
C35—C36—C32	119.4 (7)	H11W—O6W—H12W	114 (5)
C35—C36—H36	120.3	H16W—O8W—H15W	116 (5)
C32—C36—H36	120.3	H17W—O9W—H18W	115 (4)
C38—C37—C41	121.1 (7)	O3—S2—O2	112.1 (2)
C38—C37—H37	119.4	O3—S2—O1	113.3 (2)
C41—C37—H37	119.4	O2—S2—O1	110.9 (2)
N8—C38—C37	123.5 (7)	O3—S2—C1	107.7 (2)
N8—C38—H38	118.3	O2—S2—C1	107.1 (3)
C37—C38—H38	118.3	O1—S2—C1	105.3 (2)
N8—C39—C40	123.5 (7)	O20—S5—O6	113.5 (3)
N8—C39—H39	118.3	O20—S5—O5	112.6 (4)
C40—C39—H39	118.3	O6—S5—O5	111.5 (3)
N8—C39—H14W	71.8 (5)	O20—S5—C47	106.7 (3)
C40—C39—H14W	162.6 (6)	O6—S5—C47	105.2 (3)
H39—C39—H14W	47.3	O5—S5—C47	106.7 (3)

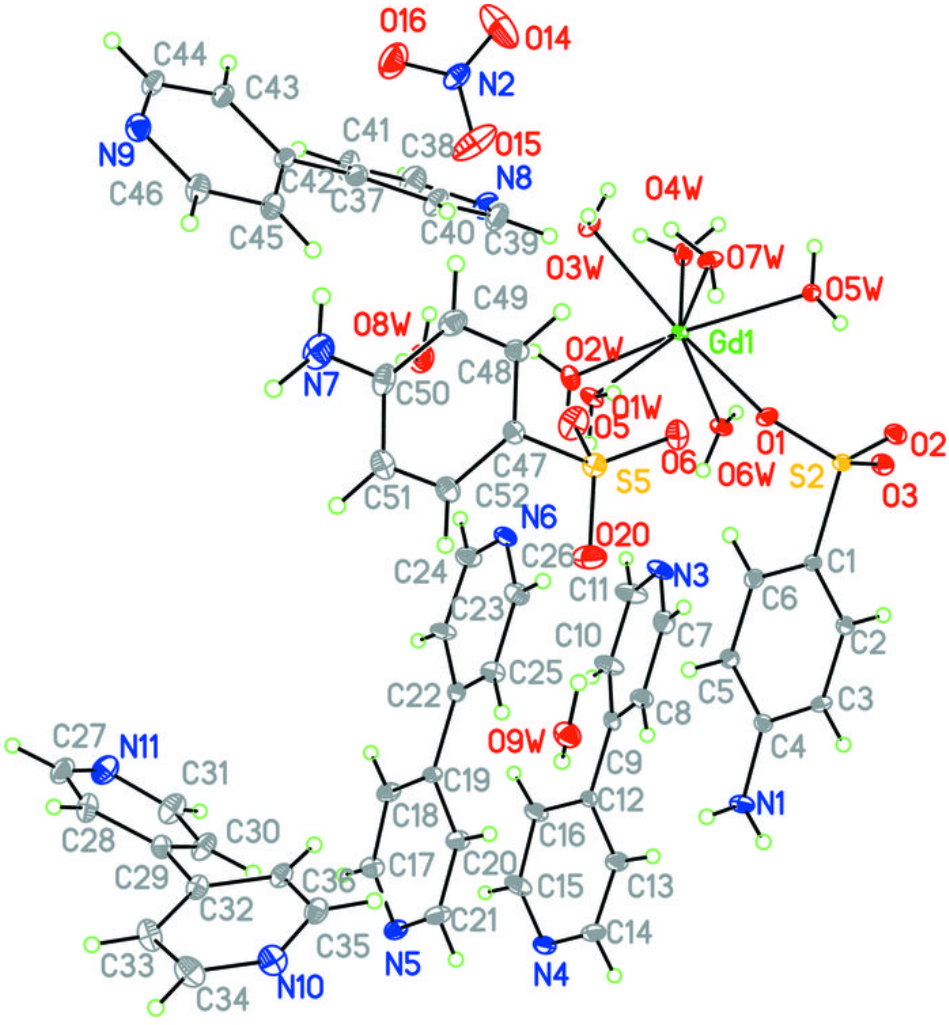
Hydrogen-bond geometry (Å, °)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
O1W—H1W···N6	0.82 (2)	2.12 (2)	2.770 (7)	136 (3)
O1W—H2W···O5	0.82 (2)	2.13 (1)	2.759 (6)	134 (3)
O2W—H3W···O8W	0.82 (2)	1.93 (1)	2.657 (7)	147 (2)
O3W—H6W···N8	0.82 (2)	1.99 (1)	2.728 (7)	149.(2)
O4W—H8W···N9^{i}	0.82 (2)	2.19 (2)	2.807 (7)	133.(1)
O5W—H9W···N4^{ii}	0.82 (1)	1.86 (1)	2.647 (7)	159.(2)
O5W—H10W···O3	0.82 (2)	2.51 (2)	3.236 (6)	148 (4)
O5W—H10W···O1	0.82 (2)	2.50 (3)	2.931 (5)	114.(2)
O6W—H11W···O3^{iii}	0.82 (3)	1.95 (3)	2.765 (6)	175 (5)
O6W—H12W···N3	0.82 (1)	1.90 (1)	2.719 (7)	178 (8)
O7W—H13W···N1^{iv}	0.82 (3)	2.19 (2)	2.902 (7)	145 (3)
O7W—H14W···N5^{ii}	0.82 (1)	2.37 (4)	2.758 (7)	110 (3)
O7W—H14W···O3W	0.82 (1)	2.29 (1)	2.709 (6)	112 (3)
O8W—H16W···N11^{v}	0.82 (3)	1.98 (3)	2.798 (9)	176 (6)
O9W—H17W···O20	0.82 (3)	2.06 (4)	2.873 (7)	169 (6)
O9W—H18W···O2^{vi}	0.82 (4)	2.24 (5)	3.028 (7)	161 (7)
N1—H1A···O6^{vi}	0.86	2.22	2.972 (7)	146
N1—H1B···O2^{vi}	0.86	2.14	2.958 (6)	159
N7—H7B···O14^{vii}	0.86	2.51	3.289 (12)	151
N7—H7A···O15^{viii}	0.86	2.63	3.345 (12)	141

N7—H7A···O16^{viii}	0.86	2.46	3.302 (13)	167

Symmetry codes: (i) −*x*+3/2, *y*−1/2, *z*; (ii) *x*, *y*, *z*−1; (iii) −*x*+2, −*y*+1, *z*; (iv) −*x*+2, −*y*+3/2, *z*−1/2; (v) −*x*+3/2, *y*, *z*−1/2; (vi) −*x*+2, −*y*+3/2, *z*+1/2; (vii) *x*, *y*+1/2, *z*+1/2; (viii) −*x*+3/2, *y*+1/2, *z*.

Fig. 1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C41
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O15
N9
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C42
C37
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C45
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O4W
O3W
O7W
O5W
C49
O8W
Gd1
O2W
N7
C50
C48
O1W
O5
O1
O2
C47
O6
O6W
S2
O3
S5
C51
C52
N6
O20
C26
C1
C24
N3
C11
C6
C23
C10
C7
C2
C25
C22
C5
C3
C8
C27
N11
O9W
C4
C31
C19
C9
C18
C12
C28
C30
C16
C17
C20
C13
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C36
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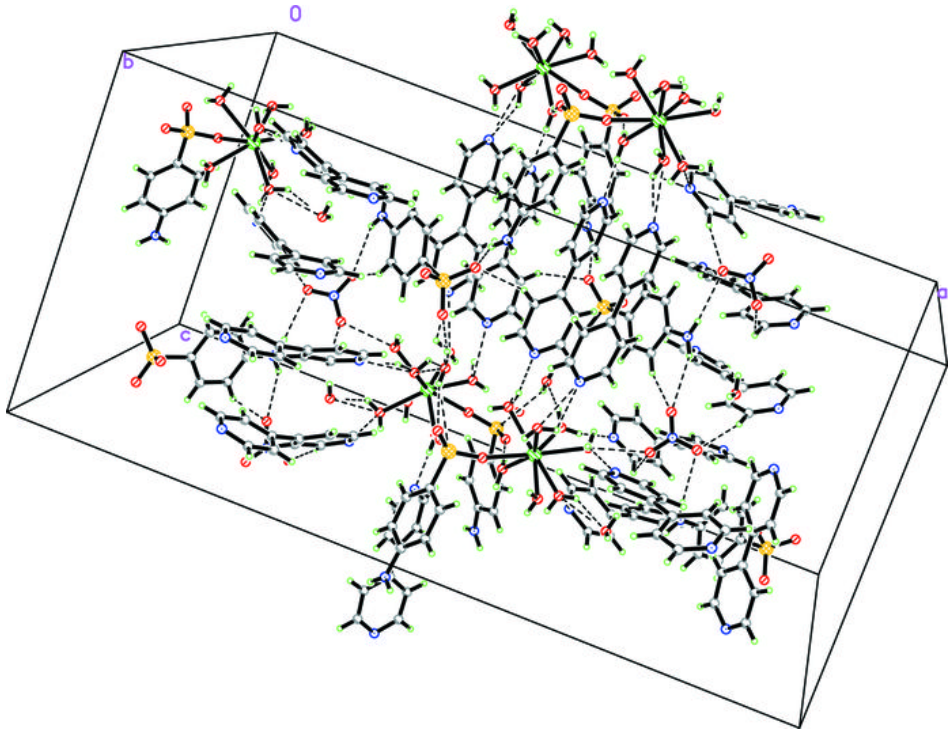
C21
C14
C35
N5
N4
C33
N10
C34
N1

Fig. 2



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Chlorido[hydridotris(pyrazol-1-yl-κN^2)-borato](1*H*-pyrazole-κN^2)(triphenylphosphine-κP)ruthenium(II)

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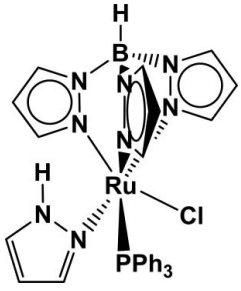
Key indicators: single-crystal X-ray study; T = 200 K; mean σ(C–C) = 0.011 Å; disorder in main residue; R factor = 0.053; wR factor = 0.118; data-to-parameter ratio = 14.7.

In the title compound, $[Ru(C_9H_{10}BN_6)Cl(C_3H_4N_2)(C_{18}H_{15}P)]$, the Ru^{II} atom is coordinated by an N,N',N''-tridentate hydridotrispyrazolylborate (Tp) ligand, a pyrazole (HPz) molecule, a chloride ion and a triphenylphosphine ligand, resulting in a distorted $RuClPN_4$ octahedral coordination for the metal ion: the tridentate N atoms occupy one octahedral face and the Cl and P atoms are *cis*. One of the phenyl rings is disordered over two orientations in a 0.547 (10):0.453 (10) ratio, and a weak intramolecular N—H···Cl hydrogen bond generates an S(5) ring.

Related literature

For general background to ruthenium coordination chemistry with pyrazole-type ligands, see: Alcock *et al.* (1992); Cheng *et al.* (2009); Deacon *et al.* (1998); Govind *et al.* (1996); Lo *et al.* (2004); Pavlik *et al.* (2005). For related structures, see: Gemel *et al.* (1996); Slugovc *et al.* (1998). Tong *et al.* (2008, 2009).



Experimental

Crystal data

$[Ru(C_9H_{10}BN_6)Cl(C_3H_4N_2)(C_{18}H_{15}P)]$
M_r = 679.91
Monoclinic, $P2_1/c$
a = 17.7782 (12) Å
b = 10.0843 (5) Å
c = 18.9139 (10) Å
β = 116.316 (3)°
V = 3039.5 (3) Å^3
Z = 4
Mo $K\alpha$ radiation
μ = 0.69 mm^{-1}
T = 200 K
0.11 × 0.08 × 0.03 mm

Data collection

Nonius KappaCCD diffractometer
Absorption correction: multi-scan (*SORTAV*; Blessing, 1995)
T_{min} = 0.928, T_{max} = 0.980
22639 measured reflections
5292 independent reflections
3470 reflections with $I > 2\sigma(I)$
R_{int} = 0.079

Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.053
$wR(F^2)$ = 0.118
S = 1.02
5292 reflections
360 parameters
H-atom parameters constrained
$\Delta\rho_{max}$ = 0.89 e Å^{-3}
$\Delta\rho_{min}$ = −0.88 e Å^{-3}

Table 1
Selected bond lengths (Å).

Ru1—N1	2.067 (4)	Ru1—N7	2.076 (4)
Ru1—N3	2.097 (4)	Ru1—P1	2.3031 (15)
Ru1—N5	2.076 (4)	Ru1—Cl1	2.4374 (14)

Table 2
Hydrogen-bond geometry (Å, °).

D—H···A	D—H	H···A	D···A	D—H···A
N8—H8′···Cl1	0.88	2.49	3.025 (6)	120

Data collection: *COLLECT* (Nonius, 1999); cell refinement: *DENZO* and *SCALEPACK* (Otwinowski & Minor, 1997); data reduction: *DENZO* and *SCALEPACK*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *ORTEP-3* (Farrugia, 1997); software used to prepare material for publication: *WinGX* (Farrugia, 1999).

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Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: HB5462).

References

Alcock, N. W., Burns, I. D., Claire, K. S. & Hill, A. F. (1992). *Inorg. Chem.* **31**, 2906–2908.

Blessing, R. H. (1995). *Acta Cryst.* A**51**, 33–38.

Cheng, C. J., Tong, H. C., Fong, Y. H., Wang, P. Y., Kuo, Y. L., Lo, Y. H. & Lin, C. H. (2009). *Dalton Trans.* pp. 4435–4438.

Deacon, G. B., Delbridge, E. E., Skelton, B. W. & White, A. H. (1998). *Angew. Chem. Int. Ed.* **37**, 2251–2554.

Farrugia, L. J. (1997). *J. Appl. Cryst.* **30**, 565.

Farrugia, L. J. (1999). *J. Appl. Cryst.* **32**, 837–838.

Gemel, C., Trimmel, G., Slugovc, C., Kremel, S., Mereiter, K., Schmid, R. & Kirchner, K. (1996). *Organometallics*, **15**, 3998–4004.

Govind, B., Satyanarayana, T. & Veera-Reddy, K. (1996). *Polyhedron*, **15**, 1009–1022.

Lo, Y. H., Lin Y.-C., Lee, G. H. & Wang, Y. W. (2004). *Eur. J. Inorg. Chem.* pp. 4616–4623.

Nonius (1999). *COLLECT*. Nonius BV, Delft, The Netherlands.

Otwinowski, Z. & Minor, W. (1997). *Methods in Enzymology*, Vol. 276, *Macromolecular Crystallography*, Part A, edited by C. W. Carter Jr & R. M. Sweet, pp. 307–326. New York: Academic Press.

Pavlik, S., Mereiter, K., Puchberger, M. & Kirchner, K. (2005). *Organometallics*, **24**, 3561–3575.

Sheldrick, G. M. (2008). *Acta Cryst.* A**64**, 112–122.

Slugovc, C., Mereiter, K., Schmid, R. & Kirchner, K. (1998). *Organometallics*, **17**, 827–831.

Tong, H.-C., Hsu, C.-Y. C., Lo, Y.-H., Lin, C.-H. & Wang, Y. (2008). *Acta Cryst.* E**64**, m1453.

Tong, H.-C., Hung, Y.-C., Wang, P.-Y., Lin, C.-H. & Lo, Y.-H. (2009). *Acta Cryst.* E**65**, m438.

supplementary materials

Acta Cryst. (2010). E**66**, m795-m796 [**doi:10.1107/S1600536810021525**]

Chlorido[hydridotris(pyrazol-1-yl-κN^2)borato](1*H*-pyrazole-κN^2)(triphenylphosphine-κP)ruthenium(II)

C.-C. Huang, H.-G. Chen, Y. H. Lo, L.-S. Hsu and C.-H. Lin

Comment

Pyrazoles and pyrazolate anions are attractive ligands that disclose a rich coordination chemistry (Deacon *et al.*, 1998). Pyrazoles and substituted pyrazoles usually perform as monodentate ligands (Lo *et al.*, 2004) and these monodentate pyrazoles may give rise to fascinating processes such as prototropic equilibrium or reversible metal-ligand binding, which are relevant to biological systems (Govind *et al.*, 1996). On the other hand, Tp (hydridotripyrazolylborate) ligand is often compared with the Cp (Cp = η^5-C_5H_5) ligand due to their charge and number of electrons donated in the formation of complex. The ruthenium chloride complex [Ru(Tp)Cl(PPh_3)$_2$] (Alcock *et al.*, 1992) has been used as the precursor for the synthesis of several complexes because of its substitutionally labile phosphines and chloride (Cheng *et al.*, 2009). TpRu complexes are of importance for stoichiometric and catalytic transformations of organic compounds (Pavlik *et al.*, 2005).

Treatment of the complex [Ru(Tp)Cl(PPh_3)$_2$] reacts with pyrazole in toluene affording the title compound [RuCl(Tp)(PPh_3)(HPz)] (Figure 1). The single crystals of the title compound suitable for X-ray structure analysis were obtained by recrystallization of the crude product from dichloromethane–ether. In the crystal structure of the title compound the ruthenium metal center is coordinated by four N, one P and one Cl atom within slightly distorted octahedron. The bite angle of the Tp ligand produces an average produces an average N—Ru—N angle of 86.6° only slightly distorted from 90°. The three Ru—N(Tp) bond lengths (2.067 (4), 2.097 (4), and 2.076 (4) Å) are slightly longer than the average distance of 2.038 Å in other ruthenium Tp complexes (Gemel *et al.* 1996; Slugovc *et al.* 1998). The Ru—Cl bond of 2.4374 (14) Å are similar to those found in other (pyrazole)ruthenium complexes, such as 2.4259 (14) Å in [Ru(Tp)Cl(PPh_3)(PhCN)] (Tong *et al.* 2008) and 2.4429 (7) Å in [Ru(Tp)Cl(PPh_3) (HN=CPh_2)] (Tong *et al.* 2009). Weak N—H——Cl hydrogen bond is observed in the crystal structure.

Experimental

To a solution of [Ru(Tp)Cl(PPh_3)$_2$] (3.95 g, 4.50 mmol) in toulene (100 ml), an excess of pyrazole were added. The mixture was heated using a warm water bath for 30 min. A deep yellow color developed during this time. The reaction mixture was stirred for a further 2 h at room temperature (298 K). Then it was concentrated to approximately half of the volume and cooled to 273 K. The yellow precipitate was filtered off, washed with ethanol and ether and dried under vacuum to give the title compound. Yellow prisms of (I) were obtained by recrystallization from dichloromethane–ether.

Refinement

The H atoms were placed in idealized positions and constrained to ride on their parent atoms, with C—H = 0.95 Å and U_{iso}(H) = 1.2 U_{eq}(C) and B—H = 1.0 Å and U_{iso}(H) = 1.2U_{eq}(B).

Figures

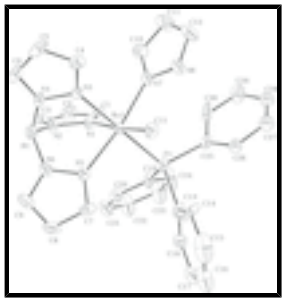


Fig. 1. Molecular structure of (I) with displacement ellipsoids drawn at the 30% probability level (H atoms are shown as spheres of arbitrary radius).

Chlorido[hydridotris(pyrazol-1-yl-κN^2)borato](1*H*-pyrazole- κN^2)(triphenylphosphine-κ*P*)ruthenium(II)

Crystal data

$[Ru(C_9H_{10}BN_6)Cl(C_3H_4N_2)(C_{18}H_{15}P)]$	$Z = 4$
$M_r = 679.91$	$F(000) = 1384$
Monoclinic, $P2_1/c$	$D_x = 1.486$ Mg m^{-3}
Hall symbol: -P 2ybc	Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å
$a = 17.7782$ (12) Å	$\mu = 0.69$ mm^{-1}
$b = 10.0843$ (5) Å	$T = 200$ K
$c = 18.9139$ (10) Å	Prism, yellow
$\beta = 116.316$ (3)°	0.11 × 0.08 × 0.03 mm
$V = 3039.5$ (3) Å^3	

Data collection

Nonius KappaCCD diffractometer	5292 independent reflections
Radiation source: fine-focus sealed tube	3470 reflections with $I > 2\sigma(I)$
graphite	$R_{int} = 0.079$
Detector resolution: 9 pixels mm^{-1}	$\theta_{max} = 25.0°$, $\theta_{min} = 2.4°$
CCD rotation images, thick slices scans	$h = -21 \rightarrow 21$
Absorption correction: multi-scan (*SORTAV*; Blessing, 1995)	$k = -11 \rightarrow 12$
$T_{min} = 0.928$, $T_{max} = 0.980$	$l = -22 \rightarrow 21$
22639 measured reflections	

Refinement

Refinement on F^2	Primary atom site location: structure-invariant direct methods
Least-squares matrix: full	Secondary atom site location: difference Fourier map
$R[F^2 > 2\sigma(F^2)] = 0.053$	Hydrogen site location: inferred from neighbouring sites
$wR(F^2) = 0.118$	H-atom parameters constrained

S = 1.02	$w = 1/[\sigma^2(F_o^2) + (0.0431P)^2 + 4.7477P]$ where $P = (F_o^2 + 2F_c^2)/3$
5292 reflections	$(\Delta/\sigma)_{max} = 0.001$
360 parameters	$\Delta\rho_{max} = 0.89$ e Å^{-3}
0 restraints	$\Delta\rho_{min} = -0.88$ e Å^{-3}

Special details

Geometry. All e.s.d.'s (except the e.s.d. in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell e.s.d.'s are taken into account individually in the estimation of e.s.d.'s in distances, angles and torsion angles; correlations between e.s.d.'s in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell e.s.d.'s is used for estimating e.s.d.'s involving l.s. planes.

Refinement. Refinement of F^2 against ALL reflections. The weighted *R*-factor *wR* and goodness of fit *S* are based on F^2, conventional *R*-factors *R* are based on *F*, with *F* set to zero for negative F^2. The threshold expression of $F^2 > \sigma(F^2)$ is used only for calculating *R*-factors(gt) *etc*. and is not relevant to the choice of reflections for refinement. *R*-factors based on F^2 are statistically about twice as large as those based on *F*, and *R*- factors based on ALL data will be even larger.

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å^2)

	x	*y*	*z*	U_{iso}*/U_{eq}	Occ. (<1)
C1	0.2902 (4)	0.3286 (6)	0.1960 (4)	0.0463 (16)	
H1	0.2738	0.2987	0.1436	0.056*	
C2	0.2953 (4)	0.4609 (6)	0.2186 (4)	0.0555 (18)	
H2	0.2837	0.5370	0.1858	0.067*	
C3	0.3205 (4)	0.4581 (6)	0.2979 (4)	0.0474 (17)	
H3	0.3290	0.5333	0.3309	0.057*	
C4	0.5121 (3)	0.0343 (6)	0.4007 (4)	0.0404 (15)	
H4	0.5261	−0.0394	0.3776	0.048*	
C5	0.5677 (4)	0.0987 (7)	0.4686 (4)	0.0539 (18)	
H5	0.6255	0.0793	0.4997	0.065*	
C6	0.5218 (4)	0.1956 (6)	0.4810 (4)	0.0480 (17)	
H6	0.5419	0.2566	0.5238	0.058*	
C7	0.2128 (4)	0.0109 (6)	0.3727 (4)	0.0402 (15)	
H7	0.1830	−0.0666	0.3468	0.048*	
C8	0.2055 (4)	0.0742 (7)	0.4345 (4)	0.0562 (19)	
H8	0.1701	0.0498	0.4580	0.067*	
C9	0.2593 (4)	0.1778 (7)	0.4543 (4)	0.057 (2)	
H9	0.2689	0.2395	0.4954	0.069*	
C10	0.4314 (4)	0.1132 (7)	0.1913 (4)	0.0540 (18)	
H10	0.4311	0.2064	0.1983	0.065*	
C11	0.4754 (5)	0.0497 (8)	0.1565 (4)	0.073 (2)	
H11	0.5096	0.0890	0.1354	0.087*	
C12	0.4589 (5)	−0.0808 (8)	0.1592 (4)	0.069 (2)	
H12	0.4799	−0.1519	0.1401	0.082*	
C13	0.1166 (4)	−0.1063 (6)	0.1829 (3)	0.0387 (15)	
C14	0.1434 (4)	−0.2266 (6)	0.2193 (5)	0.068 (2)	
H14	0.2008	−0.2507	0.2383	0.082*	

C15	0.0875 (6)	−0.3145 (8)	0.2288 (5)	0.097 (2)	
H15	0.1071	−0.3971	0.2545	0.116*	
C16	0.0059 (6)	−0.2816 (8)	0.2013 (4)	0.0853 (19)	
H16	−0.0322	−0.3420	0.2069	0.102*	
C17	−0.0222 (5)	−0.1622 (7)	0.1657 (4)	0.0608 (14)	
H17	−0.0796	−0.1390	0.1474	0.073*	
C18	0.0328 (4)	−0.0738 (6)	0.1559 (3)	0.0448 (16)	
H18	0.0126	0.0090	0.1307	0.054*	
C19	0.1261 (3)	0.1512 (5)	0.1297 (3)	0.0377 (15)	
C20	0.1150 (3)	0.2350 (5)	0.1821 (4)	0.0389 (15)	
H20	0.1442	0.2181	0.2371	0.047*	
C21	0.0622 (4)	0.3428 (7)	0.1557 (4)	0.0608 (14)	
H21	0.0536	0.3977	0.1923	0.073*	
C22	0.0221 (6)	0.3709 (8)	0.0766 (5)	0.0853 (19)	
H22	−0.0124	0.4473	0.0582	0.102*	
C23	0.0325 (6)	0.2860 (8)	0.0239 (5)	0.097 (2)	
H23	0.0037	0.3030	−0.0311	0.116*	
C24	0.0842 (5)	0.1779 (7)	0.0509 (4)	0.078 (3)	
H24	0.0909	0.1206	0.0142	0.094*	
C25	0.2000 (3)	−0.0681 (5)	0.0859 (3)	0.0391 (15)	
C26	0.2011 (7)	−0.2090 (10)	0.0842 (7)	0.039 (3)*	0.547 (10)
H26	0.1893	−0.2624	0.1194	0.047*	0.547 (10)
C27	0.2208 (7)	−0.2625 (12)	0.0263 (7)	0.052 (4)*	0.547 (10)
H27	0.2197	−0.3561	0.0204	0.063*	0.547 (10)
C28	0.2412 (8)	−0.1881 (13)	−0.0209 (9)	0.048 (3)*	0.547 (10)
H28	0.2497	−0.2303	−0.0617	0.058*	0.547 (10)
C26'	0.1488 (9)	−0.1639 (13)	0.0340 (8)	0.045 (4)*	0.453 (10)
H26'	0.1061	−0.2001	0.0454	0.054*	0.453 (10)
C27'	0.1535 (10)	−0.2134 (15)	−0.0340 (9)	0.060 (5)*	0.453 (10)
H27'	0.1188	−0.2849	−0.0632	0.072*	0.453 (10)
C28'	0.2087 (10)	−0.1562 (15)	−0.0564 (10)	0.048 (4)*	0.453 (10)
H28'	0.2167	−0.1872	−0.1000	0.057*	0.453 (10)
C29	0.2503 (5)	−0.0547 (7)	−0.0130 (4)	0.063 (2)	
H29	0.2658	−0.0021	−0.0462	0.076*	
C30	0.2354 (6)	−0.0005 (7)	0.0473 (4)	0.075 (3)	
H30	0.2511	0.0891	0.0619	0.090*	
N1	0.3114 (3)	0.2499 (4)	0.2585 (3)	0.0316 (11)	
N2	0.3313 (3)	0.3310 (4)	0.3217 (3)	0.0337 (11)	
N3	0.4364 (3)	0.0895 (4)	0.3725 (2)	0.0281 (10)	
N4	0.4429 (3)	0.1907 (4)	0.4224 (3)	0.0334 (11)	
N5	0.2680 (3)	0.0749 (4)	0.3548 (3)	0.0303 (11)	
N6	0.2968 (3)	0.1791 (4)	0.4062 (3)	0.0389 (12)	
N7	0.3897 (3)	0.0274 (4)	0.2138 (3)	0.0367 (12)	
N8	0.4080 (3)	−0.0912 (5)	0.1936 (3)	0.0476 (14)	
H8'	0.3887	−0.1669	0.2020	0.057*	
B1	0.3644 (4)	0.2722 (6)	0.4052 (4)	0.0397 (18)	
H1'	0.3771	0.3442	0.4452	0.048*	
Cl1	0.34907 (9)	−0.18597 (13)	0.31246 (9)	0.0368 (4)	
Ru1	0.32023 (3)	0.04732 (4)	0.27709 (3)	0.02453 (15)	

P1	0.19260 (9)	0.00460 (14)	0.17152 (9)	0.0329 (4)

Atomic displacement parameters (Å^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
C1	0.055 (4)	0.032 (4)	0.040 (4)	−0.002 (3)	0.010 (3)	0.011 (3)
C2	0.067 (5)	0.027 (4)	0.059 (5)	−0.006 (3)	0.016 (4)	0.020 (3)
C3	0.052 (4)	0.020 (3)	0.071 (5)	−0.007 (3)	0.028 (4)	−0.001 (3)
C4	0.034 (3)	0.037 (4)	0.045 (4)	0.003 (3)	0.013 (3)	0.005 (3)
C5	0.032 (4)	0.059 (4)	0.043 (4)	−0.006 (3)	−0.008 (3)	0.014 (4)
C6	0.052 (4)	0.047 (4)	0.026 (4)	−0.023 (4)	0.000 (3)	0.000 (3)
C7	0.032 (3)	0.034 (3)	0.052 (4)	−0.001 (3)	0.016 (3)	0.013 (3)
C8	0.055 (4)	0.063 (5)	0.072 (5)	−0.004 (4)	0.047 (4)	0.002 (4)
C9	0.078 (5)	0.054 (4)	0.068 (5)	0.003 (4)	0.058 (5)	−0.004 (4)
C10	0.064 (5)	0.061 (4)	0.049 (4)	−0.017 (4)	0.037 (4)	−0.001 (4)
C11	0.088 (6)	0.087 (6)	0.074 (6)	−0.008 (5)	0.063 (5)	0.003 (5)
C12	0.078 (6)	0.086 (6)	0.066 (5)	0.010 (5)	0.053 (5)	−0.008 (4)
C13	0.034 (3)	0.033 (3)	0.036 (4)	−0.007 (3)	0.004 (3)	−0.009 (3)
C14	0.049 (4)	0.028 (4)	0.108 (7)	−0.025 (3)	0.017 (4)	0.005 (4)
C15	0.128 (6)	0.072 (4)	0.048 (4)	0.049 (4)	0.001 (4)	0.007 (3)
C16	0.123 (5)	0.068 (4)	0.054 (4)	0.031 (4)	0.030 (4)	−0.003 (3)
C17	0.058 (3)	0.076 (4)	0.051 (3)	0.016 (3)	0.026 (3)	−0.006 (3)
C18	0.043 (4)	0.054 (4)	0.036 (4)	−0.006 (3)	0.016 (3)	−0.002 (3)
C19	0.038 (3)	0.030 (3)	0.028 (4)	0.009 (3)	−0.001 (3)	−0.005 (3)
C20	0.034 (3)	0.036 (3)	0.032 (4)	0.010 (3)	0.002 (3)	0.002 (3)
C21	0.058 (3)	0.076 (4)	0.051 (3)	0.016 (3)	0.026 (3)	−0.006 (3)
C22	0.123 (5)	0.068 (4)	0.054 (4)	0.031 (4)	0.030 (4)	−0.003 (3)
C23	0.128 (6)	0.072 (4)	0.048 (4)	0.049 (4)	0.001 (4)	0.007 (3)
C24	0.101 (6)	0.070 (5)	0.032 (4)	0.056 (5)	0.002 (4)	0.000 (4)
C25	0.030 (3)	0.031 (3)	0.045 (4)	0.001 (3)	0.007 (3)	−0.013 (3)
C29	0.087 (5)	0.061 (5)	0.040 (4)	−0.017 (4)	0.026 (4)	−0.003 (4)
C30	0.151 (8)	0.044 (4)	0.032 (4)	−0.041 (5)	0.043 (5)	−0.017 (3)
N1	0.039 (3)	0.017 (2)	0.033 (3)	−0.002 (2)	0.011 (3)	0.001 (2)
N2	0.038 (3)	0.018 (3)	0.043 (3)	−0.005 (2)	0.017 (3)	−0.003 (2)
N3	0.026 (3)	0.029 (3)	0.024 (3)	−0.001 (2)	0.008 (2)	0.000 (2)
N4	0.041 (3)	0.033 (3)	0.021 (3)	−0.009 (2)	0.008 (2)	−0.003 (2)
N5	0.030 (3)	0.025 (3)	0.034 (3)	0.002 (2)	0.012 (2)	0.001 (2)
N6	0.049 (3)	0.033 (3)	0.044 (3)	−0.001 (2)	0.029 (3)	−0.005 (2)
N7	0.042 (3)	0.035 (3)	0.037 (3)	0.001 (2)	0.021 (3)	−0.006 (2)
N8	0.058 (4)	0.044 (3)	0.052 (4)	0.001 (3)	0.034 (3)	−0.010 (3)
B1	0.049 (5)	0.029 (4)	0.045 (5)	−0.006 (3)	0.025 (4)	−0.008 (3)
Cl1	0.0399 (8)	0.0218 (7)	0.0420 (9)	0.0043 (6)	0.0120 (7)	0.0027 (6)
Ru1	0.0258 (2)	0.0193 (2)	0.0246 (3)	−0.0007 (2)	0.00759 (19)	0.0001 (2)
P1	0.0322 (9)	0.0231 (8)	0.0321 (9)	0.0004 (6)	0.0039 (7)	−0.0036 (6)

Geometric parameters (Å, °)

C1—N1	1.332 (7)	C20—C21	1.377 (8)
C1—C2	1.392 (8)	C20—H20	0.9500

C1—H1	0.9500	C21—C22	1.371 (9)
C2—C3	1.363 (9)	C21—H21	0.9500
C2—H2	0.9500	C22—C23	1.387 (10)
C3—N2	1.343 (7)	C22—H22	0.9500
C3—H3	0.9500	C23—C24	1.370 (9)
C4—N3	1.329 (6)	C23—H23	0.9500
C4—C5	1.387 (8)	C24—H24	0.9500
C4—H4	0.9500	C25—C30	1.341 (8)
C5—C6	1.359 (9)	C25—C26'	1.390 (14)
C5—H5	0.9500	C25—C26	1.422 (11)
C6—N4	1.350 (7)	C25—P1	1.835 (6)
C6—H6	0.9500	C26—C27	1.396 (14)
C7—N5	1.337 (6)	C26—H26	0.9500
C7—C8	1.387 (8)	C27—C28	1.334 (15)
C7—H7	0.9500	C27—H27	0.9500
C8—C9	1.352 (9)	C28—C29	1.355 (14)
C8—H8	0.9500	C28—H28	0.9500
C9—N6	1.346 (7)	C26'—C27'	1.416 (18)
C9—H9	0.9500	C26'—H26'	0.9500
C10—N7	1.326 (7)	C27'—C28'	1.358 (19)
C10—C11	1.382 (9)	C27'—H27'	0.9500
C10—H10	0.9500	C28'—C29	1.316 (16)
C11—C12	1.354 (9)	C28'—H28'	0.9500
C11—H11	0.9500	C29—C30	1.392 (9)
C12—N8	1.332 (7)	C29—H29	0.9500
C12—H12	0.9500	C30—H30	0.9500
C13—C14	1.371 (8)	N1—N2	1.359 (6)
C13—C18	1.384 (8)	N2—B1	1.539 (8)
C13—P1	1.838 (6)	N3—N4	1.361 (6)
C14—C15	1.402 (11)	N4—B1	1.524 (8)
C14—H14	0.9500	N5—N6	1.367 (6)
C15—C16	1.347 (11)	N6—B1	1.531 (8)
C15—H15	0.9500	N7—N8	1.339 (6)
C16—C17	1.362 (9)	N8—H8'	0.8800
C16—H16	0.9500	B1—H1'	1.0000
C17—C18	1.394 (8)	Ru1—N1	2.067 (4)
C17—H17	0.9500	Ru1—N3	2.097 (4)
C18—H18	0.9500	Ru1—N5	2.076 (4)
C19—C24	1.365 (8)	Ru1—N7	2.076 (4)
C19—C20	1.382 (7)	Ru1—P1	2.3031 (15)
C19—P1	1.839 (5)	Ru1—Cl1	2.4374 (14)
N1—C1—C2	110.2 (6)	C27—C26—C25	114.5 (9)
N1—C1—H1	124.9	C27—C26—H26	122.8
C2—C1—H1	124.9	C25—C26—H26	122.8
C3—C2—C1	105.2 (5)	C28—C27—C26	123.0 (12)
C3—C2—H2	127.4	C28—C27—H27	118.5
C1—C2—H2	127.4	C26—C27—H27	118.5
N2—C3—C2	108.5 (5)	C27—C28—C29	122.6 (12)
N2—C3—H3	125.8	C27—C28—H28	118.7

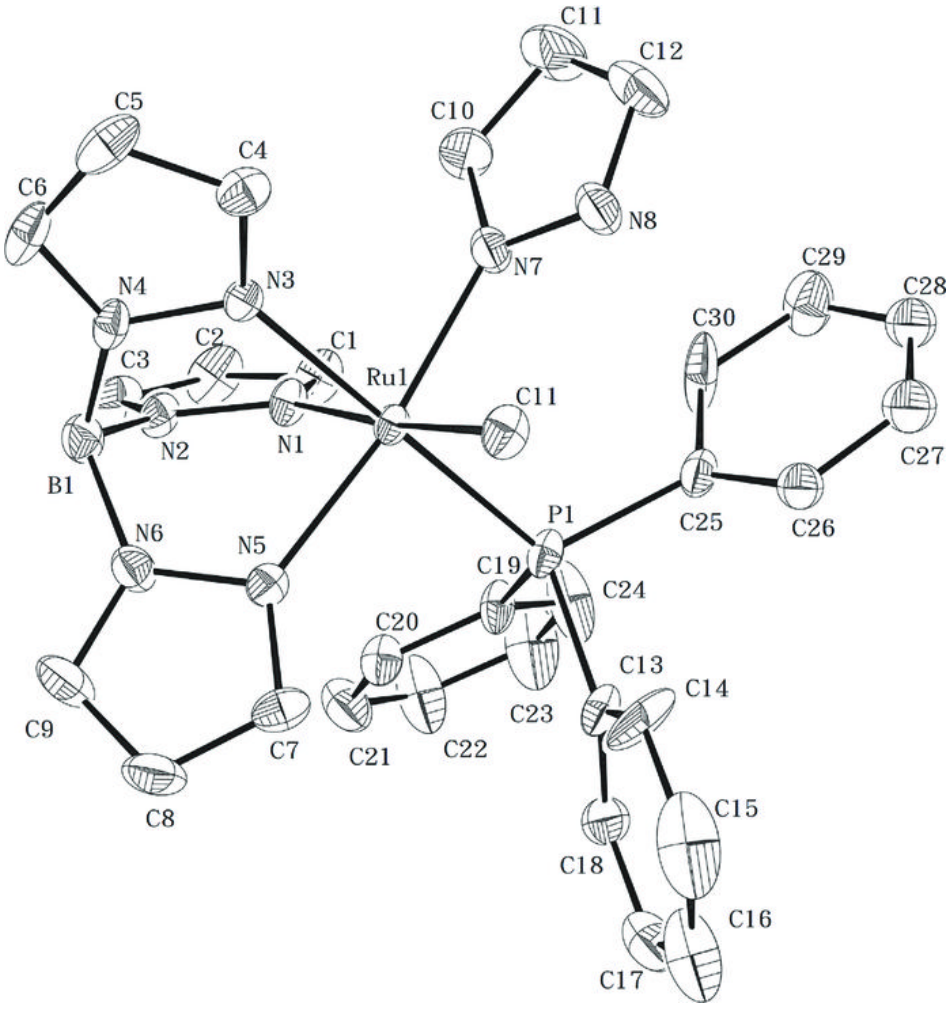
C2—C3—H3	125.8	C29—C28—H28	118.7
N3—C4—C5	110.8 (6)	C25—C26'—C27'	127.1 (12)
N3—C4—H4	124.6	C25—C26'—H26'	116.5
C5—C4—H4	124.6	C27'—C26'—H26'	116.5
C6—C5—C4	105.1 (6)	C28'—C27'—C26'	118.4 (15)
C6—C5—H5	127.5	C28'—C27'—H27'	120.8
C4—C5—H5	127.5	C26'—C27'—H27'	120.8
N4—C6—C5	108.5 (5)	C29—C28'—C27'	114.9 (13)
N4—C6—H6	125.8	C29—C28'—H28'	122.6
C5—C6—H6	125.8	C27'—C28'—H28'	122.6
N5—C7—C8	110.1 (5)	C28'—C29—C28	32.0 (7)
N5—C7—H7	124.9	C28'—C29—C30	123.9 (9)
C8—C7—H7	124.9	C28—C29—C30	115.0 (8)
C9—C8—C7	105.7 (5)	C28'—C29—H29	105.7
C9—C8—H8	127.1	C28—C29—H29	122.5
C7—C8—H8	127.1	C30—C29—H29	122.5
N6—C9—C8	108.8 (6)	C25—C30—C29	123.5 (6)
N6—C9—H9	125.6	C25—C30—H30	118.2
C8—C9—H9	125.6	C29—C30—H30	118.2
N7—C10—C11	111.4 (6)	C1—N1—N2	106.4 (4)
N7—C10—H10	124.3	C1—N1—Ru1	135.2 (4)
C11—C10—H10	124.3	N2—N1—Ru1	118.4 (3)
C12—C11—C10	104.8 (6)	C3—N2—N1	109.7 (5)
C12—C11—H11	127.6	C3—N2—B1	130.1 (5)
C10—C11—H11	127.6	N1—N2—B1	120.1 (4)
N8—C12—C11	107.4 (6)	C4—N3—N4	106.0 (5)
N8—C12—H12	126.3	C4—N3—Ru1	134.1 (4)
C11—C12—H12	126.3	N4—N3—Ru1	119.8 (3)
C14—C13—C18	118.2 (6)	C6—N4—N3	109.6 (5)
C14—C13—P1	119.2 (5)	C6—N4—B1	132.5 (5)
C18—C13—P1	122.7 (5)	N3—N4—B1	117.9 (5)
C13—C14—C15	121.0 (7)	C7—N5—N6	106.1 (4)
C13—C14—H14	119.5	C7—N5—Ru1	136.3 (4)
C15—C14—H14	119.5	N6—N5—Ru1	117.5 (3)
C16—C15—C14	119.9 (8)	C9—N6—N5	109.3 (5)
C16—C15—H15	120.0	C9—N6—B1	129.9 (5)
C14—C15—H15	120.0	N5—N6—B1	120.7 (4)
C15—C16—C17	120.3 (9)	C10—N7—N8	104.5 (5)
C15—C16—H16	119.9	C10—N7—Ru1	133.0 (4)
C17—C16—H16	119.9	N8—N7—Ru1	122.2 (4)
C16—C17—C18	120.4 (7)	C12—N8—N7	111.9 (5)
C16—C17—H17	119.8	C12—N8—H8'	124.0
C18—C17—H17	119.8	N7—N8—H8'	124.0
C13—C18—C17	120.2 (6)	N4—B1—N6	108.4 (5)
C13—C18—H18	119.9	N4—B1—N2	108.9 (5)
C17—C18—H18	119.9	N6—B1—N2	107.7 (5)
C24—C19—C20	118.7 (5)	N4—B1—H1'	110.6
C24—C19—P1	124.3 (5)	N6—B1—H1'	110.6
C20—C19—P1	116.9 (4)	N2—B1—H1'	110.6

C21—C20—C19	120.9 (6)	N1—Ru1—N5	87.90 (16)
C21—C20—H20	119.5	N1—Ru1—N7	91.02 (17)
C19—C20—H20	119.5	N5—Ru1—N7	171.23 (18)
C22—C21—C20	119.9 (6)	N1—Ru1—N3	85.26 (17)
C22—C21—H21	120.0	N5—Ru1—N3	86.71 (17)
C20—C21—H21	120.0	N7—Ru1—N3	84.53 (17)
C21—C22—C23	119.1 (7)	N1—Ru1—P1	93.79 (13)
C21—C22—H22	120.4	N5—Ru1—P1	93.51 (13)
C23—C22—H22	120.4	N7—Ru1—P1	95.25 (13)
C24—C23—C22	120.3 (7)	N3—Ru1—P1	179.02 (12)
C24—C23—H23	119.8	N1—Ru1—Cl1	172.51 (13)
C22—C23—H23	119.8	N5—Ru1—Cl1	92.33 (12)
C19—C24—C23	120.9 (6)	N7—Ru1—Cl1	87.62 (13)
C19—C24—H24	119.5	N3—Ru1—Cl1	87.28 (12)
C23—C24—H24	119.5	P1—Ru1—Cl1	93.67 (5)
C30—C25—C26'	106.7 (7)	C25—P1—C13	101.8 (3)
C30—C25—C26	118.8 (7)	C25—P1—C19	103.0 (3)
C26'—C25—C26	45.6 (6)	C13—P1—C19	100.0 (3)
C30—C25—P1	120.8 (4)	C25—P1—Ru1	114.28 (18)
C26'—C25—P1	128.3 (7)	C13—P1—Ru1	120.32 (19)
C26—C25—P1	115.2 (6)	C19—P1—Ru1	114.91 (19)

Hydrogen-bond geometry (Å, °)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
N8—H8'···Cl1	0.88	2.49	3.025 (6)	120

Fig. 1


C11
C12
C10
C5
C4
C6
N8
N7
C29
C28
N4
N3
C30
C2
C1
C3
Ru1
C11
C27
N2
N1
B1
P1
C25
C26
N6
N5
C19
C24
C20
C13
C14
C9
C7
C23
C21
C22
C15
C18
C8
C16
C17

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2,3-Dimethyl-*N*-[(*E*)-4-nitrobenzylidene]-aniline

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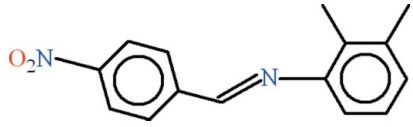
Key indicators: single-crystal X-ray study; T = 296 K; mean σ(C–C) = 0.003 Å; R factor = 0.047; wR factor = 0.111; data-to-parameter ratio = 11.0.

In the title compound, $C_{15}H_{14}N_2O_2$, the aromatic rings are oriented at a dihedral angle of 24.52 (5)°. The dihedral angle between the nitro group and its parent benzene ring is 9.22 (16)°. In the crystal, molecules interact through aromatic $\pi-\pi$ stacking interactions [centroid–centroid separations = 3.8158 (14) and 3.9139 (14) Å].

Related literature

For structural systematics of related compounds, see: Harada *et al.* (2004).



Experimental

Crystal data

$C_{15}H_{14}N_2O_2$ M_r = 254.28
Orthorhombic, $P2_12_12_1$
a = 7.1969 (5) Å
b = 11.8023 (7) Å
c = 15.3721 (8) Å
V = 1305.71 (14) Å^3
Z = 4
Mo $K\alpha$ radiation
μ = 0.09 mm^{-1}
T = 296 K
0.32 × 0.14 × 0.14 mm

Data collection

Bruker Kappa APEXII CCD diffractometer
Absorption correction: multi-scan (*SADABS*; Bruker, 2005)
T_{min} = 0.986, T_{max} = 0.987
13172 measured reflections
1917 independent reflections
1253 reflections with $I > 2\sigma(I)$
R_{int} = 0.057

Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.047
$wR(F^2)$ = 0.111
S = 1.02
1917 reflections
174 parameters
H-atom parameters constrained
$\Delta\rho_{max}$ = 0.12 e Å^{-3}
$\Delta\rho_{min}$ = −0.14 e Å^{-3}

Data collection: *APEX2* (Bruker, 2007); cell refinement: *SAINT* (Bruker, 2007); data reduction: *SAINT*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *ORTEP-3 for Windows* (Farrugia, 1997) and *PLATON* (Spek, 2009); software used to prepare material for publication: *WinGX* (Farrugia, 1999) and *PLATON*.

The authors acknowledge the provision of funds for the purchase of diffractometer and encouragement by Dr Muhammad Akram Chaudhary, Vice Chancellor, University of Sargodha, Pakistan.

Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: HB5464).

References

Bruker (2005). *SADABS*. Bruker AXS Inc., Madison, Wisconsin, USA.
Bruker (2007). *APEX2* and *SAINT*. Bruker AXS Inc., Madison, Wisconsin, USA.
Farrugia, L. J. (1997). *J. Appl. Cryst.* **30**, 565.
Farrugia, L. J. (1999). *J. Appl. Cryst.* **32**, 837–838.
Harada, J., Harakawa, M. & Ogawa, K. (2004). *Acta Cryst.* B**60**, 578–588.
Sheldrick, G. M. (2008). *Acta Cryst.* A**64**, 112–122.
Spek, A. L. (2009). *Acta Cryst.* D**65**, 148–155.

supplementary materials

Acta Cryst. (2010). E**66**, o1561 [**doi:10.1107/S160053681001932X**]

2,3-Dimethyl-*N*-[(*E*)-4-nitrobenzylidene]aniline

M. I. Tariq, S. Ahmad, M. N. Tahir, M. Sarfaraz and I. Hussain

Comment

Torsional, vibration and central bond length of *N*-benzylideneanilines (Harada *et al.*, 2004) has been studied for seven compounds at different temperatures. The title compound (I, Fig. 1) is another example due to change of substitutions at both phenyl rings for which the same study can be undertaken. The title compound has been prepared for derivatization.

The molecules of (I) are essentially monomeric having no intra or inter-molecular H-bondings. The phenyl rings A (C1—C6) and B (C10—C15) are planar with r. m. s. deviation of 0.0065 and 0.0022 Å respectively. The dihedral angle between A/B is 24.52 (5)°. The nitro group C (O1/N2/O2) is oriented at 9.22 (16)° with the parent phenyl ring. It is to be noted that the nitro substituated phenyl ring B has smaller bond lengths [1.365 (3)–1.387 (3) Å], whereas the 2,3-dimethyl substituated ring has longer bond lengths 1.373 (3)—1.401 (3) Å. The value of C═N bond length at room temperature for (I) is 1.262 (3) Å which is in compatible with the studies of Harada *et al.*, 2004. The molecules are stabilized due to π—π interactions between the centroids of phenyl rings with separation of 3.8158 (14) and 3.9139 (14) Å.

Experimental

Equimolar quantities of 2,3-dimethylaniline and 4-nitro benzaldehyde were refluxed in methanol for 15 minutes resulting in yellow color precipitates. The contents of the flask were dried at room temperature and washed with methanol and ethanol, respectively. The washed crude material affoarded yellow needles of (I) in the solution of diethyl ether at room temperature by slow evaporation after 24 h.

Refinement

In the absence of anomalous scattering, all Friedal pairs were merged. Although all H-atoms were appeared in Fourier difference map but positioned geometrically (C–H = 0.93–0.96 Å) and refined as riding with U_{iso}(H) = xU_{eq}(C), where x =1.2 for aryl C–H and x = 1.5 methyl H-atoms.

Figures

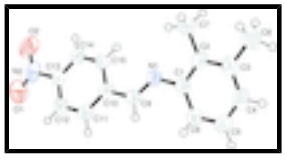


Fig. 1. View of (I) with displacement ellipsoids drawn at the 50% probability level.

2,3-Dimethyl-*N*-[(*E*)-4-nitrobenzylidene]aniline

Crystal data

$C_{15}H_{14}N_2O_2$	$F(000) = 536$
$M_r = 254.28$	$D_x = 1.294$ Mg m^{-3}
Orthorhombic, $P2_12_12_1$	Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å
Hall symbol: P 2ac 2ab	Cell parameters from 1334 reflections
$a = 7.1969$ (5) Å	$\theta = 2.1$–$25.4°$
$b = 11.8023$ (7) Å	$\mu = 0.09$ mm^{-1}
$c = 15.3721$ (8) Å	$T = 296$ K
$V = 1305.71$ (14) Å^3	Needle, yellow
$Z = 4$	0.32 × 0.14 × 0.14 mm

Data collection

Bruker Kappa APEXII CCD diffractometer	1917 independent reflections
Radiation source: fine-focus sealed tube	1253 reflections with $I > 2\sigma(I)$
graphite	$R_{int} = 0.057$
Detector resolution: 7.40 pixels mm^{-1}	$\theta_{max} = 28.6°$, $\theta_{min} = 2.2°$
ω scans	$h = -8\rightarrow9$
Absorption correction: multi-scan (*SADABS*; Bruker, 2005)	$k = -15\rightarrow15$
$T_{min} = 0.986$, $T_{max} = 0.987$	$l = -20\rightarrow20$
13172 measured reflections	

Refinement

Refinement on F^2	Primary atom site location: structure-invariant direct methods
Least-squares matrix: full	Secondary atom site location: difference Fourier map
$R[F^2 > 2\sigma(F^2)] = 0.047$	Hydrogen site location: inferred from neighbouring sites
$wR(F^2) = 0.111$	H-atom parameters constrained
$S = 1.02$	$w = 1/[\sigma^2(F_o^2) + (0.0482P)^2 + 0.0883P]$ where $P = (F_o^2 + 2F_c^2)/3$
1917 reflections	$(\Delta/\sigma)_{max} < 0.001$
174 parameters	$\Delta\rho_{max} = 0.12$ e Å^{-3}
0 restraints	$\Delta\rho_{min} = -0.14$ e Å^{-3}

Special details

Geometry. Bond distances, angles *etc*. have been calculated using the rounded fractional coordinates. All su's are estimated from the variances of the (full) variance-covariance matrix. The cell e.s.d.'s are taken into account in the estimation of distances, angles and torsion angles

Refinement. Refinement of F^2 against ALL reflections. The weighted *R*-factor *wR* and goodness of fit *S* are based on F^2, conventional *R*-factors *R* are based on *F*, with *F* set to zero for negative F^2. The threshold expression of $F^2 > \sigma(F^2)$ is used only for calculating *R*-factors(gt) *etc*. and is not relevant to the choice of reflections for refinement. *R*-factors based on F^2 are statistically about twice as large as those based on *F*, and *R*- factors based on ALL data will be even larger.

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å^2)

	x	*y*	*z*	U_{iso}*/U_{eq}
O1	0.1409 (4)	−0.19301 (18)	0.70198 (14)	0.0997 (9)
O2	0.1083 (4)	−0.06237 (19)	0.79842 (12)	0.0941 (9)
N1	0.1128 (3)	0.34130 (16)	0.47092 (11)	0.0485 (7)
N2	0.1253 (3)	−0.0943 (2)	0.72311 (16)	0.0684 (9)
C1	0.1231 (3)	0.42218 (18)	0.40278 (13)	0.0457 (7)
C2	0.1509 (3)	0.5351 (2)	0.42653 (14)	0.0488 (8)
C3	0.1581 (4)	0.61833 (19)	0.36160 (15)	0.0549 (8)
C4	0.1353 (4)	0.5864 (2)	0.27595 (17)	0.0624 (10)
C5	0.1052 (4)	0.4755 (2)	0.25272 (16)	0.0650 (10)
C6	0.0972 (4)	0.3935 (2)	0.31593 (14)	0.0550 (8)
C7	0.1768 (4)	0.5654 (2)	0.52133 (14)	0.0679 (10)
C8	0.1878 (5)	0.7409 (2)	0.38401 (19)	0.0820 (13)
C9	0.1573 (4)	0.23940 (19)	0.45751 (14)	0.0495 (8)
C10	0.1434 (3)	0.15342 (18)	0.52625 (14)	0.0448 (7)
C11	0.1832 (3)	0.04156 (19)	0.50760 (15)	0.0525 (8)
C12	0.1753 (4)	−0.0397 (2)	0.57139 (15)	0.0551 (9)
C13	0.1287 (3)	−0.0075 (2)	0.65402 (14)	0.0500 (8)
C14	0.0878 (3)	0.1021 (2)	0.67504 (15)	0.0523 (8)
C15	0.0953 (3)	0.18289 (19)	0.61064 (14)	0.0496 (8)
H4	0.14039	0.64145	0.23274	0.0748*
H5	0.09027	0.45617	0.19450	0.0779*
H6	0.07448	0.31854	0.30059	0.0659*
H7A	0.09112	0.62429	0.53696	0.1016*
H7B	0.30167	0.59128	0.53059	0.1016*
H7C	0.15399	0.49972	0.55663	0.1016*
H8A	0.18433	0.78558	0.33184	0.1229*
H8B	0.30655	0.74981	0.41166	0.1229*
H8C	0.09161	0.76571	0.42285	0.1229*
H9	0.20007	0.21822	0.40278	0.0594*
H11	0.21572	0.02105	0.45120	0.0630*
H12	0.20116	−0.11509	0.55867	0.0661*
H14	0.05543	0.12165	0.73165	0.0627*
H15	0.06802	0.25797	0.62382	0.0596*

Atomic displacement parameters (Å^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
O1	0.131 (2)	0.0586 (12)	0.1094 (16)	0.0005 (15)	0.0004 (17)	0.0307 (12)
O2	0.1205 (19)	0.1055 (16)	0.0563 (11)	−0.0025 (15)	−0.0044 (13)	0.0275 (12)

N1	0.0509 (12)	0.0484 (11)	0.0463 (11)	0.0052 (10)	0.0029 (10)	0.0042 (9)
N2	0.0614 (15)	0.0707 (16)	0.0731 (16)	−0.0068 (14)	−0.0072 (13)	0.0266 (13)
C1	0.0431 (14)	0.0477 (12)	0.0463 (12)	0.0035 (11)	0.0067 (11)	0.0043 (10)
C2	0.0454 (15)	0.0529 (13)	0.0482 (12)	0.0020 (12)	0.0069 (11)	0.0015 (11)
C3	0.0515 (16)	0.0504 (13)	0.0628 (15)	0.0051 (12)	0.0070 (12)	0.0082 (11)
C4	0.0660 (19)	0.0615 (16)	0.0596 (16)	0.0045 (15)	0.0068 (14)	0.0193 (13)
C5	0.079 (2)	0.0708 (17)	0.0453 (12)	0.0029 (16)	0.0008 (14)	0.0040 (12)
C6	0.0614 (16)	0.0526 (14)	0.0509 (14)	0.0027 (13)	0.0009 (13)	−0.0010 (12)
C7	0.081 (2)	0.0651 (16)	0.0577 (14)	−0.0020 (16)	0.0041 (14)	−0.0097 (13)
C8	0.105 (3)	0.0539 (15)	0.087 (2)	−0.0044 (18)	0.009 (2)	0.0079 (15)
C9	0.0467 (15)	0.0539 (13)	0.0479 (12)	0.0039 (12)	0.0081 (12)	0.0010 (11)
C10	0.0406 (13)	0.0467 (12)	0.0471 (13)	0.0009 (11)	0.0030 (11)	0.0026 (10)
C11	0.0578 (16)	0.0514 (13)	0.0483 (12)	0.0057 (12)	0.0043 (11)	−0.0031 (11)
C12	0.0608 (17)	0.0424 (12)	0.0621 (15)	0.0015 (12)	0.0011 (13)	0.0007 (11)
C13	0.0436 (14)	0.0550 (14)	0.0515 (12)	−0.0029 (12)	−0.0050 (12)	0.0116 (11)
C14	0.0521 (15)	0.0601 (16)	0.0447 (12)	0.0018 (13)	−0.0007 (11)	0.0014 (12)
C15	0.0521 (15)	0.0456 (12)	0.0512 (13)	0.0046 (12)	0.0015 (12)	0.0005 (11)

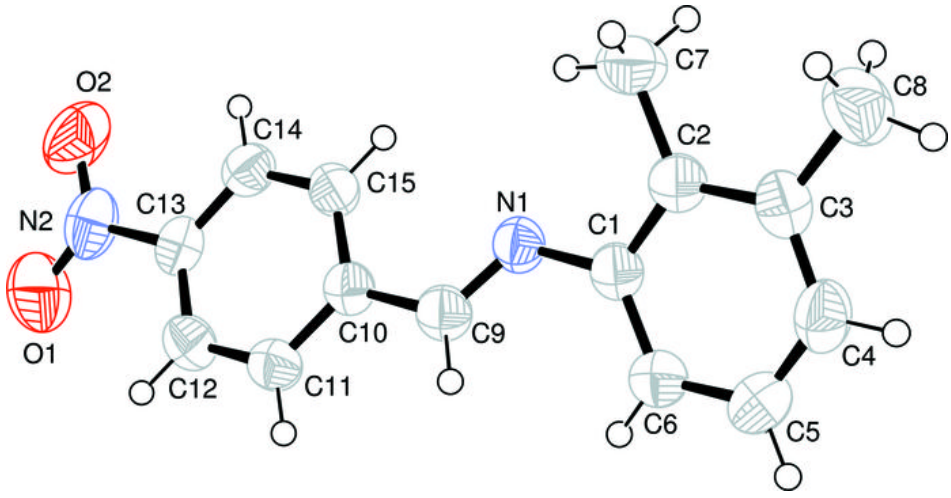
Geometric parameters (Å, °)

O1—N2	1.215 (3)	C12—C13	1.368 (3)
O2—N2	1.224 (3)	C13—C14	1.365 (3)
N1—C1	1.419 (3)	C14—C15	1.376 (3)
N1—C9	1.262 (3)	C4—H4	0.9300
N2—C13	1.476 (3)	C5—H5	0.9300
C1—C2	1.396 (3)	C6—H6	0.9300
C1—C6	1.390 (3)	C7—H7A	0.9600
C2—C3	1.401 (3)	C7—H7B	0.9600
C2—C7	1.512 (3)	C7—H7C	0.9600
C3—C4	1.379 (3)	C8—H8A	0.9600
C3—C8	1.502 (3)	C8—H8B	0.9600
C4—C5	1.374 (3)	C8—H8C	0.9600
C5—C6	1.373 (3)	C9—H9	0.9300
C9—C10	1.468 (3)	C11—H11	0.9300
C10—C11	1.381 (3)	C12—H12	0.9300
C10—C15	1.387 (3)	C14—H14	0.9300
C11—C12	1.373 (3)	C15—H15	0.9300
C1—N1—C9	120.49 (18)	C5—C4—H4	119.00
O1—N2—O2	123.9 (2)	C4—C5—H5	120.00
O1—N2—C13	118.2 (2)	C6—C5—H5	120.00
O2—N2—C13	118.0 (2)	C1—C6—H6	120.00
N1—C1—C2	117.16 (18)	C5—C6—H6	120.00
N1—C1—C6	122.56 (19)	C2—C7—H7A	109.00
C2—C1—C6	120.2 (2)	C2—C7—H7B	109.00
C1—C2—C3	119.2 (2)	C2—C7—H7C	109.00
C1—C2—C7	119.7 (2)	H7A—C7—H7B	110.00
C3—C2—C7	121.1 (2)	H7A—C7—H7C	109.00
C2—C3—C4	118.9 (2)	H7B—C7—H7C	109.00
C2—C3—C8	121.1 (2)	C3—C8—H8A	109.00

C4—C3—C8	119.9 (2)	C3—C8—H8B	109.00
C3—C4—C5	121.8 (2)	C3—C8—H8C	109.00
C4—C5—C6	119.6 (2)	H8A—C8—H8B	109.00
C1—C6—C5	120.2 (2)	H8A—C8—H8C	109.00
N1—C9—C10	121.6 (2)	H8B—C8—H8C	109.00
C9—C10—C11	119.8 (2)	N1—C9—H9	119.00
C9—C10—C15	121.1 (2)	C10—C9—H9	119.00
C11—C10—C15	119.1 (2)	C10—C11—H11	120.00
C10—C11—C12	120.7 (2)	C12—C11—H11	120.00
C11—C12—C13	118.7 (2)	C11—C12—H12	121.00
N2—C13—C12	118.7 (2)	C13—C12—H12	121.00
N2—C13—C14	118.9 (2)	C13—C14—H14	121.00
C12—C13—C14	122.4 (2)	C15—C14—H14	121.00
C13—C14—C15	118.6 (2)	C10—C15—H15	120.00
C10—C15—C14	120.6 (2)	C14—C15—H15	120.00
C3—C4—H4	119.00		

C9—N1—C1—C2	−153.3 (2)	C2—C3—C4—C5	0.2 (4)
C9—N1—C1—C6	30.1 (4)	C8—C3—C4—C5	−179.1 (3)
C1—N1—C9—C10	−178.4 (2)	C3—C4—C5—C6	0.1 (4)
O1—N2—C13—C12	−9.2 (3)	C4—C5—C6—C1	−1.3 (4)
O1—N2—C13—C14	171.7 (2)	N1—C9—C10—C11	176.3 (2)
O2—N2—C13—C12	170.3 (3)	N1—C9—C10—C15	−5.4 (4)
O2—N2—C13—C14	−8.8 (3)	C9—C10—C11—C12	178.5 (2)
N1—C1—C2—C3	−178.7 (2)	C15—C10—C11—C12	0.1 (3)
N1—C1—C2—C7	2.6 (3)	C9—C10—C15—C14	−178.2 (2)
C6—C1—C2—C3	−2.0 (3)	C11—C10—C15—C14	0.2 (3)
C6—C1—C2—C7	179.3 (2)	C10—C11—C12—C13	−0.5 (4)
N1—C1—C6—C5	178.8 (2)	C11—C12—C13—N2	−178.3 (2)
C2—C1—C6—C5	2.3 (4)	C11—C12—C13—C14	0.8 (4)
C1—C2—C3—C4	0.8 (4)	N2—C13—C14—C15	178.6 (2)
C1—C2—C3—C8	−180.0 (3)	C12—C13—C14—C15	−0.5 (3)
C7—C2—C3—C4	179.4 (2)	C13—C14—C15—C10	0.0 (3)
C7—C2—C3—C8	−1.3 (4)		

Fig. 1



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1,5-Dimethyl-4-{[1-(3-methyl-5-oxo-1-phenyl-4,5-dihydro-1*H*-pyrazol-4-ylidene)ethyl]amino}-2-phenyl-1*H*-pyrazol-3(2*H*)-one

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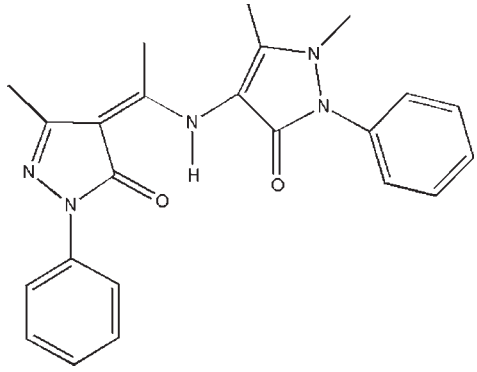
Key indicators: single-crystal X-ray study; T = 113 K; mean σ(C–C) = 0.002 Å; R factor = 0.040; wR factor = 0.105; data-to-parameter ratio = 12.7.

In the title compound, $C_{23}H_{23}N_5O_2$, an intramolecular N—H···O hydrogen bond generates an S(6) ring, and the dihedral angle between the pyrazole rings is 48.42 (8)°. The dihedral angles between the pyrazole rings and their attached phenyl rings are 10.06 (8) and 47.53 (8)°.

Related literature

For related structures and background references, see: Zhang *et al.* (2010); Zhu *et al.* (2010).



Experimental

Crystal data

$C_{23}H_{23}N_5O_2$
M_r = 401.46
Monoclinic, $C2/c$
a = 20.486 (4) Å
b = 10.209 (2) Å
c = 19.753 (4) Å
β = 102.76 (3)°
V = 4029.3 (14) Å^3
Z = 8
Mo $K\alpha$ radiation
μ = 0.09 mm^{-1}
T = 113 K
0.20 × 0.18 × 0.12 mm

Data collection

Rigaku Saturn CCD diffractometer
Absorption correction: multi-scan (*CrystalClear*; Rigaku, 2005)
T_{min} = 0.983, T_{max} = 0.990
13299 measured reflections
3553 independent reflections
2858 reflections with $I > 2\sigma(I)$
R_{int} = 0.038

Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.040
$wR(F^2)$ = 0.105
S = 1.00
3553 reflections
280 parameters
1 restraint
H atoms treated by a mixture of independent and constrained refinement
$\Delta\rho_{max}$ = 0.24 e Å^{-3}
$\Delta\rho_{min}$ = −0.20 e Å^{-3}

Table 1
Hydrogen-bond geometry (Å, °).

D—H···A	D—H	H···A	D···A	D—H···A
N3—H3A···O1	0.90 (1)	1.85 (1)	2.6459 (15)	146 (2)

Data collection: *CrystalClear* (Rigaku, 2005); cell refinement: *CrystalClear*; data reduction: *CrystalClear*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *SHELXTL* (Sheldrick, 2008); software used to prepare material for publication: *SHELXTL*.

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Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: HB5465).

References

Rigaku (2005). *CrystalClear*. Rigaku Corporation, Tokyo, Japan.
Sheldrick, G. M. (2008). *Acta Cryst.* A**64**, 112–122.
Zhang, X., Huang, M., Du, C. & Han, J. (2010). *Acta Cryst.* E**66**, o273.
Zhu, H., Shi, J., Wei, Z., Dai, R. & Zhang, X. (2010). *Acta Cryst.* E**66**, o1352.

supplementary materials

Acta Cryst. (2010). E**66**, o1583 [**doi:10.1107/S1600536810020532**]

1,5-Dimethyl-4-{[1-(3-methyl-5-oxo-1-phenyl-4,5-dihydro-1*H*-pyrazol-4-ylidene)ethyl]amino}-2-phenyl-1*H*-pyrazol-3(2*H*)-one

H. Zhu, J. Shi, Z. Wei, Y. Bai and L. Bu

Comment

As part of our onging studies of pyrazole derivatives (Zhu *et al.*, 2010), we now report the structure of the title compound, (I).

In the molecule of the title compound, (Fig.1) there is one molecule in the asymmetric unit. Atom O1, C7, C8, C11 and atom N3 form a plane, the largest deviation being 0.0132 (15) Å for atom C11. The dihedral angle between this plane and the pyrazolone ring of PMAP is 0.46 (4)°, indicating that they are essentially coplanar, as seen in Ethyl 2–{[(1*Z*)–(3–methyl–5–oxo–1–phenyl–4,5–dihydro–1*H*–pyrazol–4–ylidene) (*p*–tolyl)methyl]amino}–3–phenylpropanoate (1.52 (4)°; Zhang *et al.*, 2010). The bond lengths within this part of the molecular lie between classical single–and double–bond lengths, indicating extensive conjugation. Atoms N5,N4, C14, C13,C17 and O2 are also nearly coplanar, the largest deviation being 0.0417 (15) Å for atom C14.The dihedral angle between this plane and the phenyl ring of antipyrine is 47.41 (5)°, A strong intramolecular hydrogen bond N3—H3···O1 is observed (Table 1 & Fig. 1), stabilizing to an enamine–keto form.

Experimental

A mixture of HPMAP (15*m* mol) and 4-antipyrine (15*m* mol) in ethanol (100 ml) was refluxed over a steam bath for about 4 h, then the solution was cooled down to room temperature. After one day, pale yellow blocks were obtained and dried in air. The product was recrystallized from ethanol which afforded pale yellow blocks of (I).

Refinement

The N-bound H atom was located in a difference map and freely refined. All C-bound H atoms were geometrically positioned and refined using a riding model, with C—H = 0.95 Å for the aryl, 0.98 Å for the methyl H atoms. U_{iso}(H)= 1.2 U_{eq}(C) for aryl, 1.5U_{eq}(C) for methyl H atoms.

Figures

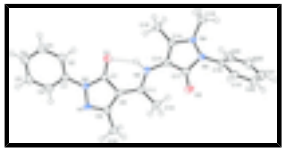


Fig. 1. The molecular structure of (I) with displacement ellipsoids drawn at the 30% probability level. H atoms are presented as spheres of arbitrary radius.

1,5-Dimethyl-4-{[1-(3-methyl-5-oxo-1-phenyl-4,5-dihydro-1*H*-pyrazol-4- ylidene)ethyl]amino}-2-phenyl-1*H*-pyrazol-3(2*H*)-one

Crystal data

$C_{23}H_{23}N_5O_2$	$F(000) = 1696$
$M_r = 401.46$	$D_x = 1.324$ Mg m^{-3}
Monoclinic, $C2/c$	Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å
Hall symbol: -C 2yc	Cell parameters from 5835 reflections
$a = 20.486$ (4) Å	$\theta = 2.0$–$27.9°$
$b = 10.209$ (2) Å	$\mu = 0.09$ mm^{-1}
$c = 19.753$ (4) Å	$T = 113$ K
$\beta = 102.76$ (3)°	Block, pale yellow
$V = 4029.3$ (14) Å^3	0.20 × 0.18 × 0.12 mm
$Z = 8$	

Data collection

Rigaku Saturn CCD diffractometer	3553 independent reflections
Radiation source: rotating anode	2858 reflections with $I > 2\sigma(I)$
confocal	$R_{int} = 0.038$
Detector resolution: 7.31 pixels mm^{-1}	$\theta_{max} = 25.0°$, $\theta_{min} = 2.0°$
ω and φ scans	$h = -24\rightarrow21$
Absorption correction: multi-scan (*CrystalClear*; Rigaku, 2005)	$k = -11\rightarrow12$
$T_{min} = 0.983$, $T_{max} = 0.990$	$l = -23\rightarrow20$
13299 measured reflections	

Refinement

Refinement on F^2	Secondary atom site location: difference Fourier map
Least-squares matrix: full	Hydrogen site location: inferred from neighbouring sites
$R[F^2 > 2\sigma(F^2)] = 0.040$	H atoms treated by a mixture of independent and constrained refinement
$wR(F^2) = 0.105$	$w = 1/[\sigma^2(F_o^2) + (0.0698P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
$S = 1.00$	$(\Delta/\sigma)_{max} = 0.001$
3553 reflections	$\Delta\rho_{max} = 0.24$ e Å^{-3}
280 parameters	$\Delta\rho_{min} = -0.20$ e Å^{-3}
1 restraint	Extinction correction: *SHELXL97* (Sheldrick, 2008), $Fc^*=kFc[1+0.001xFc^2\lambda^3/\sin(2\theta)]^{-1/4}$
Primary atom site location: structure-invariant direct methods	Extinction coefficient: 0.0113 (7)

Special details

Geometry. All e.s.d.'s (except the e.s.d. in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell e.s.d.'s are taken into account individually in the estimation of e.s.d.'s in distances, angles and torsion angles; correlations between e.s.d.'s in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell e.s.d.'s is used for estimating e.s.d.'s involving l.s. planes.

Refinement. Refinement of F^2 against ALL reflections. The weighted *R*-factor *wR* and goodness of fit *S* are based on F^2, conventional *R*-factors *R* are based on *F*, with *F* set to zero for negative F^2. The threshold expression of $F^2 > \sigma(F^2)$ is used only for calculating *R*-factors(gt) *etc*. and is not relevant to the choice of reflections for refinement. *R*-factors based on F^2 are statistically about twice as large as those based on *F*, and *R*- factors based on ALL data will be even larger.

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å^2)

	x	*y*	*z*	U_{iso}*/U_{eq}
O1	0.36779 (5)	0.46740 (9)	−0.06459 (5)	0.0331 (3)
O2	0.30384 (5)	0.76857 (9)	0.14645 (5)	0.0320 (3)
N1	0.48756 (6)	0.27136 (11)	0.04420 (6)	0.0290 (3)
N2	0.44223 (6)	0.29879 (11)	−0.01884 (6)	0.0258 (3)
N3	0.36650 (6)	0.64889 (11)	0.03072 (6)	0.0275 (3)
N4	0.31259 (6)	0.98296 (10)	0.01180 (6)	0.0265 (3)
N5	0.29411 (6)	0.95272 (11)	0.07449 (6)	0.0267 (3)
C1	0.44049 (7)	0.21464 (12)	−0.07603 (7)	0.0250 (3)
C2	0.39265 (7)	0.23181 (13)	−0.13788 (7)	0.0302 (4)
H2	0.3599	0.2988	−0.1414	0.036*
C3	0.39318 (8)	0.15100 (13)	−0.19403 (8)	0.0340 (4)
H3	0.3608	0.1633	−0.2361	0.041*
C4	0.44038 (8)	0.05234 (14)	−0.18963 (8)	0.0334 (4)
H4	0.4408	−0.0021	−0.2285	0.040*
C5	0.48688 (8)	0.03395 (13)	−0.12788 (8)	0.0325 (4)
H5	0.5188	−0.0346	−0.1243	0.039*
C6	0.48738 (7)	0.11448 (13)	−0.07107 (8)	0.0284 (3)
H6	0.5196	0.1012	−0.0290	0.034*
C7	0.40969 (7)	0.41613 (13)	−0.01570 (7)	0.0252 (3)
C8	0.43465 (7)	0.46416 (12)	0.05373 (7)	0.0246 (3)
C9	0.48298 (7)	0.36845 (13)	0.08621 (7)	0.0265 (3)
C10	0.52713 (8)	0.36606 (15)	0.15746 (8)	0.0383 (4)
H10A	0.5499	0.2812	0.1655	0.057*
H10B	0.4999	0.3793	0.1919	0.057*
H10C	0.5605	0.4361	0.1617	0.057*
C11	0.41305 (7)	0.58307 (13)	0.07650 (7)	0.0242 (3)
C12	0.43823 (8)	0.63774 (13)	0.14760 (7)	0.0296 (4)
H12A	0.4385	0.7336	0.1453	0.044*
H12B	0.4838	0.6061	0.1663	0.044*
H12C	0.4089	0.6094	0.1779	0.044*
C13	0.34091 (7)	0.77511 (12)	0.03765 (7)	0.0236 (3)
C14	0.33636 (7)	0.87041 (12)	−0.01143 (7)	0.0238 (3)
C15	0.35030 (8)	0.86237 (14)	−0.08178 (7)	0.0302 (4)

H15A	0.3841	0.7946	−0.0824	0.045*
H15B	0.3670	0.9471	−0.0940	0.045*
H15C	0.3090	0.8401	−0.1155	0.045*
C16	0.26801 (8)	1.07262 (14)	−0.03498 (8)	0.0340 (4)
H16A	0.2931	1.1167	−0.0653	0.051*
H16B	0.2502	1.1381	−0.0076	0.051*
H16C	0.2309	1.0229	−0.0634	0.051*
C17	0.31227 (7)	0.82187 (13)	0.09295 (7)	0.0252 (3)
C18	0.29907 (7)	1.05520 (13)	0.12492 (7)	0.0268 (3)
C19	0.26278 (7)	1.04378 (15)	0.17587 (7)	0.0325 (4)
H19	0.2345	0.9703	0.1765	0.039*
C20	0.26814 (8)	1.14062 (16)	0.22600 (8)	0.0412 (4)
H20	0.2439	1.1326	0.2616	0.049*
C21	0.30837 (9)	1.24844 (17)	0.22456 (9)	0.0454 (5)
H21	0.3116	1.3147	0.2589	0.054*
C22	0.34389 (9)	1.25982 (15)	0.17310 (9)	0.0429 (4)
H22	0.3712	1.3345	0.1718	0.052*
C23	0.33989 (8)	1.16264 (13)	0.12312 (8)	0.0344 (4)
H23	0.3649	1.1698	0.0881	0.041*
H3A	0.3562 (8)	0.6116 (14)	−0.0115 (6)	0.045 (5)*

Atomic displacement parameters (Å^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
O1	0.0351 (6)	0.0329 (5)	0.0257 (6)	0.0095 (5)	−0.0053 (5)	−0.0022 (4)
O2	0.0367 (6)	0.0363 (6)	0.0236 (6)	−0.0021 (5)	0.0081 (5)	0.0049 (5)
N1	0.0286 (7)	0.0338 (7)	0.0217 (7)	0.0052 (5)	−0.0003 (5)	0.0042 (5)
N2	0.0265 (7)	0.0284 (6)	0.0198 (6)	0.0039 (5)	−0.0006 (5)	0.0006 (5)
N3	0.0322 (7)	0.0267 (6)	0.0216 (6)	0.0026 (5)	0.0016 (6)	−0.0033 (5)
N4	0.0322 (7)	0.0294 (6)	0.0186 (6)	0.0050 (5)	0.0073 (5)	0.0030 (5)
N5	0.0322 (7)	0.0296 (6)	0.0198 (6)	0.0045 (5)	0.0092 (5)	0.0016 (5)
C1	0.0270 (8)	0.0253 (7)	0.0230 (8)	−0.0017 (6)	0.0063 (6)	0.0005 (6)
C2	0.0311 (9)	0.0308 (7)	0.0264 (8)	0.0043 (6)	0.0011 (7)	0.0012 (6)
C3	0.0401 (9)	0.0357 (8)	0.0236 (8)	0.0003 (7)	0.0012 (7)	−0.0004 (6)
C4	0.0404 (10)	0.0324 (8)	0.0296 (9)	−0.0027 (7)	0.0126 (7)	−0.0045 (7)
C5	0.0318 (9)	0.0279 (7)	0.0398 (9)	0.0030 (6)	0.0123 (7)	−0.0008 (7)
C6	0.0271 (8)	0.0280 (7)	0.0291 (8)	0.0001 (6)	0.0038 (6)	0.0032 (6)
C7	0.0234 (8)	0.0276 (7)	0.0232 (8)	0.0020 (6)	0.0019 (6)	0.0021 (6)
C8	0.0240 (8)	0.0281 (7)	0.0207 (8)	−0.0008 (6)	0.0027 (6)	0.0025 (6)
C9	0.0261 (8)	0.0310 (7)	0.0223 (7)	0.0017 (6)	0.0049 (6)	0.0035 (6)
C10	0.0404 (10)	0.0485 (9)	0.0226 (8)	0.0144 (8)	−0.0001 (7)	0.0007 (7)
C11	0.0236 (8)	0.0271 (7)	0.0213 (7)	−0.0031 (6)	0.0035 (6)	0.0035 (6)
C12	0.0313 (8)	0.0320 (8)	0.0233 (8)	0.0014 (6)	0.0015 (6)	−0.0008 (6)
C13	0.0239 (7)	0.0248 (7)	0.0209 (7)	−0.0005 (6)	0.0023 (6)	−0.0013 (6)
C14	0.0207 (7)	0.0298 (7)	0.0200 (7)	0.0001 (6)	0.0025 (6)	−0.0027 (6)
C15	0.0316 (9)	0.0378 (8)	0.0213 (8)	0.0026 (7)	0.0061 (6)	0.0007 (6)
C16	0.0387 (9)	0.0323 (8)	0.0308 (9)	0.0100 (7)	0.0073 (7)	0.0076 (7)
C17	0.0237 (8)	0.0294 (7)	0.0207 (7)	−0.0022 (6)	0.0009 (6)	0.0006 (6)

C18	0.0266 (8)	0.0315 (7)	0.0205 (7)	0.0087 (6)	0.0015 (6)	−0.0018 (6)
C19	0.0276 (8)	0.0443 (9)	0.0244 (8)	0.0095 (7)	0.0030 (6)	−0.0002 (7)
C20	0.0355 (10)	0.0633 (11)	0.0232 (8)	0.0165 (8)	0.0029 (7)	−0.0056 (8)
C21	0.0475 (11)	0.0484 (10)	0.0339 (10)	0.0148 (8)	−0.0048 (8)	−0.0161 (8)
C22	0.0455 (11)	0.0378 (9)	0.0407 (10)	0.0037 (8)	−0.0009 (8)	−0.0095 (8)
C23	0.0340 (9)	0.0354 (8)	0.0328 (9)	0.0044 (7)	0.0052 (7)	−0.0015 (7)

Geometric parameters (Å, °)

O1—C7	1.2559 (17)	C9—C10	1.496 (2)
O2—C17	1.2341 (16)	C10—H10A	0.9800
N1—C9	1.3093 (18)	C10—H10B	0.9800
N1—N2	1.4073 (16)	C10—H10C	0.9800
N2—C7	1.3792 (17)	C11—C12	1.4933 (19)
N2—C1	1.4133 (17)	C12—H12A	0.9800
N3—C11	1.3408 (18)	C12—H12B	0.9800
N3—C13	1.4091 (17)	C12—H12C	0.9800
N3—H3A	0.899 (9)	C13—C14	1.3622 (19)
N4—C14	1.3664 (16)	C13—C17	1.4314 (19)
N4—N5	1.4068 (16)	C14—C15	1.4814 (19)
N4—C16	1.4673 (18)	C15—H15A	0.9800
N5—C17	1.4128 (17)	C15—H15B	0.9800
N5—C18	1.4327 (17)	C15—H15C	0.9800
C1—C6	1.391 (2)	C16—H16A	0.9800
C1—C2	1.398 (2)	C16—H16B	0.9800
C2—C3	1.384 (2)	C16—H16C	0.9800
C2—H2	0.9500	C18—C19	1.382 (2)
C3—C4	1.386 (2)	C18—C23	1.385 (2)
C3—H3	0.9500	C19—C20	1.386 (2)
C4—C5	1.385 (2)	C19—H19	0.9500
C4—H4	0.9500	C20—C21	1.379 (3)
C5—C6	1.3893 (19)	C20—H20	0.9500
C5—H5	0.9500	C21—C22	1.379 (3)
C6—H6	0.9500	C21—H21	0.9500
C7—C8	1.4396 (19)	C22—C23	1.389 (2)
C8—C11	1.4000 (19)	C22—H22	0.9500
C8—C9	1.4373 (19)	C23—H23	0.9500
C9—N1—N2	106.53 (11)	N3—C11—C12	119.56 (12)
C7—N2—N1	111.35 (10)	C8—C11—C12	123.93 (12)
C7—N2—C1	129.57 (11)	C11—C12—H12A	109.5
N1—N2—C1	118.78 (11)	C11—C12—H12B	109.5
C11—N3—C13	128.11 (12)	H12A—C12—H12B	109.5
C11—N3—H3A	113.6 (11)	C11—C12—H12C	109.5
C13—N3—H3A	117.5 (11)	H12A—C12—H12C	109.5
C14—N4—N5	107.23 (10)	H12B—C12—H12C	109.5
C14—N4—C16	122.11 (12)	C14—C13—N3	123.54 (13)
N5—N4—C16	116.12 (11)	C14—C13—C17	109.25 (12)
N4—N5—C17	109.15 (10)	N3—C13—C17	127.10 (12)
N4—N5—C18	117.40 (11)	C13—C14—N4	109.58 (12)

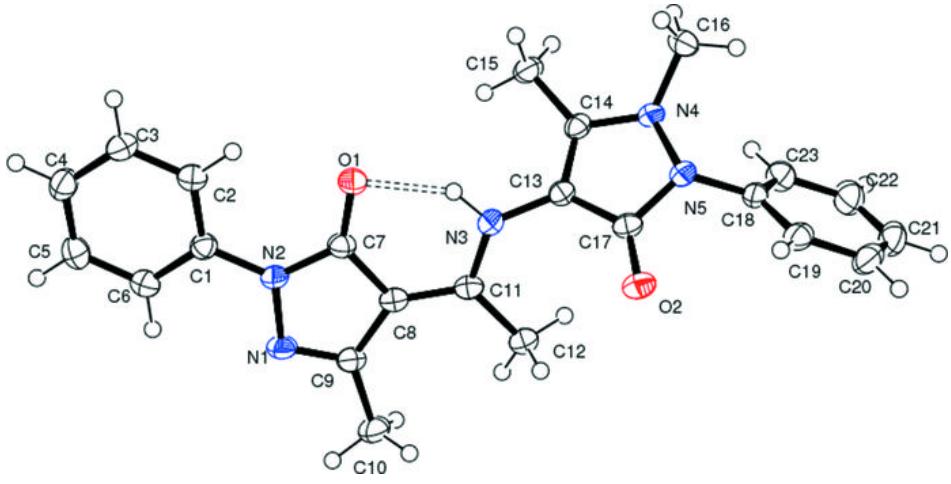
C17—N5—C18	122.47 (11)	C13—C14—C15	129.12 (12)
C6—C1—C2	119.56 (13)	N4—C14—C15	121.23 (12)
C6—C1—N2	119.69 (13)	C14—C15—H15A	109.5
C2—C1—N2	120.74 (12)	C14—C15—H15B	109.5
C3—C2—C1	119.82 (13)	H15A—C15—H15B	109.5
C3—C2—H2	120.1	C14—C15—H15C	109.5
C1—C2—H2	120.1	H15A—C15—H15C	109.5
C2—C3—C4	120.79 (14)	H15B—C15—H15C	109.5
C2—C3—H3	119.6	N4—C16—H16A	109.5
C4—C3—H3	119.6	N4—C16—H16B	109.5
C5—C4—C3	119.24 (14)	H16A—C16—H16B	109.5
C5—C4—H4	120.4	N4—C16—H16C	109.5
C3—C4—H4	120.4	H16A—C16—H16C	109.5
C4—C5—C6	120.81 (13)	H16B—C16—H16C	109.5
C4—C5—H5	119.6	O2—C17—N5	124.01 (13)
C6—C5—H5	119.6	O2—C17—C13	131.67 (13)
C5—C6—C1	119.75 (14)	N5—C17—C13	104.32 (11)
C5—C6—H6	120.1	C19—C18—C23	120.71 (13)
C1—C6—H6	120.1	C19—C18—N5	118.54 (13)
O1—C7—N2	125.62 (12)	C23—C18—N5	120.74 (13)
O1—C7—C8	128.99 (13)	C18—C19—C20	119.31 (15)
N2—C7—C8	105.38 (11)	C18—C19—H19	120.3
C11—C8—C9	132.97 (13)	C20—C19—H19	120.3
C11—C8—C7	122.03 (12)	C21—C20—C19	120.52 (16)
C9—C8—C7	104.97 (12)	C21—C20—H20	119.7
N1—C9—C8	111.75 (12)	C19—C20—H20	119.7
N1—C9—C10	118.09 (12)	C20—C21—C22	119.82 (15)
C8—C9—C10	130.15 (13)	C20—C21—H21	120.1
C9—C10—H10A	109.5	C22—C21—H21	120.1
C9—C10—H10B	109.5	C21—C22—C23	120.38 (16)
H10A—C10—H10B	109.5	C21—C22—H22	119.8
C9—C10—H10C	109.5	C23—C22—H22	119.8
H10A—C10—H10C	109.5	C18—C23—C22	119.25 (15)
H10B—C10—H10C	109.5	C18—C23—H23	120.4
N3—C11—C8	116.50 (12)	C22—C23—H23	120.4
C9—N1—N2—C7	0.73 (15)	C9—C8—C11—N3	179.24 (14)
C9—N1—N2—C1	175.01 (12)	C7—C8—C11—N3	1.6 (2)
C14—N4—N5—C17	5.07 (15)	C9—C8—C11—C12	−1.4 (2)
C16—N4—N5—C17	145.59 (12)	C7—C8—C11—C12	−179.06 (13)
C14—N4—N5—C18	150.16 (12)	C11—N3—C13—C14	130.25 (16)
C16—N4—N5—C18	−69.32 (15)	C11—N3—C13—C17	−53.9 (2)
C7—N2—C1—C6	167.10 (13)	N3—C13—C14—N4	−177.17 (12)
N1—N2—C1—C6	−5.98 (19)	C17—C13—C14—N4	6.37 (16)
C7—N2—C1—C2	−12.1 (2)	N3—C13—C14—C15	5.8 (2)
N1—N2—C1—C2	174.78 (12)	C17—C13—C14—C15	−170.70 (13)
C6—C1—C2—C3	−1.4 (2)	N5—N4—C14—C13	−7.03 (15)
N2—C1—C2—C3	177.88 (13)	C16—N4—C14—C13	−144.66 (13)
C1—C2—C3—C4	0.4 (2)	N5—N4—C14—C15	170.30 (12)
C2—C3—C4—C5	0.8 (2)	C16—N4—C14—C15	32.7 (2)

C3—C4—C5—C6	−1.1 (2)	N4—N5—C17—O2	178.14 (12)
C4—C5—C6—C1	0.2 (2)	C18—N5—C17—O2	35.2 (2)
C2—C1—C6—C5	1.0 (2)	N4—N5—C17—C13	−1.27 (14)
N2—C1—C6—C5	−178.23 (12)	C18—N5—C17—C13	−144.24 (13)
N1—N2—C7—O1	178.08 (13)	C14—C13—C17—O2	177.62 (14)
C1—N2—C7—O1	4.6 (2)	N3—C13—C17—O2	1.3 (2)
N1—N2—C7—C8	−1.39 (15)	C14—C13—C17—N5	−3.03 (15)
C1—N2—C7—C8	−174.88 (13)	N3—C13—C17—N5	−179.33 (13)
O1—C7—C8—C11	0.3 (2)	N4—N5—C18—C19	159.88 (12)
N2—C7—C8—C11	179.69 (12)	C17—N5—C18—C19	−59.97 (18)
O1—C7—C8—C9	−177.98 (14)	N4—N5—C18—C23	−20.81 (19)
N2—C7—C8—C9	1.45 (15)	C17—N5—C18—C23	119.34 (15)
N2—N1—C9—C8	0.27 (16)	C23—C18—C19—C20	−0.7 (2)
N2—N1—C9—C10	−178.89 (13)	N5—C18—C19—C20	178.58 (13)
C11—C8—C9—N1	−179.06 (14)	C18—C19—C20—C21	1.1 (2)
C7—C8—C9—N1	−1.10 (16)	C19—C20—C21—C22	−0.4 (2)
C11—C8—C9—C10	0.0 (3)	C20—C21—C22—C23	−0.7 (2)
C7—C8—C9—C10	177.93 (15)	C19—C18—C23—C22	−0.3 (2)
C13—N3—C11—C8	−173.48 (13)	N5—C18—C23—C22	−179.56 (13)
C13—N3—C11—C12	7.1 (2)	C21—C22—C23—C18	1.0 (2)

Hydrogen-bond geometry (Å, °)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
N3—H3A···O1	0.90 (1)	1.85 (1)	2.6459 (15)	146.(2)

Fig. 1


C16
C15
C14
N4
C3
C4
O1
C2
C13
C23
C22
N5
C18
C5
N2
C7
N3
C17
C21
C1
C19
C6
C11
C20
O2
C8
C12
N1
C9
C10

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Redetermination and absolute configuration of 7α-hydroxyroyleanone

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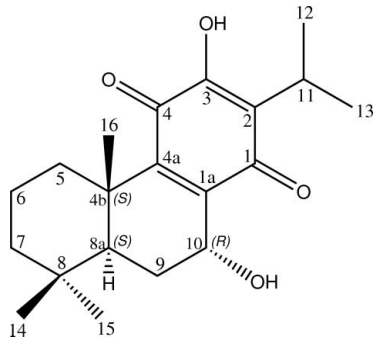
Key indicators: single-crystal X-ray study; T = 100 K; mean σ(C–C) = 0.002 Å; R factor = 0.027; wR factor = 0.074; data-to-parameter ratio = 11.2.

The title compound [systematic name: 7α,12-dihydroxy-8,12-abietadiene,11,14-dione or (4b*S*,8a*S*,10*R*)-3,10-dihydroxy-2-isopropyl-4b,8,8-trimethyl-1,4,4b,5,6,7,8,8a,9,10-decahydrophenanthrene-1,4-dione], $C_{20}H_{28}O_4$, is an abietane diterpenoid, which was isolated from the roots of *Premna obtusifolia* (Verbenaceae). Its crystal structure has been reported previously [Chen *et al.* (2000). *Jiegou Huaxue*, **19**, 122–125], but the absolute configuration could not be determined using data collected with Mo radiation. This redetermination using Cu radiation shows the the absolute configurations of the stereogenic centres at positions 4b, 8a and 10 to be *S*, *S* and *R*, respectively. Two intramolecular O—H···O hydrogen bonds [one generating an *S*(5) ring and one generating an *S*(6) ring] and a number of short C—H···O contacts occur. In the crystal, molecules are linked into infinite chains propagating in [100] by O—H···O hydrogen bonds and weak C—H···O interactions.

Related literature

For background to Verbenaceae, diterpenes and their biological activity, see: Batista *et al.* (1994); Bunluepuech & Tewtrakul (2009); Jonathan *et al.* (1989); Kabouche *et al.* (2007); Kupchan *et al.* (1968, 1969); Nagy *et al.* (1999); Ulubelen *et al.* (2001). For the previous structure determination, see: Chen *et al.* (2000). For hydrogen-bond motifs, see: Bernstein *et al.* (1995) and for ring conformations, see: Cremer & Pople (1975). For bond-length data, see: Allen *et al.* (1987). For the stability of the temperature controller used in the data collection, see Cosier & Glazer (1986).



Experimental

Crystal data

$C_{20}H_{28}O_4$
M_r = 332.42
Orthorhombic, $P2_12_12_1$
a = 7.6729 (1) Å
b = 9.3972 (1) Å
c = 24.1946 (3) Å
V = 1744.52 (4) Å^3
Z = 4
Cu $K\alpha$ radiation
μ = 0.70 mm^{-1}
T = 100 K
0.28 × 0.28 × 0.20 mm

Data collection

Bruker APEXII DUO CCD diffractometer
Absorption correction: multi-scan (*SADABS*; Bruker, 2009)
T_{min} = 0.829, T_{max} = 0.871
6475 measured reflections
2578 independent reflections
2564 reflections with $I > 2\sigma(I)$
R_{int} = 0.015

Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.027
$wR(F^2)$ = 0.074
S = 1.04
2578 reflections
230 parameters
H atoms treated by a mixture of independent and constrained refinement
$\Delta\rho_{max}$ = 0.22 e Å^{-3}
$\Delta\rho_{min}$ = −0.13 e Å^{-3}
Absolute structure: Flack (1983), 970 Friedel pairs
Flack parameter: 0.13 (16)

Table 1
Hydrogen-bond geometry (Å, °).

D—H···A	D—H	H···A	D···A	D—H···A
O1—H1*O1*···O2^{i}	0.88 (2)	2.24 (3)	2.9502 (15)	137 (2)
O1—H1*O1*···O4	0.88 (2)	2.52 (3)	2.9399 (14)	109.8 (19)
O3—H1*O3*···O2	0.83 (2)	2.075 (19)	2.5892 (14)	119.8 (19)
O3—H1*O3*···O4^{ii}	0.83 (2)	2.42 (2)	3.1635 (14)	148.8 (18)
C1—H1*A*···O2	0.97	2.33	2.9493 (18)	121
C5—H5*A*···O1	0.98	2.52	2.9933 (17)	110
C7—H7*A*···O2^{i}	0.98	2.42	3.0998 (17)	126
C15—H15*A*···O4	0.98	2.38	2.8549 (17)	109
C16—H16*C*···O3	0.96	2.58	3.1654 (19)	119
C17—H17*B*···O3	0.96	2.53	3.1204 (18)	119
C20—H20*A*···O2	0.96	2.51	3.1451 (18)	124

Symmetry codes: (i) $x-1, y, z$; (ii) $x+1, y, z$.

Data collection: *APEX2* (Bruker, 2009); cell refinement: *SAINT* (Bruker, 2009); data reduction: *SAINT*; program(s) used to solve structure: *SHELXTL* (Sheldrick, 2008); program(s) used to refine structure: *SHELXTL*; molecular graphics: *SHELXTL*; software used to prepare material for publication: *SHELXTL* and *PLATON* (Spek, 2009).

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§ Thomson Reuters ResearcherID: A-3561-2009.

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Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: HB5468).

References

Allen, F. H., Kennard, O., Watson, D. G., Brammer, L., Orpen, A. G. & Taylor, R. (1987). *J. Chem. Soc. Perkin Trans. 2*, pp. S1–S19.
Batista, O., Duarte, A., Nascimento, J. M. & Simoes, F. (1994). *J. Nat. Prod.* **57**, 858–861.
Bernstein, J., Davis, R. E., Shimoni, L. & Chang, N.-L. (1995). *Angew. Chem. Int. Ed. Engl.* **34**, 1555–1573.
Bruker (2009). *APEX2*, *SAINT* and *SADABS*. Bruker AXS Inc., Madison, Wisconsin, USA.
Bunluepuech, K. & Tewtrakul, S. (2009). *Songklanakarin J. Sci. Technol.* **31**, 289–292
Chen, X., Liao, R.-A., Weng, L.-H., Xie, Q.-L. & Deng, F.-J. (2000). *Jiegou Huaxue*, **19**, 122–125.
Cosier, J. & Glazer, A. M. (1986). *J. Appl. Cryst.* **19**, 105–107.
Cremer, D. & Pople, J. A. (1975). *J. Am. Chem. Soc.* **97**, 1354–1358.
Flack, H. D. (1983). *Acta Cryst.* A**39**, 876–881.
Jonathan, L. T., Che, C. -T., Pezzuto, J. M., Fong, H. H. S. & Farnsworth, N. R. (1989). *J. Nat. Prod.* **59**, 734–737.
Kabouche, A., Kabouche, Z., Öztürk, M., Kolak, U. & Topçu, G. (2007). *Food Chem.* **102**, 1281–1287.
Kupchan, S. M., Karim, A. & Marcks, C. (1968). *J. Am. Chem. Soc.* **90**, 5923–5924.
Kupchan, S. M., Karim, A. & Marcks, C. (1969). *J. Org. Chem.* **34**, 3912–3918.
Nagy, G., Günther, G., Máthé, I., Blunden, G., Yang, M.-H. & Crabb, T. A. (1999). *Phytochemistry*, **51**, 809–812.
Sheldrick, G. M. (2008). *Acta Cryst.* A**64**, 112–122.
Spek, A. L. (2009). *Acta Cryst.* D**65**, 148–155.
Ulubelen, A., Oksuz, S., Topgu, G., Goren, A. C. & Voelter, W. (2001). *J. Nat. Prod.* **64**, 549–551.

supplementary materials

Acta Cryst. (2010). E**66**, o1566-o1567 [**doi:10.1107/S1600536810020544**]

Redetermination and absolute configuration of 7α-hydroxyroyleanone

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Comment

The extracts of Verbenaceae plants were found to possess anti-HIV-1 integrase activity (Bunluepuech & Tewtrakul, 2009). *Premna obtusifolia* (Verbenaceae), a small tree found in the mangrove forests, is one of the Verbenaceae plants. As part of our study of chemical constituents and bioactive compounds from the roots of *Premna obtusifolia* (Verbenaceae) which were collected from Satun province in the southern part of Thailand, the title abietane diterpenoid (I) was isolated. It was known as horminone (Batista *et al.*, 1994) or 7α-hydroxyroyleanone (Nagy *et al.*, 1999) and the previous reports show that (I) exhibits significant biological activities as tumor inhibitors (Kupchan *et al.*, 1968, 1969; Jonathan *et al.*, 1989), antioxidant (Kabouche *et al.*, 2007) and antibacterial agents (Ulubelen *et al.*, 2001). The crystal structure of (I) has been reported (Chen *et al.*, 2000) but the absolute configuration could not be determined due to no large anomalous dispersion using a data set collected with Mo radiation. Our data of (I) was collected using Cu radiation with Bruker Apex-Duo CCD diffractometer and the absolute configuration at atoms C10, C5 and C7 (or positions 4b, 8a and 10 of abietane diterpenoid) were determined as *S*,*S*,*R* making use of the large anomalous scattering of Cu Kα *X*-radiation with the Flack parameter being refined to 0.13 (16). We report herein the crystal structure of (I) determined from the Cu data.

The molecule of (I) has three fused six membered rings (Fig. 1). The two cyclohexanes rings are *trans* fused. One cyclohexane ring (C1–C5/C10) is in a standard chair conformation whereas the other (C5–C10) is in half chair conformation, with the puckering parameter Q = 0.5419 (15) Å, θ = 51.68 (16)° and φ = 21.6 (2)° (Cremer & Pople, 1975). The benzoquinone ring (C8–C9/C11–C14/O2/O4) is slightly twisted with the maximum deviations of 0.060 (1) and -0.052 (1) Å for atoms C9 and C11, respectively. The O2, O3 and O4 atoms lie close to the mean plane of the C8–C9/C11–C14 ring with the *r.m.s.* of 0.0543 (1). The bond angles around C11 and C14 are indicative of sp^2 hybridization for these atoms. The orientation of the propanyl group is described by the torsion angles C14–C13–C15–C17 = -118.43 (14)° and C14–C13–C15–C16 = 116.53 (14)°. Intramolecular O1—H1O1···O4 and O3—H1O3···O2 hydrogen bonds (Table 1) generate S(6) and S(5) ring motifs, respectively (Fig. 1) (Bernstein *et al.*, 1995). The bond distances in (I) are within normal ranges (Allen *et al.*, 1987).

The crystal packing of (I) is stabilized by intermolecular O—H···O hydrogen bonds and weak C—H···O interactions (Fig. 2 and Table 1). The molecules are linked into infinite one dimensional chains along the [1 0 0] (Fig. 2) through O1—H1O1···O2 and O3—H1O3···O4 hydrogen bonds and weak C7—H7A···O2 interactions (Table 1).

Experimental

The air-dried roots of *premna obtusifolia* (4.5 kg) were extracted with CH_2Cl_2 (2 × 20 *L*) at room temperature. The combined extracts were concentrated under reduced pressure to afford a dark yellow extract (40.5 g) which was subjected to quick column chromatography (QCC) over silica gel using solvents of increasing polarity from n-hexane to EtOAc to afford 12 fractions (F1—F12). Fraction F4 was further purified by QCC using hexane-acetone (9:1), yielding the title compound (57.5 mg). Yellow blocks of (I) were recrystallized from n-hexane after several days.

Refinement

Hydroxy H atoms attached to O1 and O3 were located from the difference map and isotropically refined. The remaining H atoms were placed in calculated positions with (C—H) = 0.98 for CH, 0.97 for CH_2 and 0.96 Å for CH_3 atoms. The U_{iso} values were constrained to be $1.5U_{eq}$ of the carrier atom for methyl H atoms and $1.2U_{eq}$ for the remaining H atoms. A rotating group model was used for the methyl groups. The highest residual electron density peak is located at 0.78 Å from H7A and the deepest hole is located at 0.95 Å from C11. 970 Friedel pairs were used to determine the absolute configuration.

Figures

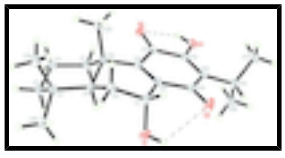


Fig. 1. The structure of (I), showing 50% probability displacement ellipsoids. Intramolecular O—H···O hydrogen bonds are shown as dashed lines.

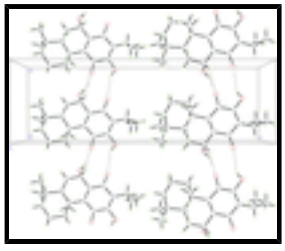


Fig. 2. The crystal packing of (I) viewed along the *b* axis, showing one dimensional chains along the [1 0 0]. Hydrogen bonds are shown as dashed lines.

(4b*S*,8a*S*,10*R*)-3,10-dihydroxy-2-isopropyl-4b,8,8-trimethyl- 1,4,4b,5,6,7,8,8a,9,10-decahydrophenanthrene-1,4-dione

Crystal data

$C_{20}H_{28}O_4$	$F(000) = 720$
$M_r = 332.42$	$D_x = 1.266$ Mg m^{-3}
Orthorhombic, $P2_12_12_1$	Cu $K\alpha$ radiation, $\lambda = 1.54178$ Å
Hall symbol: P 2ac 2ab	Cell parameters from 2578 reflections
$a = 7.6729$ (1) Å	$\theta = 5.1$–$62.5°$
$b = 9.3972$ (1) Å	$\mu = 0.70$ mm^{-1}
$c = 24.1946$ (3) Å	$T = 100$ K
$V = 1744.52$ (4) Å^3	Block, yellow
$Z = 4$	0.28 × 0.28 × 0.20 mm

Data collection

Bruker APEXII DUO CCD diffractometer	2578 independent reflections
Radiation source: sealed tube	2564 reflections with $I > 2\sigma(I)$
graphite	$R_{int} = 0.015$
φ and ω scans	$\theta_{max} = 62.5°$, $\theta_{min} = 5.1°$
Absorption correction: multi-scan	$h = -7 \rightarrow 8$

(*SADABS*; Bruker, 2009)

T_{min} = 0.829, T_{max} = 0.871

6475 measured reflections

k = −10→10

l = −27→27

Refinement

Refinement on F^2

Least-squares matrix: full

$R[F^2 > 2\sigma(F^2)]$ = 0.027

$wR(F^2)$ = 0.074

S = 1.04

2578 reflections

230 parameters

0 restraints

Primary atom site location: structure-invariant direct methods

Secondary atom site location: difference Fourier map

Hydrogen site location: inferred from neighbouring sites

H atoms treated by a mixture of independent and constrained refinement

$w = 1/[\sigma^2(F_o^2) + (0.0454P)^2 + 0.3997P]$ where $P = (F_o^2 + 2F_c^2)/3$

$(\Delta/\sigma)_{max} < 0.001$

$\Delta\rho_{max}$ = 0.22 e Å^{-3}

$\Delta\rho_{min}$ = −0.13 e Å^{-3}

Absolute structure: Flack (1983), 970 Friedel pairs

Flack parameter: 0.13 (16)

Special details

Experimental. The crystal was placed in the cold stream of an Oxford Cryosystems Cobra open-flow nitrogen cryostat (Cosier & Glazer, 1986) operating at 100.0 (1) K.

Geometry. All esds (except the esd in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell esds are taken into account individually in the estimation of esds in distances, angles and torsion angles; correlations between esds in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell esds is used for estimating esds involving l.s. planes.

Refinement. Refinement of F^2 against ALL reflections. The weighted R-factor wR and goodness of fit S are based on F^2, conventional R-factors R are based on F, with F set to zero for negative F^2. The threshold expression of $F^2 > 2$sigma(F^2) is used only for calculating R-factors(gt) etc. and is not relevant to the choice of reflections for refinement. R-factors based on F^2 are statistically about twice as large as those based on F, and R- factors based on ALL data will be even larger.

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å^2)

	x	*y*	*z*	U_{iso}*/U_{eq}
O1	0.39089 (14)	0.84016 (12)	0.26305 (4)	0.0253 (3)
H1O1	0.310 (3)	0.830 (3)	0.2374 (11)	0.077 (9)*
O2	1.09134 (13)	0.67838 (11)	0.21951 (4)	0.0216 (2)
O3	1.04729 (13)	0.73182 (11)	0.11546 (4)	0.0209 (2)
H1O3	1.132 (3)	0.720 (2)	0.1363 (8)	0.040 (6)*
O4	0.44447 (13)	0.73046 (14)	0.15053 (4)	0.0300 (3)
C1	0.98219 (19)	0.80709 (16)	0.32516 (6)	0.0198 (3)
H1A	1.0903	0.7775	0.3079	0.024*
H1B	0.9519	0.9001	0.3106	0.024*
C2	1.00975 (19)	0.81849 (16)	0.38772 (6)	0.0228 (3)
H2A	1.0508	0.7278	0.4018	0.027*

H2B	1.0988	0.8892	0.3952	0.027*
C3	0.8428 (2)	0.85964 (17)	0.41773 (6)	0.0233 (3)
H3A	0.8124	0.9564	0.4076	0.028*
H3B	0.8648	0.8584	0.4572	0.028*
C4	0.68635 (19)	0.76239 (16)	0.40536 (6)	0.0204 (3)
C5	0.66970 (18)	0.74674 (15)	0.34161 (5)	0.0173 (3)
H5A	0.6466	0.8435	0.3284	0.021*
C6	0.51347 (18)	0.66017 (16)	0.32182 (6)	0.0199 (3)
H6A	0.5401	0.5594	0.3239	0.024*
H6B	0.4137	0.6790	0.3453	0.024*
C7	0.47085 (18)	0.70050 (16)	0.26259 (6)	0.0200 (3)
H7A	0.3897	0.6310	0.2468	0.024*
C8	0.63225 (18)	0.70964 (15)	0.22719 (6)	0.0181 (3)
C9	0.79457 (18)	0.70681 (15)	0.24799 (5)	0.0158 (3)
C10	0.83719 (18)	0.70011 (15)	0.31011 (6)	0.0169 (3)
C11	0.93920 (17)	0.70252 (15)	0.20709 (6)	0.0171 (3)
C12	0.90331 (18)	0.72713 (15)	0.14720 (6)	0.0168 (3)
C13	0.74123 (19)	0.74250 (15)	0.12654 (6)	0.0182 (3)
C14	0.59663 (18)	0.72713 (15)	0.16633 (6)	0.0188 (3)
C15	0.70086 (18)	0.77406 (17)	0.06671 (6)	0.0211 (3)
H15A	0.5738	0.7793	0.0632	0.025*
C16	0.7741 (2)	0.91900 (17)	0.04969 (7)	0.0285 (4)
H16A	0.7297	0.9912	0.0740	0.043*
H16B	0.7397	0.9398	0.0124	0.043*
H16C	0.8990	0.9169	0.0520	0.043*
C17	0.7642 (2)	0.65721 (17)	0.02752 (6)	0.0260 (4)
H17A	0.7154	0.5675	0.0386	0.039*
H17B	0.8890	0.6519	0.0289	0.039*
H17C	0.7278	0.6789	−0.0095	0.039*
C18	0.5232 (2)	0.83806 (18)	0.42719 (6)	0.0266 (3)
H18A	0.5417	0.8660	0.4649	0.040*
H18B	0.4253	0.7746	0.4252	0.040*
H18C	0.5004	0.9209	0.4051	0.040*
C19	0.7033 (2)	0.62112 (17)	0.43667 (6)	0.0248 (3)
H19A	0.6847	0.6372	0.4754	0.037*
H19B	0.8178	0.5827	0.4310	0.037*
H19C	0.6179	0.5551	0.4231	0.037*
C20	0.8991 (2)	0.54667 (15)	0.32229 (6)	0.0202 (3)
H20A	0.9797	0.5171	0.2942	0.030*
H20B	0.8005	0.4838	0.3225	0.030*
H20C	0.9554	0.5439	0.3577	0.030*

Atomic displacement parameters (Å^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
O1	0.0192 (5)	0.0318 (6)	0.0248 (5)	0.0057 (5)	−0.0006 (5)	0.0037 (5)
O2	0.0130 (5)	0.0305 (6)	0.0214 (5)	0.0023 (4)	−0.0010 (4)	−0.0002 (5)
O3	0.0147 (5)	0.0290 (6)	0.0191 (5)	0.0004 (5)	0.0017 (4)	−0.0021 (5)

O4	0.0148 (5)	0.0531 (7)	0.0221 (5)	−0.0006 (5)	−0.0031 (4)	0.0068 (5)
C1	0.0162 (7)	0.0237 (7)	0.0194 (7)	−0.0028 (6)	0.0004 (6)	−0.0023 (6)
C2	0.0203 (7)	0.0257 (7)	0.0224 (7)	−0.0049 (7)	−0.0038 (6)	−0.0034 (6)
C3	0.0261 (8)	0.0248 (8)	0.0190 (7)	0.0001 (7)	−0.0014 (7)	−0.0037 (6)
C4	0.0194 (7)	0.0250 (8)	0.0168 (7)	0.0035 (6)	0.0000 (6)	0.0000 (6)
C5	0.0167 (7)	0.0185 (7)	0.0165 (6)	0.0012 (6)	−0.0003 (6)	0.0031 (6)
C6	0.0159 (7)	0.0256 (7)	0.0183 (7)	−0.0006 (6)	0.0021 (6)	0.0016 (6)
C7	0.0142 (6)	0.0268 (7)	0.0189 (7)	−0.0002 (7)	−0.0001 (6)	0.0019 (6)
C8	0.0168 (7)	0.0183 (7)	0.0192 (7)	−0.0001 (6)	−0.0008 (6)	0.0000 (6)
C9	0.0160 (7)	0.0140 (6)	0.0173 (7)	0.0003 (6)	0.0000 (6)	0.0010 (6)
C10	0.0138 (6)	0.0193 (7)	0.0177 (6)	0.0001 (6)	−0.0003 (6)	0.0003 (6)
C11	0.0160 (7)	0.0149 (7)	0.0205 (7)	−0.0008 (6)	−0.0005 (6)	−0.0026 (5)
C12	0.0163 (7)	0.0163 (6)	0.0178 (7)	−0.0003 (6)	0.0028 (6)	−0.0030 (6)
C13	0.0176 (7)	0.0184 (7)	0.0186 (7)	−0.0004 (6)	0.0007 (6)	−0.0023 (6)
C14	0.0159 (7)	0.0207 (7)	0.0198 (7)	0.0012 (6)	−0.0017 (6)	−0.0002 (6)
C15	0.0169 (7)	0.0291 (8)	0.0174 (7)	−0.0006 (7)	−0.0012 (6)	0.0005 (6)
C16	0.0341 (9)	0.0277 (8)	0.0237 (7)	0.0022 (8)	−0.0033 (7)	0.0057 (7)
C17	0.0295 (8)	0.0317 (8)	0.0169 (7)	−0.0059 (8)	0.0004 (7)	−0.0019 (6)
C18	0.0247 (8)	0.0348 (8)	0.0204 (7)	0.0048 (7)	0.0022 (6)	0.0003 (7)
C19	0.0257 (8)	0.0315 (8)	0.0171 (7)	−0.0025 (7)	−0.0007 (7)	0.0039 (6)
C20	0.0195 (7)	0.0211 (7)	0.0199 (7)	0.0019 (6)	−0.0028 (6)	−0.0007 (6)

Geometric parameters (Å, °)

O1—C7	1.4488 (18)	C8—C9	1.344 (2)
O1—H1O1	0.88 (3)	C8—C14	1.5066 (19)
O2—C11	1.2266 (17)	C9—C11	1.4874 (19)
O3—C12	1.3461 (17)	C9—C10	1.5394 (18)
O3—H1O3	0.83 (2)	C10—C20	1.546 (2)
O4—C14	1.2288 (18)	C11—C12	1.4931 (19)
C1—C2	1.5322 (19)	C12—C13	1.348 (2)
C1—C10	1.543 (2)	C13—C14	1.476 (2)
C1—H1A	0.9700	C13—C15	1.5098 (19)
C1—H1B	0.9700	C15—C17	1.530 (2)
C2—C3	1.522 (2)	C15—C16	1.530 (2)
C2—H2A	0.9700	C15—H15A	0.9800
C2—H2B	0.9700	C16—H16A	0.9600
C3—C4	1.538 (2)	C16—H16B	0.9600
C3—H3A	0.9700	C16—H16C	0.9600
C3—H3B	0.9700	C17—H17A	0.9600
C4—C18	1.534 (2)	C17—H17B	0.9600
C4—C19	1.534 (2)	C17—H17C	0.9600
C4—C5	1.5547 (18)	C18—H18A	0.9600
C5—C6	1.526 (2)	C18—H18B	0.9600
C5—C10	1.5570 (19)	C18—H18C	0.9600
C5—H5A	0.9800	C19—H19A	0.9600
C6—C7	1.5178 (19)	C19—H19B	0.9600
C6—H6A	0.9700	C19—H19C	0.9600
C6—H6B	0.9700	C20—H20A	0.9600

C7—C8	1.5082 (19)	C20—H20B	0.9600
C7—H7A	0.9800	C20—H20C	0.9600
C7—O1—H1O1	101.4 (19)	C1—C10—C20	109.94 (11)
C12—O3—H1O3	107.0 (14)	C9—C10—C5	106.92 (11)
C2—C1—C10	112.22 (12)	C1—C10—C5	107.24 (11)
C2—C1—H1A	109.2	C20—C10—C5	115.00 (12)
C10—C1—H1A	109.2	O2—C11—C9	123.52 (13)
C2—C1—H1B	109.2	O2—C11—C12	116.22 (13)
C10—C1—H1B	109.2	C9—C11—C12	120.26 (12)
H1A—C1—H1B	107.9	O3—C12—C13	122.83 (12)
C3—C2—C1	111.88 (12)	O3—C12—C11	114.03 (12)
C3—C2—H2A	109.2	C13—C12—C11	123.13 (12)
C1—C2—H2A	109.2	C12—C13—C14	116.18 (12)
C3—C2—H2B	109.2	C12—C13—C15	124.46 (13)
C1—C2—H2B	109.2	C14—C13—C15	119.36 (13)
H2A—C2—H2B	107.9	O4—C14—C13	120.59 (13)
C2—C3—C4	114.40 (12)	O4—C14—C8	118.62 (13)
C2—C3—H3A	108.7	C13—C14—C8	120.78 (12)
C4—C3—H3A	108.7	C13—C15—C17	112.84 (12)
C2—C3—H3B	108.7	C13—C15—C16	110.95 (12)
C4—C3—H3B	108.7	C17—C15—C16	110.82 (12)
H3A—C3—H3B	107.6	C13—C15—H15A	107.3
C18—C4—C19	107.48 (12)	C17—C15—H15A	107.3
C18—C4—C3	107.13 (12)	C16—C15—H15A	107.3
C19—C4—C3	110.61 (12)	C15—C16—H16A	109.5
C18—C4—C5	108.58 (11)	C15—C16—H16B	109.5
C19—C4—C5	114.52 (12)	H16A—C16—H16B	109.5
C3—C4—C5	108.26 (11)	C15—C16—H16C	109.5
C6—C5—C4	115.24 (11)	H16A—C16—H16C	109.5
C6—C5—C10	110.17 (11)	H16B—C16—H16C	109.5
C4—C5—C10	116.38 (11)	C15—C17—H17A	109.5
C6—C5—H5A	104.5	C15—C17—H17B	109.5
C4—C5—H5A	104.5	H17A—C17—H17B	109.5
C10—C5—H5A	104.5	C15—C17—H17C	109.5
C7—C6—C5	109.42 (12)	H17A—C17—H17C	109.5
C7—C6—H6A	109.8	H17B—C17—H17C	109.5
C5—C6—H6A	109.8	C4—C18—H18A	109.5
C7—C6—H6B	109.8	C4—C18—H18B	109.5
C5—C6—H6B	109.8	H18A—C18—H18B	109.5
H6A—C6—H6B	108.2	C4—C18—H18C	109.5
O1—C7—C8	107.49 (11)	H18A—C18—H18C	109.5
O1—C7—C6	108.07 (12)	H18B—C18—H18C	109.5
C8—C7—C6	111.93 (12)	C4—C19—H19A	109.5
O1—C7—H7A	109.8	C4—C19—H19B	109.5
C8—C7—H7A	109.8	H19A—C19—H19B	109.5
C6—C7—H7A	109.8	C4—C19—H19C	109.5
C9—C8—C14	122.44 (12)	H19A—C19—H19C	109.5
C9—C8—C7	123.18 (12)	H19B—C19—H19C	109.5
C14—C8—C7	114.35 (12)	C10—C20—H20A	109.5

C8—C9—C11	116.29 (12)	C10—C20—H20B	109.5
C8—C9—C10	124.29 (12)	H20A—C20—H20B	109.5
C11—C9—C10	119.34 (12)	C10—C20—H20C	109.5
C9—C10—C1	110.91 (11)	H20A—C20—H20C	109.5
C9—C10—C20	106.82 (12)	H20B—C20—H20C	109.5
C10—C1—C2—C3	−56.85 (16)	C2—C1—C10—C5	55.46 (15)
C1—C2—C3—C4	54.11 (17)	C6—C5—C10—C9	52.09 (15)
C2—C3—C4—C18	−166.79 (12)	C4—C5—C10—C9	−174.34 (12)
C2—C3—C4—C19	76.36 (15)	C6—C5—C10—C1	171.09 (11)
C2—C3—C4—C5	−49.87 (16)	C4—C5—C10—C1	−55.33 (16)
C18—C4—C5—C6	−60.53 (17)	C6—C5—C10—C20	−66.31 (15)
C19—C4—C5—C6	59.57 (16)	C4—C5—C10—C20	67.26 (16)
C3—C4—C5—C6	−176.51 (12)	C8—C9—C11—O2	−168.73 (14)
C18—C4—C5—C10	168.22 (12)	C10—C9—C11—O2	8.2 (2)
C19—C4—C5—C10	−71.68 (16)	C8—C9—C11—C12	10.76 (19)
C3—C4—C5—C10	52.23 (16)	C10—C9—C11—C12	−172.31 (12)
C4—C5—C6—C7	157.64 (12)	O2—C11—C12—O3	−5.63 (19)
C10—C5—C6—C7	−68.21 (14)	C9—C11—C12—O3	174.85 (12)
C5—C6—C7—O1	−73.43 (14)	O2—C11—C12—C13	174.01 (13)
C5—C6—C7—C8	44.75 (16)	C9—C11—C12—C13	−5.5 (2)
O1—C7—C8—C9	107.73 (15)	O3—C12—C13—C14	176.88 (13)
C6—C7—C8—C9	−10.8 (2)	C11—C12—C13—C14	−2.7 (2)
O1—C7—C8—C14	−70.35 (15)	O3—C12—C13—C15	−3.3 (2)
C6—C7—C8—C14	171.12 (12)	C11—C12—C13—C15	177.11 (13)
C14—C8—C9—C11	−7.9 (2)	C12—C13—C14—O4	−175.35 (15)
C7—C8—C9—C11	174.19 (13)	C15—C13—C14—O4	4.8 (2)
C14—C8—C9—C10	175.36 (13)	C12—C13—C14—C8	5.73 (19)
C7—C8—C9—C10	−2.6 (2)	C15—C13—C14—C8	−174.11 (13)
C8—C9—C10—C1	−134.70 (14)	C9—C8—C14—O4	−179.11 (15)
C11—C9—C10—C1	48.64 (17)	C7—C8—C14—O4	−1.0 (2)
C8—C9—C10—C20	105.50 (16)	C9—C8—C14—C13	−0.2 (2)
C11—C9—C10—C20	−71.16 (15)	C7—C8—C14—C13	177.93 (13)
C8—C9—C10—C5	−18.10 (19)	C12—C13—C15—C17	61.75 (19)
C11—C9—C10—C5	165.24 (11)	C14—C13—C15—C17	−118.43 (14)
C2—C1—C10—C9	171.86 (12)	C12—C13—C15—C16	−63.29 (18)
C2—C1—C10—C20	−70.22 (15)	C14—C13—C15—C16	116.53 (14)

Hydrogen-bond geometry (Å, °)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
O1—H1O1···O2^{i}	0.88 (2)	2.24 (3)	2.9502 (15)	137 (2)
O1—H1O1···O4	0.88 (2)	2.52 (3)	2.9399 (14)	109.8 (19)
O3—H1O3···O2	0.83 (2)	2.075 (19)	2.5892 (14)	119.8 (19)
O3—H1O3···O4^{ii}	0.83 (2)	2.42 (2)	3.1635 (14)	148.8 (18)
C1—H1A···O2	0.97	2.33	2.9493 (18)	121
C5—H5A···O1	0.98	2.52	2.9933 (17)	110
C7—H7A···O2^{i}	0.98	2.42	3.0998 (17)	126
C15—H15A···O4	0.98	2.38	2.8549 (17)	109

C16—H16C···O3	0.96	2.58	3.1654 (19)	119
C17—H17B···O3	0.96	2.53	3.1204 (18)	119
C20—H20A···O2	0.96	2.51	3.1451 (18)	124

Symmetry codes: (i) *x*−1, *y*, *z*; (ii) *x*+1, *y*, *z*.

Fig. 1

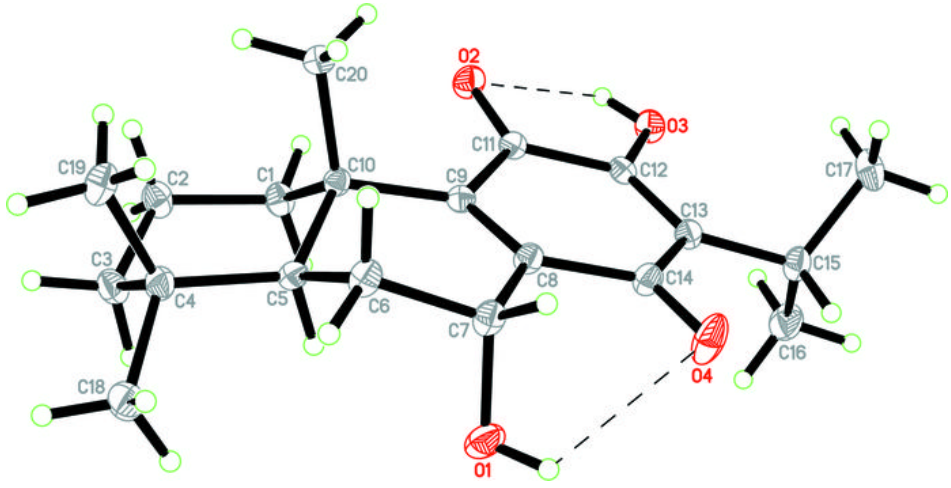
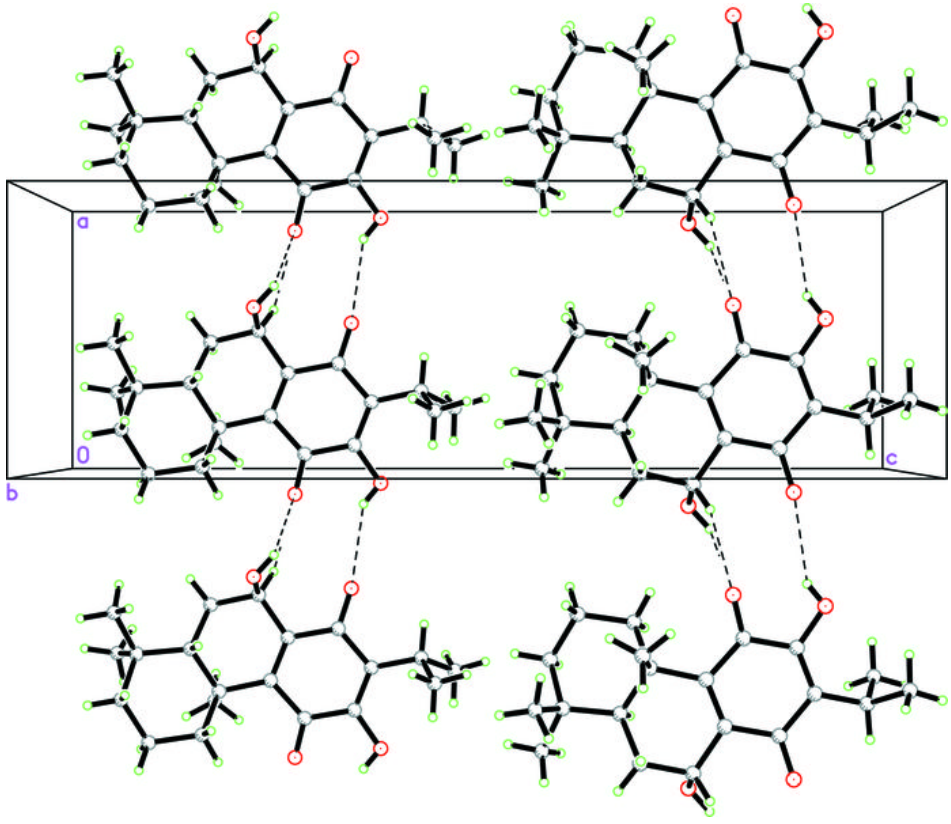

O2
C20
O3
C11
C12
C17
C19
C2
C1
C10
C9
C13
C3
C4
C5
C6
C8
C14
C15
C7
C16
O4
C18
O1

Fig. 2



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(2-Chloro-8-methoxyquinolin-3-yl)-methanol monohydrate

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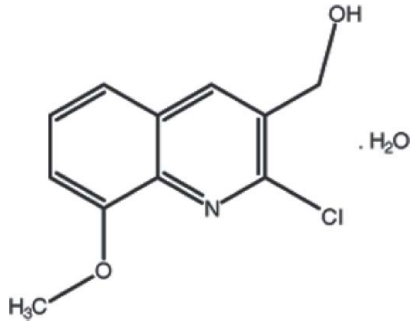
Key indicators: single-crystal X-ray study; T = 290 K; mean σ(C–C) = 0.005 Å; R factor = 0.054; wR factor = 0.134; data-to-parameter ratio = 13.4.

In the title compound, $C_{11}H_{10}ClNO_2\cdot H_2O$, the organic molecule is roughly planar (r.m.s. deviation = 0.074 Å). In the crystal structure, molecules are linked by O—H···O and O—H···N hydrogen bonds and weak C—H···π and π–π interactions [centroid–centroid distance = 3.578 (3) Å] consolidate the packing. A short Cl···O contact [3.147 (3) Å] is also observed.

Related literature

For further information on the starting material, see: Subashini *et al.* (2009). For general background to the title compound, see: Roopan *et al.* (2009). For related structures, see: Khan *et al.* (2010*a*,*b*). For bond-length data, see: Allen *et al.* (1987).



Experimental

Crystal data

$C_{11}H_{10}ClNO_2\cdot H_2O$
M_r = 241.67
Monoclinic, $P2_1/n$
a = 9.161 (5) Å
b = 14.246 (5) Å
c = 9.464 (5) Å
β = 116.819 (5)°
V = 1102.3 (9) Å^3
Z = 4
Mo $K\alpha$ radiation
μ = 0.34 mm^{-1}
T = 290 K
0.31 × 0.21 × 0.10 mm

Data collection

Oxford Xcalibur Eos (Nova) CCD detector diffractometer
Absorption correction: multi-scan (*CrysAlis RED*; Oxford Diffraction, 2009)
T_{min} = 0.903, T_{max} = 0.967
8360 measured reflections
2044 independent reflections
1212 reflections with $I > 2\sigma(I)$
R_{int} = 0.100

Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.054
$wR(F^2)$ = 0.134
S = 0.90
2044 reflections
153 parameters
H atoms treated by a mixture of independent and constrained refinement
$\Delta\rho_{max}$ = 0.40 e Å^{-3}
$\Delta\rho_{min}$ = −0.26 e Å^{-3}

Table 1
Hydrogen-bond geometry (Å, °).

*Cg*1 is the centroid of the N1/C1–C3/C8/C9 ring.

D—H···A	D—H	H···A	D···A	D—H···A
O1—H1*O*···O3^{i}	0.82	1.90	2.705 (4)	165
O3—H1*W*···N1^{ii}	0.85 (5)	2.17 (5)	2.988 (4)	163 (4)
O3—H2*W*···O1^{iii}	0.83 (4)	2.02 (4)	2.836 (4)	171 (5)
C10—H10*B*···*Cg*1^{i}	0.97	2.93	3.738 (5)	142

Symmetry codes: (i) $x-\frac{1}{2}, -y+\frac{1}{2}, z-\frac{1}{2}$; (ii) $x+1, y, z$; (iii) $x+1, y, z+1$.

Data collection: *CrysAlis PRO CCD* (Oxford Diffraction, 2009); cell refinement: *CrysAlis PRO CCD*; data reduction: *CrysAlis PRO RED* (Oxford Diffraction, 2009); program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *ORTEP-3* (Farrugia, 1997); software used to prepare material for publication: *WinGX* (Farrugia, 1999).

We thank the Department of Science and Technology, India, for use of the CCD facility set up under the FIST–DST program at SSCU, IISc. We also thank Professor T. N. Guru Row, IISc, Bangalore, for his help with the data collection. FNK thanks the DST for Fast Track Proposal funding.

Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: HB5469).

References

Allen, F. H., Kennard, O., Watson, D. G., Brammer, L., Orpen, A. G. & Taylor, R. (1987). *J. Chem. Soc. Perkin Trans. 2*, pp. S1–19.
Farrugia, L. J. (1997). *J. Appl. Cryst.* **30**, 565.
Farrugia, L. J. (1999). *J. Appl. Cryst.* **32**, 837–838.
Khan, F. N., Mohana Roopan, S., Hathwar, V. R. & Ng, S. W. (2010*a*). *Acta Cryst.* E**66**, o200.
Khan, F. N., Mohana Roopan, S., Hathwar, V. R. & Ng, S. W. (2010*b*). *Acta Cryst.* E**66**, o201.
Oxford Diffraction (2009). *CrysAlis PRO CCD* and *CrysAlis PRO RED*. Oxford Diffraction Ltd, Yarnton,England.
Roopan, S. M., Khan, F. N., Subashini, R., Hathwar, V. R. & Ng, S. W. (2009). *Acta Cryst.* E**65**, o2711.
Sheldrick, G. M. (2008). *Acta Cryst.* A**64**, 112–122.
Subashini, R., Khan, F. N., Gund, M., Hathwar, V. R. & Ng, S. W. (2009). *Acta Cryst.* E**65**, o2723.

supplementary materials

Acta Cryst. (2010). E**66**, o1542 [**doi:10.1107/S1600536810020489**]

(2-Chloro-8-methoxyquinolin-3-yl)methanol monohydrate

S. M. Roopan, F. N. Khan, A. S. Kumar, V. R. Hathwar and M. Akkurt

Comment

The importance and general background of the title compound is given in our earler paper (Roopan *et al.*, 2009).

In the main molecule of the title compound (I), (Fig. 1), all the non-H atoms are roughly coplanar (r.m.s. deviation = 0.074 Å). The bond lengths and angles are comparable to the similar structures 2-chloro-3-hydroxymethyl-7,8-dimethylquinoline and 2-chloro-3-hydroxymethyl-6-methoxyquinoline (Khan *et al.*, 2010*a*,b), and also those in literature (Allen *et al.*, 1987).

The crystal structure is stabilized by intermolecular O—H···O and O—H···N interactions between the symmetry-related molecues (Table 1, Fig. 2). Adjacent molecules are stacked along the *b* axis through weak C—H···π interactions (Table 1) and π-π interactions [*Cg*1···*Cg*2(-*x*, 1 - *y*, -*z*) = 3.578 (3) Å, where *Cg*1 and *Cg*2 are centroids of the N1/C1–C3/C8/C9 and C4–C9 rings, respectively]. In addition a short Cl1.. O2 contact of 3.15 Å is also observed.

Experimental

2-Chloro-8-methoxyquinoline-3-carbaldehyde (222 mg, 1 mmol), sodium borohydride (38 mg, 1 mmol) and catalytic amount of montmorillonite K-10 were taken in an open vessel and the resulting mixture was irradiated at 500 W for 5 min. Ethylacetate was poured into the reaction mixture and filtered off. The filtrated after removal of solvent was subjected to column chromatography packed with silica and ethyl acetate/petroleum ether was used as the eluant. Colourless slabs of (I) were grown by solvent evaporation from a solution of the compound in chloroform.

Refinement

The H atoms of the water molecule were located in difference map and its positional parameters were refined freely [O3—H1W = 0.85 (5) and O3—H2W = 0.83 (4) Å]. The remaining H atoms were positioned geometrically, with O—H = 0.82 Å (for OH) and C—H = 0.93, 0.97 and 0.96 Å for aromatic, methylene and methyl H, respectively, and refined as riding with U_{iso}(H) = 1.2 or 1.5 U_{eq}(O, C).

Figures

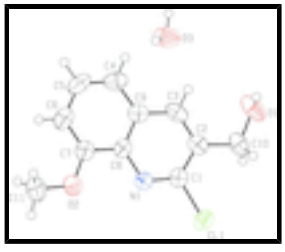


Fig. 1. The molecular structure of (I), showing 50% probability displacement ellipsoids.

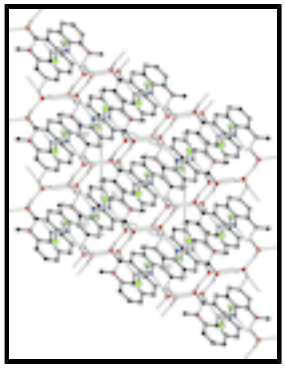


Fig. 2. Molecular packing of (I) with hydrogen bonding shown as dashed lines. The H atoms not involved in hydrogen bonds have been omitted for clarity.

(2-Chloro-8-methoxyquinolin-3-yl)methanol monohydrate

Crystal data

$C_{11}H_{10}ClNO_2 \cdot H_2O$	$F(000) = 504$
$M_r = 241.67$	$D_x = 1.456$ Mg m^{-3}
Monoclinic, $P2_1/n$	Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å
Hall symbol: -P 2yn	Cell parameters from 1021 reflections
$a = 9.161$ (5) Å	$\theta = 1.9$–$20.2°$
$b = 14.246$ (5) Å	$\mu = 0.34$ mm^{-1}
$c = 9.464$ (5) Å	$T = 290$ K
$\beta = 116.819$ (5)°	Slab, colourless
$V = 1102.3$ (9) Å^3	0.31 × 0.21 × 0.10 mm
$Z = 4$	

Data collection

Oxford Xcalibur Eos (Nova) CCD detector diffractometer	2044 independent reflections
Radiation source: Enhance (Mo) X-ray Source	1212 reflections with $I > 2\sigma(I)$
graphite	$R_{int} = 0.100$
ω scans	$\theta_{max} = 25.5°$, $\theta_{min} = 2.9°$
Absorption correction: multi-scan (*CrysAlis RED*; Oxford Diffraction, 2009)	$h = -11 \rightarrow 11$
$T_{min} = 0.903$, $T_{max} = 0.967$	$k = -17 \rightarrow 17$
8360 measured reflections	$l = -11 \rightarrow 11$

Refinement

Refinement on F^2	Primary atom site location: structure-invariant direct methods
Least-squares matrix: full	Secondary atom site location: difference Fourier map
$R[F^2 > 2\sigma(F^2)] = 0.054$	Hydrogen site location: inferred from neighbouring sites
$wR(F^2) = 0.134$	H atoms treated by a mixture of independent and constrained refinement
$S = 0.90$	$w = 1/[\sigma^2(F_o^2) + (0.0692P)^2]$

	where $P = (F_o^2 + 2F_c^2)/3$
2044 reflections	$(\Delta/\sigma)_{max} < 0.001$
153 parameters	$\Delta\rho_{max} = 0.40$ e Å^{-3}
0 restraints	$\Delta\rho_{min} = -0.26$ e Å^{-3}

Special details

Geometry. Bond distances, angles *etc*. have been calculated using the rounded fractional coordinates. All su's are estimated from the variances of the (full) variance-covariance matrix. The cell e.s.d.'s are taken into account in the estimation of distances, angles and torsion angles

Refinement. Refinement on F^2 for ALL reflections except those flagged by the user for potential systematic errors. Weighted *R*-factors *wR* and all goodnesses of fit *S* are based on F^2, conventional *R*-factors *R* are based on *F*, with *F* set to zero for negative F^2. The observed criterion of $F^2 > \sigma(F^2)$ is used only for calculating -*R*-factor-obs *etc*. and is not relevant to the choice of reflections for refinement. *R*-factors based on F^2 are statistically about twice as large as those based on *F*, and *R*-factors based on ALL data will be even larger.

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å^2)

	x	*y*	*z*	U_{iso}*/U_{eq}
Cl1	−0.12994 (10)	0.21700 (5)	−0.05478 (9)	0.0525 (3)
O1	0.0858 (3)	0.2656 (2)	−0.3822 (3)	0.0713 (10)
O2	0.1487 (3)	0.46372 (14)	0.3536 (2)	0.0515 (8)
N1	0.0521 (3)	0.35801 (15)	0.0948 (3)	0.0371 (8)
C1	0.0114 (4)	0.30580 (19)	−0.0297 (3)	0.0399 (10)
C2	0.0664 (4)	0.3140 (2)	−0.1453 (3)	0.0435 (10)
C3	0.1715 (4)	0.3870 (2)	−0.1243 (3)	0.0493 (11)
C4	0.3261 (4)	0.5254 (2)	0.0313 (4)	0.0558 (12)
C5	0.3720 (4)	0.5792 (2)	0.1620 (5)	0.0603 (14)
C6	0.3158 (4)	0.5601 (2)	0.2743 (4)	0.0545 (12)
C7	0.2105 (4)	0.4875 (2)	0.2525 (3)	0.0436 (10)
C8	0.1595 (3)	0.43029 (18)	0.1160 (3)	0.0379 (9)
C9	0.2198 (4)	0.4484 (2)	0.0056 (3)	0.0444 (11)
C10	0.0147 (4)	0.2459 (3)	−0.2813 (4)	0.0573 (11)
C11	0.2035 (5)	0.5135 (3)	0.4973 (4)	0.0678 (16)
O3	0.8868 (3)	0.3074 (2)	0.2937 (3)	0.0716 (10)
H1O	0.18120	0.24780	−0.34070	0.1070*
H3	0.21180	0.39630	−0.19750	0.0590*
H4	0.36470	0.53900	−0.04200	0.0670*
H5	0.44190	0.62970	0.17760	0.0730*
H6	0.35070	0.59720	0.36460	0.0660*
H10A	0.04510	0.18290	−0.23950	0.0690*
H10B	−0.10340	0.24780	−0.34210	0.0690*
H11A	0.32050	0.50900	0.55460	0.1020*
H11B	0.15520	0.48700	0.55960	0.1020*
H11C	0.17230	0.57820	0.47550	0.1020*
H1W	0.943 (5)	0.331 (3)	0.252 (5)	0.1080*
H2W	0.949 (6)	0.301 (3)	0.389 (5)	0.1080*

Atomic displacement parameters (Å^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Cl1	0.0537 (5)	0.0487 (5)	0.0489 (5)	−0.0099 (4)	0.0176 (4)	−0.0054 (4)
O1	0.0644 (17)	0.112 (2)	0.0369 (13)	0.0262 (15)	0.0223 (13)	0.0030 (12)
O2	0.0555 (15)	0.0550 (14)	0.0428 (12)	−0.0026 (11)	0.0212 (11)	−0.0056 (10)
N1	0.0369 (14)	0.0372 (14)	0.0321 (13)	0.0029 (11)	0.0112 (11)	0.0046 (11)
C1	0.0379 (17)	0.0400 (17)	0.0342 (17)	0.0072 (14)	0.0096 (14)	0.0066 (13)
C2	0.0369 (17)	0.054 (2)	0.0324 (17)	0.0087 (15)	0.0094 (14)	0.0063 (13)
C3	0.047 (2)	0.067 (2)	0.0379 (18)	0.0167 (18)	0.0228 (16)	0.0161 (16)
C4	0.042 (2)	0.056 (2)	0.072 (2)	0.0051 (17)	0.0280 (18)	0.0169 (19)
C5	0.043 (2)	0.040 (2)	0.090 (3)	−0.0063 (16)	0.023 (2)	0.0051 (19)
C6	0.047 (2)	0.044 (2)	0.061 (2)	−0.0025 (16)	0.0141 (18)	−0.0045 (16)
C7	0.0358 (17)	0.0434 (18)	0.0448 (19)	0.0081 (15)	0.0122 (15)	0.0033 (14)
C8	0.0317 (16)	0.0343 (16)	0.0396 (16)	0.0055 (14)	0.0089 (14)	0.0054 (13)
C9	0.0380 (18)	0.0480 (19)	0.0458 (19)	0.0053 (15)	0.0176 (16)	0.0110 (15)
C10	0.056 (2)	0.076 (2)	0.0358 (19)	0.0121 (18)	0.0170 (17)	−0.0025 (16)
C11	0.071 (3)	0.078 (3)	0.046 (2)	0.000 (2)	0.019 (2)	−0.0121 (17)
O3	0.0575 (17)	0.108 (2)	0.0480 (15)	−0.0196 (15)	0.0226 (13)	0.0007 (15)

Geometric parameters (Å, °)

Cl1—C1	1.748 (4)	C4—C9	1.413 (5)
O1—C10	1.406 (5)	C5—C6	1.401 (6)
O2—C7	1.356 (4)	C6—C7	1.365 (5)
O2—C11	1.410 (4)	C7—C8	1.417 (4)
O1—H1O	0.8200	C8—C9	1.409 (4)
O3—H1W	0.85 (5)	C3—H3	0.9300
O3—H2W	0.83 (4)	C4—H4	0.9300
N1—C1	1.298 (4)	C5—H5	0.9300
N1—C8	1.375 (4)	C6—H6	0.9300
C1—C2	1.401 (5)	C10—H10B	0.9700
C2—C3	1.369 (5)	C10—H10A	0.9700
C2—C10	1.507 (5)	C11—H11C	0.9600
C3—C9	1.408 (4)	C11—H11A	0.9600
C4—C5	1.351 (5)	C11—H11B	0.9600
Cl1···O2^{i}	3.147 (3)		
C7—O2—C11	118.3 (3)	C3—C9—C8	117.4 (3)
C10—O1—H1O	109.00	O1—C10—C2	112.8 (3)
H1W—O3—H2W	107 (5)	C2—C3—H3	119.00
C1—N1—C8	117.1 (3)	C9—C3—H3	119.00
Cl1—C1—N1	115.5 (3)	C5—C4—H4	120.00
Cl1—C1—C2	117.4 (2)	C9—C4—H4	120.00
N1—C1—C2	127.2 (3)	C6—C5—H5	120.00
C1—C2—C10	121.9 (3)	C4—C5—H5	119.00
C1—C2—C3	115.3 (3)	C7—C6—H6	120.00
C3—C2—C10	122.8 (3)	C5—C6—H6	120.00

C2—C3—C9	121.5 (3)	O1—C10—H10A	109.00
C5—C4—C9	120.2 (3)	C2—C10—H10A	109.00
C4—C5—C6	121.0 (3)	C2—C10—H10B	109.00
C5—C6—C7	120.6 (3)	O1—C10—H10B	109.00
O2—C7—C8	115.4 (3)	H10A—C10—H10B	108.00
C6—C7—C8	119.6 (3)	O2—C11—H11B	109.00
O2—C7—C6	125.0 (3)	O2—C11—H11C	110.00
N1—C8—C9	121.6 (2)	O2—C11—H11A	109.00
N1—C8—C7	118.9 (3)	H11A—C11—H11C	109.00
C7—C8—C9	119.5 (3)	H11B—C11—H11C	110.00
C3—C9—C4	123.6 (3)	H11A—C11—H11B	109.00
C4—C9—C8	119.0 (3)		
C11—O2—C7—C6	−4.0 (5)	C2—C3—C9—C8	1.8 (5)
C11—O2—C7—C8	175.5 (3)	C9—C4—C5—C6	0.0 (6)
C8—N1—C1—Cl1	−178.2 (2)	C5—C4—C9—C3	−177.5 (3)
C8—N1—C1—C2	0.8 (5)	C5—C4—C9—C8	1.6 (5)
C1—N1—C8—C7	−178.4 (3)	C4—C5—C6—C7	−1.3 (6)
C1—N1—C8—C9	1.5 (4)	C5—C6—C7—O2	−179.7 (3)
Cl1—C1—C2—C3	177.3 (2)	C5—C6—C7—C8	0.9 (5)
Cl1—C1—C2—C10	−3.6 (4)	O2—C7—C8—N1	1.1 (4)
N1—C1—C2—C3	−1.7 (5)	O2—C7—C8—C9	−178.8 (3)
N1—C1—C2—C10	177.4 (3)	C6—C7—C8—N1	−179.3 (3)
C1—C2—C3—C9	0.3 (5)	C6—C7—C8—C9	0.8 (5)
C10—C2—C3—C9	−178.8 (3)	N1—C8—C9—C3	−2.7 (4)
C1—C2—C10—O1	−179.0 (3)	N1—C8—C9—C4	178.1 (3)
C3—C2—C10—O1	0.1 (5)	C7—C8—C9—C3	177.1 (3)
C2—C3—C9—C4	−179.1 (3)	C7—C8—C9—C4	−2.0 (4)

Symmetry codes: (i) *x*−1/2, −*y*+1/2, *z*−1/2.

Hydrogen-bond geometry (Å, °)

Cg1 is the centroid of the N1/C1–C3/C8/C9 ring.

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
O1—H1O···O3^{i}	0.82	1.90	2.705 (4)	165
O3—H1W···N1^{ii}	0.85 (5)	2.17 (5)	2.988 (4)	163 (4)
O3—H2W···O1^{iii}	0.83 (4)	2.02 (4)	2.836 (4)	171 (5)
C10—H10B···Cg1^{i}	0.97	2.93	3.738 (5)	142

Symmetry codes: (i) *x*−1/2, −*y*+1/2, *z*−1/2; (ii) *x*+1, *y*, *z*; (iii) *x*+1, *y*, *z*+1.

Fig. 1

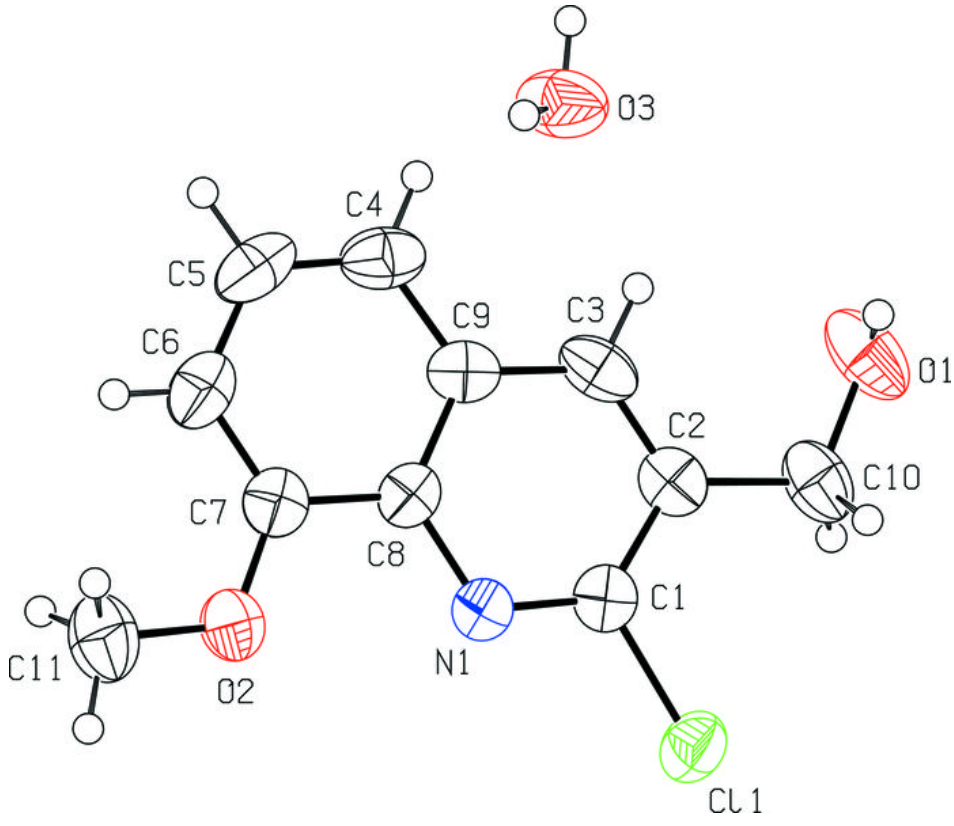
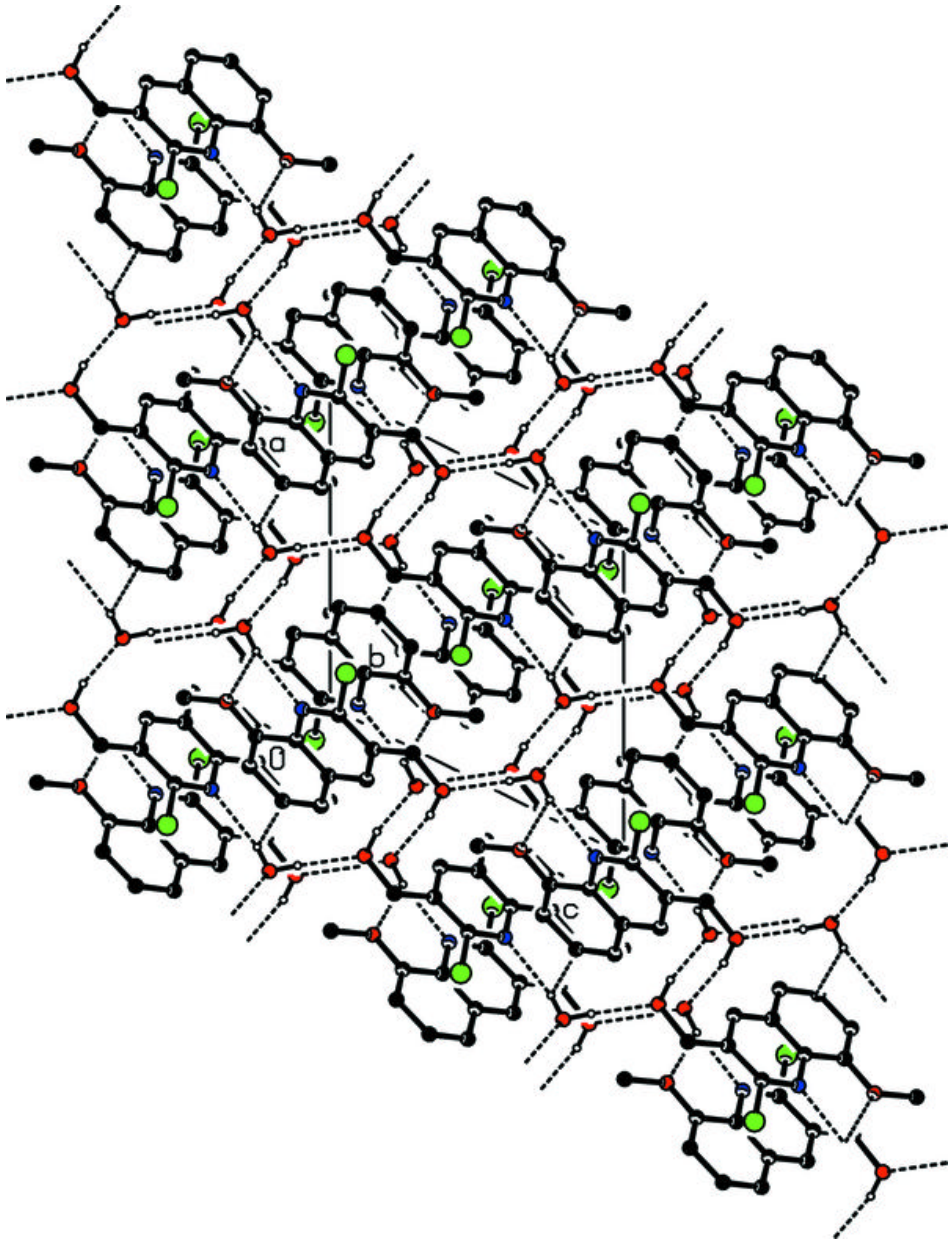


Fig. 2



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(2-Chloro-8-methylquinolin-3-yl)-methanol

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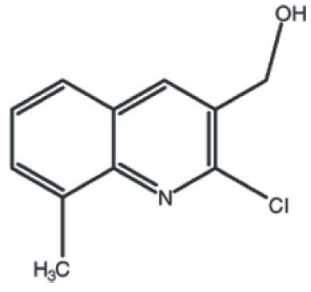
Received 25 May 2010; accepted 29 May 2010

Key indicators: single-crystal X-ray study; T = 290 K; mean σ(C–C) = 0.006 Å; R factor = 0.061; wR factor = 0.135; data-to-parameter ratio = 13.4.

The molecule of title compound, $C_{11}H_{10}ClNO$, is close to being planar (r.m.s deviation for the non-H atoms = 0.017 Å). In the crystal, molecules interact by way of O—H···O hydrogen bonds, generating $C(2)$ chains propagating in [010]. The crystal structure is consolidated by C—H···π interactions and aromatic π–π stacking interactions [centroid–centroid distance = 3.661 (2) Å].

Related literature

For a related structure and background references, see: Roopan *et al.* (2010). For a similar structure, see: Khan *et al.* (2009).



Experimental

Crystal data

$C_{11}H_{10}ClNO$
M_r = 207.65
Monoclinic, $P2_1/c$
a = 14.963 (2) Å
b = 4.632 (1) Å
c = 14.469 (2) Å
β = 103.612 (1)°
V = 974.7 (3) Å^3
Z = 4
Mo $K\alpha$ radiation
μ = 0.35 mm^{-1}
T = 290 K
0.40 × 0.24 × 0.11 mm

Data collection

Oxford Xcalibur Eos(Nova) CCD detector diffractometer
Absorption correction: multi-scan (*CrysAlis PRO* RED; Oxford Diffraction, 2009)
T_{min} = 0.871, T_{max} = 0.962
7607 measured reflections
1723 independent reflections
790 reflections with $I > 2\sigma(I)$
R_{int} = 0.167

Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.061
$wR(F^2)$ = 0.135
S = 0.85
1723 reflections
129 parameters
H-atom parameters constrained
$\Delta\rho_{max}$ = 0.23 e Å^{-3}
$\Delta\rho_{min}$ = −0.23 e Å^{-3}

Table 1
Hydrogen-bond geometry (Å, °).

*Cg*1 is a centroid of the N1/C1–C3/C8/C9 ring.

D—H···A	D—H	H···A	D···A	D—H···A
O1—H1*O*···O1^{i}	0.82	1.90	2.712 (4)	174
C10—H10*A*···*Cg*1^{ii}	0.97	2.75	3.557 (4)	141

Symmetry codes: (i) $-x, y-\frac{1}{2}, -z+\frac{1}{2}$; (ii) $x, y+1, z$.

Data collection: *CrysAlis PRO CCD* (Oxford Diffraction, 2009); cell refinement: *CrysAlis PRO CCD*; data reduction: *CrysAlis PRO RED* (Oxford Diffraction, 2009); program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *ORTEP-3* (Farrugia, 1997); software used to prepare material for publication: *WinGX* (Farrugia, 1999).

We thank the Department of Science and Technology, India, for the use of the CCD facility set up under the FIST–DST program at SSCU, IISc. We also thank Professor T. N. Guru Row, IISc, Bangalore, for his help with the data collection. FNK thanks the DST for Fast Track Proposal funding.

Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: HB5470).

References

Farrugia, L. J. (1997). *J. Appl. Cryst.* **30**, 565.
Farrugia, L. J. (1999). *J. Appl. Cryst.* **32**, 837–838.
Khan, F. N., Subashini, R., Kushwaha, A. K., Hathwar, V. R. & Ng, S. W. (2009). *Acta Cryst.* E**65**, o2722.
Oxford Diffraction (2009). *CrysAlis PRO CCD* and *CrysAlis PRO RED*. Oxford Diffraction Ltd, Yarnton, Oxfordshire, England.
Roopan, S. N., Khan, F. N., Kumar, A. S., Hathwar, V. R. & Akkurt, M. (2010). Acta Cryst. E**66**, o1542.
Sheldrick, G. M. (2008). *Acta Cryst.* A**64**, 112–122.

supplementary materials

Acta Cryst. (2010). E**66**, o1543 [**doi:10.1107/S1600536810020490**]

(2-Chloro-8-methylquinolin-3-yl)methanol

S. M. Roopan, F. N. Khan, R. Kumar, V. R. Hathwar and M. Akkurt

Comment

As part of our program which aimed to develop new selective and environmentally friendly methodologies for the preparation of 2-chloroquinolines (Roopan *et al.*, 2010), we report here crystal structure of the title compound, (I).

The title molecule (I), (Fig. 1), except the hydroxyl and methyl H atoms, close to planar (r.m.s deviation 0.017 Å). The values of the geometric parameters in (I) are comparable to those of some similar structures (Khan *et al.*, 2009).

In the solid-state, the molecules are linked *via* intermolecular O—H···O hydrogen bonds (Table 1, Fig. 2). The crystal structure is further stabilized by an intermolecular C–H···π interactions between the methylene H atom of ethenol substituent and the pyridine ring of an adjacent molecule, with a C10–H10A···*Cg*1^{ii} separation of 2.75 Å (Table 1, *Cg*1 is the centroid of N1/C1–C3/C8/C9 pyridine ring; symmetry code: (ii) *x*, *y* + 1, *z*). In addition, the packing mode results in stabilizing π-π stacking interactions [*Cg*1···*Cg*2^{ii} = 3.661 (2) Å, where *Cg*1 and *Cg*2 are the centroids of the N1/C1–C3/C8/C9 and C4–C9 rings].

Experimental

2-Chloro-8-methylquinoline-3-carbaldehyde (206 mg, 1 mmol), sodium borohydride (38 mg, 1 mmol) and catalytic amount of montmorillonite K-10 were taken in an open vessel and the resulting mixture was irradiating at 500 W for 4 min. Ethylacetate was poured into the reaction mixture and filtered off. The filtrated after removal of solvent ethy lacetate was subjected to column chromatography packed with silica and ethyl acetate/petroleum ether was used as the eluant. Colourless plates of (I) were grown by solvent evaporation from a solution of the compound in chloroform.

Refinement

H atoms were positioned geometrically, with C—H = 0.93- 0.97 Å, and refined a riding model with U_{iso}(H) = 1.2 or 1.5 U_{eq}(C). The value of R_{int} [0.167] is greater than 0.12, which may reflect the poor crystal quality.

Figures

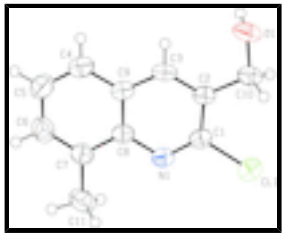


Fig. 1. The molecule of (I), showing 50% probability displacement ellipsoids.

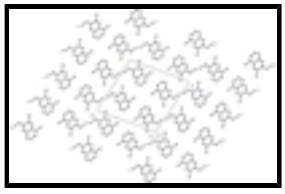


Fig. 2. A view of the packing of (I) with intermolecular O–H···O hydrogen bonding down the *b* axis. The H atoms not involved in hydrogen bonds have been omitted for clarity.

(2-Chloro-8-methylquinolin-3-yl)methanol

Crystal data

$C_{11}H_{10}ClNO$	$F(000) = 432$
$M_r = 207.65$	$D_x = 1.415$ Mg m^{-3}
Monoclinic, $P2_1/c$	Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å
Hall symbol: -P 2ybc	Cell parameters from 972 reflections
$a = 14.963$ (2) Å	$\theta = 2.0$–$20.5°$
$b = 4.632$ (1) Å	$\mu = 0.35$ mm^{-1}
$c = 14.469$ (2) Å	$T = 290$ K
$\beta = 103.612$ (1)°	Plate, colourless
$V = 974.7$ (3) Å^3	0.40 × 0.24 × 0.11 mm
$Z = 4$	

Data collection

Oxford Xcalibur Eos(Nova) CCD detector diffractometer	1723 independent reflections
Radiation source: Enhance (Mo) X-ray Source	790 reflections with $I > 2\sigma(I)$
graphite	$R_{int} = 0.167$
ω scans	$\theta_{max} = 25.0°$, $\theta_{min} = 2.9°$
Absorption correction: multi-scan (*CrysAlis PRO* RED; Oxford Diffraction, 2009)	$h = -17 \rightarrow 17$
$T_{min} = 0.871$, $T_{max} = 0.962$	$k = -5 \rightarrow 5$
7607 measured reflections	$l = -17 \rightarrow 17$

Refinement

Refinement on F^2	Primary atom site location: structure-invariant direct methods
Least-squares matrix: full	Secondary atom site location: difference Fourier map
$R[F^2 > 2\sigma(F^2)] = 0.061$	Hydrogen site location: inferred from neighbouring sites
$wR(F^2) = 0.135$	H-atom parameters constrained
$S = 0.85$	$w = 1/[\sigma^2(F_o^2) + (0.0492P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
1723 reflections	$(\Delta/\sigma)_{max} < 0.001$
129 parameters	$\Delta\rho_{max} = 0.23$ e Å^{-3}
0 restraints	$\Delta\rho_{min} = -0.23$ e Å^{-3}

Special details

Geometry. Bond distances, angles *etc*. have been calculated using the rounded fractional coordinates. All su's are estimated from the variances of the (full) variance-covariance matrix. The cell e.s.d.'s are taken into account in the estimation of distances, angles and torsion angles

Refinement. Refinement on F^2 for ALL reflections except those flagged by the user for potential systematic errors. Weighted *R*-factors *wR* and all goodnesses of fit *S* are based on F^2, conventional *R*-factors *R* are based on *F*, with *F* set to zero for negative F^2. The observed criterion of $F^2 > \sigma(F^2)$ is used only for calculating -*R*-factor-obs *etc*. and is not relevant to the choice of reflections for refinement. *R*-factors based on F^2 are statistically about twice as large as those based on *F*, and *R*-factors based on ALL data will be even larger.

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å^2)

	x	*y*	*z*	U_{iso}*/U_{eq}
Cl1	0.13301 (8)	0.6900 (2)	−0.03546 (7)	0.0599 (5)
O1	0.0342 (2)	0.8800 (5)	0.2237 (2)	0.0534 (11)
N1	0.2487 (2)	0.3588 (7)	0.0784 (2)	0.0372 (11)
C1	0.1808 (3)	0.5392 (8)	0.0749 (2)	0.0368 (14)
C2	0.1436 (3)	0.6216 (7)	0.1526 (3)	0.0340 (14)
C3	0.1835 (3)	0.4990 (8)	0.2376 (3)	0.0398 (16)
C4	0.2981 (3)	0.1674 (9)	0.3335 (3)	0.0475 (17)
C5	0.3681 (3)	−0.0242 (10)	0.3370 (3)	0.0551 (17)
C6	0.3985 (3)	−0.0855 (9)	0.2554 (3)	0.0538 (17)
C7	0.3611 (3)	0.0351 (9)	0.1686 (3)	0.0427 (17)
C8	0.2875 (3)	0.2323 (8)	0.1643 (3)	0.0365 (12)
C9	0.2566 (3)	0.3003 (8)	0.2465 (3)	0.0369 (14)
C10	0.0635 (3)	0.8293 (8)	0.1397 (3)	0.0436 (16)
C11	0.3954 (3)	−0.0328 (10)	0.0817 (3)	0.0589 (17)
H1O	0.00970	0.73400	0.23830	0.0800*
H3	0.16230	0.54700	0.29100	0.0480*
H4	0.27790	0.20970	0.38810	0.0570*
H5	0.39560	−0.11390	0.39410	0.0660*
H6	0.44670	−0.21540	0.26010	0.0640*
H10A	0.08110	1.01170	0.11630	0.0520*
H10B	0.01230	0.75250	0.09200	0.0520*
H11A	0.44600	−0.16520	0.09810	0.0880*
H11B	0.41540	0.14190	0.05710	0.0880*
H11C	0.34680	−0.11840	0.03440	0.0880*

Atomic displacement parameters (Å^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Cl1	0.0614 (8)	0.0749 (9)	0.0457 (7)	0.0113 (7)	0.0170 (6)	0.0132 (6)
O1	0.060 (2)	0.0369 (17)	0.078 (2)	0.0016 (16)	0.0457 (18)	−0.0011 (16)
N1	0.042 (2)	0.035 (2)	0.0375 (19)	−0.0031 (18)	0.0153 (17)	−0.0004 (17)
C1	0.044 (3)	0.031 (2)	0.037 (2)	−0.007 (2)	0.013 (2)	−0.0008 (19)

C2	0.040 (3)	0.028 (2)	0.037 (2)	−0.005 (2)	0.015 (2)	−0.003 (2)
C3	0.044 (3)	0.043 (3)	0.039 (2)	−0.009 (2)	0.023 (2)	−0.006 (2)
C4	0.051 (3)	0.052 (3)	0.042 (3)	−0.010 (3)	0.016 (2)	0.000 (2)
C5	0.053 (3)	0.063 (3)	0.047 (3)	−0.004 (3)	0.007 (2)	0.012 (2)
C6	0.038 (3)	0.051 (3)	0.071 (3)	−0.001 (2)	0.010 (3)	0.011 (3)
C7	0.037 (3)	0.044 (3)	0.048 (3)	−0.006 (2)	0.012 (2)	0.002 (2)
C8	0.037 (2)	0.036 (2)	0.038 (2)	−0.007 (2)	0.012 (2)	−0.002 (2)
C9	0.043 (3)	0.036 (2)	0.034 (2)	−0.007 (2)	0.014 (2)	−0.003 (2)
C10	0.046 (3)	0.038 (2)	0.053 (3)	−0.004 (2)	0.024 (2)	−0.002 (2)
C11	0.050 (3)	0.069 (3)	0.063 (3)	0.010 (3)	0.024 (2)	−0.006 (3)

Geometric parameters (Å, °)

Cl1—C1	1.735 (3)	C7—C11	1.499 (6)
O1—C10	1.406 (5)	C7—C8	1.421 (6)
O1—H1O	0.8200	C8—C9	1.409 (6)
N1—C8	1.373 (5)	C3—H3	0.9300
N1—C1	1.307 (5)	C4—H4	0.9300
C1—C2	1.419 (6)	C5—H5	0.9300
C2—C10	1.514 (6)	C6—H6	0.9300
C2—C3	1.359 (6)	C10—H10A	0.9700
C3—C9	1.412 (6)	C10—H10B	0.9700
C4—C9	1.408 (6)	C11—H11A	0.9600
C4—C5	1.365 (6)	C11—H11B	0.9600
C5—C6	1.391 (6)	C11—H11C	0.9600
C6—C7	1.368 (6)		
C10—O1—H1O	110.00	O1—C10—C2	113.5 (3)
C1—N1—C8	117.8 (3)	C2—C3—H3	119.00
Cl1—C1—N1	116.2 (3)	C9—C3—H3	119.00
Cl1—C1—C2	117.9 (3)	C5—C4—H4	120.00
N1—C1—C2	126.0 (3)	C9—C4—H4	120.00
C1—C2—C3	115.7 (4)	C4—C5—H5	120.00
C1—C2—C10	121.3 (4)	C6—C5—H5	120.00
C3—C2—C10	122.9 (4)	C5—C6—H6	118.00
C2—C3—C9	121.4 (4)	C7—C6—H6	118.00
C5—C4—C9	119.4 (4)	O1—C10—H10A	109.00
C4—C5—C6	120.2 (4)	O1—C10—H10B	109.00
C5—C6—C7	123.4 (4)	C2—C10—H10A	109.00
C6—C7—C11	122.5 (4)	C2—C10—H10B	109.00
C8—C7—C11	120.9 (4)	H10A—C10—H10B	108.00
C6—C7—C8	116.6 (4)	C7—C11—H11A	109.00
N1—C8—C9	121.0 (4)	C7—C11—H11B	109.00
C7—C8—C9	120.8 (4)	C7—C11—H11C	109.00
N1—C8—C7	118.2 (4)	H11A—C11—H11B	109.00
C3—C9—C4	122.4 (4)	H11A—C11—H11C	109.00
C4—C9—C8	119.6 (4)	H11B—C11—H11C	110.00
C3—C9—C8	118.0 (4)		
C8—N1—C1—Cl1	−179.2 (3)	C9—C4—C5—C6	0.5 (7)
C8—N1—C1—C2	1.0 (6)	C5—C4—C9—C3	179.6 (4)

C1—N1—C8—C7	179.8 (4)	C5—C4—C9—C8	0.4 (6)
C1—N1—C8—C9	−1.5 (6)	C4—C5—C6—C7	−0.7 (7)
Cl1—C1—C2—C3	−179.7 (3)	C5—C6—C7—C8	0.0 (7)
Cl1—C1—C2—C10	1.3 (5)	C5—C6—C7—C11	179.6 (4)
N1—C1—C2—C3	0.1 (6)	C6—C7—C8—N1	179.6 (4)
N1—C1—C2—C10	−178.9 (4)	C6—C7—C8—C9	0.9 (6)
C1—C2—C3—C9	−0.7 (6)	C11—C7—C8—N1	0.0 (6)
C10—C2—C3—C9	178.3 (4)	C11—C7—C8—C9	−178.7 (4)
C1—C2—C10—O1	178.4 (3)	N1—C8—C9—C3	1.0 (6)
C3—C2—C10—O1	−0.6 (5)	N1—C8—C9—C4	−179.8 (4)
C2—C3—C9—C4	−179.1 (4)	C7—C8—C9—C3	179.7 (4)
C2—C3—C9—C8	0.1 (6)	C7—C8—C9—C4	−1.1 (6)

Hydrogen-bond geometry (Å, °)

Cg1 is a centroid of the N1/C1–C3/C8/C9 ring.

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
O1—H1O···O1^{i}	0.82	1.90	2.712 (4)	174
C10—H10A···Cg1^{ii}	0.97	2.75	3.557 (4)	141

Symmetry codes: (i) −*x*, *y*−1/2, −*z*+1/2; (ii) *x*, *y*+1, *z*.

Fig. 1

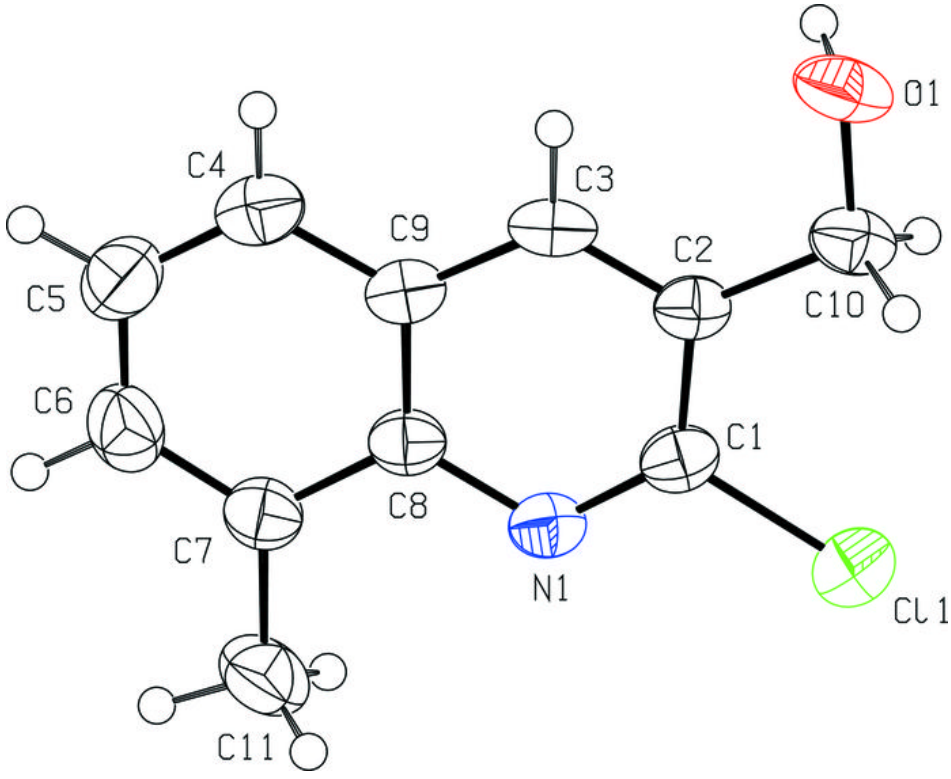
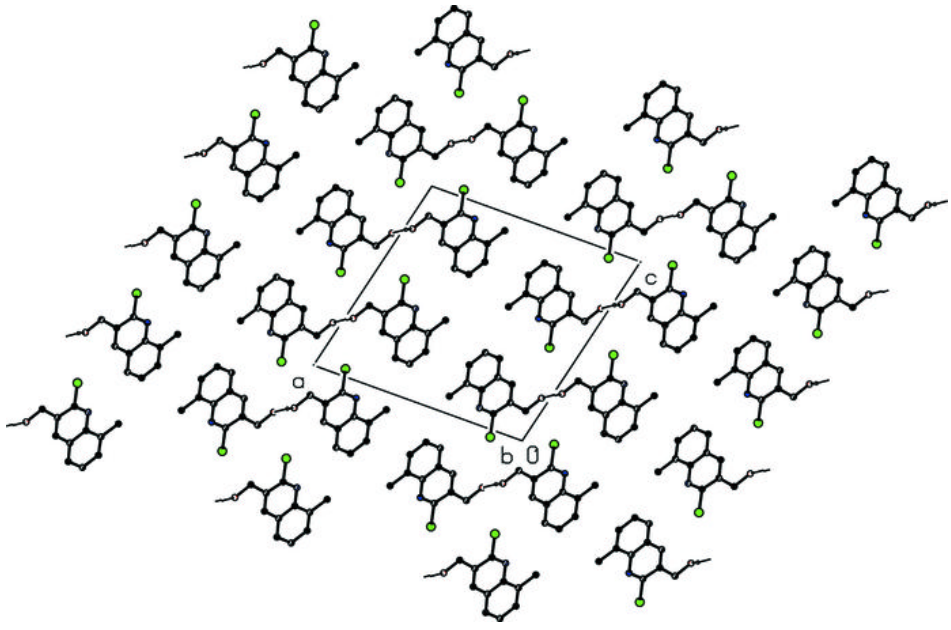


Fig. 2



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(2-Chloro-6-methylquinolin-3-yl)-methanol

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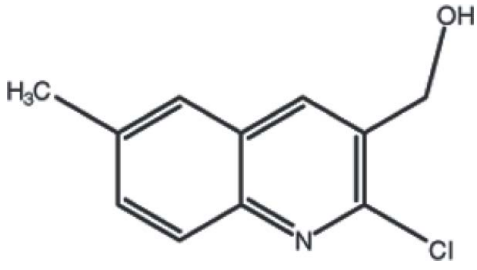
Key indicators: single-crystal X-ray study; T = 295 K; mean σ(C–C) = 0.007 Å; R factor = 0.085; wR factor = 0.222; data-to-parameter ratio = 13.1.

The title compound, $C_{11}H_{10}ClNO$, is close to being planar (r.m.s deviation for the non-H atoms = 0.026 Å). In the crystal, molecules are linked by O—H···O hydrogen bonds, generating $C(2)$ chains, and weak C—H···π interactions and aromatic π–π stacking interactions [centroid–centroid distance = 3.713 (3) Å] help to consolidate the sturcture.

Related literature

For a related structure and background references, see: Roopan *et al.* (2010). For the structure of the starting material, see: Khan *et al.* (2009). For hydrogen-bond motifs, see: Bernstein *et al.* (1995).



Experimental

Crystal data

$C_{11}H_{10}ClNO$
M_r = 207.65
Monoclinic, $P2_1/c$
a = 14.8091 (17) Å
b = 4.6387 (5) Å
c = 14.5098 (11) Å
β = 96.594 (9)°
V = 990.16 (17) Å^3
Z = 4
Mo $K\alpha$ radiation
μ = 0.35 mm^{-1}
T = 295 K
0.35 × 0.15 × 0.08 mm

Data collection

Oxford Xcalibur Eos(Nova) CCD diffractometer
Absorption correction: multi-scan *CrysAlis PRO* RED (Oxford Diffraction, 2009)
T_{min} = 0.888, T_{max} = 0.973
15485 measured reflections
1721 independent reflections
913 reflections with $I > 2\sigma(I)$
R_{int} = 0.136

Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.085
$wR(F^2)$ = 0.222
S = 0.94
1721 reflections
131 parameters
H atoms treated by a mixture of independent and constrained refinement
$\Delta\rho_{max}$ = 0.41 e Å^{-3}
$\Delta\rho_{min}$ = −0.46 e Å^{-3}

Table 1
Hydrogen-bond geometry (Å, °).

*Cg*1 is the centroid of the N1/C1/C6–C9 ring.

D—H···A	D—H	H···A	D···A	D—H···A
O1—H1*O*···O1^{i}	0.79 (6)	1.93 (6)	2.716 (5)	177 (7)
C10—H10*A*···*Cg*1^{ii}	0.97	2.73	3.526 (5)	139

Symmetry codes: (i) $-x, y-\frac{1}{2}, -z+\frac{1}{2}$; (ii) $x, y+1, z$.

Data collection: *CrysAlis PRO CCD* (Oxford Diffraction, 2009); cell refinement: *CrysAlis PRO CCD*; data reduction: *CrysAlis PRO RED* (Oxford Diffraction, 2009); program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *ORTEP-3* (Farrugia, 1997); software used to prepare material for publication: *WinGX* (Farrugia, 1999).

We thank the Department of Science and Technology, India, for use of the CCD facility set up under the FIST–DST program at SSCU, IISc. We also thank Professor T. N. Guru Row, IISc, Bangalore, for his help with the data collection. FNK thanks the DST for Fast Track Proposal funding.

Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: HB5471).

References

Bernstein, J., Davis, R. E., Shimoni, L. & Chang, N.-L. (1995). *Angew. Chem. Int. Ed. Engl.* **34**, 1555–1573.
Farrugia, L. J. (1997). *J. Appl. Cryst.* **30**, 565.
Farrugia, L. J. (1999). *J. Appl. Cryst.* **32**, 837–838.
Khan, F. N., Subashini, R., Roopan, S. M., Hathwar, V. R. & Ng, S. W. (2009). *Acta Cryst.* E**65**, o2686.
Oxford Diffraction (2009). *CrysAlis PRO CCD* and *CrysAlis PRO RED*. Oxford Diffraction Ltd, Yarnton, England.
Roopan, S. N., Khan, F. N., Kumar, A. S., Hathwar, V. R. & Akkurt, M. (2010). Acta Cryst. E00, o1542.
Sheldrick, G. M. (2008). *Acta Cryst.* A**64**, 112–122.

supplementary materials

Acta Cryst. (2010). E**66**, o1544 [**doi:10.1107/S1600536810020507**]

(2-Chloro-6-methylquinolin-3-yl)methanol

F. N. Khan, S. M. Roopan, A. K. Kushwaha, V. R. Hathwar and M. Akkurt

Comment

The importance and general background of the title compound is given in our earler paper (Roopan *et al.*, 2010).

The molecule of the title compound, (I), (Fig. 1), except the hydroxyl and methyl H atoms, is close to planar (r.m.s deviation 0.026 Å).

An intramolecular C—H···O hydrogen bond generates an S(5) ring motif (Bernstein *et al.*, 1995). Molecules of (I) are linked *via* O—H···O hydrogen bonds (Table 1, Fig. 2), an intermolecular C–H···π interactions between the aromatic H atoms of the ethenol substituent and the pyridine (N1/C1/C6–C9) ring of an adjacent molecule (Table 1), and π-π stacking interactions helping to stabilize the crystal structure [*Cg*1···*Cg*2(*x*, 1 + *y*, *z*) = 3.713 (3) Å, where *Cg*1 and *Cg*2 are centroids of the N1/C1/C6–C9 and C1–C6 rings, respectively].

Experimental

2-Chloro-6-methylquinoline-3-carbaldehyde (206 mg, 1 mmol), sodium borohydride (38 mg, 1 mmol) and catalytic amount of montmorillonite K-10 were taken in an open vessel and the resulting mixture was irradiating at 500 W for 5 min. Ethylacetate was poured into the reaction mixture and filtered off. The filtrated after removal of solvent was subjected to column chromatography packed with silica and ethyl acetate/petroleum ether was used as the eluant. Colourless plates of (I) were grown by solvent evaporation from a solution of the compound in chloroform.

Refinement

The H atom of the OH group were located in difference map and its positional parameters were refined freely [O1—H1O = 0.79 (6) Å]. The other H atoms were positioned geometrically, with C—H = 0.93–0.97 Å, and refined as riding with U_{iso}(H) = 1.2 or 1.5 U_{eq}(C). The value of R_{int} [0.136] is greater than 0.12. Since the overall quality of the data may be poor due to the crystal quality.

Figures

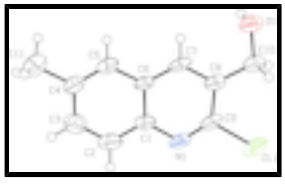


Fig. 1. View of the molecular structure of (I), showing 50% probability displacement ellipsoids.

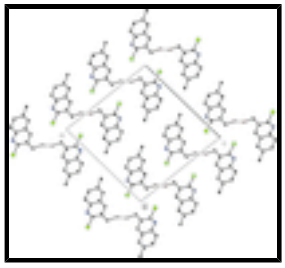


Fig. 2. Molecular packing and the hydrogen bonding of (I) viewed down *b* axis. The H atoms not involved in hydrogen bonds have been omitted for clarity.

(2-Chloro-6-methylquinolin-3-yl)methanol

Crystal data

$C_{11}H_{10}ClNO$	$F(000) = 432$
$M_r = 207.65$	$D_x = 1.393$ Mg m^{-3}
Monoclinic, $P2_1/c$	Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å
Hall symbol: -P 2ybc	Cell parameters from 865 reflections
$a = 14.8091$ (17) Å	$\theta = 2.7–21.4°$
$b = 4.6387$ (5) Å	$\mu = 0.35$ mm^{-1}
$c = 14.5098$ (11) Å	$T = 295$ K
$\beta = 96.594$ (9)°	Plate, colourless
$V = 990.16$ (17) Å^3	0.35 × 0.15 × 0.08 mm
$Z = 4$	

Data collection

Oxford Xcalibur Eos(Nova) CCD diffractometer	1721 independent reflections
Radiation source: Enhance (Mo) X-ray Source	913 reflections with $I > 2\sigma(I)$
graphite	$R_{int} = 0.136$
ω scans	$\theta_{max} = 25.0°$, $\theta_{min} = 3.0°$
Absorption correction: multi-scan *CrysAlis PRO* RED (Oxford Diffraction, 2009)	$h = -17\rightarrow17$
$T_{min} = 0.888$, $T_{max} = 0.973$	$k = -5\rightarrow5$
15485 measured reflections	$l = -17\rightarrow17$

Refinement

Refinement on F^2	Primary atom site location: structure-invariant direct methods
Least-squares matrix: full	Secondary atom site location: difference Fourier map
$R[F^2 > 2\sigma(F^2)] = 0.085$	Hydrogen site location: inferred from neighbouring sites
$wR(F^2) = 0.222$	H atoms treated by a mixture of independent and constrained refinement
$S = 0.94$	$w = 1/[\sigma^2(F_o^2) + (0.1359P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
1721 reflections	$(\Delta/\sigma)_{max} < 0.001$

131 parameters	$\Delta\rho_{max} = 0.41$ e Å^{-3}
0 restraints	$\Delta\rho_{min} = -0.46$ e Å^{-3}

Special details

Geometry. Bond distances, angles *etc*. have been calculated using the rounded fractional coordinates. All su's are estimated from the variances of the (full) variance-covariance matrix. The cell e.s.d.'s are taken into account in the estimation of distances, angles and torsion angles

Refinement. Refinement on F^2 for ALL reflections except those flagged by the user for potential systematic errors. Weighted *R*-factors *wR* and all goodnesses of fit *S* are based on F^2, conventional *R*-factors *R* are based on *F*, with *F* set to zero for negative F^2. The observed criterion of $F^2 > \sigma(F^2)$ is used only for calculating -*R*-factor-obs *etc*. and is not relevant to the choice of reflections for refinement. *R*-factors based on F^2 are statistically about twice as large as those based on *F*, and *R*-factors based on ALL data will be even larger.

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å^2)

	x	*y*	*z*	U_{iso}*/U_{eq}
Cl1	0.13152 (10)	0.6780 (3)	−0.04947 (8)	0.0717 (6)
O1	0.0334 (3)	0.9035 (7)	0.2189 (2)	0.0580 (14)
N1	0.2440 (3)	0.3573 (8)	0.0535 (2)	0.0448 (14)
C1	0.2832 (3)	0.2406 (10)	0.1357 (3)	0.0409 (16)
C2	0.3535 (3)	0.0442 (11)	0.1360 (3)	0.0554 (19)
C3	0.3939 (3)	−0.0710 (12)	0.2179 (4)	0.0583 (19)
C4	0.3645 (3)	0.0074 (11)	0.3034 (3)	0.0529 (19)
C5	0.2963 (3)	0.1980 (10)	0.3040 (3)	0.0454 (16)
C6	0.2534 (3)	0.3238 (9)	0.2222 (3)	0.0369 (16)
C7	0.1817 (3)	0.5231 (9)	0.2194 (3)	0.0438 (16)
C8	0.1412 (3)	0.6383 (9)	0.1376 (3)	0.0414 (16)
C9	0.1799 (3)	0.5394 (10)	0.0572 (3)	0.0454 (16)
C10	0.0641 (3)	0.8449 (9)	0.1312 (3)	0.0465 (17)
C11	0.4114 (4)	−0.1220 (14)	0.3929 (4)	0.078 (2)
H1O	0.014 (4)	0.756 (13)	0.235 (4)	0.0870*
H2	0.37380	−0.01050	0.08020	0.0670*
H3	0.44130	−0.20220	0.21680	0.0700*
H5	0.27670	0.24850	0.36050	0.0550*
H7	0.16080	0.57900	0.27480	0.0520*
H10A	0.08270	1.02420	0.10460	0.0560*
H10B	0.01400	0.76690	0.08970	0.0560*
H11A	0.37370	−0.09620	0.44180	0.1170*
H11B	0.46870	−0.02720	0.40930	0.1170*
H11C	0.42160	−0.32400	0.38410	0.1170*

Atomic displacement parameters (Å^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Cl1	0.0999 (12)	0.0913 (12)	0.0243 (7)	0.0084 (8)	0.0089 (6)	0.0093 (6)
O1	0.085 (3)	0.051 (2)	0.043 (2)	0.0031 (19)	0.0292 (17)	−0.0008 (17)

N1	0.066 (3)	0.048 (2)	0.0223 (19)	−0.001 (2)	0.0139 (17)	−0.0045 (16)
C1	0.048 (3)	0.051 (3)	0.025 (2)	−0.003 (2)	0.0102 (18)	−0.007 (2)
C2	0.061 (3)	0.073 (4)	0.035 (3)	−0.005 (3)	0.018 (2)	−0.007 (2)
C3	0.056 (3)	0.069 (4)	0.051 (3)	0.004 (3)	0.011 (2)	−0.009 (3)
C4	0.056 (3)	0.070 (4)	0.033 (3)	−0.001 (3)	0.007 (2)	0.006 (2)
C5	0.056 (3)	0.056 (3)	0.025 (2)	−0.005 (2)	0.008 (2)	−0.004 (2)
C6	0.050 (3)	0.041 (3)	0.021 (2)	−0.001 (2)	0.0102 (18)	−0.0049 (18)
C7	0.063 (3)	0.053 (3)	0.017 (2)	−0.009 (3)	0.0118 (19)	−0.0055 (19)
C8	0.056 (3)	0.042 (3)	0.028 (2)	−0.007 (2)	0.0125 (19)	−0.003 (2)
C9	0.068 (3)	0.049 (3)	0.020 (2)	−0.005 (3)	0.009 (2)	0.000 (2)
C10	0.070 (3)	0.037 (3)	0.035 (3)	−0.003 (2)	0.017 (2)	−0.003 (2)
C11	0.087 (4)	0.105 (5)	0.041 (3)	0.009 (3)	0.001 (3)	0.006 (3)

Geometric parameters (Å, °)

Cl1—C9	1.751 (5)	C7—C8	1.375 (6)
O1—C10	1.426 (5)	C8—C9	1.433 (6)
O1—H1O	0.79 (6)	C8—C10	1.485 (6)
N1—C9	1.276 (6)	C2—H2	0.9300
N1—C1	1.376 (5)	C3—H3	0.9300
C1—C2	1.383 (7)	C5—H5	0.9300
C1—C6	1.431 (6)	C7—H7	0.9300
C2—C3	1.376 (7)	C10—H10A	0.9700
C3—C4	1.409 (7)	C10—H10B	0.9700
C4—C11	1.524 (7)	C11—H11A	0.9600
C4—C5	1.343 (7)	C11—H11B	0.9600
C5—C6	1.407 (6)	C11—H11C	0.9600
C6—C7	1.405 (6)		
C10—O1—H1O	105 (4)	O1—C10—C8	112.9 (4)
C1—N1—C9	117.8 (4)	C1—C2—H2	120.00
N1—C1—C2	120.3 (4)	C3—C2—H2	120.00
N1—C1—C6	120.8 (4)	C2—C3—H3	120.00
C2—C1—C6	118.9 (4)	C4—C3—H3	120.00
C1—C2—C3	120.7 (4)	C4—C5—H5	119.00
C2—C3—C4	120.8 (4)	C6—C5—H5	119.00
C3—C4—C11	119.5 (4)	C6—C7—H7	119.00
C5—C4—C11	121.6 (4)	C8—C7—H7	119.00
C3—C4—C5	119.0 (4)	O1—C10—H10A	109.00
C4—C5—C6	122.3 (4)	O1—C10—H10B	109.00
C1—C6—C5	118.3 (4)	C8—C10—H10A	109.00
C5—C6—C7	124.3 (4)	C8—C10—H10B	109.00
C1—C6—C7	117.4 (4)	H10A—C10—H10B	108.00
C6—C7—C8	122.3 (4)	C4—C11—H11A	110.00
C7—C8—C10	124.1 (4)	C4—C11—H11B	110.00
C9—C8—C10	122.2 (4)	C4—C11—H11C	110.00
C7—C8—C9	113.8 (4)	H11A—C11—H11B	109.00
Cl1—C9—N1	115.9 (3)	H11A—C11—H11C	110.00
N1—C9—C8	128.0 (4)	H11B—C11—H11C	109.00
Cl1—C9—C8	116.2 (3)		

C9—N1—C1—C2	−179.4 (4)	C11—C4—C5—C6	178.8 (5)
C9—N1—C1—C6	−0.6 (7)	C4—C5—C6—C1	1.0 (7)
C1—N1—C9—Cl1	−179.3 (3)	C4—C5—C6—C7	179.8 (5)
C1—N1—C9—C8	−1.1 (7)	C1—C6—C7—C8	−0.5 (6)
N1—C1—C2—C3	179.2 (5)	C5—C6—C7—C8	−179.3 (4)
C6—C1—C2—C3	0.4 (7)	C6—C7—C8—C9	−0.9 (6)
N1—C1—C6—C5	−179.8 (4)	C6—C7—C8—C10	178.7 (4)
N1—C1—C6—C7	1.4 (6)	C7—C8—C9—Cl1	−180.0 (3)
C2—C1—C6—C5	−1.0 (6)	C7—C8—C9—N1	1.8 (7)
C2—C1—C6—C7	−179.8 (4)	C10—C8—C9—Cl1	0.4 (6)
C1—C2—C3—C4	0.2 (8)	C10—C8—C9—N1	−177.8 (4)
C2—C3—C4—C5	−0.2 (7)	C7—C8—C10—O1	−2.5 (6)
C2—C3—C4—C11	−179.4 (5)	C9—C8—C10—O1	177.1 (4)
C3—C4—C5—C6	−0.4 (7)		

Hydrogen-bond geometry (Å, °)

Cg1 is the centroid of the N1/C1/C6–C9 ring.

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
O1—H1O···O1^{i}	0.79 (6)	1.93 (6)	2.716 (5)	177 (7)
C10—H10A···Cg1^{ii}	0.97	2.73	3.526 (5)	139

Symmetry codes: (i) −*x*, *y*−1/2, −*z*+1/2; (ii) *x*, *y*+1, *z*.

Fig. 1

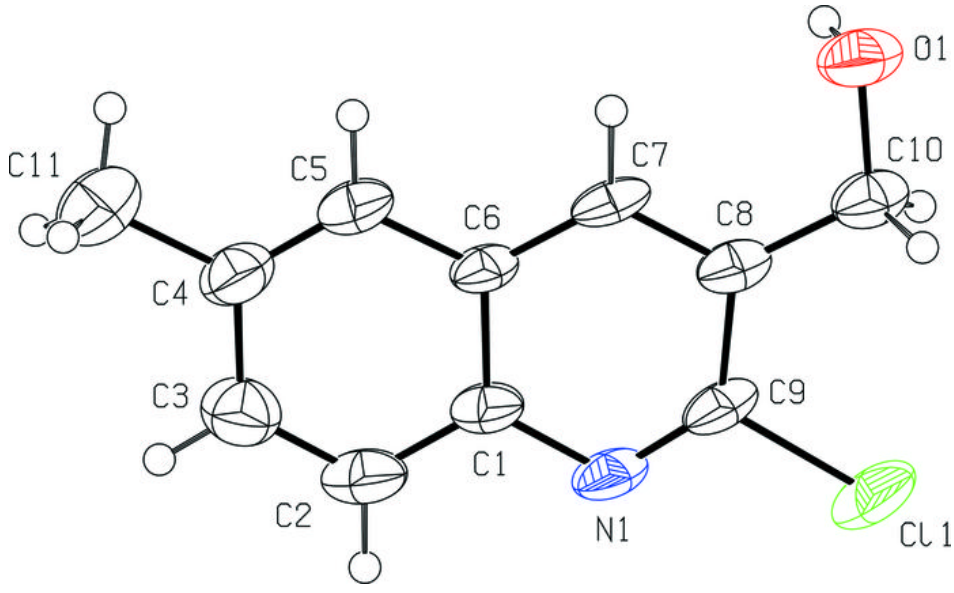
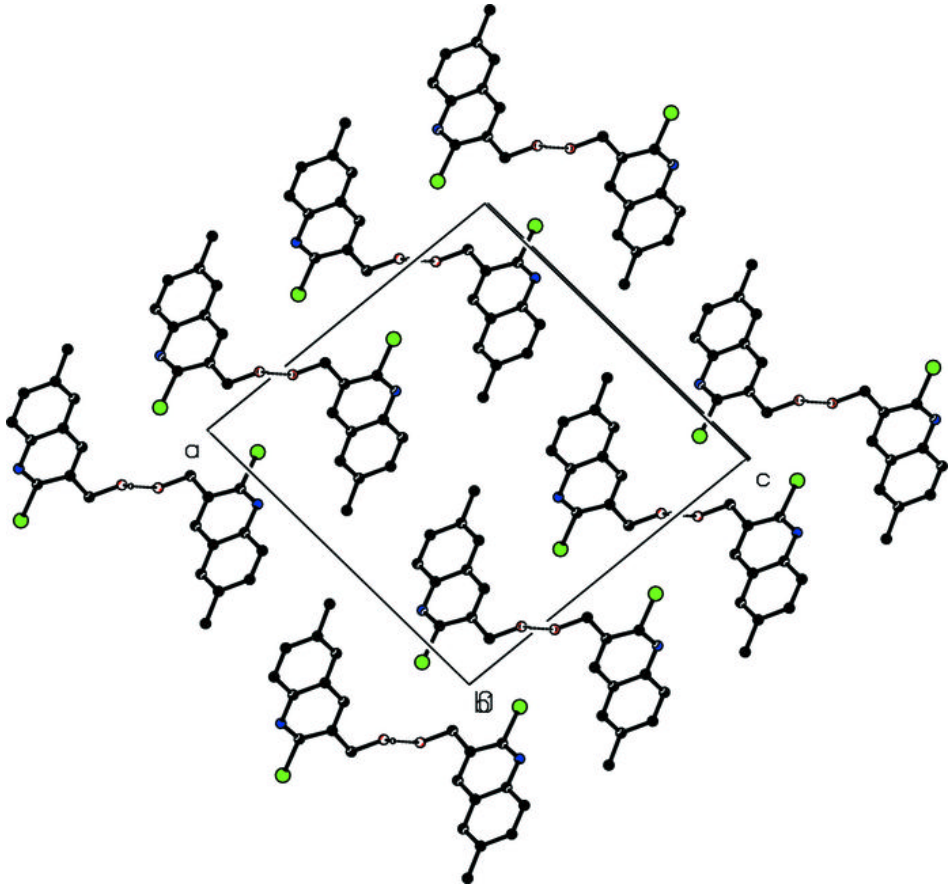


Fig. 2



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Ethyl 3-(4-methylbenzylidene)carbazate

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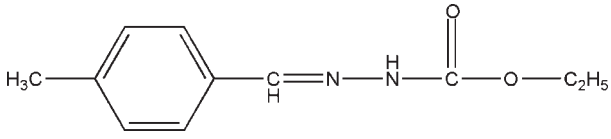
Key indicators: single-crystal X-ray study; T = 293 K; mean σ(C–C) = 0.002 Å; R factor = 0.055; wR factor = 0.185; data-to-parameter ratio = 18.9.

There are two molecules in the asymmetric unit of the title compound, $C_{11}H_{14}N_2O_2$, which have similar conformations. In the crystal, the molecules are linked by N—H···O hydrogen bonds, generating $C(4)$ chains propagating in [001].

Related literature

For background to Schiff bases with additional donor groups, see: Borisova *et al.* (2007); Gradinaru *et al.* (2007). For a related structure, see: Li *et al.* (2009).



Experimental

Crystal data

$C_{11}H_{14}N_2O_2$ M_r = 206.24
Monoclinic, $P2_1/c$
a = 15.251 (3) Å
b = 8.2853 (17) Å
c = 18.139 (4) Å
β = 101.85 (3)°
V = 2243.3 (8) Å^3
Z = 8
Mo $K\alpha$ radiation
μ = 0.09 mm^{-1}
T = 293 K
0.22 × 0.21 × 0.20 mm

Data collection

Bruker SMART CCD diffractometer
21172 measured reflections
5128 independent reflections
3927 reflections with $I > 2\sigma(I)$
R_{int} = 0.037

Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.055
$wR(F^2)$ = 0.185
S = 1.08
5128 reflections
272 parameters
H-atom parameters constrained
$\Delta\rho_{max}$ = 0.24 e Å^{-3}
$\Delta\rho_{min}$ = −0.30 e Å^{-3}

Table 1
Hydrogen-bond geometry (Å, °).

D—H···A	D—H	H···A	D···A	D—H···A
N1B—H1BA···O1A	0.86	2.03	2.8747 (17)	165
N1A—H1AA···O1B^{i}	0.86	2.13	2.9383 (17)	157

Symmetry code: (i) $x, -y+\frac{3}{2}, z+\frac{1}{2}$.

Data collection: *SMART* (Bruker, 1997); cell refinement: *SAINT* (Bruker, 1997); data reduction: *SAINT*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *SHELXTL* (Sheldrick, 2008); software used to prepare material for publication: *SHELXTL*.

Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: HB5473).

References

Borisova, N. E., Reshetova, M. D. & Ustynyuk, Y. A. (2007). *Chem. Rev.* **107**, 46–79.
Bruker (1997). *SMART* and *SAINT* Bruker AXS Inc., Madison, Wisconsin, USA.
Gradinaru, J., Forni, A. & Druta, V. (2007). *Inorg. Chem.* **46**, 884–895.
Li, Y.-F., Liu, H.-X. & Jian, F.-F. (2009). *Acta Cryst.* E**65**, o2959.
Sheldrick, G. M. (2008). *Acta Cryst.* A**64**, 112–122.

supplementary materials

Acta Cryst. (2010). E**66**, o1565 [**doi:10.1107/S1600536810020623**]

Ethyl 3-(4-methylbenzylidene)carbazate

Y.-F. Li, W.-H. Sheng and F.-F. Jian

Comment

Schiff bases bearing additional donor groups represent the important class of heteropolydentate ligands capable of forming mono-, bi-, and polynuclear complexes with metals in coordination chemistry.(Borisova, *et al.*, 2007). Meanwhile, it is an important intermediate compound which have been reported to be compounds with second-order nonlinear optical (NLO) materials (Gradinaru *et al.*, 2007). As part of our search for new schiff base compounds we synthesized the title compound (I), and describe its structure here. The title compound contains two independent molecules in the unit. The dihedral angle between the two independent benzene rings is [72.32 (11)°]. The C1A/C2A/O2A/C3A/O1A/N1A/N2A and C1B/C2B/O2B/C3B/O1B/N1B/N2B planes form dihedral angles of 4.43 (11)° and 2.33 (12)°, respectively, with the benzene planes. In the crystal lattice, the N—H···O intramolecular hydrogen bonds which form chains stable the molecule structures.

Bond lengths and angles are comparable to a related compound (Li *et al.*, 2009).

Experimental

A mixture of 4-methylbenzaldehyde (0.1 mol), and ethyl carbazate (0.1 mol) was stirred in refluxing ethanol (20 ml) for 4 h to afford the title compound (0.092 mol, yield 92%). Colourless blocks of (I) were obtained by recrystallization from ethanol at room temperature.

Refinement

H atoms were fixed geometrically and allowed to ride on their attached atoms, with C—H distances=0.97 Å, and with U_{iso}=1.2–1.5U_{eq}.

Figures

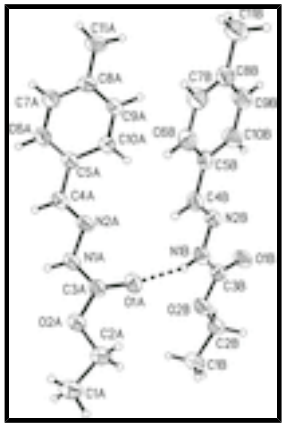


Fig. 1. The structure of (I) showing 30% probability displacement ellipsoids. The dashed line indicates a hydrogen bond.

Ethyl 3-(4-methylbenzylidene)carbazate

Crystal data

$C_{11}H_{14}N_2O_2$	$F(000) = 880$
$M_r = 206.24$	$D_x = 1.221$ Mg m^{-3}
Monoclinic, $P2_1/c$	Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å
Hall symbol: -P 2ybc	Cell parameters from 3927 reflections
$a = 15.251$ (3) Å	$\theta = 3.1$–$27.5°$
$b = 8.2853$ (17) Å	$\mu = 0.09$ mm^{-1}
$c = 18.139$ (4) Å	$T = 293$ K
$\beta = 101.85$ (3)°	Block, colorless
$V = 2243.3$ (8) Å^3	0.22 × 0.21 × 0.20 mm
$Z = 8$	

Data collection

Bruker SMART CCD diffractometer	3927 reflections with $I > 2\sigma(I)$
Radiation source: fine-focus sealed tube	$R_{int} = 0.037$
graphite	$\theta_{max} = 27.5°$, $\theta_{min} = 3.1°$
ω scans	$h = -19\rightarrow19$
21172 measured reflections	$k = -10\rightarrow10$
5128 independent reflections	$l = -20\rightarrow23$

Refinement

Refinement on F^2	Secondary atom site location: difference Fourier map
Least-squares matrix: full	Hydrogen site location: inferred from neighbouring sites
$R[F^2 > 2\sigma(F^2)] = 0.055$	H-atom parameters constrained
$wR(F^2) = 0.185$	$w = 1/[\sigma^2(F_o^2) + (0.1115P)^2 + 0.1779P]$ where $P = (F_o^2 + 2F_c^2)/3$
$S = 1.08$	$(\Delta/\sigma)_{max} < 0.001$
5128 reflections	$\Delta\rho_{max} = 0.24$ e Å^{-3}
272 parameters	$\Delta\rho_{min} = -0.30$ e Å^{-3}
0 restraints	Extinction correction: *SHELXL97* (Sheldrick, 2008), $Fc^* = kFc[1+0.001xFc^2\lambda^3/\sin(2\theta)]^{-1/4}$
Primary atom site location: structure-invariant direct methods	Extinction coefficient: 0.064 (6)

Special details

Geometry. All e.s.d.'s (except the e.s.d. in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell e.s.d.'s are taken into account individually in the estimation of e.s.d.'s in distances, angles and torsion angles; correlations

between e.s.d.'s in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell e.s.d.'s is used for estimating e.s.d.'s involving l.s. planes.

Refinement. Refinement of F^2 against ALL reflections. The weighted *R*-factor *wR* and goodness of fit *S* are based on F^2, conventional *R*-factors *R* are based on *F*, with *F* set to zero for negative F^2. The threshold expression of $F^2 > \sigma(F^2)$ is used only for calculating *R*-factors(gt) *etc*. and is not relevant to the choice of reflections for refinement. *R*-factors based on F^2 are statistically about twice as large as those based on *F*, and *R*- factors based on ALL data will be even larger.

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å^2)

	x	*y*	*z*	U_{iso}*/U_{eq}
N2A	0.37582 (8)	0.81674 (15)	0.31081 (7)	0.0581 (3)
O2A	0.59141 (7)	0.95340 (14)	0.38400 (6)	0.0669 (3)
O1B	0.46162 (7)	0.81088 (16)	0.00172 (6)	0.0724 (4)
N1A	0.46022 (8)	0.83572 (16)	0.35399 (7)	0.0617 (3)
H1AA	0.4760	0.7844	0.3958	0.074*
O2B	0.57247 (7)	0.80498 (16)	0.10534 (6)	0.0720 (3)
N1B	0.44923 (9)	0.93461 (17)	0.11143 (6)	0.0642 (4)
H1BA	0.4757	0.9577	0.1568	0.077*
N2B	0.36356 (8)	0.98639 (16)	0.08381 (6)	0.0607 (3)
C5A	0.23044 (9)	0.70401 (17)	0.29857 (8)	0.0542 (3)
O1A	0.50636 (8)	1.00212 (17)	0.26947 (6)	0.0762 (4)
C3A	0.51804 (10)	0.93606 (19)	0.32980 (7)	0.0570 (3)
C5B	0.23472 (10)	1.12384 (18)	0.10486 (7)	0.0574 (4)
C3B	0.49157 (10)	0.84683 (19)	0.06658 (8)	0.0602 (4)
C8A	0.04993 (10)	0.66046 (18)	0.22712 (9)	0.0599 (4)
C4A	0.32349 (10)	0.72637 (19)	0.33783 (8)	0.0598 (4)
H4AA	0.3444	0.6734	0.3832	0.072*
C4B	0.32641 (11)	1.06587 (18)	0.12903 (8)	0.0598 (4)
H4BA	0.3578	1.0871	0.1777	0.072*
C9A	0.10661 (10)	0.7566 (2)	0.19601 (8)	0.0646 (4)
H9AA	0.0845	0.8079	0.1504	0.077*
C10A	0.19508 (10)	0.77894 (19)	0.23044 (8)	0.0613 (4)
H10A	0.2314	0.8447	0.2079	0.074*
C6B	0.19536 (12)	1.2192 (2)	0.15151 (9)	0.0701 (4)
H6BA	0.2277	1.2459	0.1992	0.084*
C6A	0.17352 (12)	0.6081 (2)	0.32983 (9)	0.0718 (4)
H6AA	0.1954	0.5560	0.3753	0.086*
C2A	0.65982 (10)	1.0586 (2)	0.36603 (10)	0.0683 (4)
H2AB	0.6337	1.1604	0.3461	0.082*
H2AC	0.6883	1.0087	0.3286	0.082*
C10B	0.18358 (12)	1.0863 (2)	0.03459 (9)	0.0721 (4)
H10B	0.2083	1.0225	0.0019	0.087*
C8B	0.05775 (12)	1.2381 (2)	0.05846 (10)	0.0684 (4)
C9B	0.09748 (13)	1.1412 (2)	0.01226 (10)	0.0763 (5)
H9BA	0.0649	1.1128	−0.0351	0.092*
C2B	0.62646 (11)	0.7096 (3)	0.06543 (10)	0.0753 (5)
H2BB	0.6391	0.7694	0.0228	0.090*
H2BC	0.5954	0.6108	0.0470	0.090*

C7A	0.08469 (12)	0.5880 (2)	0.29489 (10)	0.0742 (5)
H7AA	0.0478	0.5240	0.3177	0.089*
C11A	−0.04662 (11)	0.6351 (3)	0.18905 (11)	0.0790 (5)
H11A	−0.0593	0.6943	0.1426	0.118*
H11B	−0.0848	0.6726	0.2214	0.118*
H11C	−0.0572	0.5222	0.1789	0.118*
C1B	0.71149 (13)	0.6717 (3)	0.12010 (12)	0.0866 (6)
H1BB	0.7493	0.6069	0.0957	0.130*
H1BC	0.6979	0.6137	0.1622	0.130*
H1BD	0.7418	0.7704	0.1375	0.130*
C11B	−0.03689 (13)	1.2974 (3)	0.03316 (13)	0.0880 (6)
H11D	−0.0531	1.3622	0.0722	0.132*
H11E	−0.0768	1.2068	0.0228	0.132*
H11F	−0.0413	1.3611	−0.0117	0.132*
C7B	0.10868 (13)	1.2758 (2)	0.12853 (10)	0.0751 (5)
H7BA	0.0841	1.3406	0.1609	0.090*
C1A	0.72665 (12)	1.0856 (3)	0.43748 (11)	0.0850 (5)
H1AB	0.7731	1.1560	0.4280	0.127*
H1AC	0.7523	0.9842	0.4563	0.127*
H1AD	0.6975	1.1342	0.4741	0.127*

Atomic displacement parameters (Å^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
N2A	0.0505 (6)	0.0690 (8)	0.0487 (6)	0.0009 (5)	−0.0044 (5)	−0.0021 (5)
O2A	0.0542 (6)	0.0850 (7)	0.0551 (6)	−0.0096 (5)	−0.0035 (5)	0.0072 (5)
O1B	0.0614 (6)	0.1030 (9)	0.0472 (6)	0.0021 (6)	−0.0020 (5)	−0.0095 (5)
N1A	0.0536 (6)	0.0772 (8)	0.0471 (6)	−0.0042 (6)	−0.0061 (5)	0.0053 (5)
O2B	0.0601 (6)	0.1023 (9)	0.0481 (5)	0.0065 (6)	−0.0017 (5)	−0.0001 (5)
N1B	0.0608 (7)	0.0869 (9)	0.0402 (6)	0.0023 (6)	−0.0008 (5)	−0.0012 (5)
N2B	0.0597 (7)	0.0715 (8)	0.0474 (6)	−0.0014 (6)	0.0031 (5)	0.0050 (5)
C5A	0.0523 (7)	0.0578 (8)	0.0488 (7)	0.0031 (5)	0.0018 (6)	−0.0010 (5)
O1A	0.0757 (7)	0.1016 (9)	0.0463 (6)	−0.0109 (6)	0.0007 (5)	0.0080 (5)
C3A	0.0547 (7)	0.0680 (9)	0.0450 (7)	0.0018 (6)	0.0023 (6)	−0.0040 (6)
C5B	0.0662 (8)	0.0594 (8)	0.0453 (7)	−0.0043 (6)	0.0082 (6)	0.0064 (6)
C3B	0.0567 (8)	0.0755 (9)	0.0442 (7)	−0.0056 (6)	0.0007 (6)	0.0042 (6)
C8A	0.0523 (7)	0.0629 (8)	0.0612 (8)	0.0035 (6)	0.0042 (6)	−0.0077 (6)
C4A	0.0572 (8)	0.0666 (9)	0.0496 (7)	0.0027 (6)	−0.0034 (6)	0.0031 (6)
C4B	0.0657 (8)	0.0679 (9)	0.0431 (6)	−0.0045 (7)	0.0051 (6)	0.0040 (6)
C9A	0.0560 (8)	0.0822 (10)	0.0514 (7)	0.0064 (7)	0.0014 (6)	0.0093 (7)
C10A	0.0529 (7)	0.0740 (9)	0.0550 (8)	0.0014 (6)	0.0061 (6)	0.0110 (7)
C6B	0.0803 (10)	0.0777 (10)	0.0496 (8)	0.0010 (8)	0.0072 (7)	−0.0044 (7)
C6A	0.0706 (9)	0.0798 (11)	0.0590 (8)	−0.0036 (8)	−0.0009 (7)	0.0188 (7)
C2A	0.0554 (8)	0.0760 (10)	0.0712 (9)	−0.0050 (7)	0.0075 (7)	0.0037 (8)
C10B	0.0715 (10)	0.0894 (12)	0.0523 (8)	0.0067 (8)	0.0053 (7)	−0.0092 (7)
C8B	0.0705 (9)	0.0667 (9)	0.0666 (9)	0.0018 (7)	0.0104 (8)	0.0097 (7)
C9B	0.0732 (10)	0.0930 (12)	0.0564 (8)	0.0049 (9)	−0.0014 (8)	−0.0046 (8)
C2B	0.0592 (9)	0.1050 (13)	0.0598 (9)	0.0058 (8)	0.0076 (7)	0.0037 (8)

C7A	0.0643 (9)	0.0819 (11)	0.0731 (10)	−0.0112 (8)	0.0068 (8)	0.0157 (8)
C11A	0.0554 (8)	0.0934 (13)	0.0820 (11)	−0.0039 (8)	0.0001 (8)	−0.0089 (9)
C1B	0.0635 (10)	0.1040 (14)	0.0834 (12)	0.0040 (9)	−0.0052 (9)	0.0051 (10)
C11B	0.0766 (12)	0.0861 (13)	0.0963 (14)	0.0124 (9)	0.0058 (10)	0.0095 (10)
C7B	0.0807 (11)	0.0774 (11)	0.0670 (10)	0.0106 (8)	0.0146 (9)	−0.0050 (8)
C1A	0.0609 (9)	0.1028 (14)	0.0836 (12)	−0.0139 (9)	−0.0028 (9)	−0.0013 (10)

Geometric parameters (Å, °)

N2A—C4A	1.2641 (19)	C6B—H6BA	0.9300
N2A—N1A	1.3716 (17)	C6A—C7A	1.383 (2)
O2A—C3A	1.3371 (17)	C6A—H6AA	0.9300
O2A—C2A	1.4471 (19)	C2A—C1A	1.492 (2)
O1B—C3B	1.2086 (18)	C2A—H2AB	0.9700
N1A—C3A	1.349 (2)	C2A—H2AC	0.9700
N1A—H1AA	0.8600	C10B—C9B	1.370 (3)
O2B—C3B	1.3345 (18)	C10B—H10B	0.9300
O2B—C2B	1.439 (2)	C8B—C7B	1.382 (3)
N1B—C3B	1.350 (2)	C8B—C9B	1.386 (3)
N1B—N2B	1.3687 (18)	C8B—C11B	1.505 (3)
N1B—H1BA	0.8600	C9B—H9BA	0.9300
N2B—C4B	1.2722 (19)	C2B—C1B	1.495 (2)
C5A—C6A	1.382 (2)	C2B—H2BB	0.9700
C5A—C10A	1.389 (2)	C2B—H2BC	0.9700
C5A—C4A	1.4631 (19)	C7A—H7AA	0.9300
O1A—C3A	1.2036 (17)	C11A—H11A	0.9600
C5B—C6B	1.382 (2)	C11A—H11B	0.9600
C5B—C10B	1.386 (2)	C11A—H11C	0.9600
C5B—C4B	1.458 (2)	C1B—H1BB	0.9600
C8A—C7A	1.373 (2)	C1B—H1BC	0.9600
C8A—C9A	1.379 (2)	C1B—H1BD	0.9600
C8A—C11A	1.507 (2)	C11B—H11D	0.9600
C4A—H4AA	0.9300	C11B—H11E	0.9600
C4B—H4BA	0.9300	C11B—H11F	0.9600
C9A—C10A	1.378 (2)	C7B—H7BA	0.9300
C9A—H9AA	0.9300	C1A—H1AB	0.9600
C10A—H10A	0.9300	C1A—H1AC	0.9600
C6B—C7B	1.384 (2)	C1A—H1AD	0.9600
C4A—N2A—N1A	116.09 (12)	C1A—C2A—H2AC	110.3
C3A—O2A—C2A	115.62 (12)	H2AB—C2A—H2AC	108.6
C3A—N1A—N2A	118.98 (12)	C9B—C10B—C5B	121.43 (16)
C3A—N1A—H1AA	120.5	C9B—C10B—H10B	119.3
N2A—N1A—H1AA	120.5	C5B—C10B—H10B	119.3
C3B—O2B—C2B	116.12 (12)	C7B—C8B—C9B	116.98 (16)
C3B—N1B—N2B	119.14 (12)	C7B—C8B—C11B	121.96 (17)
C3B—N1B—H1BA	120.4	C9B—C8B—C11B	121.05 (16)
N2B—N1B—H1BA	120.4	C10B—C9B—C8B	121.66 (16)
C4B—N2B—N1B	116.38 (12)	C10B—C9B—H9BA	119.2
C6A—C5A—C10A	117.40 (13)	C8B—C9B—H9BA	119.2

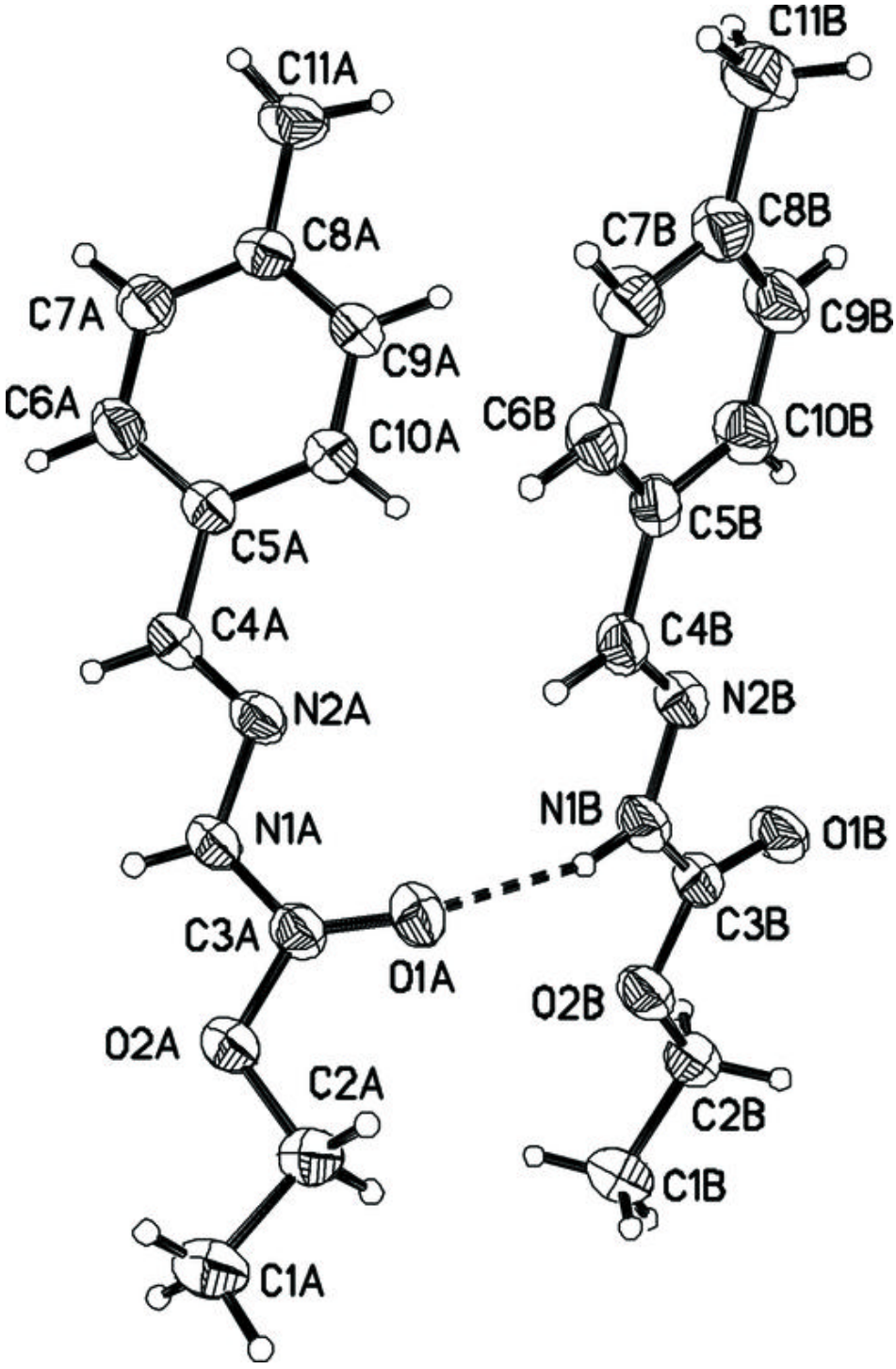
C6A—C5A—C4A	120.10 (13)	O2B—C2B—C1B	106.82 (15)
C10A—C5A—C4A	122.49 (13)	O2B—C2B—H2BB	110.4
O1A—C3A—O2A	124.40 (14)	C1B—C2B—H2BB	110.4
O1A—C3A—N1A	126.25 (14)	O2B—C2B—H2BC	110.4
O2A—C3A—N1A	109.35 (12)	C1B—C2B—H2BC	110.4
C6B—C5B—C10B	117.28 (15)	H2BB—C2B—H2BC	108.6
C6B—C5B—C4B	120.97 (13)	C8A—C7A—C6A	121.28 (15)
C10B—C5B—C4B	121.75 (15)	C8A—C7A—H7AA	119.4
O1B—C3B—O2B	124.93 (15)	C6A—C7A—H7AA	119.4
O1B—C3B—N1B	125.97 (15)	C8A—C11A—H11A	109.5
O2B—C3B—N1B	109.10 (12)	C8A—C11A—H11B	109.5
C7A—C8A—C9A	117.39 (14)	H11A—C11A—H11B	109.5
C7A—C8A—C11A	120.69 (15)	C8A—C11A—H11C	109.5
C9A—C8A—C11A	121.92 (15)	H11A—C11A—H11C	109.5
N2A—C4A—C5A	120.84 (13)	H11B—C11A—H11C	109.5
N2A—C4A—H4AA	119.6	C2B—C1B—H1BB	109.5
C5A—C4A—H4AA	119.6	C2B—C1B—H1BC	109.5
N2B—C4B—C5B	120.22 (13)	H1BB—C1B—H1BC	109.5
N2B—C4B—H4BA	119.9	C2B—C1B—H1BD	109.5
C5B—C4B—H4BA	119.9	H1BB—C1B—H1BD	109.5
C10A—C9A—C8A	122.00 (14)	H1BC—C1B—H1BD	109.5
C10A—C9A—H9AA	119.0	C8B—C11B—H11D	109.5
C8A—C9A—H9AA	119.0	C8B—C11B—H11E	109.5
C9A—C10A—C5A	120.56 (14)	H11D—C11B—H11E	109.5
C9A—C10A—H10A	119.7	C8B—C11B—H11F	109.5
C5A—C10A—H10A	119.7	H11D—C11B—H11F	109.5
C5B—C6B—C7B	121.16 (15)	H11E—C11B—H11F	109.5
C5B—C6B—H6BA	119.4	C8B—C7B—C6B	121.48 (16)
C7B—C6B—H6BA	119.4	C8B—C7B—H7BA	119.3
C5A—C6A—C7A	121.36 (14)	C6B—C7B—H7BA	119.3
C5A—C6A—H6AA	119.3	C2A—C1A—H1AB	109.5
C7A—C6A—H6AA	119.3	C2A—C1A—H1AC	109.5
O2A—C2A—C1A	106.88 (14)	H1AB—C1A—H1AC	109.5
O2A—C2A—H2AB	110.3	C2A—C1A—H1AD	109.5
C1A—C2A—H2AB	110.3	H1AB—C1A—H1AD	109.5
O2A—C2A—H2AC	110.3	H1AC—C1A—H1AD	109.5

Hydrogen-bond geometry (Å, °)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
N1B—H1BA···O1A	0.86	2.03	2.8747 (17)	165
N1A—H1AA···O1B^{i}	0.86	2.13	2.9383 (17)	157

Symmetry codes: (i) *x*, −*y*+3/2, *z*+1/2.

Fig. 1


C11B
C11A
C8B
C8A
C7B
C7A
C9B
C9A
C6B
C6A
C10B
C10A
C5B
C5A
C4B
C4A
N2B
N2A
N1B
N1A
O1B
C3B
C3A
O1A
O2B
O2A
C2B
C2A
C1B
C1A

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Ethyl 1-(2-hydroxyethyl)-2-*p*-tolyl-1*H*-benzimidazole-5-carboxylate

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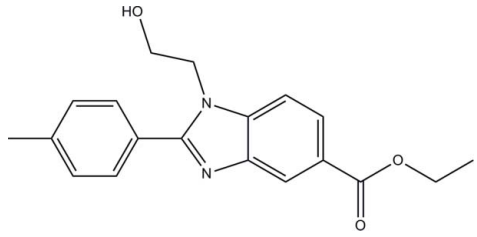
Key indicators: single-crystal X-ray study; T = 100 K; mean σ(C–C) = 0.002 Å; R factor = 0.048; wR factor = 0.194; data-to-parameter ratio = 23.9.

The asymmetric unit of the title compound, $C_{19}H_{20}N_2O_3$, contains two molecules (*A* and *B*) with slightly different orientations of the ethyl groups with respect to the attached carboxylate groups. Intramolecular C—H···O hydrogen bonds generate S(8) ring motifs in both molecules *A* and *B*. In each molecule, the benzimidazole ring system is essentially planar, with maximum deviations of 0.023 (1) and 0.020 (1) Å, respectively, for molecules *A* and *B*. The dihedral angle between the benzimidazole ring system and the phenyl ring is 37.34 (5)° for molecule *A* and 42.42 (5)° for molecule *B*. In the crystal, O—H···N and C—H···O hydrogen bonds link the molecules into [100] columns with a cross-section of two-molecule by two-molecule wide, and further stabilization is provided by weak C—H···π and π–π interactions [centroid separations = 3.5207 (7) and 3.6314 (8) Å].

Related literature

For general background to and applications of benzimidazole derivatives, see: Denny *et al.* (1990); Evans *et al.* (1997); Grassmann *et al.* (2002); Göker *et al.* (2002); Seth *et al.* (2003). For graph-set descriptions of hydrogen-bond ring motifs, see: Bernstein *et al.* (1995). For closely related benzimidazole structures, see: Arumugam *et al.* (2010*a*,*b*,*c*). For the stability of the temperature controller used for the data collection, see: Cosier & Glazer (1986).



Experimental

Crystal data

$C_{19}H_{20}N_2O_3$
M_r = 324.37
Triclinic, $P\overline{1}$
a = 9.0400 (9) Å
b = 12.6806 (13) Å
c = 15.5504 (17) Å
α = 74.170 (2)°
β = 74.360 (2)°
γ = 76.721 (2)°
V = 1627.9 (3) Å^3
Z = 4
Mo $K\alpha$ radiation
μ = 0.09 mm^{-1}
T = 100 K
0.41 × 0.32 × 0.23 mm

Data collection

Bruker APEXII DUO CCD diffractometer
Absorption correction: multi-scan (*SADABS*; Bruker, 2009)
T_{min} = 0.964, T_{max} = 0.980
30776 measured reflections
10646 independent reflections
8773 reflections with $I > 2\sigma(I)$
R_{int} = 0.030

Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.048
$wR(F^2)$ = 0.194
S = 1.13
10646 reflections
445 parameters
H atoms treated by a mixture of independent and constrained refinement
$\Delta\rho_{max}$ = 0.60 e Å^{-3}
$\Delta\rho_{min}$ = −0.65 e Å^{-3}

Table 1
Hydrogen-bond geometry (Å, °).

*Cg*1 is the centroid of the N1*B*/C7*B*/N2*B*/C8*B*/C13*B* 4,5-dihydro imidazole ring.

D—H···A	D—H	H···A	D···A	D—H···A
O3*A*—H1*OA*···N1*B*	0.96 (3)	1.83 (3)	2.7847 (14)	173 (2)
O3*B*—H1*OB*···N1*A*	0.81 (2)	2.08 (2)	2.8859 (15)	172 (3)
C1*A*—H1*AA*···O3*A*	0.93	2.37	3.2473 (16)	156
C1*B*—H1*BA*···O3*B*	0.93	2.36	3.2331 (16)	157
C12*B*—H12*B*···O3*A*^{i}	0.93	2.45	3.2788 (16)	149
C15*B*—H15*C*···O1*B*^{ii}	0.97	2.55	3.2889 (17)	133
C18*A*—H18*A*···O1*A*^{iii}	0.97	2.58	3.1928 (16)	121
C17*B*—H17*C*···*Cg*1^{iv}	0.97	2.70	3.4194 (13)	131

Symmetry codes: (i) $x-1, y, z$; (ii) $-x+1, -y, -z+1$; (iii) $x+1, y, z$; (iv) $-x+1, -y+1, -z$.

Data collection: *APEX2* (Bruker, 2009); cell refinement: *SAINT* (Bruker, 2009); data reduction: *SAINT*; program(s) used to solve structure: *SHELXTL* (Sheldrick, 2008); program(s) used to refine structure: *SHELXTL*; molecular graphics: *SHELXTL*; software used to prepare material for publication: *SHELXTL* and *PLATON* (Spek, 2009).

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¶ Thomson Reuters ResearcherID: A-3561-2009.

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Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: HB5474).

References

Arumugam, N., Abdul Rahim, A. S., Abd Hamid, S., Hemamalini, M. & Fun, H.-K. (2010*a*). *Acta Cryst.* E**66**, o796–o797.
Arumugam, N., Abdul Rahim, A. S., Osman, H., Hemamalini, M. & Fun, H.-K. (2010*b*). *Acta Cryst.* E**66**, o845.
Arumugam, N., Abdul Rahim, A. S., Osman, H., Yeap, C. S. & Fun, H.-K. (2010*c*). *Acta Cryst.* E**66**, o1214–o1215.
Bernstein, J., Davis, R. E., Shimoni, L. & Chang, N.-L. (1995). *Angew. Chem. Int. Ed. Engl.* **34**, 1555–1573.
Bruker (2009). *APEX2*, *SAINT* and *SADABS*. Bruker AXS Inc., Madison, Wisconsin, USA.
Cosier, J. & Glazer, A. M. (1986). *J. Appl. Cryst.* **19**, 105–107.
Denny, W. A., Rewcastle, G. W. & Banguly, B. C. (1990). *J. Med. Chem.* **33**, 814–819.
Evans, T. M., Gardiner, J. M., Mahmood, N. & Smis, M. (1997). *Bioorg. Med. Chem. Lett.* **7**, 409–412.
Göker, H., Kuş, C., Boykin, D. W., Yildiz, S. & Atlanlar, N. (2002). *Bioorg. Med. Chem.* **10**, 2589–2596.
Grassmann, S., Sadek, B., Ligneau, X., Elz, S., Ganellin, C. R., Arrang, J. M., Schwartz, J. C., Stark, H. & Schunack, W. (2002). *Eur. J. Pharm. Sci.* **15**, 367–378.
Seth, P. P., Jefferson, E. A., Risen, L. M. & Osgood, S. A. (2003). *Bioorg. Med. Chem. Lett.* **13**, 1669–1672.
Sheldrick, G. M. (2008). *Acta Cryst.* A**64**, 112–122.
Spek, A. L. (2009). *Acta Cryst.* D**65**, 148–155.

supplementary materials

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Ethyl 1-(2-hydroxyethyl)-2-*p*-tolyl-1*H*-benzimidazole-5-carboxylate

N. Arumugam, A. S. Abdul Rahim, H. A Wahab, J. H. Goh and H.-K. Fun

Comment

Benzimidazoles are known to exhibit anti-HIV (Evans *et al.*, 1997), anti-fungal (Göker *et al.*, 2002) and anti-parasitic (Seth *et al.*, 2003) activities. In particular, substituted benzimidazoles have proven as drug leads, generating pharmacological interests (Grassmann *et al.*, 2002). A series of substituted benzimidazole derivatives have been synthesised and evaluated for *in vitro* and *in vivo* anti-tumor activity and DNA binding affinity (Denny *et al.*, 1990). Due to their importance, the crystal structure determination of the title compound was carried out and the results are presented in this paper.

The asymmetric unit of the title benzimidazole compound (Fig. 1) comprises of two crystallographically independent molecules, designated *A* and *B*. A superposition of the non-H atoms of molecules *A* and *B* (Fig. 2) using *XP* in *SHELXTL* (Sheldrick, 2008), gave an r.m.s. deviation of 0.517 Å. Molecules *A* and *B* differ slightly in the orientation of the ethyl groups (C15 and C16) with respect to the attached carboxylate groups, as can be seen in Fig. 2. The torsion angles C14A–O2A–C15A–C16A and C14B–O2B–C15B–C16B are -77.41 (15) and -171.37 (10)°, respectively.

Intramolecular C1A—H1AA···O3A and C1B—H1BA···O3B hydrogen bonds generate eight-membered rings, producing *S*(8) ring motifs (Bernstein, 1995). In each molecule, the benzimidazole ring system (C7-C13/N1/N2) are essentially planar, with maximum deviations of 0.023 (1) and -0.020 (1) Å, respectively, at atoms C7A of molecule *A* and C8B of molecule *B*. In molecule *A*, the benzimidazole ring system is inclined at dihedral angle of 37.34 (5)° with the C1A-C6A phenyl ring; the respective angle for molecule *B* is 42.42 (5)°. The geometric parameters are comparable to those reported in closely related benzimidazole structures (Arumugam *et al.*, 2010*a,b,c*).

In the crystal packing (Fig. 3), intermolecular O3A—H1OA···N1B, O3B—H1OB···N1A, C12B—H12B···O3A, C15B—H15C···O1B and C18A—H18A···O1A hydrogen bonds link the molecules into columns with cross-section of two-molecule by two-molecule wide along the *a* axis. The crystal packing is further stabilized by intermolecular C17B—H17C···*Cg*1 interactions (Table 1) as well as weak π–π aromatic stacking interactions [*Cg*1···*Cg*2 = 3.5207 (7) and *Cg*3···*Cg*4 = 3.6314 (8) Å; symmetry code: x, y, z; *Cg*1 and *Cg*2 are the centroids of 4,5-dihydroimidazole rings (C7A/N1A/C8A/C13A/N2A and C7B/N1B/C8B/C13B/N2B), respectively; *Cg*3 and *Cg*4 are the centroids of C8A-C13A and C8B-C13B phenyl rings, respectively].

Experimental

A solution of ethyl-3-amino-4-(2-hydroxyethylamino) benzoate (0.5 g, 2.22 mmol) and sodium bisulfite adduct of *p*-methyl benzaldehyde (1.0 g, 4.46 mmol) in DMF was treated under microwave conditions at 403 K. The reaction mixture was then diluted in EtOAc (30 ml) and washed with H_2O (30 ml). The organic layer was collected and dried over Na_2SO_4. The solvent was removed under reduced pressure to afford the crude product, which upon recrystallisation from EtOAc, revealed the title compound as colourless crystals.

Refinement

Hydroxy H-atoms were located from the difference Fourier map and allowed to refine freely. The remaining H atoms were place in their calculated positions, with C–H = 0.93–0.97 Å and U_{iso}(H) = 1.2 or 1.5 U_{eq}(C). The rotating group model was applied for the methyl groups. The highest residual electron density peak is 0.49 Å from N2B and the deepest hole is 0.85 Å from C8B.

Figures

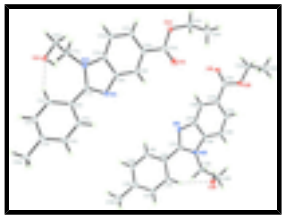


Fig. 1. The molecular structure of (I) with 50% probability displacement ellipsoids for non-H atoms. Intramolecular hydrogen bonds are shown as dashed lines.

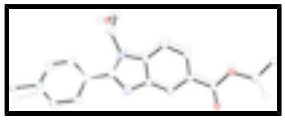


Fig. 2. Fit of molecule *A* (dashed lines) on molecule *B* (solid lines). H atoms have been omitted for clarity.

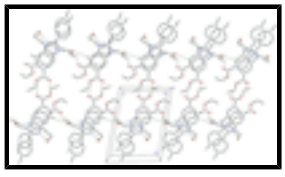


Fig. 3. The crystal packing of (I), viewed down *c* axis, showing a two-molecule by two-molecule wide column along the *a* axis. H atoms not involved in intermolecular interactions (dashed lines) have been omitted for clarity.

Ethyl 1-(2-hydroxyethyl)-2-*p*-tolyl-1*H*-benzimidazole-5-carboxylate

Crystal data

$C_{19}H_{20}N_2O_3$	$Z = 4$
$M_r = 324.37$	$F(000) = 688$
Triclinic, $P\overline{1}$	$D_x = 1.324$ Mg m^{-3}
Hall symbol: -P 1	Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å
$a = 9.0400$ (9) Å	Cell parameters from 9690 reflections
$b = 12.6806$ (13) Å	$\theta = 2.8$–$33.8°$
$c = 15.5504$ (17) Å	$\mu = 0.09$ mm^{-1}
$\alpha = 74.170$ (2)°	$T = 100$ K
$\beta = 74.360$ (2)°	Block, colourless
$\gamma = 76.721$ (2)°	0.41 × 0.32 × 0.23 mm
$V = 1627.9$ (3) Å^3	

Data collection

Bruker APEXII DUO CCD diffractometer	10646 independent reflections
Radiation source: fine-focus sealed tube	8773 reflections with $I > 2\sigma(I)$

graphite	R_{int} = 0.030
φ and ω scans	θ_{max} = 31.5°, θ_{min} = 2.4°
Absorption correction: multi-scan (*SADABS*; Bruker, 2009)	h = −13→13
T_{min} = 0.964, T_{max} = 0.980	k = −18→18
30776 measured reflections	l = −22→22

Refinement

Refinement on F^2	Primary atom site location: structure-invariant direct methods
Least-squares matrix: full	Secondary atom site location: difference Fourier map
$R[F^2 > 2\sigma(F^2)]$ = 0.048	Hydrogen site location: inferred from neighbouring sites
$wR(F^2)$ = 0.194	H atoms treated by a mixture of independent and constrained refinement
S = 1.13	$w = 1/[\sigma^2(F_o^2) + (0.1301P)^2 + 0.1152P]$ where $P = (F_o^2 + 2F_c^2)/3$
10646 reflections	$(\Delta/\sigma)_{max} < 0.001$
445 parameters	$\Delta\rho_{max}$ = 0.60 e Å^{-3}
0 restraints	$\Delta\rho_{min}$ = −0.65 e Å^{-3}

Special details

Experimental. The crystal was placed in the cold stream of an Oxford Cryosystems Cobra open-flow nitrogen cryostat (Cosier & Glazer, 1986) operating at 100.0 (1)K.

Geometry. All esds (except the esd in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell esds are taken into account individually in the estimation of esds in distances, angles and torsion angles; correlations between esds in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell esds is used for estimating esds involving l.s. planes.

Refinement. Refinement of F^2 against ALL reflections. The weighted R-factor wR and goodness of fit S are based on F^2, conventional R-factors R are based on F, with F set to zero for negative F^2. The threshold expression of $F^2 > 2\text{sigma}(F^2)$ is used only for calculating R-factors(gt) etc. and is not relevant to the choice of reflections for refinement. R-factors based on F^2 are statistically about twice as large as those based on F, and R- factors based on ALL data will be even larger.

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å^2)

	x	*y*	*z*	U_{iso}*/U_{eq}
O1A	0.07593 (12)	0.34205 (9)	0.46417 (7)	0.0276 (2)
O2A	0.22621 (11)	0.21688 (8)	0.55131 (7)	0.0214 (2)
O3A	0.96752 (10)	0.50727 (7)	0.18794 (6)	0.01475 (17)
N1A	0.44922 (12)	0.63318 (8)	0.29752 (7)	0.01358 (19)
N2A	0.68064 (11)	0.55873 (8)	0.33553 (6)	0.01221 (18)
C1A	0.79520 (14)	0.76316 (10)	0.18103 (8)	0.0153 (2)
H1AA	0.8706	0.6999	0.1772	0.018*
C2A	0.83043 (14)	0.86714 (10)	0.13230 (8)	0.0170 (2)
H2AA	0.9302	0.8723	0.0965	0.020*

C3A	0.72088 (14)	0.96366 (10)	0.13554 (8)	0.0164 (2)
C4A	0.57258 (15)	0.95372 (10)	0.19112 (8)	0.0172 (2)
H4AA	0.4977	1.0172	0.1953	0.021*
C5A	0.53556 (14)	0.85052 (10)	0.24015 (8)	0.0161 (2)
H5AA	0.4360	0.8456	0.2763	0.019*
C6A	0.64640 (13)	0.75385 (9)	0.23574 (8)	0.0132 (2)
C7A	0.59444 (13)	0.64791 (9)	0.28754 (7)	0.0127 (2)
C8A	0.43877 (13)	0.52957 (9)	0.35614 (7)	0.0123 (2)
C9A	0.31274 (13)	0.47294 (9)	0.39126 (8)	0.0139 (2)
H9AA	0.2176	0.5029	0.3748	0.017*
C10A	0.33376 (14)	0.37013 (9)	0.45175 (8)	0.0141 (2)
C11A	0.47717 (14)	0.32492 (10)	0.47744 (8)	0.0148 (2)
H11A	0.4869	0.2567	0.5191	0.018*
C12A	0.60436 (14)	0.37979 (9)	0.44210 (8)	0.0141 (2)
H12A	0.6996	0.3498	0.4584	0.017*
C13A	0.58203 (13)	0.48226 (9)	0.38085 (7)	0.0122 (2)
C14A	0.19800 (15)	0.31049 (10)	0.48803 (8)	0.0168 (2)
C15A	0.09808 (16)	0.15392 (11)	0.59046 (10)	0.0240 (3)
H15A	0.1383	0.0784	0.6190	0.029*
H15B	0.0522	0.1506	0.5418	0.029*
C16A	−0.02486 (18)	0.20524 (12)	0.66008 (10)	0.0256 (3)
H16A	−0.1042	0.1596	0.6867	0.038*
H16B	−0.0702	0.2780	0.6310	0.038*
H16C	0.0209	0.2112	0.7072	0.038*
C17A	0.84315 (13)	0.53960 (9)	0.34180 (8)	0.0138 (2)
H17A	0.8501	0.5088	0.4052	0.017*
H17B	0.8806	0.6101	0.3221	0.017*
C18A	0.94678 (13)	0.46049 (10)	0.28325 (8)	0.0145 (2)
H18A	1.0479	0.4387	0.2990	0.017*
H18B	0.9011	0.3939	0.2975	0.017*
C19A	0.75854 (17)	1.07453 (11)	0.07806 (10)	0.0230 (3)
H19A	0.8692	1.0722	0.0635	0.035*
H19B	0.7082	1.1312	0.1116	0.035*
H19C	0.7223	1.0909	0.0225	0.035*
O1B	0.62907 (11)	0.10394 (8)	0.35690 (7)	0.0212 (2)
O2B	0.38151 (10)	0.10387 (7)	0.35342 (6)	0.01744 (18)
O3B	0.29192 (11)	0.76162 (7)	0.15387 (6)	0.01769 (18)
N1B	0.71022 (11)	0.49118 (8)	0.12914 (6)	0.01173 (18)
N2B	0.48235 (11)	0.56326 (8)	0.08697 (6)	0.01134 (18)
C1B	0.62243 (14)	0.78327 (9)	0.00981 (8)	0.0148 (2)
H1BA	0.5224	0.7990	0.0449	0.018*
C2B	0.69291 (15)	0.86841 (10)	−0.05266 (9)	0.0184 (2)
H2BA	0.6389	0.9410	−0.0587	0.022*
C3B	0.84224 (15)	0.84821 (11)	−0.10662 (8)	0.0196 (2)
C4B	0.92369 (15)	0.73979 (11)	−0.09289 (9)	0.0192 (2)
H4BA	1.0255	0.7250	−0.1260	0.023*
C5B	0.85548 (14)	0.65327 (10)	−0.03060 (8)	0.0158 (2)
H5BA	0.9119	0.5814	−0.0224	0.019*
C6B	0.70215 (13)	0.67365 (9)	0.01996 (7)	0.0123 (2)

C7B	0.63190 (12)	0.57798 (9)	0.08024 (7)	0.01131 (19)
C8B	0.60714 (12)	0.41630 (9)	0.17018 (7)	0.01138 (19)
C9B	0.62468 (13)	0.31246 (9)	0.22990 (7)	0.0124 (2)
H9BA	0.7173	0.2821	0.2493	0.015*
C10B	0.49860 (13)	0.25547 (9)	0.25962 (7)	0.0128 (2)
C11B	0.35857 (13)	0.29980 (9)	0.22970 (8)	0.0138 (2)
H11B	0.2779	0.2586	0.2496	0.017*
C12B	0.33878 (13)	0.40355 (9)	0.17128 (8)	0.0130 (2)
H12B	0.2465	0.4337	0.1515	0.016*
C13B	0.46462 (12)	0.46028 (9)	0.14371 (7)	0.01133 (19)
C14B	0.51372 (13)	0.14745 (9)	0.32729 (8)	0.0141 (2)
C15B	0.38024 (15)	0.00252 (10)	0.42410 (9)	0.0191 (2)
H15C	0.3812	0.0174	0.4819	0.023*
H15D	0.4716	−0.0518	0.4078	0.023*
C16B	0.23432 (17)	−0.04128 (12)	0.43262 (10)	0.0253 (3)
H16D	0.2266	−0.1057	0.4822	0.038*
H16E	0.2383	−0.0611	0.3766	0.038*
H16F	0.1451	0.0150	0.4445	0.038*
C17B	0.35660 (13)	0.63748 (9)	0.04793 (8)	0.0135 (2)
H17C	0.3082	0.5961	0.0222	0.016*
H17D	0.3990	0.6956	−0.0014	0.016*
C18B	0.23360 (13)	0.69020 (10)	0.11993 (8)	0.0159 (2)
H18C	0.1464	0.7322	0.0932	0.019*
H18D	0.1953	0.6318	0.1706	0.019*
C19B	0.9105 (2)	0.94054 (13)	−0.17975 (10)	0.0301 (3)
H19D	1.0220	0.9215	−0.1936	0.045*
H19E	0.8801	1.0081	−0.1582	0.045*
H19F	0.8726	0.9508	−0.2340	0.045*
H1OA	0.875 (3)	0.5068 (18)	0.1692 (14)	0.039 (6)*
H1OB	0.328 (3)	0.7248 (19)	0.1973 (15)	0.035 (5)*

Atomic displacement parameters (Å^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
O1A	0.0201 (5)	0.0313 (5)	0.0292 (5)	−0.0108 (4)	−0.0094 (4)	0.0060 (4)
O2A	0.0170 (4)	0.0157 (4)	0.0259 (5)	−0.0055 (3)	−0.0013 (3)	0.0032 (3)
O3A	0.0102 (4)	0.0206 (4)	0.0134 (4)	−0.0030 (3)	−0.0024 (3)	−0.0036 (3)
N1A	0.0129 (4)	0.0138 (4)	0.0123 (4)	−0.0020 (3)	−0.0024 (3)	−0.0008 (3)
N2A	0.0108 (4)	0.0132 (4)	0.0113 (4)	−0.0018 (3)	−0.0021 (3)	−0.0011 (3)
C1A	0.0133 (5)	0.0140 (5)	0.0164 (5)	−0.0012 (4)	−0.0024 (4)	−0.0016 (4)
C2A	0.0141 (5)	0.0154 (5)	0.0187 (5)	−0.0029 (4)	−0.0031 (4)	0.0004 (4)
C3A	0.0182 (5)	0.0140 (5)	0.0173 (5)	−0.0029 (4)	−0.0062 (4)	−0.0014 (4)
C4A	0.0183 (5)	0.0131 (5)	0.0187 (5)	0.0011 (4)	−0.0047 (4)	−0.0037 (4)
C5A	0.0153 (5)	0.0151 (5)	0.0167 (5)	−0.0008 (4)	−0.0027 (4)	−0.0041 (4)
C6A	0.0129 (5)	0.0132 (5)	0.0124 (5)	−0.0016 (4)	−0.0028 (4)	−0.0018 (4)
C7A	0.0120 (5)	0.0128 (5)	0.0120 (4)	−0.0009 (4)	−0.0020 (4)	−0.0024 (4)
C8A	0.0122 (5)	0.0130 (5)	0.0106 (4)	−0.0016 (4)	−0.0017 (4)	−0.0020 (4)
C9A	0.0117 (5)	0.0155 (5)	0.0134 (5)	−0.0020 (4)	−0.0020 (4)	−0.0026 (4)

C10A	0.0148 (5)	0.0145 (5)	0.0121 (5)	−0.0035 (4)	−0.0009 (4)	−0.0027 (4)
C11A	0.0150 (5)	0.0144 (5)	0.0132 (5)	−0.0023 (4)	−0.0020 (4)	−0.0011 (4)
C12A	0.0127 (5)	0.0145 (5)	0.0131 (5)	−0.0008 (4)	−0.0029 (4)	−0.0012 (4)
C13A	0.0119 (5)	0.0130 (5)	0.0103 (4)	−0.0017 (4)	−0.0008 (3)	−0.0023 (4)
C14A	0.0177 (5)	0.0167 (5)	0.0149 (5)	−0.0049 (4)	−0.0017 (4)	−0.0021 (4)
C15A	0.0205 (6)	0.0164 (5)	0.0307 (7)	−0.0084 (4)	0.0015 (5)	−0.0008 (5)
C16A	0.0277 (7)	0.0268 (6)	0.0219 (6)	−0.0118 (5)	−0.0004 (5)	−0.0035 (5)
C17A	0.0117 (5)	0.0163 (5)	0.0137 (5)	−0.0020 (4)	−0.0038 (4)	−0.0031 (4)
C18A	0.0116 (5)	0.0164 (5)	0.0142 (5)	−0.0001 (4)	−0.0041 (4)	−0.0021 (4)
C19A	0.0263 (7)	0.0144 (5)	0.0257 (6)	−0.0042 (5)	−0.0074 (5)	0.0022 (5)
O1B	0.0168 (4)	0.0184 (4)	0.0249 (5)	−0.0033 (3)	−0.0078 (4)	0.0044 (3)
O2B	0.0155 (4)	0.0163 (4)	0.0181 (4)	−0.0053 (3)	−0.0037 (3)	0.0021 (3)
O3B	0.0189 (4)	0.0150 (4)	0.0177 (4)	−0.0003 (3)	−0.0036 (3)	−0.0039 (3)
N1B	0.0096 (4)	0.0128 (4)	0.0121 (4)	−0.0017 (3)	−0.0029 (3)	−0.0013 (3)
N2B	0.0092 (4)	0.0110 (4)	0.0126 (4)	−0.0003 (3)	−0.0035 (3)	−0.0009 (3)
C1B	0.0140 (5)	0.0136 (5)	0.0165 (5)	−0.0008 (4)	−0.0053 (4)	−0.0023 (4)
C2B	0.0203 (6)	0.0148 (5)	0.0206 (6)	−0.0038 (4)	−0.0089 (4)	0.0003 (4)
C3B	0.0213 (6)	0.0207 (6)	0.0174 (5)	−0.0093 (4)	−0.0068 (4)	0.0021 (4)
C4B	0.0142 (5)	0.0233 (6)	0.0176 (5)	−0.0059 (4)	−0.0003 (4)	−0.0016 (4)
C5B	0.0126 (5)	0.0171 (5)	0.0161 (5)	−0.0023 (4)	−0.0023 (4)	−0.0021 (4)
C6B	0.0110 (5)	0.0138 (5)	0.0117 (4)	−0.0021 (4)	−0.0038 (4)	−0.0011 (4)
C7B	0.0091 (4)	0.0129 (5)	0.0116 (4)	−0.0013 (3)	−0.0022 (3)	−0.0028 (4)
C8B	0.0092 (4)	0.0137 (5)	0.0111 (4)	−0.0015 (3)	−0.0020 (3)	−0.0031 (4)
C9B	0.0098 (4)	0.0145 (5)	0.0124 (5)	−0.0004 (3)	−0.0031 (4)	−0.0030 (4)
C10B	0.0121 (5)	0.0130 (5)	0.0121 (5)	−0.0013 (4)	−0.0020 (4)	−0.0024 (4)
C11B	0.0120 (5)	0.0145 (5)	0.0143 (5)	−0.0027 (4)	−0.0027 (4)	−0.0020 (4)
C12B	0.0100 (5)	0.0151 (5)	0.0137 (5)	−0.0019 (4)	−0.0034 (4)	−0.0027 (4)
C13B	0.0100 (4)	0.0123 (4)	0.0113 (4)	−0.0011 (3)	−0.0028 (3)	−0.0023 (4)
C14B	0.0135 (5)	0.0144 (5)	0.0137 (5)	−0.0027 (4)	−0.0021 (4)	−0.0025 (4)
C15B	0.0195 (6)	0.0163 (5)	0.0188 (5)	−0.0061 (4)	−0.0048 (4)	0.0033 (4)
C16B	0.0210 (6)	0.0237 (6)	0.0298 (7)	−0.0086 (5)	−0.0022 (5)	−0.0032 (5)
C17B	0.0108 (5)	0.0134 (5)	0.0157 (5)	0.0008 (4)	−0.0063 (4)	−0.0013 (4)
C18B	0.0107 (5)	0.0154 (5)	0.0196 (5)	0.0004 (4)	−0.0032 (4)	−0.0028 (4)
C19B	0.0342 (8)	0.0284 (7)	0.0255 (7)	−0.0173 (6)	−0.0068 (6)	0.0079 (5)

Geometric parameters (Å, °)

O1A—C14A	1.2051 (17)	O1B—C14B	1.2082 (15)
O2A—C14A	1.3422 (15)	O2B—C14B	1.3483 (14)
O2A—C15A	1.4591 (15)	O2B—C15B	1.4454 (14)
O3A—C18A	1.4160 (14)	O3B—C18B	1.4166 (15)
O3A—H1OA	0.96 (2)	O3B—H1OB	0.81 (2)
N1A—C7A	1.3302 (15)	N1B—C7B	1.3291 (14)
N1A—C8A	1.3868 (14)	N1B—C8B	1.3902 (13)
N2A—C7A	1.3752 (15)	N2B—C13B	1.3787 (14)
N2A—C13A	1.3846 (14)	N2B—C7B	1.3793 (14)
N2A—C17A	1.4586 (15)	N2B—C17B	1.4545 (14)
C1A—C2A	1.3899 (16)	C1B—C2B	1.3875 (16)
C1A—C6A	1.3959 (16)	C1B—C6B	1.3993 (16)

C1A—H1AA	0.9300	C1B—H1BA	0.9300
C2A—C3A	1.3896 (17)	C2B—C3B	1.3928 (18)
C2A—H2AA	0.9300	C2B—H2BA	0.9300
C3A—C4A	1.3978 (17)	C3B—C4B	1.3919 (19)
C3A—C19A	1.5038 (17)	C3B—C19B	1.5072 (18)
C4A—C5A	1.3875 (16)	C4B—C5B	1.3896 (16)
C4A—H4AA	0.9300	C4B—H4BA	0.9300
C5A—C6A	1.3985 (16)	C5B—C6B	1.4017 (16)
C5A—H5AA	0.9300	C5B—H5BA	0.9300
C6A—C7A	1.4729 (15)	C6B—C7B	1.4718 (15)
C8A—C9A	1.3923 (15)	C8B—C9B	1.3919 (15)
C8A—C13A	1.4037 (16)	C8B—C13B	1.4039 (15)
C9A—C10A	1.3906 (16)	C9B—C10B	1.3954 (15)
C9A—H9AA	0.9300	C9B—H9BA	0.9300
C10A—C11A	1.4078 (17)	C10B—C11B	1.4082 (16)
C10A—C14A	1.4889 (16)	C10B—C14B	1.4858 (16)
C11A—C12A	1.3879 (15)	C11B—C12B	1.3840 (16)
C11A—H11A	0.9300	C11B—H11B	0.9300
C12A—C13A	1.3945 (16)	C12B—C13B	1.3929 (14)
C12A—H12A	0.9300	C12B—H12B	0.9300
C15A—C16A	1.495 (2)	C15B—C16B	1.5060 (18)
C15A—H15A	0.9700	C15B—H15C	0.9700
C15A—H15B	0.9700	C15B—H15D	0.9700
C16A—H16A	0.9600	C16B—H16D	0.9600
C16A—H16B	0.9600	C16B—H16E	0.9600
C16A—H16C	0.9600	C16B—H16F	0.9600
C17A—C18A	1.5230 (16)	C17B—C18B	1.5272 (16)
C17A—H17A	0.9700	C17B—H17C	0.9700
C17A—H17B	0.9700	C17B—H17D	0.9700
C18A—H18A	0.9700	C18B—H18C	0.9700
C18A—H18B	0.9700	C18B—H18D	0.9700
C19A—H19A	0.9600	C19B—H19D	0.9600
C19A—H19B	0.9600	C19B—H19E	0.9600
C19A—H19C	0.9600	C19B—H19F	0.9600
C14A—O2A—C15A	115.51 (11)	C14B—O2B—C15B	116.22 (10)
C18A—O3A—H1OA	108.5 (13)	C18B—O3B—H1OB	108.2 (15)
C7A—N1A—C8A	105.16 (10)	C7B—N1B—C8B	105.51 (9)
C7A—N2A—C13A	106.47 (9)	C13B—N2B—C7B	107.03 (9)
C7A—N2A—C17A	130.53 (9)	C13B—N2B—C17B	122.50 (9)
C13A—N2A—C17A	123.00 (10)	C7B—N2B—C17B	130.43 (10)
C2A—C1A—C6A	119.88 (11)	C2B—C1B—C6B	119.85 (11)
C2A—C1A—H1AA	120.1	C2B—C1B—H1BA	120.1
C6A—C1A—H1AA	120.1	C6B—C1B—H1BA	120.1
C3A—C2A—C1A	121.93 (11)	C1B—C2B—C3B	121.82 (12)
C3A—C2A—H2AA	119.0	C1B—C2B—H2BA	119.1
C1A—C2A—H2AA	119.0	C3B—C2B—H2BA	119.1
C2A—C3A—C4A	117.82 (11)	C4B—C3B—C2B	117.94 (11)
C2A—C3A—C19A	121.07 (11)	C4B—C3B—C19B	121.33 (12)
C4A—C3A—C19A	121.05 (11)	C2B—C3B—C19B	120.70 (13)

C5A—C4A—C3A	120.93 (11)	C5B—C4B—C3B	121.13 (11)
C5A—C4A—H4AA	119.5	C5B—C4B—H4BA	119.4
C3A—C4A—H4AA	119.5	C3B—C4B—H4BA	119.4
C4A—C5A—C6A	120.73 (11)	C4B—C5B—C6B	120.40 (11)
C4A—C5A—H5AA	119.6	C4B—C5B—H5BA	119.8
C6A—C5A—H5AA	119.6	C6B—C5B—H5BA	119.8
C1A—C6A—C5A	118.69 (10)	C1B—C6B—C5B	118.70 (10)
C1A—C6A—C7A	124.55 (10)	C1B—C6B—C7B	123.14 (10)
C5A—C6A—C7A	116.72 (10)	C5B—C6B—C7B	118.15 (10)
N1A—C7A—N2A	112.70 (10)	N1B—C7B—N2B	112.04 (9)
N1A—C7A—C6A	121.20 (10)	N1B—C7B—C6B	123.42 (10)
N2A—C7A—C6A	125.93 (10)	N2B—C7B—C6B	124.34 (10)
N1A—C8A—C9A	129.96 (11)	N1B—C8B—C9B	130.89 (10)
N1A—C8A—C13A	109.82 (10)	N1B—C8B—C13B	109.62 (10)
C9A—C8A—C13A	120.21 (10)	C9B—C8B—C13B	119.49 (10)
C10A—C9A—C8A	117.82 (11)	C8B—C9B—C10B	117.73 (10)
C10A—C9A—H9AA	121.1	C8B—C9B—H9BA	121.1
C8A—C9A—H9AA	121.1	C10B—C9B—H9BA	121.1
C9A—C10A—C11A	121.28 (11)	C9B—C10B—C11B	121.69 (10)
C9A—C10A—C14A	117.03 (11)	C9B—C10B—C14B	117.90 (10)
C11A—C10A—C14A	121.70 (11)	C11B—C10B—C14B	120.37 (10)
C12A—C11A—C10A	121.52 (11)	C12B—C11B—C10B	121.18 (10)
C12A—C11A—H11A	119.2	C12B—C11B—H11B	119.4
C10A—C11A—H11A	119.2	C10B—C11B—H11B	119.4
C11A—C12A—C13A	116.56 (11)	C11B—C12B—C13B	116.38 (10)
C11A—C12A—H12A	121.7	C11B—C12B—H12B	121.8
C13A—C12A—H12A	121.7	C13B—C12B—H12B	121.8
N2A—C13A—C12A	131.53 (11)	N2B—C13B—C12B	130.72 (10)
N2A—C13A—C8A	105.85 (10)	N2B—C13B—C8B	105.80 (9)
C12A—C13A—C8A	122.58 (10)	C12B—C13B—C8B	123.46 (10)
O1A—C14A—O2A	123.30 (11)	O1B—C14B—O2B	123.54 (11)
O1A—C14A—C10A	124.42 (12)	O1B—C14B—C10B	124.61 (11)
O2A—C14A—C10A	112.29 (11)	O2B—C14B—C10B	111.84 (10)
O2A—C15A—C16A	111.79 (11)	O2B—C15B—C16B	107.68 (11)
O2A—C15A—H15A	109.3	O2B—C15B—H15C	110.2
C16A—C15A—H15A	109.3	C16B—C15B—H15C	110.2
O2A—C15A—H15B	109.3	O2B—C15B—H15D	110.2
C16A—C15A—H15B	109.3	C16B—C15B—H15D	110.2
H15A—C15A—H15B	107.9	H15C—C15B—H15D	108.5
C15A—C16A—H16A	109.5	C15B—C16B—H16D	109.5
C15A—C16A—H16B	109.5	C15B—C16B—H16E	109.5
H16A—C16A—H16B	109.5	H16D—C16B—H16E	109.5
C15A—C16A—H16C	109.5	C15B—C16B—H16F	109.5
H16A—C16A—H16C	109.5	H16D—C16B—H16F	109.5
H16B—C16A—H16C	109.5	H16E—C16B—H16F	109.5
N2A—C17A—C18A	112.15 (9)	N2B—C17B—C18B	111.50 (9)
N2A—C17A—H17A	109.2	N2B—C17B—H17C	109.3
C18A—C17A—H17A	109.2	C18B—C17B—H17C	109.3
N2A—C17A—H17B	109.2	N2B—C17B—H17D	109.3

C18A—C17A—H17B	109.2	C18B—C17B—H17D	109.3
H17A—C17A—H17B	107.9	H17C—C17B—H17D	108.0
O3A—C18A—C17A	113.28 (9)	O3B—C18B—C17B	112.66 (9)
O3A—C18A—H18A	108.9	O3B—C18B—H18C	109.1
C17A—C18A—H18A	108.9	C17B—C18B—H18C	109.1
O3A—C18A—H18B	108.9	O3B—C18B—H18D	109.1
C17A—C18A—H18B	108.9	C17B—C18B—H18D	109.1
H18A—C18A—H18B	107.7	H18C—C18B—H18D	107.8
C3A—C19A—H19A	109.5	C3B—C19B—H19D	109.5
C3A—C19A—H19B	109.5	C3B—C19B—H19E	109.5
H19A—C19A—H19B	109.5	H19D—C19B—H19E	109.5
C3A—C19A—H19C	109.5	C3B—C19B—H19F	109.5
H19A—C19A—H19C	109.5	H19D—C19B—H19F	109.5
H19B—C19A—H19C	109.5	H19E—C19B—H19F	109.5
C6A—C1A—C2A—C3A	−0.49 (18)	C6B—C1B—C2B—C3B	0.21 (18)
C1A—C2A—C3A—C4A	1.04 (18)	C1B—C2B—C3B—C4B	−3.33 (18)
C1A—C2A—C3A—C19A	−176.41 (11)	C1B—C2B—C3B—C19B	174.55 (12)
C2A—C3A—C4A—C5A	−1.06 (18)	C2B—C3B—C4B—C5B	3.20 (19)
C19A—C3A—C4A—C5A	176.39 (11)	C19B—C3B—C4B—C5B	−174.67 (12)
C3A—C4A—C5A—C6A	0.55 (18)	C3B—C4B—C5B—C6B	0.03 (19)
C2A—C1A—C6A—C5A	−0.06 (17)	C2B—C1B—C6B—C5B	3.06 (17)
C2A—C1A—C6A—C7A	177.64 (11)	C2B—C1B—C6B—C7B	−175.93 (11)
C4A—C5A—C6A—C1A	0.03 (17)	C4B—C5B—C6B—C1B	−3.18 (17)
C4A—C5A—C6A—C7A	−177.85 (11)	C4B—C5B—C6B—C7B	175.86 (11)
C8A—N1A—C7A—N2A	0.84 (12)	C8B—N1B—C7B—N2B	−0.29 (12)
C8A—N1A—C7A—C6A	−174.66 (9)	C8B—N1B—C7B—C6B	−175.30 (10)
C13A—N2A—C7A—N1A	−1.15 (12)	C13B—N2B—C7B—N1B	−0.12 (12)
C17A—N2A—C7A—N1A	178.46 (10)	C17B—N2B—C7B—N1B	177.66 (10)
C13A—N2A—C7A—C6A	174.10 (10)	C13B—N2B—C7B—C6B	174.83 (10)
C17A—N2A—C7A—C6A	−6.29 (18)	C17B—N2B—C7B—C6B	−7.39 (17)
C1A—C6A—C7A—N1A	−144.30 (12)	C1B—C6B—C7B—N1B	−142.71 (11)
C5A—C6A—C7A—N1A	33.45 (15)	C5B—C6B—C7B—N1B	38.29 (15)
C1A—C6A—C7A—N2A	40.83 (17)	C1B—C6B—C7B—N2B	42.90 (16)
C5A—C6A—C7A—N2A	−141.43 (11)	C5B—C6B—C7B—N2B	−136.10 (11)
C7A—N1A—C8A—C9A	178.75 (11)	C7B—N1B—C8B—C9B	−178.72 (11)
C7A—N1A—C8A—C13A	−0.21 (12)	C7B—N1B—C8B—C13B	0.59 (12)
N1A—C8A—C9A—C10A	−178.00 (10)	N1B—C8B—C9B—C10B	−179.58 (10)
C13A—C8A—C9A—C10A	0.88 (16)	C13B—C8B—C9B—C10B	1.16 (15)
C8A—C9A—C10A—C11A	0.54 (16)	C8B—C9B—C10B—C11B	0.93 (16)
C8A—C9A—C10A—C14A	−179.57 (10)	C8B—C9B—C10B—C14B	−176.73 (9)
C9A—C10A—C11A—C12A	−1.38 (17)	C9B—C10B—C11B—C12B	−1.80 (17)
C14A—C10A—C11A—C12A	178.74 (10)	C14B—C10B—C11B—C12B	175.80 (10)
C10A—C11A—C12A—C13A	0.71 (16)	C10B—C11B—C12B—C13B	0.48 (16)
C7A—N2A—C13A—C12A	−176.79 (11)	C7B—N2B—C13B—C12B	−178.09 (11)
C17A—N2A—C13A—C12A	3.56 (18)	C17B—N2B—C13B—C12B	3.91 (17)
C7A—N2A—C13A—C8A	0.93 (11)	C7B—N2B—C13B—C8B	0.47 (11)
C17A—N2A—C13A—C8A	−178.72 (9)	C17B—N2B—C13B—C8B	−177.53 (9)
C11A—C12A—C13A—N2A	178.14 (11)	C11B—C12B—C13B—N2B	−179.96 (11)
C11A—C12A—C13A—C8A	0.75 (16)	C11B—C12B—C13B—C8B	1.69 (16)

N1A—C8A—C13A—N2A	−0.46 (12)	N1B—C8B—C13B—N2B	−0.67 (12)
C9A—C8A—C13A—N2A	−179.55 (9)	C9B—C8B—C13B—N2B	178.74 (9)
N1A—C8A—C13A—C12A	177.51 (10)	N1B—C8B—C13B—C12B	178.03 (9)
C9A—C8A—C13A—C12A	−1.57 (17)	C9B—C8B—C13B—C12B	−2.56 (16)
C15A—O2A—C14A—O1A	0.05 (18)	C15B—O2B—C14B—O1B	3.17 (17)
C15A—O2A—C14A—C10A	179.75 (10)	C15B—O2B—C14B—C10B	−175.76 (9)
C9A—C10A—C14A—O1A	4.82 (18)	C9B—C10B—C14B—O1B	−1.86 (17)
C11A—C10A—C14A—O1A	−175.29 (12)	C11B—C10B—C14B—O1B	−179.55 (11)
C9A—C10A—C14A—O2A	−174.87 (10)	C9B—C10B—C14B—O2B	177.06 (9)
C11A—C10A—C14A—O2A	5.02 (16)	C11B—C10B—C14B—O2B	−0.64 (15)
C14A—O2A—C15A—C16A	−77.41 (15)	C14B—O2B—C15B—C16B	−171.37 (10)
C7A—N2A—C17A—C18A	−102.64 (13)	C13B—N2B—C17B—C18B	73.62 (13)
C13A—N2A—C17A—C18A	76.92 (13)	C7B—N2B—C17B—C18B	−103.86 (13)
N2A—C17A—C18A—O3A	70.06 (12)	N2B—C17B—C18B—O3B	65.15 (12)

Hydrogen-bond geometry (Å, °)

Cg1 is the centroid of the N1B/C7B/N2B/C8B/C13B 4,5-dihydro imidazole ring.

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
O3A—H1OA···N1B	0.96 (3)	1.83 (3)	2.7847 (14)	173 (2)
O3B—H1OB···N1A	0.81 (2)	2.08 (2)	2.8859 (15)	172 (3)
C1A—H1AA···O3A	0.93	2.37	3.2473 (16)	156
C1B—H1BA···O3B	0.93	2.36	3.2331 (16)	157
C12B—H12B···O3A^{i}	0.93	2.45	3.2788 (16)	149
C15B—H15C···O1B^{ii}	0.97	2.55	3.2889 (17)	133
C18A—H18A···O1A^{iii}	0.97	2.58	3.1928 (16)	121
C17B—H17C···Cg1^{iv}	0.97	2.70	3.4194 (13)	131

Symmetry codes: (i) *x*−1, *y*, *z*; (ii) −*x*+1, −*y*, −*z*+1; (iii) *x*+1, *y*, *z*; (iv) −*x*+1, −*y*+1, −*z*.

Fig. 1

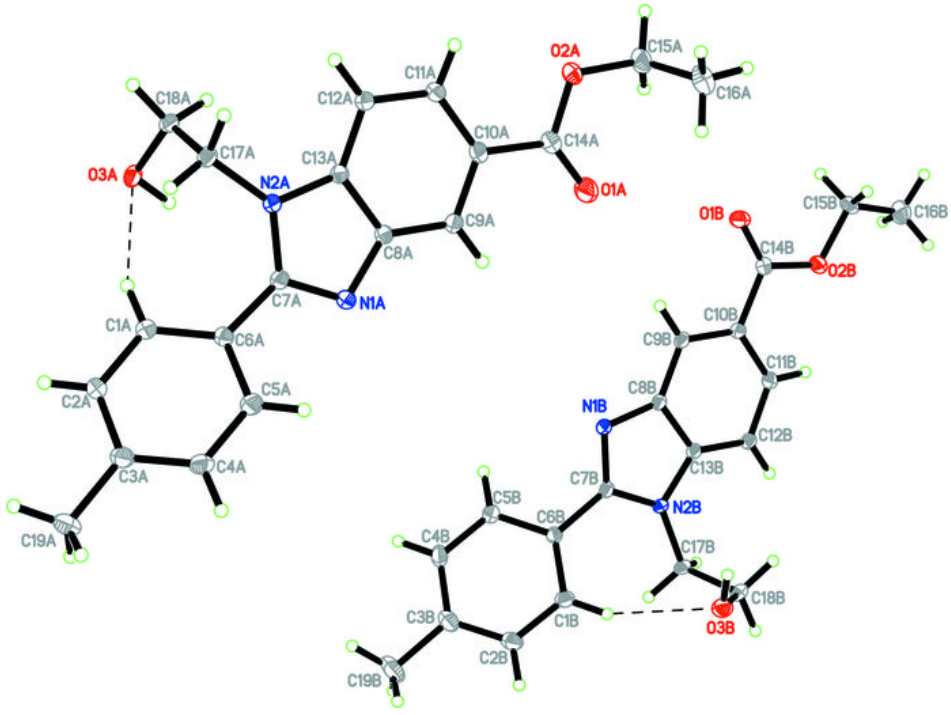

C18A
C17A
03A
N2A
C13A
C12A
C11A
C10A
C14A
02A
C15A
C16A
01A
C9A
C8A
C7A
N1A
C1A
C6A
C5A
C2A
C3A
C4A
C19A
01B
C15B
C16B
C14B
02B
C10B
C9B
C11B
C8B
N1B
C12B
C13B
C7B
N2B
C5B
C6B
C4B
C17B
C18B
03B
C3B
C1B
C2B
C19B

Fig. 2

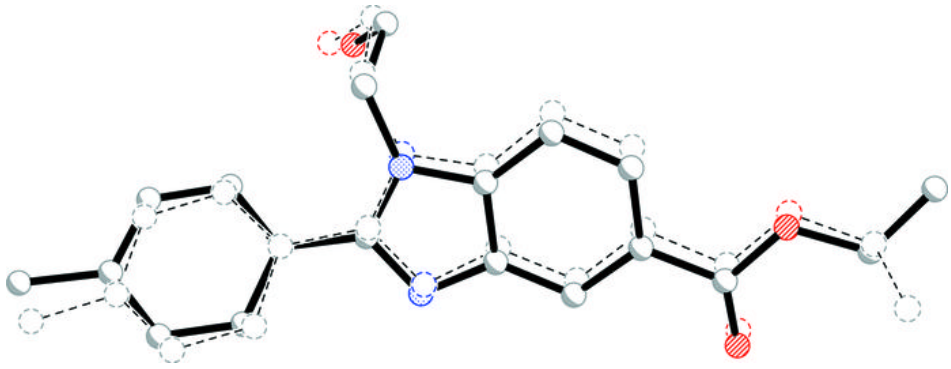
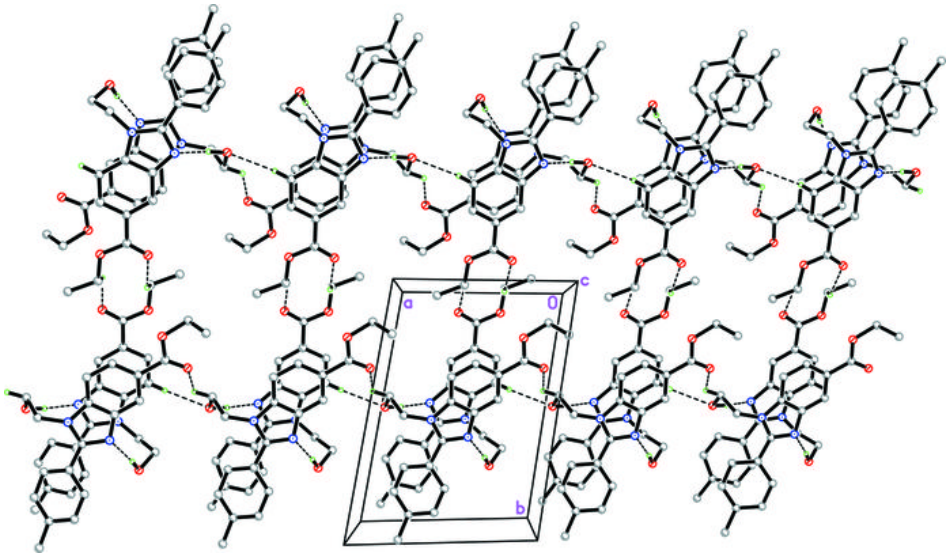


Fig. 3



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(*E*)-*N*′-[4-(Dimethylamino)benzylidene]-4-hydroxybenzohydrazide hemihydrate

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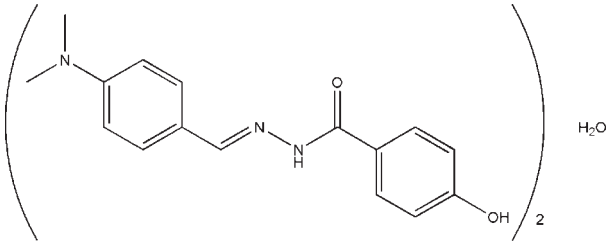
Key indicators: single-crystal X-ray study; T = 298 K; mean σ(C–C) = 0.004 Å; R factor = 0.037; wR factor = 0.094; data-to-parameter ratio = 8.0.

In the title compound, $C_{16}H_{17}N_3O_2\cdot0.5H_2O$, the two hydrazide molecules are approximately planar: the dihedral angles between the two substituted benzene rings are 7.7 (2) and 4.2 (2)°. Both hydrazone molecules exist in a *trans* geometry with respect to their methylidene units. In the crystal, the water molecule lies between the two organic molecules and makes bifurcated O—H···(N,O) hydrogen bonds to both of them. The hydrazide molecules form N—H···O and O—H···O hydrogen bonds, resulting in a three-dimensional network.

Related literature

For the biological activity of hydrazone compounds, see: Banerjee *et al.* (2009). For the structures of hydrazone compounds, see: Ahmad *et al.* (2010); Li *et al.* (2010); Naveenkumar *et al.* (2010); Zhang (2009); Fun *et al.* (2008).



Experimental

Crystal data

$C_{16}H_{17}N_3O_2\cdot0.5H_2O$
M_r = 292.34
Monoclinic, $P2_1$
a = 6.1514 (9) Å
b = 18.098 (3) Å
c = 13.356 (2) Å
β = 95.489 (2)°
V = 1480.1 (4) Å^3
Z = 4
Mo $K\alpha$ radiation
μ = 0.09 mm^{-1}
T = 298 K
0.28 × 0.27 × 0.27 mm

Data collection

Bruker SMART CCD diffractometer
Absorption correction: multi-scan (*SADABS*; Sheldrick, 1996)
T_{min} = 0.975, T_{max} = 0.976
8336 measured reflections
3254 independent reflections
2593 reflections with $I > 2\sigma(I)$
R_{int} = 0.028

Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.037
$wR(F^2)$ = 0.094
S = 1.04
3254 reflections
407 parameters
6 restraints
H atoms treated by a mixture of independent and constrained refinement
$\Delta\rho_{max}$ = 0.13 e Å^{-3}
$\Delta\rho_{min}$ = −0.11 e Å^{-3}

Table 1
Hydrogen-bond geometry (Å, °).

D—H···A	D—H	H···A	D···A	D—H···A
N5—H5*C*···O2^{i}	0.90 (1)	2.56 (3)	3.171 (3)	125 (3)
N2—H2*A*···O5^{ii}	0.90 (1)	2.12 (1)	3.003 (3)	168 (3)
O4—H4···O1^{iii}	0.82	1.90	2.688 (2)	160
O2—H2*B*···O3^{iv}	0.82	1.89	2.693 (3)	166
O5—H5*A*···O3	0.85 (1)	2.43 (2)	3.178 (3)	146 (3)
O5—H5*A*···N4	0.85 (1)	2.34 (2)	3.038 (3)	140 (3)
O5—H5*B*···O1	0.85 (1)	2.36 (2)	3.100 (3)	145 (3)
O5—H5*B*···N1	0.85 (1)	2.61 (2)	3.375 (3)	150 (3)

Symmetry codes: (i) $-x, y+\frac{1}{2}, -z+1$; (ii) $x-1, y, z$; (iii) $-x+1, y+\frac{1}{2}, -z$; (iv) $-x+1, y-\frac{1}{2}, -z+1$.

Data collection: *SMART* (Bruker, 1998); cell refinement: *SAINT* (Bruker, 1998); data reduction: *SAINT*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *SHELXTL* (Sheldrick, 2008); software used to prepare material for publication: *SHELXTL*.

The work was supported by the Guangdong Pharmaceutical University Young Teachers' Fund and the Ten Hundred Thousand Project of the Bureau of Education of Guangdong Province, China.

Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: HB5475).

References

Ahmad, T., Zia-ur-Rehman, M., Siddiqui, H. L., Mahmud, S. & Parvez, M. (2010). *Acta Cryst.* E**66**, o976.
Banerjee, S., Mondal, S., Chakraborty, W., Sen, S., Gachhui, R., Butcher, R. J., Slawin, A. M. Z., Mandal, C. & Mitra, S. (2009). *Polyhedron*, **28**, 2785–2793.
Bruker (1998). *SMART* and *SAINT*. Bruker AXS Inc., Madison, Wisconsin, USA.
Fun, H.-K., Jebas, S. R., Sujith, K. V., Patil, P. S. & Kalluraya, B. (2008). *Acta Cryst.* E**64**, o1907–o1908.
Li, C., Wang, P. & Su, Y.-Q. (2010). *Acta Cryst.* E**66**, o520.
Naveenkumar, H. S., Sadikun, A., Ibrahim, P., Hemamalini, M. & Fun, H.-K. (2010). *Acta Cryst.* E**66**, o1337–o1338.
Sheldrick, G. M. (1996). *SADABS*. University of Göttingen, Germany.
Sheldrick, G. M. (2008). *Acta Cryst.* A**64**, 112–122.
Zhang, X. (2009). *Acta Cryst.* E**65**, o2200.

supplementary materials

Acta Cryst. (2010). E**66**, o1582 [**doi:10.1107/S1600536810020763**]

(*E*)-*N*'-[4-(Dimethylamino)benzylidene]-4-hydroxybenzohydrazide hemihydrate

H. Liu

Comment

In recent years, much attention has been focused on the biological properties of hydrazone compounds (e.g. Banerjee *et al.*, 2009). A number of hydrazone compounds have been prepared and investigated for their structures (Ahmad *et al.*, 2010; Li *et al.*, 2010; Naveenkumar *et al.*, 2010; Zhang, 2009; Fun *et al.*, 2008). In the present work, a new hydrazone compound with interesting structure is reported.

The title compound consists of two hydrazone molecules and one water molecule (Fig. 1). The two hydrazone molecules are approximately parallel to each other, and are linked together by the water molecule through O—H···N and O—H···O hydrogen bonds (Table 1). Both hydrazone molecules exist in *trans* geometry with respect to the methylidene units. The dihedral angles between the two substituted benzene rings in the hydrazone molecules are 7.7 (2) and 4.2 (2)°.

In the crystal structure, the hydrazone molecules and the water molecules are linked through N—H···O, O—H···O and O—H···N hydrogen bonds (Table 1), forming a three dimensional network (Fig. 2).

Experimental

4-Dimethylaminobenzaldehyde (1.0 mmol, 149 mg) and 4-hydroxybenzohydrazide (1.0 mmol, 152 mg) were mixed in 50 ml methanol. The mixture was stirred at ambient temperature for 2 h and filtered. Colorless blocks of (I) were formed by slow evaporation of the filtrate for a week; presumably water was incorporated from the atmosphere.

Refinement

The amino hydrogen atoms were located in a difference map and refined isotropically, with the N—H distance restrained to 0.90 (1)Å. Other hydrogen atoms were placed in calculated positions (C—H = 0.93 - 0.96 Å, O—H = 0.82 Å) and refined as riding with $U_{iso}(H) = 1.2U_{eq}(C)$ and $1.5U_{eq}(O \text{ and } C_{methyl})$. In the absence of significant anomalous scattering effects, Friedel pairs were averaged.

Figures

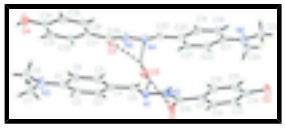


Fig. 1. Molecular structure of (I) with 30% probability displacement ellipsoids. Hydrogen bonds are shown as dashed lines.

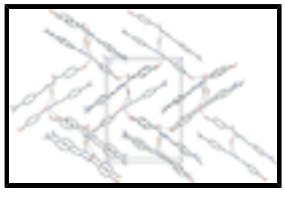


Fig. 2. Packing structure of (I), viewed along the *a* axis. Hydrogen bonds are shown as dashed lines.

(*E*)-*N*'-[4-(Dimethylamino)benzylidene]-4-hydroxybenzohydrazide hemihydrate

Crystal data

$C_{16}H_{17}N_3O_2 \cdot 0.5H_2O$	$F(000) = 620$
$M_r = 292.34$	$D_x = 1.312$ Mg m^{-3}
Monoclinic, $P2_1$	Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å
Hall symbol: P 2yb	Cell parameters from 2665 reflections
$a = 6.1514$ (9) Å	$\theta = 2.6$–$24.5°$
$b = 18.098$ (3) Å	$\mu = 0.09$ mm^{-1}
$c = 13.356$ (2) Å	$T = 298$ K
$\beta = 95.489$ (2)°	Block, colorless
$V = 1480.1$ (4) Å^3	0.28 × 0.27 × 0.27 mm
$Z = 4$	

Data collection

Bruker SMART CCD diffractometer	3254 independent reflections
Radiation source: fine-focus sealed tube	2593 reflections with $I > 2\sigma(I)$
graphite	$R_{int} = 0.028$
ω scans	$\theta_{max} = 27.0°$, $\theta_{min} = 2.3°$
Absorption correction: multi-scan (*SADABS*; Sheldrick, 1996)	$h = -7 \rightarrow 6$
$T_{min} = 0.975$, $T_{max} = 0.976$	$k = -23 \rightarrow 23$
8336 measured reflections	$l = -9 \rightarrow 17$

Refinement

Refinement on F^2	Secondary atom site location: difference Fourier map
Least-squares matrix: full	Hydrogen site location: inferred from neighbouring sites
$R[F^2 > 2\sigma(F^2)] = 0.037$	H atoms treated by a mixture of independent and constrained refinement
$wR(F^2) = 0.094$	$w = 1/[\sigma^2(F_o^2) + (0.0535P)^2 + 0.0137P]$ where $P = (F_o^2 + 2F_c^2)/3$
$S = 1.04$	$(\Delta/\sigma)_{max} < 0.001$
3254 reflections	$\Delta\rho_{max} = 0.13$ e Å^{-3}
407 parameters	$\Delta\rho_{min} = -0.11$ e Å^{-3}
6 restraints	Extinction correction: *SHELXL97* (Sheldrick, 2008), $Fc^* = kFc[1+0.001xFc^2\lambda^3/\sin(2\theta)]^{-1/4}$
Primary atom site location: structure-invariant direct methods	Extinction coefficient: 0.015 (2)

Special details

Geometry. All esds (except the esd in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell esds are taken into account individually in the estimation of esds in distances, angles and torsion angles; correlations between esds in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell esds is used for estimating esds involving l.s. planes.

Refinement. Refinement of F^2 against ALL reflections. The weighted R-factor wR and goodness of fit S are based on F^2, conventional R-factors R are based on F, with F set to zero for negative F^2. The threshold expression of $F^2 > 2\text{sigma}(F^2)$ is used only for calculating R-factors(gt) etc. and is not relevant to the choice of reflections for refinement. R-factors based on F^2 are statistically about twice as large as those based on F, and R- factors based on ALL data will be even larger.

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters ($Å^2$)

	x	*y*	*z*	U_{iso}*/U_{eq}
O1	0.4602 (3)	0.17321 (13)	0.29539 (14)	0.0654 (6)
O2	0.0189 (3)	0.07939 (12)	0.68381 (15)	0.0651 (6)
H2B	0.1181	0.0548	0.7126	0.098*
O3	0.7089 (4)	0.48243 (11)	0.21582 (13)	0.0603 (5)
O4	0.3140 (3)	0.69296 (12)	−0.13484 (15)	0.0649 (6)
H4	0.4072	0.6910	−0.1747	0.097*
O5	0.7330 (3)	0.31729 (12)	0.2971 (2)	0.0688 (6)
N1	0.2364 (3)	0.27325 (12)	0.18320 (15)	0.0465 (5)
N2	0.1558 (4)	0.24130 (13)	0.26688 (16)	0.0486 (5)
N3	0.2760 (4)	0.48063 (14)	−0.21084 (17)	0.0611 (6)
N4	0.3944 (4)	0.43505 (13)	0.32898 (16)	0.0540 (6)
N5	0.3526 (4)	0.47696 (14)	0.24264 (17)	0.0565 (6)
N6	0.2273 (4)	0.26319 (14)	0.73893 (17)	0.0574 (6)
C1	0.2382 (5)	0.44061 (15)	−0.1264 (2)	0.0478 (6)
C2	0.3964 (4)	0.39311 (15)	−0.0790 (2)	0.0500 (6)
H2	0.5311	0.3887	−0.1047	0.060*
C3	0.3556 (4)	0.35288 (15)	0.0050 (2)	0.0496 (6)
H3	0.4637	0.3219	0.0349	0.059*
C4	0.1567 (4)	0.35769 (13)	0.04580 (19)	0.0423 (6)
C5	0.0014 (5)	0.40579 (16)	−0.0010 (2)	0.0523 (7)
H5	−0.1325	0.4106	0.0253	0.063*
C6	0.0391 (5)	0.44617 (15)	−0.0841 (2)	0.0540 (7)
H6	−0.0688	0.4777	−0.1130	0.065*
C7	0.4777 (6)	0.4754 (2)	−0.2563 (2)	0.0733 (9)
H7A	0.5724	0.5152	−0.2327	0.110*
H7B	0.4487	0.4785	−0.3281	0.110*
H7C	0.5468	0.4291	−0.2386	0.110*
C8	0.1119 (6)	0.5281 (2)	−0.2596 (3)	0.0777 (10)
H8A	−0.0102	0.4989	−0.2867	0.117*
H8B	0.1715	0.5544	−0.3131	0.117*
H8C	0.0646	0.5627	−0.2118	0.117*
C9	0.1034 (4)	0.31732 (14)	0.13410 (19)	0.0475 (6)
H9	−0.0343	0.3238	0.1560	0.057*

C10	0.2801 (4)	0.19211 (14)	0.32054 (19)	0.0446 (6)
C11	0.1976 (4)	0.16137 (13)	0.41294 (18)	0.0403 (5)
C12	0.3309 (4)	0.11208 (16)	0.4684 (2)	0.0518 (7)
H12	0.4620	0.0979	0.4449	0.062*
C13	0.2740 (5)	0.08319 (17)	0.5585 (2)	0.0537 (7)
H13	0.3663	0.0501	0.5949	0.064*
C14	0.0801 (5)	0.10396 (14)	0.59334 (19)	0.0486 (6)
C15	−0.0585 (5)	0.15106 (16)	0.5375 (2)	0.0548 (7)
H15	−0.1926	0.1634	0.5598	0.066*
C16	0.0001 (4)	0.18011 (15)	0.4486 (2)	0.0510 (6)
H16	−0.0937	0.2127	0.4120	0.061*
C17	0.2277 (4)	0.30157 (14)	0.65040 (19)	0.0442 (6)
C18	0.0467 (5)	0.34222 (16)	0.6109 (2)	0.0529 (7)
H18	−0.0778	0.3437	0.6452	0.063*
C19	0.0500 (5)	0.38022 (16)	0.5216 (2)	0.0565 (7)
H19	−0.0734	0.4064	0.4965	0.068*
C20	0.2329 (4)	0.38037 (14)	0.4682 (2)	0.0484 (6)
C21	0.4131 (4)	0.34006 (14)	0.5066 (2)	0.0485 (6)
H21	0.5370	0.3391	0.4718	0.058*
C22	0.4125 (4)	0.30143 (15)	0.5953 (2)	0.0490 (6)
H22	0.5359	0.2748	0.6193	0.059*
C23	0.0321 (5)	0.25746 (19)	0.7900 (2)	0.0673 (9)
H23A	−0.0182	0.3061	0.8051	0.101*
H23B	0.0634	0.2302	0.8514	0.101*
H23C	−0.0790	0.2323	0.7476	0.101*
C24	0.4155 (6)	0.2222 (2)	0.7789 (2)	0.0712 (9)
H24A	0.4520	0.1861	0.7304	0.107*
H24B	0.3842	0.1976	0.8395	0.107*
H24C	0.5364	0.2553	0.7933	0.107*
C25	0.2250 (5)	0.42193 (15)	0.3751 (2)	0.0546 (7)
H25	0.0908	0.4399	0.3476	0.065*
C26	0.5169 (5)	0.50093 (14)	0.19151 (19)	0.0473 (6)
C27	0.4562 (4)	0.55060 (13)	0.10541 (17)	0.0421 (6)
C28	0.2589 (4)	0.58769 (15)	0.09028 (19)	0.0503 (6)
H28	0.1542	0.5804	0.1351	0.060*
C29	0.2144 (4)	0.63495 (16)	0.0107 (2)	0.0517 (7)
H29	0.0806	0.6592	0.0021	0.062*
C30	0.3686 (4)	0.64671 (14)	−0.05740 (18)	0.0456 (6)
C31	0.5696 (4)	0.61128 (15)	−0.04239 (19)	0.0491 (6)
H31	0.6753	0.6193	−0.0865	0.059*
C32	0.6112 (4)	0.56435 (14)	0.03792 (19)	0.0462 (6)
H32	0.7464	0.5411	0.0476	0.055*
H2A	0.030 (3)	0.2603 (18)	0.284 (2)	0.080*
H5C	0.213 (2)	0.4898 (19)	0.223 (2)	0.080*
H5A	0.694 (5)	0.3625 (7)	0.297 (3)	0.080*
H5B	0.617 (3)	0.2919 (14)	0.285 (3)	0.080*

Atomic displacement parameters (Å^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
O1	0.0554 (12)	0.0931 (15)	0.0510 (11)	0.0225 (11)	0.0224 (9)	0.0161 (11)
O2	0.0711 (14)	0.0726 (14)	0.0561 (12)	−0.0083 (11)	0.0306 (11)	0.0069 (10)
O3	0.0715 (14)	0.0634 (12)	0.0472 (11)	0.0164 (11)	0.0119 (10)	0.0052 (9)
O4	0.0611 (13)	0.0811 (14)	0.0558 (12)	0.0156 (11)	0.0230 (10)	0.0279 (11)
O5	0.0549 (12)	0.0606 (12)	0.0941 (16)	0.0071 (10)	0.0228 (12)	−0.0077 (12)
N1	0.0485 (13)	0.0501 (11)	0.0426 (12)	−0.0022 (10)	0.0124 (10)	0.0019 (10)
N2	0.0461 (12)	0.0555 (12)	0.0461 (12)	0.0021 (11)	0.0149 (10)	0.0063 (10)
N3	0.0613 (16)	0.0686 (15)	0.0532 (15)	−0.0010 (12)	0.0045 (12)	0.0180 (13)
N4	0.0742 (17)	0.0493 (12)	0.0392 (12)	−0.0003 (11)	0.0093 (11)	0.0065 (10)
N5	0.0670 (15)	0.0566 (13)	0.0470 (13)	0.0007 (12)	0.0109 (12)	0.0151 (11)
N6	0.0596 (15)	0.0673 (15)	0.0471 (13)	−0.0063 (12)	0.0153 (11)	0.0144 (12)
C1	0.0507 (16)	0.0488 (14)	0.0429 (14)	−0.0061 (12)	−0.0004 (12)	−0.0005 (12)
C2	0.0466 (15)	0.0570 (15)	0.0470 (15)	−0.0005 (13)	0.0070 (12)	0.0040 (13)
C3	0.0486 (15)	0.0507 (14)	0.0495 (15)	0.0032 (12)	0.0052 (13)	0.0044 (12)
C4	0.0421 (14)	0.0442 (13)	0.0407 (13)	0.0021 (11)	0.0041 (11)	0.0012 (11)
C5	0.0446 (15)	0.0592 (16)	0.0539 (16)	0.0081 (12)	0.0076 (12)	0.0011 (13)
C6	0.0537 (17)	0.0557 (16)	0.0520 (16)	0.0112 (13)	0.0017 (14)	0.0067 (13)
C7	0.081 (2)	0.082 (2)	0.0582 (19)	−0.0092 (19)	0.0156 (17)	0.0109 (17)
C8	0.083 (2)	0.080 (2)	0.068 (2)	0.0059 (19)	−0.0020 (18)	0.0280 (18)
C9	0.0431 (14)	0.0523 (14)	0.0479 (15)	0.0009 (12)	0.0084 (12)	−0.0007 (12)
C10	0.0447 (15)	0.0486 (14)	0.0416 (14)	−0.0001 (11)	0.0102 (11)	−0.0040 (11)
C11	0.0405 (13)	0.0415 (12)	0.0398 (13)	0.0002 (10)	0.0073 (11)	−0.0042 (10)
C12	0.0474 (15)	0.0624 (16)	0.0477 (15)	0.0042 (13)	0.0155 (12)	−0.0019 (13)
C13	0.0568 (17)	0.0601 (16)	0.0460 (14)	0.0065 (13)	0.0135 (13)	0.0075 (13)
C14	0.0553 (16)	0.0485 (14)	0.0440 (14)	−0.0101 (13)	0.0154 (12)	−0.0038 (12)
C15	0.0459 (15)	0.0631 (17)	0.0582 (17)	−0.0015 (14)	0.0196 (13)	−0.0019 (14)
C16	0.0466 (15)	0.0539 (15)	0.0540 (15)	−0.0003 (12)	0.0116 (12)	−0.0015 (13)
C17	0.0456 (14)	0.0443 (12)	0.0429 (14)	−0.0077 (11)	0.0054 (11)	0.0036 (11)
C18	0.0466 (16)	0.0582 (16)	0.0561 (16)	−0.0023 (13)	0.0165 (13)	0.0041 (14)
C19	0.0514 (17)	0.0561 (16)	0.0626 (18)	0.0050 (13)	0.0087 (14)	0.0123 (14)
C20	0.0573 (17)	0.0447 (13)	0.0442 (15)	−0.0021 (12)	0.0103 (13)	0.0045 (12)
C21	0.0513 (16)	0.0502 (14)	0.0463 (14)	−0.0049 (12)	0.0165 (12)	0.0013 (12)
C22	0.0466 (15)	0.0527 (14)	0.0485 (15)	0.0020 (12)	0.0095 (12)	0.0061 (12)
C23	0.075 (2)	0.075 (2)	0.0553 (17)	−0.0181 (17)	0.0228 (16)	0.0084 (16)
C24	0.086 (2)	0.074 (2)	0.0537 (18)	0.0081 (18)	0.0090 (17)	0.0218 (16)
C25	0.0645 (19)	0.0485 (15)	0.0511 (17)	0.0020 (13)	0.0079 (14)	0.0081 (13)
C26	0.0670 (19)	0.0406 (13)	0.0351 (13)	0.0054 (12)	0.0090 (13)	−0.0043 (11)
C27	0.0557 (15)	0.0371 (12)	0.0349 (12)	0.0009 (11)	0.0109 (11)	−0.0040 (10)
C28	0.0543 (16)	0.0564 (15)	0.0431 (14)	−0.0005 (13)	0.0198 (12)	0.0027 (12)
C29	0.0468 (15)	0.0615 (16)	0.0490 (16)	0.0078 (12)	0.0165 (12)	0.0070 (13)
C30	0.0527 (15)	0.0495 (14)	0.0368 (13)	0.0015 (12)	0.0158 (11)	0.0041 (11)
C31	0.0488 (15)	0.0559 (15)	0.0453 (15)	0.0045 (12)	0.0191 (12)	0.0020 (12)
C32	0.0505 (16)	0.0465 (14)	0.0428 (14)	0.0080 (11)	0.0103 (12)	0.0010 (11)

Geometric parameters (Å, °)

O1—C10	1.236 (3)	C10—C11	1.487 (3)
O2—C14	1.373 (3)	C11—C12	1.379 (4)
O2—H2B	0.8200	C11—C16	1.388 (3)
O3—C26	1.240 (3)	C12—C13	1.387 (4)
O4—C30	1.348 (3)	C12—H12	0.9300
O4—H4	0.8200	C13—C14	1.374 (4)
O5—H5A	0.852 (10)	C13—H13	0.9300
O5—H5B	0.853 (10)	C14—C15	1.374 (4)
N1—C9	1.278 (3)	C15—C16	1.378 (4)
N1—N2	1.391 (3)	C15—H15	0.9300
N2—C10	1.337 (3)	C16—H16	0.9300
N2—H2A	0.896 (10)	C17—C18	1.396 (4)
N3—C1	1.379 (3)	C17—C22	1.412 (3)
N3—C8	1.434 (4)	C18—C19	1.379 (4)
N3—C7	1.436 (4)	C18—H18	0.9300
N4—C25	1.283 (4)	C19—C20	1.389 (4)
N4—N5	1.384 (3)	C19—H19	0.9300
N5—C26	1.345 (3)	C20—C21	1.384 (4)
N5—H5C	0.903 (10)	C20—C25	1.449 (4)
N6—C17	1.371 (3)	C21—C22	1.375 (4)
N6—C24	1.435 (4)	C21—H21	0.9300
N6—C23	1.441 (3)	C22—H22	0.9300
C1—C6	1.400 (4)	C23—H23A	0.9600
C1—C2	1.403 (4)	C23—H23B	0.9600
C2—C3	1.380 (4)	C23—H23C	0.9600
C2—H2	0.9300	C24—H24A	0.9600
C3—C4	1.389 (4)	C24—H24B	0.9600
C3—H3	0.9300	C24—H24C	0.9600
C4—C5	1.395 (4)	C25—H25	0.9300
C4—C9	1.451 (4)	C26—C27	1.479 (4)
C5—C6	1.368 (4)	C27—C28	1.385 (4)
C5—H5	0.9300	C27—C32	1.396 (3)
C6—H6	0.9300	C28—C29	1.372 (4)
C7—H7A	0.9600	C28—H28	0.9300
C7—H7B	0.9600	C29—C30	1.391 (3)
C7—H7C	0.9600	C29—H29	0.9300
C8—H8A	0.9600	C30—C31	1.390 (4)
C8—H8B	0.9600	C31—C32	1.373 (4)
C8—H8C	0.9600	C31—H31	0.9300
C9—H9	0.9300	C32—H32	0.9300
C14—O2—H2B	109.5	O2—C14—C15	118.1 (2)
C30—O4—H4	109.5	C13—C14—C15	120.0 (2)
H5A—O5—H5B	107 (2)	C14—C15—C16	120.3 (3)
C9—N1—N2	114.3 (2)	C14—C15—H15	119.9
C10—N2—N1	118.5 (2)	C16—C15—H15	119.9
C10—N2—H2A	126 (2)	C15—C16—C11	120.8 (3)

N1—N2—H2A	115 (2)	C15—C16—H16	119.6
C1—N3—C8	121.3 (3)	C11—C16—H16	119.6
C1—N3—C7	122.1 (3)	N6—C17—C18	121.7 (2)
C8—N3—C7	116.5 (3)	N6—C17—C22	121.1 (2)
C25—N4—N5	114.0 (2)	C18—C17—C22	117.2 (2)
C26—N5—N4	120.7 (2)	C19—C18—C17	120.8 (2)
C26—N5—H5C	120 (2)	C19—C18—H18	119.6
N4—N5—H5C	119 (2)	C17—C18—H18	119.6
C17—N6—C24	121.0 (2)	C18—C19—C20	121.7 (3)
C17—N6—C23	121.0 (2)	C18—C19—H19	119.2
C24—N6—C23	117.8 (2)	C20—C19—H19	119.2
N3—C1—C6	121.0 (3)	C21—C20—C19	117.9 (2)
N3—C1—C2	121.8 (3)	C21—C20—C25	123.5 (2)
C6—C1—C2	117.3 (2)	C19—C20—C25	118.6 (3)
C3—C2—C1	121.2 (3)	C22—C21—C20	121.3 (2)
C3—C2—H2	119.4	C22—C21—H21	119.3
C1—C2—H2	119.4	C20—C21—H21	119.3
C2—C3—C4	121.4 (2)	C21—C22—C17	121.1 (2)
C2—C3—H3	119.3	C21—C22—H22	119.5
C4—C3—H3	119.3	C17—C22—H22	119.5
C3—C4—C5	117.0 (2)	N6—C23—H23A	109.5
C3—C4—C9	124.3 (2)	N6—C23—H23B	109.5
C5—C4—C9	118.7 (2)	H23A—C23—H23B	109.5
C6—C5—C4	122.4 (3)	N6—C23—H23C	109.5
C6—C5—H5	118.8	H23A—C23—H23C	109.5
C4—C5—H5	118.8	H23B—C23—H23C	109.5
C5—C6—C1	120.8 (3)	N6—C24—H24A	109.5
C5—C6—H6	119.6	N6—C24—H24B	109.5
C1—C6—H6	119.6	H24A—C24—H24B	109.5
N3—C7—H7A	109.5	N6—C24—H24C	109.5
N3—C7—H7B	109.5	H24A—C24—H24C	109.5
H7A—C7—H7B	109.5	H24B—C24—H24C	109.5
N3—C7—H7C	109.5	N4—C25—C20	123.1 (3)
H7A—C7—H7C	109.5	N4—C25—H25	118.5
H7B—C7—H7C	109.5	C20—C25—H25	118.5
N3—C8—H8A	109.5	O3—C26—N5	121.5 (2)
N3—C8—H8B	109.5	O3—C26—C27	122.1 (2)
H8A—C8—H8B	109.5	N5—C26—C27	116.4 (2)
N3—C8—H8C	109.5	C28—C27—C32	117.6 (2)
H8A—C8—H8C	109.5	C28—C27—C26	124.1 (2)
H8B—C8—H8C	109.5	C32—C27—C26	118.2 (2)
N1—C9—C4	123.2 (2)	C29—C28—C27	121.5 (2)
N1—C9—H9	118.4	C29—C28—H28	119.2
C4—C9—H9	118.4	C27—C28—H28	119.2
O1—C10—N2	121.4 (2)	C28—C29—C30	120.3 (2)
O1—C10—C11	120.5 (2)	C28—C29—H29	119.9
N2—C10—C11	118.1 (2)	C30—C29—H29	119.9
C12—C11—C16	117.9 (2)	O4—C30—C31	123.4 (2)
C12—C11—C10	117.1 (2)	O4—C30—C29	117.5 (2)

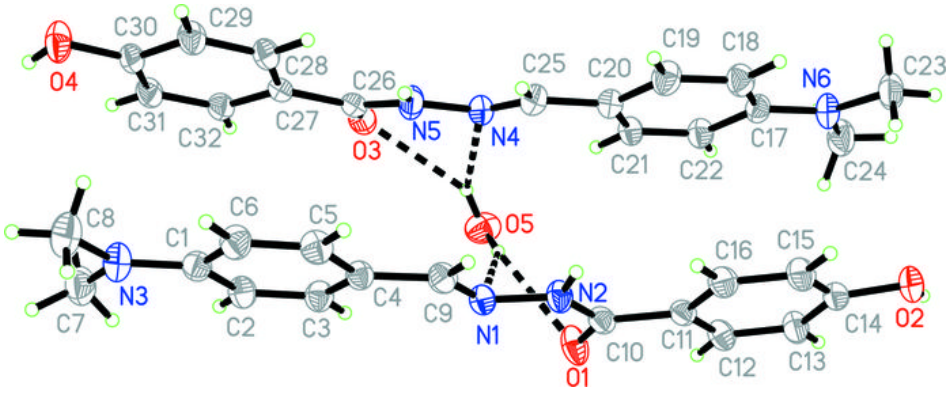
C16—C11—C10	124.9 (2)	C31—C30—C29	119.2 (2)
C11—C12—C13	121.6 (3)	C32—C31—C30	119.7 (2)
C11—C12—H12	119.2	C32—C31—H31	120.2
C13—C12—H12	119.2	C30—C31—H31	120.2
C14—C13—C12	119.3 (3)	C31—C32—C27	121.8 (2)
C14—C13—H13	120.3	C31—C32—H32	119.1
C12—C13—H13	120.3	C27—C32—H32	119.1
O2—C14—C13	122.0 (3)		

Hydrogen-bond geometry (Å, °)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
N5—H5C···O2^{i}	0.90 (1)	2.56 (3)	3.171 (3)	125 (3)
N2—H2A···O5^{ii}	0.90 (1)	2.12 (1)	3.003 (3)	168 (3)
O4—H4···O1^{iii}	0.82	1.90	2.688 (2)	160
O2—H2B···O3^{iv}	0.82	1.89	2.693 (3)	166
O5—H5A···O3	0.85 (1)	2.43 (2)	3.178 (3)	146 (3)
O5—H5A···N4	0.85 (1)	2.34 (2)	3.038 (3)	140 (3)
O5—H5B···O1	0.85 (1)	2.36 (2)	3.100 (3)	145 (3)
O5—H5B···N1	0.85 (1)	2.61 (2)	3.375 (3)	150 (3)

Symmetry codes: (i) −*x*, *y*+1/2, −*z*+1; (ii) *x*−1, *y*, *z*; (iii) −*x*+1, *y*+1/2, −*z*; (iv) −*x*+1, *y*−1/2, −*z*+1.

Fig. 1


O4
C30
C29
C28
C26
C31
C32
C27
O3
N5
N4
C25
C20
C19
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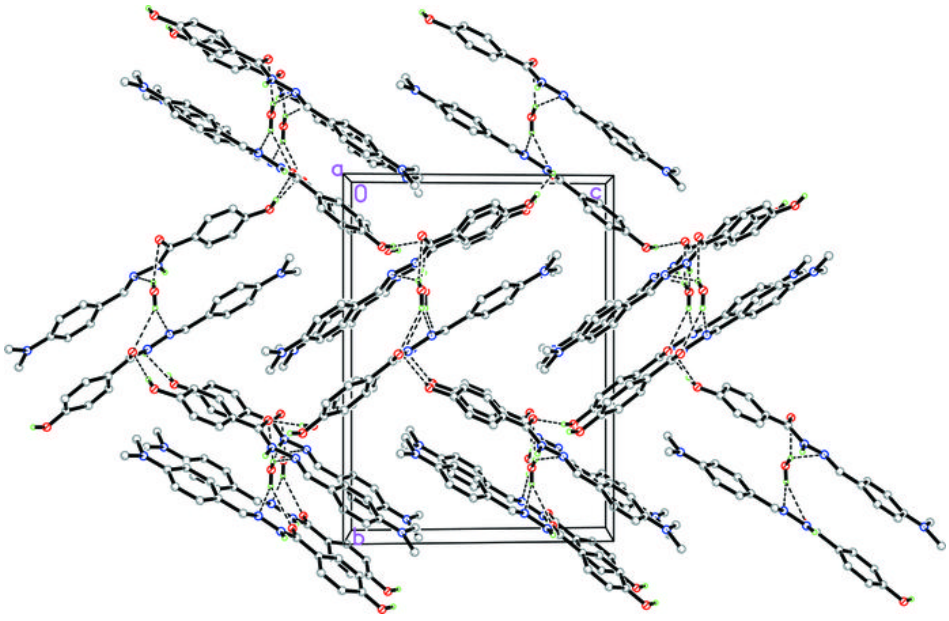
C23
C21
C22
C17
C24
O5
C8
C6
C5
C1
N3
C7
C2
C3
C4
C9
N1
N2
C16
C15
C11
C10
C12
C13
C14
O2
O1

Fig. 2



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Tris(2,2′-bipyridine)cobalt(II) μ_6-oxido-dodeca-μ_2-oxido-hexaoxidohexamolydate(VI)

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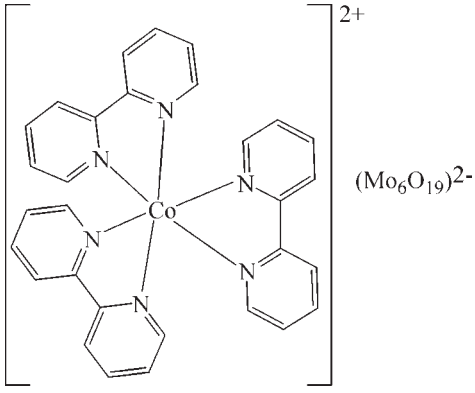
Key indicators: single-crystal X-ray study; T = 296 K; mean σ(C–C) = 0.010 Å; R factor = 0.032; wR factor = 0.092; data-to-parameter ratio = 11.6.

In the title compound, $[Co(C_{10}H_8N_2)_3][Mo_6O_{19}]$, the Co^{2+} cation is surrounded in a distorted octahedral coordination by six N atoms from three 2,2′-bipyridine ligands. The distribution of Mo—O bond lengths in the Lindqvist isopolyanion is consistent with other structures containing the same unit. In the crystal, the cations and anions are linked by C—H···O interactions.

Related literature

For general background to polyoxometalates, see: Pope & Müller (1991). For polyoxometalates modified with amines, see: Zhang, Dou *et al.* (2009); Zhang, Wei *et al.* (2009). For another structure containing the μ6-oxido-dodecakis-μ2-oxido-hexaoxidohexamolydate(VI) anion see: Dahlstrom *et al.* (1982). For Co—N bond lengths in a related structure, see: Li & Xu (2009).



Experimental

Crystal data

$[Co(C_{10}H_8N_2)_3][Mo_6O_{19}]$
M_r = 1407.12
Monoclinic, $P2_1/n$
a = 12.310 (2) Å
b = 18.979 (4) Å
c = 17.150 (4) Å
β = 100.895 (3)°
V = 3934.4 (14) Å^3
Z = 4
Mo $K\alpha$ radiation
μ = 2.35 mm^{-1}
T = 296 K
0.12 × 0.10 × 0.08 mm

Data collection

Bruker APEXII CCD diffractometer
Absorption correction: multi-scan (*SADABS*; Bruker, 2001)
T_{min} = 0.766, T_{max} = 0.834
25652 measured reflections
6500 independent reflections
4649 reflections with $I > 2\sigma(I)$
R_{int} = 0.041

Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.032
$wR(F^2)$ = 0.092
S = 1.00
6500 reflections
559 parameters
H-atom parameters constrained
$\Delta\rho_{max}$ = 0.65 e Å^{-3}
$\Delta\rho_{min}$ = −0.54 e Å^{-3}

Table 1
Selected bond lengths (Å).

Co1—N5	2.075 (5)	Co1—N4	2.081 (5)
Co1—N6	2.078 (5)	Co1—N2	2.091 (5)
Co1—N1	2.079 (5)	Co1—N3	2.100 (5)

Table 2
Hydrogen-bond geometry (Å, °).

D—H···A	D—H	H···A	D···A	D—H···A
C2—H2···O11^{i}	0.93	2.36	3.166 (9)	145
C4—H4···O17^{ii}	0.93	2.52	3.165 (9)	127
C11—H11···O4^{iii}	0.93	2.51	3.400 (8)	161
C12—H12···O2^{iii}	0.93	2.47	3.277 (10)	145
C20—H20···O14^{iv}	0.93	2.53	3.159 (9)	125
C22—H22···O8^{v}	0.93	2.54	3.230 (9)	132
C26—H26···O18	0.93	2.58	3.459 (8)	157

Symmetry codes: (i) $x, y, z-1$; (ii) $-x+\frac{3}{2}, y+\frac{1}{2}, -z+\frac{1}{2}$; (iii) $x-\frac{1}{2}, -y+\frac{1}{2}, z-\frac{1}{2}$; (iv) $-x+2, -y, -z+1$; (v) $x+\frac{1}{2}, -y+\frac{1}{2}, z-\frac{1}{2}$.

Data collection: *APEX2* (Bruker, 2004); cell refinement: *SAINT-Plus* (Bruker, 2001); data reduction: *SAINT-Plus*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *SHELXTL* (Sheldrick, 2008); software used to prepare material for publication: *SHELXTL*.

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Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: HB5476).

References

Bruker (2001). *SAINT-Plus* and *SADABS*. Bruker AXS Inc., Madison, Wisconsin, USA.

Bruker (2004). *APEX2*. Bruker AXS Inc., Madison, Wisconsin, USA.

Dahlstrom, P., Zubieta, J., Neaves, B. & Dilworth, J. R. (1982). *Cryst. Struct. Commun.* **11**, 463–469.

Li, P.-Z. & Xu, Q. (2009). *Acta Cryst.* E**65**, m508.

Pope, M. T. & Müller, A. (1991). *Angew. Chem. Int. Ed.* **30**, 34–38.

Sheldrick, G. M. (2008). *Acta Cryst.* A**64**, 112–122.

Zhang, X. T., Dou, J. M., Wei, P. H., Li, D. C., Li, B., Shi, C. W. & Hu, B. (2009). *Inorg. Chim. Acta*, **362**, 3325–3332.

Zhang, X. T., Wei, P. H., Sun, D. F., Ni, Z. H., Dou, J. M., Li, B., Shi, C. W. & Hu, B. (2009). *Cryst. Growth Des.* **9**, 4424–4428.

supplementary materials

Acta Cryst. (2010). E**66**, m756-m757 [**doi:10.1107/S1600536810020775**]

Tris(2,2'-bipyridine)cobalt(II) μ_6-oxido-dodeca-μ_2-oxido-hexaoxidohexamolydate(VI)

Y. Liu, X. Zhang, Z. Xue and J. Sheng

Comment

There has been extensive interest in heteropolyoxometalates, owing to their fascinating properties and great potential applications in many fields such as, catalysis, material science, medicine, and magnetochemistry (Pope *et al.*, 1991). The organic amines, such as 3-(2-pyridyl)pyrazole and pyrazine, are used to effectively modify heteropolyoxomolybdates under hydrothermal condictions (Zhang, Dou *et al.*, 2009; Zhang, Wei, Sun *et al.*, 2009). Here, we describe the synthesis and structural characterization of the title compound.

As shown in Figure 1, the title compound consists of two subunits, *viz.* of a complex $[Co(C_{10}H_8N_2)_3]^{2+}$ cation, one typical Lindqvist isopolyanion $[Mo_6O_{19}]^{2-}$ anion (Dahlstrom *et al.*, 1982). The Co^{2+} cation is surrounded in a distorted octahedral coordination by six N atoms from three chelating 2,2'-bipyridine ligands. The Co—N bond lengths are in the range of 2.075 (5)—2.100 (5) Å, respectively, compared to reported one (Li & Xu, 2009).

The $[Mo_6O_{19}]^{2-}$ polyoxoanion, possessing well known Lindquist structure, is formed by six MoO_6 octahedra connected with each other through edge-sharing oxygen atoms and thus exhibits approximate Oh symmetry. Three kinds of oxygen atoms exist in the cluster, that is, terminal Oa, double-bridging oxygen Ob, and central oxygen Oc. Therefore, Mo—O band lengths can be grouped into three sets: Mo—Oa 1.669 (5)—1.682 (5) Å; Mo—Ob 1.888 (4)—1.951 (5) Å; and Mo—Oc 2.299 (4)—2.318 (4) Å; these bond distances have a rule of Mo—Oa<Mo—Ob<Mo—Oc. Comparing Mo=O bond distances with that of Lindqvist isopolyanion salt (Dahlstrom, 1982), Mo=O distances have no obvious change.

Experimental

A mixture of 2,2'-bipyridine (0.5 mmoL, 0.07 g), molybdenum(VI) oxide (1 mmol, 0.14 g), oxalic aicd (10 mmol, 0.09), *p*-carboxyphenylboronic acid (0.3 mmoL, 0.05 g), and cobalt(II) sulfate heptahydrate (0.2 mmol, 0.05 g) in 14 ml distilled water was sealed in a 25 ml Teflon-lined stainless steel autoclave and was kept at 433 K for three days. Upon cooling, red blocks of (I) were obtained. Anal. Calc. for $C_{30}H_{24}CoMo_6N_6O_{19}$: C, 25.58; H, 1.71; N, 5.97. Found: C, 22.38; H, 1.52; N, 5.78%.

Refinement

All hydrogen atoms bound to carbon were refined using a riding model with distance C—H = 0.93 Å, $U_{iso} = 1.2U_{eq}$ (C) for aromatic atoms.

Figures

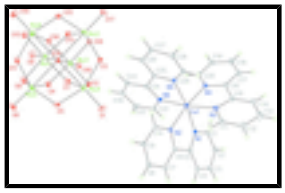


Fig. 1. The molecular structure of (I) shoiwng displacement ellipsoids drawn at the 30% probability level; H atoms are given as spheres of arbitrary radius.

Tris(2,2'-bipyridine)cobalt(II) μ_6-oxido-dodeca-μ_2-oxido-hexaoxidohexamolydate(VI)

Crystal data

$[Co(C_{10}H_8N_2)_3][Mo_6O_{19}]$	$F(000) = 2708$
$M_r = 1407.12$	$D_x = 2.376$ Mg m^{-3}
Monoclinic, $P2_1/n$	Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å
Hall symbol: -P 2yn	Cell parameters from 2413 reflections
$a = 12.310$ (2) Å	$\theta = 2.4$–$24.3°$
$b = 18.979$ (4) Å	$\mu = 2.35$ mm^{-1}
$c = 17.150$ (4) Å	$T = 296$ K
$\beta = 100.895$ (3)°	Block, red
$V = 3934.4$ (14) Å^3	0.12 × 0.10 × 0.08 mm
$Z = 4$	

Data collection

Bruker APEXII CCD diffractometer	6500 independent reflections
Radiation source: fine-focus sealed tube	4649 reflections with $I > 2\sigma(I)$
graphite	$R_{int} = 0.041$
φ and ω scans	$\theta_{max} = 24.5°$, $\theta_{min} = 2.2°$
Absorption correction: multi-scan (*SADABS*; Bruker, 2001)	$h = -14\rightarrow13$
$T_{min} = 0.766$, $T_{max} = 0.834$	$k = -22\rightarrow22$
25652 measured reflections	$l = -18\rightarrow19$

Refinement

Refinement on F^2	Primary atom site location: structure-invariant direct methods
Least-squares matrix: full	Secondary atom site location: difference Fourier map
$R[F^2 > 2\sigma(F^2)] = 0.032$	Hydrogen site location: inferred from neighbouring sites
$wR(F^2) = 0.092$	H-atom parameters constrained
$S = 1.00$	$w = 1/[\sigma^2(F_o^2) + (0.041P)^2 + 10.1791P]$ where $P = (F_o^2 + 2F_c^2)/3$
6500 reflections	$(\Delta/\sigma)_{max} = 0.003$

559 parameters

0 restraints

$\Delta\rho_{max} = 0.65$ e Å^{-3}

$\Delta\rho_{min} = -0.54$ e Å^{-3}

Special details

Geometry. All e.s.d.'s (except the e.s.d. in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell e.s.d.'s are taken into account individually in the estimation of e.s.d.'s in distances, angles and torsion angles; correlations between e.s.d.'s in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell e.s.d.'s is used for estimating e.s.d.'s involving l.s. planes.

Refinement. Refinement of F^2 against ALL reflections. The weighted *R*-factor *wR* and goodness of fit *S* are based on F^2, conventional *R*-factors *R* are based on *F*, with *F* set to zero for negative F^2. The threshold expression of $F^2 > \sigma(F^2)$ is used only for calculating *R*-factors(gt) *etc*. and is not relevant to the choice of reflections for refinement. *R*-factors based on F^2 are statistically about twice as large as those based on *F*, and *R*- factors based on ALL data will be even larger.

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å^2)

	x	*y*	*z*	U_{iso}*/U_{eq}
C1	0.8841 (6)	0.1849 (4)	0.0079 (4)	0.0458 (17)
H1	0.8962	0.1371	0.0008	0.055*
C2	0.9125 (6)	0.2314 (4)	−0.0452 (4)	0.0523 (19)
H2	0.9438	0.2154	−0.0873	0.063*
C3	0.8947 (7)	0.3012 (4)	−0.0362 (4)	0.061 (2)
H3	0.9130	0.3336	−0.0723	0.073*
C4	0.8498 (6)	0.3235 (4)	0.0264 (4)	0.0526 (19)
H4	0.8378	0.3712	0.0338	0.063*
C5	0.8221 (5)	0.2735 (3)	0.0793 (4)	0.0395 (15)
C6	0.7754 (5)	0.2926 (3)	0.1498 (4)	0.0355 (14)
C7	0.7683 (6)	0.3610 (3)	0.1751 (4)	0.0478 (17)
H7	0.7896	0.3982	0.1461	0.057*
C8	0.7294 (6)	0.3736 (4)	0.2435 (4)	0.0554 (19)
H8	0.7250	0.4196	0.2615	0.066*
C9	0.6975 (5)	0.3189 (4)	0.2848 (4)	0.0472 (17)
H9	0.6711	0.3265	0.3315	0.057*
C10	0.7051 (5)	0.2527 (4)	0.2561 (4)	0.0425 (16)
H10	0.6830	0.2152	0.2843	0.051*
C11	0.5497 (5)	0.1943 (4)	0.0374 (4)	0.0478 (17)
H11	0.5492	0.2282	0.0765	0.057*
C12	0.4747 (6)	0.1997 (5)	−0.0318 (5)	0.063 (2)
H12	0.4248	0.2369	−0.0398	0.076*
C13	0.4737 (7)	0.1496 (5)	−0.0891 (5)	0.078 (3)
H13	0.4225	0.1521	−0.1364	0.094*
C14	0.5478 (6)	0.0964 (5)	−0.0764 (4)	0.065 (2)
H14	0.5484	0.0622	−0.1151	0.078*
C15	0.6226 (5)	0.0931 (4)	−0.0056 (4)	0.0427 (16)
C16	0.7059 (6)	0.0373 (3)	0.0130 (4)	0.0447 (16)
C17	0.7080 (7)	−0.0232 (4)	−0.0324 (5)	0.067 (2)
H17	0.6542	−0.0295	−0.0779	0.080*

C18	0.7867 (8)	−0.0727 (4)	−0.0117 (6)	0.079 (3)
H18	0.7881	−0.1130	−0.0423	0.095*
C19	0.8636 (7)	−0.0623 (4)	0.0551 (5)	0.063 (2)
H19	0.9189	−0.0955	0.0709	0.076*
C20	0.8592 (6)	−0.0022 (4)	0.0993 (4)	0.0542 (19)
H20	0.9124	0.0043	0.1450	0.065*
C21	1.0059 (5)	0.1421 (3)	0.2316 (4)	0.0452 (17)
H21	1.0236	0.1587	0.1845	0.054*
C22	1.0883 (6)	0.1384 (4)	0.2973 (4)	0.0529 (19)
H22	1.1604	0.1515	0.2949	0.063*
C23	0.9551 (5)	0.0950 (4)	0.3682 (4)	0.0472 (17)
H23	0.9360	0.0791	0.4151	0.057*
C24	0.8764 (5)	0.0987 (3)	0.2994 (3)	0.0329 (14)
C25	0.7600 (5)	0.0778 (3)	0.2945 (4)	0.0330 (14)
C26	0.7195 (6)	0.0507 (3)	0.3593 (4)	0.0454 (17)
H26	0.7657	0.0443	0.4083	0.054*
C27	0.6079 (6)	0.0339 (4)	0.3479 (4)	0.0519 (18)
H27	0.5784	0.0159	0.3898	0.062*
C28	0.5422 (6)	0.0433 (4)	0.2765 (4)	0.0511 (18)
H28	0.4675	0.0316	0.2686	0.061*
C29	0.5867 (5)	0.0701 (4)	0.2165 (4)	0.0451 (17)
H29	0.5410	0.0771	0.1673	0.054*
C30	1.0613 (6)	0.1148 (4)	0.3668 (5)	0.0531 (19)
H30	1.1151	0.1124	0.4128	0.064*
Co1	0.76522 (6)	0.13938 (4)	0.14146 (4)	0.02958 (19)
Mo1	0.62552 (4)	0.16746 (3)	0.70535 (3)	0.03880 (16)
Mo2	0.68058 (5)	0.03933 (3)	0.59227 (3)	0.03863 (15)
Mo3	0.93267 (4)	0.09804 (3)	0.60537 (3)	0.04001 (16)
Mo4	0.72000 (5)	0.20190 (3)	0.54351 (3)	0.04164 (16)
Mo5	0.87672 (5)	0.22739 (3)	0.71735 (4)	0.04679 (17)
Mo6	0.83628 (5)	0.06397 (3)	0.76648 (3)	0.04393 (17)
N1	0.8397 (4)	0.2045 (3)	0.0694 (3)	0.0371 (12)
N2	0.7428 (4)	0.2385 (3)	0.1891 (3)	0.0355 (12)
N3	0.6238 (4)	0.1425 (3)	0.0512 (3)	0.0421 (13)
N4	0.7816 (4)	0.0472 (3)	0.0790 (3)	0.0401 (13)
N5	0.6935 (4)	0.0870 (3)	0.2251 (3)	0.0395 (13)
N6	0.9018 (4)	0.1232 (3)	0.2313 (3)	0.0373 (12)
O1	0.6778 (4)	0.2537 (3)	0.4646 (3)	0.0632 (14)
O2	0.8518 (4)	0.1606 (2)	0.5229 (3)	0.0467 (11)
O3	0.6467 (3)	0.1147 (2)	0.5161 (2)	0.0424 (11)
O4	0.9808 (3)	0.1811 (2)	0.6620 (3)	0.0492 (12)
O5	0.8119 (4)	0.2659 (2)	0.6171 (3)	0.0518 (12)
O6	0.9511 (4)	0.2935 (3)	0.7643 (3)	0.0744 (17)
O7	0.6093 (3)	0.2189 (2)	0.6099 (3)	0.0447 (11)
O8	0.7392 (4)	0.2354 (2)	0.7496 (3)	0.0494 (12)
O9	0.5168 (4)	0.1929 (3)	0.7438 (3)	0.0539 (12)
O10	0.7046 (3)	0.1044 (2)	0.7871 (3)	0.0484 (12)
O11	0.9111 (4)	0.1509 (3)	0.7929 (3)	0.0518 (12)
O12	0.7786 (3)	0.13302 (19)	0.6550 (2)	0.0329 (9)

O13	0.5755 (3)	0.0853 (2)	0.6474 (3)	0.0419 (11)
O14	0.8815 (4)	0.0131 (3)	0.8463 (3)	0.0705 (16)
O15	0.7458 (4)	0.0007 (2)	0.6930 (3)	0.0485 (12)
O16	0.9500 (3)	0.0484 (2)	0.7010 (3)	0.0475 (12)
O17	0.6077 (4)	−0.0283 (2)	0.5469 (3)	0.0600 (14)
O18	0.8188 (3)	0.0303 (2)	0.5606 (2)	0.0438 (11)
O19	1.0407 (4)	0.0735 (3)	0.5655 (3)	0.0565 (13)

Atomic displacement parameters (Å^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
C1	0.057 (4)	0.042 (4)	0.041 (4)	−0.006 (3)	0.017 (3)	−0.004 (3)
C2	0.064 (5)	0.061 (5)	0.034 (4)	−0.010 (4)	0.015 (4)	−0.004 (4)
C3	0.086 (6)	0.055 (5)	0.043 (4)	−0.018 (4)	0.015 (4)	0.010 (4)
C4	0.079 (5)	0.036 (4)	0.041 (4)	−0.006 (4)	0.006 (4)	0.006 (3)
C5	0.036 (4)	0.048 (4)	0.032 (4)	−0.004 (3)	0.001 (3)	0.002 (3)
C6	0.036 (4)	0.033 (4)	0.034 (4)	−0.003 (3)	−0.002 (3)	−0.001 (3)
C7	0.061 (5)	0.030 (4)	0.050 (4)	−0.001 (3)	0.006 (4)	−0.002 (3)
C8	0.064 (5)	0.042 (4)	0.057 (5)	0.009 (4)	0.003 (4)	−0.016 (4)
C9	0.049 (4)	0.049 (4)	0.043 (4)	0.009 (3)	0.008 (3)	−0.011 (4)
C10	0.043 (4)	0.055 (4)	0.029 (4)	0.011 (3)	0.005 (3)	0.005 (3)
C11	0.048 (4)	0.055 (4)	0.040 (4)	0.011 (4)	0.009 (3)	−0.003 (3)
C12	0.043 (4)	0.089 (6)	0.056 (5)	0.028 (4)	0.007 (4)	0.004 (5)
C13	0.045 (5)	0.128 (8)	0.056 (5)	0.025 (5)	−0.001 (4)	−0.008 (6)
C14	0.053 (5)	0.091 (6)	0.048 (5)	0.005 (5)	0.002 (4)	−0.022 (4)
C15	0.036 (4)	0.054 (4)	0.038 (4)	−0.008 (3)	0.006 (3)	−0.006 (3)
C16	0.055 (4)	0.035 (4)	0.048 (4)	−0.009 (3)	0.017 (4)	−0.003 (3)
C17	0.083 (6)	0.051 (5)	0.060 (5)	−0.005 (4)	0.000 (4)	−0.018 (4)
C18	0.115 (8)	0.039 (5)	0.087 (7)	0.003 (5)	0.029 (6)	−0.021 (5)
C19	0.076 (6)	0.040 (4)	0.080 (6)	0.011 (4)	0.030 (5)	0.004 (4)
C20	0.055 (5)	0.050 (5)	0.057 (5)	0.012 (4)	0.011 (4)	0.006 (4)
C21	0.046 (4)	0.041 (4)	0.050 (4)	−0.004 (3)	0.013 (3)	0.005 (3)
C22	0.038 (4)	0.048 (4)	0.068 (5)	−0.006 (3)	0.000 (4)	0.006 (4)
C23	0.047 (4)	0.051 (4)	0.040 (4)	0.007 (3)	0.000 (3)	0.004 (3)
C24	0.045 (4)	0.025 (3)	0.029 (3)	0.005 (3)	0.008 (3)	−0.001 (3)
C25	0.039 (4)	0.026 (3)	0.034 (4)	−0.001 (3)	0.008 (3)	−0.005 (3)
C26	0.056 (5)	0.045 (4)	0.036 (4)	−0.001 (3)	0.011 (3)	0.003 (3)
C27	0.058 (5)	0.054 (4)	0.049 (4)	−0.008 (4)	0.022 (4)	0.004 (4)
C28	0.043 (4)	0.057 (5)	0.055 (5)	−0.011 (3)	0.013 (4)	0.003 (4)
C29	0.039 (4)	0.057 (4)	0.037 (4)	−0.010 (3)	0.003 (3)	0.004 (3)
C30	0.042 (4)	0.046 (4)	0.065 (5)	0.002 (3)	−0.006 (4)	0.005 (4)
Co1	0.0301 (4)	0.0305 (4)	0.0280 (4)	−0.0009 (3)	0.0050 (3)	0.0012 (3)
Mo1	0.0331 (3)	0.0401 (3)	0.0451 (3)	0.0020 (2)	0.0123 (3)	−0.0020 (3)
Mo2	0.0368 (3)	0.0331 (3)	0.0451 (4)	−0.0059 (2)	0.0056 (3)	−0.0064 (3)
Mo3	0.0320 (3)	0.0490 (4)	0.0402 (3)	0.0000 (3)	0.0099 (3)	−0.0069 (3)
Mo4	0.0430 (3)	0.0396 (3)	0.0428 (3)	0.0011 (3)	0.0094 (3)	0.0095 (3)
Mo5	0.0413 (3)	0.0481 (4)	0.0522 (4)	−0.0139 (3)	0.0117 (3)	−0.0186 (3)
Mo6	0.0384 (3)	0.0556 (4)	0.0369 (3)	0.0076 (3)	0.0049 (3)	0.0077 (3)

N1	0.042 (3)	0.039 (3)	0.030 (3)	−0.003 (2)	0.007 (2)	−0.002 (2)
N2	0.036 (3)	0.041 (3)	0.028 (3)	0.001 (2)	0.001 (2)	0.001 (2)
N3	0.037 (3)	0.045 (3)	0.045 (3)	0.001 (3)	0.008 (3)	0.003 (3)
N4	0.040 (3)	0.038 (3)	0.042 (3)	−0.001 (2)	0.007 (3)	0.000 (3)
N5	0.042 (3)	0.037 (3)	0.039 (3)	−0.004 (2)	0.006 (3)	0.004 (2)
N6	0.035 (3)	0.036 (3)	0.040 (3)	−0.005 (2)	0.005 (2)	0.003 (2)
O1	0.063 (3)	0.067 (3)	0.060 (3)	0.004 (3)	0.014 (3)	0.027 (3)
O2	0.046 (3)	0.053 (3)	0.044 (3)	−0.002 (2)	0.015 (2)	0.002 (2)
O3	0.035 (2)	0.049 (3)	0.039 (3)	−0.003 (2)	−0.004 (2)	0.001 (2)
O4	0.036 (3)	0.062 (3)	0.049 (3)	−0.012 (2)	0.007 (2)	−0.014 (2)
O5	0.054 (3)	0.032 (2)	0.073 (3)	−0.008 (2)	0.019 (3)	0.003 (2)
O6	0.063 (3)	0.069 (4)	0.090 (4)	−0.023 (3)	0.012 (3)	−0.036 (3)
O7	0.041 (3)	0.040 (3)	0.054 (3)	0.005 (2)	0.011 (2)	0.004 (2)
O8	0.044 (3)	0.051 (3)	0.056 (3)	−0.001 (2)	0.015 (2)	−0.021 (2)
O9	0.039 (3)	0.066 (3)	0.061 (3)	0.006 (2)	0.018 (2)	0.000 (3)
O10	0.043 (3)	0.064 (3)	0.042 (3)	0.007 (2)	0.016 (2)	0.009 (2)
O11	0.040 (3)	0.070 (3)	0.043 (3)	−0.004 (2)	0.003 (2)	−0.012 (2)
O12	0.032 (2)	0.031 (2)	0.038 (2)	−0.0016 (18)	0.0104 (18)	−0.0038 (19)
O13	0.034 (2)	0.038 (2)	0.054 (3)	−0.0053 (19)	0.008 (2)	0.001 (2)
O14	0.056 (3)	0.096 (4)	0.057 (3)	0.017 (3)	0.006 (3)	0.026 (3)
O15	0.050 (3)	0.036 (2)	0.059 (3)	−0.001 (2)	0.008 (2)	0.010 (2)
O16	0.039 (3)	0.059 (3)	0.043 (3)	0.007 (2)	0.005 (2)	−0.001 (2)
O17	0.057 (3)	0.043 (3)	0.079 (4)	−0.010 (2)	0.008 (3)	−0.018 (3)
O18	0.044 (3)	0.044 (3)	0.043 (3)	0.004 (2)	0.008 (2)	−0.010 (2)
O19	0.041 (3)	0.080 (4)	0.050 (3)	0.006 (2)	0.014 (2)	−0.009 (3)

Geometric parameters (Å, °)

C1—N1	1.330 (8)	C25—C26	1.398 (8)
C1—C2	1.361 (9)	C26—C27	1.387 (9)
C1—H1	0.9300	C26—H26	0.9300
C2—C3	1.358 (10)	C27—C28	1.346 (9)
C2—H2	0.9300	C27—H27	0.9300
C3—C4	1.364 (10)	C28—C29	1.354 (9)
C3—H3	0.9300	C28—H28	0.9300
C4—C5	1.400 (9)	C29—N5	1.334 (8)
C4—H4	0.9300	C29—H29	0.9300
C5—N1	1.343 (8)	C30—H30	0.9300
C5—C6	1.479 (8)	Co1—N5	2.075 (5)
C6—N2	1.331 (7)	Co1—N6	2.078 (5)
C6—C7	1.376 (8)	Co1—N1	2.079 (5)
C7—C8	1.367 (9)	Co1—N4	2.081 (5)
C7—H7	0.9300	Co1—N2	2.091 (5)
C8—C9	1.358 (10)	Co1—N3	2.100 (5)
C8—H8	0.9300	Mo1—O9	1.671 (4)
C9—C10	1.359 (9)	Mo1—O7	1.884 (4)
C9—H9	0.9300	Mo1—O13	1.888 (4)
C10—N2	1.345 (7)	Mo1—O8	1.948 (4)
C10—H10	0.9300	Mo1—O10	1.957 (4)

C11—N3	1.331 (8)	Mo1—O12	2.310 (4)
C11—C12	1.362 (9)	Mo2—O17	1.671 (4)
C11—H11	0.9300	Mo2—O18	1.888 (4)
C12—C13	1.366 (11)	Mo2—O15	1.909 (4)
C12—H12	0.9300	Mo2—O3	1.929 (4)
C13—C14	1.350 (11)	Mo2—O13	1.948 (4)
C13—H13	0.9300	Mo2—O12	2.299 (4)
C14—C15	1.379 (9)	Mo3—O19	1.673 (4)
C14—H14	0.9300	Mo3—O16	1.868 (4)
C15—N3	1.350 (8)	Mo3—O4	1.888 (4)
C15—C16	1.467 (9)	Mo3—O18	1.950 (4)
C16—N4	1.336 (8)	Mo3—O2	1.968 (4)
C16—C17	1.390 (9)	Mo3—O12	2.318 (4)
C17—C18	1.349 (11)	Mo4—O1	1.673 (5)
C17—H17	0.9300	Mo4—O2	1.894 (4)
C18—C19	1.354 (11)	Mo4—O3	1.900 (4)
C18—H18	0.9300	Mo4—O5	1.951 (5)
C19—C20	1.377 (10)	Mo4—O7	1.961 (4)
C19—H19	0.9300	Mo4—O12	2.316 (4)
C20—N4	1.336 (8)	Mo5—O6	1.669 (5)
C20—H20	0.9300	Mo5—O8	1.884 (4)
C21—N6	1.330 (8)	Mo5—O5	1.900 (5)
C21—C22	1.368 (9)	Mo5—O11	1.939 (5)
C21—H21	0.9300	Mo5—O4	1.943 (4)
C22—C30	1.373 (10)	Mo5—O12	2.307 (4)
C22—H22	0.9300	Mo6—O14	1.682 (5)
C23—C30	1.365 (9)	Mo6—O10	1.887 (4)
C23—C24	1.379 (8)	Mo6—O11	1.902 (5)
C23—H23	0.9300	Mo6—O15	1.934 (4)
C24—N6	1.347 (7)	Mo6—O16	1.976 (4)
C24—C25	1.474 (8)	Mo6—O12	2.316 (4)
C25—N5	1.323 (7)		
N1—C1—C2	123.1 (7)	O17—Mo2—O18	103.3 (2)
N1—C1—H1	118.5	O17—Mo2—O15	102.9 (2)
C2—C1—H1	118.5	O18—Mo2—O15	88.73 (19)
C3—C2—C1	119.3 (7)	O17—Mo2—O3	103.1 (2)
C3—C2—H2	120.3	O18—Mo2—O3	87.96 (18)
C1—C2—H2	120.3	O15—Mo2—O3	153.89 (18)
C2—C3—C4	119.4 (7)	O17—Mo2—O13	102.9 (2)
C2—C3—H3	120.3	O18—Mo2—O13	153.82 (17)
C4—C3—H3	120.3	O15—Mo2—O13	86.36 (19)
C3—C4—C5	119.0 (7)	O3—Mo2—O13	85.28 (18)
C3—C4—H4	120.5	O17—Mo2—O12	179.2 (2)
C5—C4—H4	120.5	O18—Mo2—O12	77.50 (15)
N1—C5—C4	120.9 (6)	O15—Mo2—O12	77.28 (16)
N1—C5—C6	116.1 (5)	O3—Mo2—O12	76.72 (16)
C4—C5—C6	123.0 (6)	O13—Mo2—O12	76.34 (15)
N2—C6—C7	121.6 (6)	O19—Mo3—O16	104.5 (2)
N2—C6—C5	115.2 (5)	O19—Mo3—O4	104.3 (2)

C7—C6—C5	123.2 (6)	O16—Mo3—O4	89.9 (2)
C8—C7—C6	119.3 (7)	O19—Mo3—O18	102.9 (2)
C8—C7—H7	120.4	O16—Mo3—O18	88.10 (19)
C6—C7—H7	120.4	O4—Mo3—O18	152.37 (18)
C9—C8—C7	119.8 (6)	O19—Mo3—O2	102.0 (2)
C9—C8—H8	120.1	O16—Mo3—O2	153.38 (18)
C7—C8—H8	120.1	O4—Mo3—O2	86.13 (19)
C8—C9—C10	118.1 (6)	O18—Mo3—O2	83.50 (18)
C8—C9—H9	120.9	O19—Mo3—O12	177.44 (19)
C10—C9—H9	120.9	O16—Mo3—O12	77.75 (16)
N2—C10—C9	123.6 (6)	O4—Mo3—O12	76.77 (16)
N2—C10—H10	118.2	O18—Mo3—O12	75.87 (15)
C9—C10—H10	118.2	O2—Mo3—O12	75.71 (16)
N3—C11—C12	122.6 (7)	O1—Mo4—O2	103.8 (2)
N3—C11—H11	118.7	O1—Mo4—O3	104.5 (2)
C12—C11—H11	118.7	O2—Mo4—O3	88.71 (19)
C13—C12—C11	119.1 (7)	O1—Mo4—O5	102.2 (2)
C13—C12—H12	120.5	O2—Mo4—O5	88.06 (19)
C11—C12—H12	120.5	O3—Mo4—O5	153.15 (18)
C14—C13—C12	119.4 (7)	O1—Mo4—O7	103.3 (2)
C14—C13—H13	120.3	O2—Mo4—O7	152.92 (18)
C12—C13—H13	120.3	O3—Mo4—O7	86.39 (18)
C13—C14—C15	119.6 (7)	O5—Mo4—O7	84.46 (19)
C13—C14—H14	120.2	O1—Mo4—O12	178.4 (2)
C15—C14—H14	120.2	O2—Mo4—O12	77.12 (16)
N3—C15—C14	121.2 (7)	O3—Mo4—O12	76.83 (15)
N3—C15—C16	115.6 (6)	O5—Mo4—O12	76.46 (16)
C14—C15—C16	123.2 (6)	O7—Mo4—O12	75.83 (15)
N4—C16—C17	120.5 (7)	O6—Mo5—O8	103.8 (2)
N4—C16—C15	115.5 (6)	O6—Mo5—O5	104.2 (2)
C17—C16—C15	124.0 (7)	O8—Mo5—O5	89.3 (2)
C18—C17—C16	121.0 (8)	O6—Mo5—O11	102.1 (3)
C18—C17—H17	119.5	O8—Mo5—O11	87.6 (2)
C16—C17—H17	119.5	O5—Mo5—O11	153.44 (19)
C17—C18—C19	118.2 (8)	O6—Mo5—O4	102.9 (2)
C17—C18—H18	120.9	O8—Mo5—O4	153.17 (18)
C19—C18—H18	120.9	O5—Mo5—O4	86.3 (2)
C18—C19—C20	119.6 (8)	O11—Mo5—O4	84.69 (19)
C18—C19—H19	120.2	O6—Mo5—O12	177.9 (2)
C20—C19—H19	120.2	O8—Mo5—O12	77.15 (16)
N4—C20—C19	122.6 (7)	O5—Mo5—O12	77.63 (16)
N4—C20—H20	118.7	O11—Mo5—O12	75.97 (16)
C19—C20—H20	118.7	O4—Mo5—O12	76.05 (15)
N6—C21—C22	123.6 (6)	O14—Mo6—O10	104.1 (2)
N6—C21—H21	118.2	O14—Mo6—O11	103.5 (2)
C22—C21—H21	118.2	O10—Mo6—O11	89.9 (2)
C21—C22—C30	117.9 (7)	O14—Mo6—O15	103.6 (2)
C21—C22—H22	121.0	O10—Mo6—O15	88.0 (2)
C30—C22—H22	121.0	O11—Mo6—O15	152.55 (19)

C30—C23—C24	119.4 (7)	O14—Mo6—O16	102.5 (2)
C30—C23—H23	120.3	O10—Mo6—O16	153.36 (18)
C24—C23—H23	120.3	O11—Mo6—O16	84.39 (19)
N6—C24—C23	121.2 (6)	O15—Mo6—O16	85.39 (19)
N6—C24—C25	115.2 (5)	O14—Mo6—O12	178.3 (2)
C23—C24—C25	123.6 (6)	O10—Mo6—O12	77.53 (16)
N5—C25—C26	120.7 (6)	O11—Mo6—O12	76.43 (17)
N5—C25—C24	116.5 (5)	O15—Mo6—O12	76.39 (15)
C26—C25—C24	122.9 (6)	O16—Mo6—O12	75.83 (16)
C27—C26—C25	117.7 (6)	C1—N1—C5	118.3 (5)
C27—C26—H26	121.2	C1—N1—Co1	126.7 (4)
C25—C26—H26	121.2	C5—N1—Co1	113.9 (4)
C28—C27—C26	120.5 (6)	C6—N2—C10	117.6 (6)
C28—C27—H27	119.8	C6—N2—Co1	114.9 (4)
C26—C27—H27	119.8	C10—N2—Co1	127.3 (4)
C27—C28—C29	118.8 (7)	C11—N3—C15	118.0 (6)
C27—C28—H28	120.6	C11—N3—Co1	126.6 (5)
C29—C28—H28	120.6	C15—N3—Co1	114.0 (4)
N5—C29—C28	122.6 (6)	C20—N4—C16	118.1 (6)
N5—C29—H29	118.7	C20—N4—Co1	126.1 (5)
C28—C29—H29	118.7	C16—N4—Co1	115.7 (4)
C23—C30—C22	119.7 (7)	C25—N5—C29	119.8 (5)
C23—C30—H30	120.2	C25—N5—Co1	114.4 (4)
C22—C30—H30	120.2	C29—N5—Co1	125.3 (4)
N5—Co1—N6	78.9 (2)	C21—N6—C24	118.1 (6)
N5—Co1—N1	171.4 (2)	C21—N6—Co1	127.3 (4)
N6—Co1—N1	98.20 (19)	C24—N6—Co1	114.0 (4)
N5—Co1—N4	92.8 (2)	Mo4—O2—Mo3	116.7 (2)
N6—Co1—N4	96.5 (2)	Mo4—O3—Mo2	116.5 (2)
N1—Co1—N4	95.6 (2)	Mo3—O4—Mo5	117.2 (2)
N5—Co1—N2	93.2 (2)	Mo5—O5—Mo4	116.0 (2)
N6—Co1—N2	89.51 (19)	Mo1—O7—Mo4	116.6 (2)
N1—Co1—N2	78.62 (19)	Mo5—O8—Mo1	116.8 (2)
N4—Co1—N2	172.2 (2)	Mo6—O10—Mo1	116.3 (2)
N5—Co1—N3	97.0 (2)	Mo6—O11—Mo5	117.1 (2)
N6—Co1—N3	173.0 (2)	Mo2—O12—Mo5	179.7 (2)
N1—Co1—N3	86.7 (2)	Mo2—O12—Mo1	90.06 (13)
N4—Co1—N3	78.0 (2)	Mo5—O12—Mo1	89.99 (13)
N2—Co1—N3	96.3 (2)	Mo2—O12—Mo4	89.78 (14)
O9—Mo1—O7	103.4 (2)	Mo5—O12—Mo4	89.91 (13)
O9—Mo1—O13	103.9 (2)	Mo1—O12—Mo4	90.02 (13)
O7—Mo1—O13	90.01 (18)	Mo2—O12—Mo6	90.04 (13)
O9—Mo1—O8	103.0 (2)	Mo5—O12—Mo6	90.27 (14)
O7—Mo1—O8	86.9 (2)	Mo1—O12—Mo6	89.78 (13)
O13—Mo1—O8	152.92 (17)	Mo4—O12—Mo6	179.7 (2)
O9—Mo1—O10	102.8 (2)	Mo2—O12—Mo3	90.00 (13)
O7—Mo1—O10	153.66 (18)	Mo5—O12—Mo3	89.96 (13)
O13—Mo1—O10	86.59 (19)	Mo1—O12—Mo3	179.6 (2)
O8—Mo1—O10	84.4 (2)	Mo4—O12—Mo3	90.40 (13)

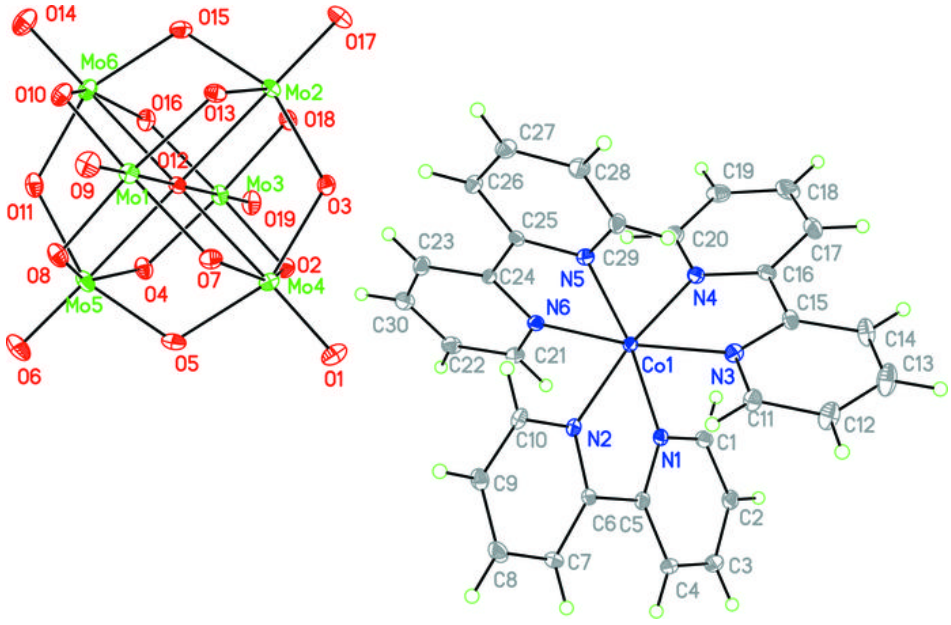
O9—Mo1—O12	178.6 (2)	Mo6—O12—Mo3	89.79 (13)
O7—Mo1—O12	77.40 (16)	Mo1—O13—Mo2	116.4 (2)
O13—Mo1—O12	77.16 (15)	Mo2—O15—Mo6	116.3 (2)
O8—Mo1—O12	75.91 (15)	Mo3—O16—Mo6	116.6 (2)
O10—Mo1—O12	76.38 (15)	Mo2—O18—Mo3	116.5 (2)

Hydrogen-bond geometry (Å, °)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
C2—H2···O11^{i}	0.93	2.36	3.166 (9)	145
C4—H4···O17^{ii}	0.93	2.52	3.165 (9)	127
C11—H11···O4^{iii}	0.93	2.51	3.400 (8)	161
C12—H12···O2^{iii}	0.93	2.47	3.277 (10)	145
C20—H20···O14^{iv}	0.93	2.53	3.159 (9)	125
C22—H22···O8^{v}	0.93	2.54	3.230 (9)	132
C26—H26···O18	0.93	2.58	3.459 (8)	157

Symmetry codes: (i) *x*, *y*, *z*−1; (ii) −*x*+3/2, *y*+1/2, −*z*+1/2; (iii) *x*−1/2, −*y*+1/2, *z*−1/2; (iv) −*x*+2, −*y*, −*z*+1; (v) *x*+1/2, −*y*+1/2, *z*−1/2.

Fig. 1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O15
O17
Mo6
O10
O16
O13
Mo2
O18
O12
O9
Mo1
Mo3
O3
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O19
O8
O2
O7
O4
Mo4
Mo5
O6
O5
O1
C27
C26
C28
C19
C18
C25
C20
C17
C23
C29
C24
N5
C16
N4
N6
C15
C30
C14
C22
C21
Co1
N3
C13
C11
C12
C10
N2
N1
C1
C9
C6
C5
C2
C8
C7
C4
C3

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Dibutyl 5-[(4-ethoxycarbonylphenyl)-diazenyl]benzene-1,3-dicarboxylate

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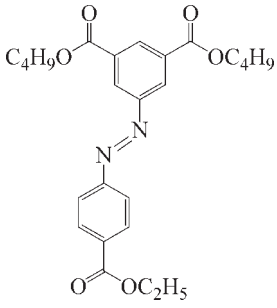
Key indicators: single-crystal X-ray study; T = 293 K; mean σ(C–C) = 0.006 Å; R factor = 0.064; wR factor = 0.218; data-to-parameter ratio = 14.2.

In the title compound, $C_{25}H_{30}N_2O_6$, the dihedral angle between the aromatic rings is 3.79 (1) Å and the N=N bond shows a *trans* conformation. Both butyl side chains show evidence of disorder.

Related literature

For general background to dendrimers related to the title compound, see: Tomalia *et al.* (1990); Bosman *et al.* (1999). For a related structure, see: Wang *et al.* (2004).



Experimental

Crystal data

$C_{25}H_{30}N_2O_6$
M_r = 454.51
Triclinic, $P\overline{1}$
a = 8.675 (2) Å
b = 11.299 (3) Å
c = 13.636 (3) Å
α = 97.311 (3)°
β = 94.806 (3)°
γ = 109.793 (2)°
V = 1235.8 (5) Å^3
Z = 2
Mo $K\alpha$ radiation
μ = 0.09 mm^{-1}
T = 293 K
0.12 × 0.10 × 0.08 mm

Data collection

Bruker APEXII CCD diffractometer
Absorption correction: multi-scan (*SADABS*; Bruker, 2001)
T_{min} = 0.990, T_{max} = 0.993
8643 measured reflections
4275 independent reflections
2736 reflections with $I > 2\sigma(I)$
R_{int} = 0.022

Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.064
$wR(F^2)$ = 0.218
S = 1.05
4275 reflections
302 parameters
13 restraints
H-atom parameters constrained
$\Delta\rho_{max}$ = 0.55 e Å^{-3}
$\Delta\rho_{min}$ = −0.32 e Å^{-3}

Data collection: *APEX2* (Bruker, 2004); cell refinement: *SAINT-Plus* (Bruker, 2001); data reduction: *SAINT-Plus*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *SHELXTL* (Sheldrick, 2008); software used to prepare material for publication: *SHELXTL*.

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Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: HB5477).

References

Bosman, A. W., Janssen, H. M. & Weijer, E. W. (1999). *Chem. Rev.* **99**, 1665–1688.
Bruker (2001). *SAINT-Plus* and *SADABS*. Bruker AXS Inc., Madison, Wisconsin, USA.
Bruker (2004). *APEX2*. Bruker AXS Inc., Madison, Wisconsin, USA.
Sheldrick, G. M. (2008). *Acta Cryst.* A**64**, 112–122.
Tomalia, D. A., Naylor, A. M. & Goddard, W. A. (1990). *Angew. Chem. Int. Ed. Engl.* **29**, 138–146.
Wang, S., Wang, X., Li, L. & Advincula, R. C. (2004). *J. Org. Chem.* **69**, 9073–9084.

supplementary materials

Acta Cryst. (2010). E**66**, o1730 [**doi:10.1107/S1600536810022762**]

Dibutyl 5-[(4-ethoxycarbonylphenyl)diazenyl]benzene-1,3-dicarboxylate

Y. Liu, X. Zhang, Z. Xue and J. Sheng

Comment

Dendrimers have been the subject of intense investigation due to both interesting structural properties and promising applications in the areas of biological and material sciences (Tomalia *et al.*, 1990; Bosman *et al.*, 1999). Here, we describe the cystallization and structural characterization of the title compound.

As shown in Fig 1. the dihedral angle between the phenyl planes of the two benzene rings is 3.79 (1) Å. The mean deviations for the two phenyl planar are 0.0058 (1) and 0.0028 (1) Å, respectively. The C=O and C—O bond distances of carbonyl groups are 1.195 (3)—1.200 (3) and 1.324 (3)—1.452 (3) Å, respectively. The N=N and N—C bond distances are 1.240 (3) and 1.423 (3)—1.431 (3) Å, respectively, which are in the normal range compared to reported Dendrimer derivatives (Wang *et al.*, 2004).

Experimental

A yellow powder of ethyl 4-((dibutyl-3',5'-biscarbonylphenyl)diazenyl)benzoate (Jinan Henghua Science & Technology Co. Ltd.) (1 mmol 0.45 g) was dissolved in 10 ml ethanol and evaporated in an open flask at room temperature. Three days later, orange blocks of (I) were obained. Anal. $C_{25}H_{30}N_2O_6$: C, 66.01; H, 6.60; N, 6.16%. Found: C, 65.98; H, 6.47; N, 6.05%.

Refinement

Hydrogen atoms were placed in geometrically calculated positions (C—H 0.95 Å for aromatic and formyl, 0.99 Å for methylene and 0.98 Å for methyl) and included in the refinement in a riding motion approximation with U_{iso}(H) = 1.2Ueq(C) [for methyl groups U_{iso}(H) = 1.5Ueq(C)].

Figures

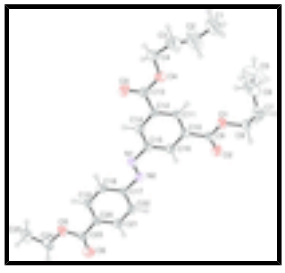


Fig. 1. The molecular sturcture of (I) with displacement ellipsoids drawn at the 30% probability level; H atoms are given as spheres of arbitrary radius.

Dibutyl 5-[(4-ethoxycarbonylphenyl)diazenyl]benzene-1,3-dicarboxylate

Crystal data

$C_{25}H_{30}N_2O_6$	$Z = 2$
$M_r = 454.51$	$F(000) = 484$
Triclinic, $P\overline{1}$	$D_x = 1.221$ Mg m^{-3}
Hall symbol: -P 1	Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å
$a = 8.675$ (2) Å	Cell parameters from 2660 reflections
$b = 11.299$ (3) Å	$\theta = 2.5$–$27.1°$
$c = 13.636$ (3) Å	$\mu = 0.09$ mm^{-1}
$\alpha = 97.311$ (3)°	$T = 293$ K
$\beta = 94.806$ (3)°	Block, yellow
$\gamma = 109.793$ (2)°	0.12 × 0.10 × 0.08 mm
$V = 1235.8$ (5) Å^3	

Data collection

Bruker APEXII CCD diffractometer	4275 independent reflections
Radiation source: fine-focus sealed tube	2736 reflections with $I > 2\sigma(I)$
graphite	$R_{int} = 0.022$
φ and ω scans	$\theta_{max} = 25.0°$, $\theta_{min} = 2.5°$
Absorption correction: multi-scan (*SADABS*; Bruker, 2001)	$h = -10 \rightarrow 10$
$T_{min} = 0.990$, $T_{max} = 0.993$	$k = -13 \rightarrow 13$
8643 measured reflections	$l = -15 \rightarrow 16$

Refinement

Refinement on F^2	Primary atom site location: structure-invariant direct methods
Least-squares matrix: full	Secondary atom site location: difference Fourier map
$R[F^2 > 2\sigma(F^2)] = 0.064$	Hydrogen site location: inferred from neighbouring sites
$wR(F^2) = 0.218$	H-atom parameters constrained
$S = 1.05$	$w = 1/[\sigma^2(F_o^2) + (0.1149P)^2 + 0.3064P]$ where $P = (F_o^2 + 2F_c^2)/3$
4275 reflections	$(\Delta/\sigma)_{max} < 0.001$
302 parameters	$\Delta\rho_{max} = 0.55$ e Å^{-3}
13 restraints	$\Delta\rho_{min} = -0.32$ e Å^{-3}

Special details

Geometry. All e.s.d.'s (except the e.s.d. in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell e.s.d.'s are taken into account individually in the estimation of e.s.d.'s in distances, angles and torsion angles; correlations

between e.s.d.'s in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell e.s.d.'s is used for estimating e.s.d.'s involving l.s. planes.

Refinement. Refinement of F^2 against ALL reflections. The weighted *R*-factor *wR* and goodness of fit *S* are based on F^2, conventional *R*-factors *R* are based on *F*, with *F* set to zero for negative F^2. The threshold expression of $F^2 > \sigma(F^2)$ is used only for calculating *R*-factors(gt) *etc*. and is not relevant to the choice of reflections for refinement. *R*-factors based on F^2 are statistically about twice as large as those based on *F*, and *R*- factors based on ALL data will be even larger.

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å^2)

	x	*y*	*z*	U_{iso}*/U_{eq}
O1	1.0434 (3)	0.2950 (2)	0.48258 (15)	0.0725 (6)
O2	0.8502 (3)	0.3718 (2)	0.52977 (16)	0.0932 (8)
O3	0.7562 (3)	−0.0204 (2)	0.05822 (16)	0.0871 (7)
O4	0.9356 (3)	−0.0106 (2)	0.18814 (15)	0.0810 (7)
O5	−0.2310 (2)	0.3824 (2)	0.02977 (15)	0.0714 (6)
O6	−0.1835 (3)	0.5354 (2)	0.1600 (2)	0.0974 (8)
N1	0.4477 (3)	0.2563 (2)	0.19969 (16)	0.0588 (6)
N2	0.4018 (3)	0.3269 (2)	0.25818 (16)	0.0577 (6)
C1	1.3390 (8)	−0.0964 (7)	0.3283 (5)	0.173 (3)
H1A	1.3681	−0.1621	0.2913	0.260*
H1B	1.3211	−0.1154	0.3940	0.260*
H1C	1.4271	−0.0159	0.3333	0.260*
C2	1.1938 (10)	−0.0905 (10)	0.2790 (6)	0.225 (4)
H2A	1.1052	−0.1568	0.3004	0.270*
H2B	1.1878	−0.0105	0.3104	0.270*
C3	1.1450 (9)	−0.0977 (7)	0.1825 (5)	0.189 (3)
H3A	1.1593	−0.1744	0.1507	0.227*
H3B	1.2301	−0.0275	0.1625	0.227*
C4	0.9940 (5)	−0.0991 (4)	0.1300 (3)	0.0905 (11)
H4A	0.9116	−0.1843	0.1198	0.109*
H4B	1.0129	−0.0745	0.0652	0.109*
C5	1.2579 (9)	0.1314 (8)	0.5848 (7)	0.207 (4)
H5A	1.2809	0.1655	0.6548	0.311*
H5B	1.3017	0.0643	0.5720	0.311*
H5C	1.1405	0.0980	0.5646	0.311*
C6	1.3321 (7)	0.2288 (7)	0.5303 (5)	0.149 (2)
H6A	1.2823	0.2014	0.4611	0.179*
H6B	1.4485	0.2407	0.5327	0.179*
C7	1.3166 (5)	0.3532 (4)	0.5670 (4)	0.1102 (14)
H7A	1.3649	0.4117	0.5223	0.132*
H7B	1.3831	0.3866	0.6319	0.132*
C8	1.1471 (4)	0.3556 (3)	0.5769 (2)	0.0842 (10)
H8A	1.1025	0.3102	0.6298	0.101*
H8B	1.1516	0.4429	0.5931	0.101*
C9	0.8992 (4)	0.3119 (3)	0.4689 (2)	0.0642 (8)
C10	0.8072 (3)	0.2505 (2)	0.36752 (19)	0.0545 (7)
C11	0.8557 (3)	0.1654 (2)	0.3055 (2)	0.0552 (7)
H11	0.9463	0.1446	0.3274	0.066*

C12	0.7685 (3)	0.1118 (2)	0.21106 (19)	0.0527 (6)
C13	0.8165 (3)	0.0201 (3)	0.1433 (2)	0.0615 (7)
C14	0.6346 (3)	0.1444 (2)	0.1786 (2)	0.0569 (7)
H14	0.5769	0.1095	0.1150	0.068*
C15	0.5867 (3)	0.2286 (2)	0.24046 (19)	0.0523 (6)
C16	0.6712 (3)	0.2805 (2)	0.33568 (19)	0.0532 (6)
H16	0.6367	0.3351	0.3779	0.064*
C17	0.2637 (3)	0.3539 (2)	0.21661 (19)	0.0523 (6)
C18	0.1725 (3)	0.2944 (3)	0.1236 (2)	0.0603 (7)
H18	0.2007	0.2334	0.0842	0.072*
C19	0.0408 (3)	0.3268 (3)	0.0906 (2)	0.0608 (7)
H19	−0.0207	0.2868	0.0287	0.073*
C20	−0.0022 (3)	0.4184 (2)	0.1480 (2)	0.0538 (6)
C21	0.0888 (3)	0.4765 (3)	0.2404 (2)	0.0631 (7)
H21	0.0611	0.5380	0.2796	0.076*
C22	0.2203 (3)	0.4437 (3)	0.2744 (2)	0.0623 (7)
H22	0.2802	0.4824	0.3369	0.075*
C23	−0.1457 (4)	0.4536 (3)	0.1153 (2)	0.0629 (7)
C24	−0.3775 (4)	0.4066 (4)	−0.0072 (3)	0.0835 (10)
H24A	−0.3473	0.4937	−0.0197	0.100*
H24B	−0.4538	0.3948	0.0419	0.100*
C25	−0.4555 (5)	0.3171 (5)	−0.0998 (4)	0.1176 (15)
H25A	−0.3772	0.3263	−0.1467	0.176*
H25B	−0.5491	0.3349	−0.1276	0.176*
H25C	−0.4913	0.2314	−0.0860	0.176*

Atomic displacement parameters (Å^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
O1	0.0697 (13)	0.0861 (14)	0.0657 (12)	0.0446 (11)	−0.0120 (10)	−0.0074 (10)
O2	0.0977 (17)	0.1285 (19)	0.0641 (13)	0.0739 (16)	−0.0125 (12)	−0.0253 (13)
O3	0.0918 (16)	0.1085 (17)	0.0657 (14)	0.0566 (14)	−0.0027 (12)	−0.0195 (12)
O4	0.0927 (16)	0.0967 (15)	0.0693 (13)	0.0649 (13)	−0.0007 (11)	−0.0106 (11)
O5	0.0609 (12)	0.0868 (14)	0.0751 (14)	0.0419 (11)	−0.0039 (10)	0.0088 (11)
O6	0.0949 (17)	0.1010 (17)	0.1112 (19)	0.0690 (15)	−0.0067 (14)	−0.0114 (14)
N1	0.0510 (13)	0.0669 (14)	0.0607 (14)	0.0285 (11)	0.0006 (10)	0.0014 (11)
N2	0.0523 (13)	0.0640 (13)	0.0594 (13)	0.0284 (11)	0.0014 (10)	0.0017 (10)
C1	0.140 (5)	0.215 (7)	0.181 (6)	0.091 (5)	−0.021 (4)	0.043 (5)
C2	0.186 (7)	0.343 (12)	0.185 (7)	0.177 (8)	−0.038 (6)	−0.012 (7)
C3	0.216 (6)	0.243 (6)	0.161 (5)	0.188 (5)	−0.031 (4)	−0.049 (4)
C4	0.099 (3)	0.097 (2)	0.091 (2)	0.065 (2)	0.0094 (19)	−0.0101 (18)
C5	0.173 (6)	0.213 (7)	0.302 (10)	0.105 (6)	0.090 (7)	0.137 (8)
C6	0.108 (4)	0.195 (6)	0.185 (6)	0.092 (4)	0.028 (4)	0.065 (5)
C7	0.080 (3)	0.120 (3)	0.124 (3)	0.036 (2)	−0.021 (2)	0.019 (3)
C8	0.084 (2)	0.092 (2)	0.073 (2)	0.0434 (19)	−0.0254 (17)	−0.0106 (17)
C9	0.0676 (18)	0.0685 (17)	0.0615 (17)	0.0375 (15)	−0.0027 (14)	−0.0014 (13)
C10	0.0532 (15)	0.0577 (15)	0.0550 (15)	0.0260 (12)	0.0036 (12)	0.0025 (12)
C11	0.0516 (15)	0.0594 (15)	0.0595 (16)	0.0272 (12)	0.0054 (12)	0.0073 (12)

C12	0.0508 (15)	0.0538 (14)	0.0560 (15)	0.0226 (12)	0.0106 (12)	0.0036 (11)
C13	0.0589 (17)	0.0664 (17)	0.0595 (18)	0.0265 (14)	0.0085 (14)	−0.0010 (13)
C14	0.0537 (15)	0.0601 (15)	0.0551 (15)	0.0213 (13)	0.0033 (12)	0.0027 (12)
C15	0.0460 (14)	0.0568 (14)	0.0560 (15)	0.0224 (12)	0.0043 (12)	0.0067 (11)
C16	0.0524 (15)	0.0555 (14)	0.0548 (15)	0.0259 (12)	0.0070 (12)	0.0011 (11)
C17	0.0455 (14)	0.0607 (15)	0.0524 (14)	0.0227 (12)	0.0033 (11)	0.0066 (11)
C18	0.0578 (16)	0.0670 (16)	0.0602 (16)	0.0338 (14)	0.0028 (13)	−0.0046 (13)
C19	0.0548 (16)	0.0701 (17)	0.0575 (16)	0.0295 (13)	−0.0034 (12)	−0.0038 (13)
C20	0.0486 (14)	0.0554 (14)	0.0606 (16)	0.0229 (12)	0.0065 (12)	0.0089 (12)
C21	0.0654 (18)	0.0652 (16)	0.0642 (17)	0.0353 (14)	0.0068 (14)	−0.0034 (13)
C22	0.0608 (17)	0.0711 (17)	0.0546 (16)	0.0312 (14)	−0.0024 (13)	−0.0064 (13)
C23	0.0593 (17)	0.0638 (16)	0.0738 (19)	0.0322 (14)	0.0088 (15)	0.0110 (14)
C24	0.0625 (19)	0.109 (3)	0.094 (2)	0.0478 (19)	−0.0003 (17)	0.027 (2)
C25	0.081 (3)	0.141 (4)	0.125 (3)	0.045 (3)	−0.026 (2)	0.012 (3)

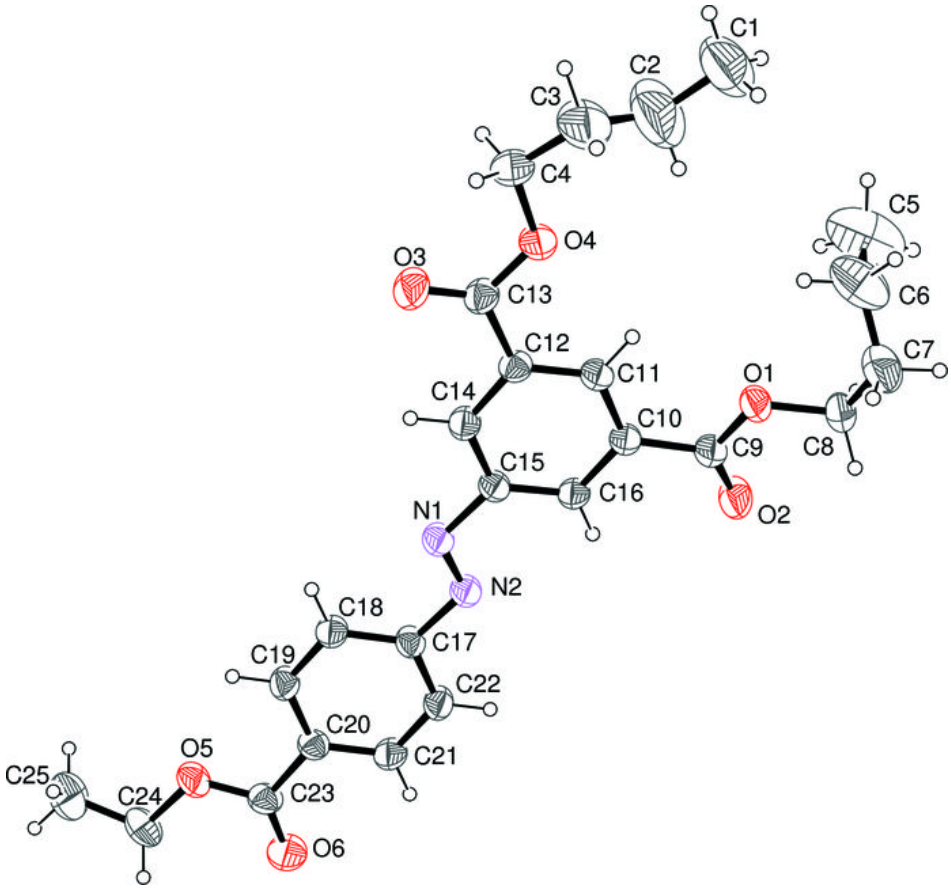
Geometric parameters (Å, °)

O1—C9	1.329 (3)	C7—H7A	0.9700
O1—C8	1.448 (3)	C7—H7B	0.9700
O2—C9	1.200 (3)	C8—H8A	0.9700
O3—C13	1.196 (3)	C8—H8B	0.9700
O4—C13	1.324 (3)	C9—C10	1.492 (4)
O4—C4	1.447 (3)	C10—C16	1.385 (3)
O5—C23	1.330 (3)	C10—C11	1.394 (3)
O5—C24	1.452 (3)	C11—C12	1.388 (4)
O6—C23	1.195 (3)	C11—H11	0.9300
N1—N2	1.240 (3)	C12—C14	1.388 (4)
N1—C15	1.431 (3)	C12—C13	1.488 (3)
N2—C17	1.423 (3)	C14—C15	1.383 (3)
C1—C2	1.403 (7)	C14—H14	0.9300
C1—H1A	0.9600	C15—C16	1.386 (4)
C1—H1B	0.9600	C16—H16	0.9300
C1—H1C	0.9600	C17—C22	1.378 (3)
C2—C3	1.331 (7)	C17—C18	1.393 (4)
C2—H2A	0.9700	C18—C19	1.372 (4)
C2—H2B	0.9700	C18—H18	0.9300
C3—C4	1.434 (7)	C19—C20	1.388 (3)
C3—H3A	0.9700	C19—H19	0.9300
C3—H3B	0.9700	C20—C21	1.384 (4)
C4—H4A	0.9700	C20—C23	1.481 (4)
C4—H4B	0.9700	C21—C22	1.377 (4)
C5—C6	1.409 (8)	C21—H21	0.9300
C5—H5A	0.9600	C22—H22	0.9300
C5—H5B	0.9600	C24—C25	1.465 (5)
C5—H5C	0.9600	C24—H24A	0.9700
C6—C7	1.485 (7)	C24—H24B	0.9700
C6—H6A	0.9700	C25—H25A	0.9600
C6—H6B	0.9700	C25—H25B	0.9600
C7—C8	1.496 (5)	C25—H25C	0.9600

C9—O1—C8	116.9 (2)	O1—C9—C10	111.9 (2)
C13—O4—C4	117.4 (2)	C16—C10—C11	120.3 (2)
C23—O5—C24	116.5 (2)	C16—C10—C9	118.2 (2)
N2—N1—C15	114.7 (2)	C11—C10—C9	121.5 (2)
N1—N2—C17	114.1 (2)	C12—C11—C10	119.8 (2)
C2—C1—H1A	109.5	C12—C11—H11	120.1
C2—C1—H1B	109.5	C10—C11—H11	120.1
H1A—C1—H1B	109.5	C14—C12—C11	119.7 (2)
C2—C1—H1C	109.5	C14—C12—C13	119.1 (2)
H1A—C1—H1C	109.5	C11—C12—C13	121.1 (2)
H1B—C1—H1C	109.5	O3—C13—O4	123.8 (2)
C3—C2—C1	131.1 (7)	O3—C13—C12	124.4 (3)
C3—C2—H2A	104.5	O4—C13—C12	111.9 (2)
C1—C2—H2A	104.5	C15—C14—C12	120.2 (2)
C3—C2—H2B	104.5	C15—C14—H14	119.9
C1—C2—H2B	104.5	C12—C14—H14	119.9
H2A—C2—H2B	105.6	C14—C15—C16	120.4 (2)
C2—C3—C4	132.1 (6)	C14—C15—N1	115.8 (2)
C2—C3—H3A	104.2	C16—C15—N1	123.8 (2)
C4—C3—H3A	104.2	C10—C16—C15	119.6 (2)
C2—C3—H3B	104.2	C10—C16—H16	120.2
C4—C3—H3B	104.2	C15—C16—H16	120.2
H3A—C3—H3B	105.5	C22—C17—C18	119.8 (2)
C3—C4—O4	108.9 (3)	C22—C17—N2	116.3 (2)
C3—C4—H4A	109.9	C18—C17—N2	123.9 (2)
O4—C4—H4A	109.9	C19—C18—C17	119.3 (2)
C3—C4—H4B	109.9	C19—C18—H18	120.3
O4—C4—H4B	109.9	C17—C18—H18	120.3
H4A—C4—H4B	108.3	C18—C19—C20	121.1 (2)
C6—C5—H5A	109.5	C18—C19—H19	119.4
C6—C5—H5B	109.5	C20—C19—H19	119.4
H5A—C5—H5B	109.5	C21—C20—C19	119.1 (2)
C6—C5—H5C	109.5	C21—C20—C23	118.5 (2)
H5A—C5—H5C	109.5	C19—C20—C23	122.4 (2)
H5B—C5—H5C	109.5	C22—C21—C20	120.2 (2)
C5—C6—C7	114.3 (6)	C22—C21—H21	119.9
C5—C6—H6A	108.7	C20—C21—H21	119.9
C7—C6—H6A	108.7	C21—C22—C17	120.5 (2)
C5—C6—H6B	108.7	C21—C22—H22	119.7
C7—C6—H6B	108.7	C17—C22—H22	119.7
H6A—C6—H6B	107.6	O6—C23—O5	123.0 (3)
C6—C7—C8	118.0 (4)	O6—C23—C20	124.8 (3)
C6—C7—H7A	107.8	O5—C23—C20	112.2 (2)
C8—C7—H7A	107.8	O5—C24—C25	108.2 (3)
C6—C7—H7B	107.8	O5—C24—H24A	110.1
C8—C7—H7B	107.8	C25—C24—H24A	110.1
H7A—C7—H7B	107.2	O5—C24—H24B	110.1
O1—C8—C7	107.9 (3)	C25—C24—H24B	110.1
O1—C8—H8A	110.1	H24A—C24—H24B	108.4

C7—C8—H8A	110.1	C24—C25—H25A	109.5
O1—C8—H8B	110.1	C24—C25—H25B	109.5
C7—C8—H8B	110.1	H25A—C25—H25B	109.5
H8A—C8—H8B	108.4	C24—C25—H25C	109.5
O2—C9—O1	124.2 (3)	H25A—C25—H25C	109.5
O2—C9—C10	123.8 (3)	H25B—C25—H25C	109.5
C15—N1—N2—C17	179.9 (2)	C12—C14—C15—N1	179.7 (2)
C1—C2—C3—C4	175.9 (8)	N2—N1—C15—C14	176.5 (2)
C2—C3—C4—O4	39.1 (12)	N2—N1—C15—C16	−3.3 (4)
C13—O4—C4—C3	166.9 (4)	C11—C10—C16—C15	−2.1 (4)
C5—C6—C7—C8	−54.1 (7)	C9—C10—C16—C15	177.7 (2)
C9—O1—C8—C7	−165.9 (3)	C14—C15—C16—C10	1.9 (4)
C6—C7—C8—O1	−52.5 (5)	N1—C15—C16—C10	−178.3 (2)
C8—O1—C9—O2	−1.0 (5)	N1—N2—C17—C22	−172.5 (2)
C8—O1—C9—C10	177.2 (3)	N1—N2—C17—C18	8.1 (4)
O2—C9—C10—C16	10.6 (5)	C22—C17—C18—C19	0.3 (4)
O1—C9—C10—C16	−167.7 (2)	N2—C17—C18—C19	179.6 (2)
O2—C9—C10—C11	−169.7 (3)	C17—C18—C19—C20	0.5 (4)
O1—C9—C10—C11	12.1 (4)	C18—C19—C20—C21	−0.7 (4)
C16—C10—C11—C12	0.8 (4)	C18—C19—C20—C23	−178.8 (3)
C9—C10—C11—C12	−179.0 (3)	C19—C20—C21—C22	0.1 (4)
C10—C11—C12—C14	0.7 (4)	C23—C20—C21—C22	178.2 (3)
C10—C11—C12—C13	−179.7 (2)	C20—C21—C22—C17	0.7 (5)
C4—O4—C13—O3	−0.4 (5)	C18—C17—C22—C21	−0.9 (4)
C4—O4—C13—C12	−179.8 (3)	N2—C17—C22—C21	179.7 (3)
C14—C12—C13—O3	6.7 (4)	C24—O5—C23—O6	−1.3 (5)
C11—C12—C13—O3	−173.0 (3)	C24—O5—C23—C20	178.1 (2)
C14—C12—C13—O4	−174.0 (2)	C21—C20—C23—O6	5.3 (5)
C11—C12—C13—O4	6.4 (4)	C19—C20—C23—O6	−176.7 (3)
C11—C12—C14—C15	−0.9 (4)	C21—C20—C23—O5	−174.1 (2)
C13—C12—C14—C15	179.5 (2)	C19—C20—C23—O5	3.9 (4)
C12—C14—C15—C16	−0.5 (4)	C23—O5—C24—C25	−178.6 (3)

Fig. 1


C1
C2
C3
C4
O4
O3
C13
C5
C6
C7
C12
C11
O1
C14
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C9
C8
C15
C16
O2
N1
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C18
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C22
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C25
C24
C23
O6

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2-(6-Bromo-3-pyridyl)-8-methylimidazo-[1,2-*a*]pyrazine

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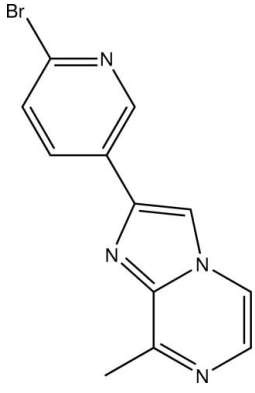
Key indicators: single-crystal X-ray study; T = 100 K; mean σ(C–C) = 0.007 Å; R factor = 0.057; wR factor = 0.154; data-to-parameter ratio = 17.2.

The structure of the title compound, $C_{12}H_9BrN_4$, prepared by the reaction of 2-bromo-1-(6-bromo-3-pyridyl)ethanone with 2-amino-3-methylpyrazine indicates that the compound with the bromopyridyl substituent at position 2 of the imidazopyrazine fused-ring system represents the major product of this reaction. The plane of the pyridine ring forms a dihedral angle of 16.2 (2)° with the essentially planar (r.m.s. deviation = 0.006 Å) imidazopyrazine system. In the crystal, molecules are linked by weak C—H···N interactions.

Related literature

For the structure of the related imidazo(1,2-*a*)pyrazine deivative, see: Lumma & Springer (1981).



Experimental

Crystal data

$C_{12}H_9BrN_4$
M_r = 289.14
Monoclinic, $P2_1/n$
a = 3.9007 (14) Å
b = 13.545 (5) Å
c = 20.673 (8) Å
β = 93.059 (5)°
V = 1090.7 (7) Å^3
Z = 4
Mo $K\alpha$ radiation
μ = 3.75 mm^{-1}
T = 100 K
0.27 × 0.11 × 0.05 mm

Data collection

Bruker APEXII CCD diffractometer
Absorption correction: multi-scan (*SADABS*; Bruker, 2001)
T_{min} = 0.431, T_{max} = 0.835
19939 measured reflections
2668 independent reflections
1887 reflections with $I > 2\sigma(I)$
R_{int} = 0.085

Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.057
$wR(F^2)$ = 0.154
S = 1.05
2668 reflections
155 parameters
H-atom parameters constrained
$\Delta\rho_{max}$ = 1.23 e Å^{-3}
$\Delta\rho_{min}$ = −1.30 e Å^{-3}

Table 1
Hydrogen-bond geometry (Å, °).

D—H···A	D—H	H···A	D···A	D—H···A
C7—H7···N1^{i}	0.95	2.52	3.438 (6)	163
C10—H10···N2^{ii}	0.95	2.60	3.484 (7)	156

Symmetry codes: (i) $-x+1, -y+2, -z+2$; (ii) $-x+\frac{5}{2}, y+\frac{1}{2}, -z+\frac{3}{2}$.

Data collection: *APEX2* (Bruker, 2007); cell refinement: *SAINT* (Bruker, 2007); data reduction: *SAINT*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *SHELXTL* (Sheldrick, 2008); software used to prepare material for publication: *SHELXTL*.

Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: HB5478).

References

Bruker (2001). *SADABS*. Bruker AXS Inc., Madison, Wisconsin, USA.
Bruker (2007). *APEX2* and *SAINT*. Bruker AXS Inc., Madison, Wisconsin, USA.
Lumma, W. C. Jr & Springer, J. P. (1981). *J. Org. Chem.* **46**, 3735–3736.
Sheldrick, G. M. (2008). *Acta Cryst.* A**64**, 112–122.

supplementary materials

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2-(6-Bromo-3-pyridyl)-8-methylimidazo[1,2-*a*]pyrazine

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Comment

The reaction of 2-bromo-1-(6-bromo3-pyridyl)ethanone with 2-amino-3-methylpyrazine may potentially produce either 2- or 3-(6-bromo3-pyridyl)-8-methylimidazo[1,2-*a*]pyrazine. The present study shows that the compound with bromopyridyl substituent in position 2 of imidazopyrazine represents the major product of this reaction (Fig. 1).

The plane of the pyridine ring N1, C1—C5 forms the dihedral angle of 16.2 (2)° with the essentially planar imidazo-pyrazine system N2, N3, N4, C6—C11. Strange though it may seem, only one purely organic structure with non-protontated non-fused imidazo(1,2 - a)pyrazine system with only carbon substituents has been published heretofore (Lumma & Springer, 1981). The geometry of the bicyclic fragment in this structure is in good agreement with that of the title compound.

Experimental

A mixture of 2-bromo-1-(6-bromo-3-pyridyl)-ethanone (2.70 g, 9.68 mmol), 2-amino-3-methylpyrazine (1.06 g, 9.68 mmol), and sodium bicarbonate (1.22 g, 14.5 mmol) in 40 ml of 2-propanol was heated at 80°C overnight. After cooling down to rt, the reaction mixture was concentrated to dryness. The resulting residue was partitioned between ethyl acetate (100 ml) and water (100 ml). The organic phase was washed with brine (1 × 100 ml), dried over sodium sulfate, concentrated to dryness, and purified by column chromatography with 0 --> 5% MeOH/EA to afford the desired product as a solid (1.25 g, 44.7% yield).

Colourless needles of (I) were grown by slow evaporation of an ethanol/dichloroethane solution.

Refinement

All H atoms were placed in geometrically calculated positions (C—H 0.95 Å for aromatic and 0.98 Å for methyl H atoms, respectively) and included in the refinement in riding motion approximation. The U_{iso}(H) were set to 1.2U_{eq} of the carrying atom (1.5U_{eq} for methyl H atoms). The maximum residual density peak 1.23 e/Å^3 is located at a distance of 0.99 Å from the Br1 atom; the deepest hole -1.30 e/Å^3 is at a distance of 0.78 Å from the Br1 atom.

Figures

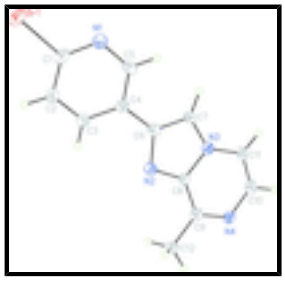


Fig. 1. Molecular structure of the title compound, showing 50% probability displacement ellipsoids. H atoms are drawn as circles of arbitrary small radius.

2-(6-Bromo-3-pyridyl)-8-methylimidazo[1,2-*a*]pyrazine

Crystal data

$C_{12}H_9BrN_4$	$F(000) = 576$
$M_r = 289.14$	$D_x = 1.761$ Mg m^{-3}
Monoclinic, $P2_1/n$	Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å
Hall symbol: -P 2yn	Cell parameters from 6098 reflections
$a = 3.9007$ (14) Å	$\theta = 3.3$–$27.2°$
$b = 13.545$ (5) Å	$\mu = 3.75$ mm^{-1}
$c = 20.673$ (8) Å	$T = 100$ K
$\beta = 93.059$ (5)°	Needle, colorless
$V = 1090.7$ (7) Å^3	0.27 × 0.11 × 0.05 mm
$Z = 4$	

Data collection

Bruker APEXII CCD diffractometer	2668 independent reflections
Radiation source: fine-focus sealed tube	1887 reflections with $I > 2\sigma(I)$
graphite	$R_{int} = 0.085$
φ and ω scans	$\theta_{max} = 28.7°$, $\theta_{min} = 1.8°$
Absorption correction: multi-scan (*SADABS*; Bruker, 2001)	$h = -5 \rightarrow 5$
$T_{min} = 0.431$, $T_{max} = 0.835$	$k = -17 \rightarrow 17$
19939 measured reflections	$l = -27 \rightarrow 26$

Refinement

Refinement on F^2	Primary atom site location: structure-invariant direct methods
Least-squares matrix: full	Secondary atom site location: difference Fourier map
$R[F^2 > 2\sigma(F^2)] = 0.057$	Hydrogen site location: inferred from neighbouring sites
$wR(F^2) = 0.154$	H-atom parameters constrained
$S = 1.05$	$w = 1/[\sigma^2(F_o^2) + (0.0701P)^2 + 3.9758P]$

	where $P = (F_o^2 + 2F_c^2)/3$
2668 reflections	$(\Delta/\sigma)_{max} = 0.001$
155 parameters	$\Delta\rho_{max} = 1.23$ e Å^{-3}
0 restraints	$\Delta\rho_{min} = -1.30$ e Å^{-3}

Special details

Geometry. All e.s.d.'s (except the e.s.d. in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell e.s.d.'s are taken into account individually in the estimation of e.s.d.'s in distances, angles and torsion angles; correlations between e.s.d.'s in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell e.s.d.'s is used for estimating e.s.d.'s involving l.s. planes.

Refinement. Refinement of F^2 against ALL reflections. The weighted *R*-factor *wR* and goodness of fit *S* are based on F^2, conventional *R*-factors *R* are based on *F*, with *F* set to zero for negative F^2. The threshold expression of $F^2 > \sigma(F^2)$ is used only for calculating *R*-factors(gt) *etc*. and is not relevant to the choice of reflections for refinement. *R*-factors based on F^2 are statistically about twice as large as those based on *F*, and *R*- factors based on ALL data will be even larger.

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å^2)

	x	*y*	*z*	U_{iso}*/U_{eq}
Br1	0.27478 (13)	0.63452 (4)	1.03763 (3)	0.0279 (2)
N1	0.5377 (11)	0.8165 (3)	1.0087 (2)	0.0247 (9)
N2	1.0290 (10)	0.9281 (3)	0.8097 (2)	0.0195 (8)
N3	1.0640 (10)	1.0898 (3)	0.83304 (19)	0.0193 (8)
N4	1.4045 (11)	1.1347 (3)	0.7232 (2)	0.0221 (9)
C1	0.4653 (12)	0.7301 (4)	0.9823 (2)	0.0215 (10)
C2	0.5223 (13)	0.7047 (4)	0.9189 (2)	0.0241 (11)
H2	0.4687	0.6407	0.9026	0.029*
C3	0.6590 (12)	0.7755 (4)	0.8807 (2)	0.0214 (10)
H3	0.7011	0.7611	0.8369	0.026*
C4	0.7370 (12)	0.8692 (3)	0.9062 (2)	0.0190 (10)
C5	0.6736 (12)	0.8850 (4)	0.9704 (2)	0.0220 (10)
H5	0.7290	0.9478	0.9887	0.026*
C6	0.8818 (12)	0.9470 (3)	0.8672 (2)	0.0185 (10)
C7	0.8997 (12)	1.0472 (3)	0.8822 (2)	0.0207 (10)
H7	0.8150	1.0790	0.9191	0.025*
C8	1.1395 (12)	1.0161 (3)	0.7898 (2)	0.0174 (9)
C9	1.3167 (12)	1.0417 (4)	0.7337 (2)	0.0207 (10)
C10	1.3238 (13)	1.2048 (4)	0.7677 (3)	0.0256 (11)
H10	1.3897	1.2710	0.7598	0.031*
C11	1.1591 (13)	1.1865 (3)	0.8214 (3)	0.0224 (10)
H11	1.1088	1.2380	0.8507	0.027*
C12	1.4005 (13)	0.9642 (4)	0.6864 (2)	0.0241 (11)
H12A	1.5153	0.9944	0.6503	0.036*
H12B	1.1887	0.9319	0.6700	0.036*
H12C	1.5530	0.9152	0.7077	0.036*

Atomic displacement parameters (Å^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Br1	0.0245 (3)	0.0267 (3)	0.0331 (3)	−0.0011 (2)	0.0081 (2)	0.0102 (2)
N1	0.027 (2)	0.024 (2)	0.023 (2)	0.0019 (18)	0.0048 (17)	0.0007 (18)
N2	0.018 (2)	0.0173 (19)	0.024 (2)	0.0029 (16)	0.0018 (16)	−0.0005 (16)
N3	0.018 (2)	0.016 (2)	0.025 (2)	0.0009 (16)	0.0031 (16)	0.0015 (16)
N4	0.021 (2)	0.018 (2)	0.027 (2)	−0.0009 (17)	0.0047 (16)	0.0024 (17)
C1	0.017 (2)	0.023 (2)	0.025 (2)	0.0025 (19)	0.0039 (18)	0.008 (2)
C2	0.024 (3)	0.019 (2)	0.029 (3)	−0.001 (2)	0.005 (2)	−0.002 (2)
C3	0.019 (2)	0.022 (2)	0.023 (2)	−0.0002 (19)	0.0032 (19)	−0.001 (2)
C4	0.017 (2)	0.020 (2)	0.020 (2)	0.0028 (19)	0.0033 (17)	0.0016 (19)
C5	0.023 (2)	0.022 (2)	0.022 (2)	0.0055 (19)	−0.0005 (19)	−0.0042 (19)
C6	0.015 (2)	0.020 (2)	0.021 (2)	0.0061 (18)	0.0003 (18)	0.0002 (19)
C7	0.025 (3)	0.016 (2)	0.022 (2)	0.0009 (19)	0.0065 (19)	−0.0035 (19)
C8	0.016 (2)	0.015 (2)	0.021 (2)	0.0013 (17)	0.0026 (18)	0.0006 (18)
C9	0.017 (2)	0.019 (2)	0.026 (2)	0.0029 (19)	0.0026 (19)	0.003 (2)
C10	0.027 (3)	0.019 (2)	0.031 (3)	−0.001 (2)	0.001 (2)	0.001 (2)
C11	0.020 (2)	0.013 (2)	0.034 (3)	0.0008 (18)	0.002 (2)	−0.003 (2)
C12	0.024 (3)	0.027 (3)	0.021 (2)	0.002 (2)	0.0069 (19)	0.000 (2)

Geometric parameters (Å, °)

Br1—C1	1.905 (5)	C3—H3	0.9500
N1—C1	1.316 (7)	C4—C5	1.381 (7)
N1—C5	1.347 (7)	C4—C6	1.458 (7)
N2—C8	1.340 (6)	C5—H5	0.9500
N2—C6	1.371 (6)	C6—C7	1.393 (7)
N3—C7	1.359 (6)	C7—H7	0.9500
N3—C8	1.382 (6)	C8—C9	1.424 (7)
N3—C11	1.386 (6)	C9—C12	1.482 (7)
N4—C9	1.327 (6)	C10—C11	1.335 (7)
N4—C10	1.371 (7)	C10—H10	0.9500
C1—C2	1.384 (7)	C11—H11	0.9500
C2—C3	1.369 (7)	C12—H12A	0.9800
C2—H2	0.9500	C12—H12B	0.9800
C3—C4	1.401 (7)	C12—H12C	0.9800
C1—N1—C5	116.8 (4)	C7—C6—C4	126.6 (4)
C8—N2—C6	104.9 (4)	N3—C7—C6	105.4 (4)
C7—N3—C8	107.6 (4)	N3—C7—H7	127.3
C7—N3—C11	132.2 (4)	C6—C7—H7	127.3
C8—N3—C11	120.2 (4)	N2—C8—N3	111.1 (4)
C9—N4—C10	118.5 (4)	N2—C8—C9	130.2 (4)
N1—C1—C2	125.0 (5)	N3—C8—C9	118.7 (4)
N1—C1—Br1	115.9 (4)	N4—C9—C8	120.4 (4)
C2—C1—Br1	119.1 (4)	N4—C9—C12	119.8 (5)
C3—C2—C1	117.3 (5)	C8—C9—C12	119.9 (4)

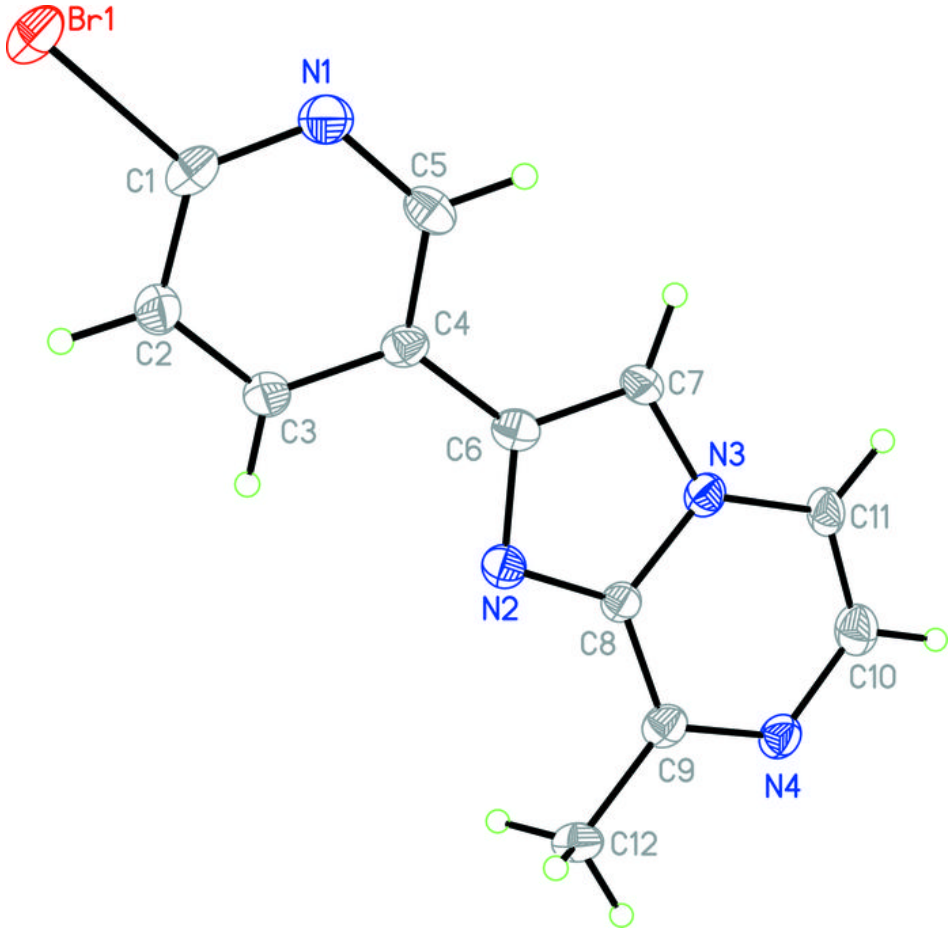
C3—C2—H2	121.3	C11—C10—N4	124.6 (5)
C1—C2—H2	121.3	C11—C10—H10	117.7
C2—C3—C4	120.2 (5)	N4—C10—H10	117.7
C2—C3—H3	119.9	C10—C11—N3	117.6 (5)
C4—C3—H3	119.9	C10—C11—H11	121.2
C5—C4—C3	117.0 (4)	N3—C11—H11	121.2
C5—C4—C6	121.0 (4)	C9—C12—H12A	109.5
C3—C4—C6	122.0 (4)	C9—C12—H12B	109.5
N1—C5—C4	123.8 (5)	H12A—C12—H12B	109.5
N1—C5—H5	118.1	C9—C12—H12C	109.5
C4—C5—H5	118.1	H12A—C12—H12C	109.5
N2—C6—C7	110.9 (4)	H12B—C12—H12C	109.5
N2—C6—C4	122.4 (4)		

Hydrogen-bond geometry (Å, °)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
C7—H7···N1^{i}	0.95	2.52	3.438 (6)	163
C10—H10···N2^{ii}	0.95	2.60	3.484 (7)	156

Symmetry codes: (i) −*x*+1, −*y*+2, −*z*+2; (ii) −*x*+5/2, *y*+1/2, −*z*+3/2.

Fig. 1



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N-[(*E*)-4-Chlorobenzylidene]-2,3-dimethylaniline

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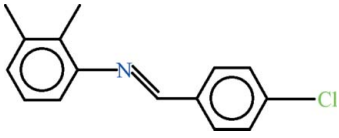
Key indicators: single-crystal X-ray study; T = 296 K; mean σ(C–C) = 0.003 Å; R factor = 0.041; wR factor = 0.116; data-to-parameter ratio = 15.1.

In the title compound, $C_{15}H_{14}ClN$, the conformation about the C=N bond is *trans* and the dihedral angle between the aromatic rings is 51.48 (4)°. In the crystal, some very weak C—H···π interactions may help to establish the packing.

Related literature

For a related structure and background to Schiff bases, see: Tariq *et al.* (2010). For related structures with different substituents at the N-bonded ring, see: Bürgi *et al.* (1968); Kazak *et al.* (2004); Ojala *et al.* (2001).



Experimental

Crystal data

$C_{15}H_{14}ClN$
M_r = 243.72
Monoclinic, $P2_1/c$
a = 12.8981 (4) Å
b = 7.7999 (2) Å
c = 15.0449 (5) Å
β = 119.315 (2)°
V = 1319.75 (7) Å^3
Z = 4
Mo $K\alpha$ radiation
μ = 0.27 mm^{-1}
T = 296 K
0.30 × 0.20 × 0.20 mm

Data collection

Bruker Kappa APEXII CCD diffractometer
Absorption correction: multi-scan (*SADABS*; Bruker, 2005)
T_{min} = 0.939, T_{max} = 0.950
10119 measured reflections
2378 independent reflections
1722 reflections with $I > 2\sigma(I)$
R_{int} = 0.026

Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.041
$wR(F^2)$ = 0.116
S = 1.05
2378 reflections
157 parameters
H-atom parameters constrained
$\Delta\rho_{max}$ = 0.15 e Å^{-3}
$\Delta\rho_{min}$ = −0.19 e Å^{-3}

Table 1
Hydrogen-bond geometry (Å, °).

*Cg*1 and *Cg*2 are the centroids of the C1–C6 and C10–C15 benzene rings, respectively.

D—H···A	D—H	H···A	D···A	D—H···A
C6—H6···*Cg*1^{i}	0.93	2.99	3.649 (2)	129
C7—H7*A*···*Cg*2^{ii}	0.96	2.93	3.757 (3)	145
C12—H12···*Cg*1^{iii}	0.93	2.96	3.793 (3)	150
C7—H7*E*···*Cg*2^{ii}	0.96	3.00	3.757 (3)	137

Symmetry codes: (i) $-x+1, y+\frac{1}{2}, -z+\frac{1}{2}$; (ii) $-x+1, -y, -z$; (iii) $-x+1, -y+1, -z$.

Data collection: *APEX2* (Bruker, 2007); cell refinement: *SAINT* (Bruker, 2007); data reduction: *SAINT*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *ORTEP-3* (Farrugia, 1997) and *PLATON* (Spek, 2009); software used to prepare material for publication: *WinGX* (Farrugia, 1999) and *PLATON* (Spek, 2009).

The authors acknowledge the provision of funds for the purchase of diffractometer and encouragement by Dr Muhammad Akram Chaudhary, Vice Chancellor, University of Sargodha.

Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: HB5479).

References

Bruker (2005). *SADABS*. Bruker AXS Inc., Madison, Wisconsin, USA.
Bruker (2007). *APEX2* and *SAINT*. Bruker AXS Inc., Madison, Wisconsin, USA.
Bürgi, H. B., Dunitz, J. D. & Züst, C. (1968). *Acta Cryst.* B**24**, 463–464.
Farrugia, L. J. (1997). *J. Appl. Cryst.* **30**, 565.
Farrugia, L. J. (1999). *J. Appl. Cryst.* **32**, 837–838.
Kazak, C., Aygün, M., Turgut, G., Odabaşoğlu, M., Büyükgüngör, O. & Kahveci, N. (2004). *Acta Cryst.* E**60**, o252–o253.
Ojala, C. R., Ojala, W. H., Gleason, W. B. & Britton, D. (2001). *J. Chem. Crystallogr.* **31**, 377–386.
Sheldrick, G. M. (2008). *Acta Cryst.* A**64**, 112–122.
Spek, A. L. (2009). *Acta Cryst.* D**65**, 148–155.
Tariq, M. I., Ahmad, S., Tahir, M. N., Sarfraz, M. & Hussain, I. (2010). *Acta Cryst.* E**66**, o1561.

supplementary materials

Acta Cryst. (2010). E**66**, o1562 [**doi:10.1107/S1600536810020933**]

N-[(*E*)-4-Chlorobenzylidene]-2,3-dimethylaniline

M. N. Tahir, M. I. Tariq, S. Ahmad, M. Sarfraz and A. Q. Ather

Comment

In continuation to synthesize various Schiff bases (Tariq *et al.*, 2010) of 2,3-dimethylaniline, the title compound (I, Fig. 1) is being reported.

The crystal structure of *p*-chlorobenzylideneaniline (Bürgi, *et al.*, 1968), *p*-cyano-*N*-(*p*-chlorobenzylidene)aniline (Ojala *et al.*, 2001) and 4-((4-Chlorobenzylidene)amino)phenol (Kazak *et al.*, 2004) have been published which contain the chloro group at *para* position. The title compound differs from these due to substitutions at the aniline.

In (I), the 2,3-dimethylanilinic group A (C1—C8/N1) and the *p*-chlorobenzaldehyde B (C9—C15/CL1) are planar with maximum r. m. s. deviations of 0.0121 and 0.0071 Å, respectively. The dihedral angle between A/B is 51.48 (4)°. The molecules are essentially monomer with no appreciable intra-molecular H-bonding. The phenyl ring of 2,3-dimethylaniline has longer bond length [1.375 (3)–1.399 (2) Å] as compared to the phenyl ring of *p*-chlorobenzaldehyde [1.364 (4)–1.386 (3) Å]. The observed value of C═N bond is 1.264 (3) Å. All these bond lengths are compareable with 2,3-dimethyl-*N*-[(*E*)-(4-nitrophenyl)methylidene]aniline (Tariq *et al.*, 2010). The molecules are stabilized due to C—H···π interactions (Table 1). The H-atoms of the methyl at *ortho* position are disordered over two set of sites with occupancy ratio 0.60 (3):0.40 (3).

Experimental

Equimolar quantities of 2,3-dimethylaniline and 4-chlorobenzaldehyde were refluxed in methanol for 45 min resulting in yellow solution. The solution was kept at room temperature which affoarded colourless prisms of (I) after 48 h.

Refinement

All H-atoms were positioned geometrically (C–H = 0.93, 0.96 Å) and refined as riding with U_{iso}(H) = xU_{eq}(C), where x = 1.2 for aryl and x = 1.5 for methyl H-atoms. From the observation of difference Fourier map, it was concluded that H-atoms of one of the *ortho* methyl are disordered.

Figures

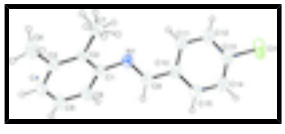


Fig. 1. View of (I) with displacement ellipsoids drawn at the 30% probability level.

N-[(*E*)-4-Chlorobenzylidene]-2,3-dimethylaniline

Crystal data

$C_{15}H_{14}ClN$	$F(000) = 512$
$M_r = 243.72$	$D_x = 1.227$ Mg m^{-3}
Monoclinic, $P2_1/c$	Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å
Hall symbol: -P 2ybc	Cell parameters from 1467 reflections
$a = 12.8981$ (4) Å	$\theta = 2.3$–$25.3°$
$b = 7.7999$ (2) Å	$\mu = 0.27$ mm^{-1}
$c = 15.0449$ (5) Å	$T = 296$ K
$\beta = 119.315$ (2)°	Prism, colourless
$V = 1319.75$ (7) Å^3	0.30 × 0.20 × 0.20 mm
$Z = 4$	

Data collection

Bruker Kappa APEXII CCD diffractometer	2378 independent reflections
Radiation source: fine-focus sealed tube	1722 reflections with $I > 2\sigma(I)$
graphite	$R_{int} = 0.026$
Detector resolution: 8.10 pixels mm^{-1}	$\theta_{max} = 25.3°$, $\theta_{min} = 2.7°$
ω scans	$h = -15 \rightarrow 15$
Absorption correction: multi-scan (*SADABS*; Bruker, 2005)	$k = -8 \rightarrow 9$
$T_{min} = 0.939$, $T_{max} = 0.950$	$l = -18 \rightarrow 18$
10119 measured reflections	

Refinement

Refinement on F^2	Primary atom site location: structure-invariant direct methods
Least-squares matrix: full	Secondary atom site location: difference Fourier map
$R[F^2 > 2\sigma(F^2)] = 0.041$	Hydrogen site location: inferred from neighbouring sites
$wR(F^2) = 0.116$	H-atom parameters constrained
$S = 1.05$	$w = 1/[\sigma^2(F_o^2) + (0.0502P)^2 + 0.2848P]$ where $P = (F_o^2 + 2F_c^2)/3$
2378 reflections	$(\Delta/\sigma)_{max} < 0.001$
157 parameters	$\Delta\rho_{max} = 0.15$ e Å^{-3}
0 restraints	$\Delta\rho_{min} = -0.19$ e Å^{-3}

Special details

Geometry. Bond distances, angles *etc*. have been calculated using the rounded fractional coordinates. All su's are estimated from the variances of the (full) variance-covariance matrix. The cell e.s.d.'s are taken into account in the estimation of distances, angles and torsion angles

Refinement. Refinement of F^2 against ALL reflections. The weighted *R*-factor *wR* and goodness of fit *S* are based on F^2, conventional *R*-factors *R* are based on *F*, with *F* set to zero for negative F^2. The threshold expression of $F^2 > \sigma(F^2)$ is used only for calculating *R*-factors(gt) *etc*. and is not relevant to the choice of reflections for refinement. *R*-factors based on F^2 are statistically about twice as large as those based on *F*, and *R*- factors based on ALL data will be even larger.

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å^2)

	x	*y*	*z*	U_{iso}*/U_{eq}	Occ. (<1)
Cl1	0.03504 (6)	0.38426 (9)	−0.38533 (4)	0.1078 (3)	
N1	0.47950 (12)	0.29383 (18)	0.09822 (10)	0.0549 (5)	
C1	0.55065 (14)	0.2685 (2)	0.20499 (12)	0.0492 (5)	
C2	0.66149 (14)	0.1905 (2)	0.24128 (12)	0.0502 (5)	
C3	0.73394 (15)	0.1691 (2)	0.34649 (13)	0.0550 (6)	
C4	0.69544 (17)	0.2286 (3)	0.41183 (14)	0.0673 (7)	
C5	0.58704 (18)	0.3083 (3)	0.37546 (14)	0.0762 (8)	
C6	0.51425 (17)	0.3277 (3)	0.27191 (14)	0.0654 (6)	
C7	0.70003 (18)	0.1280 (3)	0.16739 (15)	0.0750 (8)	
C8	0.85264 (17)	0.0805 (3)	0.39021 (15)	0.0821 (8)	
C9	0.36888 (15)	0.2672 (2)	0.05682 (13)	0.0568 (6)	
C10	0.28740 (15)	0.2988 (2)	−0.05166 (13)	0.0555 (6)	
C11	0.32577 (17)	0.3762 (2)	−0.11338 (14)	0.0642 (7)	
C12	0.24792 (19)	0.4016 (3)	−0.21581 (15)	0.0729 (7)	
C13	0.13238 (18)	0.3509 (3)	−0.25623 (14)	0.0691 (7)	
C14	0.09207 (17)	0.2742 (3)	−0.19726 (16)	0.0848 (9)	
C15	0.16989 (16)	0.2490 (3)	−0.09440 (15)	0.0753 (8)	
H4	0.74368	0.21437	0.48175	0.0807*	
H5	0.56297	0.34907	0.42059	0.0914*	
H6	0.44060	0.38061	0.24705	0.0784*	
H7A	0.68581	0.00694	0.15699	0.1125*	0.60 (3)
H7B	0.78330	0.15045	0.19446	0.1125*	0.60 (3)
H7C	0.65559	0.18672	0.10356	0.1125*	0.60 (3)
H8A	0.88586	0.06855	0.46260	0.1231*	
H8B	0.90540	0.14723	0.37604	0.1231*	
H8C	0.84233	−0.03092	0.35984	0.1231*	
H9	0.33782	0.22566	0.09688	0.0681*	
H11	0.40448	0.41135	−0.08561	0.0771*	
H12	0.27416	0.45295	−0.25702	0.0875*	
H14	0.01323	0.23925	−0.22586	0.1018*	
H15	0.14274	0.19794	−0.05375	0.0904*	
H7D	0.63260	0.08266	0.10781	0.1125*	0.40 (3)
H7E	0.75885	0.03979	0.19898	0.1125*	0.40 (3)
H7F	0.73326	0.22166	0.14822	0.1125*	0.40 (3)

Atomic displacement parameters (Å^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Cl1	0.1029 (5)	0.1121 (5)	0.0596 (4)	0.0316 (4)	0.0019 (3)	−0.0013 (3)
N1	0.0515 (8)	0.0532 (9)	0.0526 (8)	0.0013 (7)	0.0197 (7)	0.0026 (7)
C1	0.0506 (9)	0.0446 (9)	0.0496 (9)	−0.0022 (7)	0.0223 (8)	−0.0008 (7)
C2	0.0496 (9)	0.0472 (9)	0.0521 (9)	−0.0034 (7)	0.0237 (8)	−0.0011 (8)
C3	0.0507 (10)	0.0530 (10)	0.0547 (10)	−0.0025 (8)	0.0208 (8)	0.0002 (8)
C4	0.0662 (12)	0.0780 (14)	0.0478 (10)	−0.0004 (10)	0.0203 (9)	−0.0031 (10)
C5	0.0761 (14)	0.0942 (16)	0.0587 (12)	0.0091 (12)	0.0333 (10)	−0.0150 (11)
C6	0.0565 (10)	0.0693 (12)	0.0634 (11)	0.0110 (9)	0.0240 (9)	−0.0071 (10)
C7	0.0641 (12)	0.1002 (16)	0.0640 (12)	0.0125 (11)	0.0339 (10)	−0.0014 (11)
C8	0.0608 (12)	0.0989 (17)	0.0680 (12)	0.0163 (11)	0.0172 (10)	0.0052 (12)
C9	0.0553 (11)	0.0592 (11)	0.0562 (10)	−0.0001 (8)	0.0276 (9)	0.0001 (9)
C10	0.0517 (10)	0.0541 (10)	0.0549 (10)	0.0030 (8)	0.0215 (8)	−0.0039 (8)
C11	0.0590 (11)	0.0613 (12)	0.0598 (11)	−0.0094 (9)	0.0193 (9)	0.0031 (9)
C12	0.0848 (14)	0.0598 (12)	0.0607 (11)	−0.0062 (10)	0.0253 (11)	0.0057 (9)
C13	0.0657 (12)	0.0668 (13)	0.0553 (11)	0.0151 (10)	0.0145 (10)	−0.0052 (10)
C14	0.0459 (10)	0.122 (2)	0.0722 (14)	0.0036 (12)	0.0178 (10)	−0.0179 (14)
C15	0.0529 (11)	0.1084 (18)	0.0644 (12)	−0.0042 (11)	0.0285 (10)	−0.0059 (12)

Geometric parameters (Å, °)

Cl1—C13	1.740 (2)	C4—H4	0.9300
N1—C1	1.421 (2)	C5—H5	0.9300
N1—C9	1.264 (3)	C6—H6	0.9300
C1—C2	1.396 (3)	C7—H7A	0.9600
C1—C6	1.382 (3)	C7—H7B	0.9600
C2—C3	1.399 (2)	C7—H7C	0.9600
C2—C7	1.504 (3)	C7—H7D	0.9600
C3—C4	1.381 (3)	C7—H7E	0.9600
C3—C8	1.506 (3)	C7—H7F	0.9600
C4—C5	1.375 (3)	C8—H8A	0.9600
C5—C6	1.378 (3)	C8—H8B	0.9600
C9—C10	1.466 (2)	C8—H8C	0.9600
C10—C11	1.386 (3)	C9—H9	0.9300
C10—C15	1.381 (3)	C11—H11	0.9300
C11—C12	1.381 (3)	C12—H12	0.9300
C12—C13	1.364 (4)	C14—H14	0.9300
C13—C14	1.366 (3)	C15—H15	0.9300
C14—C15	1.386 (3)		
C1—N1—C9	118.88 (16)	C5—C6—H6	120.00
N1—C1—C2	118.29 (16)	C2—C7—H7A	109.00
N1—C1—C6	121.03 (17)	C2—C7—H7B	109.00
C2—C1—C6	120.59 (16)	C2—C7—H7C	109.00
C1—C2—C3	118.90 (17)	C2—C7—H7D	109.00
C1—C2—C7	119.88 (15)	C2—C7—H7E	109.00

C3—C2—C7	121.21 (18)	C2—C7—H7F	109.00
C2—C3—C4	119.44 (18)	H7A—C7—H7B	109.00
C2—C3—C8	121.46 (17)	H7A—C7—H7C	109.00
C4—C3—C8	119.10 (16)	H7B—C7—H7C	109.00
C3—C4—C5	121.24 (17)	H7D—C7—H7E	109.00
C4—C5—C6	119.8 (2)	H7D—C7—H7F	109.00
C1—C6—C5	120.0 (2)	H7E—C7—H7F	109.00
N1—C9—C10	122.83 (18)	C3—C8—H8A	109.00
C9—C10—C11	121.50 (19)	C3—C8—H8B	109.00
C9—C10—C15	119.75 (18)	C3—C8—H8C	109.00
C11—C10—C15	118.75 (17)	H8A—C8—H8B	109.00
C10—C11—C12	120.5 (2)	H8A—C8—H8C	109.00
C11—C12—C13	119.7 (2)	H8B—C8—H8C	109.00
Cl1—C13—C12	119.21 (17)	N1—C9—H9	119.00
Cl1—C13—C14	119.62 (18)	C10—C9—H9	119.00
C12—C13—C14	121.17 (19)	C10—C11—H11	120.00
C13—C14—C15	119.3 (2)	C12—C11—H11	120.00
C10—C15—C14	120.7 (2)	C11—C12—H12	120.00
C3—C4—H4	119.00	C13—C12—H12	120.00
C5—C4—H4	119.00	C13—C14—H14	120.00
C4—C5—H5	120.00	C15—C14—H14	120.00
C6—C5—H5	120.00	C10—C15—H15	120.00
C1—C6—H6	120.00	C14—C15—H15	120.00
C9—N1—C1—C2	139.41 (17)	C3—C4—C5—C6	0.9 (4)
C9—N1—C1—C6	−44.1 (2)	C4—C5—C6—C1	−0.6 (4)
C1—N1—C9—C10	176.57 (15)	N1—C9—C10—C11	−6.5 (3)
N1—C1—C2—C3	178.22 (15)	N1—C9—C10—C15	172.75 (18)
N1—C1—C2—C7	−3.0 (2)	C9—C10—C11—C12	178.72 (18)
C6—C1—C2—C3	1.7 (3)	C15—C10—C11—C12	−0.5 (3)
C6—C1—C2—C7	−179.55 (19)	C9—C10—C15—C14	−178.54 (19)
N1—C1—C6—C5	−177.17 (19)	C11—C10—C15—C14	0.7 (3)
C2—C1—C6—C5	−0.7 (3)	C10—C11—C12—C13	0.4 (3)
C1—C2—C3—C4	−1.4 (3)	C11—C12—C13—Cl1	179.79 (17)
C1—C2—C3—C8	177.88 (17)	C11—C12—C13—C14	−0.4 (4)
C7—C2—C3—C4	179.87 (19)	Cl1—C13—C14—C15	−179.61 (18)
C7—C2—C3—C8	−0.9 (3)	C12—C13—C14—C15	0.6 (4)
C2—C3—C4—C5	0.1 (3)	C13—C14—C15—C10	−0.7 (3)
C8—C3—C4—C5	−179.1 (2)		

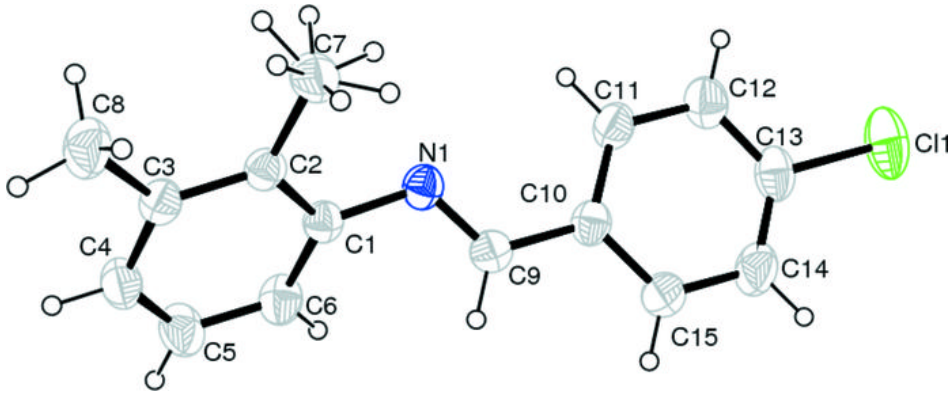
Hydrogen-bond geometry (Å, °)

Cg1 and Cg2 are the centroids of the C1–C6 and C10–C15 benzene rings, respectively.

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
C6—H6···Cg1^{i}	0.93	2.99	3.649 (2)	129
C7—H7A···Cg2^{ii}	0.96	2.93	3.757 (3)	145
C12—H12···Cg1^{iii}	0.93	2.96	3.793 (3)	150
C7—H7E···Cg2^{ii}	0.96	3.00	3.757 (3)	137

Symmetry codes: (i) −*x*+1, *y*+1/2, −*z*+1/2; (ii) −*x*+1, −*y*, −*z*; (iii) −*x*+1, −*y*+1, −*z*.

Fig. 1



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4-[(*E*)-(2,4,5-Trimethoxybenzylidene)amino]-1,5-dimethyl-2-phenyl-1*H*-pyrazol-3(2*H*)-one

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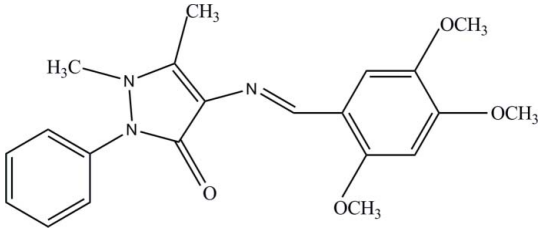
Key indicators: single-crystal X-ray study; T = 100 K; mean σ(C–C) = 0.001 Å; R factor = 0.040; wR factor = 0.123; data-to-parameter ratio = 16.3.

The title compound, $C_{21}H_{23}N_3O_4$, adopts an *E* configuration about the central C=N double bond and the pyrazolone ring is almost planar, with a maximum deviation of 0.042 (1) Å. The central pyrazolone ring makes dihedral angles of 51.96 (5) and 3.82 (5)° with the attached phenyl and the trimethoxy-substituted benzene rings, respectively. The dihedral angle between the phenyl ring and the trimethoxy-substituted benzene ring is 50.19 (5)° and an intramolecular C—H···O hydrogen bond generates an S(6) ring motif. The crystal structure is stabilized by intermolecular C—H···O and C—H···N hydrogen bonds.

Related literature

For background to the applications of Schiff bases, see: Vukovic *et al.* (2010); Ramesh & Maheswaran (2003); Dongfang *et al.* (2008); Sastry & Rao (1988); Kamel *et al.* (2010). For hydrogen-bond motifs, see: Bernstein *et al.* (1995). For the stability of the temperature controller used in the data collection, see: Cosier & Glazer (1986).



Experimental

Crystal data

$C_{21}H_{23}N_3O_4$
M_r = 381.42
Monoclinic, $P2_1/c$
a = 21.0128 (10) Å
b = 7.4242 (4) Å
c = 12.5194 (6) Å
β = 98.675 (1)°
V = 1930.72 (17) Å^3
Z = 4
Mo $K\alpha$ radiation
μ = 0.09 mm^{-1}
T = 100 K
0.67 × 0.27 × 0.15 mm

Data collection

Bruker APEXII DUO CCD diffractometer
Absorption correction: multi-scan (*SADABS*; Bruker, 2009)
T_{min} = 0.941, T_{max} = 0.987
23600 measured reflections
5614 independent reflections
4779 reflections with $I > 2\sigma(I)$
R_{int} = 0.031

Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.040
$wR(F^2)$ = 0.123
S = 1.04
5614 reflections
345 parameters
H atoms treated by a mixture of independent and constrained refinement
$\Delta\rho_{max}$ = 0.48 e Å^{-3}
$\Delta\rho_{min}$ = −0.23 e Å^{-3}

Table 1
Hydrogen-bond geometry (Å, °).

D—H···A	D—H	H···A	D···A	D—H···A
C10—H10A···O1	0.954 (13)	2.331 (13)	3.0112 (11)	127.8 (10)
C4—H4A···O1^{i}	0.969 (13)	2.541 (13)	3.2628 (12)	131.4 (10)
C20—H20A···N3^{ii}	0.996 (14)	2.577 (14)	3.5383 (13)	162.1 (12)
C20—H20C···O2^{iii}	0.977 (14)	2.509 (14)	3.4470 (13)	160.8 (12)
C20—H20C···O3^{iii}	0.977 (14)	2.495 (15)	3.2779 (13)	137.0 (11)

Symmetry codes: (i) $x, -y-\frac{1}{2}, z+\frac{1}{2}$; (ii) $x, -y+\frac{1}{2}, z-\frac{1}{2}$; (iii) $-x, -y+1, -z$.

Data collection: *APEX2* (Bruker, 2009); cell refinement: *SAINT* (Bruker, 2009); data reduction: *SAINT*; program(s) used to solve structure: *SHELXTL* (Sheldrick, 2008); program(s) used to refine structure: *SHELXTL*; molecular graphics: *SHELXTL*; software used to prepare material for publication: *SHELXTL* and *PLATON* (Spek, 2009).

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Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: HB5480).

References

Bernstein, J., Davis, R. E., Shimoni, L. & Chang, N.-L. (1995). *Angew. Chem. Int. Ed. Engl.* **34**, 1555–1573.
Bruker (2009). *APEX2*, *SAINT* and *SADABS*. Bruker AXS Inc., Madison, Wisconsin, USA.
Cosier, J. & Glazer, A. M. (1986). *J. Appl. Cryst.* **19**, 105–107.
Dongfang, X. U., Shuzhi, M. A., Guangying, D. U., Qizhuang, H. E. & Dazhi, S. (2008). *J. Rare Earths*, **26**, 643–647.
Kamel, M. M., Ali, H. I., Anwar, M. M., Mohamed, N. A. & Soliman, A. M. (2010). *Eur. J. Med. Chem.* **45**, 572–580.

‡ Thomson Reuters ResearcherID: A-3561-2009.
§ On secondment to: The Center of Excellence for Advanced Materials Research, King Abdu Aziz University, Jeddah 21589, Saudi Arabia.

Ramesh, R. & Maheswaran, S. (2003). *J. Inorg. Biochem.*, **96**, 457–462.
Sastry, C. S. P. & Rao, A. R. M. (1988). *J. Pharmacol. Methods*, **26**, 643–647.
Sheldrick, G. M. (2008). *Acta Cryst.* A**64**, 112–122.
Spek, A. L. (2009). *Acta Cryst.* D**65**, 148–155.
Vukovic, N., Sukdolak, S., Solujic, S. & Niciforovic, N. (2010). *Food Chem.* **120**, 1011–1018.

supplementary materials

Acta Cryst. (2010). E**66**, o1656-o1657 [**doi:10.1107/S1600536810021586**]

4-[(*E*)-(2,4,5-Trimethoxybenzylidene)amino]-1,5-dimethyl-2-phenyl-1*H*-pyrazol-3(2*H*)-one

H.-K. Fun, M. Hemamalini, A. M. Asiri and S. A. Khan

Comment

Compounds with the structure of AC═NB are known as Schiff base, which can be synthesized from the condensation of amino and active carbonyl groups. Schiff base compounds have shown different therapeutic properties such as antibacterial (Vukovic *et al.*, 2010), antifungal (Ramesh & Maheswaran, 2003), antitumor (Dongfang *et al.*, 2008), anti-inflammatory (Sastry & Rao, 1988) and anticancer activities (Kamel *et al.*, 2010). Due to their importance, the crystal structure determination of the title compound was carried out and the results are presented here.

In the title compound (Fig. 1), the pyrazolone ring (N1/N2/C7–C9) is almost planar, with maximum deviation of 0.042 (1) Å for atom N2. The central pyrazolone (N1/N2/C7–C9) ring makes dihedral angles of 51.96 (5)° and 3.82 (5)° with the attached phenyl ring (C1–C6) and the trimethoxy substituted phenyl ring (C11–C16), respectively. The dihedral angle between the phenyl ring(C1–C6) and the trimethoxy substituted phenyl ring (C11–C16) is 50.19 (5)°. The three methoxy groups are coplanar with the benzene ring [torsion angles C19-O2-C13-C12 = 5.04 (16)°, C20-O3-C14-C15 = -0.36 (14)° and C21-O4-C16-C15 = -1.66 (13)°].

In the crystal packing (Fig. 2), the intramolecular C10—H10A···O1 hydrogen bonding generates an *S*(6) ring motif (Bernstein *et al.*, 1995). The crystal sturcture is futher stabilized by weak intermolecular C4—H4A···O1, C20—H20C···O2, C20—H20C···O3 and C20—H20A···N3 (Table 1) hydrogen bonds.

Experimental

A mixture of 4-aminophenazone (0.50 g, 0.0033 mol) and 2,4,5-tri-methoxy- benzaldehyde (0.65 g, 0.0033 mol) in methanol (15 ml) was refluxed for 5 h with stirring to give a light yellow precipitate. It was then filtered and washed with methanol to give the pure Schiff base and yellow blocks of (I) were recrystallized from methanol. Yield: 48.18%; Mp. 381°C; IR (KBr) ν_{max} cm^{-1}: 2937 (C–H), 1644 (C═C), 1609(C═O), 1591 (C═N), 1122 (N–N). ^{1}H-NMR ($CDCl_3$) d: 10.02 ((s, 1H, CH olefinic), 7.67 (s, H3, CHaromatic), 6.49 (s, H6, CHaromatic), 7.47–7.26 (m, 5H, CHaromatic), 3.93 (s, OCH_3), 3.93 (s, OCH_3), 3.84 (s, OCH_3), 3.11(s, N-CH_3), 2.48 (s,-CH_3).

Refinement

All the H atoms were located from a difference Fourier map and refined freely [C—H = 0.945 (14)–1.008 (14) Å].

Figures

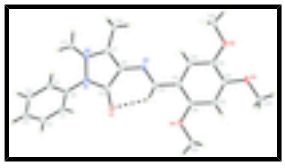


Fig. 1. The molecular structure of (I) showing 50% probability displacement ellipsoids. The intramolecular hydrogen bond is shown as a dashed line.

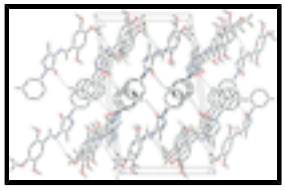


Fig. 2. The crystal packing of (I) showing hydrogen-bonded (dashed lines) networks. H atoms not involved in the hydrogen bond interactions are omitted for clarity.

4-[(*E*)-(2,4,5-Trimethoxybenzylidene)amino]-1,5-dimethyl-2-phenyl- 1*H*-pyrazol-3(2*H*)-one

Crystal data

$C_{21}H_{23}N_3O_4$	$F(000) = 808$
$M_r = 381.42$	$D_x = 1.312$ Mg m^{-3}
Monoclinic, $P2_1/c$	Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å
Hall symbol: -P 2ybc	Cell parameters from 8559 reflections
$a = 21.0128$ (10) Å	$\theta = 2.9–34.8°$
$b = 7.4242$ (4) Å	$\mu = 0.09$ mm^{-1}
$c = 12.5194$ (6) Å	$T = 100$ K
$\beta = 98.675$ (1)°	Blcok, yellow
$V = 1930.72$ (17) Å^3	0.67 × 0.27 × 0.15 mm
$Z = 4$	

Data collection

Bruker APEXII DUO CCD diffractometer	5614 independent reflections
Radiation source: fine-focus sealed tube	4779 reflections with $I > 2\sigma(I)$
graphite	$R_{int} = 0.031$
φ and ω scans	$\theta_{max} = 30.0°$, $\theta_{min} = 1.0°$
Absorption correction: multi-scan (*SADABS*; Bruker, 2009)	$h = -29\rightarrow29$
$T_{min} = 0.941$, $T_{max} = 0.987$	$k = -10\rightarrow10$
23600 measured reflections	$l = -17\rightarrow17$

Refinement

Refinement on F^2	Primary atom site location: structure-invariant direct methods
Least-squares matrix: full	Secondary atom site location: difference Fourier map
$R[F^2 > 2\sigma(F^2)] = 0.040$	Hydrogen site location: inferred from neighbouring sites

$wR(F^2) = 0.123$	H atoms treated by a mixture of independent and constrained refinement
$S = 1.04$	$w = 1/[\sigma^2(F_o^2) + (0.0771P)^2 + 0.3259P]$ where $P = (F_o^2 + 2F_c^2)/3$
5614 reflections	$(\Delta/\sigma)_{max} < 0.001$
345 parameters	$\Delta\rho_{max} = 0.48$ e Å^{-3}
0 restraints	$\Delta\rho_{min} = -0.22$ e Å^{-3}

Special details

Experimental. The crystal was placed in the cold stream of an Oxford Cryosystems Cobra open-flow nitrogen cryostat (Cosier & Glazer, 1986) operating at 100.0 (1) K.

Geometry. All s.u.'s (except the s.u. in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell s.u.'s are taken into account individually in the estimation of s.u.'s in distances, angles and torsion angles; correlations between s.u.'s in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell s.u.'s is used for estimating s.u.'s involving l.s. planes.

Refinement. Refinement of F^2 against ALL reflections. The weighted R-factor wR and goodness of fit S are based on F^2, conventional R-factors R are based on F, with F set to zero for negative F^2. The threshold expression of $F^2 > 2\sigma(F^2)$ is used only for calculating R-factors(gt) etc. and is not relevant to the choice of reflections for refinement. R-factors based on F^2 are statistically about twice as large as those based on F, and R- factors based on ALL data will be even larger.

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å^2)

	x	*y*	*z*	U_{iso}*/U_{eq}
O1	0.36912 (3)	−0.05337 (10)	0.48796 (5)	0.01654 (15)
O2	0.02634 (3)	0.14809 (11)	0.14482 (6)	0.02325 (17)
O3	0.06645 (3)	0.44390 (11)	0.06868 (6)	0.02140 (17)
O4	0.27842 (3)	0.35928 (10)	0.27787 (6)	0.01722 (15)
N1	0.35715 (4)	−0.34299 (11)	0.55298 (6)	0.01452 (16)
N2	0.30506 (4)	−0.45837 (11)	0.56225 (6)	0.01459 (16)
N3	0.22306 (4)	−0.11616 (11)	0.39236 (6)	0.01426 (16)
C1	0.47358 (5)	−0.34082 (14)	0.59345 (8)	0.01773 (19)
C2	0.52970 (5)	−0.35703 (15)	0.66770 (9)	0.0216 (2)
C3	0.52678 (5)	−0.39395 (14)	0.77564 (8)	0.0205 (2)
C4	0.46740 (5)	−0.41126 (14)	0.81062 (8)	0.01797 (19)
C5	0.41087 (5)	−0.39230 (14)	0.73777 (7)	0.01641 (18)
C6	0.41448 (4)	−0.35847 (13)	0.62948 (7)	0.01427 (18)
C7	0.25240 (4)	−0.38702 (13)	0.49748 (7)	0.01383 (18)
C8	0.26770 (4)	−0.22283 (13)	0.45728 (7)	0.01270 (17)
C9	0.33566 (4)	−0.18791 (13)	0.49592 (7)	0.01293 (17)
C10	0.24207 (4)	0.03035 (13)	0.35116 (7)	0.01384 (17)
C11	0.19674 (4)	0.14168 (13)	0.27961 (7)	0.01385 (18)
C12	0.13242 (4)	0.08699 (14)	0.24831 (7)	0.01533 (18)
C13	0.08971 (4)	0.18970 (14)	0.17891 (8)	0.01645 (18)
C14	0.11121 (4)	0.35193 (14)	0.13731 (7)	0.01642 (19)
C15	0.17427 (4)	0.40938 (14)	0.16780 (7)	0.01589 (18)
C16	0.21674 (4)	0.30561 (13)	0.24024 (7)	0.01424 (17)

C17	0.32012 (5)	−0.65126 (14)	0.55935 (8)	0.0194 (2)
C18	0.18985 (5)	−0.48412 (14)	0.47905 (8)	0.01728 (19)
C19	0.00170 (5)	−0.00727 (18)	0.19178 (11)	0.0293 (3)
C20	0.08640 (5)	0.61077 (16)	0.02644 (9)	0.0223 (2)
C21	0.29988 (5)	0.52608 (14)	0.23842 (8)	0.01750 (19)
H1A	0.4749 (7)	−0.319 (2)	0.5178 (11)	0.025 (3)*
H2A	0.5716 (7)	−0.342 (2)	0.6413 (11)	0.027 (4)*
H3A	0.5674 (7)	−0.413 (2)	0.8265 (12)	0.028 (4)*
H4A	0.4646 (6)	−0.4380 (19)	0.8855 (11)	0.020 (3)*
H5A	0.3683 (7)	−0.407 (2)	0.7601 (11)	0.024 (3)*
H10A	0.2859 (6)	0.0685 (18)	0.3651 (10)	0.016 (3)*
H12A	0.1206 (7)	−0.025 (2)	0.2767 (11)	0.022 (3)*
H15A	0.1878 (7)	0.520 (2)	0.1400 (11)	0.020 (3)*
H17A	0.2798 (7)	−0.723 (2)	0.5642 (11)	0.024 (3)*
H17B	0.3365 (7)	−0.684 (2)	0.4918 (12)	0.027 (4)*
H17C	0.3507 (7)	−0.673 (2)	0.6234 (12)	0.030 (4)*
H18A	0.1555 (7)	−0.411 (2)	0.4352 (12)	0.030 (4)*
H18B	0.1925 (8)	−0.601 (2)	0.4416 (12)	0.033 (4)*
H18C	0.1744 (7)	−0.511 (2)	0.5471 (12)	0.032 (4)*
H19A	−0.0437 (8)	−0.018 (2)	0.1586 (13)	0.037 (4)*
H19B	0.0243 (8)	−0.119 (2)	0.1720 (13)	0.038 (4)*
H19C	0.0082 (8)	0.003 (3)	0.2715 (14)	0.042 (4)*
H20A	0.1208 (7)	0.586 (2)	−0.0182 (11)	0.024 (3)*
H20B	0.1018 (7)	0.696 (2)	0.0873 (12)	0.032 (4)*
H20C	0.0475 (7)	0.656 (2)	−0.0181 (11)	0.026 (4)*
H21A	0.3011 (7)	0.515 (2)	0.1612 (12)	0.023 (3)*
H21B	0.3418 (7)	0.545 (2)	0.2761 (11)	0.025 (4)*
H21C	0.2732 (7)	0.626 (2)	0.2555 (11)	0.024 (3)*

Atomic displacement parameters (Å^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
O1	0.0170 (3)	0.0133 (3)	0.0192 (3)	−0.0013 (3)	0.0023 (2)	0.0031 (3)
O2	0.0125 (3)	0.0240 (4)	0.0322 (4)	−0.0015 (3)	0.0001 (3)	0.0114 (3)
O3	0.0138 (3)	0.0224 (4)	0.0272 (4)	0.0030 (3)	0.0007 (3)	0.0132 (3)
O4	0.0142 (3)	0.0164 (3)	0.0202 (3)	−0.0017 (3)	−0.0002 (2)	0.0061 (3)
N1	0.0139 (3)	0.0120 (4)	0.0170 (3)	−0.0004 (3)	0.0000 (3)	0.0033 (3)
N2	0.0149 (3)	0.0111 (4)	0.0172 (3)	−0.0007 (3)	0.0004 (3)	0.0030 (3)
N3	0.0153 (3)	0.0137 (4)	0.0137 (3)	0.0033 (3)	0.0020 (3)	0.0020 (3)
C1	0.0173 (4)	0.0173 (5)	0.0189 (4)	0.0029 (4)	0.0038 (3)	0.0031 (4)
C2	0.0151 (4)	0.0213 (5)	0.0281 (5)	0.0019 (4)	0.0027 (4)	0.0041 (4)
C3	0.0190 (4)	0.0159 (4)	0.0243 (5)	0.0007 (4)	−0.0041 (3)	0.0008 (4)
C4	0.0218 (4)	0.0150 (4)	0.0158 (4)	0.0018 (4)	−0.0013 (3)	−0.0005 (3)
C5	0.0173 (4)	0.0151 (4)	0.0166 (4)	0.0019 (3)	0.0020 (3)	−0.0005 (3)
C6	0.0148 (4)	0.0110 (4)	0.0163 (4)	0.0020 (3)	−0.0001 (3)	0.0004 (3)
C7	0.0153 (4)	0.0132 (4)	0.0130 (4)	0.0014 (3)	0.0023 (3)	0.0005 (3)
C8	0.0140 (4)	0.0119 (4)	0.0122 (3)	0.0020 (3)	0.0020 (3)	0.0007 (3)
C9	0.0149 (4)	0.0119 (4)	0.0122 (3)	0.0023 (3)	0.0026 (3)	0.0010 (3)

C10	0.0145 (4)	0.0131 (4)	0.0138 (4)	0.0025 (3)	0.0018 (3)	0.0012 (3)
C11	0.0146 (4)	0.0132 (4)	0.0140 (4)	0.0023 (3)	0.0027 (3)	0.0024 (3)
C12	0.0149 (4)	0.0143 (4)	0.0171 (4)	0.0020 (3)	0.0037 (3)	0.0038 (3)
C13	0.0122 (4)	0.0176 (4)	0.0197 (4)	0.0017 (3)	0.0031 (3)	0.0039 (4)
C14	0.0144 (4)	0.0175 (4)	0.0176 (4)	0.0043 (3)	0.0030 (3)	0.0056 (3)
C15	0.0155 (4)	0.0154 (4)	0.0171 (4)	0.0023 (3)	0.0035 (3)	0.0051 (3)
C16	0.0131 (4)	0.0150 (4)	0.0147 (4)	0.0013 (3)	0.0024 (3)	0.0019 (3)
C17	0.0216 (4)	0.0111 (4)	0.0244 (5)	0.0012 (4)	−0.0003 (4)	0.0034 (4)
C18	0.0166 (4)	0.0155 (4)	0.0196 (4)	−0.0020 (3)	0.0025 (3)	0.0013 (3)
C19	0.0165 (4)	0.0268 (6)	0.0443 (7)	−0.0026 (4)	0.0037 (4)	0.0137 (5)
C20	0.0179 (4)	0.0221 (5)	0.0268 (5)	0.0031 (4)	0.0028 (4)	0.0124 (4)
C21	0.0194 (4)	0.0139 (4)	0.0194 (4)	−0.0017 (4)	0.0036 (3)	0.0029 (3)

Geometric parameters (Å, °)

O1—C9	1.2341 (12)	C8—C9	1.4603 (12)
O2—C13	1.3709 (11)	C10—C11	1.4613 (12)
O2—C19	1.4268 (14)	C10—H10A	0.954 (13)
O3—C14	1.3583 (11)	C11—C16	1.4011 (13)
O3—C20	1.4342 (13)	C11—C12	1.4090 (13)
O4—C16	1.3698 (11)	C12—C13	1.3808 (13)
O4—C21	1.4311 (12)	C12—H12A	0.949 (15)
N1—C9	1.3937 (12)	C13—C14	1.4130 (14)
N1—N2	1.4084 (11)	C14—C15	1.3897 (13)
N1—C6	1.4261 (11)	C15—C16	1.4029 (12)
N2—C7	1.3754 (11)	C15—H15A	0.953 (15)
N2—C17	1.4683 (13)	C17—H17A	1.008 (14)
N3—C10	1.2927 (12)	C17—H17B	0.990 (14)
N3—C8	1.3918 (11)	C17—H17C	0.963 (15)
C1—C6	1.3898 (13)	C18—H18A	1.000 (16)
C1—C2	1.3923 (13)	C18—H18B	0.990 (17)
C1—H1A	0.965 (14)	C18—H18C	0.977 (15)
C2—C3	1.3893 (15)	C19—H19A	0.986 (17)
C2—H2A	0.992 (15)	C19—H19B	1.006 (17)
C3—C4	1.3892 (15)	C19—H19C	0.990 (18)
C3—H3A	0.995 (15)	C20—H20A	0.996 (14)
C4—C5	1.3913 (13)	C20—H20B	1.007 (16)
C4—H4A	0.969 (13)	C20—H20C	0.976 (15)
C5—C6	1.3921 (13)	C21—H21A	0.974 (14)
C5—H5A	0.984 (14)	C21—H21B	0.945 (14)
C7—C8	1.3753 (13)	C21—H21C	0.972 (15)
C7—C18	1.4863 (13)		
C13—O2—C19	116.72 (8)	C13—C12—H12A	122.3 (8)
C14—O3—C20	117.04 (8)	C11—C12—H12A	116.3 (8)
C16—O4—C21	117.65 (7)	O2—C13—C12	125.46 (9)
C9—N1—N2	110.43 (7)	O2—C13—C14	115.26 (8)
C9—N1—C6	125.90 (8)	C12—C13—C14	119.28 (8)
N2—N1—C6	118.94 (7)	O3—C14—C15	124.05 (9)
C7—N2—N1	106.45 (7)	O3—C14—C13	115.62 (8)

C7—N2—C17	121.21 (8)	C15—C14—C13	120.33 (8)
N1—N2—C17	114.72 (8)	C14—C15—C16	119.75 (9)
C10—N3—C8	119.36 (8)	C14—C15—H15A	119.3 (8)
C6—C1—C2	118.90 (9)	C16—C15—H15A	120.9 (8)
C6—C1—H1A	119.6 (8)	O4—C16—C11	116.75 (8)
C2—C1—H1A	121.5 (8)	O4—C16—C15	122.63 (9)
C3—C2—C1	120.62 (9)	C11—C16—C15	120.61 (8)
C3—C2—H2A	121.2 (8)	N2—C17—H17A	109.0 (8)
C1—C2—H2A	118.2 (8)	N2—C17—H17B	111.4 (9)
C4—C3—C2	119.89 (9)	H17A—C17—H17B	108.9 (12)
C4—C3—H3A	120.6 (9)	N2—C17—H17C	105.3 (9)
C2—C3—H3A	119.4 (9)	H17A—C17—H17C	108.8 (12)
C3—C4—C5	120.18 (9)	H17B—C17—H17C	113.3 (12)
C3—C4—H4A	120.8 (8)	C7—C18—H18A	111.7 (9)
C5—C4—H4A	119.0 (8)	C7—C18—H18B	112.7 (9)
C4—C5—C6	119.34 (9)	H18A—C18—H18B	107.7 (13)
C4—C5—H5A	121.7 (8)	C7—C18—H18C	111.5 (9)
C6—C5—H5A	118.9 (8)	H18A—C18—H18C	106.4 (12)
C1—C6—C5	121.05 (8)	H18B—C18—H18C	106.5 (13)
C1—C6—N1	118.69 (8)	O2—C19—H19A	106.4 (10)
C5—C6—N1	120.26 (8)	O2—C19—H19B	110.6 (9)
C8—C7—N2	110.21 (8)	H19A—C19—H19B	106.9 (14)
C8—C7—C18	128.54 (8)	O2—C19—H19C	110.6 (11)
N2—C7—C18	121.25 (8)	H19A—C19—H19C	114.1 (14)
C7—C8—N3	122.95 (8)	H19B—C19—H19C	108.1 (14)
C7—C8—C9	107.87 (8)	O3—C20—H20A	109.0 (9)
N3—C8—C9	129.17 (8)	O3—C20—H20B	110.2 (9)
O1—C9—N1	124.44 (8)	H20A—C20—H20B	111.3 (12)
O1—C9—C8	131.11 (8)	O3—C20—H20C	104.0 (9)
N1—C9—C8	104.37 (8)	H20A—C20—H20C	111.0 (11)
N3—C10—C11	120.57 (8)	H20B—C20—H20C	111.1 (12)
N3—C10—H10A	121.7 (8)	O4—C21—H21A	109.1 (9)
C11—C10—H10A	117.8 (8)	O4—C21—H21B	105.8 (9)
C16—C11—C12	118.58 (8)	H21A—C21—H21B	110.2 (12)
C16—C11—C10	120.31 (8)	O4—C21—H21C	111.1 (8)
C12—C11—C10	121.11 (8)	H21A—C21—H21C	112.6 (12)
C13—C12—C11	121.40 (9)	H21B—C21—H21C	107.8 (12)
C9—N1—N2—C7	8.54 (10)	C7—C8—C9—O1	−173.56 (9)
C6—N1—N2—C7	165.59 (8)	N3—C8—C9—O1	5.87 (16)
C9—N1—N2—C17	145.49 (8)	C7—C8—C9—N1	3.25 (10)
C6—N1—N2—C17	−57.45 (11)	N3—C8—C9—N1	−177.33 (9)
C6—C1—C2—C3	1.32 (16)	C8—N3—C10—C11	177.82 (8)
C1—C2—C3—C4	−1.34 (17)	N3—C10—C11—C16	176.26 (8)
C2—C3—C4—C5	0.21 (16)	N3—C10—C11—C12	−4.03 (14)
C3—C4—C5—C6	0.91 (16)	C16—C11—C12—C13	1.10 (14)
C2—C1—C6—C5	−0.17 (15)	C10—C11—C12—C13	−178.61 (9)
C2—C1—C6—N1	−179.57 (9)	C19—O2—C13—C12	5.04 (16)
C4—C5—C6—C1	−0.93 (15)	C19—O2—C13—C14	−175.23 (10)
C4—C5—C6—N1	178.45 (9)	C11—C12—C13—O2	−179.44 (9)

C9—N1—C6—C1	−65.96 (13)	C11—C12—C13—C14	0.83 (15)
N2—N1—C6—C1	140.85 (9)	C20—O3—C14—C15	−0.36 (14)
C9—N1—C6—C5	114.64 (11)	C20—O3—C14—C13	178.96 (9)
N2—N1—C6—C5	−38.55 (13)	O2—C13—C14—O3	−0.49 (13)
N1—N2—C7—C8	−6.30 (10)	C12—C13—C14—O3	179.26 (9)
C17—N2—C7—C8	−139.83 (9)	O2—C13—C14—C15	178.86 (9)
N1—N2—C7—C18	173.92 (8)	C12—C13—C14—C15	−1.40 (15)
C17—N2—C7—C18	40.39 (13)	O3—C14—C15—C16	179.28 (9)
N2—C7—C8—N3	−177.54 (8)	C13—C14—C15—C16	0.00 (15)
C18—C7—C8—N3	2.22 (15)	C21—O4—C16—C11	179.81 (8)
N2—C7—C8—C9	1.93 (10)	C21—O4—C16—C15	−1.66 (13)
C18—C7—C8—C9	−178.31 (9)	C12—C11—C16—O4	176.04 (8)
C10—N3—C8—C7	−174.99 (8)	C10—C11—C16—O4	−4.24 (13)
C10—N3—C8—C9	5.66 (14)	C12—C11—C16—C15	−2.52 (14)
N2—N1—C9—O1	169.88 (8)	C10—C11—C16—C15	177.20 (8)
C6—N1—C9—O1	14.78 (14)	C14—C15—C16—O4	−176.49 (9)
N2—N1—C9—C8	−7.20 (9)	C14—C15—C16—C11	1.98 (14)
C6—N1—C9—C8	−162.30 (8)		

Hydrogen-bond geometry (Å, °)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
C10—H10A···O1	0.954 (13)	2.331 (13)	3.0112 (11)	127.8 (10)
C4—H4A···O1^{i}	0.969 (13)	2.541 (13)	3.2628 (12)	131.4 (10)
C20—H20A···N3^{ii}	0.996 (14)	2.577 (14)	3.5383 (13)	162.1 (12)
C20—H20C···O2^{iii}	0.977 (14)	2.509 (14)	3.4470 (13)	160.8 (12)
C20—H20C···O3^{iii}	0.977 (14)	2.495 (15)	3.2779 (13)	137.0 (11)

Symmetry codes: (i) *x*, −*y*−1/2, *z*+1/2; (ii) *x*, −*y*+1/2, *z*−1/2; (iii) −*x*, −*y*+1, −*z*.

Fig. 1

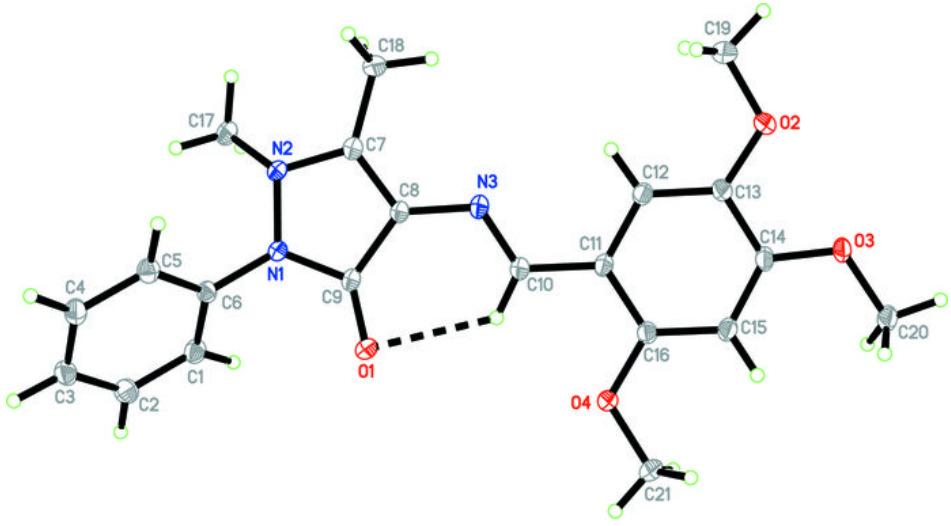
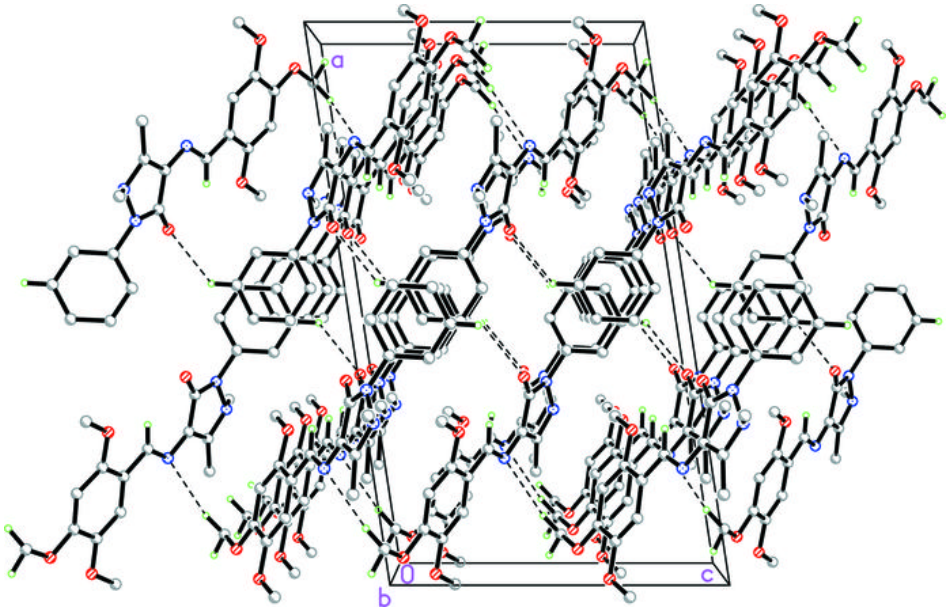

C19
C18
O2
C17
N2
C7
C12
C8
N3
C13
C14
O3
C11
C5
N1
C10
C4
C6
C9
C15
C20
C16
C1
O1
C3
C2
O4
C21

Fig. 2



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(4-Chlorophenyl)methanaminium chloride hemihydrate

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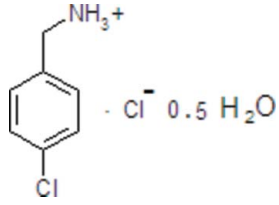
Key indicators: single-crystal X-ray study; T = 293 K; mean σ(C–C) = 0.002 Å; R factor = 0.048; wR factor = 0.130; data-to-parameter ratio = 41.7.

In the title hydrated salt, $C_7H_9ClN^+\cdot Cl^-\cdot 0.5H_2O$, the water O atom lies on a crystallographic twofold axis. In the crystal, the monoprotonated 4-chlorobenzylammonium cation forms N—H···Cl and N—H···O hydrogen bonds and the water molecule forms O—H···Cl hydrogen bonds, generating layers lying parallel to the *bc* plane.

Related literature

For the properties of benzylamines, see: Markwardt *et al.* (2005). For a related structure, see: Dhaouadi *et al.* (2008).



Experimental

Crystal data

$C_7H_9ClN^+\cdot Cl^-\cdot 0.5H_2O$
M_r = 187.06
Monoclinic, $C2/c$
a = 30.462 (2) Å
b = 4.890 (3) Å
c = 11.738 (2) Å
β = 99.97 (3)°
V = 1722.1 (11) Å^3
Z = 8
Ag $K\alpha$ radiation
λ = 0.56085 Å
μ = 0.35 mm^{-1}
T = 293 K
0.30 × 0.25 × 0.20 mm

Data collection

Enraf–Nonius TurboCAD-4 diffractometer
5908 measured reflections
4207 independent reflections
2217 reflections with $I > 2\sigma(I)$
R_{int} = 0.031
2 standard reflections every 120 min
intensity decay: 5%

Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.048
$wR(F^2)$ = 0.130
S = 1.00
4207 reflections
101 parameters
H atoms treated by a mixture of independent and constrained refinement
$\Delta\rho_{max}$ = 0.34 e Å^{-3}
$\Delta\rho_{min}$ = −0.32 e Å^{-3}

Table 1
Hydrogen-bond geometry (Å, °).

D—H···A	D—H	H···A	D···A	D—H···A
N—H0A···Cl1^{i}	0.89	2.60	3.2930 (19)	136
N—H0A···Cl1^{ii}	0.89	2.78	3.417 (2)	130
N—H0B···O	0.89	2.04	2.866 (2)	155
N—H0C···Cl1^{iii}	0.89	2.26	3.144 (2)	175
O—H1···Cl1	0.85 (3)	2.28 (3)	3.1230 (18)	171 (3)

Symmetry codes: (i) $-x, y-1, -z+\frac{1}{2}$; (ii) $x, -y, z+\frac{1}{2}$; (iii) $x, -y+1, z+\frac{1}{2}$.

Data collection: *CAD-4 EXPRESS* (Enraf–Nonius, 1994); cell refinement: *CAD-4 EXPRESS*; data reduction: *XCAD4* (Harms & Wocadlo, 1995); program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *ORTEP-3* (Farrugia, 1997); software used to prepare material for publication: *WinGX* (Farrugia, 1999).

Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: HB5481).

References

Dhaouadi, H., Marouani, H., Rzaigui, M. & Madani, A. (2008). *Mater. Res. Bull.* **43**, 3234–3244.
Enraf–Nonius (1994). *CAD-4 EXPRESS*. Enraf–Nonius, Delft, The Netherlands.
Farrugia, L. J. (1997). *J. Appl. Cryst.* **30**, 565.
Farrugia, L. J. (1999). *J. Appl. Cryst.* **32**, 837–838.
Harms, K. & Wocadlo, S. (1995). *XCAD4*. University of Marburg, Germany.
Markwardt, F., Landmann, H. & Walsmann, P. (2005). *Eur. J. Biochem.* **6**, 502–506.
Sheldrick, G. M. (2008). *Acta Cryst.* A**64**, 112–122.

supplementary materials

Acta Cryst. (2010). E**66**, o1627 [**doi:10.1107/S1600536810021100**]

(4-Chlorophenyl)methanaminium chloride hemihydrate

S. Souissi, W. Smirani Sta, S. S. Al-Deyab and M. Rzaigui

Comment

Derivatives of benzylamine were found to be competitive inhibitors of the proteolytic enzymes trypsin, plasmin, and thrombin. So, the 4-chlorobenzylamine is a strong thrombin inhibitor but only of low effectiveness against trypsin and plasmin for the hydrolysis of N-α-benzoyl catalyzed by these three enzymes. Relations between the chemical structure and the activity against trypsin, plasmin and thrombin were deduced by comparing the inhibitor constants (Markwardt, F. *et al.*, 2005). In this work, we report the crystal structure of the title compound (I). As shown in (Fig.1), the asymmetric unit of (I) is built up from one 4-chlorobenzylammonium cation, one chloride anion and one water molecule. The Cl^- anions, water molecules and R—NH_3^+ groups are lineked *via* O—H···Cl, N—H···O and N—H···Cl hydrogen bonds and ionic interactions, so as to built inorganic layers spreading around the (b,c) planes. The 4-chlorobenzylammonium cations are anchored onto the successive inorganic layers *via* hydrogen bonds and electrostatic interactions, to composite their negative charges.

The examination of the organic cation shows that the values of N—C, C—C, C—Cl distances and N—C—C, C—C—C, C—C—Cl angles range from 1.376 (3) to 1.736 (3) Å and 115.72 (19) to 122.80 (19)°, respectively. These values show no significant difference from those obtained in other organic materials associated with the same organic groups (Dhaouadi, H. *et al.*, 2008).

In this structure, the water molecules play a very important role in the cohesion of the various groups. It participates with the organic cations and chloride anions in the H-bonding scheme of N—H···O and O—H···Cl interactions in the crystal structure. The four hydrogen bonds are relatively weak, and their donor acceptor distances vary from 2.866 (2) to 3.417 (3) Å. Thus, these different interactions (hydrogen bonds, Van der Waals, and electrostatic) form a stable three-dimensional network.

Experimental

An ethanolic solution of 4-chlorobenzylamine (10 mmol, in 10 ml) was added, with stirring, to 20 ml of an aqueous HCl solution (0.5*M*) at room temperature. Colourless blocks of (I) were obtained on slow evaporation of the solvent.

Refinement

All H atoms were positioned geometrically and treated as riding on their parent atoms, [N–H = 0.89, C–H =0.96 Å (CH_3) with with U_{iso}(H) = 1.5Ueq and C–H =0.96 Å (Ar–H), with U_{iso}(H) = 1.5Ueq], but those attached to oxygen atom are located in a difference map

Figures

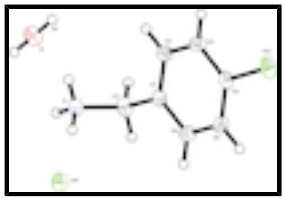


Fig. 1. View of (I) with displacement ellipsoids for non-H atoms are drawn at the 30% probability level.

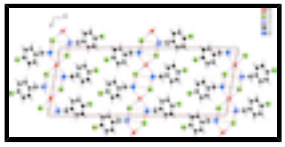


Fig. 2. A view of the packing of (I) along the *b* axis.

(4-Chlorophenyl)methanaminium chloride hemihydrate

Crystal data

$C_7H_9ClN^+\cdot Cl^-\cdot 0.5H_2O$	$F(000) = 776$
$M_r = 187.06$	$D_x = 1.443$ Mg m^{-3}
Monoclinic, *C*2/*c*	Ag *K*α radiation, λ = 0.56085 Å
Hall symbol: -C 2yc	Cell parameters from 25 reflections
a = 30.462 (2) Å	θ = 9–11°
b = 4.890 (3) Å	μ = 0.35 mm^{-1}
c = 11.738 (2) Å	*T* = 293 K
β = 99.97 (3)°	Block, colourless
V = 1722.1 (11) Å^3	0.30 × 0.25 × 0.20 mm
Z = 8	

Data collection

Enraf–Nonius TurboCAD-4 diffractometer	$R_{int} = 0.031$
Radiation source: fine-focus sealed tube	$\theta_{max} = 28.0°$, $\theta_{min} = 2.3°$
graphite	*h* = −50→50
non–profiled ω scans	*k* = 0→8
5908 measured reflections	*l* = −5→19
4207 independent reflections	2 standard reflections every 120 min
2217 reflections with $I > 2\sigma(I)$	intensity decay: 5%

Refinement

Refinement on F^2	Secondary atom site location: difference Fourier map
Least-squares matrix: full	Hydrogen site location: inferred from neighbouring sites
$R[F^2 > 2\sigma(F^2)] = 0.048$	H atoms treated by a mixture of independent and constrained refinement
$wR(F^2) = 0.130$	$w = 1/[\sigma^2(F_o^2) + (0.0585P)^2 + 0.2911P]$

	where $P = (F_o^2 + 2F_c^2)/3$
$S = 1.00$	$(\Delta/\sigma)_{max} = 0.001$
4207 reflections	$\Delta\rho_{max} = 0.34$ e Å^{-3}
101 parameters	$\Delta\rho_{min} = -0.32$ e Å^{-3}
0 restraints	Extinction correction: *SHELXL97* (Sheldrick, 2008), $Fc^*=kFc[1+0.001xFc^2\lambda^3/\sin(2\theta)]^{-1/4}$
Primary atom site location: structure-invariant direct methods	Extinction coefficient: 0.0080 (12)

Special details

Geometry. All e.s.d.'s (except the e.s.d. in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell e.s.d.'s are taken into account individually in the estimation of e.s.d.'s in distances, angles and torsion angles; correlations between e.s.d.'s in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell e.s.d.'s is used for estimating e.s.d.'s involving l.s. planes.

Refinement. Refinement of F^2 against ALL reflections. The weighted *R*-factor *wR* and goodness of fit *S* are based on F^2, conventional *R*-factors *R* are based on *F*, with *F* set to zero for negative F^2. The threshold expression of $F^2 > \sigma(F^2)$ is used only for calculating *R*-factors(gt) *etc*. and is not relevant to the choice of reflections for refinement. *R*-factors based on F^2 are statistically about twice as large as those based on *F*, and *R*- factors based on ALL data will be even larger.

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å^2)

	x	*y*	*z*	U_{iso}*/U_{eq}
Cl1	0.049348 (13)	0.63727 (9)	0.11132 (4)	0.04257 (13)
O	0.0000	0.2285 (4)	0.2500	0.0494 (5)
H1	0.0151 (8)	0.323 (5)	0.210 (2)	0.089 (9)*
C1	0.12851 (4)	0.0280 (3)	0.40289 (14)	0.0313 (3)
C2	0.12629 (5)	0.1317 (3)	0.29253 (14)	0.0364 (3)
H2	0.1048	0.0661	0.2328	0.044*
C3	0.15582 (5)	0.3328 (3)	0.26977 (14)	0.0371 (3)
H3	0.1538	0.4046	0.1957	0.045*
C4	0.18814 (4)	0.4244 (3)	0.35851 (14)	0.0329 (3)
C5	0.19059 (5)	0.3278 (4)	0.46938 (15)	0.0386 (4)
H5	0.2121	0.3947	0.5289	0.046*
C6	0.16065 (5)	0.1293 (4)	0.49129 (14)	0.0380 (3)
H6	0.1621	0.0631	0.5661	0.046*
C7	0.09748 (5)	−0.1977 (3)	0.42512 (18)	0.0399 (4)
H7A	0.0966	−0.3362	0.3656	0.048*
H7B	0.1090	−0.2824	0.4990	0.048*
Cl2	0.225682 (14)	0.66901 (9)	0.32754 (5)	0.04948 (15)
N	0.05166 (4)	−0.0999 (3)	0.42641 (13)	0.0404 (3)
H0A	0.0347	−0.2400	0.4401	0.061*
H0B	0.0406	−0.0261	0.3582	0.061*
H0C	0.0521	0.0251	0.4817	0.061*

Atomic displacement parameters (Å^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Cl1	0.0390 (2)	0.0365 (2)	0.0527 (3)	0.00140 (16)	0.00925 (17)	0.00195 (19)
O	0.0523 (11)	0.0428 (10)	0.0574 (12)	0.000	0.0215 (9)	0.000
C1	0.0289 (6)	0.0260 (6)	0.0403 (8)	0.0011 (5)	0.0097 (6)	−0.0002 (6)
C2	0.0372 (7)	0.0376 (8)	0.0333 (8)	−0.0070 (6)	0.0033 (6)	−0.0044 (7)
C3	0.0441 (8)	0.0367 (8)	0.0314 (8)	−0.0060 (7)	0.0086 (6)	0.0008 (7)
C4	0.0281 (6)	0.0281 (6)	0.0444 (9)	−0.0017 (5)	0.0117 (6)	−0.0042 (6)
C5	0.0318 (7)	0.0436 (9)	0.0388 (9)	−0.0035 (6)	0.0011 (6)	−0.0064 (7)
C6	0.0388 (7)	0.0407 (8)	0.0342 (8)	0.0015 (7)	0.0057 (6)	0.0049 (7)
C7	0.0384 (7)	0.0263 (7)	0.0577 (11)	0.0010 (6)	0.0153 (7)	0.0043 (7)
Cl2	0.0432 (2)	0.0391 (2)	0.0709 (3)	−0.01276 (17)	0.0229 (2)	−0.0055 (2)
N	0.0339 (6)	0.0355 (7)	0.0529 (9)	−0.0069 (5)	0.0101 (6)	0.0005 (6)

Geometric parameters (Å, °)

O—H1	0.84 (2)	C5—C6	1.386 (2)
C1—C2	1.382 (2)	C5—H5	0.9300
C1—C6	1.389 (2)	C6—H6	0.9300
C1—C7	1.505 (2)	C7—N	1.4779 (19)
C2—C3	1.389 (2)	C7—H7A	0.9700
C2—H2	0.9300	C7—H7B	0.9700
C3—C4	1.379 (2)	N—H0A	0.8900
C3—H3	0.9300	N—H0B	0.8900
C4—C5	1.374 (2)	N—H0C	0.8900
C4—Cl2	1.7361 (15)		
C2—C1—C6	118.89 (14)	C5—C6—C1	120.84 (15)
C2—C1—C7	120.10 (15)	C5—C6—H6	119.6
C6—C1—C7	120.98 (15)	C1—C6—H6	119.6
C1—C2—C3	120.78 (15)	N—C7—C1	112.77 (13)
C1—C2—H2	119.6	N—C7—H7A	109.0
C3—C2—H2	119.6	C1—C7—H7A	109.0
C4—C3—C2	119.10 (15)	N—C7—H7B	109.0
C4—C3—H3	120.5	C1—C7—H7B	109.0
C2—C3—H3	120.5	H7A—C7—H7B	107.8
C5—C4—C3	121.21 (14)	C7—N—H0A	109.5
C5—C4—Cl2	120.36 (12)	C7—N—H0B	109.5
C3—C4—Cl2	118.42 (13)	H0A—N—H0B	109.5
C4—C5—C6	119.14 (14)	C7—N—H0C	109.5
C4—C5—H5	120.4	H0A—N—H0C	109.5
C6—C5—H5	120.4	H0B—N—H0C	109.5

Hydrogen-bond geometry (Å, °)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
N—H0A···Cl1^{i}	0.89	2.60	3.2930 (19)	136

N—H0A···Cl1^{ii}	0.89	2.78	3.417 (2)	130
N—H0B···O	0.89	2.04	2.866 (2)	155
N—H0C···Cl1^{iii}	0.89	2.26	3.144 (2)	175
O—H1···Cl1	0.85 (3)	2.28 (3)	3.1230 (18)	171 (3)

Symmetry codes: (i) −*x*, *y*−1, −*z*+1/2; (ii) *x*, −*y*, *z*+1/2; (iii) *x*, −*y*+1, *z*+1/2.

Fig. 1

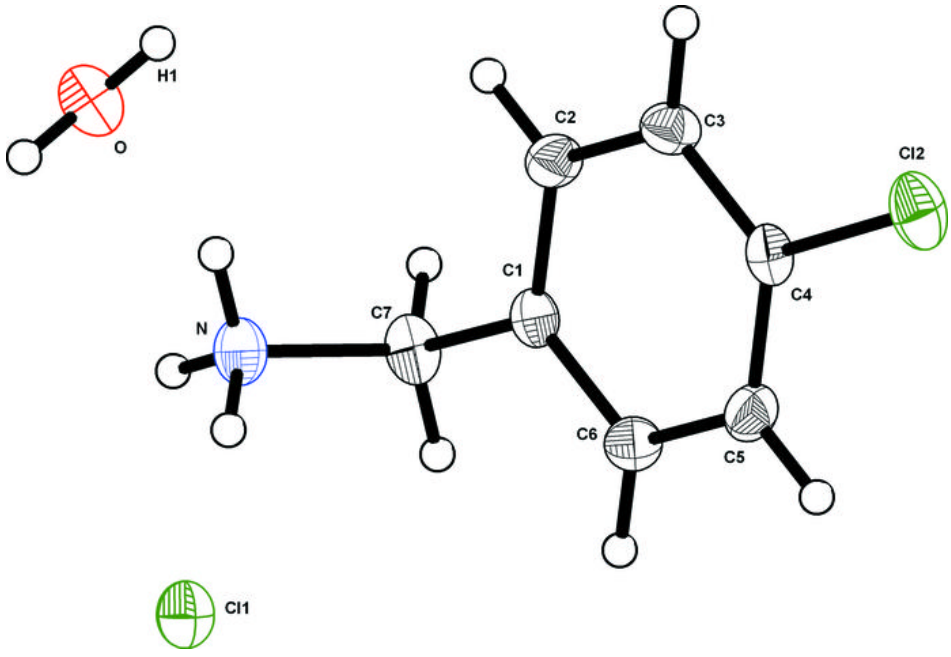
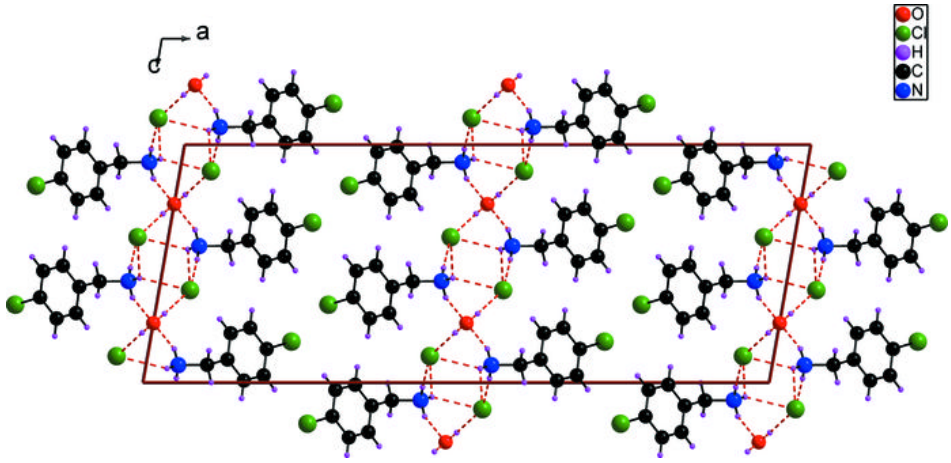


Fig. 2



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N′-(4-Hydroxybenzylidene)thiophene-2-carbohydrazide

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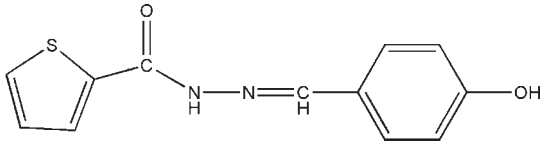
Key indicators: single-crystal X-ray study; T = 293 K; mean σ(C–C) = 0.004 Å; R factor = 0.048; wR factor = 0.181; data-to-parameter ratio = 17.1.

In the title compound, $C_{12}H_{10}N_2O_2S$, the dihedral angle between the benzene and thiophene rings is 23.34 (16)°. In the crystal structure, molecules are linked by N—H···O and O—H···O hydrogen bonds, forming (100) sheets.

Related literature

For background to the pharmacological properties of Schiff bases, see: Ren *et al.* (2002). For a related structure, see: Li *et al.* (2009).



Experimental

Crystal data

$C_{12}H_{10}N_2O_2S$ M_r = 246.28
Monoclinic, $P2_1/c$
a = 9.5622 (19) Å
b = 12.404 (3) Å
c = 9.991 (2) Å
β = 104.40 (3)°
V = 1147.8 (4) Å^3
Z = 4
Mo $K\alpha$ radiation
μ = 0.27 mm^{-1}
T = 293 K
0.22 × 0.20 × 0.18 mm

Data collection

Bruker SMART CCD diffractometer
10889 measured reflections
2629 independent reflections
1501 reflections with $I > 2\sigma(I)$
R_{int} = 0.057

Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.048
$wR(F^2)$ = 0.181
S = 1.07
2629 reflections
154 parameters
H-atom parameters constrained
$\Delta\rho_{max}$ = 0.27 e Å^{-3}
$\Delta\rho_{min}$ = −0.38 e Å^{-3}

Table 1
Hydrogen-bond geometry (Å, °).

D—H···A	D—H	H···A	D···A	D—H···A
N1—H1A···O1^{i}	0.86	2.09	2.887 (3)	154
O2—H2C···O1^{ii}	0.82	2.10	2.913 (3)	174

Symmetry codes: (i) $x, -y+\frac{1}{2}, z-\frac{1}{2}$; (ii) $-x+3, y+\frac{1}{2}, -z+\frac{1}{2}$.

Data collection: *SMART* (Bruker, 1997); cell refinement: *SAINT* (Bruker, 1997); data reduction: *SAINT*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *SHELXTL* (Sheldrick, 2008); software used to prepare material for publication: *SHELXTL*.

Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: HB5483).

References

Bruker (1997). *SMART* and *SAINT*. Bruker AXS Inc., Madison, Wisconsin, USA.
Li, Y.-F., Liu, H.-X. & Jian, F.-F. (2009). *Acta Cryst.* E**65**, o2959.
Ren, S. J., Wang, R. B. & Komatsu, K. (2002). *J. Med. Chem.* **45**, 410–419.
Sheldrick, G. M. (2008). *Acta Cryst.* A**64**, 112–122.

supplementary materials

Acta Cryst. (2010). E**66**, o1719 [**doi:10.1107/S1600536810021483**]

N'-(4-Hydroxybenzylidene)thiophene-2-carbohydrazide

Y.-F. Li, J.-H. Jiang and F.-F. Jian

Comment

Schiff bases derivatives have attracted much attention due to their pharmacological activity (Ren *et al.*, 2002). As part of an investigation of the properties of Schiff bases functioning as ligands, we synthesized the title compound (I), and describe its structure here. The title compound contains two independent molecules in the unit. The dihedral angle between the aromatic rings is [23.33 (16)°]. In the crystal lattice, the N—H···O and O—H···O intramolecular hydrogen bonds which form the molecule structures.

Bond lengths and angles are comparable to those in a related compound (Li *et al.*, 2009).

Experimental

A mixture of 4-methylbenzaldehyde (0.1 mol), and thiophene-2-carbohydrazide (0.1 mol) was stirred in refluxing ethanol (20 ml) for 4 h to afford the title compound (0.092 mol, yield 92%). Colourless blocks of (I) were obtained by recrystallization from ethanol at room temperature.

Refinement

H atoms were fixed geometrically and allowed to ride on their attached atoms, with C—H distances=0.97 Å, and with U_{iso}=1.2–1.5U_{eq}.

Figures

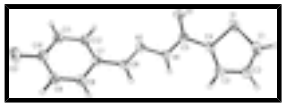


Fig. 1. The structure of (I) showing 30% probability displacement ellipsoids.

N'-(4-Hydroxybenzylidene)thiophene-2-carbohydrazide

Crystal data

$C_{12}H_{10}N_2O_2S$	$F(000)$ = 512
M_r = 246.28	D_x = 1.425 Mg m^{-3}
Monoclinic, $P2_1/c$	Mo $K\alpha$ radiation, λ = 0.71073 Å
Hall symbol: -P 2ybc	Cell parameters from 1501 reflections
a = 9.5622 (19) Å	θ = 3.1–27.5°
b = 12.404 (3) Å	μ = 0.27 mm^{-1}
c = 9.991 (2) Å	T = 293 K
β = 104.40 (3)°	Block, colorless

V = 1147.8 (4) Å^3	0.22 × 0.20 × 0.18 mm
Z = 4	

Data collection

Bruker SMART CCD diffractometer	1501 reflections with $I > 2\sigma(I)$
Radiation source: fine-focus sealed tube	R_{int} = 0.057
graphite	θ_{max} = 27.5°, θ_{min} = 3.1°
phi and ω scans	h = −12→12
10889 measured reflections	k = −16→16
2629 independent reflections	l = −11→12

Refinement

Refinement on F^2	Primary atom site location: structure-invariant direct methods
Least-squares matrix: full	Secondary atom site location: difference Fourier map
$R[F^2 > 2\sigma(F^2)]$ = 0.048	Hydrogen site location: inferred from neighbouring sites
$wR(F^2)$ = 0.181	H-atom parameters constrained
S = 1.07	$w = 1/[\sigma^2(F_o^2) + (0.1P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
2629 reflections	$(\Delta/\sigma)_{max} < 0.001$
154 parameters	$\Delta\rho_{max}$ = 0.27 e Å^{-3}
0 restraints	$\Delta\rho_{min}$ = −0.38 e Å^{-3}

Special details

Geometry. All e.s.d.'s (except the e.s.d. in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell e.s.d.'s are taken into account individually in the estimation of e.s.d.'s in distances, angles and torsion angles; correlations between e.s.d.'s in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell e.s.d.'s is used for estimating e.s.d.'s involving l.s. planes.

Refinement. Refinement of F^2 against ALL reflections. The weighted R-factor wR and goodness of fit S are based on F^2, conventional R-factors R are based on F, with F set to zero for negative F^2. The threshold expression of $F^2 > \sigma(F^2)$ is used only for calculating R-factors(gt) *etc*. and is not relevant to the choice of reflections for refinement. R-factors based on F^2 are statistically about twice as large as those based on F, and R- factors based on ALL data will be even larger.

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å^2)

	x	y	z	U_{iso}*/U_{eq}
S1	0.89443 (10)	0.07271 (7)	0.19012 (8)	0.0713 (3)
N2	1.2232 (2)	0.37439 (19)	0.1118 (2)	0.0452 (6)
O1	1.1172 (2)	0.24125 (17)	0.27388 (17)	0.0548 (6)
N1	1.1217 (2)	0.29541 (19)	0.0602 (2)	0.0482 (6)
H1A	1.0911	0.2863	−0.0275	0.058*
C12	1.4377 (3)	0.5507 (2)	0.1730 (3)	0.0464 (6)

H12A	1.4518	0.4976	0.2407	0.056*
C4	0.9590 (3)	0.1566 (2)	0.0840 (2)	0.0435 (6)
C5	1.0717 (3)	0.2334 (2)	0.1475 (2)	0.0406 (6)
C7	1.3299 (3)	0.5378 (2)	0.0519 (2)	0.0430 (6)
C6	1.2339 (3)	0.4464 (2)	0.0230 (3)	0.0483 (7)
H6A	1.1759	0.4392	−0.0663	0.058*
C11	1.5235 (3)	0.6408 (2)	0.1941 (3)	0.0506 (7)
H11A	1.5936	0.6491	0.2767	0.061*
O2	1.5867 (3)	0.81085 (19)	0.1088 (2)	0.0816 (8)
H2C	1.6718	0.7957	0.1418	0.122*
C10	1.5063 (3)	0.7198 (2)	0.0930 (3)	0.0518 (7)
C8	1.3140 (3)	0.6189 (2)	−0.0471 (3)	0.0510 (7)
H8A	1.2427	0.6120	−0.1291	0.061*
C9	1.3999 (3)	0.7083 (2)	−0.0273 (3)	0.0569 (8)
H9A	1.3866	0.7613	−0.0951	0.068*
C3	0.8883 (4)	0.1398 (3)	−0.0502 (3)	0.0647 (9)
H3A	0.9077	0.1779	−0.1237	0.078*
C2	0.7834 (4)	0.0591 (3)	−0.0662 (3)	0.0756 (11)
H2B	0.7253	0.0377	−0.1512	0.091*
C1	0.7759 (4)	0.0163 (3)	0.0548 (3)	0.0765 (11)
H1B	0.7124	−0.0386	0.0632	0.092*

Atomic displacement parameters (Å^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
S1	0.0791 (6)	0.0780 (6)	0.0592 (5)	−0.0243 (5)	0.0220 (4)	0.0166 (4)
N2	0.0506 (13)	0.0473 (14)	0.0398 (10)	−0.0127 (10)	0.0151 (10)	−0.0051 (9)
O1	0.0635 (13)	0.0682 (14)	0.0331 (9)	−0.0089 (10)	0.0129 (8)	0.0017 (8)
N1	0.0592 (15)	0.0545 (14)	0.0323 (10)	−0.0207 (11)	0.0138 (9)	−0.0059 (9)
C12	0.0476 (16)	0.0448 (15)	0.0466 (13)	−0.0047 (12)	0.0113 (12)	0.0066 (11)
C4	0.0461 (15)	0.0454 (15)	0.0416 (13)	−0.0069 (12)	0.0155 (11)	0.0010 (10)
C5	0.0446 (15)	0.0421 (14)	0.0374 (12)	−0.0003 (11)	0.0145 (10)	0.0003 (10)
C7	0.0485 (15)	0.0430 (15)	0.0398 (12)	−0.0050 (12)	0.0151 (11)	−0.0050 (10)
C6	0.0552 (17)	0.0510 (16)	0.0393 (13)	−0.0130 (13)	0.0129 (12)	−0.0049 (11)
C11	0.0465 (16)	0.0493 (17)	0.0514 (14)	−0.0048 (13)	0.0035 (12)	0.0062 (12)
O2	0.0694 (16)	0.0573 (15)	0.0975 (17)	−0.0248 (12)	−0.0184 (13)	0.0290 (12)
C10	0.0473 (16)	0.0409 (16)	0.0640 (17)	−0.0058 (13)	0.0078 (13)	0.0081 (12)
C8	0.0577 (18)	0.0497 (17)	0.0423 (13)	−0.0090 (14)	0.0064 (12)	0.0018 (11)
C9	0.063 (2)	0.0483 (18)	0.0543 (15)	−0.0072 (14)	0.0048 (14)	0.0120 (12)
C3	0.075 (2)	0.074 (2)	0.0457 (15)	−0.0327 (18)	0.0160 (15)	−0.0009 (14)
C2	0.079 (2)	0.085 (3)	0.0599 (18)	−0.041 (2)	0.0132 (17)	−0.0104 (16)
C1	0.073 (2)	0.071 (2)	0.088 (2)	−0.0361 (19)	0.0245 (19)	0.0017 (18)

Geometric parameters (Å, °)

S1—C1	1.685 (4)	C6—H6A	0.9300
S1—C4	1.707 (2)	C11—C10	1.387 (4)
N2—C6	1.281 (3)	C11—H11A	0.9300
N2—N1	1.385 (3)	O2—C10	1.354 (3)

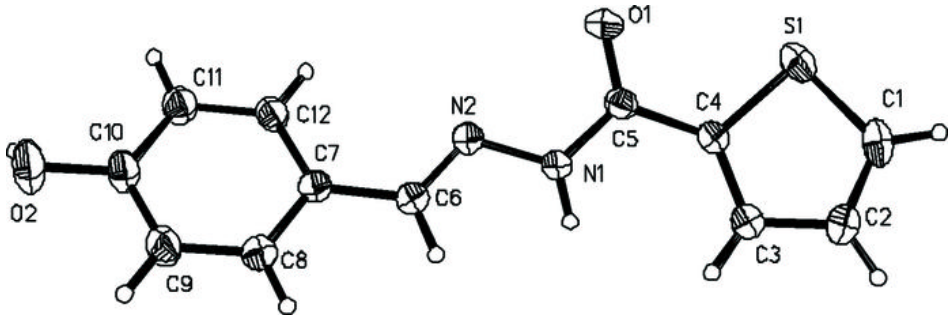
O1—C5	1.233 (3)	O2—H2C	0.8200
N1—C5	1.337 (3)	C10—C9	1.375 (4)
N1—H1A	0.8600	C8—C9	1.364 (4)
C12—C11	1.371 (4)	C8—H8A	0.9300
C12—C7	1.390 (4)	C9—H9A	0.9300
C12—H12A	0.9300	C3—C2	1.398 (4)
C4—C3	1.360 (4)	C3—H3A	0.9300
C4—C5	1.461 (4)	C2—C1	1.339 (4)
C7—C8	1.392 (4)	C2—H2B	0.9300
C7—C6	1.443 (4)	C1—H1B	0.9300
C1—S1—C4	91.70 (14)	C12—C11—H11A	119.8
C6—N2—N1	113.9 (2)	C10—C11—H11A	119.8
C5—N1—N2	119.68 (19)	C10—O2—H2C	109.5
C5—N1—H1A	120.2	O2—C10—C9	117.6 (3)
N2—N1—H1A	120.2	O2—C10—C11	122.9 (3)
C11—C12—C7	120.9 (2)	C9—C10—C11	119.5 (3)
C11—C12—H12A	119.6	C9—C8—C7	121.9 (3)
C7—C12—H12A	119.6	C9—C8—H8A	119.1
C3—C4—C5	131.4 (2)	C7—C8—H8A	119.1
C3—C4—S1	110.6 (2)	C8—C9—C10	119.9 (3)
C5—C4—S1	118.01 (18)	C8—C9—H9A	120.0
O1—C5—N1	122.0 (2)	C10—C9—H9A	120.0
O1—C5—C4	122.1 (2)	C4—C3—C2	112.9 (3)
N1—C5—C4	115.9 (2)	C4—C3—H3A	123.5
C12—C7—C8	117.5 (3)	C2—C3—H3A	123.5
C12—C7—C6	124.2 (2)	C1—C2—C3	112.3 (3)
C8—C7—C6	118.3 (2)	C1—C2—H2B	123.9
N2—C6—C7	124.5 (2)	C3—C2—H2B	123.9
N2—C6—H6A	117.8	C2—C1—S1	112.6 (3)
C7—C6—H6A	117.8	C2—C1—H1B	123.7
C12—C11—C10	120.3 (3)	S1—C1—H1B	123.7

Hydrogen-bond geometry (Å, °)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
N1—H1A···O1^{i}	0.86	2.09	2.887 (3)	154
O2—H2C···O1^{ii}	0.82	2.10	2.913 (3)	174

Symmetry codes: (i) *x*, −*y*+1/2, *z*−1/2; (ii) −*x*+3, *y*+1/2, −*z*+1/2.

Fig. 1



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Ammonium [(1*S*)-(*endo*,*anti*)]-(−)-3-bromocamphor-8-sulfonate

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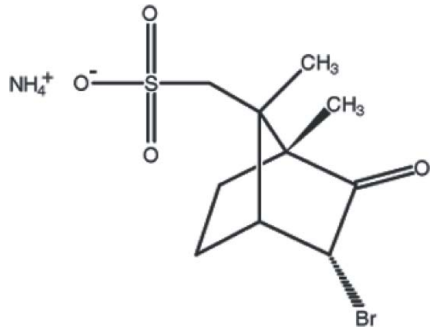
Key indicators: single-crystal X-ray study; T = 296 K; mean σ(C–C) = 0.004 Å; R factor = 0.027; wR factor = 0.065; data-to-parameter ratio = 16.5.

In the title molecular salt, $NH_4^+\cdot C_{10}H_{14}BrO_4S^-$, the norbornane skeleton of the anion is composed of two five-membered rings in envelope conformations and a six-membered ring with one Br atom, one carbonyl O atom and a methyl group held in a boat conformation by a bridging methylene group. Short intramolecular C—H···O and C—H···Br interactions occur. In the crystal, the component ions are linked by intermolecular N—H···O and C—H···O hydrogen bonds.

Related literature

For further synthetic details, see: Smith *et al.* (2008). For other structures with the norbornane skeleton, see: Jauch *et al.* (1992); Ustabaş *et al.* (2006); Ersanlı *et al.* (2005). For the use of 3-bromocamphor-8-sulfonic acid and its ammonium salts as chiral auxillaries for the optical resolution of enantiomeric amines through diasteriomeric salt formation, see: Bálint *et al.* (1999); Pellati *et al.* (2010); Roy *et al.* (2009); Zhao *et al.* (2002). For puckering parameters, see: Cremer & Pople (1975).



Experimental

Crystal data

$NH_4^+\cdot C_{10}H_{14}BrO_4S^-$
M_r = 328.22
Monoclinic, $P2_1$
a = 7.2449 (2) Å
b = 7.0049 (1) Å
c = 13.2428 (3) Å
β = 104.704 (1)°
V = 650.06 (3) Å^3
Z = 2
Mo $K\alpha$ radiation
μ = 3.33 mm^{-1}
T = 296 K
0.42 × 0.14 × 0.11 mm

Data collection

Bruker Kappa APEXII CCD diffractometer
Absorption correction: refined from ΔF (*XABS2*; Parkin *et al.*, 1995)
T_{min} = 0.336, T_{max} = 0.711
2775 measured reflections
2775 independent reflections
2586 reflections with $I > 2\sigma(I)$

Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.027
$wR(F^2)$ = 0.065
S = 1.03
2775 reflections
168 parameters
5 restraints
H atoms treated by a mixture of independent and constrained refinement
$\Delta\rho_{max}$ = 0.35 e Å^{-3}
$\Delta\rho_{min}$ = −0.47 e Å^{-3}
Absolute structure: Flack (1983), 1155 Freidel pairs
Flack parameter: −0.021 (7)

Table 1
Hydrogen-bond geometry (Å, °).

D—H···A	D—H	H···A	D···A	D—H···A
N1—H1*N*···O1^{i}	0.92 (3)	1.92 (3)	2.835 (4)	173 (3)
N1—H2*N*···O2^{ii}	0.90 (3)	2.05 (3)	2.899 (3)	157 (3)
N1—H3*N*···O2	0.92 (3)	1.97 (3)	2.887 (3)	176 (3)
N1—H4*N*···O3^{iii}	0.92 (3)	1.93 (3)	2.827 (3)	167 (4)
C4—H4*B*···Br1	0.97	2.71	3.221 (3)	113
C8—H8*A*···O2	0.96	2.44	3.104 (3)	126
C10—H10···O1^{i}	0.98	2.49	3.451 (4)	167

Symmetry codes: (i) $x, y-1, z$; (ii) $-x+2, y-\frac{1}{2}, -z+1$; (iii) $-x+1, y-\frac{1}{2}, -z+1$.

Data collection: *APEX2* (Bruker, 2007); cell refinement: *SAINT* (Bruker, 2007); data reduction: *SAINT*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *ORTEP-3* (Farrugia, 1997); software used to prepare material for publication: *WinGX* (Farrugia, 1999), *PARST* (Nardelli, 1983) and *PLATON* (Spek, 2009).

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Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: HB5484).

References

Bálint, J., Egri, G., Fogassy, E., Böcskei, Z., Simon, K., Gajáry, A. & Friesz, A. (1999). *Tetrahedron Asymmetry*, **10**, 1079–1087.
Bruker (2007). *APEX2* and *SAINT*. Bruker AXS Inc., Madison, Wisconsin, USA.
Cremer, D. & Pople, J. A. (1975). *J. Am. Chem. Soc.* **97**, 1354–1358.
Ersanlı, C. C., Çoruh, U., Hökelek, T., Vázquez-López, E. M. & Daştan, A. (2005). *Acta Cryst.* E**61**, o263–o265.
Farrugia, L. J. (1997). *J. Appl. Cryst.* **30**, 565.

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Farrugia, L. J. (1999). *J. Appl. Cryst.* **32**, 837–838.
Flack, H. D. (1983). *Acta Cryst.* A**39**, 876–881.
Jauch, J., Laderer, H. & Walz, L. (1992). *Acta Cryst.* C**48**, 1246–1248.
Nardelli, M. (1983). *Comput. Chem.* **7**, 95–98.
Parkin, S., Moezzi, B. & Hope, H. (1995). *J. Appl. Cryst.* **28**, 53–56.
Pellati, F., Cannazza, G. & Benvenuti, S. (2010). *J. Chromatogr. A*, **1217**, 3503–3510.
Roy, B. N., Singh, G. P., Srivastava, D., Jadhav, H. S., Saini, M. B. & Aher, P. (2009). *Org. Process Res. Dev.* **13**, 450–455.
Sheldrick, G. M. (2008). *Acta Cryst.* A**64**, 112–122.
Smith, E. D., Vinson, N. A., Zhong, D., Berrang, B. D., Catanzaro, J. L., Thomas, J. B., Navarro, H. A., Gilmour, B. P., Deschamps, J. & Carroll, F. I. (2008). *Bioorg. Med. Chem.* **16**, 822–829.
Spek, A. L. (2009). *Acta Cryst.* D**65**, 148–155.
Ustabaş, R., Çoruh, U., Yavuz, M., Salamci, E. & Vázquez-López, E. M. (2006). *Acta Cryst.* E**62**, o1149–o1150.
Zhao, M. M., McNamara, J. M., Ho, G.-J., Emerson, K. M., Song, Z. J., Tschaen, D. M., Brands, K. M. J., Dolling, U.-H., Grabowski, E. J. J. & Reider, P. J. (2002). *J. Org. Chem.* **67**, 6743–6747.

supplementary materials

Acta Cryst. (2010). E**66**, o1707-o1708 [**doi:10.1107/S1600536810022804**]

Ammonium [(1*S*)-(*endo*,*anti*)]-(-)-3-bromocamphor-8-sulfonate

M. A. Abbasi, Aziz-ur-Rehman, M. Akkurt, M. Jahangir, S. W. Ng and I. U. Khan

Comment

3-Bromocamphor-8-sulfonic acid and its ammonium salts have extensively been used as chiral auxillaries for the optical resolution of a number of enantiomeric amines through diasteriomeric salt formation (Bálint *et al.*, 1999; Zhao *et al.*, 2002; Roy *et al.*, 2009; Pellati *et al.*, 2010).

In the bicyclo[2.2.1]heptane (norbornane) skeleton of the title compound, (I), (Fig. 1), the two five-membered rings have envelope conformations, with atom C2 displaced by 0.365 (3) Å from the C2–C6 plane [the puckering parameters (Cremer & Pople, 1975) are Q_2 = 0.573 (3) Å and φ_2 = 5.3 (3)°] and by 0.397 (3) Å from the C2/C3/C6/C9/C10 plane [the puckering parameters: Q_2 = 0.615 (3) Å and φ_2 = 181.6 (3)°] and the six-membered ring (C3–C6/C9/C10) adopts a boat conformation by the puckering parameters Q_T = 0.970 (3) Å, θ = 92.03 (18)° and φ = 357.34 (19) °.

In (I), the C—C single-bond lengths range from 1.491 (5) to 1.575 (4) Å, with a mean value of 1.535 (4) Å. In the bicyclo[2.2.1]heptane fragment, the angles between planes A (C3/C2/C6), B (C3–C6) and C (C3/C6/C9/C10) are as follows: A/B= 53.65 (19)°, A/C= 58.14 (18)° and B/C= 68.22 (13)°.

In the crystal, adjacent molecules of (I) are linked by intermolecular N—H···O and C—H···O hydrogen bonds (Table 1, Fig. 2).

Experimental

3-Bromocamphor-8-sulfonic acid ammonium salt was prepared by modification in the reported method (Smith *et al.*, 2008). 3-Bromocamphor-8-sulfonic acid (1 g) was dissolved in 15 ml of ethanol and then 6 ml of NH_3 solution were added. The mixture was stirred until a clear solution was observed (about 20 min). The solution was slowly concentrated on water bath to half the volume over a 2 h period. The concentrate was allowed to crystallize undisturbed for 48 h. The resulting colourless prisms of (I) were carefully separated by filteration and washed with three 0.5-ml portions of petroleum ether.

Refinement

In the ammonium ion, H atoms bound to N atoms were located in difference Fourier maps and their positional parameters were refined freely using a *DFIX* instruction [N—H = 0.93 (3) Å] in *SHELXL97*, with U_{iso}(H) = 1.5U_{eq}(N). H atoms bound to C atoms were placed in idealized positions and refined using a riding model with C—H = 0.96, 0.97 and 0.98 Å for CH_3, CH_2 and CH, respectively. U_{iso}(H) values were set at 1.5U_{eq}(C) for the methyl groups, and 1.2$U_{eq}U_{eq}$(C) for other H atoms.

Figures

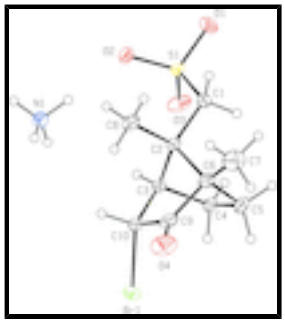


Fig. 1. View of (I) with displacement ellipsoids drawn at the 30% probability level.

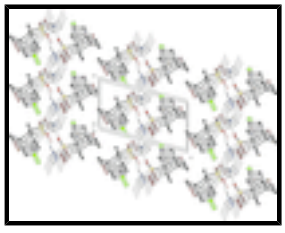


Fig. 2. The crystal packing of (I) viewed down the *b*-axis. The hydrogen-bonds are drawn as a dashed lines. H-atoms not involved in hydrogen bonds have been omitted for clarity.

Ammonium [(1*S*)-(*endo*,*anti*)]-(-)-(3-bromo-1,7- dimethyl-2-oxobicyclo[2.2.1]heptan-7-yl)methanesulfonate

Crystal data

$NH_4^+ \cdot C_{10}H_{14}BrO_4S^-$	$F(000) = 336$
$M_r = 328.22$	$D_x = 1.677$ Mg m^{-3}
Monoclinic, $P2_1$	Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å
Hall symbol: P 2yb	Cell parameters from 3356 reflections
$a = 7.2449$ (2) Å	$\theta = 2.9–28.3°$
$b = 7.0049$ (1) Å	$\mu = 3.33$ mm^{-1}
$c = 13.2428$ (3) Å	$T = 296$ K
$\beta = 104.704$ (1)°	Prism, colourless
$V = 650.06$ (3) Å^3	0.42 × 0.14 × 0.11 mm
$Z = 2$	

Data collection

Bruker Kappa APEXII CCD diffractometer	2775 independent reflections
Radiation source: sealed tube	2586 reflections with $I > 2\sigma(I)$
graphite	$R_{int} = 0.000$
φ and ω scans	$\theta_{max} = 27.5°$, $\theta_{min} = 3.3°$
Absorption correction: part of the refinement model (ΔF) (*XABS2*; Parkin *et al.*, 1995; quadratic fit to sin(θ)/λ - 18 parameters)	$h = -9 \rightarrow 9$
$T_{min} = 0.336$, $T_{max} = 0.711$	$k = -8 \rightarrow 9$
2775 measured reflections	$l = 0 \rightarrow 17$

Refinement

Refinement on F^2	Secondary atom site location: difference Fourier map
Least-squares matrix: full	Hydrogen site location: inferred from neighbouring sites
$R[F^2 > 2\sigma(F^2)] = 0.027$	H atoms treated by a mixture of independent and constrained refinement
$wR(F^2) = 0.065$	$w = 1/[\sigma^2(F_o^2) + (0.033P)^2 + 0.1814P]$ where $P = (F_o^2 + 2F_c^2)/3$
$S = 1.03$	$(\Delta/\sigma)_{max} < 0.001$
2775 reflections	$\Delta\rho_{max} = 0.35$ e Å^{-3}
168 parameters	$\Delta\rho_{min} = -0.47$ e Å^{-3}
5 restraints	Absolute structure: Flack (1983), 1155 Freidel pairs
Primary atom site location: structure-invariant direct methods	Flack parameter: −0.021 (7)

Special details

Geometry. Bond distances, angles *etc*. have been calculated using the rounded fractional coordinates. All su's are estimated from the variances of the (full) variance-covariance matrix. The cell e.s.d.'s are taken into account in the estimation of distances, angles and torsion angles

Refinement. Refinement on F^2 for ALL reflections except those flagged by the user for potential systematic errors. Weighted *R*-factors *wR* and all goodnesses of fit *S* are based on F^2, conventional *R*-factors *R* are based on *F*, with *F* set to zero for negative F^2. The observed criterion of $F^2 > \sigma(F^2)$ is used only for calculating -*R*-factor-obs *etc*. and is not relevant to the choice of reflections for refinement. *R*-factors based on F^2 are statistically about twice as large as those based on *F*, and *R*-factors based on ALL data will be even larger.

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å^2)

	x	*y*	*z*	U_{iso}*/U_{eq}
Br1	0.09450 (4)	0.00017 (4)	0.27520 (3)	0.0440 (1)
S1	0.65799 (9)	0.68509 (9)	0.36429 (5)	0.0242 (2)
O1	0.7216 (3)	0.8793 (3)	0.3541 (2)	0.0434 (8)
O2	0.8199 (3)	0.5560 (3)	0.39714 (16)	0.0332 (6)
O3	0.5283 (3)	0.6697 (4)	0.42972 (17)	0.0448 (8)
O4	0.2268 (4)	0.0517 (4)	0.0568 (2)	0.0596 (10)
C1	0.5311 (4)	0.6201 (4)	0.2339 (2)	0.0277 (8)
C2	0.4754 (4)	0.4086 (4)	0.2154 (2)	0.0213 (7)
C3	0.3597 (3)	0.3263 (4)	0.2899 (2)	0.0223 (7)
C4	0.1802 (4)	0.4500 (4)	0.2647 (2)	0.0272 (8)
C5	0.1351 (4)	0.4758 (5)	0.1462 (2)	0.0352 (9)
C6	0.3067 (4)	0.3804 (4)	0.1148 (2)	0.0310 (9)
C7	0.3318 (6)	0.4411 (6)	0.0112 (2)	0.0519 (13)
C8	0.6514 (4)	0.2949 (4)	0.2067 (2)	0.0316 (9)
C9	0.2719 (4)	0.1690 (5)	0.1248 (2)	0.0342 (9)
C10	0.3097 (4)	0.1283 (4)	0.2418 (2)	0.0298 (8)

N1	0.8032 (3)	0.1906 (4)	0.4952 (2)	0.0311 (7)
H1A	0.41550	0.69600	0.21450	0.0330*
H1B	0.60920	0.65480	0.18710	0.0330*
H3	0.42880	0.32500	0.36380	0.0270*
H4A	0.20390	0.57210	0.30010	0.0330*
H4B	0.07600	0.38650	0.28480	0.0330*
H5A	0.12590	0.61000	0.12770	0.0420*
H5B	0.01620	0.41320	0.11210	0.0420*
H7A	0.22080	0.40620	−0.04250	0.0780*
H7B	0.44200	0.37920	−0.00150	0.0780*
H7C	0.34880	0.57700	0.01080	0.0780*
H8A	0.74270	0.29220	0.27340	0.0470*
H8B	0.70750	0.35440	0.15630	0.0470*
H8C	0.61420	0.16680	0.18500	0.0470*
H10	0.42240	0.04610	0.26290	0.0360*
H1N	0.775 (5)	0.096 (4)	0.445 (2)	0.0470*
H2N	0.914 (4)	0.170 (6)	0.543 (2)	0.0470*
H3N	0.806 (5)	0.305 (4)	0.461 (3)	0.0470*
H4N	0.706 (4)	0.195 (6)	0.528 (3)	0.0470*

Atomic displacement parameters (Å^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Br1	0.0329 (2)	0.0300 (2)	0.0673 (2)	−0.0085 (1)	0.0093 (1)	0.0087 (2)
S1	0.0199 (3)	0.0209 (3)	0.0303 (3)	−0.0028 (2)	0.0036 (2)	−0.0024 (3)
O1	0.0492 (13)	0.0217 (11)	0.0526 (15)	−0.0096 (9)	0.0007 (11)	−0.0030 (9)
O2	0.0246 (9)	0.0298 (11)	0.0393 (12)	0.0024 (7)	−0.0029 (8)	−0.0036 (8)
O3	0.0304 (10)	0.0674 (17)	0.0391 (13)	−0.0101 (11)	0.0133 (9)	−0.0175 (12)
O4	0.0552 (15)	0.060 (2)	0.0580 (16)	−0.0138 (12)	0.0042 (12)	−0.0336 (13)
C1	0.0241 (13)	0.0248 (14)	0.0298 (15)	−0.0018 (11)	−0.0010 (11)	0.0010 (11)
C2	0.0168 (12)	0.0239 (13)	0.0226 (13)	−0.0016 (10)	0.0041 (10)	−0.0026 (10)
C3	0.0170 (11)	0.0207 (12)	0.0274 (14)	−0.0020 (9)	0.0022 (10)	−0.0004 (10)
C4	0.0184 (11)	0.0235 (15)	0.0403 (16)	0.0017 (9)	0.0084 (10)	−0.0020 (11)
C5	0.0222 (12)	0.0368 (19)	0.0406 (16)	0.0024 (13)	−0.0030 (11)	0.0017 (14)
C6	0.0239 (13)	0.0409 (17)	0.0248 (15)	−0.0040 (12)	−0.0002 (11)	−0.0024 (12)
C7	0.056 (2)	0.070 (3)	0.0247 (17)	−0.0134 (18)	0.0011 (15)	0.0033 (15)
C8	0.0206 (13)	0.0359 (16)	0.0382 (17)	−0.0007 (12)	0.0074 (11)	−0.0104 (13)
C9	0.0198 (12)	0.0392 (17)	0.0405 (16)	−0.0051 (12)	0.0018 (11)	−0.0130 (14)
C10	0.0213 (12)	0.0212 (13)	0.0444 (17)	−0.0006 (10)	0.0039 (11)	−0.0016 (11)
N1	0.0266 (12)	0.0334 (13)	0.0329 (13)	0.0019 (11)	0.0066 (10)	0.0030 (11)

Geometric parameters (Å, °)

Br1—C10	1.945 (3)	C6—C7	1.491 (4)
S1—O1	1.454 (2)	C6—C9	1.514 (4)
S1—O2	1.457 (2)	C9—C10	1.530 (4)
S1—O3	1.435 (2)	C1—H1B	0.9700
S1—C1	1.797 (3)	C1—H1A	0.9700
O4—C9	1.201 (4)	C3—H3	0.9800

N1—H1N	0.92 (3)	C4—H4B	0.9700
N1—H2N	0.90 (3)	C4—H4A	0.9700
N1—H3N	0.92 (3)	C5—H5A	0.9700
N1—H4N	0.92 (3)	C5—H5B	0.9700
C1—C2	1.539 (4)	C7—H7A	0.9600
C2—C3	1.558 (4)	C7—H7B	0.9600
C2—C6	1.575 (4)	C7—H7C	0.9600
C2—C8	1.532 (4)	C8—H8B	0.9600
C3—C4	1.527 (4)	C8—H8C	0.9600
C3—C10	1.531 (4)	C8—H8A	0.9600
C4—C5	1.530 (4)	C10—H10	0.9800
C5—C6	1.558 (4)		
O1—S1—O2	111.00 (13)	C3—C10—C9	102.4 (2)
O1—S1—O3	113.46 (15)	S1—C1—H1B	108.00
O1—S1—C1	104.17 (14)	S1—C1—H1A	108.00
O2—S1—O3	111.96 (14)	C2—C1—H1A	108.00
O2—S1—C1	107.84 (13)	C2—C1—H1B	108.00
O3—S1—C1	107.92 (14)	H1A—C1—H1B	107.00
H3N—N1—H4N	109 (3)	C10—C3—H3	114.00
H2N—N1—H4N	109 (3)	C4—C3—H3	114.00
H1N—N1—H3N	107 (3)	C2—C3—H3	115.00
H1N—N1—H4N	108 (3)	C5—C4—H4A	111.00
H1N—N1—H2N	113 (3)	C3—C4—H4B	111.00
H2N—N1—H3N	111 (3)	C3—C4—H4A	111.00
S1—C1—C2	116.52 (19)	C5—C4—H4B	111.00
C1—C2—C8	108.8 (2)	H4A—C4—H4B	109.00
C1—C2—C6	111.8 (2)	H5A—C5—H5B	109.00
C1—C2—C3	114.6 (2)	C4—C5—H5A	111.00
C6—C2—C8	110.7 (2)	C4—C5—H5B	111.00
C3—C2—C6	93.6 (2)	C6—C5—H5A	111.00
C3—C2—C8	116.6 (2)	C6—C5—H5B	111.00
C4—C3—C10	108.9 (2)	H7B—C7—H7C	109.00
C2—C3—C4	102.5 (2)	C6—C7—H7C	109.00
C2—C3—C10	100.4 (2)	C6—C7—H7A	110.00
C3—C4—C5	103.9 (2)	C6—C7—H7B	109.00
C4—C5—C6	104.2 (2)	H7A—C7—H7B	109.00
C7—C6—C9	114.9 (3)	H7A—C7—H7C	109.00
C2—C6—C7	119.5 (3)	C2—C8—H8B	109.00
C2—C6—C5	102.8 (2)	C2—C8—H8A	109.00
C5—C6—C9	103.6 (2)	H8A—C8—H8C	109.00
C2—C6—C9	99.2 (2)	C2—C8—H8C	109.00
C5—C6—C7	114.5 (3)	H8A—C8—H8B	109.00
O4—C9—C6	128.6 (3)	H8B—C8—H8C	110.00
O4—C9—C10	125.2 (3)	C9—C10—H10	109.00
C6—C9—C10	106.3 (2)	Br1—C10—H10	109.00
Br1—C10—C3	116.24 (18)	C3—C10—H10	109.00
Br1—C10—C9	111.62 (19)		
O1—S1—C1—C2	169.7 (2)	C2—C3—C4—C5	39.1 (3)

O2—S1—C1—C2	51.7 (2)	C10—C3—C4—C5	−66.7 (3)
O3—S1—C1—C2	−69.4 (3)	C2—C3—C10—Br1	−159.47 (17)
S1—C1—C2—C3	54.3 (3)	C2—C3—C10—C9	−37.5 (3)
S1—C1—C2—C6	159.2 (2)	C4—C3—C10—Br1	−52.3 (3)
S1—C1—C2—C8	−78.2 (3)	C4—C3—C10—C9	69.7 (3)
C1—C2—C3—C4	61.2 (3)	C3—C4—C5—C6	−5.6 (3)
C1—C2—C3—C10	173.5 (2)	C4—C5—C6—C2	−29.3 (3)
C6—C2—C3—C4	−54.8 (2)	C4—C5—C6—C7	−160.5 (3)
C6—C2—C3—C10	57.5 (2)	C4—C5—C6—C9	73.6 (3)
C8—C2—C3—C4	−170.0 (2)	C2—C6—C9—O4	−144.1 (3)
C8—C2—C3—C10	−57.8 (3)	C2—C6—C9—C10	34.8 (3)
C1—C2—C6—C5	−67.8 (3)	C5—C6—C9—O4	110.3 (4)
C1—C2—C6—C7	60.4 (4)	C5—C6—C9—C10	−70.9 (3)
C1—C2—C6—C9	−174.0 (2)	C7—C6—C9—O4	−15.4 (5)
C3—C2—C6—C5	50.6 (2)	C7—C6—C9—C10	163.5 (3)
C3—C2—C6—C7	178.7 (3)	O4—C9—C10—Br1	−54.7 (4)
C3—C2—C6—C9	−55.7 (2)	O4—C9—C10—C3	−179.8 (3)
C8—C2—C6—C5	170.7 (2)	C6—C9—C10—Br1	126.4 (2)
C8—C2—C6—C7	−61.1 (4)	C6—C9—C10—C3	1.3 (3)
C8—C2—C6—C9	64.5 (3)		

Hydrogen-bond geometry (Å, °)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
N1—H1N···O1^{i}	0.92 (3)	1.92 (3)	2.835 (4)	173 (3)
N1—H2N···O2^{ii}	0.90 (3)	2.05 (3)	2.899 (3)	157 (3)
N1—H3N···O2	0.92 (3)	1.97 (3)	2.887 (3)	176 (3)
N1—H4N···O3^{iii}	0.92 (3)	1.93 (3)	2.827 (3)	167 (4)
C4—H4B···Br1	0.97	2.71	3.221 (3)	113
C8—H8A···O2	0.96	2.44	3.104 (3)	126
C10—H10···O1^{i}	0.98	2.49	3.451 (4)	167

Symmetry codes: (i) *x*, *y*−1, *z*; (ii) −*x*+2, *y*−1/2, −*z*+1; (iii) −*x*+1, *y*−1/2, −*z*+1.

Fig. 1

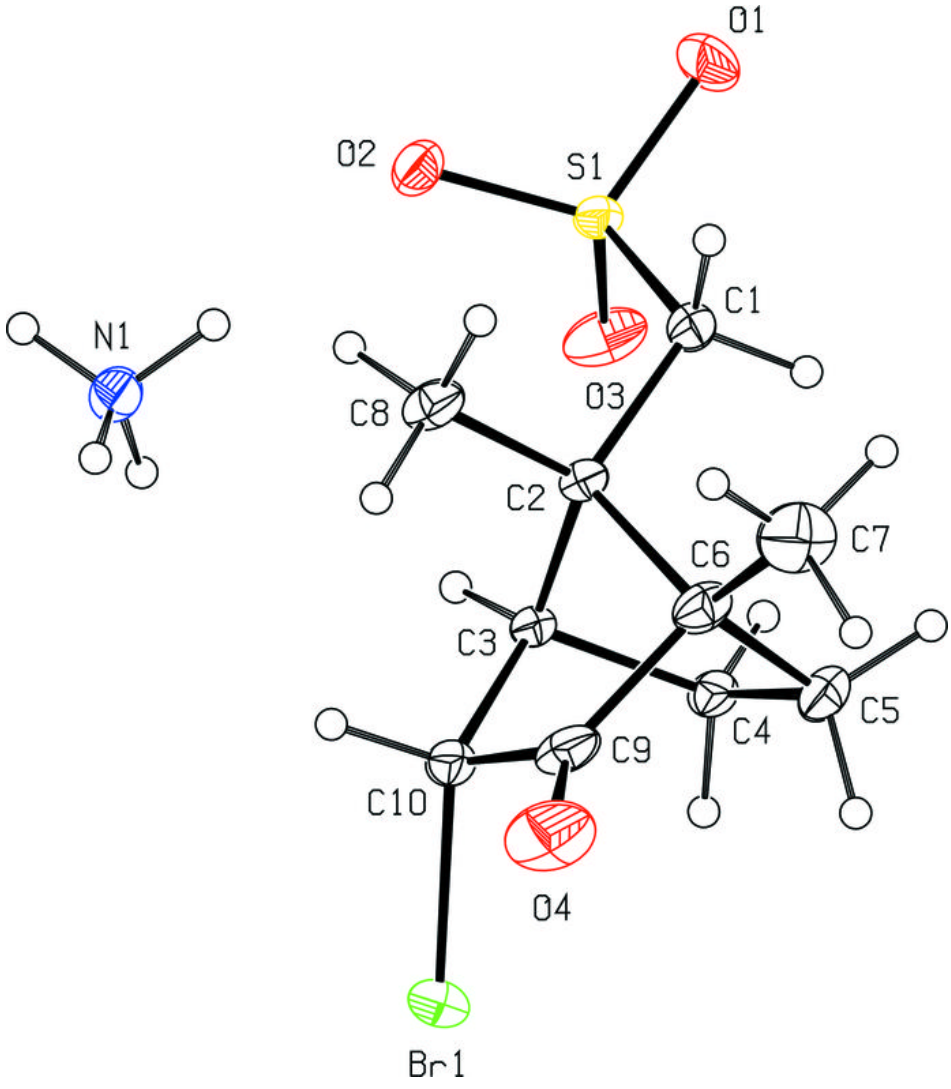
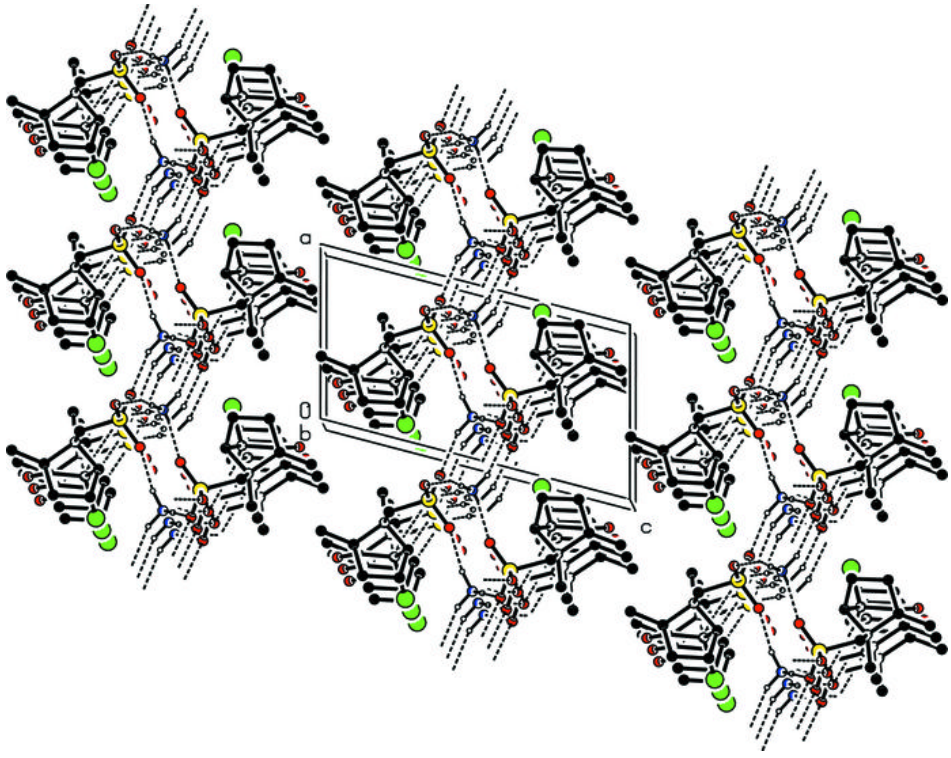


Fig. 2



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N′-Benzylidenefuran-2-carbohydrazide

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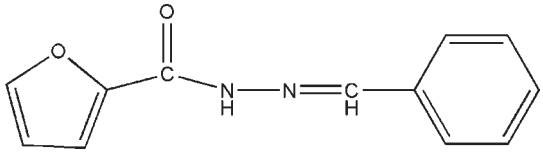
Key indicators: single-crystal X-ray study; T = 293 K; mean σ(C–C) = 0.006 Å; R factor = 0.069; wR factor = 0.182; data-to-parameter ratio = 13.1.

In the title compound, $C_{12}H_{10}N_2O_2$, the dihedral angle between the benzene ring and the furan ring is 24.6 (2)°. In the crystal, molecules are linked by N—H···O hydrogen bonds, generating $C(4)$ chains propagating in [010].

Related literature

For background to Schiff bases as ligands, see: Polt *et al.* (2003). For a related structure, see: Jiang (2010).



Experimental

Crystal data

$C_{12}H_{10}N_2O_2$ M_r = 214.22
Orthorhombic, *Pbca*
a = 11.628 (2) Å
b = 7.6638 (15) Å
c = 23.873 (5) Å
V = 2127.4 (7) Å^3
Z = 8
Mo $K\alpha$ radiation
μ = 0.09 mm^{-1}
T = 293 K
0.22 × 0.20 × 0.18 mm

Data collection

Bruker SMART CCD diffractometer
15748 measured reflections
1915 independent reflections
841 reflections with $I > 2\sigma(I)$
R_{int} = 0.180

Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.069
$wR(F^2)$ = 0.182
S = 0.87
1915 reflections
146 parameters
H-atom parameters constrained
$\Delta\rho_{max}$ = 0.48 e Å^{-3}
$\Delta\rho_{min}$ = −0.35 e Å^{-3}

Table 1
Hydrogen-bond geometry (Å, °).

D—H···A	D—H	H···A	D···A	D—H···A
N1—H1A···O2^{i}	0.86	2.06	2.911 (4)	168

Symmetry code: (i) $-x+\frac{3}{2}, y-\frac{1}{2}, z$.

Data collection: *SMART* (Bruker, 1997); cell refinement: *SAINT* (Bruker, 1997); data reduction: *SAINT*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *SHELXTL* (Sheldrick, 2008); software used to prepare material for publication: *SHELXTL*.

Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: HB5485).

References

Bruker (1997). *SMART* and *SAINT*. Bruker AXS Inc., Madison, Wisconsin, USA.
Jiang, J.-H. (2010). *Acta Cryst.* E**66**, o627.
Polt, R., Kelly, B. D. & Dangel, B. D. (2003). *Inorg. Chem.* **42**, 566–574.
Sheldrick, G. M. (2008). *Acta Cryst.* A**64**, 112–122.

supplementary materials

Acta Cryst. (2010). E**66**, o1720 [**doi:10.1107/S1600536810021471**]

N'-Benzylidenefuran-2-carbohydrazide

Y.-F. Li and F.-F. Jian

Comment

Metal complexes based on Schiff bases have attracted much attention because they can be utilized as effective ligands to form the compounds with optically active (Polt *et al.*, 2003). As part of our search for new Schiff base compounds we synthesized the title compound (I), and describe its structure here. The dihedral angle between the benzene ring and the furan ring is 24.6 (2)°. In the crystal lattice, the N—H···O hydrogen bonds which form chains stable the molecule structures.

Bond lengths and angles are comparable to those in a related material (Jiang, 2010).

Experimental

A mixture of benzaldehyde (0.1 mol), and furan-2-carbohydrazide (0.1 mol) was stirred in refluxing ethanol (20 ml) for 2 h to afford the title compound (0.096 mol, yield 96%). Colourless blocks of (I) were obtained by recrystallization from ethanol at room temperature.

Refinement

H atoms were fixed geometrically and allowed to ride on their attached atoms, with C—H distances=0.97 Å, and with U_{iso}=1.2–1.5U_{eq}.

Figures

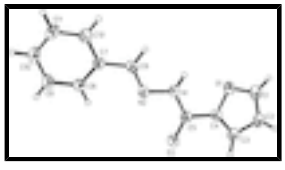


Fig. 1. The structure of (I) showing 30% probability displacement ellipsoids.

N'-Benzylidenefuran-2-carbohydrazide

Crystal data

$C_{12}H_{10}N_2O_2$	$F(000)$ = 896
M_r = 214.22	D_x = 1.338 Mg m^{-3}
Orthorhombic, *Pbca*	Mo *K*α radiation, λ = 0.71073 Å
Hall symbol: -P 2ac 2ab	Cell parameters from 2542 reflections
a = 11.628 (2) Å	θ = 2.7–25.4°
b = 7.6638 (15) Å	μ = 0.09 mm^{-1}
c = 23.873 (5) Å	*T* = 293 K

V = 2127.4 (7) Å^3	Block, colorless
Z = 8	0.22 × 0.20 × 0.18 mm

Data collection

Bruker SMART CCD diffractometer	841 reflections with $I > 2\sigma(I)$
Radiation source: fine-focus sealed tube	R_{int} = 0.180
graphite	θ_{max} = 25.3°, θ_{min} = 3.3°
phi and ω scans	h = −13→13
15748 measured reflections	k = −9→9
1915 independent reflections	l = −28→28

Refinement

Refinement on F^2	Secondary atom site location: difference Fourier map
Least-squares matrix: full	Hydrogen site location: inferred from neighbouring sites
$R[F^2 > 2\sigma(F^2)]$ = 0.069	H-atom parameters constrained
$wR(F^2)$ = 0.182	$w = 1/[\sigma^2(F_o^2) + (0.0916P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
S = 0.87	$(\Delta/\sigma)_{max} < 0.001$
1915 reflections	$\Delta\rho_{max}$ = 0.48 e Å^{-3}
146 parameters	$\Delta\rho_{min}$ = −0.35 e Å^{-3}
0 restraints	Extinction correction: *SHELXL97* (Sheldrick, 2008), $Fc^*=kFc[1+0.001xFc^2\lambda^3/\sin(2\theta)]^{-1/4}$
Primary atom site location: structure-invariant direct methods	Extinction coefficient: 0.042 (4)

Special details

Geometry. All e.s.d.'s (except the e.s.d. in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell e.s.d.'s are taken into account individually in the estimation of e.s.d.'s in distances, angles and torsion angles; correlations between e.s.d.'s in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell e.s.d.'s is used for estimating e.s.d.'s involving l.s. planes.

Refinement. Refinement of F^2 against ALL reflections. The weighted R-factor wR and goodness of fit S are based on F^2, conventional R-factors R are based on F, with F set to zero for negative F^2. The threshold expression of $F^2 > \sigma(F^2)$ is used only for calculating R-factors(gt) *etc*. and is not relevant to the choice of reflections for refinement. R-factors based on F^2 are statistically about twice as large as those based on F, and R- factors based on ALL data will be even larger.

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å^2)

	x	y	z	U_{iso}*/U_{eq}
C7	0.6392 (3)	0.2814 (4)	0.22579 (15)	0.0427 (9)
N2	0.7400 (2)	0.2911 (4)	0.13973 (12)	0.0444 (8)
O2	0.89248 (19)	0.4222 (3)	0.06644 (10)	0.0525 (7)
C6	0.6608 (3)	0.2226 (4)	0.16890 (15)	0.0464 (9)

H6A	0.6161	0.1338	0.1537	0.056*
N1	0.7595 (2)	0.2165 (4)	0.08817 (12)	0.0468 (8)
H1A	0.7204	0.1273	0.0774	0.056*
C11	0.5250 (3)	0.2748 (5)	0.30936 (18)	0.0614 (11)
H11A	0.4599	0.2357	0.3282	0.074*
C5	0.8408 (3)	0.2861 (4)	0.05515 (15)	0.0433 (9)
O1	0.8127 (2)	0.0388 (3)	−0.00680 (11)	0.0624 (8)
C12	0.5431 (3)	0.2243 (5)	0.25478 (17)	0.0565 (11)
H12A	0.4905	0.1511	0.2372	0.068*
C2	0.9298 (4)	0.0939 (6)	−0.07761 (19)	0.0717 (13)
H2B	0.9697	0.0836	−0.1112	0.086*
C8	0.7157 (3)	0.3882 (5)	0.25381 (16)	0.0499 (10)
H8A	0.7816	0.4262	0.2354	0.060*
C4	0.8663 (3)	0.1949 (4)	0.00321 (15)	0.0457 (9)
C3	0.9374 (3)	0.2318 (5)	−0.03877 (18)	0.0619 (12)
H4A	0.9835	0.3304	−0.0419	0.074*
C10	0.6010 (4)	0.3816 (5)	0.33627 (18)	0.0617 (11)
H10A	0.5884	0.4148	0.3732	0.074*
C9	0.6968 (3)	0.4393 (5)	0.30781 (17)	0.0607 (11)
H9A	0.7488	0.5134	0.3254	0.073*
C1	0.8544 (4)	−0.0182 (6)	−0.05660 (18)	0.0746 (13)
H1B	0.8329	−0.1222	−0.0737	0.090*

Atomic displacement parameters (Å^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
C7	0.047 (2)	0.0397 (19)	0.042 (2)	0.0015 (16)	0.0025 (17)	0.0011 (17)
N2	0.0508 (17)	0.0434 (17)	0.0389 (19)	−0.0018 (14)	0.0016 (14)	−0.0050 (14)
O2	0.0574 (14)	0.0490 (15)	0.0512 (18)	−0.0076 (12)	0.0024 (13)	−0.0054 (12)
C6	0.052 (2)	0.0403 (19)	0.047 (2)	−0.0016 (17)	−0.0001 (19)	−0.0025 (17)
N1	0.0558 (18)	0.0463 (17)	0.0384 (19)	−0.0070 (14)	0.0023 (15)	−0.0081 (14)
C11	0.058 (2)	0.073 (3)	0.054 (3)	0.005 (2)	0.019 (2)	0.001 (2)
C5	0.0469 (19)	0.0411 (19)	0.042 (2)	0.0030 (17)	−0.0022 (18)	0.0021 (18)
O1	0.0769 (18)	0.0604 (17)	0.0499 (19)	−0.0157 (13)	0.0153 (14)	−0.0151 (13)
C12	0.051 (2)	0.060 (2)	0.059 (3)	−0.0034 (19)	0.007 (2)	−0.006 (2)
C2	0.085 (3)	0.080 (3)	0.051 (3)	−0.011 (2)	0.024 (2)	−0.006 (2)
C8	0.051 (2)	0.051 (2)	0.047 (3)	−0.0037 (18)	0.0013 (19)	−0.0039 (18)
C4	0.051 (2)	0.0434 (19)	0.043 (3)	−0.0017 (16)	−0.0007 (18)	−0.0012 (18)
C3	0.070 (3)	0.062 (3)	0.053 (3)	−0.010 (2)	0.012 (2)	−0.005 (2)
C10	0.080 (3)	0.068 (3)	0.038 (2)	0.016 (2)	0.007 (2)	−0.001 (2)
C9	0.073 (3)	0.062 (3)	0.048 (3)	0.002 (2)	−0.003 (2)	−0.010 (2)
C1	0.101 (3)	0.069 (3)	0.053 (3)	−0.007 (3)	0.019 (2)	−0.021 (2)

Geometric parameters (Å, °)

C7—C8	1.382 (5)	O1—C4	1.370 (4)
C7—C12	1.385 (5)	C12—H12A	0.9300
C7—C6	1.453 (5)	C2—C1	1.327 (6)
N2—C6	1.268 (4)	C2—C3	1.408 (5)

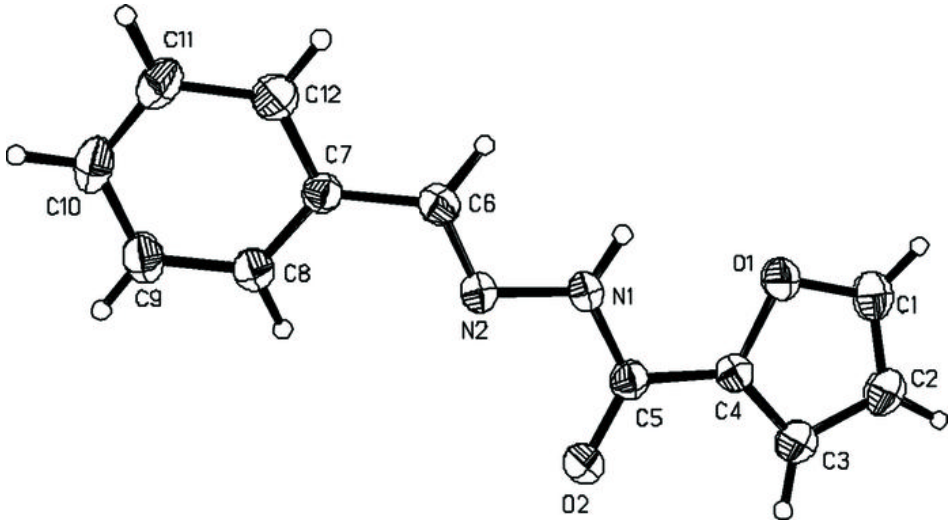
N2—N1	1.376 (4)	C2—H2B	0.9300
O2—C5	1.234 (4)	C8—C9	1.365 (5)
C6—H6A	0.9300	C8—H8A	0.9300
N1—C5	1.342 (4)	C4—C3	1.329 (5)
N1—H1A	0.8600	C3—H4A	0.9300
C11—C10	1.366 (5)	C10—C9	1.377 (5)
C11—C12	1.376 (5)	C10—H10A	0.9300
C11—H11A	0.9300	C9—H9A	0.9300
C5—C4	1.454 (5)	C1—H1B	0.9300
O1—C1	1.357 (4)		
C8—C7—C12	117.7 (4)	C1—C2—H2B	126.9
C8—C7—C6	121.6 (3)	C3—C2—H2B	126.9
C12—C7—C6	120.6 (3)	C9—C8—C7	121.6 (4)
C6—N2—N1	116.0 (3)	C9—C8—H8A	119.2
N2—C6—C7	120.7 (3)	C7—C8—H8A	119.2
N2—C6—H6A	119.6	C3—C4—O1	109.7 (3)
C7—C6—H6A	119.6	C3—C4—C5	131.9 (3)
C5—N1—N2	118.4 (3)	O1—C4—C5	118.4 (3)
C5—N1—H1A	120.8	C4—C3—C2	107.4 (3)
N2—N1—H1A	120.8	C4—C3—H4A	126.3
C10—C11—C12	121.0 (4)	C2—C3—H4A	126.3
C10—C11—H11A	119.5	C11—C10—C9	119.0 (4)
C12—C11—H11A	119.5	C11—C10—H10A	120.5
O2—C5—N1	123.5 (3)	C9—C10—H10A	120.5
O2—C5—C4	119.5 (3)	C8—C9—C10	120.2 (4)
N1—C5—C4	117.0 (3)	C8—C9—H9A	119.9
C1—O1—C4	105.8 (3)	C10—C9—H9A	119.9
C11—C12—C7	120.6 (4)	C2—C1—O1	111.0 (4)
C11—C12—H12A	119.7	C2—C1—H1B	124.5
C7—C12—H12A	119.7	O1—C1—H1B	124.5
C1—C2—C3	106.1 (4)		

Hydrogen-bond geometry (Å, °)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
N1—H1A···O2^{i}	0.86	2.06	2.911 (4)	168

Symmetry codes: (i) −*x*+3/2, *y*−1/2, *z*.

Fig. 1



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{*N*,*N*′-Bis[1-(2-pyridyl)ethylidene]-propane-1,2-diamine-κ^4N,N',N'',N'''}bis-(thiocyanato-κN)manganese(II)

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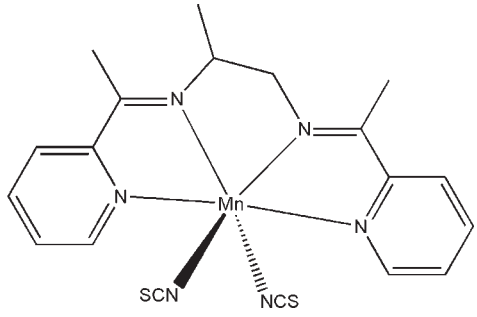
Key indicators: single-crystal X-ray study; T = 298 K; mean σ(C–C) = 0.009 Å; R factor = 0.077; wR factor = 0.224; data-to-parameter ratio = 18.0.

In the title compound, $[Mn(NCS)_2(C_{17}H_{20}N_4)]$, the Mn^{II} atom is six-coordinated by the *N*,*N*′,*N*″,*N*‴-tetradentate Schiff base ligand and by two *trans*-N atoms from two thiocyanate anions, forming a distorted octahedral geometry. The dihedral angle between the aromatic rings of the Schiff base is 9.5 (3)°.

Related literature

For another complex containing 1,2-bis(2′-pyridylmethylene-amino)propane, see: Ouyang *et al.* (2002). For related manganese(II) complexes with Schiff bases, see: Louloudi *et al.* (1999); Sra *et al.* (2000); Karmakar *et al.* (2005); Deoghoria *et al.* (2005). For the synthesis of the Schiff base, see: Gourbatsis *et al.* (1990).



Experimental

Crystal data

$[Mn(NCS)_2(C_{17}H_{20}N_4)]$ M_r = 451.47
Triclinic, $P\overline{1}$
a = 8.647 (3) Å
b = 9.135 (2) Å
c = 14.608 (3) Å
α = 84.701 (3)°
β = 79.407 (3)°
γ = 70.509 (3)°
V = 1068.6 (5) Å^3
Z = 2
Mo $K\alpha$ radiation
μ = 0.83 mm^{-1}
T = 298 K
0.33 × 0.30 × 0.30 mm

Data collection

Bruker SMART CCD diffractometer
Absorption correction: multi-scan (*SADABS*; Sheldrick, 1996)
T_{min} = 0.771, T_{max} = 0.789
11100 measured reflections
4608 independent reflections
2211 reflections with $I > 2\sigma(I)$
R_{int} = 0.078

Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.077
$wR(F^2)$ = 0.224
S = 0.99
4608 reflections
256 parameters
H-atom parameters constrained
$\Delta\rho_{max}$ = 0.68 e Å^{-3}
$\Delta\rho_{min}$ = −0.34 e Å^{-3}

Table 1
Selected bond lengths (Å).

Mn1—N5	2.127 (6)	Mn1—N3	2.260 (4)
Mn1—N6	2.149 (6)	Mn1—N4	2.334 (4)
Mn1—N2	2.258 (5)	Mn1—N1	2.346 (4)

Data collection: *SMART* (Bruker, 1998); cell refinement: *SAINT* (Bruker, 1998); data reduction: *SAINT*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *SHELXTL* (Sheldrick, 2008); software used to prepare material for publication: *SHELXTL*.

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Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: HB5486).

References

Bruker (1998). *SMART* and *SAINT*. Bruker AXS Inc., Madison, Wisconsin, USA.
Deoghoria, S., Bera, S. K., Moulton, B., Zaworotko, M. J., Tuchagues, J.-P., Mostafa, G., Lu, T.-H. & Chandra, S. K. (2005). *Polyhedron*, **24**, 343–350.
Gourbatsis, S., Perlepes, S. P., Hadjiliadis, N. & Kalkanis, G. (1990). *Transition Met. Chem.* **15**, 300–308.
Karmakar, T. K., Ghosh, B. K., Usman, A., Fun, H.-K., Riviere, E., Mallah, T., Aromi, G. & Chandra, S. K. (2005). *Inorg. Chem.* **44**, 2391–2399.
Louloudi, M., Nastopoulos, V., Gourbatsis, S., Perlepes, S. P. & Hadjiliadis, N. (1999). *Inorg. Chem. Commun.* **2**, 479–483.
Ouyang, X.-M., Fei, B.-L., Okamura, T., Sun, W.-Y., Tang, W.-X. & Ueyama, N. (2002). *Chem. Lett.* pp. 362–363.
Sheldrick, G. M. (1996). *SADABS*. University of Göttingen, Germany.
Sheldrick, G. M. (2008). *Acta Cryst.* A**64**, 112–122.
Sra, A. K., Sutter, J.-P., Guionneau, P., Chasseau, D., Yakhmi, J. V. & Kahn, O. (2000). *Inorg. Chim. Acta*, **300**, 778–782.

supplementary materials

Acta Cryst. (2010). E**66**, m777 [**doi:10.1107/S1600536810021549**]

{*N*,*N*'-Bis[1-(2-pyridyl)ethylidene]propane-1,2-diamine-κ^4*N*,*N*',*N*'',*N*'''}bis(thiocyanato-κ*N*)manganese(II)

F.-M. Wang

Comment

Metal complexes with Schiff bases have been known since 1840 but only one complex derived from 1,2-bis(2'-pyridylmethyleneamino)propane has been reported (Ouyang *et al.*, 2002). In this paper, the title new manganese(II) complex is reported.

In the title complex, Fig. 1, the Mn^{II} atom is six-coordinated by four N atoms of the Schiff base ligand 1,2-bis(2'-pyridylmethyleneamino)propane, and by two N atoms from two thiocyanate ligands, forming a distorted octahedral geometry. The coordinate bond lengths (Table 1) are comparable with those observed in other similar manganese(II) complexes with Schiff bases (Louloudi *et al.*, 1999; Sra *et al.*, 2000; Karmakar *et al.*, 2005; Deoghoria *et al.*, 2005).

Experimental

The Schiff base ligand 1,2-bis(2'-pyridylmethyleneamino)propane was synthesized according to the literature method (Gourbatsis *et al.*, 1990). To a stirred methanol solution of the Schiff base ligand (1.0 mmol, 0.280 g) was added a methanol solution of manganese acetate (1.0 mmol, 0.245 g) and ammonium thiocyanate (1.0 mmol, 0.076 g). The mixture was boiled under reflux for 2 h, then cooled to room temperature. Brown blocks of (I) were formed after slow evaporation of the solution in air for a few days.

Refinement

Hydrogen atoms were placed in geometrically idealized positions and constrained to ride on their parent atoms, with C–H distances of 0.93–0.97 Å, and with U_{iso}(H) set at 1.2U_{eq}(C) and 1.5U_{eq}(C_{methyl}).

Figures

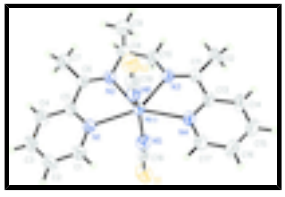


Fig. 1. The molecular structure of (I), showing displacement ellipsoids drawn at the 30% probability level.

{*N*,*N*'-Bis[1-(2-pyridyl)ethylidene]propane-1,2-diamine- κ^4*N*,*N*',*N*'',*N*'''}bis(thiocyanato- κ*N*)manganese(II)

Crystal data

$[Mn(NCS)_2(C_{17}H_{20}N_4)]$	$Z = 2$
$M_r = 451.47$	$F(000) = 466$
Triclinic, $P\overline{1}$	$D_x = 1.403$ Mg m^{-3}
Hall symbol: -P 1	Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å
$a = 8.647$ (3) Å	Cell parameters from 1307 reflections
$b = 9.135$ (2) Å	$\theta = 2.3$–$24.5°$
$c = 14.608$ (3) Å	$\mu = 0.83$ mm^{-1}
$\alpha = 84.701$ (3)°	$T = 298$ K
$\beta = 79.407$ (3)°	Block, brown
$\gamma = 70.509$ (3)°	0.33 × 0.30 × 0.30 mm
$V = 1068.6$ (5) Å^3	

Data collection

Bruker SMART CCD diffractometer	4608 independent reflections
Radiation source: fine-focus sealed tube	2211 reflections with $I > 2\sigma(I)$
graphite	$R_{int} = 0.078$
ω scan	$\theta_{max} = 27.0°$, $\theta_{min} = 2.4°$
Absorption correction: multi-scan (*SADABS*; Sheldrick, 1996)	$h = -11 \rightarrow 11$
$T_{min} = 0.771$, $T_{max} = 0.789$	$k = -11 \rightarrow 11$
11100 measured reflections	$l = -18 \rightarrow 18$

Refinement

Refinement on F^2	Primary atom site location: structure-invariant direct methods
Least-squares matrix: full	Secondary atom site location: difference Fourier map
$R[F^2 > 2\sigma(F^2)] = 0.077$	Hydrogen site location: inferred from neighbouring sites
$wR(F^2) = 0.224$	H-atom parameters constrained
$S = 0.99$	$w = 1/[\sigma^2(F_o^2) + (0.1044P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
4608 reflections	$(\Delta/\sigma)_{max} < 0.001$
256 parameters	$\Delta\rho_{max} = 0.68$ e Å^{-3}
0 restraints	$\Delta\rho_{min} = -0.34$ e Å^{-3}

Special details

Geometry. All e.s.d.'s (except the e.s.d. in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell e.s.d.'s are taken into account individually in the estimation of e.s.d.'s in distances, angles and torsion angles; correlations

between e.s.d.'s in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell e.s.d.'s is used for estimating e.s.d.'s involving l.s. planes.

Refinement. Refinement of F^2 against ALL reflections. The weighted *R*-factor *wR* and goodness of fit *S* are based on F^2, conventional *R*-factors *R* are based on *F*, with *F* set to zero for negative F^2. The threshold expression of $F^2 > \sigma(F^2)$ is used only for calculating *R*-factors(gt) *etc*. and is not relevant to the choice of reflections for refinement. *R*-factors based on F^2 are statistically about twice as large as those based on *F*, and *R*- factors based on ALL data will be even larger.

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å^2)

	x	*y*	*z*	U_{iso}*/U_{eq}
Mn1	1.02210 (10)	0.54382 (9)	0.27241 (5)	0.0601 (3)
N1	1.2061 (6)	0.6565 (5)	0.3134 (3)	0.0644 (12)
N2	1.0220 (6)	0.7580 (5)	0.1819 (3)	0.0673 (12)
N3	0.8157 (6)	0.5912 (5)	0.1875 (3)	0.0701 (13)
N4	0.9013 (5)	0.3471 (5)	0.3008 (3)	0.0665 (12)
N5	0.8737 (7)	0.6394 (7)	0.3994 (4)	0.0906 (17)
N6	1.2282 (6)	0.3744 (6)	0.1940 (4)	0.0772 (15)
S1	0.6757 (2)	0.8093 (2)	0.54416 (16)	0.1097 (7)
S2	1.4735 (2)	0.1575 (2)	0.08162 (12)	0.0855 (5)
C1	1.2937 (8)	0.6060 (8)	0.3826 (5)	0.089 (2)
H1	1.2883	0.5148	0.4151	0.107*
C2	1.3917 (9)	0.6811 (8)	0.4088 (5)	0.096 (2)
H2	1.4508	0.6422	0.4578	0.116*
C3	1.3997 (8)	0.8144 (8)	0.3608 (5)	0.088 (2)
H3	1.4654	0.8677	0.3765	0.106*
C4	1.3109 (7)	0.8693 (6)	0.2897 (5)	0.0750 (17)
H4	1.3155	0.9601	0.2565	0.090*
C5	1.2135 (6)	0.7880 (6)	0.2674 (4)	0.0574 (13)
C6	1.1124 (7)	0.8394 (7)	0.1905 (4)	0.0631 (14)
C7	1.1270 (9)	0.9785 (7)	0.1307 (5)	0.095 (2)
H7A	1.2372	0.9548	0.0956	0.142*
H7B	1.1054	1.0646	0.1696	0.142*
H7C	1.0477	1.0050	0.0888	0.142*
C8	0.9234 (8)	0.7889 (8)	0.1062 (4)	0.087 (2)
H8	0.8913	0.8996	0.0880	0.104*
C9	1.0322 (10)	0.6917 (9)	0.0230 (5)	0.106 (2)
H9A	1.1312	0.7198	0.0042	0.159*
H9B	0.9712	0.7114	−0.0281	0.159*
H9C	1.0619	0.5833	0.0409	0.159*
C10	0.7743 (8)	0.7434 (8)	0.1372 (5)	0.098 (2)
H10A	0.7250	0.7379	0.0837	0.118*
H10B	0.6935	0.8213	0.1779	0.118*
C11	0.7315 (7)	0.4988 (6)	0.1900 (4)	0.0617 (14)
C12	0.5892 (7)	0.5241 (7)	0.1393 (5)	0.0843 (19)
H12A	0.5809	0.6123	0.0970	0.126*
H12B	0.4880	0.5428	0.1833	0.126*
H12C	0.6072	0.4335	0.1050	0.126*
C13	0.7763 (6)	0.3606 (6)	0.2541 (4)	0.0613 (14)

C14	0.6956 (7)	0.2485 (8)	0.2671 (5)	0.0826 (18)
H14	0.6105	0.2573	0.2340	0.099*
C15	0.7432 (8)	0.1242 (8)	0.3297 (5)	0.094 (2)
H15	0.6899	0.0495	0.3389	0.112*
C16	0.8672 (9)	0.1124 (8)	0.3771 (5)	0.094 (2)
H16	0.9006	0.0303	0.4195	0.112*
C17	0.9429 (8)	0.2251 (7)	0.3610 (4)	0.0808 (18)
H17	1.0283	0.2165	0.3937	0.097*
C18	0.7938 (7)	0.7096 (6)	0.4577 (4)	0.0589 (14)
C19	1.3320 (7)	0.2828 (7)	0.1471 (4)	0.0631 (15)

Atomic displacement parameters (Å^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Mn1	0.0670 (6)	0.0649 (6)	0.0607 (5)	−0.0367 (5)	−0.0173 (4)	0.0090 (4)
N1	0.082 (3)	0.060 (3)	0.064 (3)	−0.036 (2)	−0.024 (2)	0.011 (2)
N2	0.078 (3)	0.075 (3)	0.066 (3)	−0.041 (3)	−0.030 (2)	0.012 (2)
N3	0.075 (3)	0.072 (3)	0.077 (3)	−0.039 (3)	−0.026 (3)	0.017 (3)
N4	0.063 (3)	0.077 (3)	0.071 (3)	−0.036 (2)	−0.018 (2)	0.009 (3)
N5	0.089 (4)	0.110 (5)	0.082 (4)	−0.051 (4)	−0.001 (3)	−0.006 (3)
N6	0.079 (4)	0.077 (4)	0.086 (4)	−0.040 (3)	−0.016 (3)	0.003 (3)
S1	0.0955 (14)	0.1071 (16)	0.1234 (16)	−0.0214 (12)	−0.0135 (12)	−0.0410 (13)
S2	0.0850 (12)	0.0822 (12)	0.0928 (12)	−0.0285 (10)	−0.0153 (9)	−0.0139 (9)
C1	0.116 (5)	0.088 (5)	0.091 (5)	−0.060 (4)	−0.049 (4)	0.026 (4)
C2	0.114 (5)	0.099 (5)	0.102 (5)	−0.051 (5)	−0.063 (4)	0.019 (4)
C3	0.096 (5)	0.078 (5)	0.115 (5)	−0.047 (4)	−0.047 (4)	0.001 (4)
C4	0.080 (4)	0.052 (3)	0.103 (5)	−0.029 (3)	−0.030 (4)	0.003 (3)
C5	0.055 (3)	0.060 (3)	0.062 (3)	−0.025 (3)	−0.010 (3)	−0.006 (3)
C6	0.065 (3)	0.067 (4)	0.064 (3)	−0.030 (3)	−0.015 (3)	0.008 (3)
C7	0.121 (6)	0.080 (5)	0.103 (5)	−0.061 (4)	−0.037 (4)	0.039 (4)
C8	0.113 (5)	0.080 (5)	0.085 (4)	−0.049 (4)	−0.042 (4)	0.027 (4)
C9	0.143 (7)	0.102 (6)	0.083 (5)	−0.051 (5)	−0.026 (5)	0.003 (4)
C10	0.108 (5)	0.110 (6)	0.110 (5)	−0.070 (5)	−0.060 (4)	0.042 (4)
C11	0.057 (3)	0.059 (3)	0.075 (4)	−0.026 (3)	−0.011 (3)	−0.005 (3)
C12	0.065 (4)	0.088 (5)	0.112 (5)	−0.032 (3)	−0.037 (4)	0.006 (4)
C13	0.056 (3)	0.064 (4)	0.069 (3)	−0.032 (3)	0.002 (3)	−0.004 (3)
C14	0.067 (4)	0.086 (5)	0.113 (5)	−0.046 (4)	−0.021 (4)	0.000 (4)
C15	0.094 (5)	0.090 (5)	0.113 (6)	−0.059 (4)	−0.015 (4)	0.022 (4)
C16	0.099 (5)	0.089 (5)	0.106 (5)	−0.054 (4)	−0.022 (4)	0.034 (4)
C17	0.087 (4)	0.086 (5)	0.088 (4)	−0.047 (4)	−0.034 (4)	0.022 (4)
C18	0.057 (4)	0.052 (4)	0.075 (4)	−0.026 (3)	−0.022 (3)	0.013 (3)
C19	0.063 (4)	0.061 (4)	0.075 (4)	−0.030 (3)	−0.024 (3)	0.013 (3)

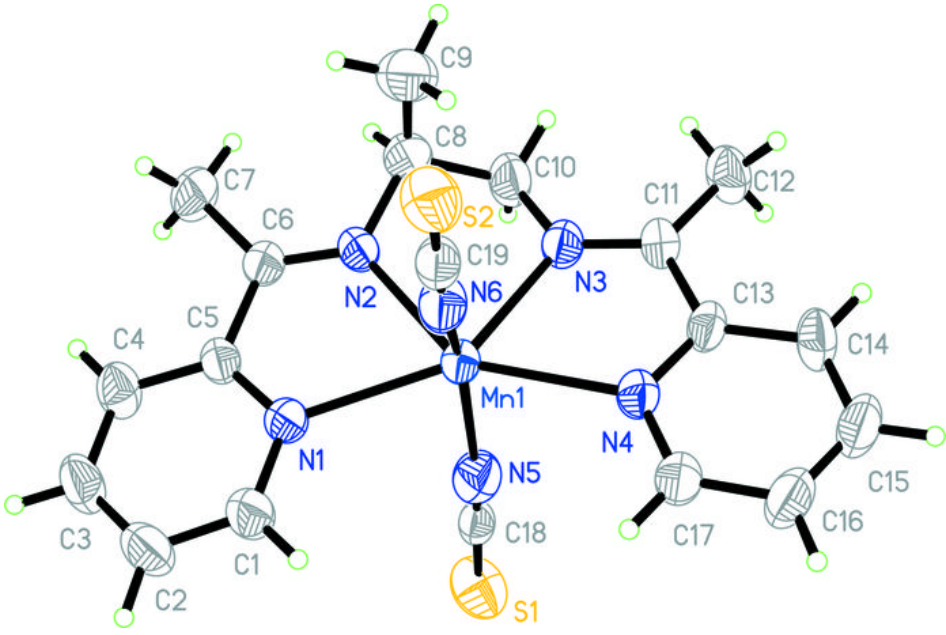
Geometric parameters (Å, °)

Mn1—N5	2.127 (6)	C5—C6	1.495 (7)
Mn1—N6	2.149 (6)	C6—C7	1.501 (8)
Mn1—N2	2.258 (5)	C7—H7A	0.9600
Mn1—N3	2.260 (4)	C7—H7B	0.9600

Mn1—N4	2.334 (4)	C7—H7C	0.9600
Mn1—N1	2.346 (4)	C8—C10	1.465 (8)
N1—C1	1.331 (7)	C8—C9	1.540 (9)
N1—C5	1.336 (6)	C8—H8	0.9800
N2—C6	1.274 (6)	C9—H9A	0.9600
N2—C8	1.470 (7)	C9—H9B	0.9600
N3—C11	1.281 (6)	C9—H9C	0.9600
N3—C10	1.476 (7)	C10—H10A	0.9700
N4—C17	1.345 (7)	C10—H10B	0.9700
N4—C13	1.348 (6)	C11—C13	1.486 (8)
N5—C18	1.097 (7)	C11—C12	1.493 (7)
N6—C19	1.164 (7)	C12—H12A	0.9600
S1—C18	1.608 (7)	C12—H12B	0.9600
S2—C19	1.600 (7)	C12—H12C	0.9600
C1—C2	1.376 (8)	C13—C14	1.402 (7)
C1—H1	0.9300	C14—C15	1.389 (8)
C2—C3	1.364 (9)	C14—H14	0.9300
C2—H2	0.9300	C15—C16	1.351 (8)
C3—C4	1.364 (8)	C15—H15	0.9300
C3—H3	0.9300	C16—C17	1.376 (8)
C4—C5	1.389 (7)	C16—H16	0.9300
C4—H4	0.9300	C17—H17	0.9300
N5—Mn1—N6	152.6 (2)	H7A—C7—H7B	109.5
N5—Mn1—N2	102.5 (2)	C6—C7—H7C	109.5
N6—Mn1—N2	99.53 (18)	H7A—C7—H7C	109.5
N5—Mn1—N3	98.1 (2)	H7B—C7—H7C	109.5
N6—Mn1—N3	103.71 (18)	C10—C8—N2	109.6 (5)
N2—Mn1—N3	73.15 (16)	C10—C8—C9	109.9 (6)
N5—Mn1—N4	86.78 (19)	N2—C8—C9	107.8 (5)
N6—Mn1—N4	85.41 (17)	C10—C8—H8	109.8
N2—Mn1—N4	142.80 (16)	N2—C8—H8	109.8
N3—Mn1—N4	69.88 (16)	C9—C8—H8	109.8
N5—Mn1—N1	82.92 (18)	C8—C9—H9A	109.5
N6—Mn1—N1	89.82 (17)	C8—C9—H9B	109.5
N2—Mn1—N1	69.50 (15)	H9A—C9—H9B	109.5
N3—Mn1—N1	141.88 (17)	C8—C9—H9C	109.5
N4—Mn1—N1	147.69 (16)	H9A—C9—H9C	109.5
C1—N1—C5	117.9 (5)	H9B—C9—H9C	109.5
C1—N1—Mn1	125.2 (4)	C8—C10—N3	110.8 (5)
C5—N1—Mn1	116.7 (3)	C8—C10—H10A	109.5
C6—N2—C8	121.8 (5)	N3—C10—H10A	109.5
C6—N2—Mn1	122.4 (4)	C8—C10—H10B	109.5
C8—N2—Mn1	115.5 (3)	N3—C10—H10B	109.5
C11—N3—C10	122.6 (5)	H10A—C10—H10B	108.1
C11—N3—Mn1	122.1 (4)	N3—C11—C13	115.4 (5)
C10—N3—Mn1	114.9 (3)	N3—C11—C12	125.6 (5)
C17—N4—C13	117.9 (5)	C13—C11—C12	118.9 (5)
C17—N4—Mn1	125.7 (4)	C11—C12—H12A	109.5
C13—N4—Mn1	116.3 (3)	C11—C12—H12B	109.5

C18—N5—Mn1	169.2 (6)	H12A—C12—H12B	109.5
C19—N6—Mn1	174.9 (5)	C11—C12—H12C	109.5
N1—C1—C2	123.6 (6)	H12A—C12—H12C	109.5
N1—C1—H1	118.2	H12B—C12—H12C	109.5
C2—C1—H1	118.2	N4—C13—C14	120.4 (5)
C3—C2—C1	118.0 (6)	N4—C13—C11	116.3 (5)
C3—C2—H2	121.0	C14—C13—C11	123.3 (5)
C1—C2—H2	121.0	C15—C14—C13	119.7 (6)
C2—C3—C4	119.7 (6)	C15—C14—H14	120.2
C2—C3—H3	120.1	C13—C14—H14	120.2
C4—C3—H3	120.1	C16—C15—C14	119.6 (6)
C3—C4—C5	119.2 (6)	C16—C15—H15	120.2
C3—C4—H4	120.4	C14—C15—H15	120.2
C5—C4—H4	120.4	C15—C16—C17	118.2 (6)
N1—C5—C4	121.6 (5)	C15—C16—H16	120.9
N1—C5—C6	115.6 (4)	C17—C16—H16	120.9
C4—C5—C6	122.8 (5)	N4—C17—C16	124.2 (6)
N2—C6—C5	115.6 (5)	N4—C17—H17	117.9
N2—C6—C7	126.2 (5)	C16—C17—H17	117.9
C5—C6—C7	118.2 (5)	N5—C18—S1	178.7 (6)
C6—C7—H7A	109.5	N6—C19—S2	179.4 (6)
C6—C7—H7B	109.5		

Fig. 1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C8
C7
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C11
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C13
C5
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C14
Mn1
N1
N4
N5
C15
C3
C18
C17
C16
C1
C2
S1

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(*E*)-*N*′-(3-Nitrobenzylidene)-4-(8-quinolyloxy)butanohydrazide

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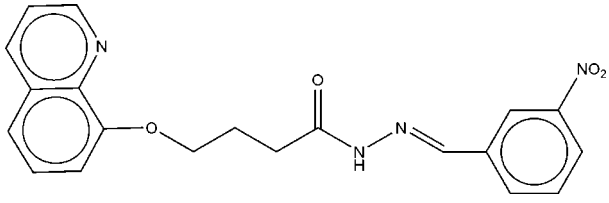
Key indicators: single-crystal X-ray study; T = 296 K; mean σ(C–C) = 0.006 Å; R factor = 0.065; wR factor = 0.268; data-to-parameter ratio = 13.5.

In the title Schiff base compound, $C_{20}H_{18}N_4O_4$, the conformation along the bond sequence linking the benzene and quinoline rings is *trans*–(+)*gauche*–*trans*–*trans*–(+)*gauche*–*trans*–*trans*. The dihedral angle between the aromatic ring systems is 80.3 (6)°. In the crystal, a pair of intermolecular N—H···N hydrogen bonds link the molecules into centrosymmetric $R_2^2(20)$ dimers, which are aggregated *via* π–π interactions into sheets [quinoline–benzene ring centroid–centroid separation = 3.572 (2)–3.773 (3) Å].

Related literature

For a closely related isomeric structure and background references, see: XiaHou *et al.* (2010). For further synthetic details, see: Zheng *et al.* (2006). For reference bond lengths, see: Allen *et al.* (1987). For hydrogen-bond motifs, see: Bernstein *et al.* (1995).



Experimental

Crystal data

$C_{20}H_{18}N_4O_4$
M_r = 378.38
Triclinic, $P\overline{1}$
a = 8.3664 (12) Å
b = 10.4882 (15) Å
c = 11.5855 (16) Å
α = 100.595 (3)°
β = 91.968 (3)°
γ = 101.898 (4)°
V = 975.0 (2) Å^3
Z = 2
Mo $K\alpha$ radiation
μ = 0.09 mm^{-1}
T = 296 K
0.19 × 0.17 × 0.15 mm

Data collection

Bruker SMART CCD diffractometer
Absorption correction: multi-scan (*SADABS*; Sheldrick, 1996)
T_{min} = 0.983, T_{max} = 0.986
5434 measured reflections
3409 independent reflections
1926 reflections with $I > 2\sigma(I)$
R_{int} = 0.023

Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.065
$wR(F^2)$ = 0.268
S = 1.08
3409 reflections
253 parameters
H-atom parameters constrained
$\Delta\rho_{max}$ = 0.45 e Å^{-3}
$\Delta\rho_{min}$ = −0.26 e Å^{-3}

Table 1
Hydrogen-bond geometry (Å, °).

D—H···A	D—H	H···A	D···A	D—H···A
N2—H2A···N1^{i}	0.86	2.19	3.022 (4)	162

Symmetry code: (i) $-x+1, -y, -z+2$.

Data collection: *SMART* (Bruker, 2007); cell refinement: *SAINT* (Bruker, 2007); data reduction: *SAINT*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *SHELXTL* (Sheldrick, 2008); software used to prepare material for publication: *SHELXTL*.

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Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: HB5488).

References

Allen, F. H., Kennard, O., Watson, D. G., Brammer, L., Orpen, A. G. & Taylor, R. J. (1987). *J. Chem. Soc. Perkin Trans. 2*, pp. S1–19.
Bernstein, J., Davis, R. E., Shimoni, L. & Chang, N.-L. (1995). *Angew. Chem. Int. Ed. Engl.* **34**, 1555–1573.
Bruker (2007). *SMART* and *SAINT*. Bruker AXS Inc., Madison, Wisconsin, USA.
Sheldrick, G. M. (1996). *SADABS*. University of Göttingen, Germany.
Sheldrick, G. M. (2008). *Acta Cryst.* A**64**, 112–122.
XiaHou, G.-L., Ding, Y.-C. & Fan, X.-N. (2010). *Acta Cryst.* E**66**, o1522.
Zheng, P.-W., Qiu, Q.-M., Lin, Y.-Y. & Liu, K.-F. (2006). *Acta Cryst.* E**62**, o1913–o1914.

supplementary materials

Acta Cryst. (2010). E**66**, o1659 [**doi:10.1107/S1600536810022257**]

(*E*)-*N*'-(3-Nitrobenzylidene)-4-(8-quinolyloxy)butanohydrazide

L. Zeng, X.-S. Zhou, L.-H. Lv and G.-X. Li

Comment

In this article, we present the synthesis and crystal structure of a new Schiff base, (I), which contains oxygen and nitrogen donors and flexible aliphatic spacers. A closely related structure with the nitro group at the 4-position was reported recently (XiaHou *et al.*, 2010). X-ray diffraction analysis reveals that (I) contains a *trans*-(+)*gauche*-*trans*-*trans*-(+)*gauche*-*trans*-*trans* conformation along the quinoline ring–benzene ring bond sequence [torsion angles (°): C8–O1–C10–C11, 178.5 (3); O1–C10–C11–C12, 70.1 (4); C10–C11–C12–C13, -173.2 (3); C11–C12–C13–N2, -174.8 (3); C12–C13–N2–N3, 0.8 (5); C13–N2–N3–C14, -176.8 (3); N2–N3–C14–C15, -180.0 (3)] (Fig.1). The bond lengths and angles in (I) are in good agreement with the expected values (Allen *et al.*, 1987). The C14—N3 and C13—O2 bond length of 1.276 (5) and 1.214 (4) Å, respectively, indicate the presence of a typical C═N and C═O. The C═N–N angle of 116.6 (3) ° is significantly smaller than the ideal value of 120 ° expected for sp^2-hybridized N atoms. This is probably a consequence of repulsion between the nitrogen lone pairs and the adjacent N atom (Zheng *et al.*, 2006). In the crystal structure, a pair of intermolecular N—H···N hydrogen bonds link the molecules into centrosymmetric cyclic $R^2_2(20)$ (Bernstein *et al.*, 1995) dimers(Fig.2) which are aggregated *via* π–π interactions into parallel sheets [quinoline–benzene ring centroid separation = 3.572 (2)–3.773 (3) Å], giving a supramolecular two dimensional network(Fig. 3).

Experimental

The title compound was synthesized according to the method of Zheng *et al.* (2006): 4-(quinolin-8-yloxy)butanehydrazide (0.01 mol), 3-nitrobenzaldehyde (0.01 mol), ethanol (40 ml) and some drops of acetic acid were added to a 100 ml flask and refluxed for 6 h. After cooling to room temperature, the solid product was separated by filtration. Yellow blocks of (I) were obtained by slow evaporation of a tetrahydrofuran solution of the title compound over a period of six days.

Refinement

All H atoms were placed in idealized positions (C—H = 0.93–0.97 Å, N—H = 0.86 Å and refined as riding atoms with U_{iso}(H) = 1.2U_{eq}(C or N).

Figures

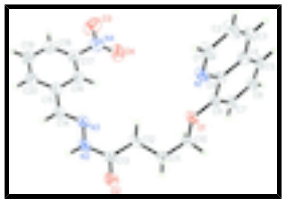


Fig. 1. The molecular structure of (I), with displacement ellipsoids at the 30% probability level.

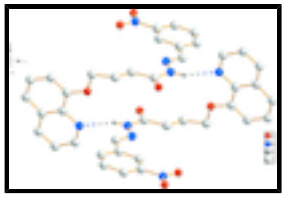


Fig. 2. The cyclic hydrogen-bonded dimer in (I) with hydrogen bonds shown as dashed lines. H atoms, except for those involved in hydrogen bonds, are not included.

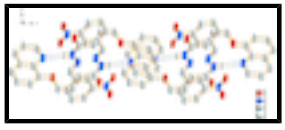


Fig. 3. Part of the crystal structure of (I) showing hydrogen bonds as dashed lines. H atoms, except for those involved in hydrogen bonds, are not included.

(*E*)-*N*'-(3-Nitrobenzylidene)-4-(8-quinolyloxy)butanohydrazide

Crystal data

$C_{20}H_{18}N_4O_4$	$Z = 2$
$M_r = 378.38$	$F(000) = 396$
Triclinic, $P\overline{1}$	$D_x = 1.289$ Mg m^{-3}
Hall symbol: -P 1	Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å
$a = 8.3664$ (12) Å	Cell parameters from 1258 reflections
$b = 10.4882$ (15) Å	$\theta = 2.4$–$24.1°$
$c = 11.5855$ (16) Å	$\mu = 0.09$ mm^{-1}
$\alpha = 100.595$ (3)°	$T = 296$ K
$\beta = 91.968$ (3)°	Block, yellow
$\gamma = 101.898$ (4)°	0.19 × 0.17 × 0.15 mm
$V = 975.0$ (2) Å^3	

Data collection

Bruker SMART CCD diffractometer	3409 independent reflections
Radiation source: fine-focus sealed tube	1926 reflections with $I > 2\sigma(I)$
graphite	$R_{int} = 0.023$
φ and ω scans	$\theta_{max} = 25.1°$, $\theta_{min} = 1.8°$
Absorption correction: multi-scan (*SADABS*; Sheldrick, 1996)	$h = -9 \rightarrow 9$
$T_{min} = 0.983$, $T_{max} = 0.986$	$k = -12 \rightarrow 11$
5434 measured reflections	$l = -13 \rightarrow 12$

Refinement

Refinement on F^2	Primary atom site location: structure-invariant direct methods
Least-squares matrix: full	Secondary atom site location: difference Fourier map
$R[F^2 > 2\sigma(F^2)] = 0.065$	Hydrogen site location: inferred from neighbouring sites
$wR(F^2) = 0.268$	H-atom parameters constrained
$S = 1.08$	$w = 1/[\sigma^2(F_o^2) + (0.1425P)^2 + 0.1889P]$

	where $P = (F_o^2 + 2F_c^2)/3$
3409 reflections	$(\Delta/\sigma)_{max} < 0.001$
253 parameters	$\Delta\rho_{max} = 0.45$ e Å^{-3}
0 restraints	$\Delta\rho_{min} = -0.26$ e Å^{-3}

Special details

Geometry. All e.s.d.'s (except the e.s.d. in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell e.s.d.'s are taken into account individually in the estimation of e.s.d.'s in distances, angles and torsion angles; correlations between e.s.d.'s in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell e.s.d.'s is used for estimating e.s.d.'s involving l.s. planes.

Refinement. Refinement of F^2 against ALL reflections. The weighted *R*-factor *wR* and goodness of fit *S* are based on F^2, conventional *R*-factors *R* are based on *F*, with *F* set to zero for negative F^2. The threshold expression of $F^2 > \sigma(F^2)$ is used only for calculating *R*-factors(gt) *etc*. and is not relevant to the choice of reflections for refinement. *R*-factors based on F^2 are statistically about twice as large as those based on *F*, and *R*- factors based on ALL data will be even larger.

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å^2)

	x	*y*	*z*	U_{iso}*/U_{eq}
O1	0.2886 (3)	−0.1013 (3)	0.68540 (19)	0.0613 (8)
O2	0.2305 (4)	−0.0360 (3)	1.0959 (2)	0.0740 (9)
O3	0.8883 (6)	0.6809 (5)	0.8111 (4)	0.1341 (17)
O4	0.6888 (6)	0.5092 (4)	0.7739 (3)	0.1053 (12)
N1	0.5334 (4)	−0.2125 (3)	0.6100 (2)	0.0625 (9)
N2	0.4230 (4)	0.1503 (3)	1.1241 (3)	0.0642 (9)
H2A	0.4367	0.1491	1.1978	0.077*
N3	0.5149 (4)	0.2515 (3)	1.0792 (3)	0.0566 (8)
C1	0.6550 (6)	−0.2666 (5)	0.5723 (4)	0.0872 (15)
H1	0.7215	−0.2894	0.6277	0.105*
C2	0.6912 (7)	−0.2923 (6)	0.4538 (4)	0.0991 (17)
H2	0.7791	−0.3306	0.4316	0.119*
C3	0.5935 (6)	−0.2595 (5)	0.3724 (4)	0.0786 (13)
H3	0.6141	−0.2765	0.2933	0.094*
C4	0.4625 (5)	−0.2005 (4)	0.4064 (3)	0.0592 (10)
C5	0.3618 (6)	−0.1590 (4)	0.3276 (3)	0.0685 (12)
H5	0.3790	−0.1723	0.2478	0.082*
C6	0.2416 (6)	−0.1004 (4)	0.3671 (3)	0.0711 (12)
H6	0.1778	−0.0709	0.3147	0.085*
C7	0.2099 (5)	−0.0826 (4)	0.4869 (3)	0.0670 (11)
H7	0.1221	−0.0456	0.5119	0.080*
C8	0.3055 (5)	−0.1187 (4)	0.5660 (3)	0.0558 (10)
C9	0.4356 (5)	−0.1781 (4)	0.5281 (3)	0.0524 (9)
C10	0.1507 (5)	−0.0514 (5)	0.7282 (3)	0.0621 (10)
H10A	0.0496	−0.1098	0.6910	0.074*
H10B	0.1552	0.0363	0.7112	0.074*
C11	0.1582 (5)	−0.0454 (4)	0.8588 (3)	0.0617 (11)
H11A	0.0553	−0.0295	0.8878	0.074*

H11B	0.1703	−0.1309	0.8740	0.074*
C12	0.2951 (5)	0.0599 (4)	0.9259 (3)	0.0560 (10)
H12A	0.2762	0.1465	0.9191	0.067*
H12B	0.3971	0.0506	0.8913	0.067*
C13	0.3110 (5)	0.0523 (4)	1.0542 (3)	0.0507 (9)
C14	0.6227 (5)	0.3359 (4)	1.1503 (3)	0.0624 (10)
H14	0.6351	0.3263	1.2282	0.075*
C15	0.7263 (5)	0.4469 (4)	1.1114 (3)	0.0629 (11)
C16	0.7079 (5)	0.4681 (4)	0.9964 (3)	0.0597 (10)
H16	0.6269	0.4117	0.9428	0.072*
C17	0.8108 (5)	0.5730 (4)	0.9636 (4)	0.0637 (11)
C18	0.9289 (6)	0.6604 (4)	1.0400 (5)	0.0755 (13)
H18	0.9950	0.7321	1.0160	0.091*
C19	0.9478 (6)	0.6398 (5)	1.1533 (5)	0.0840 (14)
H19	1.0292	0.6964	1.2064	0.101*
C20	0.8451 (6)	0.5343 (5)	1.1875 (4)	0.0761 (13)
H20	0.8571	0.5224	1.2646	0.091*
N4	0.7921 (6)	0.5887 (4)	0.8403 (4)	0.0813 (11)

Atomic displacement parameters (Å^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
O1	0.0655 (17)	0.0903 (19)	0.0358 (12)	0.0323 (15)	0.0088 (11)	0.0135 (12)
O2	0.077 (2)	0.095 (2)	0.0570 (16)	0.0159 (17)	0.0094 (14)	0.0357 (16)
O3	0.118 (3)	0.132 (3)	0.157 (4)	−0.016 (3)	−0.020 (3)	0.094 (3)
O4	0.135 (3)	0.091 (2)	0.082 (2)	−0.001 (2)	−0.010 (2)	0.030 (2)
N1	0.069 (2)	0.087 (2)	0.0414 (16)	0.0367 (19)	0.0070 (15)	0.0150 (16)
N2	0.076 (2)	0.081 (2)	0.0409 (16)	0.020 (2)	0.0077 (16)	0.0199 (16)
N3	0.062 (2)	0.068 (2)	0.0473 (17)	0.0246 (17)	0.0096 (15)	0.0160 (16)
C1	0.105 (4)	0.119 (4)	0.056 (2)	0.064 (3)	0.011 (2)	0.020 (2)
C2	0.114 (4)	0.135 (5)	0.065 (3)	0.070 (4)	0.018 (3)	0.010 (3)
C3	0.082 (3)	0.106 (3)	0.047 (2)	0.031 (3)	0.011 (2)	0.001 (2)
C4	0.064 (3)	0.071 (3)	0.0405 (19)	0.011 (2)	0.0023 (17)	0.0085 (17)
C5	0.087 (3)	0.078 (3)	0.0318 (18)	0.002 (2)	−0.0028 (19)	0.0081 (18)
C6	0.081 (3)	0.086 (3)	0.044 (2)	0.013 (3)	−0.013 (2)	0.013 (2)
C7	0.065 (3)	0.092 (3)	0.047 (2)	0.029 (2)	−0.0074 (18)	0.009 (2)
C8	0.067 (3)	0.067 (2)	0.0328 (17)	0.017 (2)	−0.0001 (16)	0.0066 (16)
C9	0.057 (2)	0.065 (2)	0.0346 (17)	0.0117 (19)	0.0013 (15)	0.0093 (16)
C10	0.046 (2)	0.085 (3)	0.055 (2)	0.013 (2)	0.0090 (17)	0.013 (2)
C11	0.049 (2)	0.090 (3)	0.050 (2)	0.020 (2)	0.0113 (17)	0.014 (2)
C12	0.067 (3)	0.072 (2)	0.0379 (18)	0.032 (2)	0.0137 (17)	0.0140 (17)
C13	0.046 (2)	0.067 (2)	0.047 (2)	0.0224 (19)	0.0096 (17)	0.0211 (19)
C14	0.064 (3)	0.079 (3)	0.049 (2)	0.024 (2)	0.0043 (19)	0.012 (2)
C15	0.060 (3)	0.073 (3)	0.059 (2)	0.030 (2)	0.0037 (19)	0.002 (2)
C16	0.064 (3)	0.056 (2)	0.061 (2)	0.024 (2)	0.0003 (19)	0.0053 (18)
C17	0.064 (3)	0.057 (2)	0.078 (3)	0.030 (2)	0.006 (2)	0.014 (2)
C18	0.066 (3)	0.054 (3)	0.104 (4)	0.018 (2)	0.011 (3)	0.000 (2)
C19	0.066 (3)	0.082 (3)	0.088 (4)	0.016 (3)	−0.005 (2)	−0.021 (3)

C20	0.072 (3)	0.083 (3)	0.065 (3)	0.019 (3)	0.005 (2)	−0.007 (2)
N4	0.087 (3)	0.070 (3)	0.097 (3)	0.022 (2)	0.005 (2)	0.035 (2)

Geometric parameters (Å, °)

O1—C8	1.378 (4)	C7—H7	0.9300
O1—C10	1.429 (4)	C8—C9	1.406 (5)
O2—C13	1.214 (4)	C10—C11	1.501 (5)
O3—N4	1.231 (5)	C10—H10A	0.9700
O4—N4	1.207 (5)	C10—H10B	0.9700
N1—C1	1.313 (5)	C11—C12	1.495 (5)
N1—C9	1.377 (4)	C11—H11A	0.9700
N2—C13	1.355 (5)	C11—H11B	0.9700
N2—N3	1.372 (4)	C12—C13	1.505 (5)
N2—H2A	0.8600	C12—H12A	0.9700
N3—C14	1.276 (5)	C12—H12B	0.9700
C1—C2	1.406 (6)	C14—C15	1.454 (6)
C1—H1	0.9300	C14—H14	0.9300
C2—C3	1.363 (6)	C15—C20	1.368 (6)
C2—H2	0.9300	C15—C16	1.399 (5)
C3—C4	1.399 (6)	C16—C17	1.372 (5)
C3—H3	0.9300	C16—H16	0.9300
C4—C5	1.407 (5)	C17—C18	1.367 (6)
C4—C9	1.419 (5)	C17—N4	1.474 (6)
C5—C6	1.334 (6)	C18—C19	1.379 (7)
C5—H5	0.9300	C18—H18	0.9300
C6—C7	1.408 (5)	C19—C20	1.382 (6)
C6—H6	0.9300	C19—H19	0.9300
C7—C8	1.350 (5)	C20—H20	0.9300
C8—O1—C10	117.5 (3)	C12—C11—C10	114.0 (3)
C1—N1—C9	117.9 (3)	C12—C11—H11A	108.8
C13—N2—N3	120.9 (3)	C10—C11—H11A	108.8
C13—N2—H2A	119.5	C12—C11—H11B	108.8
N3—N2—H2A	119.5	C10—C11—H11B	108.8
C14—N3—N2	116.6 (3)	H11A—C11—H11B	107.7
N1—C1—C2	124.3 (4)	C11—C12—C13	112.4 (3)
N1—C1—H1	117.9	C11—C12—H12A	109.1
C2—C1—H1	117.9	C13—C12—H12A	109.1
C3—C2—C1	118.0 (4)	C11—C12—H12B	109.1
C3—C2—H2	121.0	C13—C12—H12B	109.1
C1—C2—H2	121.0	H12A—C12—H12B	107.9
C2—C3—C4	120.8 (4)	O2—C13—N2	119.8 (3)
C2—C3—H3	119.6	O2—C13—C12	123.5 (4)
C4—C3—H3	119.6	N2—C13—C12	116.6 (3)
C3—C4—C5	123.5 (3)	N3—C14—C15	120.9 (4)
C3—C4—C9	117.2 (3)	N3—C14—H14	119.6
C5—C4—C9	119.2 (4)	C15—C14—H14	119.6
C6—C5—C4	120.1 (3)	C20—C15—C16	118.1 (4)
C6—C5—H5	119.9	C20—C15—C14	120.4 (4)

C4—C5—H5	119.9	C16—C15—C14	121.5 (4)
C5—C6—C7	121.0 (4)	C17—C16—C15	119.2 (4)
C5—C6—H6	119.5	C17—C16—H16	120.4
C7—C6—H6	119.5	C15—C16—H16	120.4
C8—C7—C6	120.8 (4)	C18—C17—C16	122.5 (4)
C8—C7—H7	119.6	C18—C17—N4	119.9 (4)
C6—C7—H7	119.6	C16—C17—N4	117.6 (4)
C7—C8—O1	125.3 (3)	C17—C18—C19	118.5 (5)
C7—C8—C9	119.8 (3)	C17—C18—H18	120.7
O1—C8—C9	114.9 (3)	C19—C18—H18	120.7
N1—C9—C8	119.1 (3)	C18—C19—C20	119.6 (4)
N1—C9—C4	121.9 (3)	C18—C19—H19	120.2
C8—C9—C4	119.0 (3)	C20—C19—H19	120.2
O1—C10—C11	107.0 (3)	C15—C20—C19	122.1 (4)
O1—C10—H10A	110.3	C15—C20—H20	118.9
C11—C10—H10A	110.3	C19—C20—H20	118.9
O1—C10—H10B	110.3	O4—N4—O3	124.2 (4)
C11—C10—H10B	110.3	O4—N4—C17	118.8 (4)
H10A—C10—H10B	108.6	O3—N4—C17	116.9 (5)
C13—N2—N3—C14	−176.8 (3)	C8—O1—C10—C11	178.5 (3)
C9—N1—C1—C2	−0.4 (8)	O1—C10—C11—C12	70.1 (4)
N1—C1—C2—C3	−0.3 (9)	C10—C11—C12—C13	−173.2 (3)
C1—C2—C3—C4	0.8 (8)	N3—N2—C13—O2	−179.7 (3)
C2—C3—C4—C5	177.1 (5)	N3—N2—C13—C12	0.8 (5)
C2—C3—C4—C9	−0.7 (7)	C11—C12—C13—O2	5.7 (5)
C3—C4—C5—C6	−178.3 (4)	C11—C12—C13—N2	−174.8 (3)
C9—C4—C5—C6	−0.7 (6)	N2—N3—C14—C15	−180.0 (3)
C4—C5—C6—C7	−1.9 (7)	N3—C14—C15—C20	−177.9 (3)
C5—C6—C7—C8	3.2 (7)	N3—C14—C15—C16	2.4 (5)
C6—C7—C8—O1	177.6 (4)	C20—C15—C16—C17	1.4 (5)
C6—C7—C8—C9	−1.8 (6)	C14—C15—C16—C17	−178.9 (3)
C10—O1—C8—C7	5.6 (6)	C15—C16—C17—C18	−1.7 (5)
C10—O1—C8—C9	−175.0 (3)	C15—C16—C17—N4	177.5 (3)
C1—N1—C9—C8	−179.3 (4)	C16—C17—C18—C19	1.8 (6)
C1—N1—C9—C4	0.5 (6)	N4—C17—C18—C19	−177.3 (4)
C7—C8—C9—N1	179.0 (4)	C17—C18—C19—C20	−1.7 (6)
O1—C8—C9—N1	−0.3 (5)	C16—C15—C20—C19	−1.3 (6)
C7—C8—C9—C4	−0.8 (6)	C14—C15—C20—C19	178.9 (4)
O1—C8—C9—C4	179.8 (3)	C18—C19—C20—C15	1.5 (6)
C3—C4—C9—N1	0.0 (6)	C18—C17—N4—O4	178.7 (4)
C5—C4—C9—N1	−177.8 (4)	C16—C17—N4—O4	−0.4 (6)
C3—C4—C9—C8	179.8 (4)	C18—C17—N4—O3	1.3 (6)
C5—C4—C9—C8	2.0 (6)	C16—C17—N4—O3	−177.9 (4)

Hydrogen-bond geometry (Å, °)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
N2—H2A···N1^{i}	0.86	2.19	3.022 (4)	162

Symmetry codes: (i) −*x*+1, −*y*, −*z*+2.

Fig. 1

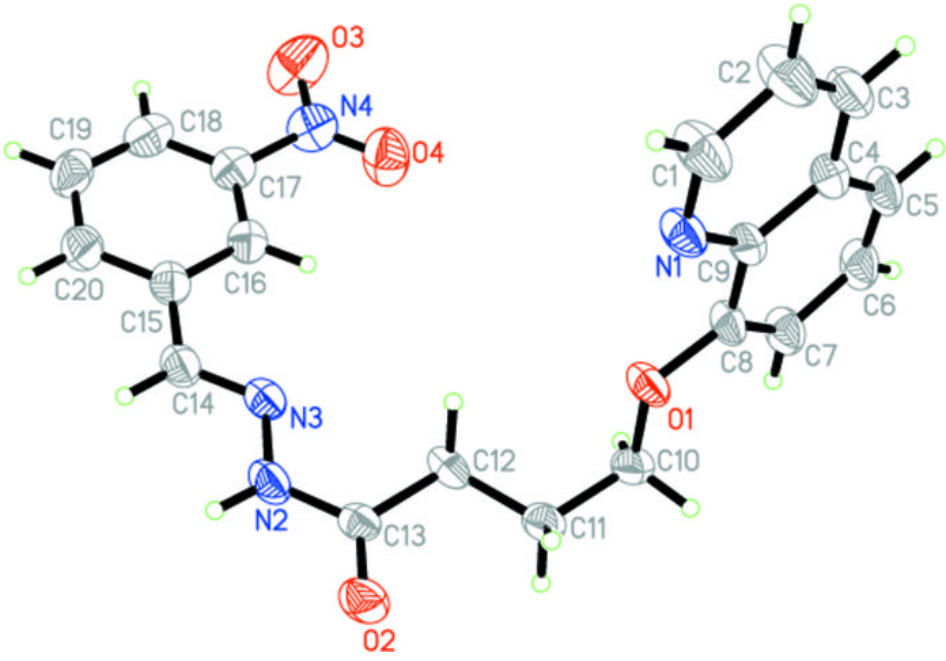

O3
N4
O4
C19
C18
C17
C20
C16
C15
C14
N3
N2
C13
O2
C12
C11
C10
O1
C8
C7
C6
C5
C4
C3
C2
C1
N1
C9

Fig. 2

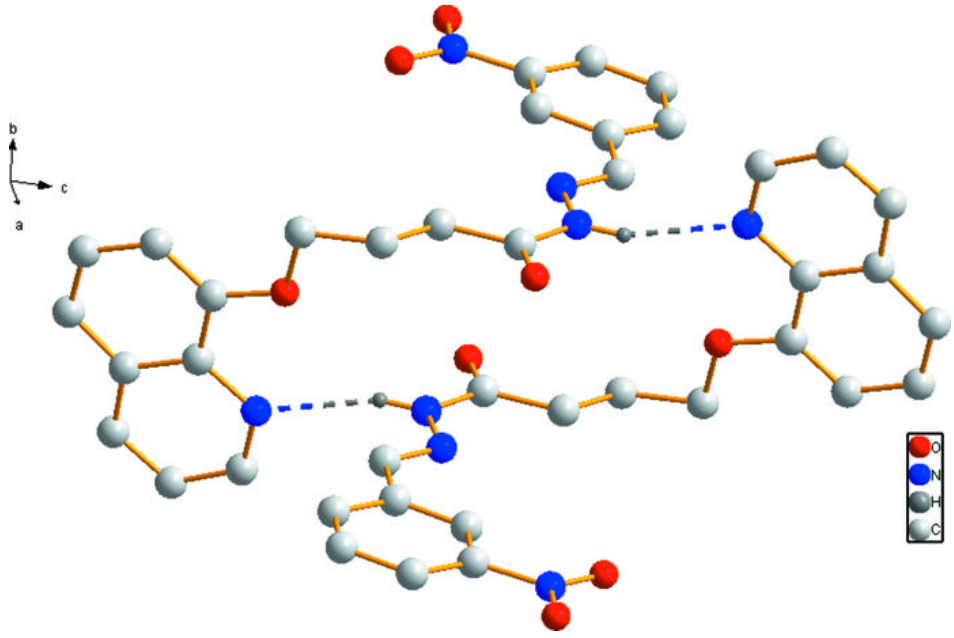
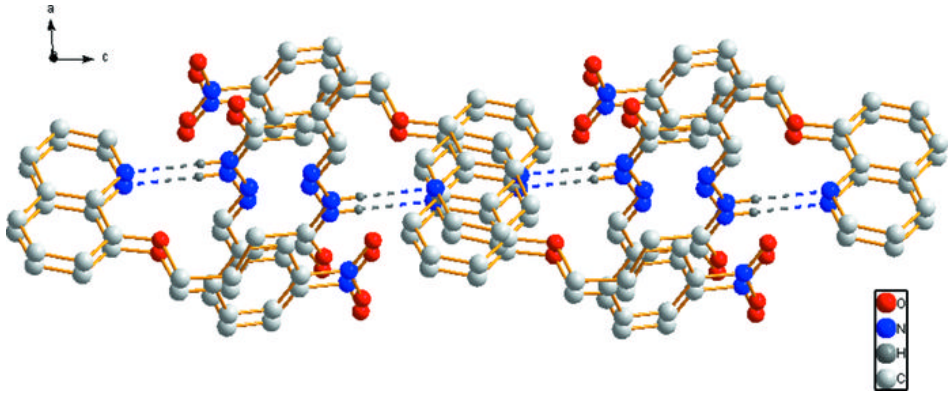


Fig. 3



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(2-Methoxybenzyl)(2-methoxybenzylidene)azanium (2-methoxyphenyl)methanaminium tetrachloridozincate(II) monohydrate

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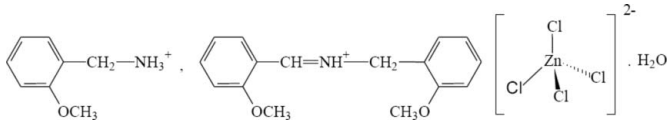
Key indicators: single-crystal X-ray study; T = 293 K; mean σ(C–C) = 0.003 Å; R factor = 0.036; wR factor = 0.087; data-to-parameter ratio = 20.0.

The title compound, $(C_8H_{12}NO)(C_{16}H_{18}NO_2)[ZnCl_4]\cdot H_2O$, was obtained as a by-product of the Zn^{2+} and HCl catalyzed condensation of (2-methoxyphenyl)methanamine in water. Both cations feature an intramolecular N—H···O hydrogen bond. In the crystal, the components are linked by an extensive three-dimensional network of N—H···O, O—H···Cl and N—H···Cl hydrogen bonds (three of them bifurcated). Weak C—H···O interactions also occur.

Related literature

For related *meta*-chlorido complexes, see: Ben Gharbia *et al.* (2005, 2008). For Zn—Cl distances and Cl—Zn—Cl bond angles, see: Gayathri *et al.* (2008); Hosseinian & Mahjoub (2009).



Experimental

Crystal data

$(C_8H_{12}NO)(C_{16}H_{18}NO_2)[ZnCl_4]\cdot H_2O$
M_r = 619.69
Triclinic, $P\overline{1}$
a = 8.0884 (9) Å
b = 12.424 (2) Å
c = 14.678 (2) Å
α = 98.23 (1)°
β = 97.43 (1)°
γ = 90.29 (1)°
V = 1447.1 (3) Å^3
Z = 2
Mo $K\alpha$ radiation
μ = 1.25 mm^{-1}
T = 293 K
0.54 × 0.47 × 0.25 mm

Data collection

Oxford Diffraction Xcalibur diffractometer
Absorption correction: analytical (*CrysAlis PRO*; Oxford Diffraction, 2009; Clark & Reid, 1995)
T_{min} = 0.576, T_{max} = 0.749
12584 measured reflections
6583 independent reflections
4644 reflections with $I > 2\sigma(I)$
R_{int} = 0.028

Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.036
$wR(F^2)$ = 0.087
S = 0.98
6583 reflections
329 parameters
3 restraints
H atoms treated by a mixture of independent and constrained refinement
$\Delta\rho_{max}$ = 0.72 e Å^{-3}
$\Delta\rho_{min}$ = −0.64 e Å^{-3}

Table 1
Hydrogen-bond geometry (Å, °).

D—H···A	D—H	H···A	D···A	D—H···A
N1—H1···O2	0.89 (1)	2.07 (2)	2.680 (2)	125 (2)
N1—H1···Cl2^{i}	0.89 (1)	2.64 (2)	3.3221 (18)	135 (2)
N2—H2A···O4	0.89	2.30	3.102 (3)	151
N2—H2A···O3	0.89	2.37	2.877 (2)	116
N2—H2B···O4^{ii}	0.89	2.04	2.881 (3)	158
N2—H2B···Cl3^{iii}	0.89	2.98	3.502 (2)	120
N2—H2C···Cl1^{iv}	0.89	2.45	3.306 (2)	162
O4—H4B···Cl4^{iii}	0.80 (2)	2.44 (2)	3.2323 (19)	168 (3)
O4—H4A···Cl1^{v}	0.80 (2)	2.72 (2)	3.4165 (19)	147 (3)
C8—H8A···Cl3	0.97	2.67	3.474 (2)	140
C11—H11···Cl2	0.93	2.82	3.687 (2)	155
C24—H24A···Cl4^{vi}	0.97	2.76	3.707 (3)	166

Symmetry codes: (i) $x+1, y, z$; (ii) $-x+1, -y+1, -z$; (iii) $x, y, z-1$; (iv) $-x+1, -y+1, -z+1$; (v) $-x, -y+1, -z+1$; (vi) $x+1, y, z-1$.

Data collection: *CrysAlis PRO* (Oxford Diffraction, 2009); cell refinement: *CrysAlis PRO*; data reduction: *CrysAlis PRO*; program(s) used to solve structure: *SIR97* (Altomare *et al.*, 1999); program(s) used to refine structure: *SHELXTL* (Sheldrick, 2008); molecular graphics: *SHELXTL*; software used to prepare material for publication: *SHELXTL*.

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Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: HB5489).

References

Altomare, A., Burla, M. C., Camalli, M., Cascarano, G. L., Giacovazzo, C., Guagliardi, A., Moliterni, A. G. G., Polidori, G. & Spagna, R. (1999). *J. Appl. Cryst.* **32**, 115–119.
Ben Gharbia, I., Kefi, R., El Glaoui, M., Jeanneau, E. & Ben Nasr, C. (2008). *Acta Cryst.* E**64**, m880.
Ben Gharbia, I., Kefi, R., Rayes, A. & Ben Nasr, C. (2005). *Z. Kristallogr. New Cryst. Struct.* **220**, 333–334.
Clark, R. C. & Reid, J. S. (1995). *Acta Cryst.* A**51**, 887–897.
Gayathri, D., Velmurugan, D., Hemalatha, P., Veeravazhuthi, V. & Ravikumar, K. (2008). *Acta Cryst.* E**64**, m848–m849.
Hosseinian, A. & Mahjoub, A. R. (2009). *Acta Cryst.* E**65**, m1456.
Oxford Diffraction (2009). *CrysAlis PRO*. Oxford Diffraction Ltd, Yarnton, USA.
Sheldrick, G. M. (2008). *Acta Cryst.* A**64**, 112–122.

supplementary materials

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(2-Methoxybenzyl)(2-methoxybenzylidene)azanium (2-methoxyphenyl)methanaminium tetrachloridozincate(II) monohydrate

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Comment

As a part of our ongoing investigations in molecular salts containing *meta*-chlorido complexes (Ben Gharbia *et al.*, 2005; Ben Gharbia *et al.*, 2008), we report here the crystal structure of one such compound, $(C_{16}H_{18}NO_2)(C_8H_{12}NO)[ZnCl_4].H_2O$. The title compound was obtained as a byproduct of the Zn^{2+} and HCl catalyzed condensation of (2-methoxyphenyl) methanamine in water. Subsequent crystallization from the reaction mixture yielded among the main reaction products crystals of the title compound that consist of one *N*-(2-methoxybenzylidene)-1-(2-methoxyphenyl)methanaminnium cation, one (2-methoxyphenyl) methanaminium cation, one $ZnCl_4^{2-}$ anion and one interstitial water molecule (Fig. 1).

The distance N1—C9 [1.273 (2) Å] is substantially shorter than the one of N1—C8 [1.477 (2) Å], indicating the presence of a double bond in the condensation product, thus indicating the nature of the organic molecules in the crystal as indictated in Scheme 1. Preliminary NMR data on the material indicate that the bulk of the reaction product is not identical with the title compound. Further investigations into the nature of the bulk material are under way.

The Cl—Zn—Cl bond angles in the title compound show relatively little distortion from a regular tetrahedron [spread values 104.45 (3)–111.78 (2)] (Gayathri *et al.*, 2008, Hosseinian *et al.*, 2009). Classic N—H···O, O—H···Cl and N—H···Cl hydrogen bonds are observed, which link the two types of organic ammonium cations, the anionic complexes $[ZnCl_4]^{2-}$ and the uncoordinated water molecules into a 3-D hydrogen bonded network, as shown in Fig. 2. Three of the hydrogen bonds are bifurcated: N1—H1··· (Cl2,O2), N2—H2A···(O3,O4) and N2—H2B···(O4,Cl3).

Experimental

An aqueous solution of (2-methoxyphenyl) methanamine (2-methoxybenzylamine), zinc chloride and 1 *M* hydrochloric acid in a Petri disk was slowly evaporated at room temperature. A colourless block of (I), which remained stable under normal conditions of temperature and humidity, was isolated as a byproduct of the reaction.

Refinement

C—H and ammonium H atoms were placed in calculated positions with C—H in the range 0.93–0.97 and N—H equal to 0.89 Å. The imminium and the water hydrogen atom postitions were refined with N—H and O—H distance restraints of 0.89 (2) and 0.82 (2) Å. The U_{iso}(H) values of all H atoms were constrained to 1.2 or 1.5 times U_{eq} of the respective parent atom.

Figures

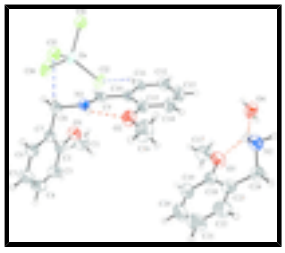


Fig. 1. A view of the title compound, showing 50% probability displacement ellipsoids (arbitrary spheres for the H atoms).

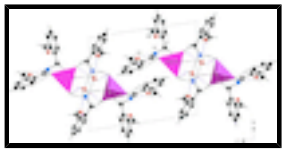


Fig. 2. Projection of the structure along the *a* axis. Hydrogen bonds are denoted by dotted lines.

(2-Methoxybenzyl)(2-methoxybenzylidene)azanium (2-methoxyphenyl)methanaminium tetrachloridozincate(II) monohydrate

Crystal data

$(C_8H_{12}NO)(C_{16}H_{18}NO_2)[ZnCl_4]\cdot H_2O$	$Z = 2$
$M_r = 619.69$	$F(000) = 640$
Triclinic, $P\overline{1}$	$D_x = 1.422$ Mg m^{-3}
Hall symbol: -P 1	Mo $K\alpha$ radiation, $\lambda = 0.71069$ Å
$a = 8.0884$ (9) Å	Cell parameters from 5313 reflections
$b = 12.424$ (2) Å	$\theta = 3.0$–$29.2°$
$c = 14.678$ (2) Å	$\mu = 1.25$ mm^{-1}
$\alpha = 98.23$ (1)°	$T = 293$ K
$\beta = 97.43$ (1)°	Block, colourless
$\gamma = 90.29$ (1)°	0.54 × 0.47 × 0.25 mm
$V = 1447.1$ (3) Å^3	

Data collection

Oxford Diffraction Xcalibur diffractometer	6583 independent reflections
Radiation source: fine-focus sealed tube	4644 reflections with $I > 2\sigma(I)$
graphite	$R_{int} = 0.028$
ω scans	$\theta_{max} = 29.5°$, $\theta_{min} = 3.0°$
Absorption correction: analytical (*CrysAlis PRO*; Oxford Diffraction, 2009; Clark & Reid, 1995)	$h = -10 \rightarrow 11$
$T_{min} = 0.576$, $T_{max} = 0.749$	$k = -15 \rightarrow 16$
12584 measured reflections	$l = -19 \rightarrow 19$

Refinement

Refinement on F^2	Primary atom site location: structure-invariant direct methods
Least-squares matrix: full	Secondary atom site location: difference Fourier map
$R[F^2 > 2\sigma(F^2)] = 0.036$	Hydrogen site location: inferred from neighbouring sites
$wR(F^2) = 0.087$	H atoms treated by a mixture of independent and constrained refinement
$S = 0.98$	$w = 1/[\sigma^2(F_o^2) + (0.0435P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
6583 reflections	$(\Delta/\sigma)_{max} = 0.001$
329 parameters	$\Delta\rho_{max} = 0.72$ e Å^{-3}
3 restraints	$\Delta\rho_{min} = -0.64$ e Å^{-3}

Special details

Geometry. All e.s.d.'s (except the e.s.d. in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell e.s.d.'s are taken into account individually in the estimation of e.s.d.'s in distances, angles and torsion angles; correlations between e.s.d.'s in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell e.s.d.'s is used for estimating e.s.d.'s involving l.s. planes.

Refinement. Refinement of F^2 against ALL reflections. The weighted *R*-factor *wR* and goodness of fit *S* are based on F^2, conventional *R*-factors *R* are based on *F*, with *F* set to zero for negative F^2. The threshold expression of $F^2 > \sigma(F^2)$ is used only for calculating *R*-factors(gt) *etc*. and is not relevant to the choice of reflections for refinement. *R*-factors based on F^2 are statistically about twice as large as those based on *F*, and *R*- factors based on ALL data will be even larger.

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å^2)

	x	*y*	*z*	U_{iso}*/U_{eq}
C1	0.2523 (3)	0.0313 (2)	0.58855 (19)	0.0669 (8)
H1A	0.2600	−0.0055	0.5272	0.100*
H1B	0.1579	0.0778	0.5869	0.100*
H1C	0.2392	−0.0214	0.6292	0.100*
C2	0.5461 (3)	0.04191 (18)	0.63917 (14)	0.0377 (5)
C3	0.5657 (3)	−0.06829 (19)	0.61983 (16)	0.0486 (6)
H3	0.4754	−0.1130	0.5916	0.058*
C4	0.7185 (3)	−0.1128 (2)	0.64206 (17)	0.0559 (6)
H4	0.7313	−0.1875	0.6285	0.067*
C5	0.8521 (3)	−0.0475 (2)	0.68406 (17)	0.0535 (6)
H5	0.9549	−0.0779	0.6999	0.064*
C6	0.8333 (3)	0.06297 (19)	0.70261 (14)	0.0421 (5)
H6	0.9247	0.1070	0.7303	0.051*
C7	0.6816 (2)	0.11022 (17)	0.68108 (13)	0.0331 (4)
C8	0.6598 (3)	0.23148 (16)	0.70157 (13)	0.0367 (5)
H8A	0.5629	0.2461	0.7336	0.044*
H8B	0.7568	0.2646	0.7418	0.044*

C9	0.5018 (2)	0.31536 (16)	0.57852 (13)	0.0331 (4)
H9	0.4129	0.3162	0.6129	0.040*
C10	0.4693 (2)	0.35513 (16)	0.49025 (13)	0.0326 (4)
C11	0.3132 (2)	0.39947 (17)	0.46852 (15)	0.0390 (5)
H11	0.2380	0.4048	0.5117	0.047*
C12	0.2683 (3)	0.43548 (18)	0.38452 (16)	0.0485 (6)
H12	0.1641	0.4649	0.3709	0.058*
C13	0.3800 (3)	0.42721 (19)	0.32143 (16)	0.0536 (6)
H13	0.3498	0.4506	0.2643	0.064*
C14	0.5355 (3)	0.3854 (2)	0.34018 (15)	0.0469 (6)
H14	0.6098	0.3814	0.2965	0.056*
C15	0.5808 (2)	0.34898 (17)	0.42502 (14)	0.0360 (5)
C16	0.8537 (3)	0.2994 (3)	0.38782 (19)	0.0764 (9)
H16A	0.8119	0.2554	0.3301	0.115*
H16B	0.9527	0.2678	0.4153	0.115*
H16C	0.8797	0.3714	0.3766	0.115*
C17	0.2513 (3)	0.1890 (3)	0.1188 (2)	0.0783 (9)
H17A	0.2140	0.1149	0.0986	0.117*
H17B	0.1647	0.2370	0.1003	0.117*
H17C	0.2776	0.2010	0.1852	0.117*
C18	0.5273 (3)	0.14345 (19)	0.08828 (15)	0.0467 (6)
C19	0.5371 (4)	0.0578 (2)	0.14046 (17)	0.0616 (7)
H19	0.4496	0.0425	0.1722	0.074*
C20	0.6792 (4)	−0.0042 (2)	0.14433 (19)	0.0741 (8)
H20	0.6864	−0.0621	0.1783	0.089*
C21	0.8083 (4)	0.0192 (3)	0.0987 (2)	0.0772 (9)
H21	0.9038	−0.0221	0.1023	0.093*
C22	0.7973 (3)	0.1043 (2)	0.04706 (19)	0.0641 (7)
H22	0.8862	0.1200	0.0164	0.077*
C23	0.6558 (3)	0.16659 (19)	0.04026 (15)	0.0435 (5)
C24	0.6378 (3)	0.2543 (2)	−0.02067 (16)	0.0512 (6)
H24A	0.7340	0.2540	−0.0539	0.061*
H24B	0.5397	0.2379	−0.0663	0.061*
Cl3	0.40847 (6)	0.41374 (5)	0.81903 (4)	0.04914 (15)
Cl2	0.04753 (7)	0.32552 (5)	0.63718 (3)	0.05224 (16)
Cl1	0.03902 (8)	0.57253 (6)	0.81699 (4)	0.06066 (18)
Cl4	0.03288 (9)	0.29378 (6)	0.88415 (4)	0.0746 (2)
N1	0.6383 (2)	0.27933 (13)	0.61445 (11)	0.0334 (4)
H1	0.729 (2)	0.2772 (17)	0.5852 (13)	0.040*
N2	0.6225 (2)	0.36549 (15)	0.03186 (13)	0.0488 (5)
H2A	0.5218	0.3717	0.0501	0.073*
H2B	0.6365	0.4152	−0.0047	0.073*
H2C	0.7000	0.3756	0.0814	0.073*
O1	0.40047 (18)	0.09490 (13)	0.62188 (11)	0.0508 (4)
O2	0.72997 (17)	0.30455 (13)	0.44960 (10)	0.0458 (4)
O3	0.3943 (2)	0.20972 (14)	0.07819 (12)	0.0616 (5)
O4	0.2655 (2)	0.45092 (16)	0.04551 (11)	0.0573 (5)
H4B	0.220 (3)	0.412 (2)	0.0009 (15)	0.086*
H4A	0.208 (3)	0.473 (3)	0.0836 (17)	0.086*

Zn1	0.12911 (3)	0.39816 (2)	0.786811 (15)	0.03902 (9)

Atomic displacement parameters (Å^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
C1	0.0402 (13)	0.079 (2)	0.0807 (19)	−0.0143 (13)	0.0011 (13)	0.0147 (16)
C2	0.0393 (12)	0.0406 (14)	0.0358 (11)	−0.0040 (10)	0.0081 (9)	0.0113 (10)
C3	0.0548 (14)	0.0362 (14)	0.0524 (14)	−0.0100 (11)	0.0027 (11)	0.0031 (12)
C4	0.0713 (18)	0.0304 (14)	0.0637 (16)	0.0043 (12)	0.0050 (13)	0.0018 (12)
C5	0.0504 (14)	0.0428 (16)	0.0665 (16)	0.0090 (11)	0.0044 (12)	0.0085 (13)
C6	0.0401 (12)	0.0393 (14)	0.0461 (13)	−0.0011 (10)	0.0011 (10)	0.0075 (11)
C7	0.0400 (11)	0.0314 (12)	0.0299 (10)	−0.0007 (9)	0.0076 (8)	0.0080 (9)
C8	0.0462 (12)	0.0327 (12)	0.0311 (10)	0.0012 (9)	0.0046 (9)	0.0050 (9)
C9	0.0349 (11)	0.0276 (11)	0.0367 (11)	−0.0013 (8)	0.0073 (9)	0.0024 (9)
C10	0.0343 (10)	0.0275 (11)	0.0357 (11)	−0.0030 (8)	0.0015 (8)	0.0061 (9)
C11	0.0349 (11)	0.0307 (12)	0.0504 (13)	−0.0035 (9)	0.0017 (10)	0.0061 (10)
C12	0.0416 (12)	0.0413 (14)	0.0599 (15)	−0.0027 (10)	−0.0104 (11)	0.0142 (12)
C13	0.0635 (16)	0.0510 (16)	0.0454 (13)	−0.0112 (12)	−0.0118 (12)	0.0208 (12)
C14	0.0510 (14)	0.0531 (15)	0.0377 (12)	−0.0075 (11)	0.0052 (10)	0.0118 (11)
C15	0.0355 (11)	0.0327 (12)	0.0393 (11)	−0.0066 (9)	0.0008 (9)	0.0073 (10)
C16	0.0522 (16)	0.116 (3)	0.0707 (18)	0.0130 (16)	0.0307 (14)	0.0248 (18)
C17	0.0612 (17)	0.080 (2)	0.104 (2)	0.0048 (15)	0.0403 (17)	0.0217 (19)
C18	0.0518 (14)	0.0454 (15)	0.0433 (13)	0.0018 (11)	0.0046 (11)	0.0090 (12)
C19	0.0748 (18)	0.0559 (18)	0.0588 (16)	0.0021 (14)	0.0137 (14)	0.0202 (14)
C20	0.101 (2)	0.058 (2)	0.0637 (18)	0.0116 (17)	−0.0055 (17)	0.0245 (16)
C21	0.069 (2)	0.075 (2)	0.084 (2)	0.0259 (16)	−0.0060 (16)	0.0126 (18)
C22	0.0508 (15)	0.066 (2)	0.0751 (18)	0.0077 (13)	0.0082 (13)	0.0080 (16)
C23	0.0402 (12)	0.0427 (14)	0.0457 (13)	0.0002 (10)	0.0025 (10)	0.0019 (11)
C24	0.0579 (15)	0.0516 (16)	0.0472 (13)	−0.0012 (12)	0.0177 (11)	0.0080 (12)
Cl3	0.0335 (3)	0.0638 (4)	0.0473 (3)	0.0050 (3)	0.0046 (2)	−0.0010 (3)
Cl2	0.0449 (3)	0.0768 (5)	0.0322 (3)	−0.0055 (3)	0.0033 (2)	0.0003 (3)
Cl1	0.0586 (4)	0.0643 (5)	0.0540 (4)	0.0230 (3)	−0.0034 (3)	0.0003 (3)
Cl4	0.0860 (5)	0.0963 (6)	0.0413 (3)	−0.0483 (4)	0.0023 (3)	0.0165 (4)
N1	0.0369 (9)	0.0298 (10)	0.0347 (9)	−0.0008 (8)	0.0067 (7)	0.0067 (8)
N2	0.0512 (11)	0.0436 (12)	0.0522 (11)	−0.0044 (9)	0.0039 (9)	0.0118 (10)
O1	0.0377 (8)	0.0492 (10)	0.0652 (10)	−0.0031 (7)	0.0023 (7)	0.0120 (8)
O2	0.0374 (8)	0.0595 (11)	0.0444 (8)	0.0057 (7)	0.0109 (7)	0.0159 (8)
O3	0.0493 (10)	0.0612 (12)	0.0850 (13)	0.0119 (8)	0.0259 (9)	0.0309 (10)
O4	0.0568 (11)	0.0688 (13)	0.0442 (10)	−0.0155 (9)	0.0040 (8)	0.0048 (10)
Zn1	0.03518 (14)	0.05046 (18)	0.03133 (14)	−0.00161 (11)	0.00427 (10)	0.00579 (12)

Geometric parameters (Å, °)

C1—O1	1.424 (3)	C16—O2	1.431 (2)
C1—H1A	0.9600	C16—H16A	0.9600
C1—H1B	0.9600	C16—H16B	0.9600
C1—H1C	0.9600	C16—H16C	0.9600
C2—O1	1.365 (2)	C17—O3	1.407 (3)
C2—C3	1.372 (3)	C17—H17A	0.9600

C2—C7	1.402 (3)	C17—H17B	0.9600
C3—C4	1.377 (3)	C17—H17C	0.9600
C3—H3	0.9300	C18—O3	1.364 (3)
C4—C5	1.372 (3)	C18—C23	1.380 (3)
C4—H4	0.9300	C18—C19	1.394 (3)
C5—C6	1.374 (3)	C19—C20	1.386 (4)
C5—H5	0.9300	C19—H19	0.9300
C6—C7	1.382 (3)	C20—C21	1.362 (4)
C6—H6	0.9300	C20—H20	0.9300
C7—C8	1.509 (3)	C21—C22	1.384 (4)
C8—N1	1.477 (2)	C21—H21	0.9300
C8—H8A	0.9700	C22—C23	1.386 (3)
C8—H8B	0.9700	C22—H22	0.9300
C9—N1	1.273 (2)	C23—C24	1.501 (3)
C9—C10	1.445 (3)	C24—N2	1.497 (3)
C9—H9	0.9300	C24—H24A	0.9700
C10—C15	1.392 (3)	C24—H24B	0.9700
C10—C11	1.397 (3)	Cl3—Zn1	2.2495 (6)
C11—C12	1.377 (3)	Cl2—Zn1	2.2639 (6)
C11—H11	0.9300	Cl1—Zn1	2.2903 (8)
C12—C13	1.369 (3)	Cl4—Zn1	2.2664 (7)
C12—H12	0.9300	N1—H1	0.893 (14)
C13—C14	1.373 (3)	N2—H2A	0.8900
C13—H13	0.9300	N2—H2B	0.8900
C14—C15	1.391 (3)	N2—H2C	0.8900
C14—H14	0.9300	O4—H4B	0.801 (17)
C15—O2	1.357 (2)	O4—H4A	0.795 (17)
O1—C1—H1A	109.5	H16A—C16—H16B	109.5
O1—C1—H1B	109.5	O2—C16—H16C	109.5
H1A—C1—H1B	109.5	H16A—C16—H16C	109.5
O1—C1—H1C	109.5	H16B—C16—H16C	109.5
H1A—C1—H1C	109.5	O3—C17—H17A	109.5
H1B—C1—H1C	109.5	O3—C17—H17B	109.5
O1—C2—C3	125.4 (2)	H17A—C17—H17B	109.5
O1—C2—C7	114.2 (2)	O3—C17—H17C	109.5
C3—C2—C7	120.4 (2)	H17A—C17—H17C	109.5
C2—C3—C4	120.2 (2)	H17B—C17—H17C	109.5
C2—C3—H3	119.9	O3—C18—C23	114.11 (19)
C4—C3—H3	119.9	O3—C18—C19	124.9 (2)
C5—C4—C3	120.3 (2)	C23—C18—C19	121.0 (2)
C5—C4—H4	119.9	C20—C19—C18	119.1 (2)
C3—C4—H4	119.9	C20—C19—H19	120.4
C4—C5—C6	119.6 (2)	C18—C19—H19	120.4
C4—C5—H5	120.2	C21—C20—C19	120.4 (3)
C6—C5—H5	120.2	C21—C20—H20	119.8
C5—C6—C7	121.5 (2)	C19—C20—H20	119.8
C5—C6—H6	119.3	C20—C21—C22	120.1 (3)
C7—C6—H6	119.3	C20—C21—H21	120.0
C6—C7—C2	118.0 (2)	C22—C21—H21	120.0

C6—C7—C8	121.79 (19)	C21—C22—C23	121.0 (3)
C2—C7—C8	120.23 (18)	C21—C22—H22	119.5
N1—C8—C7	110.25 (16)	C23—C22—H22	119.5
N1—C8—H8A	109.6	C18—C23—C22	118.4 (2)
C7—C8—H8A	109.6	C18—C23—C24	120.1 (2)
N1—C8—H8B	109.6	C22—C23—C24	121.5 (2)
C7—C8—H8B	109.6	N2—C24—C23	113.39 (18)
H8A—C8—H8B	108.1	N2—C24—H24A	108.9
N1—C9—C10	127.33 (18)	C23—C24—H24A	108.9
N1—C9—H9	116.3	N2—C24—H24B	108.9
C10—C9—H9	116.3	C23—C24—H24B	108.9
C15—C10—C11	118.40 (18)	H24A—C24—H24B	107.7
C15—C10—C9	124.36 (18)	C9—N1—C8	124.65 (17)
C11—C10—C9	117.20 (18)	C9—N1—H1	120.6 (13)
C12—C11—C10	121.4 (2)	C8—N1—H1	114.6 (13)
C12—C11—H11	119.3	C24—N2—H2A	109.5
C10—C11—H11	119.3	C24—N2—H2B	109.5
C13—C12—C11	118.8 (2)	H2A—N2—H2B	109.5
C13—C12—H12	120.6	C24—N2—H2C	109.5
C11—C12—H12	120.6	H2A—N2—H2C	109.5
C12—C13—C14	121.8 (2)	H2B—N2—H2C	109.5
C12—C13—H13	119.1	C2—O1—C1	118.18 (19)
C14—C13—H13	119.1	C15—O2—C16	119.14 (17)
C13—C14—C15	119.4 (2)	C18—O3—C17	119.08 (19)
C13—C14—H14	120.3	H4B—O4—H4A	115 (3)
C15—C14—H14	120.3	Cl3—Zn1—Cl2	111.78 (2)
O2—C15—C14	123.99 (19)	Cl3—Zn1—Cl4	108.77 (3)
O2—C15—C10	115.83 (17)	Cl2—Zn1—Cl4	110.35 (3)
C14—C15—C10	120.17 (19)	Cl3—Zn1—Cl1	104.45 (3)
O2—C16—H16A	109.5	Cl2—Zn1—Cl1	111.19 (3)
O2—C16—H16B	109.5	Cl4—Zn1—Cl1	110.14 (3)
O1—C2—C3—C4	−178.8 (2)	C11—C10—C15—C14	−0.7 (3)
C7—C2—C3—C4	0.5 (3)	C9—C10—C15—C14	177.2 (2)
C2—C3—C4—C5	0.3 (4)	O3—C18—C19—C20	179.4 (2)
C3—C4—C5—C6	−1.0 (4)	C23—C18—C19—C20	0.5 (4)
C4—C5—C6—C7	0.9 (3)	C18—C19—C20—C21	0.8 (4)
C5—C6—C7—C2	−0.2 (3)	C19—C20—C21—C22	−0.9 (5)
C5—C6—C7—C8	179.77 (18)	C20—C21—C22—C23	−0.4 (4)
O1—C2—C7—C6	178.82 (17)	O3—C18—C23—C22	179.3 (2)
C3—C2—C7—C6	−0.5 (3)	C19—C18—C23—C22	−1.7 (4)
O1—C2—C7—C8	−1.1 (3)	O3—C18—C23—C24	−3.2 (3)
C3—C2—C7—C8	179.54 (18)	C19—C18—C23—C24	175.8 (2)
C6—C7—C8—N1	108.7 (2)	C21—C22—C23—C18	1.6 (4)
C2—C7—C8—N1	−71.3 (2)	C21—C22—C23—C24	−175.8 (2)
N1—C9—C10—C15	7.4 (3)	C18—C23—C24—N2	64.7 (3)
N1—C9—C10—C11	−174.7 (2)	C22—C23—C24—N2	−117.9 (2)
C15—C10—C11—C12	0.7 (3)	C10—C9—N1—C8	−174.76 (19)
C9—C10—C11—C12	−177.4 (2)	C7—C8—N1—C9	108.3 (2)
C10—C11—C12—C13	0.0 (3)	C3—C2—O1—C1	5.8 (3)

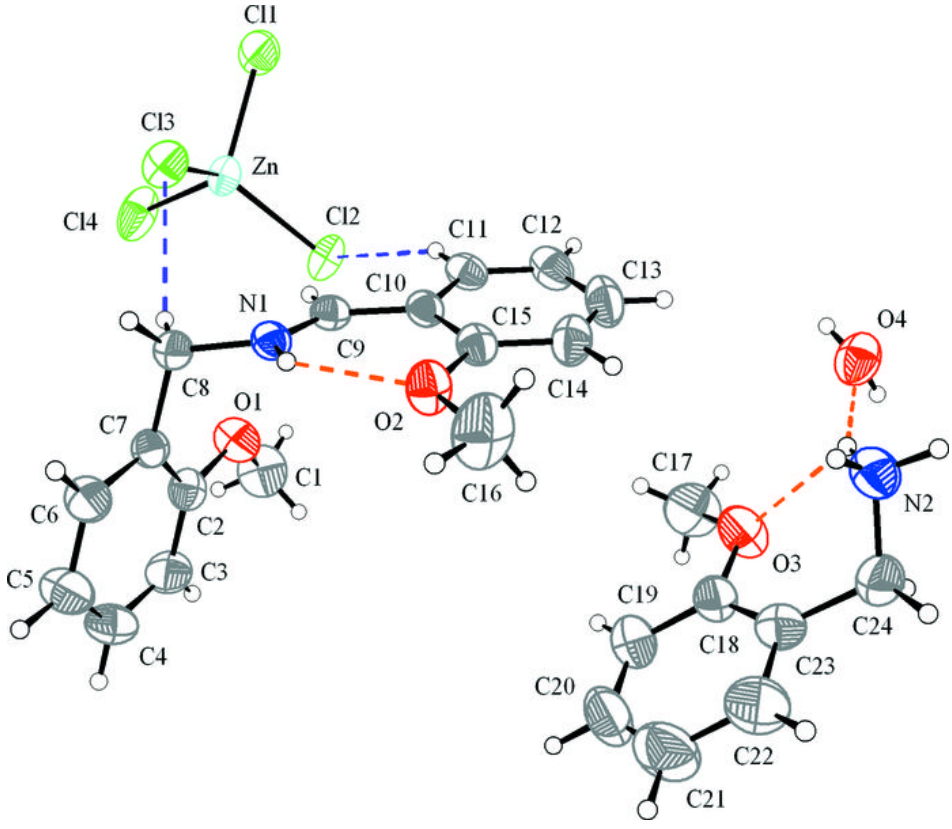
C11—C12—C13—C14	−0.8 (4)	C7—C2—O1—C1	−173.46 (18)
C12—C13—C14—C15	0.8 (4)	C14—C15—O2—C16	3.6 (3)
C13—C14—C15—O2	178.8 (2)	C10—C15—O2—C16	−177.5 (2)
C13—C14—C15—C10	−0.1 (3)	C23—C18—O3—C17	175.7 (2)
C11—C10—C15—O2	−179.57 (19)	C19—C18—O3—C17	−3.3 (4)
C9—C10—C15—O2	−1.7 (3)		

Hydrogen-bond geometry (Å, °)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
N1—H1···O2	0.89 (1)	2.07 (2)	2.680 (2)	125.(2)
N1—H1···Cl2^{i}	0.89 (1)	2.64 (2)	3.3221 (18)	135.(2)
N2—H2A···O4	0.89	2.30	3.102 (3)	151
N2—H2A···O3	0.89	2.37	2.877 (2)	116
N2—H2B···O4^{ii}	0.89	2.04	2.881 (3)	158
N2—H2B···Cl3^{iii}	0.89	2.98	3.502 (2)	120
N2—H2C···Cl1^{iv}	0.89	2.45	3.306 (2)	162
O4—H4B···Cl4^{iii}	0.80 (2)	2.44 (2)	3.2323 (19)	168 (3)
O4—H4A···Cl1^{v}	0.80 (2)	2.72 (2)	3.4165 (19)	147 (3)
C8—H8A···Cl3	0.97	2.67	3.474 (2)	140
C11—H11···Cl2	0.93	2.82	3.687 (2)	155
C24—H24A···Cl4^{vi}	0.97	2.76	3.707 (3)	166

Symmetry codes: (i) *x*+1, *y*, *z*; (ii) −*x*+1, −*y*+1, −*z*; (iii) *x*, *y*, *z*−1; (iv) −*x*+1, −*y*+1, −*z*+1; (v) −*x*, −*y*+1, −*z*+1; (vi) *x*+1, *y*, *z*−1.

Fig. 1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Cl4
Cl2
C11
C12
C13
C10
N1
C15
C9
C14
O2
C8
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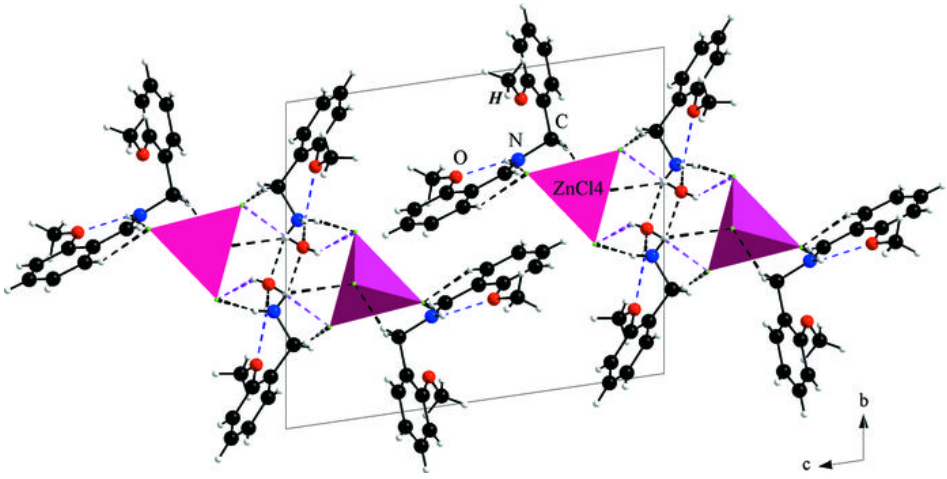
C7
C16
C1
C6
C2
C5
C3
C4
O4
C17
N2
O3
C19
C24
C18
C23
C20
C22
C21

Fig. 2



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N′-(4-Cyanobenzylidene)furan-2-carbohydrazide monohydrate

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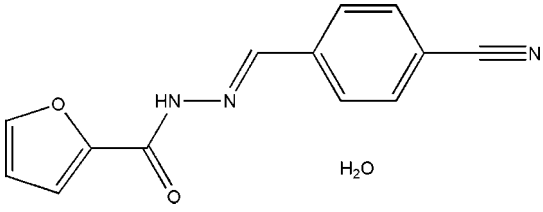
Key indicators: single-crystal X-ray study; T = 293 K; mean σ(C–C) = 0.003 Å; R factor = 0.048; wR factor = 0.135; data-to-parameter ratio = 15.7.

In the title compound, $C_{13}H_9N_3O_2\cdot H_2O$, the dihedral angle between the aromatic rings is 10.7 (4)° and an intramolecular N—H···O hydrogen bond occurs. In the crystal, the components are linked by N—H···O, O—H···N and O—H···O hydrogen bonds.

Related literature

For a related structure and background references, see: Li *et al.* (2010).



Experimental

Crystal data

$C_{13}H_9N_3O_2\cdot H_2O$
M_r = 257.25
Monoclinic, $P2_1/n$
a = 7.0501 (14) Å
b = 14.295 (3) Å
c = 12.640 (3) Å
β = 103.38 (3)°
V = 1239.3 (4) Å^3
Z = 4
Mo $K\alpha$ radiation
μ = 0.10 mm^{-1}
T = 293 K
0.22 × 0.20 × 0.18 mm

Data collection

Bruker SMART CCD diffractometer
11389 measured reflections
2834 independent reflections
1568 reflections with $I > 2\sigma(I)$
R_{int} = 0.043

Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.048
$wR(F^2)$ = 0.135
S = 0.98
2834 reflections
180 parameters
H atoms treated by a mixture of independent and constrained refinement
$\Delta\rho_{max}$ = 0.24 e Å^{-3}
$\Delta\rho_{min}$ = −0.16 e Å^{-3}

Table 1
Hydrogen-bond geometry (Å, °).

D—H···A	D—H	H···A	D···A	D—H···A
N1—H1A···O1	0.86	2.33	2.692 (2)	106
N1—H1A···O3	0.86	2.07	2.920 (2)	169
O3—H3B···N3^{i}	1.00 (4)	1.99 (4)	2.980 (2)	172 (3)
O3—H3C···O2^{ii}	0.88 (3)	1.98 (3)	2.848 (2)	171 (3)

Symmetry codes: (i) $x-\frac{1}{2}, -y+\frac{3}{2}, z-\frac{1}{2}$; (ii) $x-\frac{1}{2}, -y+\frac{1}{2}, z-\frac{1}{2}$.

Data collection: *SMART* (Bruker, 1997); cell refinement: *SAINT* (Bruker, 1997); data reduction: *SAINT*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *SHELXTL* (Sheldrick, 2008); software used to prepare material for publication: *SHELXTL*.

Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: HB5490).

References

Bruker (1997). *SMART* and *SAINT*. Bruker AXS Inc., Madison, Wisconsin, USA.
Li, Y.-F., Zhang, F.-G. & Jian, F.-F. (2010). *Acta Cryst.* E**66**, o1471.
Sheldrick, G. M. (2008). *Acta Cryst.* A**64**, 112–122.

supplementary materials

Acta Cryst. (2010). E**66**, o1670 [**doi:10.1107/S1600536810022221**]

N'-(4-Cyanobenzylidene)furan-2-carbohydrazide monohydrate

Y.-F. Li and F.-F. Jian

Experimental

A mixture of 4-formylbenzonitrile (0.1 mol), and furan-2-carbohydrazide (0.1 mol) was stirred in refluxing ethanol (20 mL) for 2 h to afford the title compound (0.090 mol, yield 90%). Colourless blocks of (I) were obtained by recrystallization from ethanol at room temperature.

Refinement

H atoms were fixed geometrically and allowed to ride on their attached atoms, with C—H distances=0.97 Å, and with U_{iso}=1.2–1.5U_{eq}.

Figures

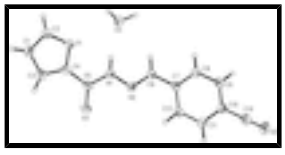


Fig. 1. The structure of the title compound showing 30% probability displacement ellipsoids.

N'-(4-Cyanobenzylidene)furan-2-carbohydrazide monohydrate

Crystal data

$C_{13}H_9N_3O_2·H_2O$	$F(000)$ = 536
M_r = 257.25	D_x = 1.379 Mg m^{-3}
Monoclinic, $P2_1/n$	Mo $K\alpha$ radiation, λ = 0.71073 Å
Hall symbol: -P 2yn	Cell parameters from 1568 reflections
a = 7.0501 (14) Å	θ = 2.7–25.5°
b = 14.295 (3) Å	μ = 0.10 mm^{-1}
c = 12.640 (3) Å	T = 293 K
β = 103.38 (3)°	Block, colorless
V = 1239.3 (4) Å^3	0.22 × 0.20 × 0.18 mm
Z = 4	

Data collection

Bruker SMART CCD diffractometer	1568 reflections with $I > 2\sigma(I)$
Radiation source: fine-focus sealed tube	R_{int} = 0.043
graphite	θ_{max} = 27.5°, θ_{min} = 3.3°

φ and ω scans	$h = -8 \rightarrow 9$
11389 measured reflections	$k = -18 \rightarrow 18$
2834 independent reflections	$l = -16 \rightarrow 16$

Refinement

Refinement on F^2	Primary atom site location: structure-invariant direct methods
Least-squares matrix: full	Secondary atom site location: difference Fourier map
$R[F^2 > 2\sigma(F^2)] = 0.048$	Hydrogen site location: inferred from neighbouring sites
$wR(F^2) = 0.135$	H atoms treated by a mixture of independent and constrained refinement
$S = 0.98$	$w = 1/[\sigma^2(F_o^2) + (0.0694P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
2834 reflections	$(\Delta/\sigma)_{max} < 0.001$
180 parameters	$\Delta\rho_{max} = 0.24$ e Å^{-3}
0 restraints	$\Delta\rho_{min} = -0.16$ e Å^{-3}

Special details

Geometry. All e.s.d.'s (except the e.s.d. in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell e.s.d.'s are taken into account individually in the estimation of e.s.d.'s in distances, angles and torsion angles; correlations between e.s.d.'s in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell e.s.d.'s is used for estimating e.s.d.'s involving l.s. planes.

Refinement. Refinement of F^2 against ALL reflections. The weighted *R*-factor *wR* and goodness of fit *S* are based on F^2, conventional *R*-factors *R* are based on *F*, with *F* set to zero for negative F^2. The threshold expression of $F^2 > \sigma(F^2)$ is used only for calculating *R*-factors(gt) *etc*. and is not relevant to the choice of reflections for refinement. *R*-factors based on F^2 are statistically about twice as large as those based on *F*, and *R*- factors based on ALL data will be even larger.

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å^2)

	x	*y*	*z*	U_{iso}*/U_{eq}
N2	0.2572 (2)	0.42473 (10)	0.51829 (12)	0.0431 (4)
N1	0.2142 (2)	0.34390 (9)	0.45997 (12)	0.0440 (4)
H1A	0.1704	0.3458	0.3906	0.053*
O1	0.10154 (18)	0.19128 (9)	0.33670 (10)	0.0526 (4)
C6	0.2239 (3)	0.50009 (12)	0.46228 (15)	0.0461 (5)
H6A	0.1747	0.4964	0.3875	0.055*
C4	0.1844 (3)	0.17816 (13)	0.44486 (15)	0.0442 (5)
O3	0.0883 (2)	0.37589 (11)	0.22607 (12)	0.0654 (5)
C13	0.3865 (3)	0.85907 (14)	0.65549 (17)	0.0548 (5)
O2	0.3075 (2)	0.25365 (9)	0.61179 (11)	0.0595 (4)
C12	0.3138 (3)	0.60216 (13)	0.62661 (16)	0.0525 (5)
H12A	0.3218	0.5497	0.6709	0.063*
C7	0.2620 (3)	0.59186 (12)	0.51417 (15)	0.0420 (4)
C5	0.2414 (3)	0.26093 (12)	0.51272 (15)	0.0436 (4)

C8	0.2453 (3)	0.67132 (13)	0.44979 (16)	0.0518 (5)
H8A	0.2069	0.6655	0.3746	0.062*
C11	0.3534 (3)	0.68908 (13)	0.67294 (16)	0.0551 (5)
H11A	0.3887	0.6952	0.7482	0.066*
C10	0.3405 (3)	0.76786 (12)	0.60708 (16)	0.0453 (5)
C2	0.0589 (3)	0.10477 (13)	0.29261 (18)	0.0566 (6)
H2B	0.0003	0.0931	0.2200	0.068*
N3	0.4234 (3)	0.93164 (12)	0.69148 (17)	0.0721 (6)
C1	0.1133 (3)	0.03943 (15)	0.36854 (18)	0.0654 (6)
H1B	0.1006	−0.0249	0.3588	0.078*
C9	0.2850 (3)	0.75903 (13)	0.49571 (16)	0.0521 (5)
H9A	0.2741	0.8118	0.4516	0.062*
C3	0.1943 (3)	0.08674 (13)	0.46686 (18)	0.0617 (6)
H3A	0.2449	0.0593	0.5342	0.074*
H3B	0.025 (5)	0.438 (3)	0.208 (3)	0.156 (14)*
H3C	−0.005 (4)	0.337 (2)	0.197 (3)	0.120 (12)*

Atomic displacement parameters (Å^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
N2	0.0504 (9)	0.0360 (8)	0.0404 (9)	0.0034 (7)	0.0056 (7)	−0.0056 (7)
N1	0.0572 (9)	0.0360 (8)	0.0346 (9)	0.0018 (7)	0.0023 (7)	−0.0016 (6)
O1	0.0708 (9)	0.0435 (7)	0.0389 (8)	−0.0040 (7)	0.0030 (6)	0.0018 (6)
C6	0.0560 (11)	0.0405 (10)	0.0384 (11)	0.0028 (9)	0.0037 (8)	−0.0023 (8)
C4	0.0466 (10)	0.0473 (11)	0.0366 (11)	0.0005 (9)	0.0052 (8)	0.0017 (8)
O3	0.0897 (11)	0.0468 (9)	0.0497 (9)	−0.0047 (9)	−0.0044 (8)	0.0021 (7)
C13	0.0600 (12)	0.0438 (11)	0.0576 (13)	0.0031 (10)	0.0073 (10)	−0.0013 (10)
O2	0.0829 (10)	0.0532 (8)	0.0369 (8)	0.0059 (7)	0.0026 (7)	0.0064 (6)
C12	0.0739 (14)	0.0408 (10)	0.0418 (11)	0.0062 (10)	0.0114 (10)	0.0024 (8)
C7	0.0435 (10)	0.0381 (10)	0.0428 (11)	0.0050 (8)	0.0072 (8)	−0.0002 (8)
C5	0.0451 (10)	0.0468 (11)	0.0377 (11)	0.0064 (9)	0.0074 (8)	0.0064 (8)
C8	0.0653 (12)	0.0467 (11)	0.0392 (12)	0.0028 (9)	0.0038 (9)	−0.0003 (8)
C11	0.0768 (14)	0.0483 (11)	0.0369 (11)	0.0042 (10)	0.0064 (10)	−0.0036 (9)
C10	0.0469 (10)	0.0383 (10)	0.0490 (12)	0.0020 (8)	0.0077 (8)	−0.0048 (8)
C2	0.0708 (14)	0.0460 (11)	0.0488 (12)	−0.0087 (10)	0.0052 (10)	−0.0062 (9)
N3	0.0868 (14)	0.0448 (11)	0.0786 (14)	−0.0037 (10)	0.0064 (11)	−0.0129 (9)
C1	0.0812 (15)	0.0401 (11)	0.0656 (15)	−0.0037 (11)	−0.0021 (12)	−0.0018 (10)
C9	0.0625 (12)	0.0396 (10)	0.0513 (13)	0.0008 (9)	0.0075 (10)	0.0067 (9)
C3	0.0757 (14)	0.0430 (11)	0.0575 (14)	0.0020 (10)	−0.0030 (11)	0.0125 (9)

Geometric parameters (Å, °)

N2—C6	1.281 (2)	C12—C11	1.374 (3)
N2—N1	1.3664 (18)	C12—C7	1.391 (3)
N1—C5	1.352 (2)	C12—H12A	0.9300
N1—H1A	0.8600	C7—C8	1.386 (2)
O1—C2	1.361 (2)	C8—C9	1.383 (2)
O1—C4	1.370 (2)	C8—H8A	0.9300
C6—C7	1.464 (2)	C11—C10	1.391 (3)

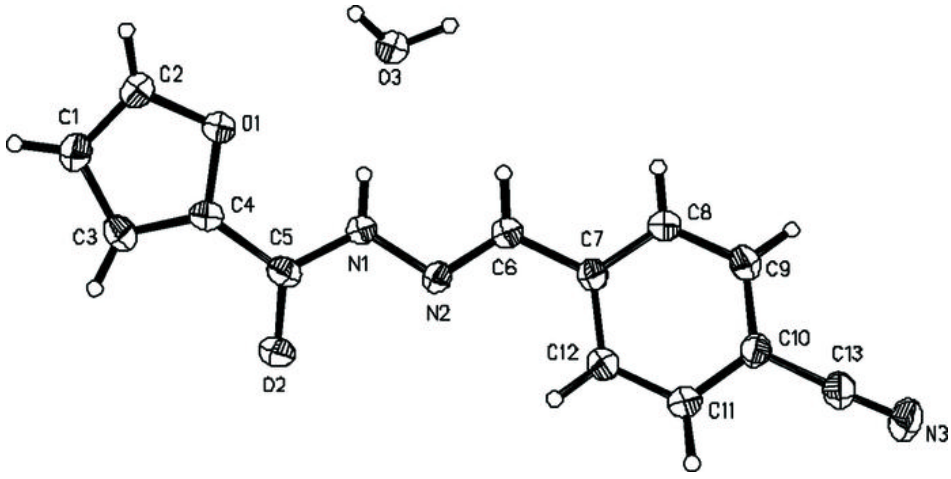
C6—H6A	0.9300	C11—H11A	0.9300
C4—C3	1.335 (2)	C10—C9	1.377 (3)
C4—C5	1.462 (2)	C2—C1	1.331 (3)
O3—H3B	1.00 (4)	C2—H2B	0.9300
O3—H3C	0.87 (3)	C1—C3	1.414 (3)
C13—N3	1.139 (2)	C1—H1B	0.9300
C13—C10	1.445 (3)	C9—H9A	0.9300
O2—C5	1.235 (2)	C3—H3A	0.9300
C6—N2—N1	115.07 (15)	C9—C8—C7	121.00 (18)
C5—N1—N2	119.16 (15)	C9—C8—H8A	119.5
C5—N1—H1A	120.4	C7—C8—H8A	119.5
N2—N1—H1A	120.4	C12—C11—C10	119.89 (18)
C2—O1—C4	106.68 (15)	C12—C11—H11A	120.1
N2—C6—C7	121.01 (17)	C10—C11—H11A	120.1
N2—C6—H6A	119.5	C9—C10—C11	120.09 (17)
C7—C6—H6A	119.5	C9—C10—C13	119.90 (17)
C3—C4—O1	109.38 (16)	C11—C10—C13	120.01 (18)
C3—C4—C5	132.55 (18)	C1—C2—O1	110.06 (19)
O1—C4—C5	118.07 (15)	C1—C2—H2B	125.0
H3B—O3—H3C	102 (3)	O1—C2—H2B	125.0
N3—C13—C10	178.5 (2)	C2—C1—C3	106.77 (19)
C11—C12—C7	120.69 (17)	C2—C1—H1B	126.6
C11—C12—H12A	119.7	C3—C1—H1B	126.6
C7—C12—H12A	119.7	C10—C9—C8	119.63 (17)
C8—C7—C12	118.66 (16)	C10—C9—H9A	120.2
C8—C7—C6	119.31 (17)	C8—C9—H9A	120.2
C12—C7—C6	122.03 (16)	C4—C3—C1	107.11 (19)
O2—C5—N1	123.42 (16)	C4—C3—H3A	126.4
O2—C5—C4	120.96 (16)	C1—C3—H3A	126.4
N1—C5—C4	115.60 (16)		

Hydrogen-bond geometry (Å, °)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
N1—H1A···O1	0.86	2.33	2.692 (2)	106
N1—H1A···O3	0.86	2.07	2.920 (2)	169
O3—H3B···N3^{i}	1.00 (4)	1.99 (4)	2.980 (2)	172 (3)
O3—H3C···O2^{ii}	0.88 (3)	1.98 (3)	2.848 (2)	171 (3)

Symmetry codes: (i) *x*−1/2, −*y*+3/2, *z*−1/2; (ii) *x*−1/2, −*y*+1/2, *z*−1/2.

Fig. 1



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1-Chloromethyl-4-nitrobenzene

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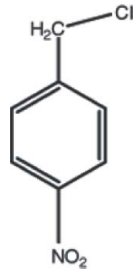
Key indicators: single-crystal X-ray study; T = 296 K; mean σ(C–C) = 0.003 Å; R factor = 0.041; wR factor = 0.103; data-to-parameter ratio = 18.2.

In the title compound, $C_7H_6ClNO_2$, the nitro group is almost coplanar with the aromatic ring [dihedral angle = 2.9 (2)°], but the Cl atom deviates from the ring plane by 1.129 (1) Å. In the crystal, molecules are linked by weak C—H···O interactions to generate chains.

Related literature

For background on the toxicity of nitro-aromatic compounds, see: Moreno *et al.* (1986). For the synthesis of the title compound, see: Livermore & Sealock (1947). For bond-length data, see: Allen *et al.* (1987).



Experimental

Crystal data

$C_7H_6ClNO_2$
M_r = 171.58
Orthorhombic, $P2_12_12_1$
a = 4.7434 (1) Å
b = 6.4189 (2) Å
c = 24.9413 (11) Å
V = 759.40 (4) Å^3
Z = 4
Mo $K\alpha$ radiation
μ = 0.45 mm^{-1}
T = 296 K
0.35 × 0.11 × 0.10 mm

Data collection

Bruker APEXII CCD diffractometer
4389 measured reflections
1816 independent reflections
1586 reflections with $I > 2\sigma(I)$
R_{int} = 0.018

Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.041
$wR(F^2)$ = 0.103
S = 1.04
1816 reflections
100 parameters
H-atom parameters constrained
$\Delta\rho_{max}$ = 0.33 e Å^{-3}
$\Delta\rho_{min}$ = −0.34 e Å^{-3}
Absolute structure: Flack (1983), 662 Freidel pairs
Flack parameter: 0.02 (11)

Table 1
Hydrogen-bond geometry (Å, °).

D—H···A	D—H	H···A	D···A	D—H···A
C7—H7B···O1^{i}	0.97	2.48	3.396 (3)	158

Symmetry code: (i) $x-1, y+1, z$.

Data collection: *APEX2* (Bruker, 2007); cell refinement: *SAINT* (Bruker, 2007); data reduction: *SAINT*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *ORTEP-3* (Farrugia, 1997); software used to prepare material for publication: *WinGX* (Farrugia, 1999), *PARST* (Nardelli, 1983) and *PLATON* (Spek, 2009).

The authors are grateful to the Higher Education Commission for providing financial support. Professor Islam Ullah Khan is also gratefully acknowledged for providing single-crystal X-ray diffraction facilities at the Materials Chemistry Laboratory, GC University Lahore.

Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: HB5491).

References

Allen, F. H., Kennard, O., Watson, D. G., Brammer, L., Orpen, A. G. & Taylor, R. (1987). *J. Chem. Soc. Perkin Trans. 2*, pp. S1–19.
Bruker (2007). *APEX2* and *SAINT*. Bruker AXS Inc., Madison, Wisconsin, USA.
Farrugia, L. J. (1997). *J. Appl. Cryst.* **30**, 565.
Farrugia, L. J. (1999). *J. Appl. Cryst.* **32**, 837–838.
Flack, H. D. (1983). *Acta Cryst.* A**39**, 876–881.
Livermore, A. H. & Sealock, R. R. (1947). *J. Biol. Chem.* **167**, 699–704.
Moreno, S. N. J., Schreiber, J. & Mason, R. P. (1986). *J. Biol. Chem.* **261**, 7811–7815.
Nardelli, M. (1983). *Comput. Chem.* **7**, 95–98.
Sheldrick, G. M. (2008). *Acta Cryst.* A**64**, 112–122.
Spek, A. L. (2009). *Acta Cryst.* D**65**, 148–155.

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supplementary materials

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1-Chloromethyl-4-nitrobenzene

Aziz-ur-Rehman, A. Yasir, M. Akkurt, M. A. Abbasi, M. Jahangir and I. U. Khan

Comment

The irreversible binding of the reductive intermediates of nitroaromatic compounds to protein and DNA is thought to be responsible for the carcinogenicity and mutagenicity of this class of compounds. Several studies revealed that some nitro radical metabolites with special features are expected to decompose to form neutral carbon-centered free radicals with not net reduction of the nitro group occurring. The radicals anions of *p*-and *o*-nitrobenzyl chloride are known to expel chloride to form the corresponding carbon-centered nitrobenzyl radicals with rate constants of 1 × 104 and 4 × 103 s^{-1}. Such species are highly reactive and could account for the unusual cytotoxicity of these nitrocompounds (Moreno *et al.*, 1986). This structural report on 1-(chloromethyl)-4-nitrobenzene (*p*-nitrobenzyl chloride) might be helpful to carry out such studies on these nitroaromatic compounds in future.

The title molecule (I), (Fig. 1), is non-planar and the dihedral angle between the plane of the NO_2 group and benzene (C1–C6) ring is 2.9 (2)°, while the C5—C4—C7—Cl1 torsion angle is 83.8 (2)°. In (I), the bond lengths (Allen *et al.*, 1987) and angles have values within the normal ranges.

In the crystal structure, there is no classic hydrogen bonds. A weak intermolecular C—H···O interaction contrubutes to the stability of the structure (Table 1, Fig. 2).

Experimental

The title *p*-nitrobenzyl chloride was prepared by adding 5.3 ml of benzyl chloride slowly and with stirring to 27.5 ml of a mixture of equal parts of concentrated nitric and sulfuric acids cooled to 283 K. The temperature rose to 303 K during the 10 min required for the addition. The mixture was stirred for 30 min and then poured into 50 g of crushed ice. The crude material was recrystallized from ethanol. Product obtained was dissolved in ethanol and crystallized by slow evaporation of the solvent to yield colourless needles of (I) in an over-all yield of 46% (Livermore & Sealock, 1947).

Refinement

H atoms were positioned geometrically (C—H = 0.93 and 0.97 Å) and allowed to ride on their parent atoms, with U_{iso}(H) = 1.2U_{eq}(C).

Figures

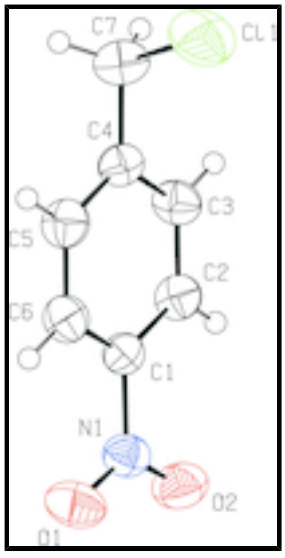


Fig. 1. View of the title molecule, with displacement ellipsoids drawn at the 50% probability level.

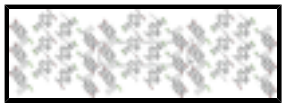


Fig. 2. The crystal packing and the hydrogen bonding of (I) viewed down the *a*-axis. H-atoms not involved in hydrogen bonds have been omitted for clarity.

1-Chloromethyl-4-nitrobenzene

Crystal data

$C_7H_6ClNO_2$	$F(000) = 352$
$M_r = 171.58$	$D_x = 1.501$ Mg m^{-3}
Orthorhombic, $P2_12_12_1$	Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å
Hall symbol: P 2ac 2ab	Cell parameters from 1957 reflections
$a = 4.7434$ (1) Å	$\theta = 3.3$–$26.7°$
$b = 6.4189$ (2) Å	$\mu = 0.45$ mm^{-1}
$c = 24.9413$ (11) Å	$T = 296$ K
$V = 759.40$ (4) Å^3	Needle, colourless
$Z = 4$	0.35 × 0.11 × 0.10 mm

Data collection

Bruker APEXII CCD diffractometer	1586 reflections with $I > 2\sigma(I)$
Radiation source: sealed tube	$R_{int} = 0.018$
graphite	$\theta_{max} = 28.3°$, $\theta_{min} = 3.3°$
φ and ω scans	$h = -5 \rightarrow 6$
4389 measured reflections	$k = -8 \rightarrow 5$
1816 independent reflections	$l = -33 \rightarrow 17$

Refinement

Refinement on F^2	Secondary atom site location: difference Fourier map
Least-squares matrix: full	Hydrogen site location: inferred from neighbouring sites
$R[F^2 > 2\sigma(F^2)] = 0.041$	H-atom parameters constrained
$wR(F^2) = 0.103$	$w = 1/[\sigma^2(F_o^2) + (0.049P)^2 + 0.1709P]$ where $P = (F_o^2 + 2F_c^2)/3$
$S = 1.04$	$(\Delta/\sigma)_{max} < 0.001$
1816 reflections	$\Delta\rho_{max} = 0.33$ e Å^{-3}
100 parameters	$\Delta\rho_{min} = -0.34$ e Å^{-3}
0 restraints	Absolute structure: Flack (1983), 662 Freidel pairs
Primary atom site location: structure-invariant direct methods	Flack parameter: 0.02 (11)

Special details

Geometry. Bond distances, angles *etc*. have been calculated using the rounded fractional coordinates. All su's are estimated from the variances of the (full) variance-covariance matrix. The cell e.s.d.'s are taken into account in the estimation of distances, angles and torsion angles

Refinement. Refinement on F^2 for ALL reflections except those flagged by the user for potential systematic errors. Weighted *R*-factors *wR* and all goodnesses of fit *S* are based on F^2, conventional *R*-factors *R* are based on *F*, with *F* set to zero for negative F^2. The observed criterion of $F^2 > \sigma(F^2)$ is used only for calculating -*R*-factor-obs *etc*. and is not relevant to the choice of reflections for refinement. *R*-factors based on F^2 are statistically about twice as large as those based on *F*, and *R*-factors based on ALL data will be even larger.

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å^2)

	x	*y*	*z*	U_{iso}*/U_{eq}
Cl1	0.75015 (18)	0.45250 (12)	0.22343 (3)	0.0812 (3)
O1	1.4188 (4)	−0.3381 (3)	0.07002 (7)	0.0621 (6)
O2	1.4761 (4)	−0.0854 (3)	0.01453 (7)	0.0601 (6)
N1	1.3647 (3)	−0.1634 (3)	0.05351 (7)	0.0434 (5)
C1	1.1532 (4)	−0.0398 (3)	0.08269 (7)	0.0364 (5)
C2	1.0829 (4)	0.1540 (3)	0.06377 (7)	0.0421 (6)
C3	0.8901 (4)	0.2704 (3)	0.09215 (8)	0.0437 (6)
C4	0.7690 (4)	0.1928 (3)	0.13883 (7)	0.0393 (5)
C5	0.8402 (5)	−0.0046 (3)	0.15629 (8)	0.0472 (6)
C6	1.0341 (5)	−0.1235 (3)	0.12836 (8)	0.0459 (6)
C7	0.5663 (5)	0.3213 (4)	0.17034 (8)	0.0533 (7)
H2	1.16370	0.20560	0.03250	0.0510*
H3	0.84040	0.40230	0.08000	0.0520*
H5	0.75690	−0.05800	0.18710	0.0570*
H6	1.08280	−0.25630	0.14000	0.0550*
H7A	0.42040	0.23280	0.18530	0.0640*
H7B	0.47710	0.42290	0.14710	0.0640*

Atomic displacement parameters (Å^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Cl1	0.0957 (5)	0.0831 (5)	0.0647 (4)	0.0041 (4)	0.0047 (4)	−0.0299 (3)
O1	0.0677 (11)	0.0514 (9)	0.0671 (10)	0.0222 (8)	−0.0024 (8)	0.0041 (8)
O2	0.0584 (10)	0.0629 (11)	0.0591 (9)	0.0072 (8)	0.0175 (8)	0.0010 (8)
N1	0.0412 (8)	0.0450 (9)	0.0440 (8)	0.0046 (8)	−0.0047 (7)	−0.0051 (7)
C1	0.0336 (8)	0.0382 (9)	0.0374 (8)	0.0008 (7)	−0.0048 (7)	−0.0001 (7)
C2	0.0446 (10)	0.0451 (11)	0.0366 (9)	0.0024 (9)	0.0012 (7)	0.0076 (8)
C3	0.0496 (11)	0.0409 (10)	0.0406 (9)	0.0079 (9)	−0.0016 (8)	0.0079 (8)
C4	0.0362 (9)	0.0460 (10)	0.0357 (8)	0.0024 (9)	−0.0033 (7)	−0.0008 (7)
C5	0.0526 (11)	0.0495 (12)	0.0394 (9)	−0.0012 (9)	0.0046 (8)	0.0080 (8)
C6	0.0500 (11)	0.0405 (10)	0.0471 (10)	0.0015 (9)	0.0001 (9)	0.0084 (8)
C7	0.0510 (12)	0.0613 (13)	0.0475 (11)	0.0111 (12)	0.0033 (9)	−0.0004 (10)

Geometric parameters (Å, °)

Cl1—C7	1.795 (2)	C4—C7	1.491 (3)
O1—N1	1.222 (3)	C5—C6	1.383 (3)
O2—N1	1.215 (2)	C2—H2	0.9300
N1—C1	1.472 (3)	C3—H3	0.9300
C1—C2	1.372 (3)	C5—H5	0.9300
C1—C6	1.380 (3)	C6—H6	0.9300
C2—C3	1.377 (3)	C7—H7A	0.9700
C3—C4	1.391 (3)	C7—H7B	0.9700
C4—C5	1.382 (3)		
O1—N1—O2	123.83 (19)	C1—C2—H2	121.00
O1—N1—C1	118.12 (17)	C3—C2—H2	121.00
O2—N1—C1	118.05 (18)	C2—C3—H3	120.00
N1—C1—C2	118.98 (16)	C4—C3—H3	120.00
N1—C1—C6	118.51 (17)	C4—C5—H5	120.00
C2—C1—C6	122.51 (18)	C6—C5—H5	120.00
C1—C2—C3	118.48 (17)	C1—C6—H6	121.00
C2—C3—C4	120.69 (18)	C5—C6—H6	121.00
C3—C4—C5	119.43 (18)	Cl1—C7—H7A	110.00
C3—C4—C7	120.64 (18)	Cl1—C7—H7B	110.00
C5—C4—C7	119.93 (18)	C4—C7—H7A	110.00
C4—C5—C6	120.65 (18)	C4—C7—H7B	110.00
C1—C6—C5	118.22 (18)	H7A—C7—H7B	108.00
Cl1—C7—C4	109.58 (16)		
O1—N1—C1—C2	−177.90 (18)	C1—C2—C3—C4	−0.2 (3)
O1—N1—C1—C6	2.4 (3)	C2—C3—C4—C5	−1.0 (3)
O2—N1—C1—C2	2.4 (3)	C2—C3—C4—C7	178.30 (19)
O2—N1—C1—C6	−177.28 (19)	C3—C4—C5—C6	1.2 (3)
N1—C1—C2—C3	−178.37 (17)	C7—C4—C5—C6	−178.1 (2)
C6—C1—C2—C3	1.3 (3)	C3—C4—C7—Cl1	−95.5 (2)
N1—C1—C6—C5	178.55 (18)	C5—C4—C7—Cl1	83.8 (2)

C2—C1—C6—C5	−1.1 (3)	C4—C5—C6—C1	−0.2 (3)

Hydrogen-bond geometry (Å, °)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
C7—H7B···O1^{i}	0.97	2.48	3.396 (3)	158

Symmetry codes: (i) *x*−1, *y*+1, *z*.

Fig. 1

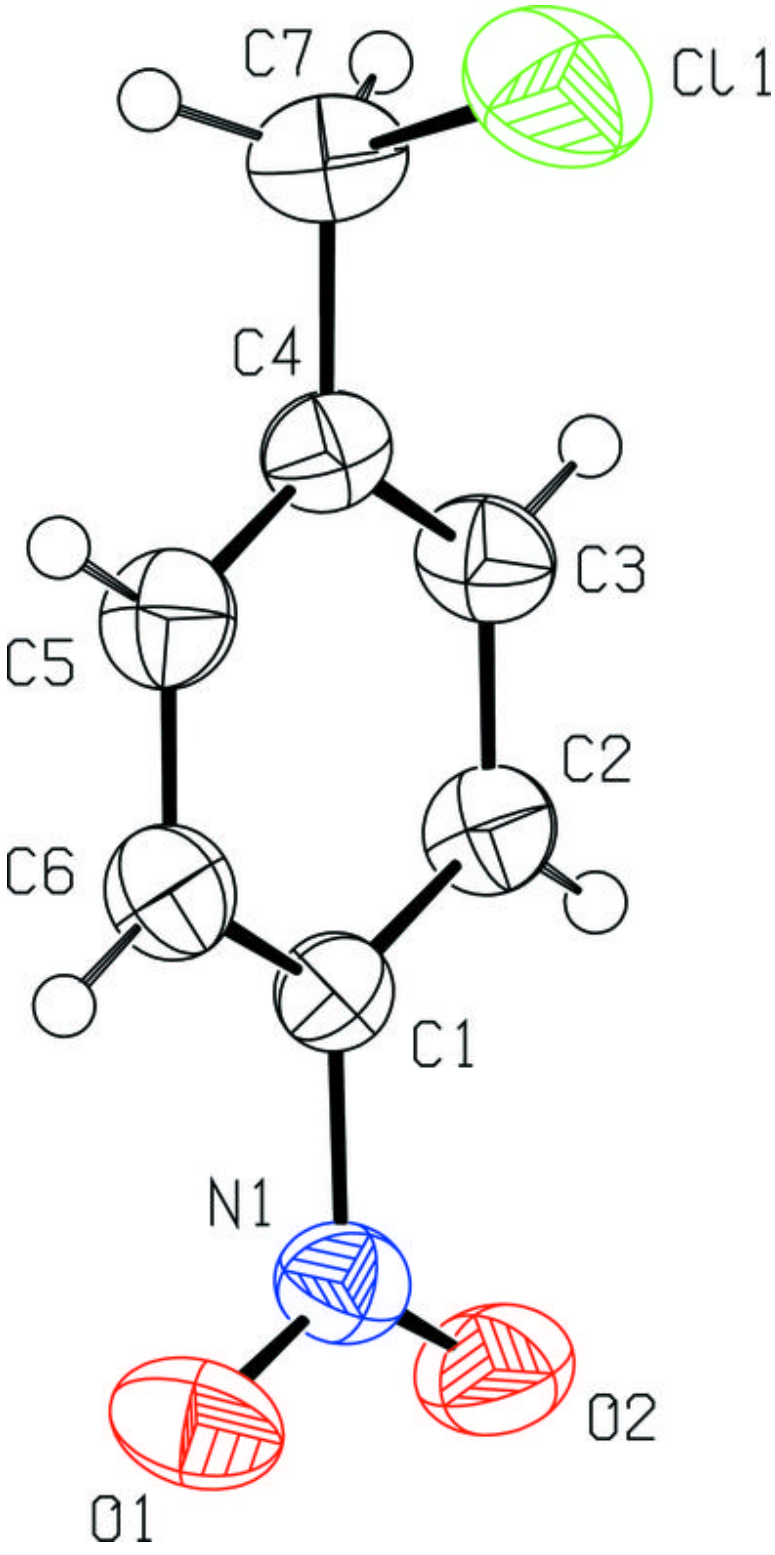
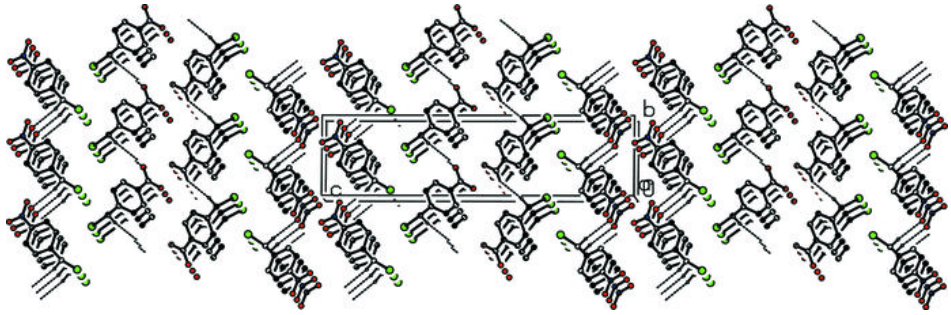


Fig. 2



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4-Ethyl-1-(4-methoxybenzylidene)thiosemicarbazide

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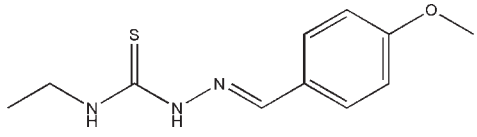
Key indicators: single-crystal X-ray study; T = 293 K; mean σ(C–C) = 0.003 Å; R factor = 0.053; wR factor = 0.160; data-to-parameter ratio = 20.1.

In the title compound, $C_{11}H_{15}N_3OS$, the dihedral angle between the aromatic ring and the thiourea unit is 4.28 (7)° and an intramolecular N—H···N hydrogen bond generates an S(5) ring. In the crystal, molecules are linked into (001) sheets by N—H···S hydrogen bonds.

Related literature

For background to the reactions and properties of thiosemicarbazones, see: Casas *et al.* (2000); Lobana *et al.* (2009); Quiroga & Ranninger (2004). For a related structure, see: Li & Jian (2010).



Experimental

Crystal data

$C_{11}H_{15}N_3OS$
M_r = 237.32
Orthorhombic, *Pbca*
a = 13.066 (3) Å
b = 10.128 (2) Å
c = 19.224 (4) Å
V = 2543.9 (9) Å^3
Z = 8
Mo $K\alpha$ radiation
μ = 0.24 mm^{-1}
T = 293 K
0.22 × 0.20 × 0.18 mm

Data collection

Bruker SMART CCD diffractometer
22633 measured reflections
2912 independent reflections
2302 reflections with $I > 2\sigma(I)$
R_{int} = 0.044

Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.053
$wR(F^2)$ = 0.160
S = 1.05
2912 reflections
145 parameters
H-atom parameters constrained
$\Delta\rho_{max}$ = 0.26 e Å^{-3}
$\Delta\rho_{min}$ = −0.34 e Å^{-3}

Table 1
Hydrogen-bond geometry (Å, °).

D—H···A	D—H	H···A	D···A	D—H···A
N1—H1A···S1^{i}	0.86	2.60	3.4080 (17)	156
N3—H3A···N2	0.86	2.26	2.634 (2)	106
N3—H3A···S1^{ii}	0.86	2.78	3.4670 (17)	137

Symmetry codes: (i) $-x, -y+2, -z+1$; (ii) $-x+\frac{1}{2}, y-\frac{1}{2}, z$.

Data collection: *SMART* (Bruker, 1997); cell refinement: *SAINT* (Bruker, 1997); data reduction: *SAINT*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *SHELXTL* (Sheldrick, 2008); software used to prepare material for publication: *SHELXTL*.

Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: HB5492).

References

Bruker (1997). *SMART* and *SAINT*. Bruker AXS Inc., Madison, Wisconsin, USA.
Casas, J. S., Garcia-T, M. S. & Sordo, J. (2000). *Coord. Chem. Rev.* **209**, 197–261.
Li, Y.-F. & Jian, F.-F. (2010). *Acta Cryst.* E**66**, o1399.
Lobana, T. S., Khanna, S., Hundal, G., Kaur, P., Thakur, B., Attri, S. & Butcher, R. J. (2009). *Polyhedron*, **28**, 1583–1593.
Quiroga, A. G. & Ranninger, C. N. (2004). *Coord. Chem. Rev.* **248**, 119–133.
Sheldrick, G. M. (2008). *Acta Cryst.* A**64**, 112–122.

supplementary materials

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4-Ethyl-1-(4-methoxybenzylidene)thiosemicarbazide

Y.-F. Li and F.-F. Jian

Comment

Thiosemicarbazones have attracted much attention because they can be utilized as effective ligands to form the compounds with antitumoral drugs. (Quiroga & Ranninger, 2004).They are important versatile coordination agents which have been reported to be coordination compounds (Casas *et al.*, 2000) (Lobana *et al.*, 2009). As part of our search for new thiosemicarbazones compounds we synthesized the title compound (I), and describe its structure here. The dihedral angle between the benzene ring and the thiourea unit is [4.28 (7)°]. Intermolecular N—H···S hydrogen bonds generate chains.

Bond lengths and angles agree with those observed in a related compound (Li & Jian, 2010).

Experimental

A mixture of 4-methoxybenzaldehyde (0.1 mol) and 4-ethylthiosemicarbazide (0.1 mol) was stirred in refluxing ethanol (20 ml) for 2 h to afford the title compound (0.086 mol, yield 86%). Colourless blocks of (I) were obtained by recrystallization from ethanol at room temperature.

Refinement

H atoms were fixed geometrically and allowed to ride on their attached atoms, with C—H = 0.97 Å, and with U_{iso}(H) = 1.2–1.5U_{eq}(C).

Figures

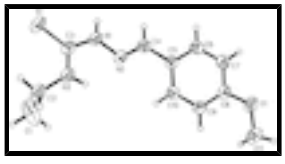


Fig. 1. The structure of (I) showing 30% probability displacement ellipsoids.

4-Ethyl-1-(4-methoxybenzylidene)thiosemicarbazide

Crystal data

$C_{11}H_{15}N_3OS$	F(000) = 1008
M_r = 237.32	D_x = 1.239 Mg m^{-3}
Orthorhombic, *Pbca*	Mo $K\alpha$ radiation, λ = 0.71073 Å
Hall symbol: -P 2ac 2ab	Cell parameters from 2302 reflections
a = 13.066 (3) Å	θ = 2.8–25.3°
b = 10.128 (2) Å	μ = 0.24 mm^{-1}

c = 19.224 (4) Å	T = 293 K
V = 2543.9 (9) Å^3	Block, colorless
Z = 8	0.22 × 0.20 × 0.18 mm

Data collection

Bruker SMART CCD diffractometer	2302 reflections with $I > 2\sigma(I)$
Radiation source: fine-focus sealed tube	R_{int} = 0.044
graphite	θ_{max} = 27.5°, θ_{min} = 3.1°
phi and ω scans	h = −16→16
22633 measured reflections	k = −13→13
2912 independent reflections	l = −24→24

Refinement

Refinement on F^2	Primary atom site location: structure-invariant direct methods
Least-squares matrix: full	Secondary atom site location: difference Fourier map
$R[F^2 > 2\sigma(F^2)]$ = 0.053	Hydrogen site location: inferred from neighbouring sites
$wR(F^2)$ = 0.160	H-atom parameters constrained
S = 1.05	$w = 1/[\sigma^2(F_o^2) + (0.0997P)^2 + 0.2868P]$ where $P = (F_o^2 + 2F_c^2)/3$
2912 reflections	$(\Delta/\sigma)_{max}$ = 0.001
145 parameters	$\Delta\rho_{max}$ = 0.26 e Å^{-3}
0 restraints	$\Delta\rho_{min}$ = −0.34 e Å^{-3}

Special details

Geometry. All e.s.d.'s (except the e.s.d. in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell e.s.d.'s are taken into account individually in the estimation of e.s.d.'s in distances, angles and torsion angles; correlations between e.s.d.'s in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell e.s.d.'s is used for estimating e.s.d.'s involving l.s. planes.

Refinement. Refinement of F^2 against ALL reflections. The weighted R-factor wR and goodness of fit S are based on F^2, conventional R-factors R are based on F, with F set to zero for negative F^2. The threshold expression of $F^2 > \sigma(F^2)$ is used only for calculating R-factors(gt) *etc*. and is not relevant to the choice of reflections for refinement. R-factors based on F^2 are statistically about twice as large as those based on F, and R- factors based on ALL data will be even larger.

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å^2)

	x	y	z	U_{iso}*/U_{eq}
S1	0.12047 (4)	1.04218 (4)	0.57631 (3)	0.0768 (2)
N1	0.09565 (11)	0.83299 (14)	0.49802 (8)	0.0648 (4)
H1A	0.0548	0.8818	0.4742	0.078*
N2	0.11117 (10)	0.70368 (14)	0.47913 (8)	0.0598 (3)
C9	0.12596 (13)	0.30355 (18)	0.41061 (9)	0.0637 (4)

H9A	0.1545	0.2367	0.4375	0.076*
C3	0.14420 (12)	0.88334 (15)	0.55374 (9)	0.0596 (4)
N3	0.21067 (12)	0.80566 (14)	0.58550 (9)	0.0719 (4)
H3A	0.2271	0.7331	0.5651	0.086*
O1	0.09603 (11)	0.15651 (14)	0.31258 (7)	0.0803 (4)
C5	0.07418 (12)	0.53144 (16)	0.39807 (8)	0.0576 (4)
C10	0.11699 (13)	0.42999 (18)	0.43678 (9)	0.0621 (4)
H10A	0.1403	0.4476	0.4815	0.075*
C4	0.06596 (13)	0.66625 (17)	0.42425 (9)	0.0626 (4)
H4A	0.0262	0.7267	0.3999	0.075*
C8	0.09189 (12)	0.27751 (17)	0.34373 (9)	0.0621 (4)
C6	0.04087 (15)	0.5032 (2)	0.33114 (10)	0.0719 (5)
H6A	0.0115	0.5696	0.3044	0.086*
C11	0.14227 (19)	0.05082 (19)	0.34942 (13)	0.0866 (6)
H11A	0.1397	−0.0278	0.3216	0.130*
H11B	0.1061	0.0363	0.3922	0.130*
H11C	0.2123	0.0725	0.3594	0.130*
C2	0.25846 (16)	0.8338 (2)	0.65277 (13)	0.0910 (7)
H2B	0.2628	0.9285	0.6594	0.109*
H2C	0.3275	0.7984	0.6532	0.109*
C7	0.05071 (16)	0.3784 (2)	0.30398 (10)	0.0769 (5)
H7A	0.0296	0.3616	0.2586	0.092*
C1	0.1984 (3)	0.7743 (4)	0.71090 (15)	0.1455 (13)
H1B	0.2311	0.7943	0.7544	0.218*
H1C	0.1952	0.6803	0.7049	0.218*
H1D	0.1304	0.8100	0.7108	0.218*

Atomic displacement parameters (Å^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
S1	0.0653 (3)	0.0441 (3)	0.1211 (5)	0.00297 (16)	−0.0100 (2)	−0.0109 (2)
N1	0.0687 (8)	0.0469 (7)	0.0786 (9)	0.0078 (6)	−0.0085 (7)	0.0005 (6)
N2	0.0596 (7)	0.0479 (7)	0.0720 (8)	0.0022 (5)	−0.0015 (6)	−0.0004 (6)
C9	0.0672 (9)	0.0567 (10)	0.0673 (9)	0.0013 (7)	−0.0052 (7)	0.0071 (7)
C3	0.0526 (7)	0.0447 (8)	0.0814 (10)	−0.0024 (6)	0.0014 (7)	−0.0002 (7)
N3	0.0716 (9)	0.0512 (8)	0.0929 (10)	0.0102 (6)	−0.0169 (8)	−0.0137 (7)
O1	0.0857 (8)	0.0647 (8)	0.0905 (9)	0.0036 (6)	−0.0126 (7)	−0.0171 (7)
C5	0.0515 (8)	0.0583 (9)	0.0632 (8)	0.0022 (6)	−0.0032 (6)	−0.0007 (6)
C10	0.0695 (10)	0.0594 (10)	0.0575 (8)	−0.0005 (7)	−0.0070 (7)	0.0017 (7)
C4	0.0604 (9)	0.0585 (9)	0.0688 (9)	0.0067 (7)	−0.0063 (7)	0.0016 (7)
C8	0.0547 (8)	0.0613 (10)	0.0702 (9)	−0.0008 (7)	−0.0022 (7)	−0.0071 (7)
C6	0.0762 (11)	0.0698 (10)	0.0697 (10)	0.0143 (9)	−0.0188 (8)	0.0012 (8)
C11	0.0946 (14)	0.0568 (11)	0.1083 (16)	0.0024 (9)	0.0065 (13)	−0.0021 (10)
C2	0.0766 (12)	0.0677 (12)	0.1285 (18)	0.0107 (9)	−0.0402 (13)	−0.0265 (11)
C7	0.0856 (12)	0.0772 (12)	0.0679 (10)	0.0109 (9)	−0.0231 (9)	−0.0102 (9)
C1	0.120 (2)	0.232 (4)	0.0849 (16)	−0.025 (2)	−0.0161 (16)	−0.032 (2)

Geometric parameters (Å, °)

S1—C3	1.6948 (17)	C10—H10A	0.9300
N1—C3	1.345 (2)	C4—H4A	0.9300
N1—N2	1.3742 (19)	C8—C7	1.385 (3)
N1—H1A	0.8600	C6—C7	1.373 (3)
N2—C4	1.267 (2)	C6—H6A	0.9300
C9—C10	1.381 (2)	C11—H11A	0.9600
C9—C8	1.386 (3)	C11—H11B	0.9600
C9—H9A	0.9300	C11—H11C	0.9600
C3—N3	1.321 (2)	C2—C1	1.492 (4)
N3—C2	1.464 (2)	C2—H2B	0.9700
N3—H3A	0.8600	C2—H2C	0.9700
O1—C8	1.365 (2)	C7—H7A	0.9300
O1—C11	1.419 (3)	C1—H1B	0.9600
C5—C10	1.387 (2)	C1—H1C	0.9600
C5—C6	1.388 (2)	C1—H1D	0.9600
C5—C4	1.459 (2)		
C3—N1—N2	120.14 (13)	C7—C8—C9	119.75 (16)
C3—N1—H1A	119.9	C7—C6—C5	120.86 (16)
N2—N1—H1A	119.9	C7—C6—H6A	119.6
C4—N2—N1	115.87 (14)	C5—C6—H6A	119.6
C10—C9—C8	119.16 (16)	O1—C11—H11A	109.5
C10—C9—H9A	120.4	O1—C11—H11B	109.5
C8—C9—H9A	120.4	H11A—C11—H11B	109.5
N3—C3—N1	116.89 (14)	O1—C11—H11C	109.5
N3—C3—S1	124.54 (13)	H11A—C11—H11C	109.5
N1—C3—S1	118.51 (12)	H11B—C11—H11C	109.5
C3—N3—C2	124.95 (15)	N3—C2—C1	111.03 (19)
C3—N3—H3A	117.5	N3—C2—H2B	109.4
C2—N3—H3A	117.5	C1—C2—H2B	109.4
C8—O1—C11	118.37 (16)	N3—C2—H2C	109.4
C10—C5—C6	118.11 (16)	C1—C2—H2C	109.4
C10—C5—C4	122.54 (15)	H2B—C2—H2C	108.0
C6—C5—C4	119.32 (15)	C6—C7—C8	120.37 (16)
C9—C10—C5	121.73 (16)	C6—C7—H7A	119.8
C9—C10—H10A	119.1	C8—C7—H7A	119.8
C5—C10—H10A	119.1	C2—C1—H1B	109.5
N2—C4—C5	122.20 (15)	C2—C1—H1C	109.5
N2—C4—H4A	118.9	H1B—C1—H1C	109.5
C5—C4—H4A	118.9	C2—C1—H1D	109.5
O1—C8—C7	115.83 (15)	H1B—C1—H1D	109.5
O1—C8—C9	124.41 (16)	H1C—C1—H1D	109.5

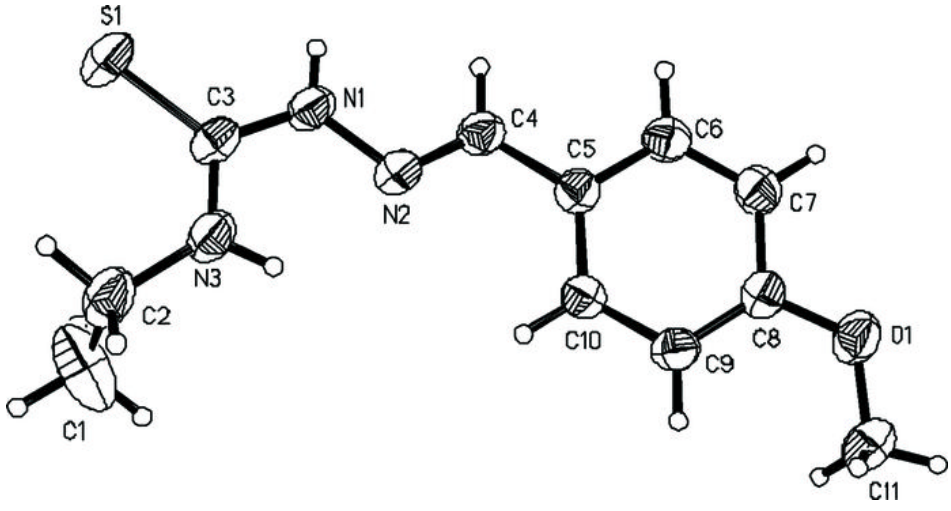
Hydrogen-bond geometry (Å, °)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
N1—H1A···S1^{i}	0.86	2.60	3.4080 (17)	156

N3—H3A···N2	0.86	2.26	2.634 (2)	106
N3—H3A···S1^{ii}	0.86	2.78	3.4670 (17)	137

Symmetry codes: (i) −*x*, −*y*+2, −*z*+1; (ii) −*x*+1/2, *y*−1/2, *z*.

Fig. 1



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2-Methylpropan-2-aminium 4-hydroxybenzoate

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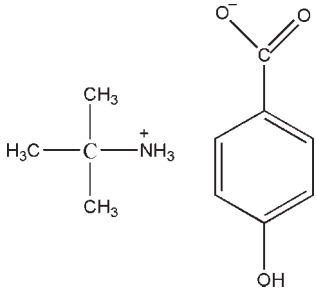
Key indicators: single-crystal X-ray study; T = 293 K; mean σ(C–C) = 0.003 Å; R factor = 0.057; wR factor = 0.168; data-to-parameter ratio = 18.0.

In the crystal of the title molecular salt, $C_4H_{12}N^+\cdot C_7H_5O_3^-$, the cation is linked to three nearby anions by N—H···O hydrogen bonds. An O—H···O hydrogen bond between anions further consolidates the packing.

Related literature

For a related structure, see: Scholz & Gorls (2002).



Experimental

Crystal data

$C_4H_{12}N^+\cdot C_7H_5O_3^-$ M_r = 211.26
Monoclinic, $P2_1/c$
a = 6.8300 (14) Å
b = 9.2790 (19) Å
c = 19.831 (4) Å
β = 99.58 (3)°
V = 1239.3 (4) Å^3
Z = 4
Mo $K\alpha$ radiation
μ = 0.08 mm^{-1}
T = 293 K
0.10 × 0.09 × 0.08 mm

Data collection

Bruker SMART CCD diffractometer
2899 measured reflections
2677 independent reflections
1804 reflections with $I > 2\sigma(I)$
R_{int} = 0.039

Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.057
$wR(F^2)$ = 0.168
S = 1.04
2677 reflections
149 parameters
H atoms treated by a mixture of independent and constrained refinement
$\Delta\rho_{max}$ = 0.22 e Å^{-3}
$\Delta\rho_{min}$ = −0.29 e Å^{-3}

Table 1
Hydrogen-bond geometry (Å, °).

D—H···A	D—H	H···A	D···A	D—H···A
O3—H3B···O1^{i}	0.82	1.83	2.621 (2)	163
N1—H1···O2^{ii}	0.92 (2)	1.93 (2)	2.835 (2)	168.2 (18)
N1—H3···O2	0.94 (2)	1.93 (2)	2.842 (2)	162.2 (18)
N1—H2···O1^{iii}	0.87 (2)	1.92 (3)	2.796 (2)	174.7 (19)

Symmetry codes: (i) $-x, y-\frac{1}{2}, -z+\frac{1}{2}$; (ii) $-x+1, -y+2, -z+1$; (iii) $x+1, y, z$.

Data collection: *SMART* (Bruker, 2003); cell refinement: *SAINT* (Bruker, 2003); data reduction: *SAINT*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *SHELXTL* (Sheldrick, 2008); software used to prepare material for publication: *SHELXTL*.

Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: HB5493).

References

Bruker (2003). *SMART* and *SAINT*. Bruker AXS Inc., Madison, Wisconsin, USA.
Scholz, J. & Gorls, H. (2002). *Polyhedron*, **21**, 305–312.
Sheldrick, G. M. (2008). *Acta Cryst.* A**64**, 112–122.

supplementary materials

Acta Cryst. (2010). E**66**, o1706 [**doi:10.1107/S1600536810022592**]

2-Methylpropan-2-aminium 4-hydroxybenzoate

S.-L. Yu

Experimental

A mixture of 2-methylpropan-2-amine(0.02 mol) and 4-hydroxybenzoic acid (0.02 mol) was stirred in ethanol (30 ml) at 353 K for 3 h to afford the title compound (yield 50%). Colourless bars of (I) were obtained by recrystallization from acetone at room temperature.

Refinement

H atoms were positioned geometrically and allowed to ride on their parent atoms, with N—H and C—H distances of 0.86 and 0.93–0.96 Å, respectively, and with $U_{iso}(H) = 1.2U_{eq}$ of the parent atoms.

Figures

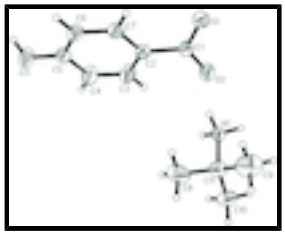


Fig. 1. The molecular structure of (I) with displacement ellipsoids drawn at the 30% probability level.

2-Methylpropan-2-aminium 4-hydroxybenzoate

Crystal data

$C_4H_{12}N^+·C_7H_5O_3^-$	$F(000) = 456$
$M_r = 211.26$	$D_x = 1.132$ Mg m^{-3}
Monoclinic, $P2_1/c$	Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å
Hall symbol: -P 2ybc	Cell parameters from 1804 reflections
$a = 6.8300$ (14) Å	$\theta = 2.1$–$27.0°$
$b = 9.2790$ (19) Å	$\mu = 0.08$ mm^{-1}
$c = 19.831$ (4) Å	$T = 293$ K
$\beta = 99.58$ (3)°	Bar, colorless
$V = 1239.3$ (4) Å^3	0.10 × 0.09 × 0.08 mm
$Z = 4$	

Data collection

Bruker SMART CCD diffractometer	1804 reflections with $I > 2\sigma(I)$

Radiation source: fine-focus sealed tube	$R_{int} = 0.039$
graphite	$\theta_{max} = 27.0°$, $\theta_{min} = 2.1°$
phi and ω scans	$h = 0 \rightarrow 8$
2899 measured reflections	$k = 0 \rightarrow 11$
2677 independent reflections	$l = -23 \rightarrow 23$

Refinement

Refinement on F^2	Secondary atom site location: difference Fourier map
Least-squares matrix: full	Hydrogen site location: inferred from neighbouring sites
$R[F^2 > 2\sigma(F^2)] = 0.057$	H atoms treated by a mixture of independent and constrained refinement
$wR(F^2) = 0.168$	$w = 1/[\sigma^2(F_o^2) + (0.0928P)^2 + 0.1735P]$ where $P = (F_o^2 + 2F_c^2)/3$
$S = 1.04$	$(\Delta/\sigma)_{max} < 0.001$
2677 reflections	$\Delta\rho_{max} = 0.22$ e Å^{-3}
149 parameters	$\Delta\rho_{min} = -0.29$ e Å^{-3}
0 restraints	Extinction correction: *SHELXL97* (Sheldrick, 2008), $Fc^* = kFc[1+0.001xFc^2\lambda^3/\sin(2\theta)]^{-1/4}$
Primary atom site location: structure-invariant direct methods	Extinction coefficient: 0.59 (3)

Special details

Geometry. All e.s.d.'s (except the e.s.d. in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell e.s.d.'s are taken into account individually in the estimation of e.s.d.'s in distances, angles and torsion angles; correlations between e.s.d.'s in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell e.s.d.'s is used for estimating e.s.d.'s involving l.s. planes.

Refinement. Refinement of F^2 against ALL reflections. The weighted *R*-factor *wR* and goodness of fit *S* are based on F^2, conventional *R*-factors *R* are based on *F*, with *F* set to zero for negative F^2. The threshold expression of $F^2 > \sigma(F^2)$ is used only for calculating *R*-factors(gt) *etc*. and is not relevant to the choice of reflections for refinement. *R*-factors based on F^2 are statistically about twice as large as those based on *F*, and *R*- factors based on ALL data will be even larger.

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å^2)

	x	*y*	*z*	U_{iso}*/U_{eq}
C1	0.1770 (3)	0.81042 (19)	0.40216 (9)	0.0475 (4)
C2	0.2054 (2)	0.70697 (18)	0.34696 (8)	0.0435 (4)
C3	0.3911 (3)	0.6882 (2)	0.32850 (10)	0.0618 (6)
H3A	0.4999	0.7372	0.3523	0.074*
C4	0.4170 (3)	0.5976 (3)	0.27512 (12)	0.0728 (7)
H4A	0.5423	0.5872	0.2632	0.087*
C5	0.2577 (3)	0.5225 (2)	0.23940 (10)	0.0571 (5)
C6	0.0722 (3)	0.5367 (2)	0.25849 (10)	0.0558 (5)
H6A	−0.0351	0.4843	0.2359	0.067*
C7	0.0470 (2)	0.6290 (2)	0.31113 (9)	0.0513 (5)

H7A	−0.0785	0.6393	0.3229	0.062*
O1	0.00062 (19)	0.84869 (15)	0.40644 (6)	0.0606 (4)
O2	0.3246 (2)	0.85859 (16)	0.44198 (7)	0.0667 (5)
O3	0.2922 (2)	0.4377 (2)	0.18682 (9)	0.0863 (6)
H3B	0.1865	0.4187	0.1622	0.129*
C8	0.7450 (4)	0.6075 (3)	0.50722 (16)	0.0949 (9)
H8A	0.6109	0.6040	0.4832	0.142*
H8B	0.7693	0.5259	0.5372	0.142*
H8C	0.8352	0.6053	0.4749	0.142*
C9	0.6313 (5)	0.7601 (4)	0.59955 (17)	0.1178 (12)
H9A	0.6486	0.8522	0.6218	0.177*
H9B	0.6563	0.6850	0.6331	0.177*
H9C	0.4977	0.7520	0.5754	0.177*
C10	0.9911 (4)	0.7600 (3)	0.58411 (13)	0.0806 (7)
H10A	1.0103	0.8519	0.6065	0.121*
H10B	1.0772	0.7522	0.5507	0.121*
H10C	1.0213	0.6845	0.6173	0.121*
C11	0.7764 (3)	0.7461 (2)	0.54907 (11)	0.0632 (6)
N1	0.7346 (2)	0.86993 (18)	0.49897 (8)	0.0483 (4)
H1	0.734 (3)	0.958 (2)	0.5202 (10)	0.058*
H2	0.815 (3)	0.869 (2)	0.4690 (12)	0.058*
H3	0.608 (3)	0.859 (2)	0.4718 (10)	0.058*

Atomic displacement parameters (Å^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
C1	0.0461 (10)	0.0530 (10)	0.0442 (8)	0.0012 (8)	0.0095 (7)	0.0012 (7)
C2	0.0394 (9)	0.0475 (9)	0.0439 (8)	−0.0014 (7)	0.0077 (7)	0.0004 (7)
C3	0.0401 (10)	0.0804 (13)	0.0662 (11)	−0.0155 (9)	0.0120 (8)	−0.0224 (10)
C4	0.0406 (10)	0.1022 (17)	0.0781 (14)	−0.0061 (10)	0.0176 (9)	−0.0322 (12)
C5	0.0449 (10)	0.0678 (12)	0.0576 (10)	0.0055 (8)	0.0055 (8)	−0.0158 (9)
C6	0.0394 (9)	0.0673 (12)	0.0583 (10)	−0.0050 (8)	0.0008 (7)	−0.0132 (9)
C7	0.0356 (8)	0.0661 (11)	0.0523 (9)	−0.0023 (8)	0.0070 (7)	−0.0036 (8)
O1	0.0513 (8)	0.0813 (10)	0.0505 (7)	0.0161 (7)	0.0122 (6)	−0.0023 (6)
O2	0.0521 (8)	0.0788 (10)	0.0674 (9)	−0.0015 (7)	0.0051 (6)	−0.0267 (7)
O3	0.0537 (8)	0.1141 (13)	0.0890 (11)	0.0104 (8)	0.0058 (7)	−0.0525 (10)
C8	0.0918 (18)	0.0576 (14)	0.127 (2)	−0.0112 (12)	−0.0065 (16)	0.0126 (14)
C9	0.098 (2)	0.161 (3)	0.107 (2)	0.013 (2)	0.0542 (18)	0.056 (2)
C10	0.0671 (14)	0.0876 (16)	0.0802 (15)	0.0001 (12)	−0.0078 (12)	0.0154 (13)
C11	0.0545 (11)	0.0673 (12)	0.0678 (12)	−0.0024 (10)	0.0105 (9)	0.0151 (10)
N1	0.0421 (8)	0.0528 (9)	0.0510 (8)	−0.0009 (7)	0.0108 (7)	−0.0036 (7)

Geometric parameters (Å, °)

C1—O2	1.255 (2)	C8—H8A	0.9600
C1—O1	1.272 (2)	C8—H8B	0.9600
C1—C2	1.493 (2)	C8—H8C	0.9600
C2—C3	1.388 (2)	C9—C11	1.527 (3)
C2—C7	1.394 (2)	C9—H9A	0.9600

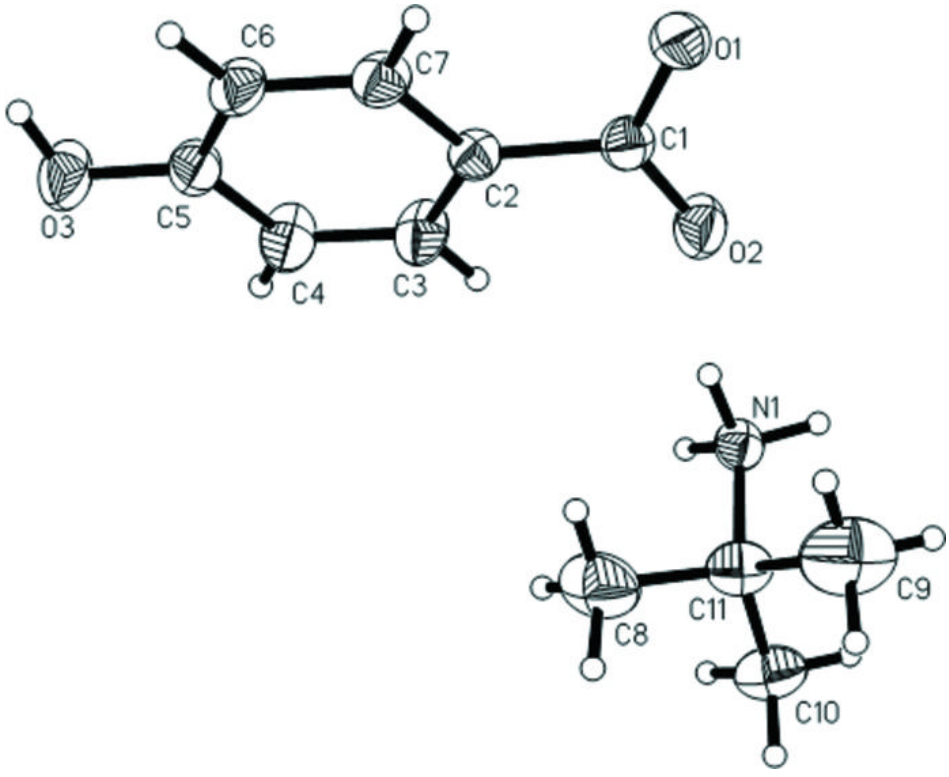
C3—C4	1.386 (3)	C9—H9B	0.9600
C3—H3A	0.9300	C9—H9C	0.9600
C4—C5	1.384 (3)	C10—C11	1.520 (3)
C4—H4A	0.9300	C10—H10A	0.9600
C5—O3	1.358 (2)	C10—H10B	0.9600
C5—C6	1.388 (3)	C10—H10C	0.9600
C6—C7	1.383 (3)	C11—N1	1.515 (2)
C6—H6A	0.9300	N1—H1	0.92 (2)
C7—H7A	0.9300	N1—H2	0.87 (2)
O3—H3B	0.8200	N1—H3	0.94 (2)
C8—C11	1.527 (3)		
O2—C1—O1	121.95 (16)	H8A—C8—H8C	109.5
O2—C1—C2	120.11 (16)	H8B—C8—H8C	109.5
O1—C1—C2	117.93 (15)	C11—C9—H9A	109.5
C3—C2—C7	117.80 (15)	C11—C9—H9B	109.5
C3—C2—C1	120.66 (15)	H9A—C9—H9B	109.5
C7—C2—C1	121.53 (15)	C11—C9—H9C	109.5
C4—C3—C2	121.05 (17)	H9A—C9—H9C	109.5
C4—C3—H3A	119.5	H9B—C9—H9C	109.5
C2—C3—H3A	119.5	C11—C10—H10A	109.5
C5—C4—C3	120.47 (18)	C11—C10—H10B	109.5
C5—C4—H4A	119.8	H10A—C10—H10B	109.5
C3—C4—H4A	119.8	C11—C10—H10C	109.5
O3—C5—C4	117.57 (17)	H10A—C10—H10C	109.5
O3—C5—C6	123.22 (17)	H10B—C10—H10C	109.5
C4—C5—C6	119.21 (17)	N1—C11—C10	107.33 (16)
C7—C6—C5	119.93 (16)	N1—C11—C8	106.78 (18)
C7—C6—H6A	120.0	C10—C11—C8	110.92 (19)
C5—C6—H6A	120.0	N1—C11—C9	107.08 (19)
C6—C7—C2	121.50 (16)	C10—C11—C9	112.0 (2)
C6—C7—H7A	119.3	C8—C11—C9	112.4 (2)
C2—C7—H7A	119.3	C11—N1—H1	113.0 (13)
C5—O3—H3B	109.5	C11—N1—H2	111.4 (13)
C11—C8—H8A	109.5	H1—N1—H2	111.9 (19)
C11—C8—H8B	109.5	C11—N1—H3	110.4 (12)
H8A—C8—H8B	109.5	H1—N1—H3	106.4 (18)
C11—C8—H8C	109.5	H2—N1—H3	103.3 (18)

Hydrogen-bond geometry (Å, °)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
O3—H3B···O1^{i}	0.82	1.83	2.621 (2)	163
N1—H1···O2^{ii}	0.92 (2)	1.93 (2)	2.835 (2)	168.2 (18)
N1—H3···O2	0.94 (2)	1.93 (2)	2.842 (2)	162.2 (18)
N1—H2···O1^{iii}	0.87 (2)	1.92 (3)	2.796 (2)	174.7 (19)

Symmetry codes: (i) −*x*, *y*−1/2, −*z*+1/2; (ii) −*x*+1, −*y*+2, −*z*+1; (iii) *x*+1, *y*, *z*.

Fig. 1



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4-Ethyl-1-[4-(methylsulfanyl)benzylidene]thiosemicarbazide

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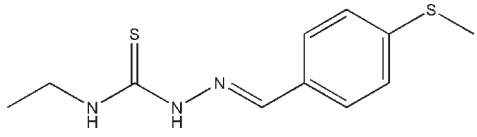
Key indicators: single-crystal X-ray study; T = 293 K; mean σ(C–C) = 0.004 Å; R factor = 0.053; wR factor = 0.201; data-to-parameter ratio = 20.9.

There are four independent molecules in the asymmetric unit of the title compound, $C_{11}H_{15}N_3S_2$, with different conformations: the dihedral angles between the benzene rings and thiourea units are 16.85 (9), 0.56 (10), 8.05 (12) and 4.56 (8)°. Each molecule contains an intramolecular N—H···N hydrogen bond, generating an S(5) ring. The crystal structure is stabilized by intermolecular N—H···S hydrogen bonds.

Related literature

For a related structure and background references to thiosemicarbazones, see: Li & Jian (2010).



Experimental

Crystal data

$C_{11}H_{15}N_3S_2$
M_r = 253.38
Triclinic, $P\overline{1}$
a = 10.496 (2) Å
b = 15.737 (3) Å
c = 17.542 (4) Å
α = 111.07 (3)°
β = 91.62 (3)°
γ = 100.43 (3)°
V = 2645.4 (9) Å^3
Z = 8
Mo $K\alpha$ radiation
μ = 0.38 mm^{-1}
T = 293 K
0.22 × 0.20 × 0.18 mm

Data collection

Bruker SMART CCD diffractometer
26033 measured reflections
12032 independent reflections
8042 reflections with $I > 2\sigma(I)$
R_{int} = 0.042

Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.053
$wR(F^2)$ = 0.201
S = 1.31
12032 reflections
577 parameters
H-atom parameters constrained
$\Delta\rho_{max}$ = 0.68 e Å^{-3}
$\Delta\rho_{min}$ = −0.44 e Å^{-3}

Table 1
Hydrogen-bond geometry (Å, °).

D—H···A	D—H	H···A	D···A	D—H···A
N1A—H1AA···N2A	0.86	2.20	2.602 (3)	108
N1B—H1BA···N3B	0.86	2.17	2.585 (3)	109
N1C—H1CA···N3C	0.86	2.23	2.624 (3)	108
N3D—H3DA···N1D	0.86	2.22	2.610 (3)	107
N3A—H3AA···S1D^{i}	0.86	2.59	3.398 (2)	156
N2D—H2DA···S2A^{ii}	0.86	2.57	3.402 (2)	163
N1A—H1AA···S1B	0.86	2.81	3.4798 (19)	136
N2B—H2BA···S1C	0.86	2.72	3.579 (2)	174
N2C—H2CA···S1B	0.86	2.64	3.487 (3)	168

Symmetry codes: (i) $x, y-1, z$; (ii) $x, y+1, z$.

Data collection: *SMART* (Bruker, 1997); cell refinement: *SAINT* (Bruker, 1997); data reduction: *SAINT*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *SHELXTL* (Sheldrick, 2008); software used to prepare material for publication: *SHELXTL*.

Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: HB5494).

References

Bruker (1997). *SMART* and *SAINT*. Bruker AXS Inc., Madison, Wisconsin, USA.
Li, Y.-F. & Jian, F.-F. (2010). *Acta Cryst.* E**66**, o1399.
Sheldrick, G. M. (2008). *Acta Cryst.* A**64**, 112–122.

supplementary materials

Acta Cryst. (2010). E**66**, o1715 [**doi:10.1107/S1600536810022920**]

4-Ethyl-1-[4-(methylsulfanyl)benzylidene]thiosemicarbazide

Y.-F. Li and F.-F. Jian

Comment

As part of our ongoing studies of thiosemicarbazone compounds (Li & Jian, 2010), we synthesized the title compound (I), and describe its structure here. In the four independent molecules, the dihedral angle between the benzene ring and the thiourea unit is [16.85 (9)°], [0.56 (10)°], [8.05 (12)°], [4.56 (8)°] respectively.

Experimental

A mixture of 4-ethylthiosemicarbazide (0.1 mol), and 4-(methylthio)benzaldehyde (0.1 mol) was stirred in refluxing ethanol (20 ml) for 2 h to afford the title compound (0.086 mol, yield 86%). Colourless blocks of (I) were obtained by recrystallization from ethanol at room temperature.

Refinement

H atoms were fixed geometrically and allowed to ride on their attached atoms, with C—H distances=0.97 Å, and with U_{iso}=1.2–1.5U_{eq}.

Figures

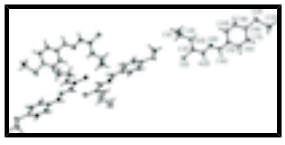


Fig. 1. The structure of (I) showing 30% probability displacement ellipsoids.

4-Ethyl-1-[4-(methylsulfanyl)benzylidene]thiosemicarbazide

Crystal data

$C_{11}H_{15}N_3S_2$	Z = 8
M_r = 253.38	F(000) = 1072
Triclinic, $P\overline{1}$	D_x = 1.272 Mg m^{-3}
Hall symbol: -P 1	Mo $K\alpha$ radiation, λ = 0.71073 Å
a = 10.496 (2) Å	Cell parameters from 8042 reflections
b = 15.737 (3) Å	θ = 3.0–27.5°
c = 17.542 (4) Å	μ = 0.38 mm^{-1}
α = 111.07 (3)°	T = 293 K
β = 91.62 (3)°	Block, colorless
γ = 100.43 (3)°	0.22 × 0.20 × 0.18 mm
V = 2645.4 (9) Å^3	

Data collection

Bruker SMART CCD diffractometer	8042 reflections with $I > 2\sigma(I)$
Radiation source: fine-focus sealed tube	$R_{int} = 0.042$
graphite	$\theta_{max} = 27.5°$, $\theta_{min} = 3.0°$
phi and ω scans	$h = -13\rightarrow13$
26033 measured reflections	$k = -20\rightarrow20$
12032 independent reflections	$l = -22\rightarrow22$

Refinement

Refinement on F^2	Primary atom site location: structure-invariant direct methods
Least-squares matrix: full	Secondary atom site location: difference Fourier map
$R[F^2 > 2\sigma(F^2)] = 0.053$	Hydrogen site location: inferred from neighbouring sites
$wR(F^2) = 0.201$	H-atom parameters constrained
$S = 1.31$	$w = 1/[\sigma^2(F_o^2) + (0.1P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
12032 reflections	$(\Delta/\sigma)_{max} = 0.001$
577 parameters	$\Delta\rho_{max} = 0.68$ e Å^{-3}
0 restraints	$\Delta\rho_{min} = -0.44$ e Å^{-3}

Special details

Geometry. All e.s.d.'s (except the e.s.d. in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell e.s.d.'s are taken into account individually in the estimation of e.s.d.'s in distances, angles and torsion angles; correlations between e.s.d.'s in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell e.s.d.'s is used for estimating e.s.d.'s involving l.s. planes.

Refinement. Refinement of F^2 against ALL reflections. The weighted *R*-factor *wR* and goodness of fit *S* are based on F^2, conventional *R*-factors *R* are based on *F*, with *F* set to zero for negative F^2. The threshold expression of $F^2 > \sigma(F^2)$ is used only for calculating *R*-factors(gt) *etc*. and is not relevant to the choice of reflections for refinement. *R*-factors based on F^2 are statistically about twice as large as those based on *F*, and *R*- factors based on ALL data will be even larger.

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å^2)

	x	*y*	*z*	U_{iso}*/U_{eq}
S1D	0.70888 (7)	0.63167 (4)	0.27855 (3)	0.06536 (19)
S2A	0.77477 (8)	−0.09229 (4)	0.25247 (3)	0.0713 (2)
S1B	0.81356 (8)	−0.20823 (4)	−0.11837 (3)	0.0747 (2)
S2D	0.91253 (8)	1.22890 (5)	0.82918 (4)	0.0787 (2)
S1C	0.59612 (10)	−0.26828 (5)	−0.35997 (4)	0.0909 (3)
S2C	0.57360 (9)	0.35118 (5)	0.15668 (5)	0.0892 (3)
S1A	0.63732 (9)	−0.69992 (6)	−0.29039 (5)	0.0952 (3)
S2B	1.00646 (10)	−0.79759 (6)	−0.60067 (5)	0.0999 (3)

N3A	0.72112 (19)	−0.26196 (13)	0.14045 (10)	0.0570 (5)
H3AA	0.6975	−0.2804	0.1795	0.068*
N3D	0.6760 (2)	0.68551 (12)	0.43757 (10)	0.0601 (5)
H3DA	0.6771	0.7297	0.4842	0.072*
N2A	0.71480 (17)	−0.32505 (12)	0.06176 (10)	0.0522 (4)
N2D	0.75067 (19)	0.80099 (12)	0.39072 (10)	0.0562 (4)
H2DA	0.7700	0.8205	0.3517	0.067*
N1D	0.76168 (17)	0.86248 (12)	0.46999 (10)	0.0528 (4)
N1A	0.7964 (2)	−0.14877 (13)	0.09172 (10)	0.0604 (5)
H1AA	0.7847	−0.1934	0.0445	0.072*
C3D	0.7090 (2)	0.70904 (15)	0.37417 (11)	0.0507 (5)
C3A	0.7648 (2)	−0.17061 (15)	0.15602 (12)	0.0541 (5)
N3B	0.8723 (2)	−0.42118 (14)	−0.30377 (11)	0.0618 (5)
C5A	0.66625 (19)	−0.48223 (14)	−0.03193 (12)	0.0493 (5)
C4A	0.6790 (2)	−0.41118 (15)	0.05027 (13)	0.0512 (5)
H4AA	0.6608	−0.4286	0.0948	0.061*
C5D	0.8371 (2)	1.01651 (15)	0.56714 (12)	0.0517 (5)
C4D	0.8144 (2)	0.94679 (15)	0.48379 (12)	0.0534 (5)
H4DA	0.8388	0.9642	0.4401	0.064*
N3C	0.5771 (2)	−0.04440 (14)	−0.17236 (11)	0.0680 (5)
N2B	0.8282 (2)	−0.34282 (14)	−0.25800 (10)	0.0663 (5)
H2BA	0.7763	−0.3203	−0.2807	0.080*
N1B	0.9511 (2)	−0.34109 (14)	−0.14897 (11)	0.0666 (5)
H1BA	0.9764	−0.3872	−0.1845	0.080*
C3B	0.8681 (2)	−0.30171 (16)	−0.17630 (13)	0.0608 (6)
C6A	0.6774 (2)	−0.45969 (16)	−0.10174 (13)	0.0610 (6)
H6AA	0.6934	−0.3976	−0.0963	0.073*
C8D	0.8865 (2)	1.15085 (16)	0.72642 (13)	0.0573 (5)
C10D	0.8050 (2)	0.99256 (16)	0.63471 (13)	0.0583 (5)
H10A	0.7679	0.9313	0.6269	0.070*
N2C	0.6029 (3)	−0.12828 (16)	−0.22144 (11)	0.0800 (7)
H2CA	0.6489	−0.1564	−0.2009	0.096*
C8B	0.9502 (2)	−0.69882 (16)	−0.54091 (14)	0.0610 (5)
C6D	0.8938 (2)	1.10765 (16)	0.58141 (14)	0.0598 (5)
H6DA	0.9158	1.1247	0.5372	0.072*
C8C	0.5907 (2)	0.24294 (16)	0.08527 (14)	0.0609 (5)
C8A	0.6428 (2)	−0.62037 (17)	−0.18858 (14)	0.0635 (6)
C5B	0.8749 (2)	−0.53968 (16)	−0.43370 (13)	0.0573 (5)
C9A	0.6289 (2)	−0.64442 (17)	−0.12059 (16)	0.0666 (6)
H9AA	0.6117	−0.7068	−0.1268	0.080*
C7B	0.8681 (3)	−0.65617 (18)	−0.56913 (13)	0.0729 (7)
H7BA	0.8373	−0.6800	−0.6245	0.087*
C10A	0.6406 (2)	−0.57573 (16)	−0.04307 (14)	0.0591 (5)
H10B	0.6311	−0.5927	0.0024	0.071*
C9D	0.8283 (2)	1.05956 (17)	0.71286 (13)	0.0632 (6)
H9DA	0.8046	1.0433	0.7572	0.076*
C7A	0.6651 (3)	−0.52784 (19)	−0.17804 (14)	0.0705 (7)
H7AA	0.6721	−0.5113	−0.2238	0.085*
C4B	0.8349 (3)	−0.45683 (17)	−0.37994 (13)	0.0646 (6)

H4BA	0.7803	−0.4292	−0.4019	0.078*
C10B	0.9567 (2)	−0.58410 (18)	−0.40533 (13)	0.0650 (6)
H10C	0.9866	−0.5609	−0.3499	0.078*
C2D	0.6381 (3)	0.59073 (18)	0.43388 (14)	0.0745 (7)
H2DB	0.6588	0.5894	0.4876	0.089*
H2DC	0.6886	0.5522	0.3957	0.089*
C3C	0.5568 (3)	−0.16705 (18)	−0.30147 (14)	0.0713 (7)
C6C	0.5343 (3)	0.13004 (18)	−0.05242 (15)	0.0656 (6)
H6CA	0.4886	0.1116	−0.1038	0.079*
C9B	0.9939 (3)	−0.66138 (19)	−0.45749 (15)	0.0693 (6)
H9BA	1.0496	−0.6896	−0.4370	0.083*
C7D	0.9188 (2)	1.17422 (16)	0.66004 (14)	0.0628 (6)
H7DA	0.9577	1.2352	0.6681	0.075*
C4C	0.6275 (3)	−0.0129 (2)	−0.09849 (15)	0.0810 (8)
H4CA	0.6772	−0.0480	−0.0823	0.097*
C5C	0.6116 (3)	0.07495 (17)	−0.03801 (13)	0.0659 (6)
C2A	0.8492 (3)	−0.05562 (18)	0.09475 (15)	0.0809 (9)
H2AB	0.8181	−0.0110	0.1408	0.097*
H2AC	0.8168	−0.0496	0.0450	0.097*
N1C	0.4853 (3)	−0.12191 (17)	−0.32778 (13)	0.0853 (7)
H1CA	0.4686	−0.0718	−0.2926	0.102*
C6B	0.8302 (3)	−0.57779 (18)	−0.51630 (14)	0.0746 (7)
H6BA	0.7735	−0.5502	−0.5367	0.089*
C7C	0.5234 (3)	0.21250 (18)	0.00832 (16)	0.0709 (7)
H7CA	0.4696	0.2484	−0.0027	0.085*
C10C	0.6784 (4)	0.1063 (2)	0.03940 (17)	0.1071 (13)
H10D	0.7324	0.0706	0.0507	0.129*
C9C	0.6676 (4)	0.1891 (2)	0.10045 (16)	0.0900 (10)
H9CA	0.7132	0.2078	0.1520	0.108*
C2B	1.0029 (3)	−0.3124 (2)	−0.06345 (15)	0.0783 (7)
H2BB	0.9320	−0.3077	−0.0288	0.094*
H2BC	1.0604	−0.2517	−0.0462	0.094*
C11D	0.9757 (3)	1.3390 (2)	0.82323 (17)	0.0862 (9)
H11A	0.9925	1.3859	0.8775	0.129*
H11B	0.9135	1.3537	0.7913	0.129*
H11C	1.0553	1.3367	0.7976	0.129*
C1B	1.0759 (4)	−0.3812 (3)	−0.05415 (18)	0.1076 (12)
H1BB	1.1090	−0.3622	0.0023	0.161*
H1BC	1.1470	−0.3848	−0.0876	0.161*
H1BD	1.0187	−0.4412	−0.0711	0.161*
C11A	0.5706 (3)	−0.8097 (2)	−0.2859 (2)	0.1097 (12)
H11D	0.5645	−0.8573	−0.3395	0.165*
H11E	0.4854	−0.8092	−0.2675	0.165*
H11F	0.6258	−0.8221	−0.2482	0.165*
C1A	0.9928 (4)	−0.0328 (2)	0.1032 (2)	0.1091 (12)
H1AB	1.0221	0.0298	0.1060	0.164*
H1AC	1.0243	−0.0750	0.0566	0.164*
H1AD	1.0256	−0.0384	0.1525	0.164*
C11C	0.6779 (4)	0.3679 (2)	0.24419 (17)	0.0959 (10)

H11G	0.6743	0.4263	0.2867	0.144*
H11H	0.7655	0.3683	0.2299	0.144*
H11I	0.6503	0.3183	0.2635	0.144*
C1D	0.4976 (4)	0.5507 (2)	0.4078 (2)	0.1096 (12)
H1DB	0.4785	0.4877	0.4054	0.164*
H1DC	0.4764	0.5516	0.3546	0.164*
H1DD	0.4470	0.5869	0.4466	0.164*
C11B	0.9299 (4)	−0.8277 (2)	−0.70075 (18)	0.1145 (13)
H11J	0.9563	−0.8820	−0.7376	0.172*
H11K	0.9548	−0.7770	−0.7190	0.172*
H11L	0.8371	−0.8407	−0.6999	0.172*
C2C	0.4309 (5)	−0.1508 (3)	−0.4138 (2)	0.1359 (18)
H2CB	0.4887	−0.1851	−0.4491	0.163*
H2CC	0.3478	−0.1933	−0.4218	0.163*
C1C	0.4128 (6)	−0.0818 (4)	−0.4382 (3)	0.172 (2)
H1CB	0.3779	−0.1075	−0.4948	0.258*
H1CC	0.4945	−0.0398	−0.4319	0.258*
H1CD	0.3529	−0.0487	−0.4053	0.258*

Atomic displacement parameters (Å^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
S1D	0.0967 (5)	0.0526 (3)	0.0385 (3)	0.0130 (3)	0.0152 (3)	0.0077 (2)
S2A	0.1070 (5)	0.0539 (3)	0.0419 (3)	0.0123 (3)	0.0111 (3)	0.0065 (2)
S1B	0.1203 (6)	0.0505 (3)	0.0483 (3)	0.0269 (3)	0.0128 (3)	0.0075 (2)
S2D	0.0965 (5)	0.0675 (4)	0.0514 (3)	0.0182 (4)	0.0026 (3)	−0.0028 (3)
S1C	0.1435 (7)	0.0710 (5)	0.0468 (3)	0.0242 (5)	0.0222 (4)	0.0065 (3)
S2C	0.1155 (6)	0.0633 (4)	0.0799 (4)	0.0435 (4)	0.0096 (4)	0.0041 (3)
S1A	0.1066 (6)	0.0885 (6)	0.0643 (4)	0.0383 (5)	0.0037 (4)	−0.0109 (4)
S2B	0.1272 (7)	0.0838 (5)	0.0892 (5)	0.0574 (5)	0.0367 (5)	0.0136 (4)
N3A	0.0729 (11)	0.0503 (10)	0.0397 (8)	0.0053 (9)	0.0075 (8)	0.0106 (7)
N3D	0.0909 (13)	0.0461 (10)	0.0395 (8)	0.0157 (9)	0.0130 (9)	0.0101 (7)
N2A	0.0592 (10)	0.0494 (10)	0.0410 (8)	0.0119 (8)	0.0037 (7)	0.0082 (7)
N2D	0.0743 (11)	0.0474 (10)	0.0395 (8)	0.0061 (8)	0.0095 (8)	0.0102 (7)
N1D	0.0615 (10)	0.0479 (10)	0.0411 (8)	0.0110 (8)	0.0028 (8)	0.0075 (7)
N1A	0.0905 (13)	0.0443 (10)	0.0422 (9)	0.0149 (9)	0.0042 (9)	0.0108 (7)
C3D	0.0574 (11)	0.0493 (11)	0.0402 (9)	0.0110 (9)	0.0043 (9)	0.0105 (8)
C3A	0.0659 (12)	0.0485 (11)	0.0436 (10)	0.0150 (10)	0.0040 (9)	0.0104 (9)
N3B	0.0800 (12)	0.0551 (11)	0.0453 (9)	0.0186 (9)	0.0140 (9)	0.0100 (8)
C5A	0.0441 (9)	0.0489 (11)	0.0492 (10)	0.0115 (8)	0.0030 (8)	0.0106 (9)
C4A	0.0556 (11)	0.0486 (12)	0.0478 (10)	0.0104 (9)	0.0065 (9)	0.0161 (9)
C5D	0.0540 (11)	0.0493 (11)	0.0469 (10)	0.0130 (9)	0.0074 (9)	0.0106 (9)
C4D	0.0621 (12)	0.0494 (12)	0.0451 (10)	0.0117 (10)	0.0070 (9)	0.0130 (9)
N3C	0.0942 (14)	0.0589 (12)	0.0491 (10)	0.0246 (11)	0.0133 (10)	0.0130 (9)
N2B	0.0976 (14)	0.0554 (11)	0.0430 (9)	0.0286 (10)	0.0108 (10)	0.0082 (8)
N1B	0.0814 (13)	0.0629 (12)	0.0460 (9)	0.0213 (10)	0.0070 (9)	0.0057 (8)
C3B	0.0774 (14)	0.0512 (12)	0.0452 (11)	0.0066 (11)	0.0152 (10)	0.0101 (9)
C6A	0.0747 (14)	0.0515 (13)	0.0503 (11)	0.0073 (11)	0.0003 (11)	0.0145 (10)

C8D	0.0573 (11)	0.0520 (12)	0.0506 (11)	0.0149 (10)	0.0039 (10)	0.0034 (9)
C10D	0.0697 (13)	0.0490 (12)	0.0479 (11)	0.0070 (10)	0.0019 (10)	0.0110 (9)
N2C	0.1209 (18)	0.0689 (14)	0.0436 (10)	0.0397 (13)	0.0111 (11)	0.0033 (9)
C8B	0.0715 (13)	0.0535 (13)	0.0585 (12)	0.0197 (11)	0.0223 (11)	0.0169 (10)
C6D	0.0714 (14)	0.0493 (12)	0.0526 (11)	0.0095 (10)	0.0107 (10)	0.0129 (9)
C8C	0.0732 (14)	0.0511 (12)	0.0585 (12)	0.0226 (11)	0.0109 (11)	0.0154 (10)
C8A	0.0585 (12)	0.0613 (14)	0.0571 (12)	0.0210 (11)	0.0045 (10)	0.0019 (11)
C5B	0.0706 (13)	0.0556 (13)	0.0444 (10)	0.0187 (11)	0.0105 (10)	0.0139 (9)
C9A	0.0701 (14)	0.0455 (12)	0.0763 (15)	0.0192 (11)	0.0077 (12)	0.0097 (11)
C7B	0.106 (2)	0.0682 (16)	0.0422 (11)	0.0349 (15)	0.0066 (12)	0.0091 (11)
C10A	0.0672 (13)	0.0519 (12)	0.0585 (12)	0.0164 (10)	0.0078 (11)	0.0186 (10)
C9D	0.0747 (14)	0.0642 (14)	0.0463 (11)	0.0131 (12)	0.0064 (11)	0.0159 (10)
C7A	0.0849 (16)	0.0728 (17)	0.0473 (11)	0.0153 (13)	0.0049 (12)	0.0150 (11)
C4B	0.0866 (16)	0.0567 (13)	0.0472 (11)	0.0237 (12)	0.0081 (11)	0.0107 (10)
C10B	0.0782 (15)	0.0688 (15)	0.0458 (11)	0.0223 (12)	0.0016 (11)	0.0156 (10)
C2D	0.121 (2)	0.0592 (14)	0.0466 (11)	0.0271 (15)	0.0150 (13)	0.0188 (10)
C3C	0.0975 (18)	0.0653 (15)	0.0440 (11)	0.0066 (14)	0.0162 (12)	0.0161 (11)
C6C	0.0747 (14)	0.0615 (14)	0.0585 (13)	0.0219 (12)	−0.0009 (11)	0.0165 (11)
C9B	0.0745 (15)	0.0723 (16)	0.0648 (14)	0.0324 (13)	0.0087 (12)	0.0214 (12)
C7D	0.0689 (14)	0.0452 (12)	0.0634 (13)	0.0093 (10)	0.0091 (11)	0.0082 (10)
C4C	0.120 (2)	0.0703 (17)	0.0514 (13)	0.0495 (16)	−0.0003 (14)	0.0073 (11)
C5C	0.0911 (17)	0.0586 (14)	0.0498 (11)	0.0332 (13)	0.0062 (12)	0.0137 (10)
C2A	0.150 (3)	0.0504 (14)	0.0482 (12)	0.0322 (16)	0.0097 (15)	0.0191 (10)
N1C	0.1164 (19)	0.0747 (15)	0.0538 (11)	0.0089 (14)	−0.0073 (12)	0.0169 (11)
C6B	0.110 (2)	0.0676 (16)	0.0466 (11)	0.0409 (15)	0.0020 (13)	0.0111 (11)
C7C	0.0818 (16)	0.0571 (14)	0.0741 (15)	0.0285 (12)	0.0001 (13)	0.0183 (12)
C10C	0.174 (3)	0.086 (2)	0.0610 (15)	0.083 (2)	−0.0183 (19)	0.0023 (14)
C9C	0.139 (3)	0.0724 (17)	0.0543 (13)	0.0541 (18)	−0.0147 (16)	0.0044 (12)
C2B	0.0872 (17)	0.0840 (19)	0.0493 (12)	0.0206 (15)	−0.0004 (12)	0.0069 (12)
C11D	0.0785 (17)	0.0711 (17)	0.0765 (17)	0.0053 (14)	0.0112 (14)	−0.0065 (13)
C1B	0.125 (3)	0.136 (3)	0.0639 (16)	0.062 (2)	0.0024 (18)	0.0238 (18)
C11A	0.0859 (19)	0.083 (2)	0.114 (3)	0.0141 (17)	0.0107 (19)	−0.0176 (18)
C1A	0.133 (3)	0.067 (2)	0.118 (3)	−0.0126 (19)	0.008 (2)	0.0404 (18)
C11C	0.133 (3)	0.0739 (19)	0.0641 (16)	0.0293 (18)	0.0092 (17)	0.0015 (13)
C1D	0.124 (3)	0.082 (2)	0.112 (3)	−0.014 (2)	0.011 (2)	0.040 (2)
C11B	0.177 (4)	0.074 (2)	0.0721 (18)	0.026 (2)	0.041 (2)	0.0006 (15)
C2C	0.217 (5)	0.098 (3)	0.074 (2)	0.007 (3)	−0.044 (3)	0.0247 (19)
C1C	0.240 (6)	0.159 (5)	0.125 (3)	0.067 (4)	−0.062 (4)	0.054 (3)

Geometric parameters (Å, °)

S1D—C3D	1.681 (2)	C9A—C10A	1.385 (3)
S2A—C3A	1.684 (2)	C9A—H9AA	0.9300
S1B—C3B	1.670 (3)	C7B—C6B	1.384 (3)
S2D—C8D	1.758 (2)	C7B—H7BA	0.9300
S2D—C11D	1.780 (3)	C10A—H10B	0.9300
S1C—C3C	1.688 (3)	C9D—H9DA	0.9300
S2C—C8C	1.758 (2)	C7A—H7AA	0.9300
S2C—C11C	1.770 (3)	C4B—H4BA	0.9300

S1A—C8A	1.767 (2)	C10B—C9B	1.364 (3)
S1A—C11A	1.773 (4)	C10B—H10C	0.9300
S2B—C8B	1.749 (2)	C2D—C1D	1.483 (5)
S2B—C11B	1.771 (4)	C2D—H2DB	0.9700
N3A—C3A	1.350 (3)	C2D—H2DC	0.9700
N3A—N2A	1.372 (2)	C3C—N1C	1.300 (4)
N3A—H3AA	0.8600	C6C—C5C	1.369 (3)
N3D—C3D	1.329 (3)	C6C—C7C	1.378 (3)
N3D—C2D	1.450 (3)	C6C—H6CA	0.9300
N3D—H3DA	0.8600	C9B—H9BA	0.9300
N2A—C4A	1.278 (3)	C7D—H7DA	0.9300
N2D—C3D	1.353 (3)	C4C—C5C	1.451 (3)
N2D—N1D	1.366 (2)	C4C—H4CA	0.9300
N2D—H2DA	0.8600	C5C—C10C	1.385 (4)
N1D—C4D	1.273 (3)	C2A—C1A	1.476 (5)
N1A—C3A	1.326 (3)	C2A—H2AB	0.9700
N1A—C2A	1.451 (3)	C2A—H2AC	0.9700
N1A—H1AA	0.8600	N1C—C2C	1.474 (4)
N3B—C4B	1.267 (3)	N1C—H1CA	0.8600
N3B—N2B	1.377 (3)	C6B—H6BA	0.9300
C5A—C10A	1.386 (3)	C7C—H7CA	0.9300
C5A—C6A	1.394 (3)	C10C—C9C	1.383 (4)
C5A—C4A	1.457 (3)	C10C—H10D	0.9300
C4A—H4AA	0.9300	C9C—H9CA	0.9300
C5D—C6D	1.378 (3)	C2B—C1B	1.485 (4)
C5D—C10D	1.399 (3)	C2B—H2BB	0.9700
C5D—C4D	1.460 (3)	C2B—H2BC	0.9700
C4D—H4DA	0.9300	C11D—H11A	0.9600
N3C—C4C	1.268 (3)	C11D—H11B	0.9600
N3C—N2C	1.372 (3)	C11D—H11C	0.9600
N2B—C3B	1.360 (3)	C1B—H1BB	0.9600
N2B—H2BA	0.8600	C1B—H1BC	0.9600
N1B—C3B	1.326 (3)	C1B—H1BD	0.9600
N1B—C2B	1.459 (3)	C11A—H11D	0.9600
N1B—H1BA	0.8600	C11A—H11E	0.9600
C6A—C7A	1.366 (3)	C11A—H11F	0.9600
C6A—H6AA	0.9300	C1A—H1AB	0.9600
C8D—C7D	1.375 (3)	C1A—H1AC	0.9600
C8D—C9D	1.386 (3)	C1A—H1AD	0.9600
C10D—C9D	1.378 (3)	C11C—H11G	0.9600
C10D—H10A	0.9300	C11C—H11H	0.9600
N2C—C3C	1.347 (3)	C11C—H11I	0.9600
N2C—H2CA	0.8600	C1D—H1DB	0.9600
C8B—C7B	1.364 (3)	C1D—H1DC	0.9600
C8B—C9B	1.394 (3)	C1D—H1DD	0.9600
C6D—C7D	1.382 (3)	C11B—H11J	0.9600
C6D—H6DA	0.9300	C11B—H11K	0.9600
C8C—C9C	1.357 (4)	C11B—H11L	0.9600
C8C—C7C	1.382 (3)	C2C—C1C	1.344 (5)

C8A—C7A	1.375 (4)	C2C—H2CB	0.9700
C8A—C9A	1.379 (4)	C2C—H2CC	0.9700
C5B—C6B	1.384 (3)	C1C—H1CB	0.9600
C5B—C10B	1.384 (3)	C1C—H1CC	0.9600
C5B—C4B	1.450 (3)	C1C—H1CD	0.9600
C8D—S2D—C11D	104.40 (13)	H2DB—C2D—H2DC	107.8
C8C—S2C—C11C	104.08 (13)	N1C—C3C—N2C	116.4 (2)
C8A—S1A—C11A	104.33 (15)	N1C—C3C—S1C	124.9 (2)
C8B—S2B—C11B	104.45 (16)	N2C—C3C—S1C	118.7 (2)
C3A—N3A—N2A	119.28 (17)	C5C—C6C—C7C	120.8 (2)
C3A—N3A—H3AA	120.4	C5C—C6C—H6CA	119.6
N2A—N3A—H3AA	120.4	C7C—C6C—H6CA	119.6
C3D—N3D—C2D	124.72 (18)	C10B—C9B—C8B	121.3 (2)
C3D—N3D—H3DA	117.6	C10B—C9B—H9BA	119.4
C2D—N3D—H3DA	117.6	C8B—C9B—H9BA	119.4
C4A—N2A—N3A	117.34 (18)	C8D—C7D—C6D	120.4 (2)
C3D—N2D—N1D	119.31 (17)	C8D—C7D—H7DA	119.8
C3D—N2D—H2DA	120.3	C6D—C7D—H7DA	119.8
N1D—N2D—H2DA	120.3	N3C—C4C—C5C	123.3 (2)
C4D—N1D—N2D	117.00 (18)	N3C—C4C—H4CA	118.3
C3A—N1A—C2A	125.21 (19)	C5C—C4C—H4CA	118.3
C3A—N1A—H1AA	117.4	C6C—C5C—C10C	117.1 (2)
C2A—N1A—H1AA	117.4	C6C—C5C—C4C	124.1 (2)
N3D—C3D—N2D	116.24 (18)	C10C—C5C—C4C	118.8 (2)
N3D—C3D—S1D	123.83 (17)	N1A—C2A—C1A	113.2 (2)
N2D—C3D—S1D	119.84 (15)	N1A—C2A—H2AB	108.9
N1A—C3A—N3A	115.98 (18)	C1A—C2A—H2AB	108.9
N1A—C3A—S2A	124.11 (17)	N1A—C2A—H2AC	108.9
N3A—C3A—S2A	119.91 (16)	C1A—C2A—H2AC	108.9
C4B—N3B—N2B	117.1 (2)	H2AB—C2A—H2AC	107.8
C10A—C5A—C6A	117.6 (2)	C3C—N1C—C2C	124.4 (3)
C10A—C5A—C4A	120.3 (2)	C3C—N1C—H1CA	117.8
C6A—C5A—C4A	122.0 (2)	C2C—N1C—H1CA	117.8
N2A—C4A—C5A	120.58 (19)	C5B—C6B—C7B	121.3 (2)
N2A—C4A—H4AA	119.7	C5B—C6B—H6BA	119.3
C5A—C4A—H4AA	119.7	C7B—C6B—H6BA	119.3
C6D—C5D—C10D	118.2 (2)	C6C—C7C—C8C	121.4 (2)
C6D—C5D—C4D	120.6 (2)	C6C—C7C—H7CA	119.3
C10D—C5D—C4D	121.2 (2)	C8C—C7C—H7CA	119.3
N1D—C4D—C5D	121.0 (2)	C9C—C10C—C5C	122.2 (3)
N1D—C4D—H4DA	119.5	C9C—C10C—H10D	118.9
C5D—C4D—H4DA	119.5	C5C—C10C—H10D	118.9
C4C—N3C—N2C	115.7 (2)	C8C—C9C—C10C	120.1 (2)
C3B—N2B—N3B	118.8 (2)	C8C—C9C—H9CA	120.0
C3B—N2B—H2BA	120.6	C10C—C9C—H9CA	120.0
N3B—N2B—H2BA	120.6	N1B—C2B—C1B	110.0 (2)
C3B—N1B—C2B	125.2 (2)	N1B—C2B—H2BB	109.7
C3B—N1B—H1BA	117.4	C1B—C2B—H2BB	109.7
C2B—N1B—H1BA	117.4	N1B—C2B—H2BC	109.7

N1B—C3B—N2B	115.0 (2)	C1B—C2B—H2BC	109.7
N1B—C3B—S1B	124.81 (17)	H2BB—C2B—H2BC	108.2
N2B—C3B—S1B	120.1 (2)	S2D—C11D—H11A	109.5
C7A—C6A—C5A	120.7 (2)	S2D—C11D—H11B	109.5
C7A—C6A—H6AA	119.6	H11A—C11D—H11B	109.5
C5A—C6A—H6AA	119.6	S2D—C11D—H11C	109.5
C7D—C8D—C9D	118.8 (2)	H11A—C11D—H11C	109.5
C7D—C8D—S2D	124.82 (18)	H11B—C11D—H11C	109.5
C9D—C8D—S2D	116.42 (18)	C2B—C1B—H1BB	109.5
C9D—C10D—C5D	120.1 (2)	C2B—C1B—H1BC	109.5
C9D—C10D—H10A	119.9	H1BB—C1B—H1BC	109.5
C5D—C10D—H10A	119.9	C2B—C1B—H1BD	109.5
C3C—N2C—N3C	120.6 (2)	H1BB—C1B—H1BD	109.5
C3C—N2C—H2CA	119.7	H1BC—C1B—H1BD	109.5
N3C—N2C—H2CA	119.7	S1A—C11A—H11D	109.5
C7B—C8B—C9B	118.1 (2)	S1A—C11A—H11E	109.5
C7B—C8B—S2B	125.57 (19)	H11D—C11A—H11E	109.5
C9B—C8B—S2B	116.4 (2)	S1A—C11A—H11F	109.5
C5D—C6D—C7D	121.4 (2)	H11D—C11A—H11F	109.5
C5D—C6D—H6DA	119.3	H11E—C11A—H11F	109.5
C7D—C6D—H6DA	119.3	C2A—C1A—H1AB	109.5
C9C—C8C—C7C	118.4 (2)	C2A—C1A—H1AC	109.5
C9C—C8C—S2C	124.19 (19)	H1AB—C1A—H1AC	109.5
C7C—C8C—S2C	117.39 (18)	C2A—C1A—H1AD	109.5
C7A—C8A—C9A	118.9 (2)	H1AB—C1A—H1AD	109.5
C7A—C8A—S1A	116.1 (2)	H1AC—C1A—H1AD	109.5
C9A—C8A—S1A	125.0 (2)	S2C—C11C—H11G	109.5
C6B—C5B—C10B	117.6 (2)	S2C—C11C—H11H	109.5
C6B—C5B—C4B	120.2 (2)	H11G—C11C—H11H	109.5
C10B—C5B—C4B	122.3 (2)	S2C—C11C—H11I	109.5
C8A—C9A—C10A	120.0 (2)	H11G—C11C—H11I	109.5
C8A—C9A—H9AA	120.0	H11H—C11C—H11I	109.5
C10A—C9A—H9AA	120.0	C2D—C1D—H1DB	109.5
C8B—C7B—C6B	120.7 (2)	C2D—C1D—H1DC	109.5
C8B—C7B—H7BA	119.6	H1DB—C1D—H1DC	109.5
C6B—C7B—H7BA	119.6	C2D—C1D—H1DD	109.5
C9A—C10A—C5A	121.3 (2)	H1DB—C1D—H1DD	109.5
C9A—C10A—H10B	119.3	H1DC—C1D—H1DD	109.5
C5A—C10A—H10B	119.3	S2B—C11B—H11J	109.5
C10D—C9D—C8D	121.1 (2)	S2B—C11B—H11K	109.5
C10D—C9D—H9DA	119.5	H11J—C11B—H11K	109.5
C8D—C9D—H9DA	119.5	S2B—C11B—H11L	109.5
C6A—C7A—C8A	121.4 (2)	H11J—C11B—H11L	109.5
C6A—C7A—H7AA	119.3	H11K—C11B—H11L	109.5
C8A—C7A—H7AA	119.3	C1C—C2C—N1C	115.8 (4)
N3B—C4B—C5B	121.7 (2)	C1C—C2C—H2CB	108.3
N3B—C4B—H4BA	119.2	N1C—C2C—H2CB	108.3
C5B—C4B—H4BA	119.2	C1C—C2C—H2CC	108.3
C9B—C10B—C5B	121.0 (2)	N1C—C2C—H2CC	108.3

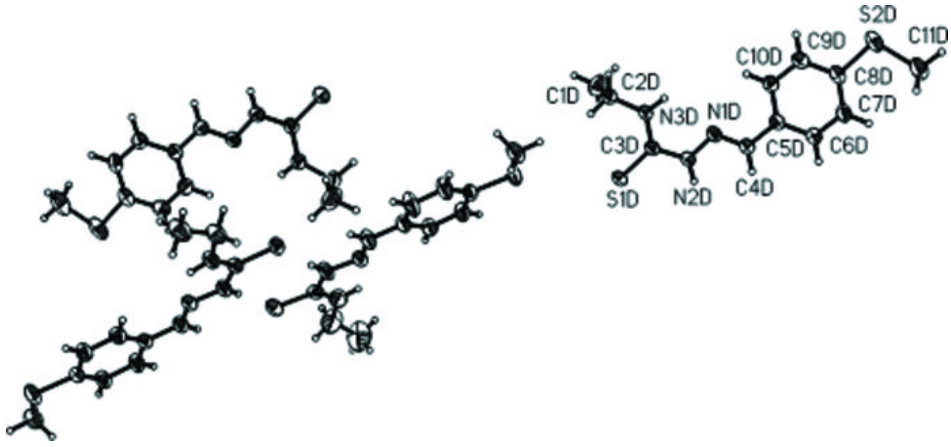
C9B—C10B—H10C	119.5	H2CB—C2C—H2CC	107.4
C5B—C10B—H10C	119.5	C2C—C1C—H1CB	109.5
N3D—C2D—C1D	113.1 (3)	C2C—C1C—H1CC	109.5
N3D—C2D—H2DB	109.0	H1CB—C1C—H1CC	109.5
C1D—C2D—H2DB	109.0	C2C—C1C—H1CD	109.5
N3D—C2D—H2DC	109.0	H1CB—C1C—H1CD	109.5
C1D—C2D—H2DC	109.0	H1CC—C1C—H1CD	109.5

Hydrogen-bond geometry (Å, °)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
N1A—H1AA···N2A	0.86	2.20	2.602 (3)	108
N1B—H1BA···N3B	0.86	2.17	2.585 (3)	109
N1C—H1CA···N3C	0.86	2.23	2.624 (3)	108
N3D—H3DA···N1D	0.86	2.22	2.610 (3)	107
N3A—H3AA···S1D^{i}	0.86	2.59	3.398 (2)	156
N2D—H2DA···S2A^{ii}	0.86	2.57	3.402 (2)	163
N1A—H1AA···S1B	0.86	2.81	3.4798 (19)	136
N2B—H2BA···S1C	0.86	2.72	3.579 (2)	174
N2C—H2CA···S1B	0.86	2.64	3.487 (3)	168

Symmetry codes: (i) *x*, *y*−1, *z*; (ii) *x*, *y*+1, *z*.

Fig. 1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C2D
N3D
N1D
C3D
C4D
S1D
N2D

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N-Cyclohexylbenzamide

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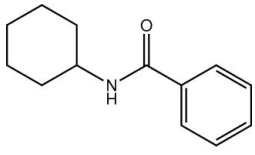
Key indicators: single-crystal X-ray study; T = 293 K; mean σ(C–C) = 0.005 Å; R factor = 0.045; wR factor = 0.163; data-to-parameter ratio = 10.2.

The structure of the title compound, $C_{13}H_{17}NO$, features an *anti* disposition of the N—H and carbonyl groups. The amide group is twisted with respect to the benzene ring [N–C(=O)–C–C torsion angle = −30.8 (4)°]. In the crystal, $C(4)$ chains propagating in [100] are formed by intermolecular N–H···O hydrogen bonds. Weak C—H···π interactions link the chains into sheets.

Related literature

For biological applications of benzamides, see: Clark *et al.* (1988); Leander *et al.* (1988); Diouf *et al.* (1997).



Experimental

Crystal data

$C_{13}H_{17}NO$
M_r = 203.28
Monoclinic, $P2_1$
a = 5.2372 (3) Å
b = 6.5841 (4) Å
c = 16.6029 (12) Å
β = 91.176 (2)°
V = 572.38 (6) Å^3
Z = 2
Mo $K\alpha$ radiation
μ = 0.07 mm^{-1}
T = 293 K
0.28 × 0.17 × 0.12 mm

Data collection

Bruker APEXII CCD diffractometer
5479 measured reflections
1423 independent reflections
1105 reflections with $I > 2\sigma(I)$
R_{int} = 0.033

Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.045
$wR(F^2)$ = 0.163
S = 1.07
1423 reflections
140 parameters
1 restraint
H atoms treated by a mixture of independent and constrained refinement
$\Delta\rho_{max}$ = 0.22 e Å^{-3}
$\Delta\rho_{min}$ = −0.21 e Å^{-3}

Table 1
Hydrogen-bond geometry (Å, °).

*Cg*1 is the centroid of the C2–C7 ring.

D—H···A	D—H	H···A	D···A	D—H···A
N1—H1*n*···O1^{i}	0.80 (3)	2.32 (3)	3.065 (3)	157 (3)
C13—H13a···*Cg*1^{ii}	0.97	2.82	3.722 (4)	154
C5—H5···*Cg*1^{iii}	0.93	2.96	3.729 (4)	141

Symmetry codes: (i) $x-1, y, z$; (ii) $x, y-1, z$; (iii) $-x+1, y+\frac{1}{2}, -z$.

Data collection: *APEX2* (Bruker, 2007); cell refinement: *SAINT* (Bruker, 2007); data reduction: *SAINT*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *ORTEP-3* (Farrugia, 1997) and *DIAMOND* (Brandenburg, 2006); software used to prepare material for publication: *publCIF* (Westrip, 2010).

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Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: HB5496).

References

Brandenburg, K. (2006). *DIAMOND*. Crystal Impact GbR, Bonn, Germany.
Bruker (2007). *APEX2* & *SAINT*. Bruker AXS Inc., Madison, Wisconsin, USA.
Clark, C. R. (1988). *Epilepsia*, **29**, 198–203.
Diouf, O., Bourhim, M., Lambert, D. M., Poupaert, J. H., Stables, J. P. & Vamecq, J. (1997). *Biomed. Pharmacother.* **51**, 131–136.
Farrugia, L. J. (1997). *J. Appl. Cryst.* **30**, 565.
Leander, J. D., Robertson, D. W., Clark, C. R., Lawson, R. R. & Rathbun, R. C. (1988). *Epilepsia*, **29**, 83–90.
Sheldrick, G. M. (2008). *Acta Cryst.* A**64**, 112–122.
Westrip, S. P. (2010). *J. Appl. Cryst.* **43**. Submitted.

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supplementary materials

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N-Cyclohexylbenzamide

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Comment

Benzamides are frequently used in the synthesis of new and potent anti-convulsant agents (Clark *et al.*, 1988; Leander *et al.*, 1988; Diouf *et al.*, 1997). The structure of the title compound, (I), a benzamide derivative, is reported herein (Fig. 1).

The benzene ring, adjacent to the carbonyl group, twisted with respect to the plane formed through the central amide group; the N1–C1–C2–C3 torsion angle = -30.8 (4) °. In the same way, the putative mirror plane through the cyclohexyl ring (having a chair conformation) is twisted away from the central plane; the O1–N1–C8–C11 torsion angle is 151.3 (4) °. The anti-disposition of the NH and carbonyl groups allows for the formation of N–H···O hydrogen bonds which leads to the formation supramolecular chains aligned along the *a* axis, Fig. 2 and Table 1. These are connected into layers in the *ab* plane *via* C–H···π interactions, Fig. 2 and Table 1.

Experimental

A solution of cyclohexyl amine (0.458 µl, 4 mmol) in dichloromethane (15 ml) was treated dropwise with benzoyl chloride (0.463 µl, 4 mmol) in the presence of triethanol amine (5 ml) as a catalyst. The resulting mixture was stirred for 1 h. The precipitates that formed were filtered, dried and crystallized from methanol to yield colourless blocks of (I).

Refinement

The C-bound H atoms were geometrically placed (C–H = 0.93–0.98 Å) and refined as riding with U_{iso}(H) = 1.2U_{eq}(C). The N-bound H atom was refined freely. In the absence of significant anomalous scattering effects, 1130 Friedel pairs were averaged in the final refinement.

Figures

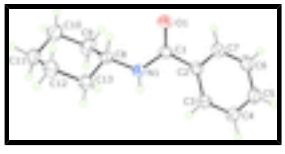


Fig. 1. The molecular structure of (I) showing displacement ellipsoids at the 35% probability level.

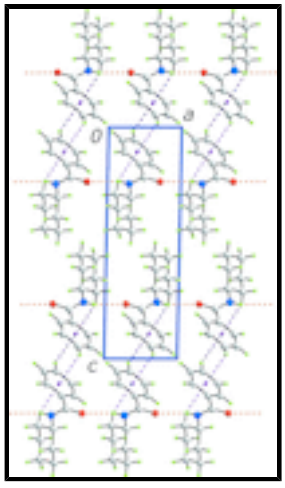


Fig. 2. A view in projection down the *b* axis of the unit-cell contents for (I), highlighting the formation of layers in the *ab* plane. The N–H···O and C–H···π interactions are shown as orange and purple dashed lines, respectively. Colour code: O, red; N, blue; C, grey; and H, green.

N-Cyclohexylbenzamide

Crystal data

$C_{13}H_{17}NO$	$Z = 2$
$M_r = 203.28$	$F(000) = 220$
Monoclinic, $P2_1$	$D_x = 1.179$ Mg m^{-3}
Hall symbol: P 2yb	Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å
$a = 5.2372$ (3) Å	$\mu = 0.07$ mm^{-1}
$b = 6.5841$ (4) Å	$T = 293$ K
$c = 16.6029$ (12) Å	Block, colourless
$\beta = 91.176$ (2)°	0.28 × 0.17 × 0.12 mm
$V = 572.38$ (6) Å^3	

Data collection

Bruker APEXII CCD diffractometer	1105 reflections with $I > 2\sigma(I)$
Radiation source: fine-focus sealed tube	$R_{int} = 0.033$
graphite	$\theta_{max} = 27.5°$, $\theta_{min} = 1.2°$
φ and ω scans	$h = -6 \rightarrow 6$
5479 measured reflections	$k = -8 \rightarrow 8$
1423 independent reflections	$l = -21 \rightarrow 21$

Refinement

Refinement on F^2	Secondary atom site location: difference Fourier map
Least-squares matrix: full	Hydrogen site location: inferred from neighbouring sites
$R[F^2 > 2\sigma(F^2)] = 0.045$	H atoms treated by a mixture of independent and constrained refinement
$wR(F^2) = 0.163$	$w = 1/[\sigma^2(F_o^2) + (0.1083P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$

S = 1.07	$(\Delta/\sigma)_{max} < 0.001$
1423 reflections	$\Delta\rho_{max} = 0.22$ e Å^{-3}
140 parameters	$\Delta\rho_{min} = -0.21$ e Å^{-3}
1 restraint	Absolute structure: unk
Primary atom site location: structure-invariant direct methods	

Special details

Geometry. All s.u.'s (except the s.u. in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell s.u.'s are taken into account individually in the estimation of s.u.'s in distances, angles and torsion angles; correlations between s.u.'s in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell s.u.'s is used for estimating s.u.'s involving l.s. planes.

Refinement. Refinement of F^2 against ALL reflections. The weighted *R*-factor *wR* and goodness of fit *S* are based on F^2, conventional *R*-factors *R* are based on *F*, with *F* set to zero for negative F^2. The threshold expression of $F^2 > 2\sigma(F^2)$ is used only for calculating *R*-factors(gt) *etc*. and is not relevant to the choice of reflections for refinement. *R*-factors based on F^2 are statistically about twice as large as those based on *F*, and *R*- factors based on ALL data will be even larger.

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å^2)

	x	*y*	*z*	U_{iso}*/U_{eq}
O1	0.7158 (3)	0.9885 (4)	0.23591 (14)	0.0636 (8)
N1	0.2952 (5)	0.9238 (4)	0.24441 (15)	0.0424 (6)
H1n	0.157 (6)	0.969 (6)	0.2345 (18)	0.045 (9)*
C1	0.4923 (5)	1.0267 (4)	0.21584 (18)	0.0415 (7)
C2	0.4362 (5)	1.1979 (5)	0.15919 (15)	0.0381 (6)
C3	0.2245 (5)	1.2004 (6)	0.10682 (16)	0.0460 (7)
H3	0.1077	1.0941	0.1071	0.055*
C4	0.1894 (6)	1.3614 (7)	0.05468 (18)	0.0575 (9)
H4	0.0488	1.3620	0.0195	0.069*
C5	0.3571 (6)	1.5201 (6)	0.05375 (19)	0.0602 (10)
H5	0.3321	1.6270	0.0179	0.072*
C6	0.5654 (6)	1.5203 (6)	0.1069 (2)	0.0586 (9)
H6	0.6785	1.6292	0.1076	0.070*
C7	0.6038 (6)	1.3593 (6)	0.15818 (19)	0.0495 (8)
H7	0.7455	1.3591	0.1929	0.059*
C8	0.3233 (5)	0.7589 (4)	0.30240 (17)	0.0405 (7)
H8	0.4904	0.6958	0.2945	0.049*
C9	0.3184 (8)	0.8399 (6)	0.3885 (2)	0.0611 (9)
H9A	0.4570	0.9358	0.3968	0.073*
H9B	0.1588	0.9108	0.3969	0.073*
C10	0.3452 (8)	0.6680 (7)	0.4484 (2)	0.0683 (11)
H10A	0.5140	0.6088	0.4443	0.082*
H10B	0.3296	0.7218	0.5024	0.082*
C11	0.1481 (6)	0.5051 (6)	0.4349 (2)	0.0636 (10)
H11A	−0.0198	0.5593	0.4461	0.076*
H11B	0.1814	0.3937	0.4719	0.076*

C12	0.1507 (7)	0.4266 (6)	0.3493 (2)	0.0620 (9)
H12A	0.0120	0.3306	0.3413	0.074*
H12B	0.3100	0.3556	0.3405	0.074*
C13	0.1224 (6)	0.5985 (5)	0.2888 (2)	0.0482 (8)
H13A	0.1362	0.5444	0.2347	0.058*
H13B	−0.0455	0.6591	0.2934	0.058*

Atomic displacement parameters (Å^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
O1	0.0330 (10)	0.0681 (17)	0.0893 (17)	0.0023 (11)	−0.0042 (10)	0.0243 (15)
N1	0.0333 (12)	0.0437 (14)	0.0500 (14)	0.0042 (11)	−0.0005 (9)	0.0077 (11)
C1	0.0359 (13)	0.0405 (16)	0.0479 (15)	0.0036 (13)	0.0009 (11)	−0.0004 (13)
C2	0.0356 (12)	0.0421 (15)	0.0368 (14)	0.0029 (12)	0.0050 (10)	−0.0031 (13)
C3	0.0398 (14)	0.0546 (18)	0.0436 (15)	0.0001 (14)	−0.0021 (11)	0.0020 (16)
C4	0.0471 (16)	0.080 (2)	0.0453 (16)	0.0045 (18)	−0.0018 (13)	0.0133 (19)
C5	0.0554 (17)	0.067 (2)	0.059 (2)	0.0138 (18)	0.0137 (15)	0.024 (2)
C6	0.0552 (17)	0.0512 (19)	0.070 (2)	−0.0060 (17)	0.0147 (15)	0.0140 (18)
C7	0.0426 (14)	0.0538 (19)	0.0523 (17)	−0.0035 (14)	0.0059 (12)	0.0047 (16)
C8	0.0354 (12)	0.0391 (15)	0.0470 (16)	0.0060 (12)	0.0010 (11)	0.0046 (13)
C9	0.084 (2)	0.051 (2)	0.0476 (17)	−0.0102 (19)	−0.0115 (16)	−0.0008 (16)
C10	0.082 (2)	0.071 (3)	0.0513 (19)	−0.001 (2)	−0.0104 (17)	0.010 (2)
C11	0.0624 (19)	0.062 (2)	0.067 (2)	0.010 (2)	0.0116 (16)	0.022 (2)
C12	0.0633 (19)	0.0396 (18)	0.083 (3)	−0.0053 (16)	0.0001 (17)	0.0068 (18)
C13	0.0457 (15)	0.0427 (17)	0.0560 (19)	−0.0010 (14)	−0.0021 (13)	−0.0011 (15)

Geometric parameters (Å, °)

O1—C1	1.236 (3)	C8—C9	1.526 (4)
N1—C1	1.331 (4)	C8—H8	0.9800
N1—C8	1.456 (4)	C9—C10	1.511 (5)
N1—H1n	0.80 (3)	C9—H9A	0.9700
C1—C2	1.493 (4)	C9—H9B	0.9700
C2—C7	1.379 (4)	C10—C11	1.502 (5)
C2—C3	1.395 (4)	C10—H10A	0.9700
C3—C4	1.379 (5)	C10—H10B	0.9700
C3—H3	0.9300	C11—C12	1.512 (5)
C4—C5	1.365 (5)	C11—H11A	0.9700
C4—H4	0.9300	C11—H11B	0.9700
C5—C6	1.389 (5)	C12—C13	1.519 (5)
C5—H5	0.9300	C12—H12A	0.9700
C6—C7	1.372 (5)	C12—H12B	0.9700
C6—H6	0.9300	C13—H13A	0.9700
C7—H7	0.9300	C13—H13B	0.9700
C8—C13	1.505 (4)		
C1—N1—C8	123.1 (2)	C10—C9—C8	110.6 (3)
C1—N1—H1N	116 (3)	C10—C9—H9A	109.5
C8—N1—H1N	120 (2)	C8—C9—H9A	109.5

O1—C1—N1	122.5 (3)	C10—C9—H9B	109.5
O1—C1—C2	119.8 (2)	C8—C9—H9B	109.5
N1—C1—C2	117.7 (2)	H9A—C9—H9B	108.1
C7—C2—C3	118.8 (3)	C11—C10—C9	112.5 (3)
C7—C2—C1	118.2 (2)	C11—C10—H10A	109.1
C3—C2—C1	123.0 (3)	C9—C10—H10A	109.1
C4—C3—C2	119.7 (3)	C11—C10—H10B	109.1
C4—C3—H3	120.2	C9—C10—H10B	109.1
C2—C3—H3	120.2	H10A—C10—H10B	107.8
C5—C4—C3	121.2 (3)	C10—C11—C12	111.4 (3)
C5—C4—H4	119.4	C10—C11—H11A	109.4
C3—C4—H4	119.4	C12—C11—H11A	109.4
C4—C5—C6	119.4 (3)	C10—C11—H11B	109.4
C4—C5—H5	120.3	C12—C11—H11B	109.4
C6—C5—H5	120.3	H11A—C11—H11B	108.0
C7—C6—C5	119.8 (3)	C11—C12—C13	111.4 (3)
C7—C6—H6	120.1	C11—C12—H12A	109.4
C5—C6—H6	120.1	C13—C12—H12A	109.4
C6—C7—C2	121.2 (3)	C11—C12—H12B	109.4
C6—C7—H7	119.4	C13—C12—H12B	109.4
C2—C7—H7	119.4	H12A—C12—H12B	108.0
N1—C8—C13	111.3 (2)	C8—C13—C12	111.4 (2)
N1—C8—C9	110.8 (3)	C8—C13—H13A	109.3
C13—C8—C9	111.1 (3)	C12—C13—H13A	109.3
N1—C8—H8	107.8	C8—C13—H13B	109.3
C13—C8—H8	107.8	C12—C13—H13B	109.3
C9—C8—H8	107.8	H13A—C13—H13B	108.0
C8—N1—C1—O1	0.7 (5)	C3—C2—C7—C6	−0.1 (4)
C8—N1—C1—C2	−177.6 (2)	C1—C2—C7—C6	179.2 (3)
O1—C1—C2—C7	−28.3 (4)	C1—N1—C8—C13	−146.5 (3)
N1—C1—C2—C7	150.1 (3)	C1—N1—C8—C9	89.3 (3)
O1—C1—C2—C3	150.9 (3)	N1—C8—C9—C10	179.5 (3)
N1—C1—C2—C3	−30.8 (4)	C13—C8—C9—C10	55.2 (3)
C7—C2—C3—C4	1.0 (4)	C8—C9—C10—C11	−54.8 (4)
C1—C2—C3—C4	−178.2 (3)	C9—C10—C11—C12	54.6 (4)
C2—C3—C4—C5	−0.6 (5)	C10—C11—C12—C13	−54.1 (4)
C3—C4—C5—C6	−0.7 (5)	N1—C8—C13—C12	−179.8 (3)
C4—C5—C6—C7	1.6 (5)	C9—C8—C13—C12	−55.8 (3)
C5—C6—C7—C2	−1.2 (5)	C11—C12—C13—C8	55.2 (4)

Hydrogen-bond geometry (Å, °)

Cg1 is the centroid of the C2–C7 ring.

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
N1—H1n···O1^{i}	0.80 (3)	2.32 (3)	3.065 (3)	157 (3)
C13—H13a···Cg1^{ii}	0.97	2.82	3.722 (4)	154
C5—H5···Cg1^{iii}	0.93	2.96	3.729 (4)	141

Symmetry codes: (i) *x*−1, *y*, *z*; (ii) *x*, *y*−1, *z*; (iii) −*x*+1, *y*+1/2, −*z*.

Fig. 1

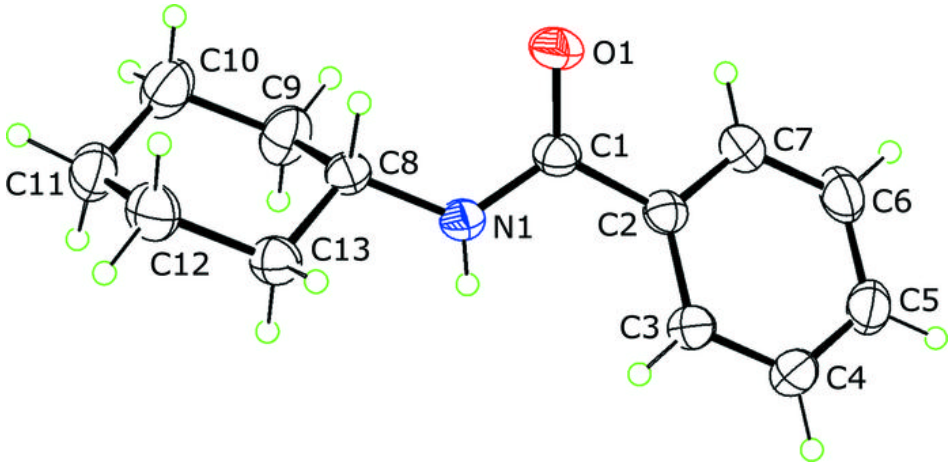
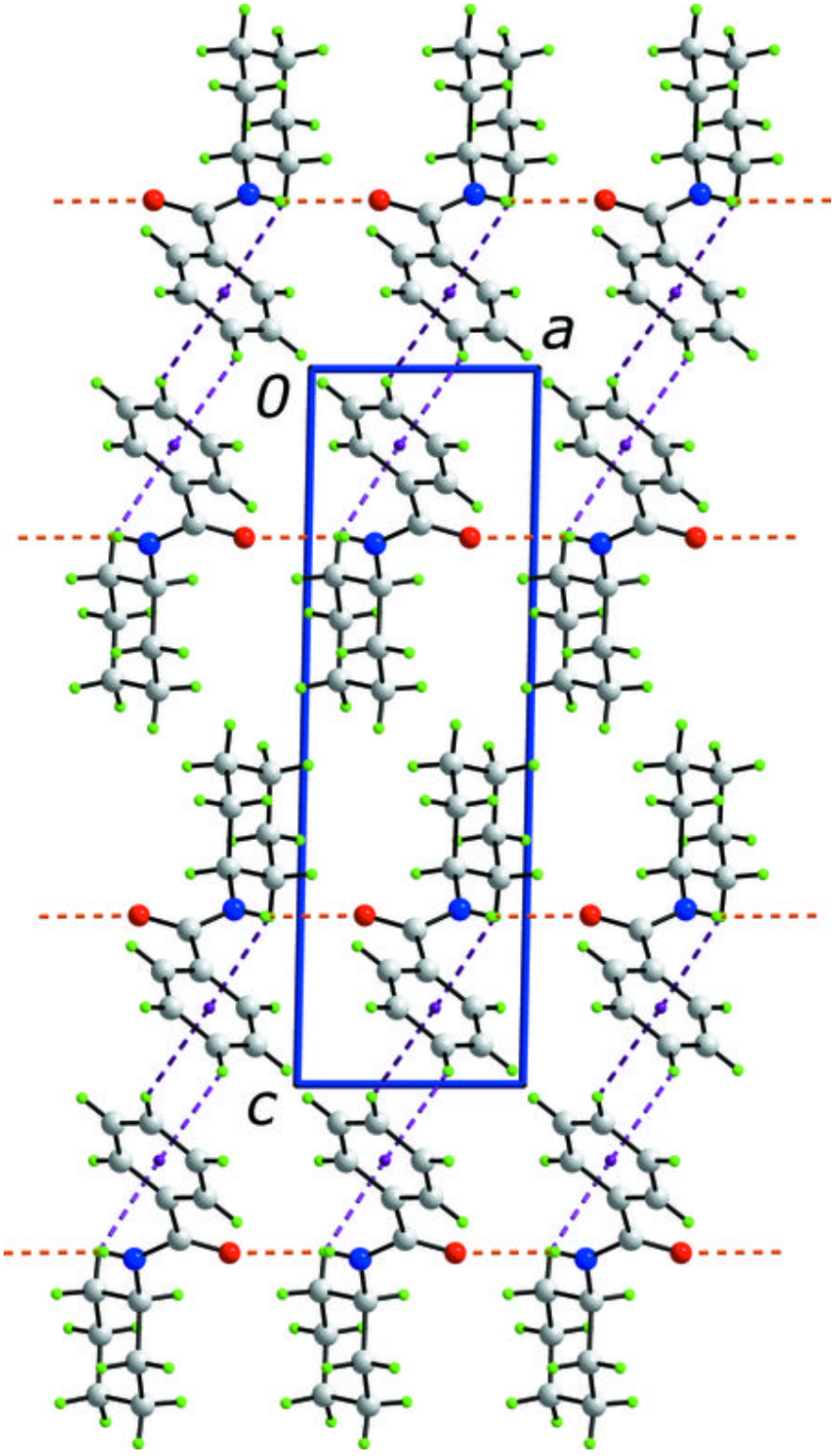


Fig. 2



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Tris(1,10-phenanthroline)cobalt(II) bis(perrhenate) monohydrate

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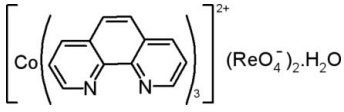
Key indicators: single-crystal X-ray study; T = 293 K; mean σ(C–C) = 0.012 Å; R factor = 0.083; wR factor = 0.244; data-to-parameter ratio = 35.0.

In the title compound, $[Co(C_{12}H_8N_2)_3][ReO_4]_2\cdot H_2O$, the Co^{II} atom is coordinated by three 1,10-phenanthroline ligands in a distorted octahedral arrangement. In the crystal, the components are linked by O—H···O, C—H···O and aromatic π–π stacking [shortest centroid–centroid separation = 3.659 (5) Å] interactions.

Related literature

For a related structure and biological background information, see: Li *et al.* (2010). For geometrical features in related structures, see: Ikotun *et al.* (2008); Addison *et al.* (1984).



Experimental

Crystal data

$[Co(C_{12}H_8N_2)_3][ReO_4]_2\cdot H_2O$
M_r = 1117.96
Triclinic, $P\overline{1}$
a = 10.350 (5) Å
b = 13.133 (3) Å
c = 14.392 (2) Å
α = 73.58 (2)°
β = 71.18 (2)°
γ = 78.50 (3)°
V = 1763.6 (10) Å^3
Z = 2
Ag $K\alpha$ radiation
λ = 0.56087 Å
μ = 3.97 mm^{-1}
T = 293 K
0.17 × 0.15 × 0.13 mm

Data collection

Enraf–Nonius CAD-4 diffractometer
24086 measured reflections
17274 independent reflections
8056 reflections with $I > 2\sigma(I)$
R_{int} = 0.027
2 standard reflections every 120 min
intensity decay: 3%

Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.083
$wR(F^2)$ = 0.244
S = 0.98
17274 reflections
493 parameters
3 restraints
H atoms treated by a mixture of independent and constrained refinement
$\Delta\rho_{max}$ = 5.34 e Å^{-3}
$\Delta\rho_{min}$ = −5.31 e Å^{-3}

Table 1
Selected bond lengths (Å).

Re2—O7	1.549 (15)	Re1—O4	1.724 (10)
Re2—O5	1.685 (8)	Co1—N6	2.122 (5)
Re2—O6	1.708 (8)	Co1—N2	2.122 (5)
Re2—O8	1.728 (8)	Co1—N1	2.136 (5)
Re1—O3	1.688 (9)	Co1—N4	2.147 (5)
Re1—O2	1.691 (9)	Co1—N3	2.148 (6)
Re1—O1	1.700 (7)	Co1—N5	2.151 (6)

Table 2
Hydrogen-bond geometry (Å, °).

D—H···A	D—H	H···A	D···A	D—H···A
O9—H209···O1^{i}	0.85 (10)	1.99 (8)	2.802 (13)	157 (19)
O9—H109···O8	0.86 (14)	2.26 (17)	2.953 (17)	139 (23)
C15—H15···O9^{ii}	0.93	2.56	3.271 (14)	134
C33—H33···O5^{iii}	0.93	2.51	3.116 (12)	123
C5—H5···O4^{iv}	0.93	2.45	3.309 (13)	154
C33—H33···O5^{iii}	0.93	2.51	3.116 (12)	123

Symmetry codes: (i) $x, y, z+1$; (ii) $x, y+1, z-1$; (iii) $-x+2, -y+1, -z+1$; (iv) $x+1, y, z$.

Data collection: *CAD-4 EXPRESS* (Enraf–Nonius, 1994); cell refinement: *CAD-4 EXPRESS*; data reduction: *XCAD4* (Harms & Wocadlo, 1995); program(s) used to solve structure: *SHELXS86* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *ORTEP-3* (Farrugia, 1997) and *DIAMOND* (Brandenburg & Putz, 2005); software used to prepare material for publication: *WinGX* (Farrugia, 1999).

Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: HB5497).

References

Addison, A. W., Rao, T. N., Reedijk, J., Rijn, J. V. & Verschoor, G. C. (1984). *J. Chem. Soc. Dalton Trans.* pp. 1349–1356.
Brandenburg, K. & Putz, H. (2005). *DIAMOND*. Crystal impact GbR, Bonn, Germany.
Enraf–Nonius (1994). *CAD-4 EXPRESS*. Enraf–Nonius, Delft, The Netherlands.
Farrugia, L. J. (1997). *J. Appl. Cryst.* **30**, 565.
Farrugia, L. J. (1999). *J. Appl. Cryst.* **32**, 837–838.
Harms, K. & Wocadlo, S. (1995). *XCAD4*. University of Marburg, Germany.
Ikotun, O. F., Ouellette, W., Lloret, F., Kruger, P. E., Julve, M. & Doyle, R. P. (2008). *Eur. J. Inorg. Chem.* **17**, 2691–2697.
Li, M. X., Chen, C. L., Zhang, D., Niu, J. Y. & Ji, B. S. (2010). *Eur. J. Med. Chem.* **45**, 3169–3177.
Sheldrick, G. M. (2008). *Acta Cryst.* A**64**, 112–122.

supplementary materials

Acta Cryst. (2010). E**66**, m816 [**doi:10.1107/S1600536810022750**]

Tris(1,10-phenanthroline)cobalt(II) bis(perrhenate) monohydrate

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Comment

As part of our exploration of metal complexes with possible biological applications (Li *et al.*, 2010), we now report the structure of the title compound, (I)> It contains one cationic mononuclear species $[Co(phen)_3]^{2+}$, two perrhenate anions, and one lattice water molecule (Fig. 1). The unique crystallographically independent Co^{II} exhibits a distorted octahedral environment with a τ value of 0.05 (2) calaculated using the approach of Reedijk and co-workers (Addison *et al.*, 1984). Six nitrogen donors from three bidendate phen ligands are coordinated to Co^{II}. The Co^{II} is slightly displaced from the octahedron centroid by 0.053 (1) Å. The structural data are in good agreement with those of the cobalt(II) complexes which exhibit a similar geometry (Li *et al.*, 2010). The phen molecules are nearly planar (mean deviation is 0.048 (3) Å). The mean dihedral angle between the two pyridyl planes being 3.0 (2)°. The intra-ring C—N and C—C bond distances have respectively the usual mean values 1,344 (8) Å) and 1.397 (11)Å (Ikotun *et al.*, 2008). The angles subtended by the bidentate phen ligand at the cobalt atom are comparable with a mean value 77,9(2)°. The charges are counterbalanced by uncoordinated perrhenate anions which are connected through hydrogen bonds (C—H ···O) to the coordinated phen molecules (Table 1 and Fig. 2). The mononuclear units are also interconnected through intermolecular hydrogen bonds involving the uncoordinated water molecule and perrhenate oxygen atoms (Table 1) to form trinuclear unit which is further stabilized by the inter-phen ring *p*-p stacking (Fig. 2). The mean interplanar distance is 3.719 Å and the angle made by ring normal and the vector between the ring centroids is 7.95° (mean value).

Experimental

An aqueous solution (15 ml) of NH_4ReO_4 (0.54 g; 2 mmol) was slowly added under stirring to a mixture of ethanol (5 ml) and water (15 ml) containing phen (0,42 g; 3 mmol) and $CoCl_2$ (0.2 g; 1 mmol). The purple solution was left in air for a week and pink prisms of (I) were recovered.

Refinement

The water H atoms were located in a difference map and freely refined. All H atoms attached to C atoms were fixed geometrically and treated as riding, with C—H = 0.93 Å and with U_{iso}(H) = 1.2Ueq(C).

Figures

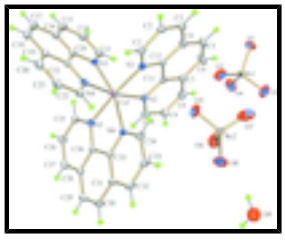


Fig. 1. The structure of (I) with displacement ellipsoids drawn at the 30% probability level.

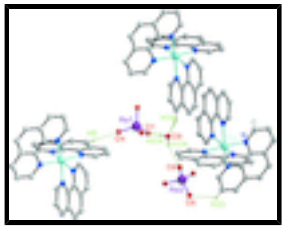


Fig. 2. Hydrogen-bonding interactions in (I); the H-atoms not involved in H-bonding are omitted.

Tris(1,10-phenanthroline)cobalt(II) bis(perrhenate) monohydrate

Crystal data

$[Co(C_{12}H_8N_2)_3][ReO_4]_2 \cdot H_2O$	$Z = 2$
$M_r = 1117.96$	$F(000) = 1066$
Triclinic, $P\overline{1}$	$D_x = 2.105$ Mg m^{-3}
Hall symbol: -P 1	Ag $K\alpha$ radiation, $\lambda = 0.56087$ Å
$a = 10.350$ (5) Å	Cell parameters from 25 reflections
$b = 13.133$ (3) Å	$\theta = 9$–$11°$
$c = 14.392$ (2) Å	$\mu = 3.97$ mm^{-1}
$\alpha = 73.58$ (2)°	$T = 293$ K
$\beta = 71.18$ (2)°	Prism, pink
$\gamma = 78.50$ (3)°	0.17 × 0.15 × 0.13 mm
$V = 1763.6$ (10) Å^3	

Data collection

Enraf–Nonius CAD-4 diffractometer	$R_{int} = 0.027$
Radiation source: fine-focus sealed tube	$\theta_{max} = 28.0°$, $\theta_{min} = 2.2°$
graphite	$h = -17 \rightarrow 17$
non–profiled ω scans	$k = -21 \rightarrow 21$
24086 measured reflections	$l = -6 \rightarrow 24$
17274 independent reflections	2 standard reflections every 120 min
8056 reflections with $I > 2\sigma(I)$	intensity decay: 3%

Refinement

Refinement on F^2	Primary atom site location: structure-invariant direct methods

Least-squares matrix: full	Secondary atom site location: difference Fourier map
$R[F^2 > 2\sigma(F^2)] = 0.083$	Hydrogen site location: inferred from neighbouring sites
$wR(F^2) = 0.244$	H atoms treated by a mixture of independent and constrained refinement
$S = 0.98$	$w = 1/[\sigma^2(F_o^2) + (0.1366P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
17274 reflections	$(\Delta/\sigma)_{max} = 0.035$
493 parameters	$\Delta\rho_{max} = 5.34$ e Å^{-3}
3 restraints	$\Delta\rho_{min} = -5.31$ e Å^{-3}

Special details

Geometry. All e.s.d.'s (except the e.s.d. in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell e.s.d.'s are taken into account individually in the estimation of e.s.d.'s in distances, angles and torsion angles; correlations between e.s.d.'s in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell e.s.d.'s is used for estimating e.s.d.'s involving l.s. planes.

Refinement. Refinement of F^2 against ALL reflections. The weighted *R*-factor *wR* and goodness of fit *S* are based on F^2, conventional *R*-factors *R* are based on *F*, with *F* set to zero for negative F^2. The threshold expression of $F^2 > \sigma(F^2)$ is used only for calculating *R*-factors(gt) *etc*. and is not relevant to the choice of reflections for refinement. *R*-factors based on F^2 are statistically about twice as large as those based on *F*, and *R*- factors based on ALL data will be even larger.

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å^2)

	x	*y*	*z*	U_{iso}*/U_{eq}
Re2	0.81148 (4)	0.32794 (3)	0.47046 (3)	0.05237 (11)
Re1	0.42492 (4)	0.26252 (3)	0.05290 (2)	0.05389 (11)
Co1	0.77573 (8)	0.78259 (7)	0.30120 (6)	0.03267 (17)
N1	0.9503 (5)	0.6807 (4)	0.2371 (4)	0.0360 (11)
N2	0.6819 (5)	0.6648 (4)	0.2795 (4)	0.0373 (11)
N3	0.7832 (6)	0.8921 (5)	0.1575 (4)	0.0386 (11)
N4	0.8990 (5)	0.8977 (4)	0.2982 (4)	0.0357 (10)
N5	0.5837 (5)	0.8693 (5)	0.3666 (5)	0.0383 (11)
N6	0.7463 (5)	0.7149 (4)	0.4579 (4)	0.0353 (10)
O1	0.5215 (9)	0.2398 (7)	−0.0613 (6)	0.087 (2)
O2	0.4816 (12)	0.3588 (9)	0.0815 (7)	0.119 (4)
O3	0.4311 (14)	0.1461 (8)	0.1403 (7)	0.125 (4)
O4	0.2576 (10)	0.2997 (10)	0.0475 (10)	0.123 (4)
O5	0.8842 (9)	0.4410 (6)	0.4074 (8)	0.089 (3)
O6	0.6492 (9)	0.3431 (8)	0.4588 (8)	0.102 (3)
O7	0.9060 (11)	0.2337 (12)	0.4291 (8)	0.132 (4)
O8	0.7999 (11)	0.3087 (9)	0.5966 (6)	0.113 (4)
O9	0.6895 (13)	0.1463 (10)	0.7811 (8)	0.118 (3)
H109	0.69 (2)	0.180 (17)	0.721 (4)	0.230*
H209	0.622 (12)	0.166 (14)	0.828 (8)	0.153*
C1	1.0837 (7)	0.6876 (6)	0.2185 (6)	0.0453 (15)
H1	1.1092	0.7374	0.2421	0.054*

C2	1.1877 (7)	0.6209 (6)	0.1635 (6)	0.0485 (17)
H2	1.2798	0.6291	0.1495	0.058*
C3	1.1533 (8)	0.5461 (7)	0.1318 (7)	0.0541 (19)
H3	1.2216	0.5025	0.0959	0.065*
C4	1.0142 (8)	0.5333 (6)	0.1528 (6)	0.0463 (15)
C5	0.9697 (9)	0.4542 (7)	0.1245 (8)	0.062 (2)
H5	1.0338	0.4069	0.0904	0.074*
C6	0.8313 (10)	0.4475 (8)	0.1478 (9)	0.070 (3)
H6	0.8038	0.3948	0.1291	0.084*
C7	0.7289 (9)	0.5179 (6)	0.1990 (6)	0.0483 (16)
C8	0.5883 (10)	0.5129 (7)	0.2260 (8)	0.061 (2)
H8	0.5557	0.4645	0.2053	0.073*
C9	0.5006 (9)	0.5762 (7)	0.2806 (8)	0.060 (2)
H9	0.4071	0.5694	0.3022	0.073*
C10	0.5501 (7)	0.6541 (6)	0.3057 (6)	0.0476 (16)
H10	0.4873	0.6999	0.3423	0.057*
C11	0.7723 (7)	0.5954 (5)	0.2277 (5)	0.0362 (12)
C12	0.9166 (6)	0.6051 (5)	0.2043 (5)	0.0345 (12)
C13	0.7240 (8)	0.8886 (7)	0.0902 (6)	0.0498 (17)
H13	0.6849	0.8275	0.0987	0.060*
C14	0.7176 (9)	0.9729 (8)	0.0066 (6)	0.060 (2)
H14	0.6715	0.9689	−0.0378	0.072*
C15	0.7792 (9)	1.0608 (7)	−0.0092 (6)	0.060 (2)
H15	0.7780	1.1167	−0.0656	0.072*
C16	0.8444 (8)	1.0663 (5)	0.0601 (6)	0.0474 (17)
C17	0.9158 (10)	1.1552 (7)	0.0493 (8)	0.062 (2)
H17	0.9184	1.2130	−0.0062	0.075*
C18	0.9789 (9)	1.1563 (6)	0.1182 (8)	0.063 (2)
H18	1.0231	1.2148	0.1098	0.076*
C19	0.9781 (7)	1.0697 (6)	0.2024 (7)	0.0468 (17)
C20	1.0409 (9)	1.0668 (7)	0.2771 (8)	0.059 (2)
H20	1.0872	1.1230	0.2717	0.071*
C21	1.0327 (8)	0.9808 (8)	0.3570 (7)	0.056 (2)
H21	1.0757	0.9774	0.4056	0.067*
C22	0.9605 (7)	0.8977 (6)	0.3669 (6)	0.0443 (15)
H22	0.9549	0.8405	0.4230	0.053*
C23	0.9084 (6)	0.9817 (5)	0.2161 (5)	0.0373 (13)
C24	0.8440 (6)	0.9794 (5)	0.1435 (5)	0.0374 (13)
C25	0.5018 (7)	0.9451 (6)	0.3215 (6)	0.0445 (15)
H25	0.5289	0.9676	0.2515	0.053*
C26	0.3778 (8)	0.9917 (7)	0.3749 (7)	0.0548 (19)
H26	0.3242	1.0447	0.3406	0.066*
C27	0.3352 (7)	0.9605 (6)	0.4761 (7)	0.0524 (19)
H27	0.2509	0.9902	0.5117	0.063*
C28	0.4194 (7)	0.8820 (6)	0.5285 (6)	0.0434 (15)
C29	0.3850 (8)	0.8462 (7)	0.6356 (6)	0.0514 (18)
H29	0.3023	0.8739	0.6748	0.062*
C30	0.4710 (8)	0.7722 (7)	0.6816 (6)	0.0528 (18)
H30	0.4472	0.7517	0.7517	0.063*

C31	0.5963 (7)	0.7258 (6)	0.6245 (5)	0.0436 (15)
C32	0.6871 (8)	0.6473 (7)	0.6673 (6)	0.0530 (18)
H32	0.6695	0.6252	0.7371	0.064*
C33	0.8045 (9)	0.6025 (7)	0.6043 (6)	0.0548 (19)
H33	0.8642	0.5482	0.6313	0.066*
C34	0.8303 (7)	0.6406 (6)	0.5006 (5)	0.0451 (15)
H34	0.9105	0.6125	0.4590	0.054*
C35	0.6306 (6)	0.7583 (5)	0.5182 (5)	0.0363 (12)
C36	0.5425 (6)	0.8397 (5)	0.4702 (5)	0.0359 (12)

Atomic displacement parameters (Å^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Re2	0.0577 (2)	0.05247 (19)	0.04822 (18)	−0.01579 (14)	−0.01504 (15)	−0.00749 (14)
Re1	0.0644 (2)	0.0581 (2)	0.03748 (16)	−0.00922 (15)	−0.00999 (14)	−0.01234 (13)
Co1	0.0324 (4)	0.0366 (4)	0.0285 (4)	−0.0069 (3)	−0.0071 (3)	−0.0067 (3)
N1	0.035 (2)	0.042 (3)	0.032 (2)	−0.007 (2)	−0.011 (2)	−0.008 (2)
N2	0.035 (2)	0.039 (3)	0.036 (3)	−0.012 (2)	−0.006 (2)	−0.005 (2)
N3	0.036 (2)	0.044 (3)	0.033 (3)	−0.007 (2)	−0.009 (2)	−0.005 (2)
N4	0.035 (2)	0.042 (3)	0.035 (3)	−0.007 (2)	−0.012 (2)	−0.012 (2)
N5	0.031 (2)	0.042 (3)	0.042 (3)	−0.003 (2)	−0.012 (2)	−0.010 (2)
N6	0.033 (2)	0.039 (3)	0.031 (2)	−0.007 (2)	−0.006 (2)	−0.006 (2)
O1	0.087 (5)	0.113 (6)	0.060 (4)	0.007 (5)	−0.019 (4)	−0.033 (4)
O2	0.165 (10)	0.136 (8)	0.082 (6)	−0.086 (7)	−0.030 (7)	−0.025 (6)
O3	0.219 (13)	0.079 (6)	0.077 (6)	−0.036 (7)	−0.055 (8)	0.007 (5)
O4	0.071 (5)	0.132 (9)	0.166 (11)	0.012 (6)	−0.023 (6)	−0.064 (8)
O5	0.087 (5)	0.063 (4)	0.113 (7)	−0.024 (4)	−0.033 (5)	0.001 (4)
O6	0.088 (6)	0.115 (7)	0.126 (8)	−0.038 (5)	−0.046 (6)	−0.027 (6)
O7	0.114 (8)	0.201 (12)	0.082 (7)	−0.069 (8)	−0.021 (6)	−0.011 (8)
O8	0.122 (7)	0.151 (9)	0.046 (4)	0.025 (7)	−0.025 (5)	−0.017 (5)
O9	0.141 (10)	0.137 (9)	0.087 (7)	−0.011 (8)	−0.042 (7)	−0.035 (7)
C1	0.036 (3)	0.055 (4)	0.044 (4)	−0.008 (3)	−0.014 (3)	−0.005 (3)
C2	0.037 (3)	0.054 (4)	0.046 (4)	−0.002 (3)	−0.006 (3)	−0.007 (3)
C3	0.042 (4)	0.051 (4)	0.055 (5)	0.006 (3)	−0.004 (3)	−0.010 (4)
C4	0.044 (3)	0.046 (4)	0.048 (4)	−0.005 (3)	−0.010 (3)	−0.014 (3)
C5	0.060 (5)	0.049 (4)	0.074 (6)	0.004 (4)	−0.009 (4)	−0.031 (4)
C6	0.070 (6)	0.066 (6)	0.091 (8)	−0.003 (5)	−0.017 (5)	−0.052 (6)
C7	0.054 (4)	0.046 (4)	0.048 (4)	−0.019 (3)	−0.011 (3)	−0.010 (3)
C8	0.063 (5)	0.059 (5)	0.071 (6)	−0.023 (4)	−0.026 (5)	−0.014 (4)
C9	0.047 (4)	0.059 (5)	0.079 (6)	−0.021 (4)	−0.009 (4)	−0.022 (5)
C10	0.039 (3)	0.055 (4)	0.049 (4)	−0.010 (3)	−0.008 (3)	−0.012 (3)
C11	0.036 (3)	0.034 (3)	0.038 (3)	−0.008 (2)	−0.010 (2)	−0.004 (2)
C12	0.036 (3)	0.032 (3)	0.031 (3)	−0.002 (2)	−0.008 (2)	−0.003 (2)
C13	0.055 (4)	0.060 (4)	0.036 (3)	−0.003 (3)	−0.016 (3)	−0.013 (3)
C14	0.061 (5)	0.079 (6)	0.039 (4)	0.003 (4)	−0.026 (4)	−0.008 (4)
C15	0.067 (5)	0.060 (5)	0.034 (4)	0.002 (4)	−0.012 (4)	0.009 (3)
C16	0.049 (4)	0.034 (3)	0.045 (4)	0.000 (3)	−0.006 (3)	0.001 (3)
C17	0.067 (5)	0.038 (4)	0.069 (6)	−0.010 (3)	−0.013 (5)	0.002 (4)

C18	0.054 (4)	0.040 (4)	0.088 (7)	−0.014 (3)	−0.007 (5)	−0.013 (4)
C19	0.036 (3)	0.041 (3)	0.061 (5)	−0.009 (3)	−0.003 (3)	−0.018 (3)
C20	0.049 (4)	0.057 (5)	0.077 (6)	−0.013 (4)	−0.012 (4)	−0.027 (5)
C21	0.041 (4)	0.074 (5)	0.067 (5)	−0.008 (3)	−0.019 (4)	−0.036 (5)
C22	0.040 (3)	0.054 (4)	0.045 (4)	−0.011 (3)	−0.013 (3)	−0.017 (3)
C23	0.027 (2)	0.036 (3)	0.044 (3)	−0.005 (2)	−0.003 (2)	−0.010 (3)
C24	0.034 (3)	0.040 (3)	0.033 (3)	−0.003 (2)	−0.006 (2)	−0.005 (2)
C25	0.044 (3)	0.043 (3)	0.047 (4)	−0.005 (3)	−0.019 (3)	−0.007 (3)
C26	0.039 (3)	0.056 (4)	0.068 (5)	−0.002 (3)	−0.018 (4)	−0.012 (4)
C27	0.034 (3)	0.054 (4)	0.069 (5)	0.004 (3)	−0.008 (3)	−0.028 (4)
C28	0.037 (3)	0.049 (4)	0.045 (4)	−0.010 (3)	−0.002 (3)	−0.019 (3)
C29	0.045 (4)	0.066 (5)	0.045 (4)	−0.016 (3)	0.002 (3)	−0.026 (4)
C30	0.051 (4)	0.070 (5)	0.035 (3)	−0.015 (4)	0.000 (3)	−0.019 (3)
C31	0.043 (3)	0.061 (4)	0.028 (3)	−0.018 (3)	−0.003 (3)	−0.012 (3)
C32	0.052 (4)	0.070 (5)	0.030 (3)	−0.022 (4)	−0.006 (3)	0.001 (3)
C33	0.053 (4)	0.056 (4)	0.047 (4)	−0.011 (3)	−0.020 (4)	0.011 (3)
C34	0.044 (3)	0.052 (4)	0.034 (3)	−0.005 (3)	−0.010 (3)	−0.003 (3)
C35	0.031 (3)	0.044 (3)	0.032 (3)	−0.012 (2)	−0.005 (2)	−0.004 (2)
C36	0.031 (3)	0.042 (3)	0.038 (3)	−0.008 (2)	−0.009 (2)	−0.012 (3)

Geometric parameters (Å, °)

Re2—O7	1.549 (15)	C9—C10	1.407 (11)
Re2—O5	1.685 (8)	C9—H9	0.9300
Re2—O6	1.708 (8)	C10—H10	0.9300
Re2—O8	1.728 (8)	C11—C12	1.445 (9)
Re1—O3	1.688 (9)	C13—C14	1.395 (11)
Re1—O2	1.691 (9)	C13—H13	0.9300
Re1—O1	1.700 (7)	C14—C15	1.357 (14)
Re1—O4	1.724 (10)	C14—H14	0.9300
Co1—N6	2.122 (5)	C15—C16	1.397 (13)
Co1—N2	2.122 (5)	C15—H15	0.9300
Co1—N1	2.136 (5)	C16—C24	1.403 (9)
Co1—N4	2.147 (5)	C16—C17	1.450 (12)
Co1—N3	2.148 (6)	C17—C18	1.357 (15)
Co1—N5	2.151 (6)	C17—H17	0.9300
N1—C1	1.336 (8)	C18—C19	1.407 (12)
N1—C12	1.356 (8)	C18—H18	0.9300
N2—C10	1.318 (8)	C19—C20	1.414 (13)
N2—C11	1.362 (8)	C19—C23	1.417 (9)
N3—C13	1.317 (9)	C20—C21	1.359 (14)
N3—C24	1.352 (9)	C20—H20	0.9300
N4—C22	1.337 (9)	C21—C22	1.392 (11)
N4—C23	1.362 (9)	C21—H21	0.9300
N5—C25	1.336 (9)	C22—H22	0.9300
N5—C36	1.373 (9)	C23—C24	1.418 (10)
N6—C34	1.324 (9)	C25—C26	1.389 (11)
N6—C35	1.360 (8)	C25—H25	0.9300
O9—H109	0.85 (10)	C26—C27	1.342 (13)

O9—H209	0.86 (14)	C26—H26	0.9300
C1—C2	1.422 (11)	C27—C28	1.420 (11)
C1—H1	0.9300	C27—H27	0.9300
C2—C3	1.341 (12)	C28—C36	1.388 (9)
C2—H2	0.9300	C28—C29	1.424 (11)
C3—C4	1.407 (11)	C29—C30	1.358 (13)
C3—H3	0.9300	C29—H29	0.9300
C4—C12	1.411 (9)	C30—C31	1.418 (10)
C4—C5	1.417 (12)	C30—H30	0.9300
C5—C6	1.378 (13)	C31—C32	1.398 (11)
C5—H5	0.9300	C31—C35	1.410 (9)
C6—C7	1.418 (12)	C32—C33	1.397 (12)
C6—H6	0.9300	C32—H32	0.9300
C7—C8	1.390 (12)	C33—C34	1.386 (10)
C7—C11	1.396 (9)	C33—H33	0.9300
C8—C9	1.319 (13)	C34—H34	0.9300
C8—H8	0.9300	C35—C36	1.432 (9)
O7—Re2—O5	108.3 (5)	N2—C11—C12	116.7 (6)
O7—Re2—O6	113.2 (5)	C7—C11—C12	121.2 (6)
O5—Re2—O6	109.3 (5)	N1—C12—C4	123.8 (6)
O7—Re2—O8	109.7 (5)	N1—C12—C11	117.5 (5)
O5—Re2—O8	107.7 (6)	C4—C12—C11	118.7 (6)
O6—Re2—O8	108.5 (5)	N3—C13—C14	122.7 (8)
O3—Re1—O2	111.0 (5)	N3—C13—H13	118.7
O3—Re1—O1	107.9 (5)	C14—C13—H13	118.7
O2—Re1—O1	111.5 (5)	C15—C14—C13	119.4 (8)
O3—Re1—O4	108.4 (6)	C15—C14—H14	120.3
O2—Re1—O4	110.6 (6)	C13—C14—H14	120.3
O1—Re1—O4	107.4 (5)	C14—C15—C16	119.3 (7)
N6—Co1—N2	94.4 (2)	C14—C15—H15	120.3
N6—Co1—N1	101.4 (2)	C16—C15—H15	120.3
N2—Co1—N1	78.1 (2)	C15—C16—C24	118.1 (7)
N6—Co1—N4	93.0 (2)	C15—C16—C17	123.8 (8)
N2—Co1—N4	169.5 (2)	C24—C16—C17	118.1 (8)
N1—Co1—N4	93.2 (2)	C18—C17—C16	121.6 (8)
N6—Co1—N3	163.7 (2)	C18—C17—H17	119.2
N2—Co1—N3	96.8 (2)	C16—C17—H17	119.2
N1—Co1—N3	92.5 (2)	C17—C18—C19	120.6 (8)
N4—Co1—N3	77.5 (2)	C17—C18—H18	119.7
N6—Co1—N5	78.0 (2)	C19—C18—H18	119.7
N2—Co1—N5	94.3 (2)	C18—C19—C20	123.1 (7)
N1—Co1—N5	172.3 (2)	C18—C19—C23	119.6 (8)
N4—Co1—N5	94.5 (2)	C20—C19—C23	117.3 (8)
N3—Co1—N5	89.4 (2)	C21—C20—C19	119.1 (7)
C1—N1—C12	117.7 (6)	C21—C20—H20	120.5
C1—N1—Co1	129.0 (5)	C19—C20—H20	120.5
C12—N1—Co1	113.1 (4)	C20—C21—C22	120.7 (8)
C10—N2—C11	117.6 (6)	C20—C21—H21	119.7
C10—N2—Co1	128.5 (5)	C22—C21—H21	119.7

C11—N2—Co1	113.8 (4)	N4—C22—C21	122.1 (8)
C13—N3—C24	118.8 (6)	N4—C22—H22	119.0
C13—N3—Co1	127.8 (5)	C21—C22—H22	119.0
C24—N3—Co1	113.0 (4)	N4—C23—C19	122.3 (7)
C22—N4—C23	118.5 (6)	N4—C23—C24	117.6 (6)
C22—N4—Co1	128.4 (5)	C19—C23—C24	120.1 (7)
C23—N4—Co1	113.1 (4)	N3—C24—C16	121.7 (7)
C25—N5—C36	117.2 (6)	N3—C24—C23	118.2 (6)
C25—N5—Co1	129.7 (5)	C16—C24—C23	120.1 (7)
C36—N5—Co1	113.1 (4)	N5—C25—C26	122.8 (8)
C34—N6—C35	118.8 (6)	N5—C25—H25	118.6
C34—N6—Co1	127.0 (5)	C26—C25—H25	118.6
C35—N6—Co1	114.2 (4)	C27—C26—C25	120.1 (8)
H109—O9—H209	116 (16)	C27—C26—H26	119.9
N1—C1—C2	121.7 (7)	C25—C26—H26	119.9
N1—C1—H1	119.1	C26—C27—C28	119.7 (7)
C2—C1—H1	119.1	C26—C27—H27	120.1
C3—C2—C1	120.1 (7)	C28—C27—H27	120.1
C3—C2—H2	120.0	C36—C28—C27	117.0 (7)
C1—C2—H2	120.0	C36—C28—C29	119.2 (7)
C2—C3—C4	120.2 (7)	C27—C28—C29	123.9 (7)
C2—C3—H3	119.9	C30—C29—C28	121.2 (7)
C4—C3—H3	119.9	C30—C29—H29	119.4
C3—C4—C12	116.5 (7)	C28—C29—H29	119.4
C3—C4—C5	123.6 (7)	C29—C30—C31	121.1 (7)
C12—C4—C5	120.0 (7)	C29—C30—H30	119.4
C6—C5—C4	119.8 (7)	C31—C30—H30	119.4
C6—C5—H5	120.1	C32—C31—C35	117.7 (7)
C4—C5—H5	120.1	C32—C31—C30	123.8 (7)
C5—C6—C7	122.6 (8)	C35—C31—C30	118.5 (7)
C5—C6—H6	118.7	C33—C32—C31	119.4 (7)
C7—C6—H6	118.7	C33—C32—H32	120.3
C8—C7—C11	117.4 (8)	C31—C32—H32	120.3
C8—C7—C6	124.7 (8)	C34—C33—C32	118.7 (7)
C11—C7—C6	117.8 (7)	C34—C33—H33	120.6
C9—C8—C7	120.7 (8)	C32—C33—H33	120.6
C9—C8—H8	119.6	N6—C34—C33	123.2 (7)
C7—C8—H8	119.6	N6—C34—H34	118.4
C8—C9—C10	119.2 (8)	C33—C34—H34	118.4
C8—C9—H9	120.4	N6—C35—C31	122.2 (6)
C10—C9—H9	120.4	N6—C35—C36	117.7 (6)
N2—C10—C9	122.7 (8)	C31—C35—C36	120.1 (6)
N2—C10—H10	118.7	N5—C36—C28	123.2 (6)
C9—C10—H10	118.7	N5—C36—C35	117.0 (6)
N2—C11—C7	122.1 (6)	C28—C36—C35	119.8 (6)
N6—Co1—N1—C1	−86.0 (6)	Co1—N1—C12—C4	175.3 (6)
N2—Co1—N1—C1	−178.2 (6)	C1—N1—C12—C11	177.9 (6)
N4—Co1—N1—C1	7.8 (6)	Co1—N1—C12—C11	−7.4 (7)
N3—Co1—N1—C1	85.4 (6)	C3—C4—C12—N1	−2.7 (11)

N5—Co1—N1—C1	−170.6 (15)	C5—C4—C12—N1	177.6 (7)
N6—Co1—N1—C12	100.1 (4)	C3—C4—C12—C11	−179.9 (7)
N2—Co1—N1—C12	7.9 (4)	C5—C4—C12—C11	0.4 (11)
N4—Co1—N1—C12	−166.2 (4)	N2—C11—C12—N1	1.2 (9)
N3—Co1—N1—C12	−88.6 (4)	C7—C11—C12—N1	−178.3 (6)
N5—Co1—N1—C12	15.5 (19)	N2—C11—C12—C4	178.6 (6)
N6—Co1—N2—C10	75.1 (7)	C7—C11—C12—C4	−0.9 (10)
N1—Co1—N2—C10	175.8 (7)	C24—N3—C13—C14	−2.1 (11)
N4—Co1—N2—C10	−149.6 (11)	Co1—N3—C13—C14	169.5 (6)
N3—Co1—N2—C10	−93.0 (7)	N3—C13—C14—C15	2.8 (13)
N5—Co1—N2—C10	−3.2 (7)	C13—C14—C15—C16	−1.8 (13)
N6—Co1—N2—C11	−108.0 (5)	C14—C15—C16—C24	0.4 (12)
N1—Co1—N2—C11	−7.3 (5)	C14—C15—C16—C17	178.6 (8)
N4—Co1—N2—C11	27.3 (14)	C15—C16—C17—C18	−179.3 (9)
N3—Co1—N2—C11	83.8 (5)	C24—C16—C17—C18	−1.1 (13)
N5—Co1—N2—C11	173.7 (5)	C16—C17—C18—C19	0.7 (14)
N6—Co1—N3—C13	−123.2 (8)	C17—C18—C19—C20	−179.4 (9)
N2—Co1—N3—C13	10.0 (6)	C17—C18—C19—C23	−1.2 (12)
N1—Co1—N3—C13	88.3 (6)	C18—C19—C20—C21	178.7 (8)
N4—Co1—N3—C13	−179.0 (6)	C23—C19—C20—C21	0.5 (11)
N5—Co1—N3—C13	−84.2 (6)	C19—C20—C21—C22	−1.6 (12)
N6—Co1—N3—C24	48.9 (9)	C23—N4—C22—C21	0.3 (10)
N2—Co1—N3—C24	−177.9 (4)	Co1—N4—C22—C21	−177.0 (5)
N1—Co1—N3—C24	−99.6 (5)	C20—C21—C22—N4	1.3 (12)
N4—Co1—N3—C24	−6.9 (4)	C22—N4—C23—C19	−1.5 (9)
N5—Co1—N3—C24	87.8 (5)	Co1—N4—C23—C19	176.2 (5)
N6—Co1—N4—C22	16.2 (6)	C22—N4—C23—C24	179.2 (6)
N2—Co1—N4—C22	−119.2 (12)	Co1—N4—C23—C24	−3.1 (7)
N1—Co1—N4—C22	−85.4 (6)	C18—C19—C23—N4	−177.2 (7)
N3—Co1—N4—C22	−177.2 (6)	C20—C19—C23—N4	1.1 (10)
N5—Co1—N4—C22	94.4 (6)	C18—C19—C23—C24	2.2 (10)
N6—Co1—N4—C23	−161.2 (4)	C20—C19—C23—C24	−179.6 (6)
N2—Co1—N4—C23	63.4 (13)	C13—N3—C24—C16	0.6 (10)
N1—Co1—N4—C23	97.2 (4)	Co1—N3—C24—C16	−172.2 (5)
N3—Co1—N4—C23	5.3 (4)	C13—N3—C24—C23	−179.5 (6)
N5—Co1—N4—C23	−83.0 (4)	Co1—N3—C24—C23	7.7 (7)
N6—Co1—N5—C25	−179.1 (6)	C15—C16—C24—N3	0.2 (11)
N2—Co1—N5—C25	−85.5 (6)	C17—C16—C24—N3	−178.1 (7)
N1—Co1—N5—C25	−93.0 (18)	C15—C16—C24—C23	−179.7 (7)
N4—Co1—N5—C25	88.7 (6)	C17—C16—C24—C23	2.0 (10)
N3—Co1—N5—C25	11.3 (6)	N4—C23—C24—N3	−3.1 (9)
N6—Co1—N5—C36	0.7 (4)	C19—C23—C24—N3	177.5 (6)
N2—Co1—N5—C36	94.3 (5)	N4—C23—C24—C16	176.8 (6)
N1—Co1—N5—C36	86.8 (17)	C19—C23—C24—C16	−2.6 (9)
N4—Co1—N5—C36	−91.5 (5)	C36—N5—C25—C26	−1.6 (11)
N3—Co1—N5—C36	−168.9 (5)	Co1—N5—C25—C26	178.1 (6)
N2—Co1—N6—C34	88.4 (6)	N5—C25—C26—C27	−0.4 (13)
N1—Co1—N6—C34	9.6 (6)	C25—C26—C27—C28	1.9 (13)
N4—Co1—N6—C34	−84.2 (6)	C26—C27—C28—C36	−1.2 (11)

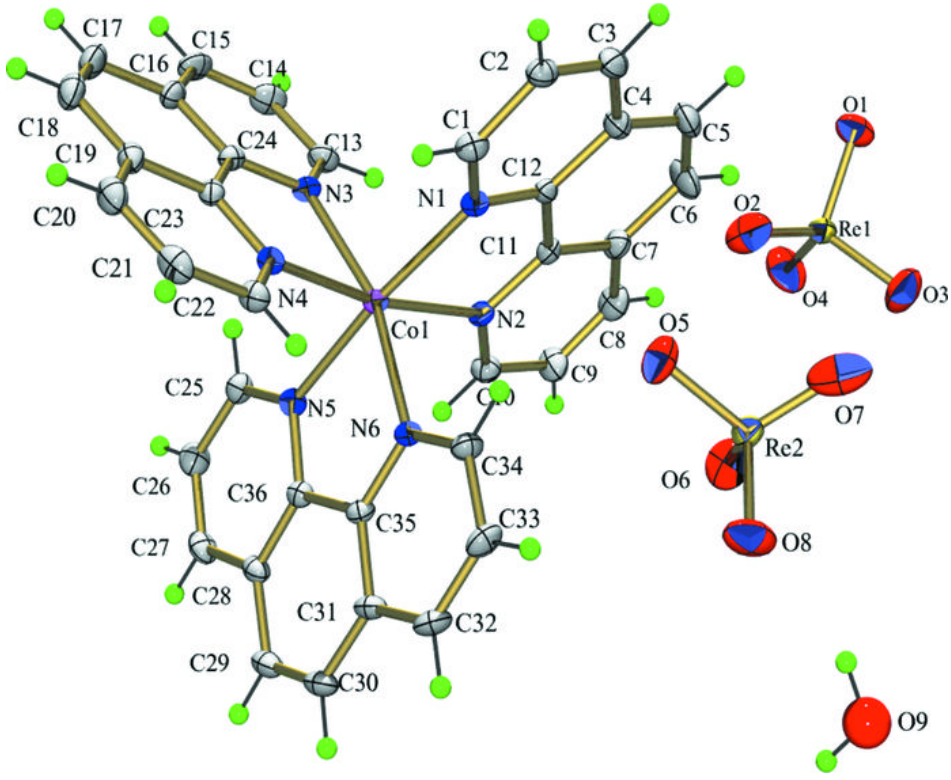
N3—Co1—N6—C34	−138.2 (8)	C26—C27—C28—C29	178.0 (8)
N5—Co1—N6—C34	−178.2 (6)	C36—C28—C29—C30	0.5 (11)
N2—Co1—N6—C35	−94.8 (5)	C27—C28—C29—C30	−178.7 (8)
N1—Co1—N6—C35	−173.6 (4)	C28—C29—C30—C31	−1.8 (12)
N4—Co1—N6—C35	92.6 (5)	C29—C30—C31—C32	−178.2 (8)
N3—Co1—N6—C35	38.6 (10)	C29—C30—C31—C35	0.2 (12)
N5—Co1—N6—C35	−1.4 (4)	C35—C31—C32—C33	−1.8 (11)
C12—N1—C1—C2	1.9 (10)	C30—C31—C32—C33	176.6 (8)
Co1—N1—C1—C2	−171.8 (5)	C31—C32—C33—C34	2.6 (12)
N1—C1—C2—C3	−2.3 (12)	C35—N6—C34—C33	1.7 (11)
C1—C2—C3—C4	0.0 (13)	Co1—N6—C34—C33	178.4 (6)
C2—C3—C4—C12	2.3 (12)	C32—C33—C34—N6	−2.6 (13)
C2—C3—C4—C5	−178.0 (9)	C34—N6—C35—C31	−0.8 (10)
C3—C4—C5—C6	−179.8 (10)	Co1—N6—C35—C31	−177.9 (5)
C12—C4—C5—C6	−0.2 (14)	C34—N6—C35—C36	179.0 (6)
C4—C5—C6—C7	0.4 (17)	Co1—N6—C35—C36	1.9 (7)
C5—C6—C7—C8	−178.6 (10)	C32—C31—C35—N6	0.9 (10)
C5—C6—C7—C11	−1.0 (16)	C30—C31—C35—N6	−177.6 (7)
C11—C7—C8—C9	−3.0 (14)	C32—C31—C35—C36	−178.9 (7)
C6—C7—C8—C9	174.6 (10)	C30—C31—C35—C36	2.6 (10)
C7—C8—C9—C10	4.2 (16)	C25—N5—C36—C28	2.3 (10)
C11—N2—C10—C9	−1.3 (12)	Co1—N5—C36—C28	−177.5 (5)
Co1—N2—C10—C9	175.5 (7)	C25—N5—C36—C35	179.9 (6)
C8—C9—C10—N2	−2.1 (15)	Co1—N5—C36—C35	0.1 (7)
C10—N2—C11—C7	2.5 (10)	C27—C28—C36—N5	−0.9 (10)
Co1—N2—C11—C7	−174.7 (5)	C29—C28—C36—N5	179.8 (7)
C10—N2—C11—C12	−177.0 (6)	C27—C28—C36—C35	−178.5 (6)
Co1—N2—C11—C12	5.8 (7)	C29—C28—C36—C35	2.2 (10)
C8—C7—C11—N2	−0.5 (11)	N6—C35—C36—N5	−1.4 (9)
C6—C7—C11—N2	−178.3 (8)	C31—C35—C36—N5	178.5 (6)
C8—C7—C11—C12	179.0 (7)	N6—C35—C36—C28	176.3 (6)
C6—C7—C11—C12	1.2 (12)	C31—C35—C36—C28	−3.8 (10)
C1—N1—C12—C4	0.6 (10)		

Hydrogen-bond geometry (Å, °)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
O9—H209···O1^{i}	0.85 (10)	1.99 (8)	2.802 (13)	157 (19)
O9—H109···O8	0.86 (14)	2.26 (17)	2.953 (17)	139 (23)
C15—H15···O9^{ii}	0.93	2.56	3.271 (14)	134
C33—H33···O5^{iii}	0.93	2.51	3.116 (12)	123
C5—H5···O4^{iv}	0.93	2.45	3.309 (13)	154
C33—H33···O5^{iii}	0.93	2.51	3.116 (12)	123

Symmetry codes: (i) *x*, *y*, *z*+1; (ii) *x*, *y*+1, *z*−1; (iii) −*x*+2, −*y*+1, −*z*+1; (iv) *x*+1, *y*, *z*.

Fig. 1


C17
C15
C16
C14
C18
C24
C13
C19
N3
C20
C23
C21
N4
C22
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C1
C2
C3
C4
C5
C12
C6
C11
C7
N2
C8
C9
C10
O1
O2
Re1
O4
O3
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O7
Re2
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O8
O9
C25
N5
N6
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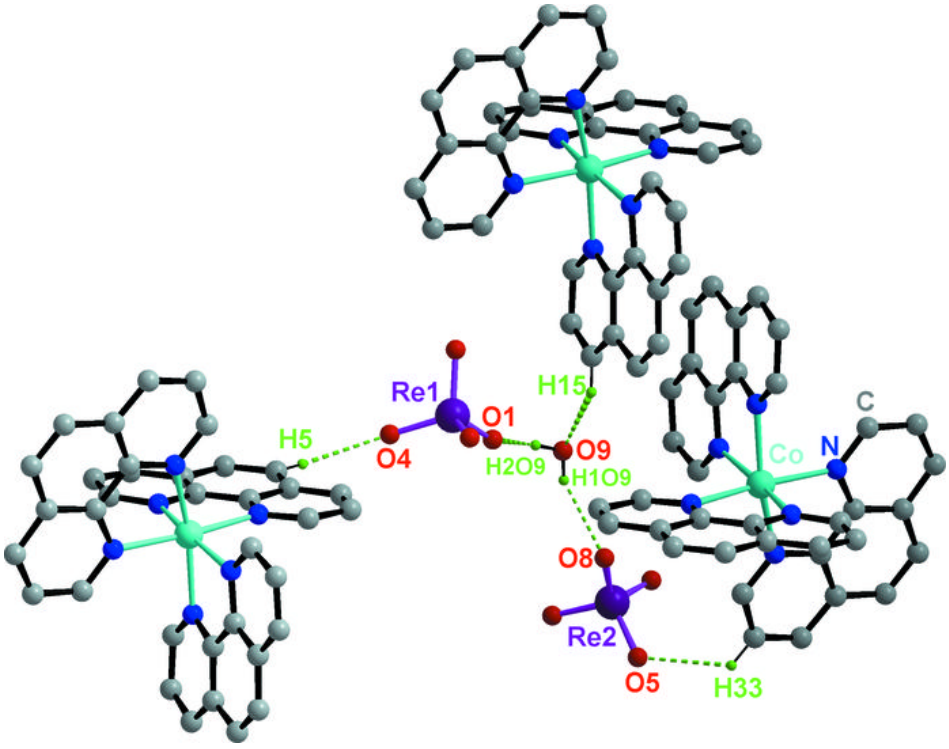
C26
C36
C35
C33
C27
C28
C31
C32
C29
C30

Fig. 2



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Structure Reports Online
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1-Acetyl-3-[2-(2,3,5,6-tetrafluorophenyl)hydrazin-1-ylidene]indolin-2-one

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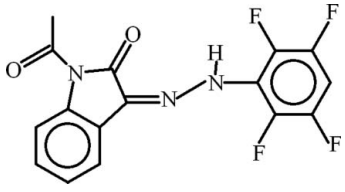
Key indicators: single-crystal X-ray study; T = 296 K; mean σ(C–C) = 0.008 Å; R factor = 0.046; wR factor = 0.080; data-to-parameter ratio = 6.4.

In the title compound, $C_{16}H_9F_4N_3O_2$, the dihedral angle between the aromatic ring systems is 4.10 (14)° and a bifurcated intramolecular N—H···(O,F) hydrogen bond generates an S(6) ring for the O-atom acceptor and an S(5) ring for the F-atom acceptor. A short C—H···O conact also occurs. In the crystal, molecules are linked by C—H···O interactions.

Related literature

For background on related isatin derivatives, see: Pervez *et al.* (2007, 2008, 2010*a*). For related structures, see: Abad *et al.* (2006); Pervez *et al.* (2010*b*). For graph-set notation, see: Bernstein *et al.* (1995).



Experimental

Crystal data

$C_{16}H_9F_4N_3O_2$
M_r = 351.26
Monoclinic, $P2_1$
a = 9.8993 (19) Å
b = 4.7740 (6) Å
c = 16.066 (3) Å
β = 104.807 (8)°
V = 734.0 (2) Å^3
Z = 2
Mo $K\alpha$ radiation
μ = 0.14 mm^{-1}
T = 296 K
0.32 × 0.24 × 0.22 mm

Data collection

Bruker Kappa APEXII CCD diffractometer
Absorption correction: multi-scan (*SADABS*; Bruker, 2005)
T_{min} = 0.942, T_{max} = 0.952
6095 measured reflections
1462 independent reflections
749 reflections with $I > 2\sigma(I)$
R_{int} = 0.087

Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.046
$wR(F^2)$ = 0.080
S = 0.96
1462 reflections
227 parameters
1 restraint
H-atom parameters constrained
$\Delta\rho_{max}$ = 0.14 e Å^{-3}
$\Delta\rho_{min}$ = −0.18 e Å^{-3}

Table 1
Hydrogen-bond geometry (Å, °).

D—H···A	D—H	H···A	D···A	D—H···A
N2—H2···O2	0.86	1.99	2.694 (5)	139
N2—H2···F1	0.86	2.29	2.658 (5)	106
C6—H6···O1	0.93	2.33	2.857 (8)	116
C14—H14···O1^{i}	0.93	2.32	3.217 (7)	163

Symmetry code: (i) $x+1, y-2, z$.

Data collection: *APEX2* (Bruker, 2007); cell refinement: *SAINT* (Bruker, 2007); data reduction: *SAINT*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *ORTEP-3* (Farrugia, 1997) and *PLATON* (Spek, 2009); software used to prepare material for publication: *WinGX* (Farrugia, 1999) and *PLATON*.

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Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: HB5498).

References

Abad, A., Agulló, C., Cuñat, A. C., Vilanova, C. & de Arellano, M. C. R. (2006). *Cryst. Growth Des.* **6**, 46–57.
Bernstein, J., Davis, R. E., Shimoni, L. & Chang, N.-L. (1995). *Angew. Chem. Int. Ed. Engl.* **34**, 1555–1573.
Bruker (2005). *SADABS*. Bruker AXS Inc., Madison, Wisconsin, USA.
Bruker (2007). *APEX2* and *SAINT*. Bruker AXS Inc., Madison, Wisconsin, USA.
Farrugia, L. J. (1997). *J. Appl. Cryst.* **30**, 565.
Farrugia, L. J. (1999). *J. Appl. Cryst.* **32**, 837–838.
Pervez, H., Iqbal, M. S., Tahir, M. Y., Choudhary, M. I. & Khan, K. M. (2007). *Nat. Prod. Res.* **21**, 1178–1186.
Pervez, H., Iqbal, M. S., Tahir, M. Y., Nasim, F. H., Choudhary, M. I. & Khan, K. M. & Yaqub, M. (2008). *J. Enz. Inhib. Med. Chem.* **23**, 848–854.
Pervez, H., Manzoor, N., Yaqub, M., Khan, A., Khan, K. M., Nasim, F. H. & Choudhary, M. I. (2010*a*). *Lett. Drug Des. Discov.* **7**, 102–108.
Pervez, H., Yaqub, M., Ramzan, M., Iqbal, M. S. & Tahir, M. N. (2010*b*). *Acta Cryst.* E**66**, o1018.
Sheldrick, G. M. (2008). *Acta Cryst.* A**64**, 112–122.
Spek, A. L. (2009). *Acta Cryst.* D**65**, 148–155.

supplementary materials

Acta Cryst. (2010). E**66**, o1686 [**doi:10.1107/S1600536810022580**]

1-Acetyl-3-[2-(2,3,5,6-tetrafluorophenyl)hydrazin-1-ylidene]indolin-2-one

H. Pervez, M. Yaqub, M. Ahmad, M. N. Tahir and R. Akhtar

Comment

In continuation of our previous work on the synthesis of isatin derivatives having physiological properties (Pervez *et al.*, 2007, 2008, 2010*a*, 2010*b*), we report herein the synthesis and crystal structure of the title compound (I), (Fig. 1).

The crystal structure of *N*-(2-chloropyrid-4-yl)-*N*'-(2,3,5,6-tetrafluorophenyl)urea (Abad *et al.*, 2006) has been published which contains the same flouro substituted phenyl group as in (I).

In (I), the 2-oxoindolin-3-hydrazono group A (N3/C1–C8/O2/N1/N2) and tetrafluorophenyl B (C11—C16/F1–F4) are planar with r. m. s. deviations of 0.0197 and 0.0121 Å, respectively. The dihedral angle between A/B is 4.10 (14)°. The acetyl moiety (O1/C9/C10) is oriented at 6.21 (83)° with its parent group A. One S(5) ring motif (Bernstein *et al.*, 1995) is formed due to intramolecular H-bonding of N—H···F type, two S(6) ring motifs due to N—H···O and C—H···O interactions (Table 1, Fig. 1) are formed. The molecules are stabilized in the form of one dimensional polymeric chains extending along the *a* axis (Fig. 2).

Experimental

A solution of 1-acetylisatin (0.95 g, 5.0 mmol) in ethanol (50 ml) was added to the solution of 2,3,5,6-tetrafluorophenyl hydrazine (0.90 g, 5.0 mmol) made in concentrated sulfuric acid (8 ml) and diluted with ethanol (50 ml). The reaction mixture was then refluxed for 30 min. The bright yellow crystalline solid formed during refluxing was collected by suction filtration. Thorough washing with hot ethanol furnished the desired compound (I) in pure form (0.40 g, 23%), m.p. 445 K. Bright yellow prisms of (I) were grown in chloroform by slow evaporation method at room temperature.

Refinement

In the absence of anamolous scattering, the Friedal pairs were merged before refinement. The H-atoms were positioned geometrically (N–H = 0.86 Å, C–H = 0.93–0.96 Å) and refined as riding with U_{iso}(H) = xU_{eq}(C, N), where x = 1.5 for methyl and x = 1.2 for all other H-atoms.

Figures

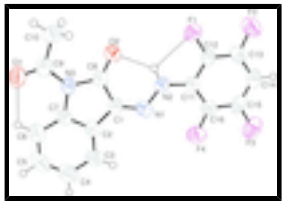


Fig. 1. View of (I) with displacement ellipsoids drawn at the 50% probability level. The dotted lines indicate the intra-molecular H-bondings.

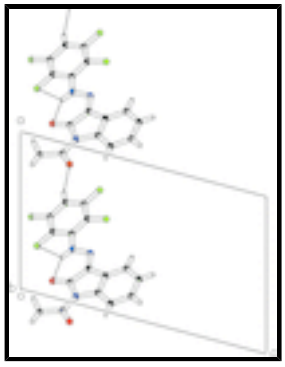


Fig. 2. The partial packing of (I), which shows that molecules form one-dimensional polymeric chains extending along the *a* axis.

1-Acetyl-3-[2-(2,3,5,6-tetrafluorophenyl)hydrazin-1-ylidene]indolin-2-one

Crystal data

$C_{16}H_9F_4N_3O_2$	$F(000) = 356$
$M_r = 351.26$	$D_x = 1.589$ Mg m^{-3}
Monoclinic, $P2_1$	Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å
Hall symbol: P 2yb	Cell parameters from 749 reflections
$a = 9.8993$ (19) Å	$\theta = 2.6$–$25.3°$
$b = 4.7740$ (6) Å	$\mu = 0.14$ mm^{-1}
$c = 16.066$ (3) Å	$T = 296$ K
$\beta = 104.807$ (8)°	Prism, yellow
$V = 734.0$ (2) Å^3	0.32 × 0.24 × 0.22 mm
$Z = 2$	

Data collection

Bruker Kappa APEXII CCD diffractometer	1462 independent reflections
Radiation source: fine-focus sealed tube	749 reflections with $I > 2\sigma(I)$
graphite	$R_{int} = 0.087$
Detector resolution: 8.10 pixels mm^{-1}	$\theta_{max} = 25.3°$, $\theta_{min} = 2.1°$
ω scans	$h = -11 \rightarrow 11$
Absorption correction: multi-scan (*SADABS*; Bruker, 2005)	$k = -5 \rightarrow 5$
$T_{min} = 0.942$, $T_{max} = 0.952$	$l = -19 \rightarrow 19$
6095 measured reflections	

Refinement

Refinement on F^2	Primary atom site location: structure-invariant direct methods
Least-squares matrix: full	Secondary atom site location: difference Fourier map
$R[F^2 > 2\sigma(F^2)] = 0.046$	Hydrogen site location: inferred from neighbouring sites
$wR(F^2) = 0.080$	H-atom parameters constrained

$S = 0.96$	$w = 1/[\sigma^2(F_o^2) + (0.0218P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
1462 reflections	$(\Delta/\sigma)_{max} < 0.001$
227 parameters	$\Delta\rho_{max} = 0.14$ e Å^{-3}
1 restraint	$\Delta\rho_{min} = -0.18$ e Å^{-3}

Special details

Geometry. Bond distances, angles *etc*. have been calculated using the rounded fractional coordinates. All su's are estimated from the variances of the (full) variance-covariance matrix. The cell e.s.d.'s are taken into account in the estimation of distances, angles and torsion angles

Refinement. Refinement of F^2 against ALL reflections. The weighted *R*-factor *wR* and goodness of fit *S* are based on F^2, conventional *R*-factors *R* are based on *F*, with *F* set to zero for negative F^2. The threshold expression of $F^2 > \sigma(F^2)$ is used only for calculating *R*-factors(gt) *etc*. and is not relevant to the choice of reflections for refinement. *R*-factors based on F^2 are statistically about twice as large as those based on *F*, and *R*- factors based on ALL data will be even larger.

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å^2)

	x	*y*	*z*	U_{iso}*/U_{eq}
F1	0.3005 (3)	−0.4142 (6)	0.06872 (17)	0.0638 (12)
F2	0.4748 (3)	−0.8205 (7)	0.0458 (2)	0.0791 (16)
F3	0.7604 (3)	−0.6503 (7)	0.3236 (2)	0.0843 (14)
F4	0.5877 (3)	−0.2576 (8)	0.34942 (19)	0.0820 (14)
O1	−0.1264 (4)	0.8071 (9)	0.2007 (3)	0.0780 (17)
O2	0.1041 (3)	0.1514 (8)	0.1326 (2)	0.0613 (14)
N1	0.3432 (4)	0.0297 (9)	0.2843 (3)	0.0520 (17)
N2	0.3382 (4)	−0.1238 (9)	0.2140 (3)	0.0492 (17)
N3	0.0446 (4)	0.4800 (9)	0.2270 (3)	0.0472 (17)
C1	0.2424 (5)	0.2126 (11)	0.2794 (3)	0.045 (2)
C2	0.2254 (6)	0.3936 (11)	0.3472 (3)	0.048 (2)
C3	0.3062 (6)	0.4269 (12)	0.4321 (4)	0.067 (3)
C4	0.2608 (7)	0.6204 (15)	0.4832 (4)	0.085 (3)
C5	0.1400 (8)	0.7727 (13)	0.4520 (4)	0.082 (3)
C6	0.0581 (6)	0.7417 (12)	0.3682 (4)	0.064 (3)
C7	0.1054 (5)	0.5532 (10)	0.3168 (3)	0.046 (2)
C8	0.1251 (5)	0.2667 (11)	0.2034 (3)	0.047 (2)
C9	−0.0694 (6)	0.6214 (14)	0.1721 (4)	0.057 (2)
C10	−0.1145 (5)	0.5317 (13)	0.0791 (3)	0.078 (3)
C11	0.4358 (5)	−0.3222 (11)	0.2091 (3)	0.0415 (19)
C12	0.4162 (5)	−0.4726 (11)	0.1331 (3)	0.046 (2)
C13	0.5063 (6)	−0.6775 (12)	0.1212 (4)	0.055 (2)
C14	0.6244 (6)	−0.7476 (12)	0.1850 (4)	0.058 (3)
C15	0.6455 (6)	−0.5977 (13)	0.2589 (4)	0.055 (2)
C16	0.5565 (6)	−0.3921 (11)	0.2732 (3)	0.052 (2)
H2	0.26986	−0.09659	0.16945	0.0589*
H3	0.38710	0.32286	0.45329	0.0808*
H4	0.31279	0.64831	0.53964	0.1016*

H5	0.11238	0.90027	0.48823	0.0984*
H6	−0.02410	0.84251	0.34781	0.0768*
H10A	−0.19107	0.64643	0.04892	0.1164*
H10B	−0.14341	0.33917	0.07589	0.1164*
H10C	−0.03772	0.55230	0.05320	0.1164*
H14	0.68534	−0.88833	0.17772	0.0692*

Atomic displacement parameters (Å^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
F1	0.059 (2)	0.066 (2)	0.058 (2)	0.0084 (17)	−0.0006 (16)	0.0018 (17)
F2	0.096 (3)	0.066 (2)	0.078 (3)	0.010 (2)	0.027 (2)	−0.013 (2)
F3	0.062 (2)	0.101 (3)	0.083 (2)	0.018 (2)	0.006 (2)	0.024 (2)
F4	0.077 (2)	0.098 (3)	0.060 (2)	0.013 (2)	−0.0025 (19)	−0.010 (2)
O1	0.075 (3)	0.076 (3)	0.083 (3)	0.029 (3)	0.020 (2)	0.002 (2)
O2	0.061 (2)	0.070 (3)	0.052 (2)	0.010 (2)	0.013 (2)	−0.010 (2)
N1	0.062 (3)	0.047 (3)	0.048 (3)	−0.006 (3)	0.016 (2)	−0.002 (3)
N2	0.042 (3)	0.055 (3)	0.048 (3)	0.008 (2)	0.007 (2)	−0.001 (3)
N3	0.048 (3)	0.039 (3)	0.055 (3)	0.008 (2)	0.014 (3)	0.006 (2)
C1	0.048 (4)	0.038 (4)	0.051 (4)	0.003 (3)	0.015 (3)	0.008 (3)
C2	0.058 (4)	0.043 (4)	0.045 (4)	−0.004 (3)	0.018 (3)	0.002 (3)
C3	0.075 (4)	0.069 (5)	0.055 (4)	0.010 (4)	0.011 (4)	−0.004 (4)
C4	0.105 (6)	0.083 (6)	0.062 (5)	0.003 (5)	0.014 (4)	−0.015 (4)
C5	0.112 (6)	0.068 (5)	0.073 (5)	0.001 (5)	0.035 (4)	−0.020 (4)
C6	0.067 (4)	0.056 (4)	0.074 (5)	0.007 (3)	0.027 (4)	−0.003 (4)
C7	0.053 (4)	0.037 (4)	0.050 (4)	−0.004 (3)	0.016 (3)	−0.001 (3)
C8	0.049 (4)	0.042 (4)	0.051 (4)	−0.003 (3)	0.017 (3)	0.006 (3)
C9	0.051 (4)	0.057 (4)	0.066 (4)	0.005 (3)	0.022 (3)	0.008 (3)
C10	0.072 (4)	0.095 (5)	0.057 (4)	0.019 (4)	0.000 (3)	0.000 (4)
C11	0.040 (3)	0.037 (3)	0.051 (4)	−0.001 (3)	0.018 (3)	0.010 (3)
C12	0.046 (4)	0.040 (4)	0.052 (4)	0.006 (3)	0.013 (3)	0.006 (3)
C13	0.068 (4)	0.045 (4)	0.055 (4)	0.001 (3)	0.020 (4)	−0.002 (3)
C14	0.057 (4)	0.044 (4)	0.078 (5)	0.008 (3)	0.028 (4)	0.012 (4)
C15	0.044 (4)	0.057 (4)	0.064 (4)	0.009 (3)	0.012 (3)	0.021 (4)
C16	0.051 (4)	0.056 (4)	0.048 (4)	−0.009 (3)	0.013 (3)	−0.006 (3)

Geometric parameters (Å, °)

F1—C12	1.362 (6)	C4—C5	1.380 (10)
F2—C13	1.356 (7)	C5—C6	1.391 (9)
F3—C15	1.354 (7)	C6—C7	1.382 (8)
F4—C16	1.347 (6)	C9—C10	1.508 (8)
O1—C9	1.203 (8)	C11—C16	1.404 (7)
O2—C8	1.233 (6)	C11—C12	1.387 (7)
N1—N2	1.337 (6)	C12—C13	1.370 (8)
N1—C1	1.313 (7)	C13—C14	1.385 (9)
N2—C11	1.370 (7)	C14—C15	1.356 (9)
N3—C7	1.457 (7)	C15—C16	1.377 (8)
N3—C8	1.404 (7)	C3—H3	0.9300

N3—C9	1.414 (8)	C4—H4	0.9300
N2—H2	0.8600	C5—H5	0.9300
C1—C8	1.477 (7)	C6—H6	0.9300
C1—C2	1.434 (7)	C10—H10A	0.9600
C2—C7	1.391 (8)	C10—H10B	0.9600
C2—C3	1.403 (8)	C10—H10C	0.9600
C3—C4	1.385 (9)	C14—H14	0.9300
N2—N1—C1	116.8 (4)	F1—C12—C13	119.4 (5)
N1—N2—C11	123.6 (4)	C11—C12—C13	122.9 (5)
C7—N3—C8	108.8 (4)	F1—C12—C11	117.7 (4)
C7—N3—C9	124.4 (4)	C12—C13—C14	121.7 (5)
C8—N3—C9	126.6 (5)	F2—C13—C12	118.4 (5)
N1—N2—H2	118.00	F2—C13—C14	119.9 (5)
C11—N2—H2	118.00	C13—C14—C15	115.6 (6)
N1—C1—C2	126.2 (5)	F3—C15—C16	116.9 (5)
N1—C1—C8	126.2 (5)	C14—C15—C16	124.1 (6)
C2—C1—C8	107.6 (4)	F3—C15—C14	119.1 (5)
C1—C2—C3	131.2 (5)	C11—C16—C15	120.5 (5)
C3—C2—C7	120.2 (5)	F4—C16—C11	120.5 (5)
C1—C2—C7	108.6 (4)	F4—C16—C15	118.9 (5)
C2—C3—C4	117.5 (6)	C2—C3—H3	121.00
C3—C4—C5	121.2 (6)	C4—C3—H3	121.00
C4—C5—C6	122.2 (6)	C3—C4—H4	119.00
C5—C6—C7	116.4 (6)	C5—C4—H4	119.00
C2—C7—C6	122.5 (5)	C4—C5—H5	119.00
N3—C7—C2	108.4 (4)	C6—C5—H5	119.00
N3—C7—C6	129.1 (5)	C5—C6—H6	122.00
N3—C8—C1	106.5 (4)	C7—C6—H6	122.00
O2—C8—N3	126.9 (5)	C9—C10—H10A	110.00
O2—C8—C1	126.6 (5)	C9—C10—H10B	109.00
O1—C9—N3	119.4 (6)	C9—C10—H10C	109.00
O1—C9—C10	122.6 (6)	H10A—C10—H10B	109.00
N3—C9—C10	118.0 (5)	H10A—C10—H10C	109.00
N2—C11—C12	117.8 (4)	H10B—C10—H10C	109.00
C12—C11—C16	115.1 (5)	C13—C14—H14	122.00
N2—C11—C16	127.1 (5)	C15—C14—H14	122.00
C1—N1—N2—C11	179.8 (5)	C1—C2—C7—C6	177.8 (5)
N2—N1—C1—C2	178.5 (5)	C3—C2—C7—N3	178.8 (5)
N2—N1—C1—C8	−0.7 (8)	C3—C2—C7—C6	−2.1 (8)
N1—N2—C11—C12	178.2 (5)	C2—C3—C4—C5	0.6 (10)
N1—N2—C11—C16	−2.2 (8)	C3—C4—C5—C6	−0.3 (11)
C8—N3—C7—C2	2.2 (6)	C4—C5—C6—C7	−1.2 (10)
C8—N3—C7—C6	−176.7 (5)	C5—C6—C7—N3	−178.8 (5)
C9—N3—C7—C2	−172.7 (5)	C5—C6—C7—C2	2.4 (8)
C9—N3—C7—C6	8.4 (8)	N2—C11—C12—F1	−0.5 (7)
C7—N3—C8—O2	179.4 (5)	N2—C11—C12—C13	−179.4 (5)
C7—N3—C8—C1	−2.2 (5)	C16—C11—C12—F1	179.8 (4)
C9—N3—C8—O2	−5.9 (9)	C16—C11—C12—C13	0.9 (8)

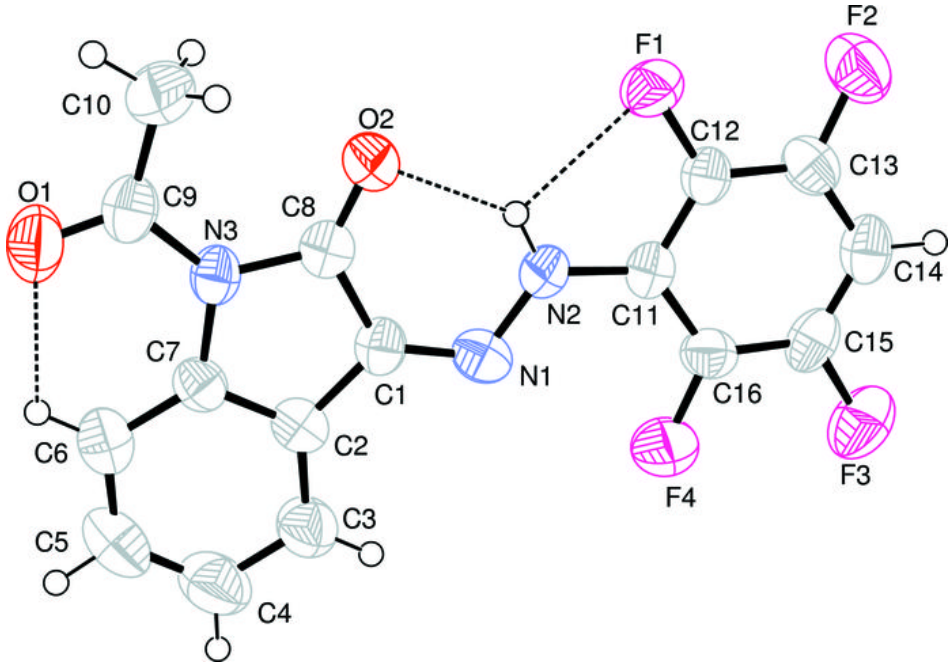
C9—N3—C8—C1	172.6 (5)	N2—C11—C16—F4	−0.6 (8)
C7—N3—C9—O1	−3.7 (9)	N2—C11—C16—C15	180.0 (5)
C7—N3—C9—C10	176.2 (5)	C12—C11—C16—F4	179.1 (5)
C8—N3—C9—O1	−177.7 (5)	C12—C11—C16—C15	−0.4 (8)
C8—N3—C9—C10	2.3 (8)	F1—C12—C13—F2	−1.6 (8)
N1—C1—C2—C3	0.5 (10)	F1—C12—C13—C14	−179.1 (5)
N1—C1—C2—C7	−179.4 (5)	C11—C12—C13—F2	177.3 (5)
C8—C1—C2—C3	179.8 (6)	C11—C12—C13—C14	−0.2 (9)
C8—C1—C2—C7	0.0 (6)	F2—C13—C14—C15	−178.4 (5)
N1—C1—C8—O2	−0.8 (9)	C12—C13—C14—C15	−0.9 (9)
N1—C1—C8—N3	−179.3 (5)	C13—C14—C15—F3	−178.6 (5)
C2—C1—C8—O2	179.9 (5)	C13—C14—C15—C16	1.5 (9)
C2—C1—C8—N3	1.4 (6)	F3—C15—C16—F4	−0.2 (8)
C1—C2—C3—C4	−179.3 (6)	F3—C15—C16—C11	179.3 (5)
C7—C2—C3—C4	0.6 (9)	C14—C15—C16—F4	179.7 (5)
C1—C2—C7—N3	−1.3 (6)	C14—C15—C16—C11	−0.9 (9)

Hydrogen-bond geometry (Å, °)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
N2—H2···O2	0.86	1.99	2.694 (5)	139
N2—H2···F1	0.86	2.29	2.658 (5)	106
C6—H6···O1	0.93	2.33	2.857 (8)	116
C14—H14···O1^{i}	0.93	2.32	3.217 (7)	163

Symmetry codes: (i) *x*+1, *y*−2, *z*.

Fig. 1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O2
C12
C13
O1
C9
C8
N3
C14
N2
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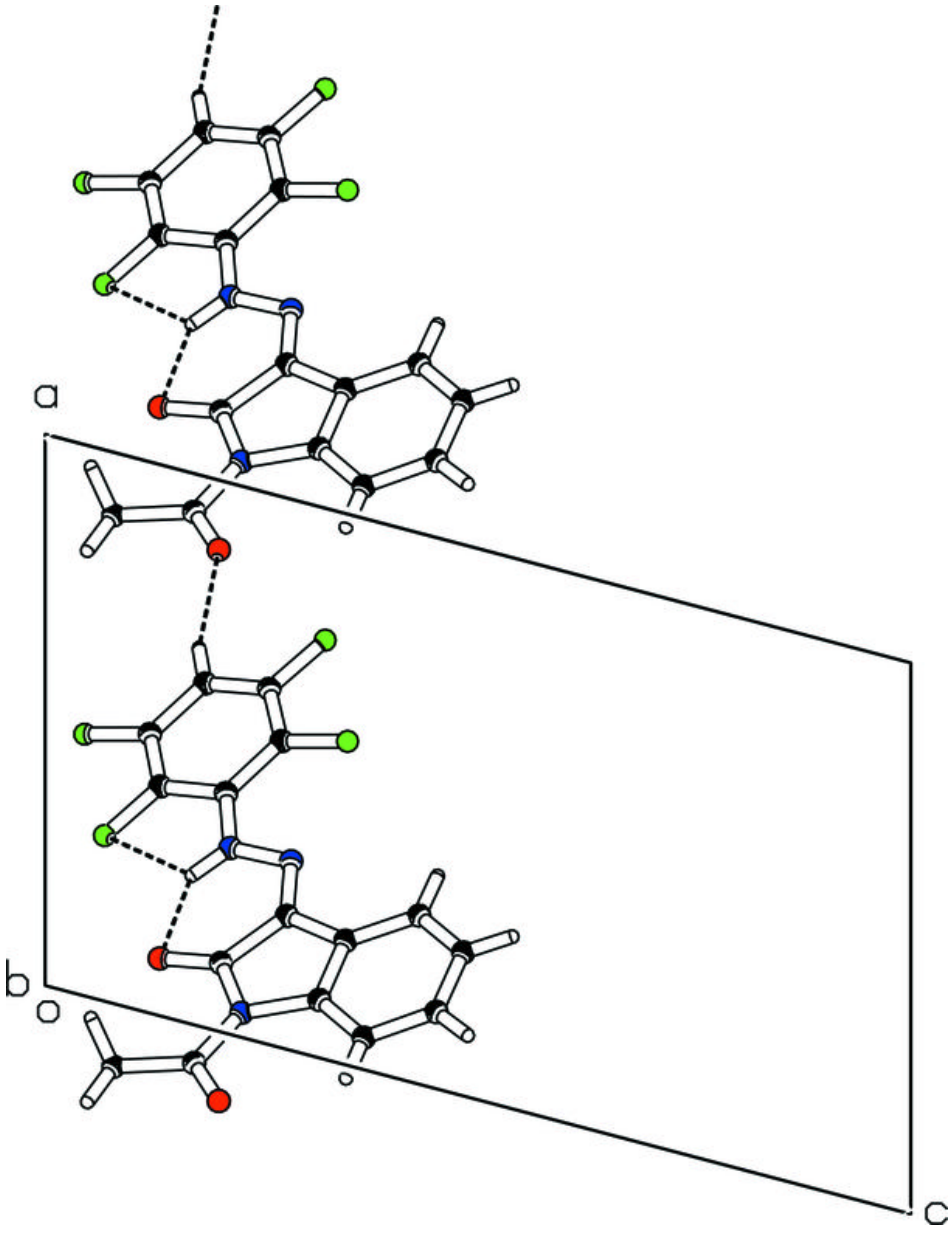
C1
C16
C6
C2
F3
F4
C3
C5
C4

Fig. 2



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1-[1-(4-Bromophenyl)ethylidene]-4-(2,4-dimethoxyphenyl)thiosemicarbazide

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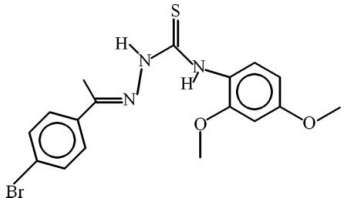
Key indicators: single-crystal X-ray study; T = 296 K; mean σ(C–C) = 0.004 Å; R factor = 0.041; wR factor = 0.100; data-to-parameter ratio = 19.8.

In the title compound, $C_{17}H_{18}BrN_3O_2S$, the dihedral angle between the aromatic rings is 9.15 (17)°. A bifurcated intramolecular N—H···(N,O) hydrogen bond generates two S(5) rings and a weak intramolecular C—H···S interaction completes an S(6) ring motif. In the crystal, inversion dimers linked by pairs of N—H···S hydrogen bonds generate $R_2^2(8)$ loops and weak C—H···S and C—H···π interactions are also present.

Related literature

For the pharmacological applications of thiosemicarbazones see: Beraldo & Gambino (2004); Pervez *et al.* (2008, 2010*a*,*b*). For related structures, see: Jian *et al.* (2005); Martínez *et al.* (2006). For graph-set notation, see: Bernstein *et al.* (1995).



Experimental

Crystal data

$C_{17}H_{18}BrN_3O_2S$
M_r = 408.31
Monoclinic, $P2_1/n$
a = 5.8390 (2) Å
b = 30.3335 (11) Å
c = 9.9423 (4) Å
β = 94.910 (2)°
V = 1754.49 (11) Å^3
Z = 4
Mo $K\alpha$ radiation
μ = 2.48 mm^{-1}
T = 296 K
0.25 × 0.22 × 0.20 mm

Data collection

Bruker Kappa APEXII CCD diffractometer
Absorption correction: multi-scan (*SADABS*; Bruker, 2005)
T_{min} = 0.642, T_{max} = 0.652
17115 measured reflections
4346 independent reflections
2654 reflections with $I > 2\sigma(I)$
R_{int} = 0.044

Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.041
$wR(F^2)$ = 0.100
S = 1.01
4346 reflections
220 parameters
H-atom parameters constrained
$\Delta\rho_{max}$ = 0.42 e Å^{-3}
$\Delta\rho_{min}$ = −0.36 e Å^{-3}

Table 1
Hydrogen-bond geometry (Å, °).

*Cg*1 is the centroid of C1–C6 ring.

D—H···A	D—H	H···A	D···A	D—H···A
N1—H1···O1	0.86	2.12	2.573 (3)	113
N1—H1···N3	0.86	2.05	2.538 (3)	115
N2—H2A···S1^{i}	0.86	2.84	3.662 (2)	161
C2—H2···S1	0.93	2.58	3.248 (3)	129
C17—H17A···S1^{ii}	0.96	2.86	3.774 (3)	161
C8—H8A···Cg1^{iii}	0.96	2.98	3.860 (3)	153

Symmetry codes: (i) $-x+2, -y, -z+2$; (ii) $x+1, y, z$; (iii) $x-1, y, z$.

Data collection: *APEX2* (Bruker, 2007); cell refinement: *SAINT* (Bruker, 2007); data reduction: *SAINT*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *ORTEP-3* (Farrugia, 1997) and *PLATON* (Spek, 2009); software used to prepare material for publication: *WinGX* (Farrugia, 1999) and *PLATON*.

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Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: HB5499).

References

Beraldo, H. & Gambino, D. (2004). *Mini Rev. Med. Chem.* **4**, 159–165.
Bernstein, J., Davis, R. E., Shimoni, L. & Chang, N.-L. (1995). *Angew. Chem. Int. Ed. Engl.* **34**, 1555–1573.
Bruker (2005). *SADABS*. Bruker AXS Inc., Madison, Wisconsin, USA.
Bruker (2007). *APEX2* and *SAINT*. Bruker AXS Inc., Madison, Wisconsin, USA.
Farrugia, L. J. (1997). *J. Appl. Cryst.* **30**, 565.
Farrugia, L. J. (1999). *J. Appl. Cryst.* **32**, 837–838.
Jian, F., Li, Y. & Xiao, H. (2005). *Acta Cryst.* E**61**, o2219–o2220.
Martínez, J., Adrio, L. A., Antelo, J. M., Ortigueira, J. M., Pereira, M. T., López-Torres, M. & Vila, M. J. (2006). *J. Organomet. Chem.* 691, 2891–2901.
Pervez, H., Iqbal, M. S., Tahir, M. Y., Nasim, F. H., Choudhary, M. I. Khan, K. M. & Yaqub, M. (2008). *J. Enz. Inhib. Med. Chem.* **23**, 848–854.
Pervez, H., Manzoor, N., Yaqub, M., Khan, A., Khan, K. M., Nasim, F. H. & Choudhary, M. I. (2010*a*). *Lett. Drug Des. Discov.* **7**, 102–108.
Pervez, H., Iqbal, M. S., Saira, N., Yaqub, M. & Tahir, M. N. (2010*b*). *Acta Cryst.* E**66**, o1169–01170.
Sheldrick, G. M. (2008). *Acta Cryst.* A**64**, 112–122.
Spek, A. L. (2009). *Acta Cryst.* D**65**, 148–155.

supplementary materials

Acta Cryst. (2010). E**66**, o1696 [**doi:10.1107/S1600536810022622**]

1-[1-(4-Bromophenyl)ethylidene]-4-(2,4-dimethoxyphenyl)thiosemicarbazide

M. Yaqub, H. Pervez, N. Arif, M. N. Tahir and M. Hussain

Comment

Thiosemicarbazones have wide pharmacological properties (Beraldo & Gambino, 2004). Prompted by this, we recently reported the synthesis and medicinal importance of some isatins-thiosemicarbazones (Pervez *et al.*, 2008, 2010*a*,*b*). Now, we report the synthesis and crystal structure of the title compound (I), (Fig. I).

The crystal structure of (II) *i.e.* 4-fluoroacetophenone-*N*-propylthiosemicarbazone (Martinez *et al.*, 2006) and (III) *i.e.* 4-phenyl-1-(1-phenylethylidene)thiosemicarbazide (Jian, *et al.*, 2005) have been published. The title compound (I) is different from (II) and (III) due to attachment of substituants at the phenyl rings.

In (I), the phenyl ring A (C1–C6) of 2,4-dimethoxyanilino group, B (C11—C16) of 4-bromophenyl are planar with r. m. s. deviations of 0.0034 and 0.0036 Å, respectively. The thiosemicarbazone moiety C (N1—N3/C9/S1) is also planar with r. m. s. deviation of 0.0062 Å from its mean square plane. The dihedral angle between A/B, A/C and B/C is 9.15 (17), 2.07 (17) and 9.12 (16)°, respectively. Two S(5) ring motifs (Bernstein *et al.*, 1995) (Table 1, Fig. 1) are formed due to strong intramolecular H-bonding of N—H···N and N—H···O types. The weak interaction of C—H···S type completes an S(6) ring motif. The molecules are dimerized due to intermolecular interactions of N—H···S type and complete $R_2^2(8)$ ring motif (Fig. 2). The dimers are interlinked through C—H···S interactions (Table 1). The C—H···π interaction (Table 1) also play role in stabilizing the molecules.

Experimental

A solution of 4-(2,4-dimethoxyphenyl)thiosemicarbazide (0.15 g, 0.66 mole) in warm ethanol (20 ml) was added drop wise to the stirred solution of 4-bromoacetophenone (0.13 g, 0.66 mol) in warm ethanol (10 ml) containing 2–3 drops of acetic acid. The resultant mixture was then heated under reflux for 30 min. After cooling the reaction mixture to room temperature, the yellow solid was collected by suction filtration, washing with ethanol furnished the title compound in pure form (0.21 g, 95%), m.p. 502 K. Colourless prisms of (I) were grown in chloroform-petroleum ether (1:5) system at room temperature by diffusion method.

Refinement

The H-atoms were positioned geometrically (N–H = 0.86 Å, C–H = 0.93–0.96 Å) and refined as riding with U_{iso}(H) = xU_{eq}(C, N), where x = 1.5 for methyl and x = 1.2 for all other H-atoms.

Figures

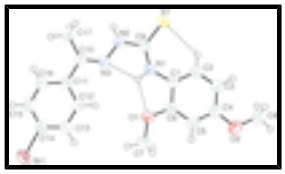


Fig. 1. View of (I) with displacement ellipsoids drawn at the 50% probability level. The dotted lines indicate the intra-molecular H-bonds.

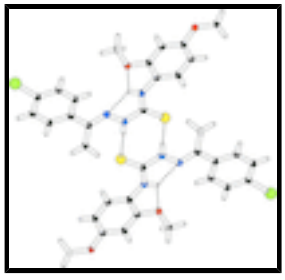


Fig. 2. The partial packing of (I), which shows that molecules form dimers.

1-[1-(4-Bromophenyl)ethylidene]-4-(2,4-dimethoxyphenyl)thiosemicarbazide

Crystal data

$C_{17}H_{18}BrN_3O_2S$	$F(000) = 832$
$M_r = 408.31$	$D_x = 1.546$ Mg m^{-3}
Monoclinic, $P2_1/n$	Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å
Hall symbol: -P 2yn	Cell parameters from 2654 reflections
$a = 5.8390$ (2) Å	$\theta = 2.2$–$28.3°$
$b = 30.3335$ (11) Å	$\mu = 2.48$ mm^{-1}
$c = 9.9423$ (4) Å	$T = 296$ K
$\beta = 94.910$ (2)°	Prism, colorless
$V = 1754.49$ (11) Å^3	0.25 × 0.22 × 0.20 mm
$Z = 4$	

Data collection

Bruker Kappa APEXII CCD diffractometer	4346 independent reflections
Radiation source: fine-focus sealed tube	2654 reflections with $I > 2\sigma(I)$
graphite	$R_{int} = 0.044$
Detector resolution: 7.5 pixels mm^{-1}	$\theta_{max} = 28.3°$, $\theta_{min} = 2.2°$
ω scans	$h = -4 \rightarrow 7$
Absorption correction: multi-scan (*SADABS*; Bruker, 2005)	$k = -40 \rightarrow 40$
$T_{min} = 0.642$, $T_{max} = 0.652$	$l = -13 \rightarrow 13$
17115 measured reflections	

Refinement

Refinement on F^2	Primary atom site location: structure-invariant direct methods

Least-squares matrix: full	Secondary atom site location: difference Fourier map
$R[F^2 > 2\sigma(F^2)] = 0.041$	Hydrogen site location: inferred from neighbouring sites
$wR(F^2) = 0.100$	H-atom parameters constrained
$S = 1.01$	$w = 1/[\sigma^2(F_o^2) + (0.0413P)^2 + 0.4088P]$ where $P = (F_o^2 + 2F_c^2)/3$
4346 reflections	$(\Delta/\sigma)_{max} = 0.001$
220 parameters	$\Delta\rho_{max} = 0.42$ e Å^{-3}
0 restraints	$\Delta\rho_{min} = -0.36$ e Å^{-3}

Special details

Geometry. Bond distances, angles *etc*. have been calculated using the rounded fractional coordinates. All su's are estimated from the variances of the (full) variance-covariance matrix. The cell e.s.d.'s are taken into account in the estimation of distances, angles and torsion angles

Refinement. Refinement of F^2 against ALL reflections. The weighted *R*-factor *wR* and goodness of fit *S* are based on F^2, conventional *R*-factors *R* are based on *F*, with *F* set to zero for negative F^2. The threshold expression of $F^2 > \sigma(F^2)$ is used only for calculating *R*-factors(gt) *etc*. and is not relevant to the choice of reflections for refinement. *R*-factors based on F^2 are statistically about twice as large as those based on *F*, and *R*- factors based on ALL data will be even larger.

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å^2)

	x	*y*	*z*	U_{iso}*/U_{eq}
Br1	1.68144 (7)	0.28876 (1)	0.66065 (3)	0.0846 (1)
S1	0.69373 (12)	0.00989 (2)	0.87217 (7)	0.0577 (2)
O1	0.7242 (3)	0.14610 (6)	0.55058 (18)	0.0598 (7)
O2	0.0390 (3)	0.09126 (7)	0.3147 (2)	0.0710 (8)
N1	0.7530 (3)	0.08160 (7)	0.7192 (2)	0.0504 (7)
N2	1.0174 (3)	0.06989 (7)	0.8946 (2)	0.0490 (7)
N3	1.1192 (3)	0.10729 (7)	0.8520 (2)	0.0465 (7)
C1	0.5629 (4)	0.08091 (8)	0.6222 (2)	0.0453 (8)
C2	0.3956 (5)	0.04927 (10)	0.6085 (3)	0.0684 (11)
C3	0.2178 (5)	0.05173 (10)	0.5075 (3)	0.0707 (11)
C4	0.2059 (4)	0.08609 (9)	0.4186 (3)	0.0536 (9)
C5	0.3721 (4)	0.11870 (9)	0.4316 (3)	0.0519 (9)
C6	0.5493 (4)	0.11606 (8)	0.5315 (2)	0.0449 (8)
C7	0.7459 (5)	0.17845 (10)	0.4497 (3)	0.0718 (11)
C8	−0.1278 (5)	0.05715 (11)	0.2945 (3)	0.0714 (11)
C9	0.8214 (4)	0.05526 (8)	0.8225 (2)	0.0426 (8)
C10	1.2991 (4)	0.12299 (8)	0.9180 (2)	0.0413 (8)
C11	1.3922 (4)	0.16334 (8)	0.8596 (2)	0.0397 (7)
C12	1.2659 (4)	0.18592 (9)	0.7571 (3)	0.0522 (9)
C13	1.3493 (5)	0.22333 (9)	0.7001 (3)	0.0585 (10)
C14	1.5632 (4)	0.23844 (9)	0.7440 (3)	0.0511 (9)
C15	1.6935 (5)	0.21732 (9)	0.8453 (3)	0.0560 (10)
C16	1.6074 (4)	0.17997 (9)	0.9025 (3)	0.0508 (9)
C17	1.4082 (5)	0.10312 (9)	1.0456 (3)	0.0565 (9)

H1	0.84389	0.10350	0.71009	0.0605*
H2	0.40157	0.02564	0.66831	0.0820*
H2A	1.07456	0.05588	0.96481	0.0587*
H3	0.10583	0.02985	0.50022	0.0849*
H5	0.36375	0.14251	0.37241	0.0623*
H7A	0.61321	0.19727	0.44397	0.1075*
H7B	0.75783	0.16426	0.36429	0.1075*
H7C	0.88133	0.19576	0.47252	0.1075*
H8A	−0.21919	0.05609	0.37027	0.1075*
H8B	−0.05148	0.02938	0.28602	0.1075*
H8C	−0.22514	0.06296	0.21373	0.1075*
H12	1.12106	0.17552	0.72613	0.0626*
H13	1.26085	0.23820	0.63226	0.0701*
H15	1.83820	0.22799	0.87536	0.0672*
H16	1.69579	0.16564	0.97145	0.0610*
H17A	1.48971	0.07685	1.02462	0.0848*
H17B	1.29134	0.09589	1.10418	0.0848*
H17C	1.51361	0.12388	1.08973	0.0848*

Atomic displacement parameters (Å^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Br1	0.1088 (3)	0.0700 (2)	0.0736 (2)	−0.0456 (2)	0.0001 (2)	0.0106 (2)
S1	0.0585 (4)	0.0489 (4)	0.0642 (4)	−0.0114 (3)	−0.0030 (3)	0.0194 (3)
O1	0.0677 (12)	0.0508 (11)	0.0587 (12)	−0.0148 (9)	−0.0080 (9)	0.0172 (9)
O2	0.0668 (12)	0.0697 (14)	0.0712 (13)	0.0015 (11)	−0.0242 (10)	0.0076 (11)
N1	0.0543 (12)	0.0453 (12)	0.0496 (12)	−0.0150 (10)	−0.0074 (10)	0.0128 (10)
N2	0.0522 (12)	0.0458 (12)	0.0470 (12)	−0.0095 (10)	−0.0066 (10)	0.0129 (10)
N3	0.0493 (12)	0.0431 (12)	0.0464 (12)	−0.0070 (9)	−0.0005 (10)	0.0087 (9)
C1	0.0483 (14)	0.0439 (14)	0.0429 (13)	−0.0044 (11)	−0.0008 (11)	0.0061 (11)
C2	0.077 (2)	0.0571 (18)	0.0670 (19)	−0.0215 (15)	−0.0181 (16)	0.0215 (15)
C3	0.0721 (19)	0.063 (2)	0.072 (2)	−0.0253 (16)	−0.0223 (16)	0.0155 (16)
C4	0.0529 (16)	0.0520 (16)	0.0540 (16)	0.0031 (12)	−0.0056 (13)	−0.0032 (13)
C5	0.0644 (17)	0.0443 (14)	0.0462 (15)	0.0062 (12)	−0.0006 (13)	0.0072 (11)
C6	0.0517 (15)	0.0390 (13)	0.0442 (14)	−0.0022 (11)	0.0051 (12)	0.0012 (10)
C7	0.090 (2)	0.0543 (19)	0.070 (2)	−0.0172 (16)	0.0010 (17)	0.0197 (15)
C8	0.0591 (18)	0.076 (2)	0.075 (2)	0.0018 (16)	−0.0180 (15)	−0.0104 (17)
C9	0.0461 (14)	0.0407 (13)	0.0412 (13)	−0.0013 (10)	0.0043 (11)	0.0027 (10)
C10	0.0435 (14)	0.0416 (13)	0.0384 (13)	0.0037 (10)	0.0018 (11)	−0.0006 (10)
C11	0.0417 (13)	0.0388 (13)	0.0384 (12)	−0.0005 (10)	0.0025 (10)	−0.0044 (10)
C12	0.0475 (15)	0.0506 (15)	0.0572 (16)	−0.0094 (12)	−0.0030 (12)	0.0095 (13)
C13	0.0617 (18)	0.0552 (17)	0.0567 (17)	−0.0082 (13)	−0.0053 (14)	0.0109 (13)
C14	0.0603 (16)	0.0469 (15)	0.0465 (15)	−0.0135 (12)	0.0075 (13)	−0.0047 (12)
C15	0.0539 (16)	0.0591 (18)	0.0544 (16)	−0.0181 (13)	0.0004 (13)	−0.0090 (13)
C16	0.0507 (15)	0.0525 (16)	0.0480 (14)	−0.0024 (12)	−0.0029 (12)	0.0005 (12)
C17	0.0650 (17)	0.0505 (16)	0.0515 (16)	−0.0036 (13)	−0.0099 (13)	0.0063 (12)

Geometric parameters (Å, °)

Br1—C14	1.895 (3)	C11—C12	1.387 (4)
S1—C9	1.660 (2)	C12—C13	1.376 (4)
O1—C6	1.370 (3)	C13—C14	1.366 (4)
O1—C7	1.417 (3)	C14—C15	1.368 (4)
O2—C4	1.367 (3)	C15—C16	1.382 (4)
O2—C8	1.423 (4)	C2—H2	0.9300
N1—C1	1.407 (3)	C3—H3	0.9300
N1—C9	1.335 (3)	C5—H5	0.9300
N2—N3	1.365 (3)	C7—H7A	0.9600
N2—C9	1.371 (3)	C7—H7B	0.9600
N3—C10	1.282 (3)	C7—H7C	0.9600
N1—H1	0.8600	C8—H8A	0.9600
N2—H2A	0.8600	C8—H8B	0.9600
C1—C2	1.368 (4)	C8—H8C	0.9600
C1—C6	1.394 (3)	C12—H12	0.9300
C2—C3	1.383 (4)	C13—H13	0.9300
C3—C4	1.365 (4)	C15—H15	0.9300
C4—C5	1.384 (4)	C16—H16	0.9300
C5—C6	1.374 (3)	C17—H17A	0.9600
C10—C11	1.478 (3)	C17—H17B	0.9600
C10—C17	1.497 (4)	C17—H17C	0.9600
C11—C16	1.387 (3)		
C6—O1—C7	118.27 (19)	C14—C15—C16	119.2 (3)
C4—O2—C8	117.3 (2)	C11—C16—C15	121.6 (3)
C1—N1—C9	133.2 (2)	C1—C2—H2	119.00
N3—N2—C9	118.23 (19)	C3—C2—H2	119.00
N2—N3—C10	120.6 (2)	C2—C3—H3	120.00
C9—N1—H1	113.00	C4—C3—H3	120.00
C1—N1—H1	113.00	C4—C5—H5	120.00
N3—N2—H2A	121.00	C6—C5—H5	120.00
C9—N2—H2A	121.00	O1—C7—H7A	109.00
C2—C1—C6	118.1 (2)	O1—C7—H7B	109.00
N1—C1—C6	115.5 (2)	O1—C7—H7C	109.00
N1—C1—C2	126.4 (2)	H7A—C7—H7B	109.00
C1—C2—C3	121.3 (3)	H7A—C7—H7C	109.00
C2—C3—C4	120.3 (3)	H7B—C7—H7C	109.00
O2—C4—C3	124.8 (2)	O2—C8—H8A	109.00
O2—C4—C5	115.9 (2)	O2—C8—H8B	109.00
C3—C4—C5	119.3 (3)	O2—C8—H8C	109.00
C4—C5—C6	120.3 (3)	H8A—C8—H8B	109.00
O1—C6—C5	124.6 (2)	H8A—C8—H8C	109.00
C1—C6—C5	120.7 (2)	H8B—C8—H8C	109.00
O1—C6—C1	114.75 (19)	C11—C12—H12	119.00
S1—C9—N1	127.77 (18)	C13—C12—H12	119.00
S1—C9—N2	119.25 (17)	C12—C13—H13	120.00
N1—C9—N2	112.9 (2)	C14—C13—H13	120.00

C11—C10—C17	121.5 (2)	C14—C15—H15	120.00
N3—C10—C11	114.80 (19)	C16—C15—H15	120.00
N3—C10—C17	123.7 (2)	C11—C16—H16	119.00
C10—C11—C16	122.3 (2)	C15—C16—H16	119.00
C12—C11—C16	117.2 (2)	C10—C17—H17A	109.00
C10—C11—C12	120.5 (2)	C10—C17—H17B	109.00
C11—C12—C13	121.7 (2)	C10—C17—H17C	109.00
C12—C13—C14	119.4 (3)	H17A—C17—H17B	109.00
Br1—C14—C13	119.2 (2)	H17A—C17—H17C	109.00
C13—C14—C15	120.9 (3)	H17B—C17—H17C	110.00
Br1—C14—C15	119.90 (19)		
C7—O1—C6—C1	169.2 (2)	C2—C3—C4—O2	179.3 (3)
C7—O1—C6—C5	−10.1 (3)	C2—C3—C4—C5	−0.8 (4)
C8—O2—C4—C3	−3.1 (4)	O2—C4—C5—C6	−178.9 (2)
C8—O2—C4—C5	176.9 (2)	C3—C4—C5—C6	1.1 (4)
C9—N1—C1—C2	−2.8 (4)	C4—C5—C6—O1	178.5 (2)
C9—N1—C1—C6	178.0 (2)	C4—C5—C6—C1	−0.8 (4)
C1—N1—C9—S1	0.2 (4)	N3—C10—C11—C12	11.5 (3)
C1—N1—C9—N2	−177.7 (2)	N3—C10—C11—C16	−167.7 (2)
C9—N2—N3—C10	178.1 (2)	C17—C10—C11—C12	−167.6 (2)
N3—N2—C9—S1	−179.91 (16)	C17—C10—C11—C16	13.1 (4)
N3—N2—C9—N1	−1.8 (3)	C10—C11—C12—C13	−179.4 (2)
N2—N3—C10—C11	179.44 (19)	C16—C11—C12—C13	−0.1 (4)
N2—N3—C10—C17	−1.4 (3)	C10—C11—C16—C15	178.9 (2)
N1—C1—C2—C3	−179.0 (3)	C12—C11—C16—C15	−0.3 (4)
C6—C1—C2—C3	0.2 (4)	C11—C12—C13—C14	0.9 (4)
N1—C1—C6—O1	0.1 (3)	C12—C13—C14—Br1	177.8 (2)
N1—C1—C6—C5	179.5 (2)	C12—C13—C14—C15	−1.2 (4)
C2—C1—C6—O1	−179.3 (2)	Br1—C14—C15—C16	−178.2 (2)
C2—C1—C6—C5	0.2 (4)	C13—C14—C15—C16	0.7 (4)
C1—C2—C3—C4	0.1 (4)	C14—C15—C16—C11	0.1 (4)

Hydrogen-bond geometry (Å, °)

Cg1 is the centroid of C1–C6 ring.

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
N1—H1···O1	0.86	2.12	2.573 (3)	113
N1—H1···N3	0.86	2.05	2.538 (3)	115
N2—H2A···S1^{i}	0.86	2.84	3.662 (2)	161
C2—H2···S1	0.93	2.58	3.248 (3)	129
C17—H17A···S1^{ii}	0.96	2.86	3.774 (3)	161
C8—H8A···Cg1^{iii}	0.96	2.98	3.860 (3)	153

Symmetry codes: (i) −*x*+2, −*y*, −*z*+2; (ii) *x*+1, *y*, *z*; (iii) *x*−1, *y*, *z*.

Fig. 1

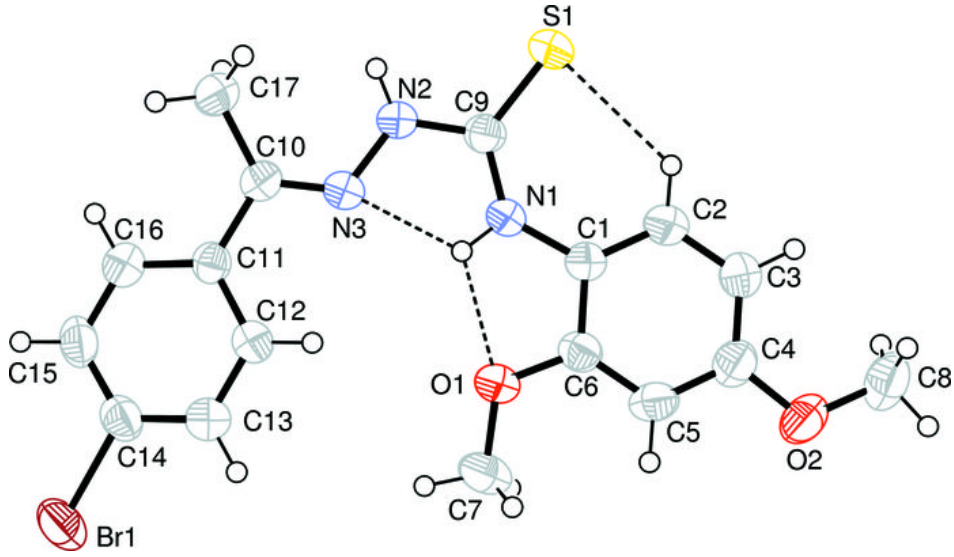
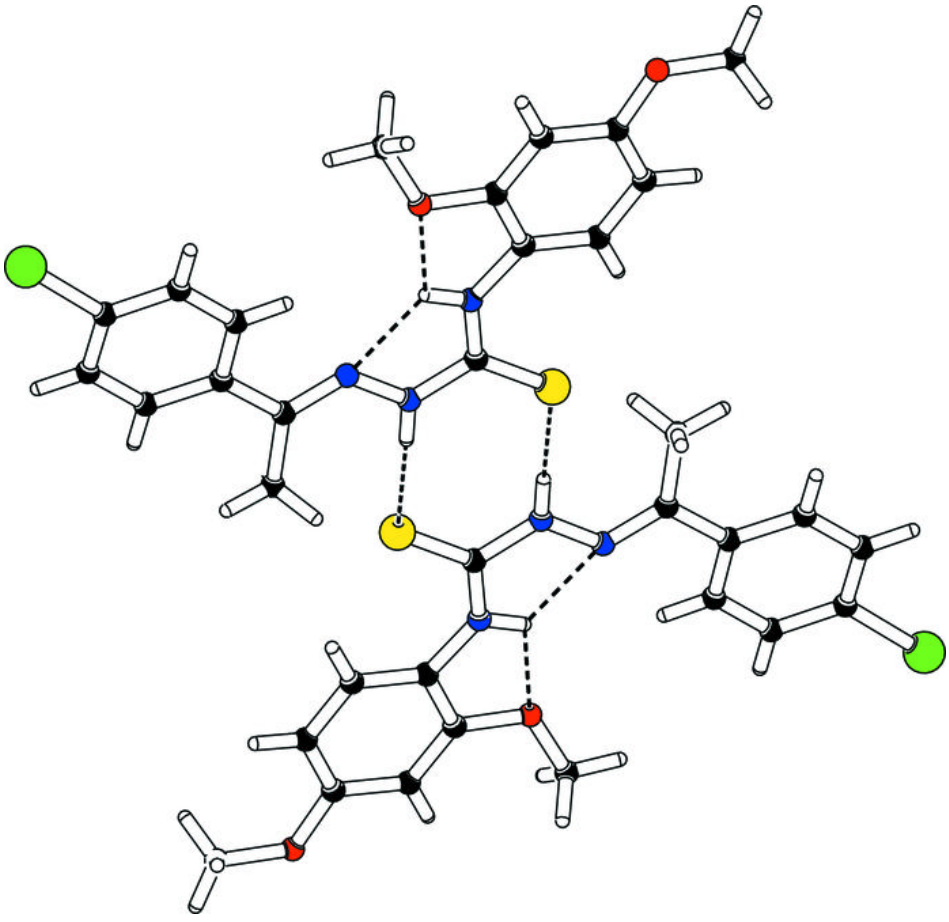

S1
C17
N2
C9
C10
N1
C2
C16
N3
C1
C11
C3
C12
C15
O1
C6
C4
C8
C13
C5
C14
O2
C7
Br1

Fig. 2



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N-(2-Methoxyphenyl)benzenesulfonamide

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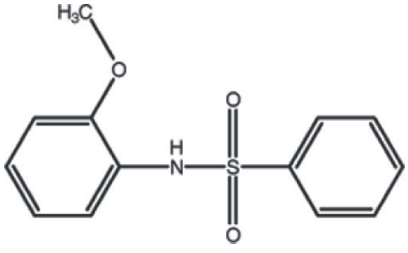
Key indicators: single-crystal X-ray study; T = 296 K; mean σ(C–C) = 0.004 Å; R factor = 0.047; wR factor = 0.113; data-to-parameter ratio = 19.0.

The asymmetric unit of the title compound, $C_{13}H_{13}NO_3S$, contains two crystallographically independent molecules in which the dihedral angles between the phenyl and benzene rings are 88.16 (12) and 44.50 (12)°. One of the molecules features an intramolecular N—H···O hydrogen bond. In the crystal, the molecules are linked into dimers by pairs of N—H···O hydrogen bonds. The dimers are further connected by C—H···O and C—H···π interactions, forming a three-dimensional network.

Related literature

For the biological activity of sulfonamides, see: Arshad *et al.* (2008); Gennarti *et al.* (1994); Kayser *et al.* (2004); Rough *et al.* (1998).



Experimental

Crystal data

$C_{13}H_{13}NO_3S$
M_r = 263.31
Monoclinic, $P2_1/n$
a = 8.7705 (2) Å
b = 28.1684 (7) Å
c = 10.7256 (3) Å
β = 105.968 (1)°
V = 2547.53 (11) Å^3
Z = 8
Mo $K\alpha$ radiation
μ = 0.25 mm^{-1}
T = 296 K
0.25 × 0.17 × 0.07 mm

Data collection

Bruker APEXII CCD diffractometer
24823 measured reflections
6318 independent reflections
4145 reflections with $I > 2\sigma(I)$
R_{int} = 0.043

Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.047
$wR(F^2)$ = 0.113
S = 1.02
6318 reflections
333 parameters
2 restraints
H atoms treated by a mixture of independent and constrained refinement
$\Delta\rho_{max}$ = 0.29 e Å^{-3}
$\Delta\rho_{min}$ = −0.29 e Å^{-3}

Table 1
Hydrogen-bond geometry (Å, °).

*Cg*4 is the centroid of the C7′–C12′ phenyl ring.

D—H···A	D—H	H···A	D···A	D—H···A
N1′—H1*N*′···O2	0.828 (18)	2.310 (17)	3.074 (2)	153.6 (17)
N1—H1*N*···O1′	0.843 (17)	2.129 (17)	2.961 (2)	168.7 (17)
N1—H1*N*···O3	0.843 (17)	2.258 (18)	2.592 (2)	103.8 (14)
C4—H4···O2′^{i}	0.93	2.47	3.377 (3)	167
C4′—H4′···*Cg*4^{ii}	0.93	2.85	3.601 (2)	138

Symmetry codes: (i) $-x+1, -y+2, -z+1$; (ii) $-x, -y+2, -z$.

Data collection: *APEX2* (Bruker, 2007); cell refinement: *SAINT* (Bruker, 2007); data reduction: *SAINT*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *ORTEP-3* (Farrugia, 1997); software used to prepare material for publication: *WinGX* (Farrugia, 1999) and *PLATON* (Spek, 2009).

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Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: HB5501).

References

Arshad, M. N., Khan, I. U. & Zia-ur-Rehman, M. (2008). *Acta Cryst.* E**64**, o2283–o2284.
Bruker (2007). *APEX2* and *SAINT*. Bruker AXS Inc., Madison, Wisconsin, USA.
Farrugia, L. J. (1997). *J. Appl. Cryst.* **30**, 565.
Farrugia, L. J. (1999). *J. Appl. Cryst.* **32**, 837–838.
Gennarti, C., Salom, B., Potenza, D. & Williams, A. (1994). Angew. *Chem. Int. Ed. Engl.* **33**, 2067–2069.
Kayser, F. H., Bienz, K. A., Eckert, J. & Zinkernagel, R. M. (2004). *Medical Microbiology*, pp. 1–20. Berlin: Thieme Medical.
Rough, W. R., Gwaltney, S. L., Cheng, J., Scheidt, K. A., Mc Kerrow, J. H. & Hansell, E. (1998). *J. Am. Chem. Soc.* **120**, 10994–10995.
Sheldrick, G. M. (2008). *Acta Cryst.* A**64**, 112–122.
Spek, A. L. (2009). *Acta Cryst.* D**65**, 148–155.

supplementary materials

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N-(2-Methoxyphenyl)benzenesulfonamide

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Comment

Sulfonamides are well known for their enormous potential as biologically active molecules (Rough *et al.*, 1998) in areas such as anti-microbial (Kayser *et al.*, 2004), anti-convulsant (Arshad *et al.*, 2008), anti-cancer agents and for the treatment of inflammatory rheumatic and non-rheumatic processes including onsets and traumatologic lesions (Gennarti *et al.*, 1994). In the present paper, the structure of *N*-(2-methoxyphenyl)benzene sulfonamide has been determined as part of a research program involving the synthesis and biological evaluation of sulfur containing compounds.

In the crystal structure of the title compound (I), (Fig. 1), there exist two independent molecules, A (with S1) and B (with S1'). Both independent molecules are bent at their *S* atoms with the C—S—N(H)—C torsion angles of 67.25 (15)° in molecule A and -81.17 (16)° in molecule B. The dihedral angles between the phenyl and benzene rings is 88.16 (12)° in molecule A and 44.50 (12)° in molecule B.

Molecular packing of (I) is stabilized by N–H···O, C—H···O interactions and C—H···π interactions, forming a three dimensional network (Table 1). Fig. 2 shows N—H···O hydrogen bonds between the molecules A and B in the asymmetric unit.

Experimental

A mixture benzenesulfonyl chloride (10.0 mmol; 1.45 ml), *ortho*-methoxy aniline (*o*-anisidine) (10.0 mmol; 1.12 ml), aqueous sodium carbonate (10%; 15.0 ml) and water (25 ml) was stirred for one hour at room temperature. The crude mixture was washed with water and dried. The product was dissolved in methanol and recrystallized by slow evaporation of the solvent, to generate colourless blocks of (I) in 74% yield.

Refinement

The H atoms of the NH groups were located in a difference Fourier map and refined with the N—H distance restrained to 0.86 (2) %A. The other H atoms were positioned geometrically using a riding model with C–H = 0.93 and 0.96 Å. All H atoms were refined with isotropic displacement parameters with U_{iso}(H) = 1.2U_{eq}(aromatic, NH) and U_{iso}(H) = 1.5U_{eq}(methyl).

Figures

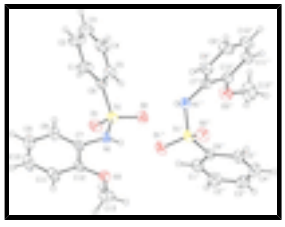


Fig. 1. View of the two independent molecules in the asymmetric unit of (I0 with displacement ellipsoids drawn at the 30% probability level.

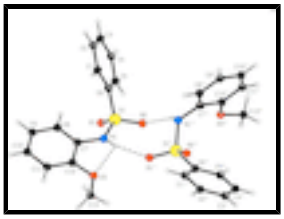


Fig. 2. View of N—H···O hydrogen bonds shown as dashed lines between the two independent molecules in the asymmetric unit.

N-(2-Methoxyphenyl)benzenesulfonamide

Crystal data

$C_{13}H_{13}NO_3S$	$F(000) = 1104$
$M_r = 263.31$	$D_x = 1.373$ Mg m^{-3}
Monoclinic, $P2_1/n$	Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å
Hall symbol: -P 2yn	Cell parameters from 5117 reflections
$a = 8.7705$ (2) Å	$\theta = 2.5$–$23.9°$
$b = 28.1684$ (7) Å	$\mu = 0.25$ mm^{-1}
$c = 10.7256$ (3) Å	$T = 296$ K
$\beta = 105.968$ (1)°	Block, colourless
$V = 2547.53$ (11) Å^3	0.25 × 0.17 × 0.07 mm
$Z = 8$	

Data collection

Bruker APEXII CCD diffractometer	4145 reflections with $I > 2\sigma(I)$
Radiation source: sealed tube	$R_{int} = 0.043$
graphite	$\theta_{max} = 28.3°$, $\theta_{min} = 3.3°$
φ and ω scans	$h = -11 \rightarrow 11$
24823 measured reflections	$k = -37 \rightarrow 37$
6318 independent reflections	$l = -14 \rightarrow 14$

Refinement

Refinement on F^2	Primary atom site location: structure-invariant direct methods
Least-squares matrix: full	Secondary atom site location: difference Fourier map
$R[F^2 > 2\sigma(F^2)] = 0.047$	Hydrogen site location: inferred from neighbouring sites
$wR(F^2) = 0.113$	H atoms treated by a mixture of independent and constrained refinement
$S = 1.02$	$w = 1/[\sigma^2(F_o^2) + (0.0488P)^2 + 0.3381P]$ where $P = (F_o^2 + 2F_c^2)/3$
6318 reflections	$(\Delta/\sigma)_{max} = 0.001$
333 parameters	$\Delta\rho_{max} = 0.29$ e Å^{-3}
2 restraints	$\Delta\rho_{min} = -0.29$ e Å^{-3}

Special details

Geometry. Bond distances, angles *etc*. have been calculated using the rounded fractional coordinates. All su's are estimated from the variances of the (full) variance-covariance matrix. The cell e.s.d.'s are taken into account in the estimation of distances, angles and torsion angles

Refinement. Refinement on F^2 for ALL reflections except those flagged by the user for potential systematic errors. Weighted *R*-factors *wR* and all goodnesses of fit *S* are based on F^2, conventional *R*-factors *R* are based on *F*, with *F* set to zero for negative F^2. The observed criterion of $F^2 > \sigma(F^2)$ is used only for calculating -*R*-factor-obs *etc*. and is not relevant to the choice of reflections for refinement. *R*-factors based on F^2 are statistically about twice as large as those based on *F*, and *R*-factors based on ALL data will be even larger.

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å^2)

	x	*y*	*z*	U_{iso}*/U_{eq}
S1	0.33115 (5)	0.81887 (2)	0.56961 (5)	0.0412 (2)
O1	0.29814 (16)	0.77142 (5)	0.59898 (15)	0.0561 (5)
O2	0.21225 (14)	0.84480 (5)	0.47617 (14)	0.0518 (5)
O3	0.68975 (15)	0.82034 (5)	0.38159 (14)	0.0507 (5)
N1	0.48440 (18)	0.81979 (6)	0.51516 (16)	0.0430 (5)
C1	0.3503 (3)	0.83266 (9)	0.8243 (2)	0.0681 (9)
C2	0.3878 (4)	0.85873 (11)	0.9379 (3)	0.0865 (11)
C3	0.4523 (3)	0.90282 (11)	0.9397 (3)	0.0764 (10)
C4	0.4848 (3)	0.92123 (8)	0.8326 (3)	0.0663 (9)
C5	0.4496 (2)	0.89536 (7)	0.7189 (2)	0.0511 (7)
C6	0.3823 (2)	0.85108 (7)	0.71581 (19)	0.0424 (6)
C7	0.6322 (2)	0.79744 (6)	0.57144 (18)	0.0388 (6)
C8	0.6717 (3)	0.77602 (7)	0.6914 (2)	0.0536 (7)
C9	0.8209 (3)	0.75621 (9)	0.7392 (3)	0.0681 (9)
C10	0.9276 (3)	0.75748 (9)	0.6684 (3)	0.0728 (9)
C11	0.8897 (2)	0.77854 (8)	0.5478 (3)	0.0596 (8)
C12	0.7411 (2)	0.79839 (6)	0.4983 (2)	0.0417 (6)
C13	0.7966 (3)	0.82674 (9)	0.3050 (2)	0.0653 (9)
S1'	0.31232 (5)	0.92918 (2)	0.25688 (5)	0.0434 (2)
O1'	0.41671 (16)	0.89021 (5)	0.30204 (16)	0.0599 (5)
O2'	0.37153 (17)	0.97058 (5)	0.21000 (15)	0.0587 (5)
O3'	−0.07087 (16)	0.95549 (5)	0.29180 (16)	0.0619 (5)
N1'	0.24881 (18)	0.94574 (6)	0.37937 (16)	0.0432 (6)
C1'	0.1023 (3)	0.86096 (7)	0.1393 (2)	0.0540 (7)
C2'	−0.0250 (3)	0.84437 (9)	0.0434 (3)	0.0675 (9)
C3'	−0.1041 (3)	0.87391 (10)	−0.0551 (2)	0.0720 (10)
C4'	−0.0567 (3)	0.92019 (9)	−0.0586 (2)	0.0687 (9)
C5'	0.0710 (3)	0.93721 (8)	0.0355 (2)	0.0542 (7)
C6'	0.1504 (2)	0.90740 (7)	0.13445 (18)	0.0412 (6)
C7'	0.1746 (2)	0.99118 (7)	0.37841 (18)	0.0415 (6)
C8'	0.2668 (3)	1.02998 (7)	0.4245 (2)	0.0570 (8)
C9'	0.1992 (3)	1.07399 (8)	0.4279 (3)	0.0711 (10)

C10'	0.0390 (3)	1.07863 (9)	0.3853 (3)	0.0694 (10)
C11'	−0.0561 (3)	1.04027 (8)	0.3392 (2)	0.0593 (8)
C12'	0.0103 (2)	0.99586 (7)	0.33485 (19)	0.0453 (7)
C13'	−0.2368 (3)	0.95970 (11)	0.2309 (3)	0.0931 (13)
H1	0.30370	0.80290	0.82150	0.0820*
H1N	0.476 (2)	0.8381 (6)	0.4514 (17)	0.0520*
H2	0.36910	0.84620	1.01260	0.1040*
H3	0.47460	0.92060	1.01560	0.0910*
H4	0.53060	0.95110	0.83600	0.0800*
H5	0.47120	0.90770	0.64510	0.0610*
H8	0.59870	0.77490	0.74000	0.0640*
H9	0.84830	0.74190	0.82050	0.0820*
H10	1.02730	0.74400	0.70170	0.0870*
H11	0.96360	0.77940	0.50010	0.0710*
H13A	0.88270	0.84670	0.35050	0.0980*
H13B	0.74210	0.84140	0.22420	0.0980*
H13C	0.83730	0.79650	0.28840	0.0980*
H1'	0.15550	0.84110	0.20650	0.0650*
H1N'	0.210 (2)	0.9225 (6)	0.4068 (19)	0.0520*
H2'	−0.05770	0.81300	0.04530	0.0810*
H3'	−0.19020	0.86250	−0.11970	0.0860*
H4'	−0.11130	0.94010	−0.12520	0.0820*
H5'	0.10370	0.96850	0.03280	0.0650*
H8'	0.37640	1.02660	0.45380	0.0680*
H9'	0.26260	1.10020	0.45910	0.0850*
H10'	−0.00680	1.10830	0.38740	0.0830*
H11'	−0.16560	1.04410	0.31080	0.0710*
H13D	−0.28950	0.97050	0.29310	0.1400*
H13E	−0.27860	0.92930	0.19770	0.1400*
H13F	−0.25390	0.98210	0.16090	0.1400*

Atomic displacement parameters (Å^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
S1	0.0350 (2)	0.0431 (3)	0.0485 (3)	0.0004 (2)	0.0165 (2)	−0.0006 (2)
O1	0.0577 (9)	0.0437 (8)	0.0721 (11)	−0.0080 (7)	0.0265 (8)	−0.0027 (7)
O2	0.0329 (7)	0.0658 (9)	0.0574 (9)	0.0070 (6)	0.0137 (6)	0.0053 (7)
O3	0.0403 (7)	0.0654 (9)	0.0508 (8)	0.0048 (7)	0.0200 (6)	0.0008 (7)
N1	0.0351 (8)	0.0546 (10)	0.0419 (9)	0.0105 (7)	0.0148 (7)	0.0079 (7)
C1	0.0940 (18)	0.0595 (15)	0.0663 (16)	−0.0063 (13)	0.0479 (14)	−0.0035 (12)
C2	0.114 (2)	0.098 (2)	0.0639 (18)	0.0013 (19)	0.0522 (17)	−0.0102 (16)
C3	0.0722 (17)	0.093 (2)	0.0642 (17)	0.0062 (15)	0.0193 (14)	−0.0275 (15)
C4	0.0516 (13)	0.0576 (15)	0.0858 (19)	−0.0042 (11)	0.0126 (13)	−0.0189 (13)
C5	0.0466 (11)	0.0494 (12)	0.0588 (14)	−0.0019 (10)	0.0169 (10)	0.0001 (10)
C6	0.0410 (10)	0.0436 (11)	0.0469 (11)	0.0050 (8)	0.0195 (9)	0.0004 (9)
C7	0.0333 (9)	0.0354 (10)	0.0463 (11)	0.0035 (8)	0.0084 (8)	−0.0031 (8)
C8	0.0521 (12)	0.0505 (13)	0.0560 (13)	0.0049 (10)	0.0114 (10)	0.0089 (10)
C9	0.0635 (15)	0.0601 (15)	0.0686 (16)	0.0082 (12)	−0.0022 (13)	0.0190 (12)

C10	0.0448 (12)	0.0618 (16)	0.101 (2)	0.0167 (11)	0.0017 (13)	0.0162 (14)
C11	0.0365 (11)	0.0537 (13)	0.0886 (18)	0.0076 (10)	0.0174 (11)	−0.0007 (12)
C12	0.0328 (9)	0.0362 (10)	0.0543 (12)	0.0000 (8)	0.0091 (8)	−0.0062 (9)
C13	0.0596 (13)	0.0753 (16)	0.0730 (16)	−0.0073 (12)	0.0383 (13)	−0.0062 (13)
S1'	0.0351 (2)	0.0419 (3)	0.0543 (3)	0.0050 (2)	0.0143 (2)	0.0066 (2)
O1'	0.0452 (8)	0.0579 (9)	0.0768 (11)	0.0199 (7)	0.0172 (7)	0.0121 (8)
O2'	0.0542 (8)	0.0521 (9)	0.0770 (11)	−0.0079 (7)	0.0304 (8)	0.0062 (8)
O3'	0.0368 (7)	0.0664 (10)	0.0780 (11)	−0.0051 (7)	0.0085 (7)	−0.0066 (8)
N1'	0.0405 (9)	0.0425 (10)	0.0463 (10)	0.0013 (7)	0.0113 (7)	0.0067 (7)
C1'	0.0641 (13)	0.0433 (12)	0.0555 (13)	0.0007 (10)	0.0178 (11)	0.0076 (10)
C2'	0.0769 (16)	0.0555 (15)	0.0686 (16)	−0.0142 (12)	0.0174 (14)	−0.0068 (12)
C3'	0.0709 (16)	0.0831 (19)	0.0549 (15)	−0.0082 (14)	0.0053 (12)	−0.0136 (13)
C4'	0.0729 (16)	0.0741 (17)	0.0503 (14)	0.0100 (13)	0.0023 (12)	0.0064 (12)
C5'	0.0635 (13)	0.0466 (12)	0.0515 (13)	0.0081 (10)	0.0141 (11)	0.0089 (10)
C6'	0.0431 (10)	0.0406 (11)	0.0429 (11)	0.0061 (8)	0.0168 (9)	0.0027 (8)
C7'	0.0403 (10)	0.0456 (11)	0.0391 (10)	0.0035 (8)	0.0120 (8)	0.0001 (8)
C8'	0.0460 (11)	0.0542 (13)	0.0696 (15)	−0.0039 (10)	0.0141 (11)	−0.0114 (11)
C9'	0.0695 (16)	0.0507 (14)	0.094 (2)	−0.0067 (12)	0.0242 (14)	−0.0202 (13)
C10'	0.0766 (17)	0.0563 (15)	0.0807 (18)	0.0155 (13)	0.0306 (14)	−0.0106 (13)
C11'	0.0474 (12)	0.0714 (16)	0.0611 (15)	0.0170 (11)	0.0183 (11)	−0.0006 (12)
C12'	0.0389 (10)	0.0543 (13)	0.0433 (11)	0.0013 (9)	0.0122 (9)	−0.0005 (9)
C13'	0.0414 (13)	0.098 (2)	0.123 (3)	−0.0113 (13)	−0.0060 (14)	−0.0054 (18)

Geometric parameters (Å, °)

S1—O1	1.4212 (15)	C5—H5	0.9300
S1—O2	1.4319 (15)	C8—H8	0.9300
S1—N1	1.6063 (17)	C9—H9	0.9300
S1—C6	1.760 (2)	C10—H10	0.9300
S1'—C6'	1.7582 (19)	C11—H11	0.9300
S1'—N1'	1.6299 (17)	C13—H13A	0.9600
S1'—O1'	1.4260 (15)	C13—H13C	0.9600
S1'—O2'	1.4235 (15)	C13—H13B	0.9600
O3—C12	1.357 (2)	C1'—C2'	1.375 (4)
O3—C13	1.417 (3)	C1'—C6'	1.380 (3)
O3'—C12'	1.354 (2)	C2'—C3'	1.374 (4)
O3'—C13'	1.427 (3)	C3'—C4'	1.372 (4)
N1—C7	1.418 (2)	C4'—C5'	1.372 (3)
N1—H1N	0.843 (17)	C5'—C6'	1.382 (3)
N1'—C7'	1.435 (3)	C7'—C12'	1.394 (3)
N1'—H1N'	0.828 (18)	C7'—C8'	1.369 (3)
C1—C2	1.383 (4)	C8'—C9'	1.379 (3)
C1—C6	1.372 (3)	C9'—C10'	1.359 (4)
C2—C3	1.363 (4)	C10'—C11'	1.371 (4)
C3—C4	1.360 (4)	C11'—C12'	1.386 (3)
C4—C5	1.381 (4)	C1'—H1'	0.9300
C5—C6	1.376 (3)	C2'—H2'	0.9300
C7—C12	1.393 (3)	C3'—H3'	0.9300
C7—C8	1.376 (3)	C4'—H4'	0.9300

C8—C9	1.385 (4)	C5'—H5'	0.9300
C9—C10	1.358 (4)	C8'—H8'	0.9300
C10—C11	1.378 (4)	C9'—H9'	0.9300
C11—C12	1.383 (3)	C10'—H10'	0.9300
C1—H1	0.9300	C11'—H11'	0.9300
C2—H2	0.9300	C13'—H13D	0.9600
C3—H3	0.9300	C13'—H13E	0.9600
C4—H4	0.9300	C13'—H13F	0.9600
O1—S1—O2	118.77 (9)	C9—C10—H10	120.00
O1—S1—N1	109.73 (9)	C11—C10—H10	120.00
O1—S1—C6	107.75 (9)	C10—C11—H11	120.00
O2—S1—N1	104.98 (9)	C12—C11—H11	120.00
O2—S1—C6	108.59 (9)	O3—C13—H13A	109.00
N1—S1—C6	106.38 (9)	H13A—C13—H13C	109.00
O1'—S1'—O2'	119.21 (9)	H13B—C13—H13C	109.00
O1'—S1'—N1'	106.05 (9)	H13A—C13—H13B	109.00
O1'—S1'—C6'	107.24 (9)	O3—C13—H13B	109.00
O2'—S1'—N1'	106.80 (9)	O3—C13—H13C	110.00
O2'—S1'—C6'	108.68 (9)	C2'—C1'—C6'	119.2 (2)
N1'—S1'—C6'	108.48 (9)	C1'—C2'—C3'	120.3 (2)
C12—O3—C13	119.21 (16)	C2'—C3'—C4'	120.3 (2)
C12'—O3'—C13'	117.44 (18)	C3'—C4'—C5'	120.3 (2)
S1—N1—C7	126.62 (14)	C4'—C5'—C6'	119.3 (2)
C7—N1—H1N	118.8 (12)	S1'—C6'—C5'	119.63 (16)
S1—N1—H1N	114.2 (12)	C1'—C6'—C5'	120.68 (19)
S1'—N1'—C7'	120.30 (13)	S1'—C6'—C1'	119.68 (15)
C7'—N1'—H1N'	118.5 (13)	C8'—C7'—C12'	119.96 (19)
S1'—N1'—H1N'	109.0 (13)	N1'—C7'—C8'	119.22 (18)
C2—C1—C6	119.5 (2)	N1'—C7'—C12'	120.80 (17)
C1—C2—C3	119.6 (3)	C7'—C8'—C9'	120.8 (2)
C2—C3—C4	121.2 (3)	C8'—C9'—C10'	119.3 (2)
C3—C4—C5	119.8 (2)	C9'—C10'—C11'	121.0 (2)
C4—C5—C6	119.3 (2)	C10'—C11'—C12'	120.3 (2)
C1—C6—C5	120.58 (19)	C7'—C12'—C11'	118.65 (19)
S1—C6—C1	119.96 (16)	O3'—C12'—C7'	115.67 (17)
S1—C6—C5	119.42 (15)	O3'—C12'—C11'	125.68 (18)
C8—C7—C12	119.97 (19)	C2'—C1'—H1'	120.00
N1—C7—C8	123.93 (19)	C6'—C1'—H1'	120.00
N1—C7—C12	116.10 (16)	C1'—C2'—H2'	120.00
C7—C8—C9	119.5 (2)	C3'—C2'—H2'	120.00
C8—C9—C10	120.6 (3)	C2'—C3'—H3'	120.00
C9—C10—C11	120.7 (3)	C4'—C3'—H3'	120.00
C10—C11—C12	119.5 (2)	C3'—C4'—H4'	120.00
C7—C12—C11	119.7 (2)	C5'—C4'—H4'	120.00
O3—C12—C7	115.04 (16)	C4'—C5'—H5'	120.00
O3—C12—C11	125.23 (19)	C6'—C5'—H5'	120.00
C6—C1—H1	120.00	C7'—C8'—H8'	120.00
C2—C1—H1	120.00	C9'—C8'—H8'	120.00
C3—C2—H2	120.00	C8'—C9'—H9'	120.00

C1—C2—H2	120.00	C10'—C9'—H9'	120.00
C4—C3—H3	119.00	C9'—C10'—H10'	119.00
C2—C3—H3	119.00	C11'—C10'—H10'	120.00
C5—C4—H4	120.00	C10'—C11'—H11'	120.00
C3—C4—H4	120.00	C12'—C11'—H11'	120.00
C4—C5—H5	120.00	O3'—C13'—H13D	109.00
C6—C5—H5	120.00	O3'—C13'—H13E	109.00
C7—C8—H8	120.00	O3'—C13'—H13F	109.00
C9—C8—H8	120.00	H13D—C13'—H13E	109.00
C10—C9—H9	120.00	H13D—C13'—H13F	109.00
C8—C9—H9	120.00	H13E—C13'—H13F	110.00
O1—S1—N1—C7	−49.05 (18)	C4—C5—C6—S1	177.86 (17)
O2—S1—N1—C7	−177.75 (15)	C4—C5—C6—C1	0.0 (3)
C6—S1—N1—C7	67.25 (18)	C12—C7—C8—C9	1.0 (3)
O1—S1—C6—C1	−14.8 (2)	N1—C7—C12—O3	−0.7 (2)
O1—S1—C6—C5	167.32 (15)	N1—C7—C8—C9	−178.4 (2)
O2—S1—C6—C1	115.07 (18)	C8—C7—C12—O3	179.93 (17)
O2—S1—C6—C5	−62.83 (17)	C8—C7—C12—C11	−1.2 (3)
N1—S1—C6—C1	−132.41 (18)	N1—C7—C12—C11	178.21 (18)
N1—S1—C6—C5	49.70 (18)	C7—C8—C9—C10	−0.5 (4)
N1'—S1'—C6'—C5'	95.33 (18)	C8—C9—C10—C11	0.1 (4)
O1'—S1'—N1'—C7'	163.92 (14)	C9—C10—C11—C12	−0.3 (4)
O2'—S1'—N1'—C7'	35.80 (17)	C10—C11—C12—C7	0.8 (3)
C6'—S1'—N1'—C7'	−81.17 (16)	C10—C11—C12—O3	179.6 (2)
O1'—S1'—C6'—C1'	30.5 (2)	C6'—C1'—C2'—C3'	−0.7 (4)
O1'—S1'—C6'—C5'	−150.54 (17)	C2'—C1'—C6'—S1'	179.66 (19)
O2'—S1'—C6'—C1'	160.64 (17)	C2'—C1'—C6'—C5'	0.7 (3)
O2'—S1'—C6'—C5'	−20.4 (2)	C1'—C2'—C3'—C4'	0.0 (4)
N1'—S1'—C6'—C1'	−83.61 (19)	C2'—C3'—C4'—C5'	0.7 (4)
C13—O3—C12—C7	174.60 (17)	C3'—C4'—C5'—C6'	−0.6 (4)
C13—O3—C12—C11	−4.2 (3)	C4'—C5'—C6'—S1'	−179.01 (18)
C13'—O3'—C12'—C7'	−172.1 (2)	C4'—C5'—C6'—C1'	−0.1 (3)
C13'—O3'—C12'—C11'	8.2 (3)	N1'—C7'—C8'—C9'	−178.5 (2)
S1—N1—C7—C8	−8.1 (3)	C12'—C7'—C8'—C9'	−0.3 (3)
S1—N1—C7—C12	172.47 (14)	N1'—C7'—C12'—O3'	−1.5 (3)
S1'—N1'—C7'—C8'	−88.1 (2)	N1'—C7'—C12'—C11'	178.22 (18)
S1'—N1'—C7'—C12'	93.8 (2)	C8'—C7'—C12'—O3'	−179.62 (18)
C2—C1—C6—C5	−0.7 (4)	C8'—C7'—C12'—C11'	0.1 (3)
C6—C1—C2—C3	1.6 (4)	C7'—C8'—C9'—C10'	0.3 (4)
C2—C1—C6—S1	−178.6 (2)	C8'—C9'—C10'—C11'	0.1 (4)
C1—C2—C3—C4	−1.9 (5)	C9'—C10'—C11'—C12'	−0.3 (4)
C2—C3—C4—C5	1.2 (4)	C10'—C11'—C12'—O3'	179.9 (2)
C3—C4—C5—C6	−0.2 (4)	C10'—C11'—C12'—C7'	0.2 (3)

Hydrogen-bond geometry (Å, °)

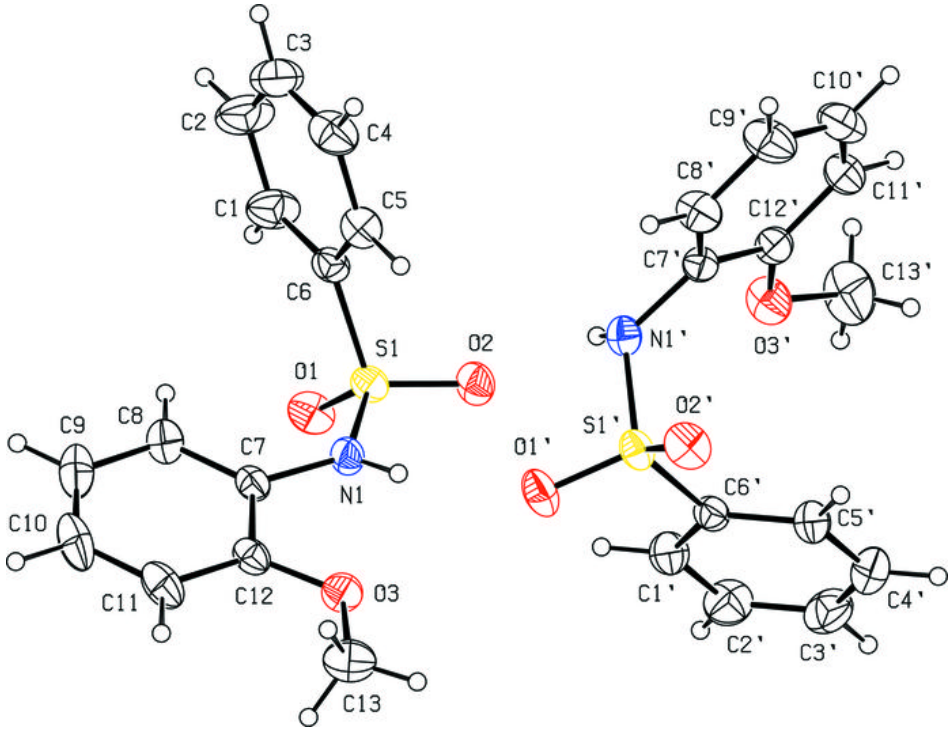
Cg4 is the centroid of the C7'–C12' phenyl ring.

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
N1'—H1N'···O2	0.828 (18)	2.310 (17)	3.074 (2)	153.6 (17)

N1—H1N···O1'	0.843 (17)	2.129 (17)	2.961 (2)	168.7 (17)
N1—H1N···O3	0.843 (17)	2.258 (18)	2.592 (2)	103.8 (14)
C4—H4···O2'^{i}	0.93	2.47	3.377 (3)	167
C4'—H4'···Cg4^{ii}	0.93	2.85	3.601 (2)	138

Symmetry codes: (i) −*x*+1, −*y*+2, −*z*+1; (ii) −*x*, −*y*+2, −*z*.

Fig. 1


C3
C2
C4
C1
C5
C6
S1
O2
O1
C9
C8
C7
N1
C10
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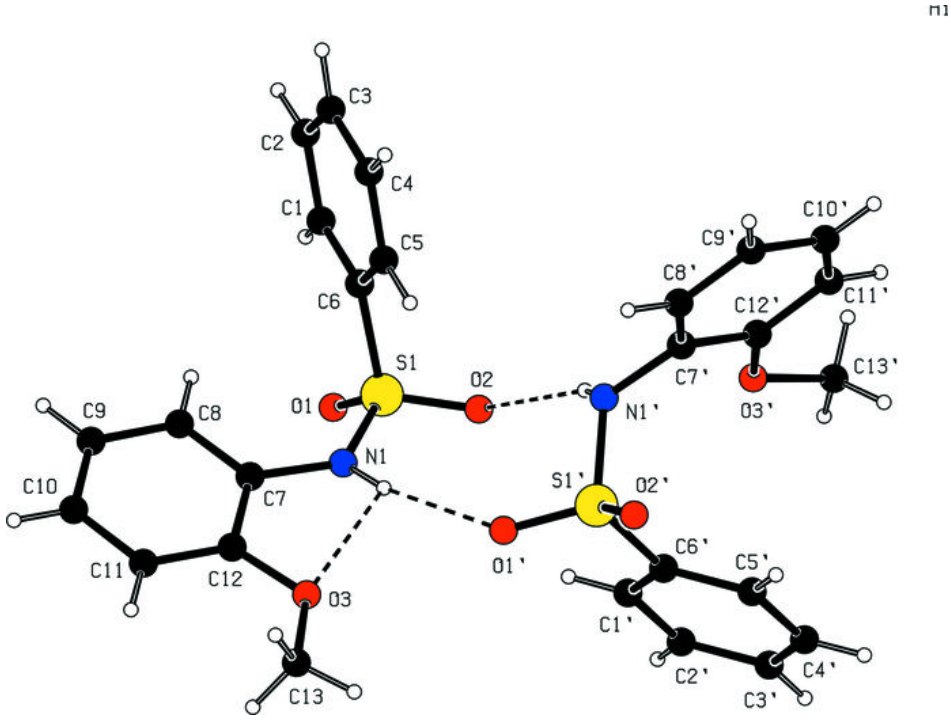
O3
C13
C10'
C9'
C8'
C11'
C12'
C7'
C13'
N1'
O3'
S1'
O2'
O1'
C6'
C5'
C1'
C4'
C2'
C3'

Fig. 2


C3
C2
C4
C1
C5
C6
S1
O2
O1
N1
C9
C8
C10
C7
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C12
O3
C13
C10'
C9'
C8'
C12'
C11'
C7'
C13'
O3'
N1'
S1'
O2'
O1'
C6'
C5'
C1'
C2'
C4'
C3'

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N-{[4-(4-Methoxybenzenesulfonamido)-phenyl]sulfonyl}acetamide

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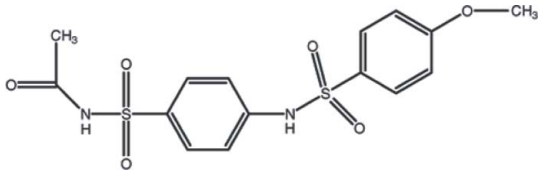
Key indicators: single-crystal X-ray study; T = 296 K; mean σ(C–C) = 0.008 Å; R factor = 0.084; wR factor = 0.189; data-to-parameter ratio = 16.7.

In the title compound, $C_{15}H_{16}N_2O_6S_2$, the dihedral angle between the benzene rings is 83.2 (3)°. The molecular conformation is stabilized by an intramolecular C—H···O interaction. In the crystal structure, molecules are linked by N—H···O and C—H···O hydrogen bonds and additional stabilization is provided by weak C—H···π interactions.

Related literature

For previous studies on the synthesis of sulfonamide derivatives with phenyl glycine, see: Ashfaq *et al.* (2009, 2010).



Experimental

Crystal data

$C_{15}H_{16}N_2O_6S_2$
M_r = 384.44
Monoclinic, $P2_1/c$
a = 5.3651 (10) Å
b = 20.551 (3) Å
c = 15.034 (2) Å
β = 94.040 (7)°
V = 1653.5 (4) Å^3
Z = 4
Mo $K\alpha$ radiation
μ = 0.36 mm^{-1}
T = 296 K
0.25 × 0.08 × 0.07 mm

Data collection

Bruker Kappa APEXII CCD diffractometer
13678 measured reflections
3771 independent reflections
1608 reflections with $I > 2\sigma(I)$
R_{int} = 0.114

Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.084
$wR(F^2)$ = 0.189
S = 0.89
3771 reflections
226 parameters
H-atom parameters constrained
$\Delta\rho_{max}$ = 0.83 e Å^{-3}
$\Delta\rho_{min}$ = −0.32 e Å^{-3}

Table 1
Hydrogen-bond geometry (Å, °).

*Cg*1 and *Cg*2 are the centroids of the C1–C6 and C8–C13 rings, respectively.

D—H···A	D—H	H···A	D···A	D—H···A
N1—H1···O4^{i}	0.86	2.09	2.932 (5)	168
N2—H2···O5^{ii}	0.86	2.26	3.071 (5)	157
C13—H13···O2	0.93	2.35	2.986 (6)	126
C15—H15*C*···O6^{ii}	0.96	2.45	3.348 (7)	156
C15—H15*B*···*Cg*1^{iii}	0.96	2.79	3.722 (6)	164
C15—H15*A*···*Cg*2^{iii}	0.96	2.79	3.589 (6)	141

Symmetry codes: (i) $x, -y+\frac{1}{2}, z-\frac{1}{2}$; (ii) $x+1, y, z$; (iii) $-x+2, -y, -z+2$.

Data collection: *APEX2* (Bruker, 2007); cell refinement: *SAINT* (Bruker, 2007); data reduction: *SAINT*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *ORTEP-3* (Farrugia, 1997); software used to prepare material for publication: *WinGX* (Farrugia, 1999) and *PLATON* (Spek, 2009).

GM greatly acknowledge the Vice Chancellor, University of Gujrat, Professor Dr Nizam Uddin, for creating a healthy research environment in the University of Gujrat.

Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: HB5502).

References

Ashfaq, M., Khan, I. U., Arshad, M. N., Ahmad, H. & Asghar, M. N. (2010). *Acta Cryst.* E**66**, o299.
Ashfaq, M., Tahir, M. N., Khan, I. U., Arshad, M. N. & Saeed-ul-Hassan, S. (2009). *Acta Cryst.* E**65**, o1180.
Bruker (2007). *APEX2* and *SAINT*. Bruker AXS Inc., Madison, Wisconsin, USA.
Farrugia, L. J. (1997). *J. Appl. Cryst.* **30**, 565.
Farrugia, L. J. (1999). *J. Appl. Cryst.* **32**, 837–838.
Sheldrick, G. M. (2008). *Acta Cryst.* A**64**, 112–122.
Spek, A. L. (2009). *Acta Cryst.* D**65**, 148–155.

supplementary materials

Acta Cryst. (2010). E**66**, o1768 [**doi:10.1107/S1600536810023925**]

N-{[4-(4-Methoxybenzenesulfonamido)phenyl]sulfonyl}acetamide

G. Mustafa, M. Akkurt, I. U. Khan, R. Naseem and B. Sajjad

Comment

Sulphacetamide sodium is an antibiotic which is being used for eye infections. Because the antiobiotics lose their efficacy after long term used, so there is a need to derivatize them to get better therapeutic result. In this paper, a new derivative of it is being reported. Previously this drug has also been derivatized by other researchers (Ashfaq *et al.*, 2009, 2010). Here we present the crystal structure of the title compound (I), (Fig. 1).

In (I), the benzene rings (C1–C6) and (C8–C13) are twisted with a dihedral angle of 83.2 (3) ° to each other. Molecular conformation is stabilized by intramolecular C–H···O interactions. Intermolecular N—H···O and C—H···O hydrogen bonds and C—H···π interactions contribute to the stabilization of the crystal structure (Table 1, Fig. 2).

Experimental

Sodium sulphacetamide (0.5 g, 2.32 mmol) was taken in 50 ml round bottom flask and dissolved in 20 ml of distilled water. Then, methoxy benzene sulfonyl chloride (0.46 g, 2.32 mmol) was added with continuous stirring at ambient temperature. The pH of this solution was strictly maintained between 8 and 9 by using $NaHCO_3$ (3 *M*). The consumption of suspended methoxy benzene sulfonyl chloride was an indication of reaction completion. Then pH was adjusted to 2–3 using HCl (3 N). The precipitates formed were filtered, washed three to four times with distilled water and recrystallised using methanol to yield colourless rods of (I).

Refinement

All H-atoms were positioned geometrically and refined using a riding model with d(N—H) = 0.86 Å, $U_{iso} = 1.2U_{eq}$(N) for NH, 0.93 Å, $U_{iso} = 1.2U_{eq}$(C) for aromatic and 0.96 Å, $U_{iso} = 1.5U_{eq}$(C) for CH_3 hydrogen atoms.

Figures

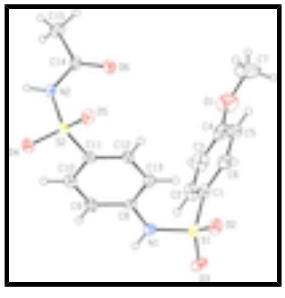


Fig. 1. The title molecule with displacement ellipsoids for non-H atoms drawn at the 30% probability level.

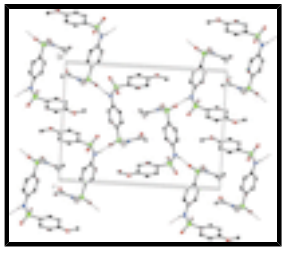


Fig. 2. The packing and hydrogen bonding of (I) viewed down *a* axis. H atoms not participating in hydrogen bonding have been omitted for clarity.

N-{[4-(4-Methoxybenzenesulfonamido)phenyl]sulfonyl}acetamide

Crystal data

$C_{15}H_{16}N_2O_6S_2$	$F(000) = 800$
$M_r = 384.44$	$D_x = 1.544$ Mg m^{-3}
Monoclinic, $P2_1/c$	Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å
Hall symbol: -P 2ybc	Cell parameters from 1463 reflections
$a = 5.3651$ (10) Å	$\theta = 2.9$–$20.1°$
$b = 20.551$ (3) Å	$\mu = 0.36$ mm^{-1}
$c = 15.034$ (2) Å	$T = 296$ K
$\beta = 94.040$ (7)°	Rod, colourless
$V = 1653.5$ (4) Å^3	0.25 × 0.08 × 0.07 mm
$Z = 4$	

Data collection

Bruker Kappa APEXII CCD diffractometer	1608 reflections with $I > 2\sigma(I)$
Radiation source: sealed tube	$R_{int} = 0.114$
graphite	$\theta_{max} = 28.4°$, $\theta_{min} = 3.3°$
phi and ω scans	$h = -7 \rightarrow 7$
13678 measured reflections	$k = -27 \rightarrow 26$
3771 independent reflections	$l = -20 \rightarrow 20$

Refinement

Refinement on F^2	Primary atom site location: structure-invariant direct methods
Least-squares matrix: full	Secondary atom site location: difference Fourier map
$R[F^2 > 2\sigma(F^2)] = 0.084$	Hydrogen site location: inferred from neighbouring sites
$wR(F^2) = 0.189$	H-atom parameters constrained
$S = 0.89$	$w = 1/[\sigma^2(F_o^2) + (0.068P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
3771 reflections	$(\Delta/\sigma)_{max} < 0.001$
226 parameters	$\Delta\rho_{max} = 0.83$ e Å^{-3}
0 restraints	$\Delta\rho_{min} = -0.32$ e Å^{-3}

Special details

Geometry. Bond distances, angles *etc*. have been calculated using the rounded fractional coordinates. All su's are estimated from the variances of the (full) variance-covariance matrix. The cell e.s.d.'s are taken into account in the estimation of distances, angles and torsion angles

Refinement. Refinement on F^2 for ALL reflections except those flagged by the user for potential systematic errors. Weighted *R*-factors *wR* and all goodnesses of fit *S* are based on F^2, conventional *R*-factors *R* are based on *F*, with *F* set to zero for negative F^2. The observed criterion of $F^2 > \sigma(F^2)$ is used only for calculating -*R*-factor-obs *etc*. and is not relevant to the choice of reflections for refinement. *R*-factors based on F^2 are statistically about twice as large as those based on *F*, and *R*-factors based on ALL data will be even larger.

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å^2)

	x	*y*	*z*	U_{iso}*/U_{eq}
S1	0.3465 (3)	0.17871 (7)	0.68802 (9)	0.0373 (5)
S2	0.7590 (2)	0.14262 (6)	1.14309 (8)	0.0290 (4)
O1	0.7672 (11)	−0.0692 (3)	0.5765 (3)	0.082 (2)
O2	0.1176 (7)	0.16711 (19)	0.7264 (2)	0.0455 (14)
O3	0.3551 (7)	0.2208 (2)	0.6128 (2)	0.0515 (16)
O4	0.8828 (6)	0.19627 (17)	1.1877 (2)	0.0386 (11)
O5	0.5388 (6)	0.11632 (18)	1.1764 (2)	0.0377 (11)
O6	0.7458 (7)	0.00642 (18)	1.0809 (3)	0.0444 (14)
N1	0.5446 (8)	0.2099 (2)	0.7634 (2)	0.0348 (14)
N2	0.9779 (7)	0.0863 (2)	1.1487 (3)	0.0335 (14)
C1	0.4677 (10)	0.1033 (3)	0.6585 (3)	0.0373 (19)
C2	0.6748 (11)	0.1020 (3)	0.6078 (4)	0.051 (2)
C3	0.7658 (13)	0.0438 (4)	0.5824 (4)	0.060 (3)
C4	0.6569 (12)	−0.0140 (4)	0.6055 (4)	0.055 (2)
C5	0.4498 (13)	−0.0129 (3)	0.6561 (4)	0.054 (2)
C6	0.3601 (11)	0.0463 (3)	0.6810 (4)	0.0450 (19)
C7	0.671 (2)	−0.1301 (4)	0.5999 (5)	0.102 (4)
C8	0.5896 (9)	0.1915 (2)	0.8531 (3)	0.0274 (16)
C9	0.7968 (9)	0.2181 (3)	0.8989 (3)	0.0345 (17)
C10	0.8521 (9)	0.2034 (3)	0.9879 (3)	0.0353 (17)
C11	0.6938 (9)	0.1611 (2)	1.0304 (3)	0.0278 (16)
C12	0.4918 (9)	0.1342 (2)	0.9844 (3)	0.0322 (17)
C13	0.4361 (10)	0.1492 (3)	0.8956 (3)	0.0345 (17)
C14	0.9434 (9)	0.0225 (3)	1.1177 (3)	0.0310 (17)
C15	1.1613 (10)	−0.0206 (3)	1.1364 (4)	0.0426 (17)
H1	0.63300	0.24180	0.74610	0.0420*
H2	1.12300	0.09690	1.17230	0.0400*
H2A	0.75010	0.14060	0.59160	0.0610*
H3	0.90470	0.04290	0.54880	0.0720*
H5	0.37410	−0.05130	0.67260	0.0650*
H6	0.22080	0.04750	0.71450	0.0540*
H7A	0.66710	−0.13270	0.66350	0.1520*

H7B	0.77580	−0.16400	0.57940	0.1520*
H7C	0.50490	−0.13500	0.57270	0.1520*
H9	0.90000	0.24620	0.86980	0.0420*
H10	0.99190	0.22120	1.01900	0.0420*
H12	0.39030	0.10540	1.01310	0.0380*
H13	0.29670	0.13110	0.86470	0.0420*
H15A	1.12360	−0.06320	1.11290	0.0640*
H15B	1.19890	−0.02350	1.19970	0.0640*
H15C	1.30280	−0.00320	1.10880	0.0640*

Atomic displacement parameters (Å^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
S1	0.0361 (8)	0.0443 (9)	0.0310 (7)	0.0051 (6)	−0.0015 (6)	0.0047 (6)
S2	0.0303 (7)	0.0313 (7)	0.0256 (6)	0.0004 (5)	0.0039 (5)	−0.0046 (5)
O1	0.110 (4)	0.070 (4)	0.066 (3)	0.033 (3)	0.003 (3)	−0.024 (3)
O2	0.032 (2)	0.054 (3)	0.050 (2)	0.0047 (18)	−0.0006 (17)	−0.0042 (19)
O3	0.061 (3)	0.058 (3)	0.034 (2)	0.008 (2)	−0.0071 (19)	0.0161 (19)
O4	0.045 (2)	0.034 (2)	0.0362 (19)	−0.0048 (17)	−0.0013 (17)	−0.0108 (17)
O5	0.0298 (19)	0.050 (2)	0.0343 (19)	0.0003 (17)	0.0090 (15)	−0.0001 (17)
O6	0.034 (2)	0.035 (2)	0.063 (3)	−0.0026 (17)	−0.0055 (18)	−0.0050 (19)
N1	0.040 (2)	0.036 (3)	0.028 (2)	−0.006 (2)	−0.0013 (19)	0.0099 (19)
N2	0.027 (2)	0.038 (3)	0.034 (2)	−0.0021 (19)	−0.0081 (18)	0.001 (2)
C1	0.033 (3)	0.048 (4)	0.030 (3)	−0.001 (3)	−0.005 (2)	−0.002 (2)
C2	0.046 (4)	0.056 (4)	0.050 (4)	−0.010 (3)	0.003 (3)	−0.011 (3)
C3	0.050 (4)	0.083 (5)	0.048 (4)	0.006 (4)	0.010 (3)	−0.018 (4)
C4	0.054 (4)	0.067 (5)	0.042 (3)	0.019 (4)	−0.014 (3)	−0.015 (3)
C5	0.072 (5)	0.045 (4)	0.043 (3)	0.007 (3)	−0.010 (3)	0.002 (3)
C6	0.048 (3)	0.052 (4)	0.035 (3)	0.003 (3)	0.004 (3)	0.003 (3)
C7	0.189 (10)	0.054 (5)	0.060 (5)	0.039 (6)	−0.002 (6)	−0.005 (4)
C8	0.029 (3)	0.025 (3)	0.028 (2)	0.004 (2)	0.001 (2)	0.005 (2)
C9	0.036 (3)	0.033 (3)	0.035 (3)	−0.014 (2)	0.007 (2)	0.005 (2)
C10	0.033 (3)	0.036 (3)	0.037 (3)	−0.004 (2)	0.003 (2)	−0.004 (2)
C11	0.033 (3)	0.026 (3)	0.025 (2)	0.002 (2)	0.006 (2)	−0.002 (2)
C12	0.034 (3)	0.029 (3)	0.033 (3)	−0.009 (2)	−0.001 (2)	0.003 (2)
C13	0.031 (3)	0.039 (3)	0.033 (3)	−0.004 (2)	−0.002 (2)	0.004 (2)
C14	0.026 (3)	0.037 (3)	0.030 (3)	−0.004 (2)	0.002 (2)	0.003 (2)
C15	0.037 (3)	0.041 (3)	0.050 (3)	0.013 (3)	0.004 (2)	−0.002 (3)

Geometric parameters (Å, °)

S1—O2	1.413 (4)	C8—C13	1.384 (7)
S1—O3	1.427 (4)	C8—C9	1.379 (7)
S1—N1	1.629 (4)	C9—C10	1.383 (7)
S1—C1	1.750 (6)	C10—C11	1.401 (7)
S2—O4	1.430 (4)	C11—C12	1.361 (7)
S2—O5	1.422 (3)	C12—C13	1.382 (6)
S2—N2	1.647 (4)	C14—C15	1.478 (8)
S2—C11	1.747 (5)	C2—H2A	0.9300

O1—C4	1.365 (10)	C3—H3	0.9300
O1—C7	1.408 (10)	C5—H5	0.9300
O6—C14	1.207 (6)	C6—H6	0.9300
N1—C8	1.405 (5)	C7—H7A	0.9600
N2—C14	1.399 (7)	C7—H7B	0.9600
N1—H1	0.8600	C7—H7C	0.9600
N2—H2	0.8600	C9—H9	0.9300
C1—C6	1.359 (9)	C10—H10	0.9300
C1—C2	1.391 (8)	C12—H12	0.9300
C2—C3	1.357 (10)	C13—H13	0.9300
C3—C4	1.379 (11)	C15—H15A	0.9600
C4—C5	1.390 (9)	C15—H15B	0.9600
C5—C6	1.370 (9)	C15—H15C	0.9600
O2—S1—O3	120.2 (2)	S2—C11—C12	120.1 (3)
O2—S1—N1	109.0 (2)	C10—C11—C12	120.5 (4)
O2—S1—C1	107.7 (3)	C11—C12—C13	120.7 (4)
O3—S1—N1	104.9 (2)	C8—C13—C12	119.4 (5)
O3—S1—C1	107.6 (2)	O6—C14—C15	125.5 (5)
N1—S1—C1	106.8 (2)	N2—C14—C15	114.5 (4)
O4—S2—O5	119.9 (2)	O6—C14—N2	120.0 (5)
O4—S2—N2	102.2 (2)	C1—C2—H2A	120.00
O4—S2—C11	110.0 (2)	C3—C2—H2A	120.00
O5—S2—N2	108.8 (2)	C2—C3—H3	119.00
O5—S2—C11	108.0 (2)	C4—C3—H3	119.00
N2—S2—C11	107.2 (2)	C4—C5—H5	121.00
C4—O1—C7	119.0 (6)	C6—C5—H5	121.00
S1—N1—C8	128.4 (3)	C1—C6—H6	119.00
S2—N2—C14	124.4 (3)	C5—C6—H6	119.00
S1—N1—H1	116.00	O1—C7—H7A	109.00
C8—N1—H1	116.00	O1—C7—H7B	109.00
S2—N2—H2	118.00	O1—C7—H7C	109.00
C14—N2—H2	118.00	H7A—C7—H7B	110.00
S1—C1—C2	118.8 (5)	H7A—C7—H7C	110.00
S1—C1—C6	121.9 (4)	H7B—C7—H7C	110.00
C2—C1—C6	119.3 (6)	C8—C9—H9	120.00
C1—C2—C3	119.2 (6)	C10—C9—H9	120.00
C2—C3—C4	121.4 (6)	C9—C10—H10	121.00
O1—C4—C5	124.7 (7)	C11—C10—H10	121.00
C3—C4—C5	119.5 (7)	C11—C12—H12	120.00
O1—C4—C3	115.8 (6)	C13—C12—H12	120.00
C4—C5—C6	118.3 (6)	C8—C13—H13	120.00
C1—C6—C5	122.3 (6)	C12—C13—H13	120.00
C9—C8—C13	120.2 (4)	C14—C15—H15A	109.00
N1—C8—C9	116.8 (4)	C14—C15—H15B	109.00
N1—C8—C13	123.0 (4)	C14—C15—H15C	109.00
C8—C9—C10	120.5 (5)	H15A—C15—H15B	109.00
C9—C10—C11	118.8 (5)	H15A—C15—H15C	109.00
S2—C11—C10	119.4 (4)	H15B—C15—H15C	110.00

O2—S1—N1—C8	42.8 (5)	S2—N2—C14—O6	3.0 (7)
O3—S1—N1—C8	172.7 (4)	S2—N2—C14—C15	−175.4 (4)
C1—S1—N1—C8	−73.3 (5)	S1—C1—C2—C3	−178.1 (5)
O2—S1—C1—C2	171.0 (4)	C6—C1—C2—C3	−0.4 (8)
O2—S1—C1—C6	−6.7 (5)	S1—C1—C6—C5	178.2 (5)
O3—S1—C1—C2	40.0 (5)	C2—C1—C6—C5	0.6 (9)
O3—S1—C1—C6	−137.6 (5)	C1—C2—C3—C4	0.2 (9)
N1—S1—C1—C2	−72.1 (5)	C2—C3—C4—O1	−179.5 (6)
N1—S1—C1—C6	110.2 (5)	C2—C3—C4—C5	−0.2 (10)
O4—S2—N2—C14	176.6 (4)	O1—C4—C5—C6	179.6 (6)
O5—S2—N2—C14	48.9 (5)	C3—C4—C5—C6	0.3 (9)
C11—S2—N2—C14	−67.7 (4)	C4—C5—C6—C1	−0.5 (9)
O4—S2—C11—C10	30.0 (5)	N1—C8—C9—C10	178.9 (5)
O4—S2—C11—C12	−150.4 (4)	C13—C8—C9—C10	−0.7 (8)
O5—S2—C11—C10	162.5 (4)	N1—C8—C13—C12	−179.2 (4)
O5—S2—C11—C12	−17.9 (4)	C9—C8—C13—C12	0.4 (8)
N2—S2—C11—C10	−80.4 (4)	C8—C9—C10—C11	0.0 (8)
N2—S2—C11—C12	99.2 (4)	C9—C10—C11—S2	−179.4 (4)
C7—O1—C4—C3	178.1 (6)	C9—C10—C11—C12	1.1 (8)
C7—O1—C4—C5	−1.2 (9)	S2—C11—C12—C13	179.0 (4)
S1—N1—C8—C9	169.1 (4)	C10—C11—C12—C13	−1.4 (7)
S1—N1—C8—C13	−11.4 (7)	C11—C12—C13—C8	0.7 (8)

Hydrogen-bond geometry (Å, °)

Cg1 and Cg2 are the centroids of the C1–C6 and C8–C13 rings, respectively.

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
N1—H1···O4^{i}	0.86	2.09	2.932 (5)	168
N2—H2···O5^{ii}	0.86	2.26	3.071 (5)	157
C13—H13···O2	0.93	2.35	2.986 (6)	126
C15—H15C···O6^{ii}	0.96	2.45	3.348 (7)	156
C15—H15B···Cg1^{iii}	0.96	2.79	3.722 (6)	164
C15—H15A···Cg2^{iii}	0.96	2.79	3.589 (6)	141

Symmetry codes: (i) *x*, −*y*+1/2, *z*−1/2; (ii) *x*+1, *y*, *z*; (iii) −*x*+2, −*y*, −*z*+2.

Fig. 1

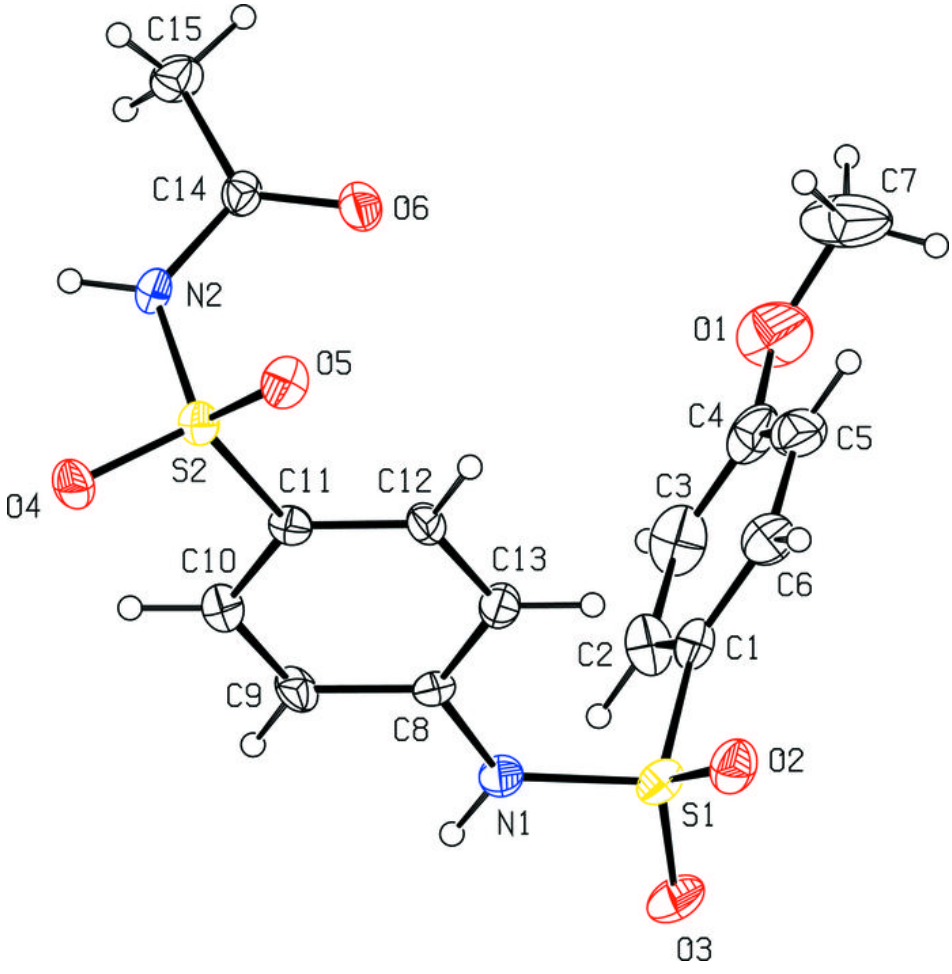
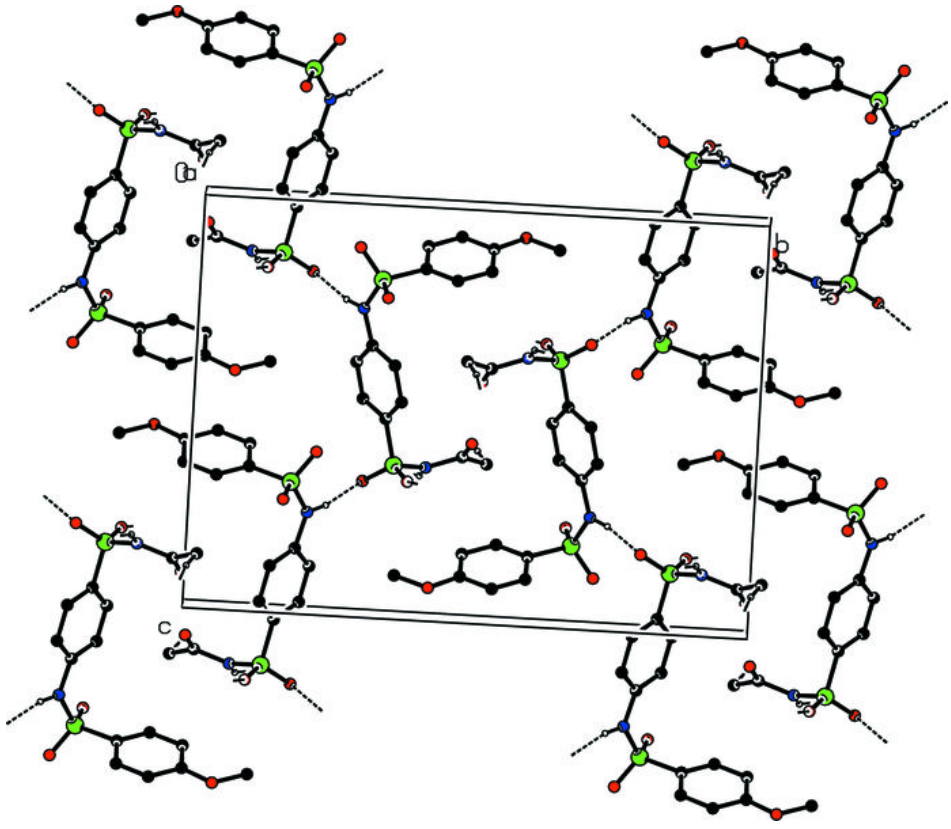

C15
C14
O6
N2
O5
S2
O4
C11
C12
C10
C13
C9
C8
N1
S1
O2
O3
C7
O1
C4
C5
C3
C6
C2
C1

Fig. 2



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2-Amino-4-methylpyridinium 3-chlorobenzoate

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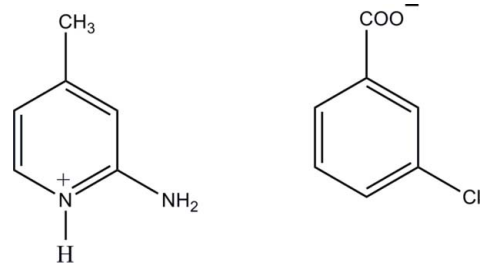
Key indicators: single-crystal X-ray study; T = 100 K; mean σ(C–C) = 0.002 Å; R factor = 0.029; wR factor = 0.117; data-to-parameter ratio = 25.7.

In the title salt, $C_6H_9N_2^+\cdot C_7H_4ClO_2^-$, the 2-amino-4-methylpyridinium cation is almost planar, with a maximum deviation of 0.010 (1) Å. In the crystal, the protonated N atom and the 2-amino group of the cation are hydrogen bonded to the carboxylate O atoms of the anion *via* a pair of N—H···O hydrogen bonds, forming an $R_2^2(8)$ ring motif. The ion pairs are further connected *via* N—H···O and C—H···O hydrogen bonds, forming a two-dimensional network parallel to the *bc* plane.

Related literature

For details of non-covalent interactions, see: Remenar *et al.* (2003); Aakeröy *et al.* (2001); Sokolov *et al.* (2006). For related structures, see: Kvick & Noordik (1977); Shen *et al.* (2008); Hemamalini & Fun (2010*a*,*b*). For details of hydrogen bonding, see: Jeffrey & Saenger (1991); Jeffrey (1997); Scheiner (1997). For hydrogen-bond motifs, see: Bernstein *et al.* (1995). For bond-length data, see: Allen *et al.* (1987). For the stability of the temperature controller used in the data collection, see: Cosier & Glazer (1986).



Experimental

Crystal data

$C_6H_9N_2^+\cdot C_7H_4ClO_2^-$ M_r = 264.70
Monoclinic, $P2_1$
a = 7.9930 (6) Å
b = 6.8608 (5) Å
c = 11.2148 (9) Å
β = 93.526 (2)°
V = 613.84 (8) Å^3
Z = 2
Mo $K\alpha$ radiation
μ = 0.31 mm^{-1}
T = 100 K
0.28 × 0.17 × 0.10 mm

Data collection

Bruker APEXII DUO CCD diffractometer
Absorption correction: multi-scan (*SADABS*; Bruker, 2009)
T_{min} = 0.919, T_{max} = 0.971
9325 measured reflections
4207 independent reflections
4076 reflections with $I > 2\sigma(I)$
R_{int} = 0.019

Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.029
$wR(F^2)$ = 0.117
S = 1.22
4207 reflections
164 parameters
1 restraint
H-atom parameters constrained
$\Delta\rho_{max}$ = 0.64 e Å^{-3}
$\Delta\rho_{min}$ = −0.54 e Å^{-3}
Absolute structure: Flack (1983), 1860 Friedel pairs
Flack parameter: −0.01 (4)

Table 1
Hydrogen-bond geometry (Å, °).

D—H···A	D—H	H···A	D···A	D—H···A
N1—H1A···O1^{i}	0.86	1.83	2.6921 (16)	175
N2—H2B···O2^{i}	0.86	1.93	2.786 (2)	177
N2—H2C···O2^{ii}	0.86	1.96	2.8146 (14)	173
C5—H5A···O1^{iii}	0.93	2.50	3.1707 (13)	129

Symmetry codes: (i) $x, y+1, z$; (ii) $-x+1, y+\frac{1}{2}, -z+2$; (iii) $-x+1, y+\frac{1}{2}, -z+1$.

Data collection: *APEX2* (Bruker, 2009); cell refinement: *SAINT* (Bruker, 2009); data reduction: *SAINT*; program(s) used to solve structure: *SHELXTL* (Sheldrick, 2008); program(s) used to refine structure: *SHELXTL*; molecular graphics: *SHELXTL*; software used to prepare material for publication: *SHELXTL* and *PLATON* (Spek, 2009).

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Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: HB5503).

References

Aakeröy, C. B., Beatty, A. M. & Helfrich, B. A. (2001). *Angew. Chem. Int. Ed.* **40**, 3240–3242.
Allen, F. H., Kennard, O., Watson, D. G., Brammer, L., Orpen, A. G. & Taylor, R. (1987). *J. Chem. Soc. Perkin Trans. 2*, pp. S1–19.
Bernstein, J., Davis, R. E., Shimoni, L. & Chang, N.-L. (1995). *Angew. Chem. Int. Ed. Engl.* **34**, 1555–1573.
Bruker (2009). *APEX2*, *SAINT* and *SADABS*. Bruker AXS Inc., Madison, Wisconsin, USA.
Cosier, J. & Glazer, A. M. (1986). *J. Appl. Cryst.* **19**, 105–107.
Flack, H. D. (1983). *Acta Cryst.* A**39**, 876–881.
Hemamalini, M. & Fun, H.-K. (2010*a*). *Acta Cryst.* E**66**, o335.
Hemamalini, M. & Fun, H.-K. (2010*b*). *Acta Cryst.* E**66**, o781–o782.
Jeffrey, G. A. (1997). *An Introduction to Hydrogen Bonding*. Oxford University Press.
Jeffrey, G. A. & Saenger, W. (1991). *Hydrogen Bonding in Biological Structures*. Berlin: Springer.

‡ Thomson Reuters ResearcherID: A-3561-2009.

Kvick, Å. & Noordik, J. (1977). *Acta Cryst.* B**33**, 2862–2866.
Remenar, J. F., Morissette, S. L., Peterson, M. L., Moulton, B., MacPhee, J. M., GuzmaÅ, H. R. & Almarsson, O. È. (2003). *J. Am. Chem. Soc.* **125**, 8456–8457.
Scheiner, S. (1997). *Hydrogen Bonding. A Theoretical Perspective.* Oxford University Press.
Sheldrick, G. M. (2008). *Acta Cryst.* A**64**, 112–122.
Shen, H., Nie, J.-J. & Xu, D.-J. (2008). *Acta Cryst.* E**64**, o1129.
Sokolov, A. N., FrisïcïcÅ, T. & MacGillivray, L. R. (2006). *J. Am. Chem. Soc.* **128**, 2806–2807.
Spek, A. L. (2009). *Acta Cryst.* D**65**, 148–155.

supplementary materials

Acta Cryst. (2010). E**66**, o1843-o1844 [**doi:10.1107/S160053681002444X**]

2-Amino-4-methylpyridinium 3-chlorobenzoate

M. Hemamalini and H.-K. Fun

Comment

Recently, much attention has been devoted to the design and synthesis of supramolecular architectures assembled via various weak noncovalent interactions, such as hydrogen bonds, π···π stacking and C—H···π interactions (Remenar *et al.*, 2003; Aakeröy *et al.*, 2001; Sokolov *et al.*, 2006). 2-Aminopyridine and its derivatives are used in the manufacture of pharmaceuticals, hair dyes and other dyes. They are often involved in hydrogen-bond interactions (Jeffrey & Saenger, 1991; Jeffrey, 1997; Scheiner, 1997). The crystal structures of 2-amino-4-methyl pyridine (Kvick & Noordik, 1977) and 2-amino-4-methylpyridinium 4-aminobenzoate (Shen *et al.*, 2008) have been reported. We have recently reported the crystal structures of 2-amino-4-methylpyridinium 4-nitrobenzoate (Hemamalini & Fun, 2010*a*) and 2-Amino-4-methylpyridinium trifluoroacetate (Hemamalini & Fun, 2010*b*) from our laboratory. In continuation of our studies of pyridinium derivatives, the crystal structure determination of the title salt has been undertaken.

The asymmetric unit of the title compound, (Fig 1), contains a protonated 2-amino-4-methylpyridinium cation and a 3-chlorobenzoate anion. The 2-amino-4-methylpyridinium cation is planar, with a maximum deviation of 0.010 (1) Å for atom C1. The protonated N1 atom has lead to a slight increase in the C1—N1—C5 angle to 121.66 (11)°, compared to the corresponding angle of 117.3 (1)° in neutral 2-amino-4-methylpyridine (Kvick & Noordik, 1977). The bond lengths (Allen *et al.*, 1987) and angles are normal.

In the crystal packing, (Fig. 2), the protonated N atom and 2-amino group (N2) is hydrogen-bonded to the carboxylate oxygen atoms (O1 and O2) via a pair of N—H···O hydrogen bonds leading to the formation of a $R^2_2(8)$ ring (Bernstein *et al.*, 1995). Furthermore, these motifs are connected via N2—H2C···O2 and C5—H5A···O1 hydrogen bonds to form two-dimensional networks parallel to the *bc*-plane.

Experimental

A hot methanol solution (20 ml) of 2-amino-4-methylpyridine (54 mg, Aldrich) and 3-chlorobenzoic acid (78 mg, Merck) were mixed and warmed over a heating magnetic-stirrer hotplate for a few minutes. The resulting solution was allowed to cool slowly at room temperature and colourless needles of (I) appeared after a few days.

Refinement

All hydrogen atoms were positioned geometrically [C–H = 0.93 or 0.96 Å] and were refined using a riding model, with U_{iso}(H) = 1.2 or 1.5 U_{eq}(C). A rotating group model was used for the methyl group. 1860 Friedel pairs were used to determine the absolute configuration.

Figures

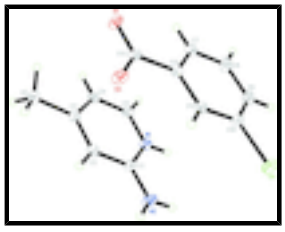


Fig. 1. The asymmetric unit of (I). Displacement ellipsoids are drawn at the 50% probability level.

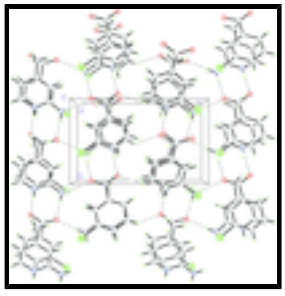


Fig. 2. The crystal packing of (I), showing hydrogen-bonded (dashed lines) 2D networks parallel to the *bc*-plane.

2-Amino-4-methylpyridinium 3-chlorobenzoate

Crystal data

$C_6H_9N_2^+ \cdot C_7H_4ClO_2^-$	$F(000) = 276$
$M_r = 264.70$	$D_x = 1.432$ Mg m^{-3}
Monoclinic, $P2_1$	Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å
Hall symbol: P 2yb	Cell parameters from 6601 reflections
$a = 7.9930$ (6) Å	$\theta = 3.9$–$35.1°$
$b = 6.8608$ (5) Å	$\mu = 0.31$ mm^{-1}
$c = 11.2148$ (9) Å	$T = 100$ K
$\beta = 93.526$ (2)°	Needle, colourless
$V = 613.84$ (8) Å^3	0.28 × 0.17 × 0.10 mm
$Z = 2$	

Data collection

Bruker APEXII DUO CCD diffractometer	4207 independent reflections
Radiation source: fine-focus sealed tube	4076 reflections with $I > 2\sigma(I)$
graphite	$R_{int} = 0.019$
φ and ω scans	$\theta_{max} = 32.5°$, $\theta_{min} = 3.9°$
Absorption correction: multi-scan (*SADABS*; Bruker, 2009)	$h = -12 \rightarrow 12$
$T_{min} = 0.919$, $T_{max} = 0.971$	$k = -10 \rightarrow 10$
9325 measured reflections	$l = -16 \rightarrow 16$

Refinement

Refinement on F^2	Secondary atom site location: difference Fourier map
Least-squares matrix: full	Hydrogen site location: inferred from neighbouring sites
$R[F^2 > 2\sigma(F^2)] = 0.029$	H-atom parameters constrained
$wR(F^2) = 0.117$	$w = 1/[\sigma^2(F_o^2) + (0.0801P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
$S = 1.22$	$(\Delta/\sigma)_{max} < 0.001$
4207 reflections	$\Delta\rho_{max} = 0.64$ e Å^{-3}
164 parameters	$\Delta\rho_{min} = -0.54$ e Å^{-3}
1 restraint	Absolute structure: Flack (1983), 1860 Friedel pairs
Primary atom site location: structure-invariant direct methods	Flack parameter: −0.01 (4)

Special details

Experimental. The crystal was placed in the cold stream of an Oxford Cryosystems Cobra open-flow nitrogen cryostat (Cosier & Glazer, 1986) operating at 100.0 (1) K.

Geometry. All s.u.'s (except the s.u. in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell s.u.'s are taken into account individually in the estimation of s.u.'s in distances, angles and torsion angles; correlations between s.u.'s in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell s.u.'s is used for estimating s.u.'s involving l.s. planes.

Refinement. Refinement of F^2 against ALL reflections. The weighted R-factor wR and goodness of fit S are based on F^2, conventional R-factors R are based on F, with F set to zero for negative F^2. The threshold expression of $F^2 > 2\sigma(F^2)$ is used only for calculating R-factors(gt) etc. and is not relevant to the choice of reflections for refinement. R-factors based on F^2 are statistically about twice as large as those based on F, and R- factors based on ALL data will be even larger.

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å^2)

	x	*y*	*z*	U_{iso}*/U_{eq}
Cl1	0.03584 (4)	1.13218 (6)	0.91629 (3)	0.02460 (10)
O1	0.36548 (12)	0.41445 (16)	0.66474 (7)	0.01744 (18)
O2	0.36855 (12)	0.47553 (16)	0.86099 (7)	0.01876 (19)
C7	0.18473 (15)	0.7570 (2)	0.61091 (10)	0.0158 (2)
H7A	0.2131	0.6782	0.5478	0.019*
C8	0.09543 (15)	0.9288 (2)	0.58796 (11)	0.0197 (2)
H8A	0.0654	0.9648	0.5096	0.024*
C9	0.05103 (16)	1.0466 (2)	0.68188 (12)	0.0195 (2)
H9A	−0.0078	1.1618	0.6671	0.023*
C10	0.09626 (15)	0.9890 (2)	0.79852 (10)	0.0159 (2)
C11	0.18604 (14)	0.8195 (2)	0.82290 (10)	0.0148 (2)
H11A	0.2155	0.7838	0.9014	0.018*
C12	0.23182 (14)	0.70259 (19)	0.72825 (10)	0.01258 (19)
C13	0.32902 (14)	0.51628 (19)	0.75345 (10)	0.0131 (2)
N1	0.53373 (13)	1.07928 (17)	0.70756 (8)	0.01350 (18)

H1A	0.4786	1.1863	0.6979	0.016*
N2	0.53701 (13)	1.1268 (3)	0.91147 (8)	0.0185 (2)
H2B	0.4837	1.2344	0.8986	0.022*
H2C	0.5638	1.0902	0.9835	0.022*
C1	0.57797 (14)	1.01721 (19)	0.82012 (10)	0.0133 (2)
C2	0.66378 (14)	0.8378 (2)	0.83484 (10)	0.0144 (2)
H2A	0.6936	0.7919	0.9112	0.017*
C3	0.70348 (14)	0.73057 (19)	0.73661 (10)	0.0141 (2)
C4	0.65921 (14)	0.8046 (2)	0.62099 (10)	0.0152 (2)
H4A	0.6878	0.7364	0.5535	0.018*
C5	0.57458 (14)	0.9762 (2)	0.60956 (9)	0.0143 (2)
H5A	0.5441	1.0239	0.5337	0.017*
C6	0.79035 (16)	0.5371 (2)	0.75110 (12)	0.0195 (2)
H6A	0.9016	0.5472	0.7239	0.029*
H6B	0.7286	0.4404	0.7048	0.029*
H6C	0.7964	0.5002	0.8338	0.029*

Atomic displacement parameters (Å^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Cl1	0.02597 (15)	0.02386 (18)	0.02371 (15)	0.00755 (12)	−0.00058 (10)	−0.00950 (12)
O1	0.0271 (4)	0.0139 (4)	0.0114 (3)	0.0054 (3)	0.0016 (3)	−0.0014 (3)
O2	0.0299 (4)	0.0157 (5)	0.0104 (3)	0.0044 (4)	−0.0002 (3)	0.0000 (3)
C7	0.0166 (4)	0.0184 (6)	0.0123 (4)	0.0012 (4)	0.0013 (3)	0.0016 (4)
C8	0.0203 (5)	0.0227 (7)	0.0160 (5)	0.0047 (5)	0.0006 (4)	0.0050 (5)
C9	0.0189 (5)	0.0184 (7)	0.0213 (5)	0.0041 (4)	0.0007 (4)	0.0019 (5)
C10	0.0147 (4)	0.0158 (6)	0.0173 (4)	0.0005 (4)	0.0016 (3)	−0.0023 (4)
C11	0.0159 (4)	0.0148 (6)	0.0135 (4)	0.0000 (4)	0.0007 (3)	−0.0009 (4)
C12	0.0131 (4)	0.0126 (5)	0.0121 (4)	−0.0009 (4)	0.0013 (3)	0.0007 (4)
C13	0.0175 (4)	0.0108 (5)	0.0109 (4)	−0.0016 (4)	0.0013 (3)	0.0000 (4)
N1	0.0177 (4)	0.0123 (5)	0.0106 (4)	−0.0005 (3)	0.0009 (3)	0.0017 (3)
N2	0.0292 (5)	0.0162 (5)	0.0100 (4)	0.0049 (4)	0.0009 (3)	−0.0003 (4)
C1	0.0164 (4)	0.0130 (5)	0.0104 (4)	−0.0015 (4)	0.0017 (3)	0.0018 (4)
C2	0.0175 (4)	0.0135 (6)	0.0123 (4)	0.0005 (4)	0.0012 (3)	0.0027 (4)
C3	0.0138 (4)	0.0133 (6)	0.0152 (4)	−0.0010 (4)	0.0016 (3)	0.0007 (4)
C4	0.0161 (4)	0.0164 (6)	0.0130 (4)	−0.0008 (4)	0.0012 (3)	−0.0014 (4)
C5	0.0169 (4)	0.0161 (6)	0.0099 (4)	−0.0021 (4)	0.0012 (3)	0.0001 (4)
C6	0.0199 (5)	0.0158 (6)	0.0228 (5)	0.0032 (4)	0.0024 (4)	0.0010 (4)

Geometric parameters (Å, °)

Cl1—C10	1.7383 (13)	N1—H1A	0.8600
O1—C13	1.2643 (14)	N2—C1	1.3280 (18)
O2—C13	1.2593 (14)	N2—H2B	0.8600
C7—C8	1.3934 (19)	N2—H2C	0.8600
C7—C12	1.3972 (16)	C1—C2	1.4138 (18)
C7—H7A	0.9300	C2—C3	1.3779 (16)
C8—C9	1.3909 (19)	C2—H2A	0.9300
C8—H8A	0.9300	C3—C4	1.4170 (16)

C9—C10	1.3927 (17)	C3—C6	1.5019 (19)
C9—H9A	0.9300	C4—C5	1.3599 (18)
C10—C11	1.3849 (19)	C4—H4A	0.9300
C11—C12	1.3968 (17)	C5—H5A	0.9300
C11—H11A	0.9300	C6—H6A	0.9600
C12—C13	1.5134 (18)	C6—H6B	0.9600
N1—C1	1.3582 (14)	C6—H6C	0.9600
N1—C5	1.3636 (15)		
C8—C7—C12	120.35 (12)	C1—N2—H2B	120.0
C8—C7—H7A	119.8	C1—N2—H2C	120.0
C12—C7—H7A	119.8	H2B—N2—H2C	120.0
C9—C8—C7	120.21 (11)	N2—C1—N1	118.49 (12)
C9—C8—H8A	119.9	N2—C1—C2	122.93 (11)
C7—C8—H8A	119.9	N1—C1—C2	118.57 (11)
C8—C9—C10	118.87 (12)	C3—C2—C1	120.36 (10)
C8—C9—H9A	120.6	C3—C2—H2A	119.8
C10—C9—H9A	120.6	C1—C2—H2A	119.8
C11—C10—C9	121.68 (12)	C2—C3—C4	118.91 (11)
C11—C10—Cl1	119.30 (9)	C2—C3—C6	120.86 (11)
C9—C10—Cl1	119.01 (10)	C4—C3—C6	120.22 (11)
C10—C11—C12	119.26 (11)	C5—C4—C3	119.42 (11)
C10—C11—H11A	120.4	C5—C4—H4A	120.3
C12—C11—H11A	120.4	C3—C4—H4A	120.3
C11—C12—C7	119.63 (12)	C4—C5—N1	121.04 (11)
C11—C12—C13	119.90 (10)	C4—C5—H5A	119.5
C7—C12—C13	120.47 (11)	N1—C5—H5A	119.5
O2—C13—O1	125.07 (12)	C3—C6—H6A	109.5
O2—C13—C12	117.52 (10)	C3—C6—H6B	109.5
O1—C13—C12	117.41 (10)	H6A—C6—H6B	109.5
C1—N1—C5	121.66 (11)	C3—C6—H6C	109.5
C1—N1—H1A	119.2	H6A—C6—H6C	109.5
C5—N1—H1A	119.2	H6B—C6—H6C	109.5
C12—C7—C8—C9	−0.62 (19)	C11—C12—C13—O1	179.10 (11)
C7—C8—C9—C10	−0.5 (2)	C7—C12—C13—O1	0.27 (16)
C8—C9—C10—C11	0.9 (2)	C5—N1—C1—N2	178.68 (11)
C8—C9—C10—Cl1	−178.18 (10)	C5—N1—C1—C2	−2.06 (17)
C9—C10—C11—C12	−0.32 (18)	N2—C1—C2—C3	−179.79 (12)
Cl1—C10—C11—C12	178.81 (9)	N1—C1—C2—C3	0.98 (17)
C10—C11—C12—C7	−0.79 (17)	C1—C2—C3—C4	0.97 (17)
C10—C11—C12—C13	−179.62 (10)	C1—C2—C3—C6	−178.29 (10)
C8—C7—C12—C11	1.26 (18)	C2—C3—C4—C5	−1.91 (17)
C8—C7—C12—C13	−179.91 (11)	C6—C3—C4—C5	177.35 (11)
C11—C12—C13—O2	−1.50 (17)	C3—C4—C5—N1	0.90 (17)
C7—C12—C13—O2	179.67 (11)	C1—N1—C5—C4	1.13 (17)

Hydrogen-bond geometry (Å, °)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*

N1—H1A···O1^{i}	0.86	1.83	2.6921 (16)	175
N2—H2B···O2^{i}	0.86	1.93	2.786 (2)	177
N2—H2C···O2^{ii}	0.86	1.96	2.8146 (14)	173
C5—H5A···O1^{iii}	0.93	2.50	3.1707 (13)	129

Symmetry codes: (i) *x*, *y*+1, *z*; (ii) −*x*+1, *y*+1/2, −*z*+2; (iii) −*x*+1, *y*+1/2, −*z*+1.

Fig. 1

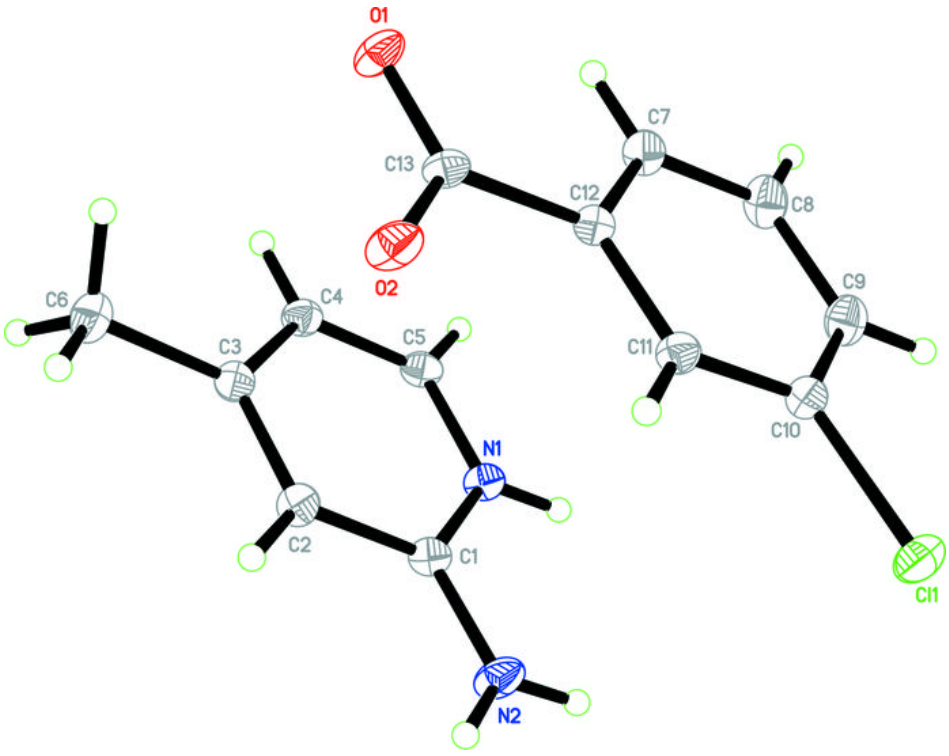
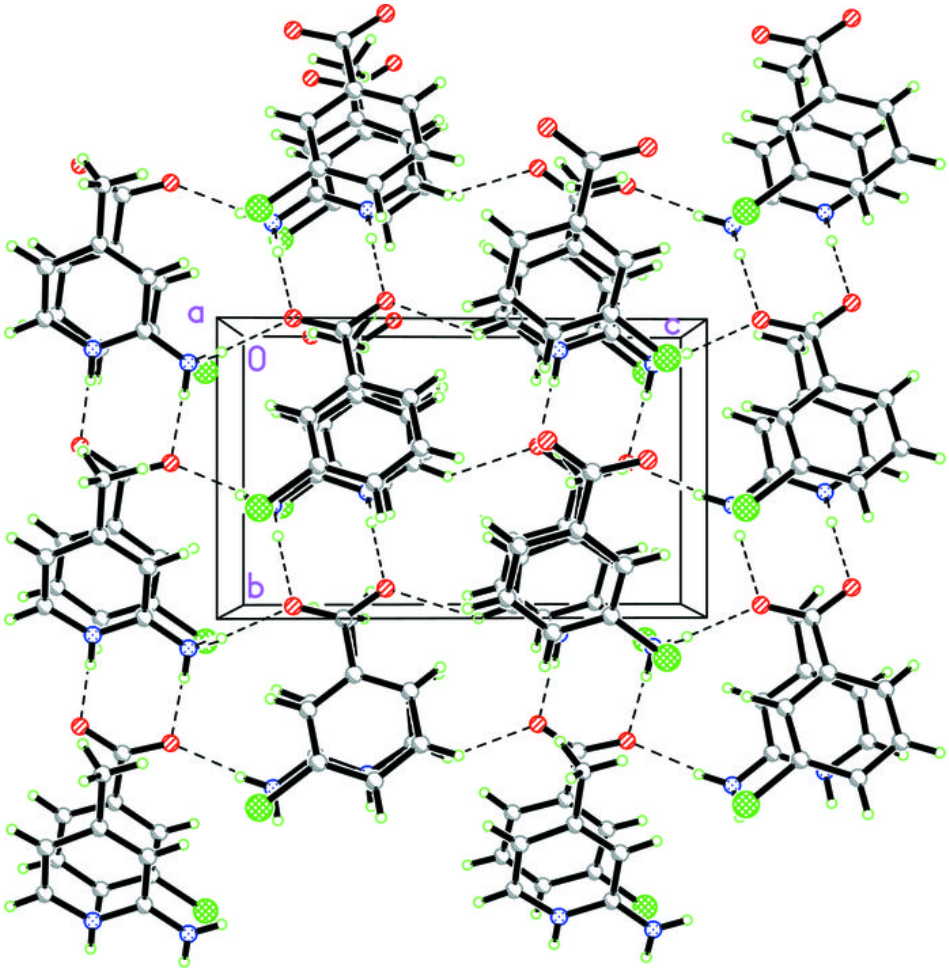


Fig. 2



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2,3-Dimethyl-6-nitroquinoxaline

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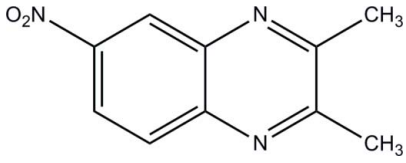
Key indicators: single-crystal X-ray study; T = 100 K; mean σ(C–C) = 0.001 Å; R factor = 0.045; wR factor = 0.136; data-to-parameter ratio = 27.3.

The asymmetric unit of the title quinoxaline compound, $C_{10}H_9N_3O_2$, contains two crystallographically independent molecules (*A* and *B*). The quinoxaline ring systems are essentially planar, with maximum deviations of 0.006 (1) and 0.017 (1) Å, respectively, for molecules *A* and *B*. In molecule *A*, the dihedral angle formed between the quinoxaline ring system and nitro group is 10.94 (3)° [6.31 (13)° for molecule *B*]. In the crystal, molecules are linked into chains propagating along [001]: one forms zigzag chains linked by C—H···O hydrogen bonds, whilst the other forms ladder-like chains by way of C—H···N and C—H···O hydrogen bonds. The packing is further consolidated by weak π–π interactions [range of centroid–centroid distances = 3.5895 (7)–3.6324 (7) Å].

Related literature

For general background to and applications of the title quinoxaline compound, see: Darabi *et al.* (2008). For the synthesis, see: Ajaikumar & Pandurangan (2009); Darabi *et al.* (2009). For related quinoxaline structures, see: Ghalib *et al.* (2010); Wozniak *et al.* (1993). For graph-set descriptions of hydrogen-bond ring motifs, see: Bernstein *et al.* (1995). For the stability of the temperature controller used for the data collection, see: Cosier & Glazer (1986).



‡ Thomson Reuters ResearcherID: C-7576-2009.
§ Thomson Reuters ResearcherID: A-3561-2009.

Experimental

Crystal data

$C_{10}H_9N_3O_2$
M_r = 203.20
Monoclinic, $P2_1/c$
a = 7.1125 (7) Å
b = 22.490 (2) Å
c = 12.9596 (10) Å
β = 115.026 (4)°
V = 1878.4 (3) Å^3
Z = 8
Mo $K\alpha$ radiation
μ = 0.10 mm^{-1}
T = 100 K
0.26 × 0.21 × 0.10 mm

Data collection

Bruker APEXII DUO CCD diffractometer
Absorption correction: multi-scan (*SADABS*; Bruker, 2009)
T_{min} = 0.973, T_{max} = 0.990
52279 measured reflections
7510 independent reflections
5559 reflections with $I > 2\sigma(I)$
R_{int} = 0.043

Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.045
$wR(F^2)$ = 0.136
S = 1.03
7510 reflections
275 parameters
H-atom parameters constrained
$\Delta\rho_{max}$ = 0.55 e Å^{-3}
$\Delta\rho_{min}$ = −0.20 e Å^{-3}

Table 1
Hydrogen-bond geometry (Å, °).

D—H···A	D—H	H···A	D···A	D—H···A
C3*A*—H3*A*···N2*A*^{i}	0.93	2.56	3.4486 (14)	160
C9*B*—H9*D*···O1*B*^{ii}	0.96	2.58	3.5380 (14)	176
C10*A*—H10*A*···O2*A*^{i}	0.96	2.38	3.3355 (15)	171

Symmetry codes: (i) $x, -y+\frac{3}{2}, z-\frac{1}{2}$; (ii) $x, -y+\frac{3}{2}, z+\frac{1}{2}$.

Data collection: *APEX2* (Bruker, 2009); cell refinement: *SAINT* (Bruker, 2009); data reduction: *SAINT*; program(s) used to solve structure: *SHELXTL* (Sheldrick, 2008); program(s) used to refine structure: *SHELXTL*; molecular graphics: *SHELXTL*; software used to prepare material for publication: *SHELXTL* and *PLATON* (Spek, 2009).

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Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: HB5504).

References

Ajaikumar, S. & Pandurangan, A. (2009). *Appl. Catal. A*, **357**, 184–192.
Bernstein, J., Davis, R. E., Shimoni, L. & Chang, N.-L. (1995). *Angew. Chem. Int. Ed. Engl.* **34**, 1555–1573.
Bruker (2009). *APEX2*, *SAINT* and *SADABS*. Bruker AXS Inc., Madison, Wisconsin, USA.
Cosier, J. & Glazer, A. M. (1986). *J. Appl. Cryst.* **19**, 105–107.
Darabi, H. R., Aghapoor, K., Mohsenzadeh, F., Taala, F., Asadollahnejad, N. & Badiei, A. (2009). *Catal. Lett.* **133**, 84–89.
Darabi, H. R., Tahoori, F., Aghapoor, K., Taala, F. & Mohsenzadeh, F. (2008). *J. Braz. Chem. Soc.* **19**, 1646–1652.

Ghalib, R. M., Hashim, R., Sulaiman, O., Hemamalini, M. & Fun, H.-K. (2010). *Acta Cryst.* E**66**, o1494.
Sheldrick, G. M. (2008). *Acta Cryst.* A**64**, 112–122.
Spek, A. L. (2009). *Acta Cryst.* D**65**, 148–155.
Wozniak, K., Krygowski, T. M., Grech, E., Kolodziejski, W. & Klinowski, J. (1993). *J. Phys. Chem.* **97**, 1862–1867.

supplementary materials

Acta Cryst. (2010). E**66**, o1830-o1831 [**doi:10.1107/S1600536810024463**]

2,3-Dimethyl-6-nitroquinoxaline

R. M. Ghalib, R. Hashim, S. H. Mehdi, J. H. Goh and H.-K. Fun

Comment

The direct condensation of various benzene-1,2-diamines with 1,2-dicarboxyl compounds has been successfully achieved in excellent yields using (NH_4Cl-CH_3OH) catalyst system at room temperature (Darabi *et al.*, 2008). Here in this study our method comprises the synthesis of the title compound by the reaction of 4-nitro-o-phenylenediamine and butanedione in distilled water. The procedure can be performed for a broad scope of quinoxaline derivatives and is eco-friendly.

The asymmetric unit of the title quinoxaline compound comprises of two crystallographically independent 2,3-dimethyl-6-nitroquinoxaline molecules, designated molecules *A* and *B* (Fig. 1). The two independent molecules having closely similar geometries, as shown in the superposition of the non-H atoms of molecules *A* and *B* (Fig. 2) using *XP* in *SHELXTL* (Sheldrick, 2008), giving an r.m.s. deviation of 0.116 Å.

In each molecule, the quinoxaline ring system (C1-C8/N1/N2) is essentially planar, with maximum deviations of -0.006 (1) and -0.017 (1) Å, respectively, for atoms C1A of molecule *A* and C3B of molecule *B*. There are slight inclinations between the quinoxaline ring systems and nitro groups, as indicated by the dihedral angles formed of 10.94 (3) and 6.31 (13)°, respectively, for molecules *A* and *B*. The bond lengths and angles are comparable to those observed in the reported quinoxaline structures (Ghalib *et al.*, 2010; Wozniak *et al.*, 1993).

The interesting feature of the crystal packing (Fig. 3) is that no intermolecular hydrogen bond is observed between the two independent molecules and they are packed in different manners. Adjacent molecules *A* are linked by intermolecular C3A—H3A···N2A and C10A—H10A···O2A hydrogen bonds (Table 1) into ladder-like chains incorporating $R^2_2(13)$ ring motifs (Bernstein *et al.*, 1995) whereas intermolecular C9B—H9D···O1B hydrogen bonds (Table 1) link adjacent molecules *B* into zig-zag shaped chains. Both chains are running along the [001] direction. Further consolidation of the crystal packing is provided by weak *Cg*1···*Cg*2 and *Cg*1···*Cg*3 interactions [*Cg*1···*Cg*2 = 3.5895 (7) Å, symmetry code: x, y, z; *Cg*1···*Cg*2 = 3.6324 (7) Å, symmetry code: x-1, y, z; *Cg*1···*Cg*3 = 3.6228 (7) Å, symmetry code: x, y, z; *Cg*1 and *Cg*2 are the centroids of the C2A–C7A and C2B–C7B benzene rings, respectively; *Cg*3 is the centroid of the C1B/N1B/C2B/C7B/N2B/C8B pyrazine ring].

Experimental

The title compound was synthesized as reported in the literatures (Darabi *et al.*, 2009; Ajaikumar & Pandurangan, 2009). A mixture of 4-nitro-o-phenylenediamine (1.5310 g) and butanedione (0.8775 g) in molar ratio 1:1 were refluxed in distilled water for 1 h. The reaction mixture was dried on rota vapor at low pressure and then recrystallized with a 1:1 mixture of alcohol-chloroform to afford brownish crystals of the title compound (1.76 g, *M.p.* 406 K).

Refinement

All H atoms were placed in their calculated positions, with C—H = 0.93 or 0.96 Å, and refined using a riding model, with U_{iso} = 1.2 or 1.5 U_{eq}(C). The rotating group model is applied to the methyl groups.

Figures

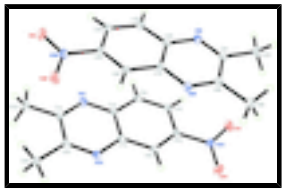


Fig. 1. The molecular structure of (I) showing 30 % probability displacement ellipsoids for non-H atoms.

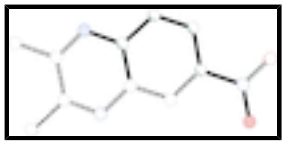


Fig. 2. Fit of molecule *A* (dashed lines) on molecule *B* (solid lines). H atoms have been omitted for clarity.

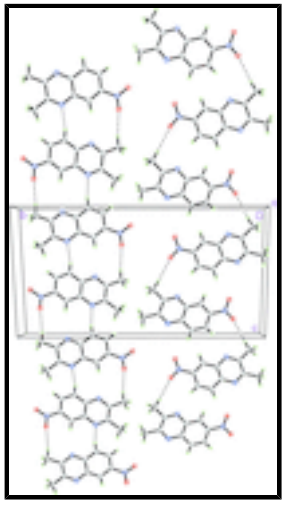


Fig. 3. The crystal structure of (I), viewed along the *a* axis, showing the molecules being linked into one-dimensional chains along the [001] direction. Intermolecular hydrogen bonds are shown as dashed lines.

2,3-Dimethyl-6-nitroquinoxaline

Crystal data

$C_{10}H_9N_3O_2$	$F(000)$ = 848
M_r = 203.20	D_x = 1.437 Mg m^{-3}
Monoclinic, $P2_1/c$	Mo $K\alpha$ radiation, λ = 0.71073 Å
Hall symbol: -P 2ybc	Cell parameters from 9916 reflections
a = 7.1125 (7) Å	θ = 3.4–33.5°
b = 22.490 (2) Å	μ = 0.10 mm^{-1}
c = 12.9596 (10) Å	T = 100 K
β = 115.026 (4)°	Block, brown
V = 1878.4 (3) Å^3	0.26 × 0.21 × 0.10 mm
Z = 8	

Data collection

Bruker APEXII DUO CCD diffractometer	7510 independent reflections
Radiation source: fine-focus sealed tube	5559 reflections with $I > 2\sigma(I)$
graphite	$R_{int} = 0.043$
φ and ω scans	$\theta_{max} = 33.8°$, $\theta_{min} = 1.8°$
Absorption correction: multi-scan (*SADABS*; Bruker, 2009)	$h = -10 \rightarrow 11$
$T_{min} = 0.973$, $T_{max} = 0.990$	$k = -35 \rightarrow 35$
52279 measured reflections	$l = -20 \rightarrow 20$

Refinement

Refinement on F^2	Primary atom site location: structure-invariant direct methods
Least-squares matrix: full	Secondary atom site location: difference Fourier map
$R[F^2 > 2\sigma(F^2)] = 0.045$	Hydrogen site location: inferred from neighbouring sites
$wR(F^2) = 0.136$	H-atom parameters constrained
$S = 1.03$	$w = 1/[\sigma^2(F_o^2) + (0.077P)^2 + 0.2747P]$ where $P = (F_o^2 + 2F_c^2)/3$
7510 reflections	$(\Delta/\sigma)_{max} = 0.001$
275 parameters	$\Delta\rho_{max} = 0.55$ e Å^{-3}
0 restraints	$\Delta\rho_{min} = -0.20$ e Å^{-3}

Special details

Experimental. The crystal was placed in the cold stream of an Oxford Cryosystems Cobra open-flow nitrogen cryostat (Cosier & Glazer, 1986) operating at 100.0 (1)K.

Geometry. All esds (except the esd in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell esds are taken into account individually in the estimation of esds in distances, angles and torsion angles; correlations between esds in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell esds is used for estimating esds involving l.s. planes.

Refinement. Refinement of F^2 against ALL reflections. The weighted R-factor wR and goodness of fit S are based on F^2, conventional R-factors R are based on F, with F set to zero for negative F^2. The threshold expression of $F^2 > 2\text{sigma}(F^2)$ is used only for calculating R-factors(gt) etc. and is not relevant to the choice of reflections for refinement. R-factors based on F^2 are statistically about twice as large as those based on F, and R- factors based on ALL data will be even larger.

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å^2)

	x	*y*	*z*	U_{iso}*/U_{eq}
O1A	0.42483 (15)	0.54231 (3)	0.13432 (7)	0.03320 (19)
O2A	0.40149 (14)	0.57864 (4)	0.28272 (7)	0.03070 (18)
N1A	0.46872 (13)	0.81176 (4)	0.03295 (7)	0.02043 (16)
N2A	0.50093 (12)	0.79631 (4)	0.25642 (7)	0.01853 (15)

N3A	0.41730 (13)	0.58434 (4)	0.19278 (7)	0.02205 (16)
C1A	0.49512 (15)	0.85691 (4)	0.10172 (8)	0.02068 (17)
C2A	0.45607 (13)	0.75638 (4)	0.07370 (8)	0.01702 (16)
C3A	0.42621 (14)	0.70659 (4)	0.00252 (8)	0.01940 (17)
H3A	0.4160	0.7116	−0.0709	0.023*
C4A	0.41210 (14)	0.65075 (4)	0.04132 (8)	0.01985 (17)
H4A	0.3915	0.6177	−0.0053	0.024*
C5A	0.42934 (14)	0.64452 (4)	0.15257 (8)	0.01822 (16)
C6A	0.45822 (14)	0.69133 (4)	0.22529 (8)	0.01792 (16)
H6A	0.4686	0.6855	0.2985	0.022*
C7A	0.47173 (13)	0.74866 (4)	0.18519 (7)	0.01652 (15)
C8A	0.51266 (14)	0.84900 (4)	0.21625 (8)	0.01909 (16)
C9A	0.54442 (18)	0.90164 (5)	0.29221 (9)	0.0257 (2)
H9A	0.5650	0.8884	0.3667	0.039*
H9B	0.4244	0.9269	0.2613	0.039*
H9C	0.6642	0.9234	0.2975	0.039*
C10A	0.5085 (2)	0.91790 (5)	0.05931 (10)	0.0309 (2)
H10A	0.4890	0.9156	−0.0186	0.046*
H10B	0.6425	0.9346	0.1049	0.046*
H10C	0.4027	0.9426	0.0643	0.046*
O1B	1.02498 (14)	0.88142 (4)	0.11899 (7)	0.03279 (18)
O2B	1.01367 (14)	0.86371 (3)	0.28010 (7)	0.03235 (18)
N1B	0.91353 (13)	0.60539 (4)	0.08423 (7)	0.02072 (15)
N2B	0.96057 (12)	0.64557 (4)	0.30076 (7)	0.01937 (15)
N3B	1.00834 (13)	0.84739 (4)	0.18868 (8)	0.02304 (17)
C1B	0.91658 (15)	0.56851 (4)	0.16330 (8)	0.02119 (17)
C2B	0.93380 (13)	0.66464 (4)	0.11081 (8)	0.01795 (16)
C3B	0.92863 (15)	0.70603 (4)	0.02753 (8)	0.02017 (17)
H3B	0.9091	0.6928	−0.0443	0.024*
C4B	0.95218 (14)	0.76554 (4)	0.05198 (8)	0.02043 (17)
H4B	0.9496	0.7930	−0.0022	0.025*
C5B	0.98036 (14)	0.78392 (4)	0.16108 (8)	0.01887 (16)
C6B	0.98399 (14)	0.74548 (4)	0.24403 (8)	0.01843 (16)
H6B	1.0023	0.7595	0.3152	0.022*
C7B	0.95944 (13)	0.68435 (4)	0.21894 (8)	0.01721 (16)
C8B	0.93904 (15)	0.58899 (4)	0.27364 (8)	0.02046 (17)
C9B	0.93881 (19)	0.54547 (5)	0.36108 (9)	0.0285 (2)
H9D	0.9554	0.5664	0.4289	0.043*
H9E	1.0512	0.5179	0.3786	0.043*
H9F	0.8097	0.5242	0.3318	0.043*
C10B	0.8977 (2)	0.50367 (5)	0.13618 (11)	0.0306 (2)
H10D	0.8890	0.4978	0.0609	0.046*
H10E	0.7747	0.4883	0.1399	0.046*
H10F	1.0171	0.4832	0.1903	0.046*

Atomic displacement parameters (Å^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}

O1A	0.0509 (5)	0.0197 (3)	0.0321 (4)	−0.0016 (3)	0.0206 (4)	−0.0041 (3)
O2A	0.0432 (5)	0.0283 (4)	0.0244 (4)	−0.0055 (3)	0.0179 (3)	0.0018 (3)
N1A	0.0232 (4)	0.0210 (4)	0.0172 (4)	0.0026 (3)	0.0086 (3)	0.0016 (3)
N2A	0.0196 (3)	0.0201 (3)	0.0165 (3)	0.0004 (3)	0.0082 (3)	−0.0012 (3)
N3A	0.0244 (4)	0.0203 (4)	0.0210 (4)	−0.0024 (3)	0.0092 (3)	−0.0006 (3)
C1A	0.0230 (4)	0.0203 (4)	0.0185 (4)	0.0031 (3)	0.0085 (3)	0.0016 (3)
C2A	0.0161 (4)	0.0199 (4)	0.0152 (4)	0.0017 (3)	0.0067 (3)	0.0005 (3)
C3A	0.0208 (4)	0.0232 (4)	0.0153 (4)	0.0006 (3)	0.0086 (3)	−0.0019 (3)
C4A	0.0204 (4)	0.0216 (4)	0.0182 (4)	−0.0013 (3)	0.0088 (3)	−0.0033 (3)
C5A	0.0174 (4)	0.0188 (4)	0.0187 (4)	−0.0010 (3)	0.0079 (3)	−0.0003 (3)
C6A	0.0175 (4)	0.0208 (4)	0.0157 (4)	−0.0001 (3)	0.0073 (3)	−0.0004 (3)
C7A	0.0149 (3)	0.0201 (4)	0.0145 (4)	0.0004 (3)	0.0061 (3)	−0.0010 (3)
C8A	0.0195 (4)	0.0202 (4)	0.0178 (4)	0.0013 (3)	0.0081 (3)	−0.0011 (3)
C9A	0.0338 (5)	0.0209 (4)	0.0239 (5)	−0.0006 (4)	0.0137 (4)	−0.0044 (4)
C10A	0.0488 (7)	0.0204 (4)	0.0243 (5)	0.0037 (4)	0.0162 (5)	0.0043 (4)
O1B	0.0440 (5)	0.0202 (3)	0.0365 (5)	−0.0034 (3)	0.0192 (4)	0.0045 (3)
O2B	0.0469 (5)	0.0206 (3)	0.0330 (4)	−0.0026 (3)	0.0203 (4)	−0.0061 (3)
N1B	0.0221 (4)	0.0186 (3)	0.0209 (4)	−0.0005 (3)	0.0085 (3)	−0.0020 (3)
N2B	0.0200 (3)	0.0183 (3)	0.0195 (4)	0.0003 (3)	0.0081 (3)	0.0010 (3)
N3B	0.0229 (4)	0.0176 (3)	0.0284 (4)	−0.0011 (3)	0.0106 (3)	−0.0001 (3)
C1B	0.0223 (4)	0.0171 (4)	0.0234 (4)	0.0008 (3)	0.0089 (3)	−0.0009 (3)
C2B	0.0159 (4)	0.0186 (4)	0.0187 (4)	−0.0005 (3)	0.0066 (3)	−0.0011 (3)
C3B	0.0208 (4)	0.0212 (4)	0.0188 (4)	−0.0017 (3)	0.0086 (3)	−0.0003 (3)
C4B	0.0194 (4)	0.0207 (4)	0.0213 (4)	−0.0007 (3)	0.0087 (3)	0.0018 (3)
C5B	0.0174 (4)	0.0160 (4)	0.0233 (4)	−0.0009 (3)	0.0087 (3)	−0.0006 (3)
C6B	0.0180 (4)	0.0181 (4)	0.0198 (4)	−0.0009 (3)	0.0085 (3)	−0.0017 (3)
C7B	0.0157 (3)	0.0173 (4)	0.0186 (4)	−0.0006 (3)	0.0072 (3)	−0.0010 (3)
C8B	0.0206 (4)	0.0190 (4)	0.0209 (4)	0.0009 (3)	0.0079 (3)	0.0014 (3)
C9B	0.0386 (6)	0.0209 (4)	0.0255 (5)	−0.0002 (4)	0.0131 (4)	0.0042 (4)
C10B	0.0433 (6)	0.0176 (4)	0.0334 (6)	−0.0009 (4)	0.0188 (5)	−0.0027 (4)

Geometric parameters (Å, °)

O1A—N3A	1.2267 (11)	O1B—N3B	1.2272 (11)
O2A—N3A	1.2242 (11)	O2B—N3B	1.2255 (12)
N1A—C1A	1.3111 (12)	N1B—C1B	1.3114 (12)
N1A—C2A	1.3705 (12)	N1B—C2B	1.3686 (12)
N2A—C8A	1.3111 (12)	N2B—C8B	1.3117 (12)
N2A—C7A	1.3717 (11)	N2B—C7B	1.3703 (12)
N3A—C5A	1.4658 (12)	N3B—C5B	1.4646 (12)
C1A—C8A	1.4469 (13)	C1B—C8B	1.4454 (14)
C1A—C10A	1.4956 (14)	C1B—C10B	1.4927 (14)
C2A—C3A	1.4087 (13)	C2B—C7B	1.4062 (13)
C2A—C7A	1.4121 (12)	C2B—C3B	1.4138 (13)
C3A—C4A	1.3722 (13)	C3B—C4B	1.3693 (13)
C3A—H3A	0.9300	C3B—H3B	0.9300
C4A—C5A	1.4014 (13)	C4B—C5B	1.4036 (13)
C4A—H4A	0.9300	C4B—H4B	0.9300
C5A—C6A	1.3691 (13)	C5B—C6B	1.3711 (13)

C6A—C7A	1.4086 (13)	C6B—C7B	1.4066 (12)
C6A—H6A	0.9300	C6B—H6B	0.9300
C8A—C9A	1.4944 (13)	C8B—C9B	1.4978 (14)
C9A—H9A	0.9600	C9B—H9D	0.9600
C9A—H9B	0.9600	C9B—H9E	0.9600
C9A—H9C	0.9600	C9B—H9F	0.9600
C10A—H10A	0.9600	C10B—H10D	0.9600
C10A—H10B	0.9600	C10B—H10E	0.9600
C10A—H10C	0.9600	C10B—H10F	0.9600
C1A—N1A—C2A	117.11 (8)	C1B—N1B—C2B	117.01 (8)
C8A—N2A—C7A	117.13 (8)	C8B—N2B—C7B	116.63 (8)
O2A—N3A—O1A	123.57 (9)	O2B—N3B—O1B	123.47 (9)
O2A—N3A—C5A	118.55 (8)	O2B—N3B—C5B	118.27 (8)
O1A—N3A—C5A	117.88 (8)	O1B—N3B—C5B	118.27 (9)
N1A—C1A—C8A	121.84 (9)	N1B—C1B—C8B	121.99 (9)
N1A—C1A—C10A	118.27 (8)	N1B—C1B—C10B	117.64 (9)
C8A—C1A—C10A	119.90 (9)	C8B—C1B—C10B	120.37 (9)
N1A—C2A—C3A	119.10 (8)	N1B—C2B—C7B	120.87 (8)
N1A—C2A—C7A	121.09 (8)	N1B—C2B—C3B	118.88 (8)
C3A—C2A—C7A	119.80 (8)	C7B—C2B—C3B	120.25 (8)
C4A—C3A—C2A	120.12 (8)	C4B—C3B—C2B	120.38 (9)
C4A—C3A—H3A	119.9	C4B—C3B—H3B	119.8
C2A—C3A—H3A	119.9	C2B—C3B—H3B	119.8
C3A—C4A—C5A	118.70 (8)	C3B—C4B—C5B	118.18 (9)
C3A—C4A—H4A	120.6	C3B—C4B—H4B	120.9
C5A—C4A—H4A	120.6	C5B—C4B—H4B	120.9
C6A—C5A—C4A	123.62 (8)	C6B—C5B—C4B	123.47 (9)
C6A—C5A—N3A	118.66 (8)	C6B—C5B—N3B	117.86 (8)
C4A—C5A—N3A	117.72 (8)	C4B—C5B—N3B	118.67 (8)
C5A—C6A—C7A	117.63 (8)	C5B—C6B—C7B	118.40 (9)
C5A—C6A—H6A	121.2	C5B—C6B—H6B	120.8
C7A—C6A—H6A	121.2	C7B—C6B—H6B	120.8
N2A—C7A—C6A	118.79 (8)	N2B—C7B—C2B	121.76 (8)
N2A—C7A—C2A	121.09 (8)	N2B—C7B—C6B	118.93 (8)
C6A—C7A—C2A	120.12 (8)	C2B—C7B—C6B	119.31 (8)
N2A—C8A—C1A	121.74 (8)	N2B—C8B—C1B	121.72 (9)
N2A—C8A—C9A	118.14 (8)	N2B—C8B—C9B	117.94 (9)
C1A—C8A—C9A	120.12 (8)	C1B—C8B—C9B	120.34 (9)
C8A—C9A—H9A	109.5	C8B—C9B—H9D	109.5
C8A—C9A—H9B	109.5	C8B—C9B—H9E	109.5
H9A—C9A—H9B	109.5	H9D—C9B—H9E	109.5
C8A—C9A—H9C	109.5	C8B—C9B—H9F	109.5
H9A—C9A—H9C	109.5	H9D—C9B—H9F	109.5
H9B—C9A—H9C	109.5	H9E—C9B—H9F	109.5
C1A—C10A—H10A	109.5	C1B—C10B—H10D	109.5
C1A—C10A—H10B	109.5	C1B—C10B—H10E	109.5
H10A—C10A—H10B	109.5	H10D—C10B—H10E	109.5
C1A—C10A—H10C	109.5	C1B—C10B—H10F	109.5
H10A—C10A—H10C	109.5	H10D—C10B—H10F	109.5

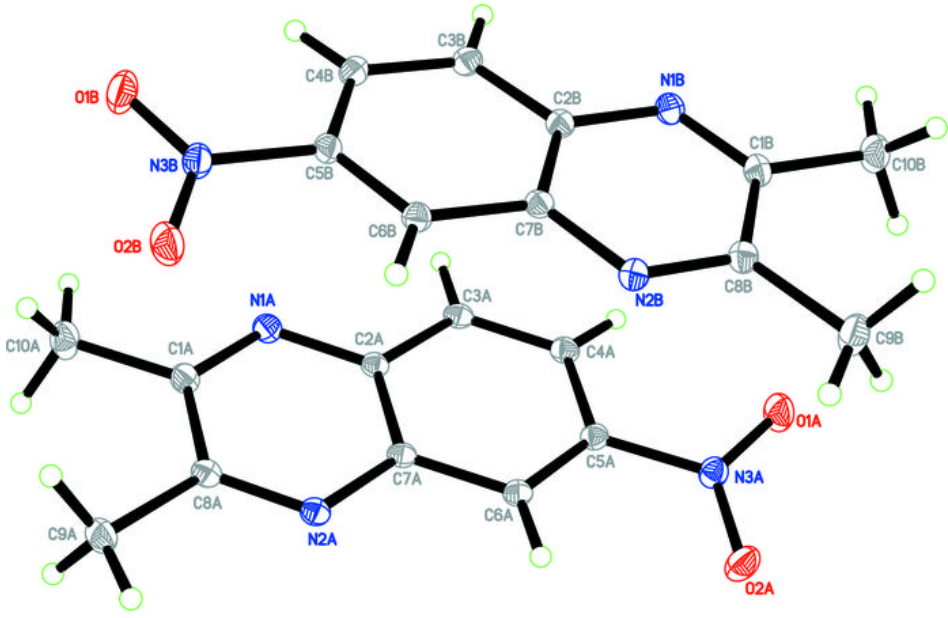
H10B—C10A—H10C	109.5	H10E—C10B—H10F	109.5
C2A—N1A—C1A—C8A	0.68 (14)	C2B—N1B—C1B—C8B	0.35 (14)
C2A—N1A—C1A—C10A	−179.74 (9)	C2B—N1B—C1B—C10B	−179.15 (9)
C1A—N1A—C2A—C3A	179.54 (9)	C1B—N1B—C2B—C7B	0.83 (13)
C1A—N1A—C2A—C7A	−0.23 (13)	C1B—N1B—C2B—C3B	−179.19 (9)
N1A—C2A—C3A—C4A	−179.69 (8)	N1B—C2B—C3B—C4B	−178.82 (9)
C7A—C2A—C3A—C4A	0.09 (13)	C7B—C2B—C3B—C4B	1.16 (14)
C2A—C3A—C4A—C5A	−0.42 (14)	C2B—C3B—C4B—C5B	−0.29 (14)
C3A—C4A—C5A—C6A	0.49 (14)	C3B—C4B—C5B—C6B	−0.49 (14)
C3A—C4A—C5A—N3A	−178.99 (8)	C3B—C4B—C5B—N3B	179.24 (8)
O2A—N3A—C5A—C6A	11.04 (13)	O2B—N3B—C5B—C6B	−6.86 (13)
O1A—N3A—C5A—C6A	−168.57 (9)	O1B—N3B—C5B—C6B	173.21 (9)
O2A—N3A—C5A—C4A	−169.46 (9)	O2B—N3B—C5B—C4B	173.39 (9)
O1A—N3A—C5A—C4A	10.93 (13)	O1B—N3B—C5B—C4B	−6.54 (13)
C4A—C5A—C6A—C7A	−0.20 (14)	C4B—C5B—C6B—C7B	0.38 (14)
N3A—C5A—C6A—C7A	179.27 (8)	N3B—C5B—C6B—C7B	−179.35 (8)
C8A—N2A—C7A—C6A	−179.96 (8)	C8B—N2B—C7B—C2B	0.80 (13)
C8A—N2A—C7A—C2A	0.28 (13)	C8B—N2B—C7B—C6B	−179.40 (8)
C5A—C6A—C7A—N2A	−179.91 (8)	N1B—C2B—C7B—N2B	−1.47 (13)
C5A—C6A—C7A—C2A	−0.15 (13)	C3B—C2B—C7B—N2B	178.54 (8)
N1A—C2A—C7A—N2A	−0.27 (13)	N1B—C2B—C7B—C6B	178.72 (8)
C3A—C2A—C7A—N2A	179.96 (8)	C3B—C2B—C7B—C6B	−1.26 (13)
N1A—C2A—C7A—C6A	179.98 (8)	C5B—C6B—C7B—N2B	−179.31 (8)
C3A—C2A—C7A—C6A	0.21 (13)	C5B—C6B—C7B—C2B	0.50 (13)
C7A—N2A—C8A—C1A	0.16 (13)	C7B—N2B—C8B—C1B	0.39 (13)
C7A—N2A—C8A—C9A	179.99 (8)	C7B—N2B—C8B—C9B	−179.77 (9)
N1A—C1A—C8A—N2A	−0.68 (15)	N1B—C1B—C8B—N2B	−1.02 (15)
C10A—C1A—C8A—N2A	179.74 (9)	C10B—C1B—C8B—N2B	178.47 (9)
N1A—C1A—C8A—C9A	179.49 (9)	N1B—C1B—C8B—C9B	179.14 (9)
C10A—C1A—C8A—C9A	−0.08 (14)	C10B—C1B—C8B—C9B	−1.37 (15)

Hydrogen-bond geometry (Å, °)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
C3A—H3A···N2A^{i}	0.93	2.56	3.4486 (14)	160
C9B—H9D···O1B^{ii}	0.96	2.58	3.5380 (14)	176
C10A—H10A···O2A^{i}	0.96	2.38	3.3355 (15)	171

Symmetry codes: (i) *x*, −*y*+3/2, *z*−1/2; (ii) *x*, −*y*+3/2, *z*+1/2.

Fig. 1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O1B
N1B
C2B
N3B
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C1B
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C6B
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C8B
N1A
C3A
C10A
C1A
C2A
C4A
C9B
O1A
C5A
N3A
C7A
C8A
C6A
C9A
N2A
O2A

Fig. 2

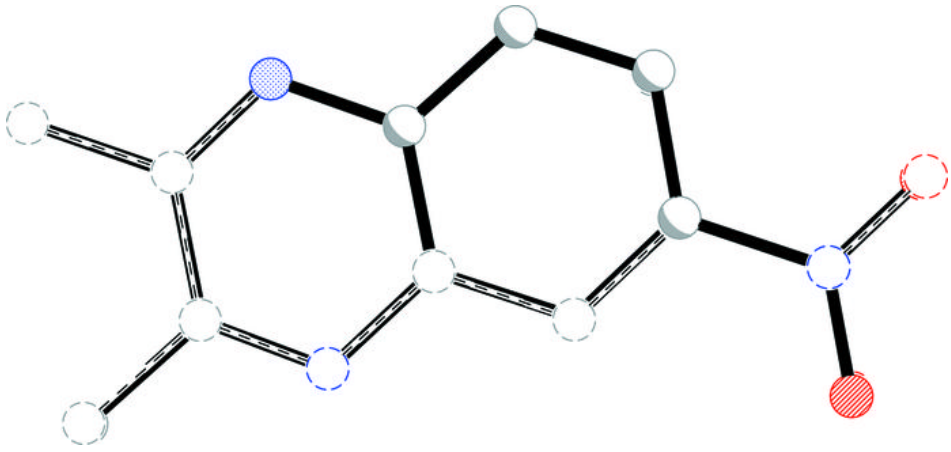
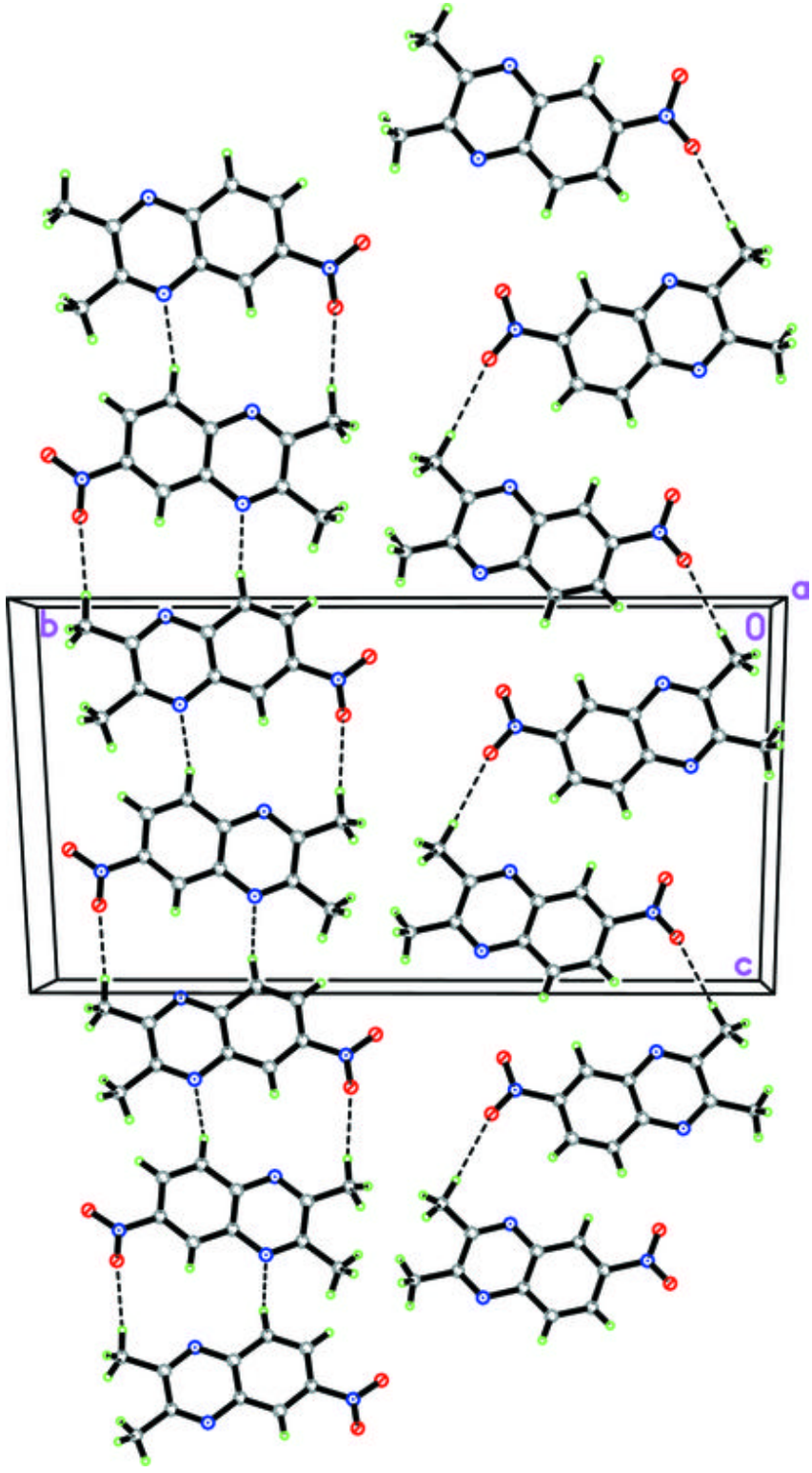


Fig. 3



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2-(7-Methoxy-1-naphthyl)acetonitrile

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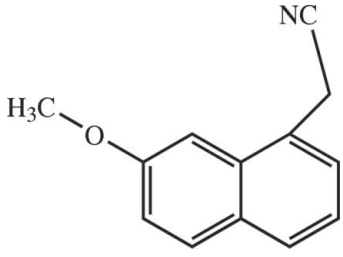
Key indicators: single-crystal X-ray study; T = 293 K; mean σ(C–C) = 0.004 Å; R factor = 0.059; wR factor = 0.163; data-to-parameter ratio = 13.9.

The molecule of the title compound, $C_{13}H_{11}NO$, is almost planar (r.m.s. deviation = 0.013 Å), apart from the cyanide group, for which the C and N atoms deviate from the mean plane of the other atoms by 0.341 (3) and 0.571 (4) Å, respectively. In the crystal, weak aromatic π–π stacking [centroid–centroid distance = 3.758 (3) Å] may help to stabilize the structure.

Related literature

For background to the use of naphthylethyl acetonitrile as an intermediate for the synthesisis of *N*-naphthylethyl amide derivatives, see: Depreux & Lesieur (1994). For further synthetic details, see: Yous & Andrieux (1992).



Experimental

Crystal data

$C_{13}H_{11}NO$
M_r = 197.23
Monoclinic, $P2_1/n$
a = 7.5110 (15) Å
b = 9.6170 (19) Å
c = 14.731 (3) Å
β = 101.03 (3)°
V = 1044.4 (4) Å^3
Z = 4
Mo $K\alpha$ radiation
μ = 0.08 mm^{-1}
T = 293 K
0.30 × 0.20 × 0.10 mm

Data collection

Enraf–Nonius CAD-4 diffractometer
Absorption correction: ψ scan (North *et al.*, 1968)
T_{min} = 0.976, T_{max} = 0.992
1971 measured reflections
1897 independent reflections
1045 reflections with $I > 2\sigma(I)$
R_{int} = 0.011
3 standard reflections every 200 reflections
intensity decay: 1%

Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.059
$wR(F^2)$ = 0.163
S = 1.00
1897 reflections
136 parameters
H-atom parameters constrained
$\Delta\rho_{max}$ = 0.14 e Å^{-3}
$\Delta\rho_{min}$ = −0.14 e Å^{-3}

Data collection: *CAD-4 EXPRESS* (Enraf–Nonius, 1994); cell refinement: *CAD-4 EXPRESS*; data reduction: *XCAD4* (Harms & Wocadlo, 1995); program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *PLATON* (Spek, 2009); software used to prepare material for publication: *PLATON*.

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Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: HB5505).

References

Depreux, P. & Lesieur, D. (1994). *J. Med. Chem.* **37**, 3231–3239.
Enraf–Nonius (1994). *CAD-4 EXPRESS*. Enraf–Nonius, Delft, The Netherlands.
Harms, K. & Wocadlo, S. (1995). *XCAD4*. University of Marburg, Germany.
North, A. C. T., Phillips, D. C. & Mathews, F. S. (1968). *Acta Cryst.* A**24**, 351–359.
Sheldrick, G. M. (2008). *Acta Cryst.* A**64**, 112–122.
Spek, A. L. (2009). *Acta Cryst.* D**65**, 148–155.
Yous, S. & Andrieux, J. (1992). *J. Med. Chem.* **35**, 1484–1486.

supplementary materials

Acta Cryst. (2010). E**66**, o1868 [**doi:10.1107/S1600536810024372**]

2-(7-Methoxy-1-naphthyl)acetonitrile

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Comment

Naphthylethyl acetonitrile is an important pharmaceutical intermediate for synthesizing *N*-naphthylethyl amide derivatives which was evaluated as melatonin receptor ligands (Depreux & Lesieur, 1994). We report herein the crystal structure of the title compound, (I).

In the molecule of the title compound (Fig 1), the bond lengths and angles are within normal ranges. Rings A (C3—C7/C12), B (C8—C12)are, of course, planar, and they are oriented at dihedral angle A/B= 1.10 (3) °. So, they are nearly co-planar. No classical hydrogen bond was found in the molecule. The π–π contacts between the naphthalene rings, *Cg*1—*Cg*2^{i} [symmetry codes: -*x*,1 - *y*,1 - *z*, where *Cg*1 and *Cg*2 are centroids of the rings A (C3—C7/C10/C12), and B (C8—C12), respectively] may further stabilize the structure, with centroid-centroid distances of 3.758 (3) Å.

Experimental

(7-Methoxy-1-naphthyl)acetic acid was reacted with thionyl chloride in $CHCl_3$, and the crude acid chloride was treated with aqueous ammonia to produce (7-Methoxy-1-naphthyl)acetamide. Dehydration of this amide with trifluoroacetic anhydride in THF at 273 K gave the title compound (Yous & Andrieux, 1992). Crystals suitable for X-ray analysis were obtained by slow evaporation of a methanol solution (yield; 66%, m.p. 353 K).

Refinement

H atoms were positioned geometrically, with C—H = 0.93 Å for aromatic H and C—H = 0.96 and 0.97 Å for methyl and methylene H, respectively, and constrained to ride on their parent atoms, with U_{iso}(H) = xU_{eq}(C,*O*), where *x* = 1.5 for OH H and *x* = 1.2 for all other H atoms.

Figures

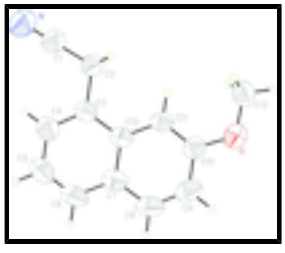


Fig. 1. View of the title compound with displacement ellipsoids for non-H atoms drawn at the 50% probability level.

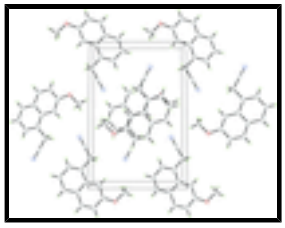


Fig. 2. A packing diagram of title molecule.

2-(7-Methoxy-1-naphthyl)acetonitrile

Crystal data

$C_{13}H_{11}NO$	$F(000) = 416$
$M_r = 197.23$	$D_x = 1.254$ Mg m^{-3}
Monoclinic, $P2_1/n$	Melting point: 353 K
Hall symbol: -P 2yn	Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å
$a = 7.5110$ (15) Å	Cell parameters from 25 reflections
$b = 9.6170$ (19) Å	$\theta = 9$–$13°$
$c = 14.731$ (3) Å	$\mu = 0.08$ mm^{-1}
$\beta = 101.03$ (3)°	$T = 293$ K
$V = 1044.4$ (4) Å^3	Block, colorless
$Z = 4$	0.30 × 0.20 × 0.10 mm

Data collection

Enraf–Nonius CAD-4 diffractometer	1045 reflections with $I > 2\sigma(I)$
Radiation source: fine-focus sealed tube	$R_{int} = 0.011$
graphite	$\theta_{max} = 25.3°$, $\theta_{min} = 2.5°$
$\omega/2\theta$ scans	$h = -9 \rightarrow 8$
Absorption correction: ψ scan (North *et al.*, 1968)	$k = -11 \rightarrow 0$
$T_{min} = 0.976$, $T_{max} = 0.992$	$l = 0 \rightarrow 17$
1971 measured reflections	3 standard reflections every 200 reflections
1897 independent reflections	intensity decay: 1%

Refinement

Refinement on F^2	Primary atom site location: structure-invariant direct methods
Least-squares matrix: full	Secondary atom site location: difference Fourier map
$R[F^2 > 2\sigma(F^2)] = 0.059$	Hydrogen site location: inferred from neighbouring sites
$wR(F^2) = 0.163$	H-atom parameters constrained
$S = 1.00$	$w = 1/[\sigma^2(F_o^2) + (0.069P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
1897 reflections	$(\Delta/\sigma)_{max} < 0.001$
136 parameters	$\Delta\rho_{max} = 0.14$ e Å^{-3}

0 restraints $\Delta\rho_{min} = -0.14$ e Å^{-3}

Special details

Geometry. All e.s.d.'s (except the e.s.d. in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell e.s.d.'s are taken into account individually in the estimation of e.s.d.'s in distances, angles and torsion angles; correlations between e.s.d.'s in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell e.s.d.'s is used for estimating e.s.d.'s involving l.s. planes.

Refinement. Refinement of F^2 against ALL reflections. The weighted *R*-factor *wR* and goodness of fit *S* are based on F^2, conventional *R*-factors *R* are based on *F*, with *F* set to zero for negative F^2. The threshold expression of $F^2 > \sigma(F^2)$ is used only for calculating *R*-factors(gt) *etc*. and is not relevant to the choice of reflections for refinement. *R*-factors based on F^2 are statistically about twice as large as those based on *F*, and *R*- factors based on ALL data will be even larger.

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å^2)

	x	*y*	*z*	U_{iso}*/U_{eq}
O	0.8616 (3)	−0.2547 (2)	0.13823 (13)	0.0718 (6)
N	0.7349 (5)	0.1342 (3)	−0.3297 (2)	0.1076 (12)
C1	0.7327 (4)	0.0786 (3)	−0.2623 (2)	0.0691 (9)
C2	0.7316 (4)	0.0085 (3)	−0.17484 (17)	0.0565 (7)
H2A	0.8471	−0.0380	−0.1550	0.068*
H2B	0.6376	−0.0620	−0.1842	0.068*
C3	0.6992 (3)	0.1069 (3)	−0.09873 (18)	0.0484 (7)
C4	0.6435 (4)	0.2412 (3)	−0.1174 (2)	0.0622 (8)
H4A	0.6228	0.2727	−0.1782	0.075*
C5	0.6171 (4)	0.3319 (3)	−0.0472 (3)	0.0716 (9)
H5A	0.5794	0.4227	−0.0613	0.086*
C6	0.6466 (4)	0.2874 (3)	0.0411 (2)	0.0685 (9)
H6A	0.6293	0.3486	0.0876	0.082*
C7	0.7028 (4)	0.1504 (3)	0.06461 (19)	0.0552 (8)
C8	0.7346 (4)	0.1027 (3)	0.1570 (2)	0.0675 (9)
H8A	0.7200	0.1635	0.2042	0.081*
C9	0.7857 (4)	−0.0299 (4)	0.1779 (2)	0.0685 (9)
H9A	0.8060	−0.0596	0.2391	0.082*
C10	0.8086 (4)	−0.1236 (3)	0.10760 (19)	0.0564 (7)
C11	0.7816 (3)	−0.0820 (3)	0.01827 (18)	0.0495 (7)
H11A	0.7979	−0.1448	−0.0275	0.059*
C12	0.7285 (3)	0.0571 (3)	−0.00618 (18)	0.0471 (7)
C13	0.8857 (4)	−0.3548 (3)	0.0708 (2)	0.0723 (9)
H13A	0.9233	−0.4415	0.1007	0.108*
H13B	0.9768	−0.3229	0.0380	0.108*
H13C	0.7733	−0.3677	0.0280	0.108*

Atomic displacement parameters (Å^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
O	0.0897 (16)	0.0689 (14)	0.0570 (12)	0.0037 (12)	0.0148 (11)	0.0088 (11)

N	0.177 (4)	0.085 (2)	0.062 (2)	−0.005 (2)	0.024 (2)	0.0025 (17)
C1	0.092 (2)	0.064 (2)	0.0507 (18)	−0.0084 (18)	0.0111 (16)	−0.0041 (16)
C2	0.0636 (19)	0.0525 (17)	0.0549 (17)	−0.0034 (14)	0.0150 (14)	−0.0016 (14)
C3	0.0441 (15)	0.0478 (16)	0.0553 (17)	−0.0072 (13)	0.0142 (13)	−0.0041 (13)
C4	0.065 (2)	0.0532 (18)	0.070 (2)	−0.0012 (15)	0.0164 (15)	0.0030 (16)
C5	0.074 (2)	0.0490 (18)	0.097 (3)	0.0035 (16)	0.0285 (19)	−0.0043 (18)
C6	0.073 (2)	0.057 (2)	0.084 (2)	−0.0069 (16)	0.0352 (18)	−0.0222 (17)
C7	0.0506 (17)	0.0552 (19)	0.0636 (19)	−0.0093 (14)	0.0210 (14)	−0.0135 (15)
C8	0.074 (2)	0.073 (2)	0.062 (2)	−0.0102 (18)	0.0293 (16)	−0.0217 (17)
C9	0.078 (2)	0.082 (2)	0.0499 (17)	−0.0113 (19)	0.0234 (16)	−0.0027 (17)
C10	0.0572 (18)	0.0583 (18)	0.0552 (18)	−0.0043 (14)	0.0141 (14)	0.0006 (15)
C11	0.0491 (16)	0.0508 (17)	0.0519 (17)	−0.0058 (13)	0.0182 (13)	−0.0061 (13)
C12	0.0384 (15)	0.0485 (16)	0.0565 (17)	−0.0098 (12)	0.0142 (12)	−0.0069 (13)
C13	0.078 (2)	0.0579 (19)	0.079 (2)	0.0039 (16)	0.0087 (18)	0.0028 (17)

Geometric parameters (Å, °)

O—C10	1.372 (3)	C6—H6A	0.9300
O—C13	1.419 (3)	C7—C8	1.413 (4)
N—C1	1.130 (4)	C7—C12	1.417 (3)
C1—C2	1.456 (4)	C8—C9	1.350 (4)
C2—C3	1.522 (3)	C8—H8A	0.9300
C2—H2A	0.9700	C9—C10	1.407 (4)
C2—H2B	0.9700	C9—H9A	0.9300
C3—C4	1.369 (4)	C10—C11	1.353 (4)
C3—C12	1.422 (3)	C11—C12	1.422 (4)
C4—C5	1.396 (4)	C11—H11A	0.9300
C4—H4A	0.9300	C13—H13A	0.9600
C5—C6	1.347 (4)	C13—H13B	0.9600
C5—H5A	0.9300	C13—H13C	0.9600
C6—C7	1.406 (4)		
C10—O—C13	117.4 (2)	C8—C7—C12	118.8 (3)
N—C1—C2	179.1 (4)	C9—C8—C7	120.9 (3)
C1—C2—C3	113.2 (2)	C9—C8—H8A	119.5
C1—C2—H2A	108.9	C7—C8—H8A	119.5
C3—C2—H2A	108.9	C8—C9—C10	120.4 (3)
C1—C2—H2B	108.9	C8—C9—H9A	119.8
C3—C2—H2B	108.9	C10—C9—H9A	119.8
H2A—C2—H2B	107.8	C11—C10—O	124.9 (3)
C4—C3—C12	119.7 (3)	C11—C10—C9	120.6 (3)
C4—C3—C2	121.6 (3)	O—C10—C9	114.5 (3)
C12—C3—C2	118.7 (2)	C10—C11—C12	120.5 (3)
C3—C4—C5	121.5 (3)	C10—C11—H11A	119.8
C3—C4—H4A	119.2	C12—C11—H11A	119.8
C5—C4—H4A	119.2	C7—C12—C3	118.3 (3)
C6—C5—C4	119.8 (3)	C7—C12—C11	118.7 (2)
C6—C5—H5A	120.1	C3—C12—C11	123.0 (2)
C4—C5—H5A	120.1	O—C13—H13A	109.5
C5—C6—C7	121.4 (3)	O—C13—H13B	109.5

C5—C6—H6A	119.3	H13A—C13—H13B	109.5
C7—C6—H6A	119.3	O—C13—H13C	109.5
C6—C7—C8	121.9 (3)	H13A—C13—H13C	109.5
C6—C7—C12	119.3 (3)	H13B—C13—H13C	109.5

Fig. 1

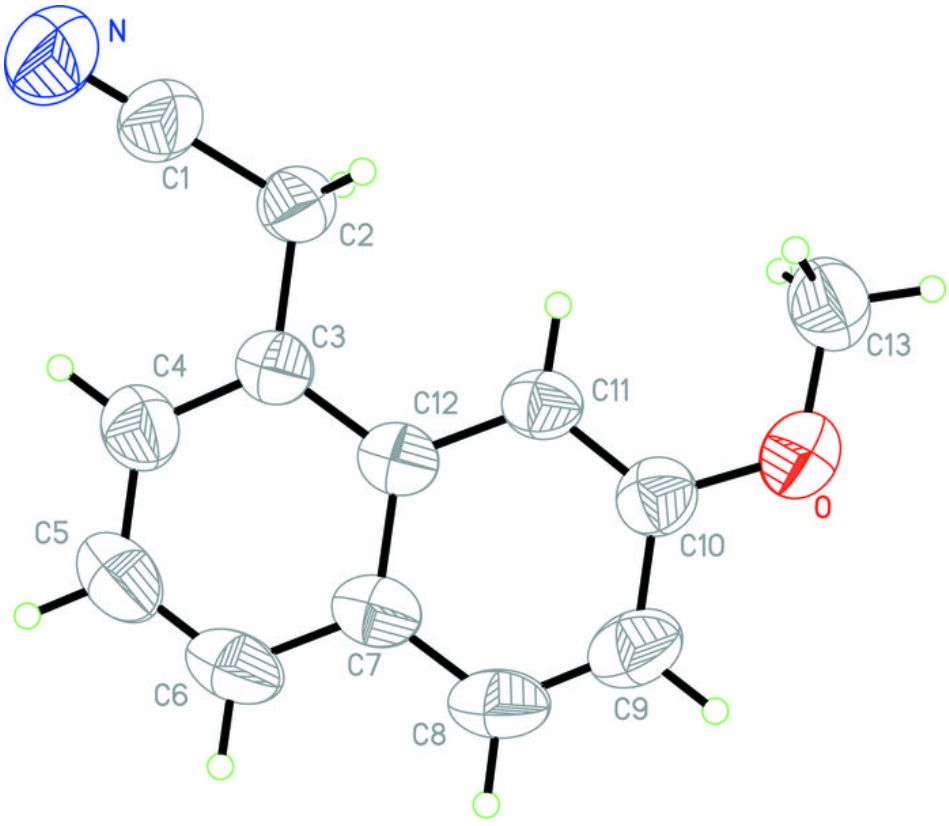
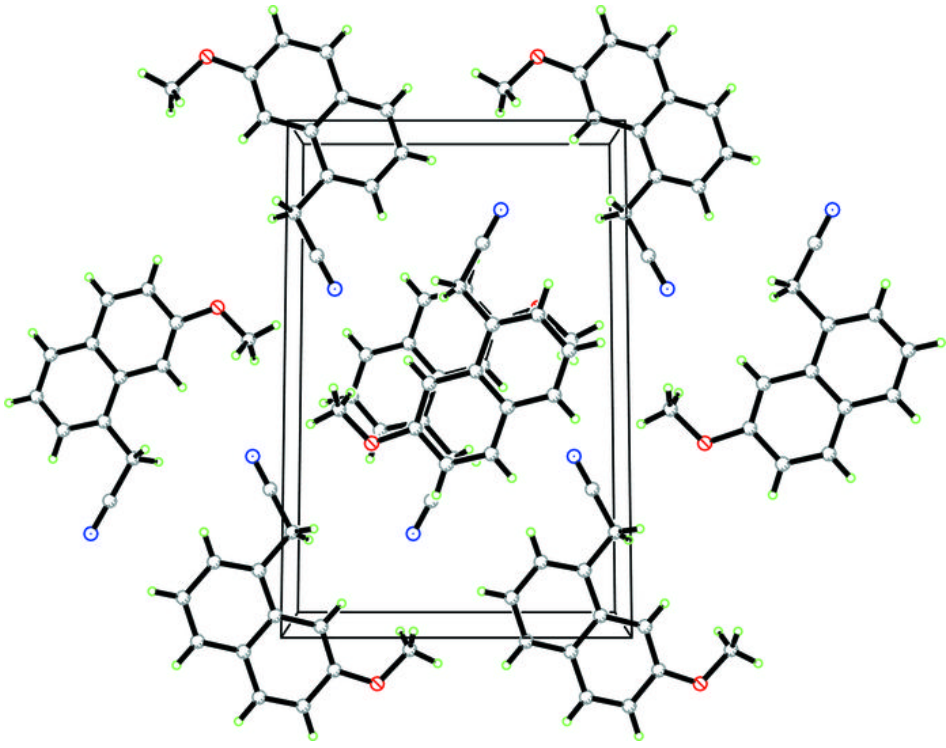


Fig. 2



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2-[(2-Hydroxy-4-methoxybenzylidene)-azaniumyl]benzoate monohydrate

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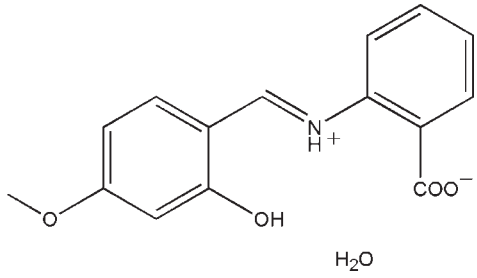
Key indicators: single-crystal X-ray study; T = 298 K; mean σ(C–C) = 0.003 Å; R factor = 0.043; wR factor = 0.122; data-to-parameter ratio = 13.8.

In the title compound, $C_{15}H_{13}NO_4\cdot H_2O$, the Schiff base exists in a zwitterionic form and a bifurcated intramolecular N—H···(O,O) hydrogen bond generates two S(6) rings. The dihedral angle between the two benzene rings is 25.8 (2)°. The crystal structure is stabilized by intermolecular O—H···O hydrogen bonds.

Related literature

For a related compound and background references to Schiff bases, see: Hang (2010). For related structures, see: Alpaslan *et al.* (2010*a*,*b*); Aritake *et al.* (2010); Bahron *et al.* (2010).



Experimental

Crystal data

$C_{15}H_{13}NO_4\cdot H_2O$
M_r = 289.28
Triclinic, $P\overline{1}$
a = 8.7240 (5) Å
b = 8.9252 (4) Å
c = 10.7967 (5) Å
α = 111.312 (2)°
β = 93.084 (3)°
γ = 117.500 (2)°
V = 669.24 (6) Å^3
Z = 2
Mo $K\alpha$ radiation
μ = 0.11 mm^{-1}
T = 298 K
0.30 × 0.28 × 0.28 mm

Data collection

Bruker SMART CCD diffractometer
Absorption correction: multi-scan (*SADABS*; Sheldrick, 1996)
T_{min} = 0.968, T_{max} = 0.970
4045 measured reflections
2810 independent reflections
1992 reflections with $I > 2\sigma(I)$
R_{int} = 0.013

Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.043
$wR(F^2)$ = 0.122
S = 1.08
2810 reflections
203 parameters
5 restraints
H atoms treated by a mixture of independent and constrained refinement
$\Delta\rho_{max}$ = 0.15 e Å^{-3}
$\Delta\rho_{min}$ = −0.18 e Å^{-3}

Table 1
Hydrogen-bond geometry (Å, °).

D—H···A	D—H	H···A	D···A	D—H···A
N1—H1···O1	0.91 (1)	2.14 (2)	2.7257 (17)	121 (2)
N1—H1···O2	0.91 (1)	1.88 (2)	2.6366 (17)	139 (2)
O1—H1*A*···O2^{i}	0.86 (1)	1.72 (1)	2.5675 (16)	165 (2)
O5—H5*A*···O3^{ii}	0.85 (1)	2.07 (1)	2.907 (2)	169 (2)
O5—H5*B*···O3	0.86 (1)	1.95 (1)	2.806 (2)	178 (2)

Symmetry codes: (i) $-x+1, -y, -z$; (ii) $-x+1, -y, -z+1$.

Data collection: *SMART* (Bruker, 2002); cell refinement: *SAINT* (Bruker, 2002); data reduction: *SAINT*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *SHELXTL* (Sheldrick, 2008); software used to prepare material for publication: *SHELXL97*.

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Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: HB5506).

References

Alpaslan, Y. B., Alpaslan, G., Agar, A. & Isik, S. (2010*b*). *Acta Cryst.* E**66**, o510.
Alpaslan, G., Macit, M., Büyükgüngör, O. & Erdönmez, A. (2010*a*). *Acta Cryst.* E**66**, o1178.
Aritake, Y., Watanabe, Y. & Akitsu, T. (2010). *Acta Cryst.* E**66**, o749.
Bahron, H., Bakar, S. N. A., Kassim, K., Yeap, C. S. & Fun, H.-K. (2010). *Acta Cryst.* E**66**, o883.
Bruker (2002). *SAINT* and *SMART*. Bruker AXS Inc., Madison, Wisconsin, USA.
Hang, Z.-X. (2010). *Acta Cryst.* E**66**, o1650.
Sheldrick, G. M. (1996). *SADABS*. University of Göttingen, Germany.
Sheldrick, G. M. (2008). *Acta Cryst.* A**64**, 112–122.

supplementary materials

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2-[(2-Hydroxy-4-methoxybenzylidene)azaniumyl]benzoate monohydrate

Z.-X. Hang, B. Dong and X.-W. Wang

Comment

The crystal structures of Schiff bases have been widely reported (Alpaslan *et al.*, 2010*a*,*b*; Aritake *et al.*, 2010; Bahron *et al.*, 2010). As a continuation of our work on Schiff bases (Hang, 2010), the present paper reports the title Schiff base compound.

The title compound contains a Schiff base molecule and a water molecule of crystallization (Fig. 1). There exist two intramolecular N–H···O hydrogen bonds in the molecule of the compound. The dihedral angle between the two benzene rings is 25.8 (2)°. The crystal structure is stabilized by intermolecular O–H···O hydrogen bonds (Table 1, Fig. 2).

Experimental

Equimolar quantities (1 mmol each) of 2-aminobenzoic acid and 4-methoxysalicylaldehyde were mixed and stirred in methanol for 2 h at ambient temperature. The resulting mixture was concentrated under recuced pressure. The residue, purified by washing with cold methanol and diethyl ether, afforded the pure product of the hydrazone compound. Colorless blocks of (I) were obtained by recrystallization of the product from 95% ethanol.

Refinement

The H atoms attached to N and O atoms were found from a difference Fourier map and refined isotropically, with N–H, O–H, and H···H distances restrained to 0.90 (1), 0.85 (1), and 1.37 (2) Å, respectively. The remaining H atoms were positioned geometrically and refined using a riding model with C–H = 0.93 and 0.96 Å, and U_{iso}(H) = 1.2 or 1.5U_{eq}(C).

Figures

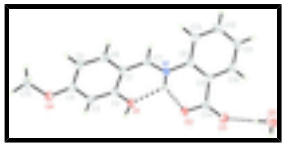


Fig. 1. Ellipsoid plot of the title compound at the 30% probability level. Hydrogen atoms are drawn as spheres of arbitrary radius. O–H···N hydrogen bond is drawn by a dashed line.

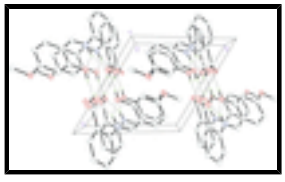


Fig. 2. The molecular packing of the title compound, viewed along the *c* axis. Hydrogen bonds are drawn as dashed lines.

2-[(2-Hydroxy-4-methoxybenzylidene)azaniumyl]benzoate monohydrate

Crystal data

$C_{15}H_{13}NO_4·H_2O$ $Z = 2$

M_r = 289.28	F(000) = 304
Triclinic, $P\overline{1}$	D_x = 1.436 Mg m^{-3}
Hall symbol: -P 1	Mo $K\alpha$ radiation, λ = 0.71073 Å
a = 8.7240 (5) Å	Cell parameters from 1109 reflections
b = 8.9252 (4) Å	θ = 2.6–26.2°
c = 10.7967 (5) Å	μ = 0.11 mm^{-1}
α = 111.312 (2)°	T = 298 K
β = 93.084 (3)°	Block, colorless
γ = 117.500 (2)°	0.30 × 0.28 × 0.28 mm
V = 669.24 (6) Å^3	

Data collection

Bruker SMART CCD diffractometer	2810 independent reflections
Radiation source: fine-focus sealed tube	1992 reflections with $I > 2\sigma(I)$
graphite	R_{int} = 0.013
ω scans	θ_{max} = 27.0°, θ_{min} = 2.1°
Absorption correction: multi-scan (*SADABS*; Sheldrick, 1996)	h = −6→11
T_{min} = 0.968, T_{max} = 0.970	k = −11→11
4045 measured reflections	l = −13→13

Refinement

Refinement on F^2	Primary atom site location: structure-invariant direct methods
Least-squares matrix: full	Secondary atom site location: difference Fourier map
$R[F^2 > 2\sigma(F^2)]$ = 0.043	Hydrogen site location: inferred from neighbouring sites
$wR(F^2)$ = 0.122	H atoms treated by a mixture of independent and constrained refinement
S = 1.08	$w = 1/[\sigma^2(F_o^2) + (0.0595P)^2 + 0.0161P]$ where $P = (F_o^2 + 2F_c^2)/3$
2810 reflections	$(\Delta/\sigma)_{max} < 0.001$
203 parameters	$\Delta\rho_{max}$ = 0.15 e Å^{-3}
5 restraints	$\Delta\rho_{min}$ = −0.18 e Å^{-3}

Special details

Geometry. All e.s.d.'s (except the e.s.d. in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell e.s.d.'s are taken into account individually in the estimation of e.s.d.'s in distances, angles and torsion angles; correlations between e.s.d.'s in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell e.s.d.'s is used for estimating e.s.d.'s involving l.s. planes.

Refinement. Refinement of F^2 against ALL reflections. The weighted R-factor wR and goodness of fit S are based on F^2, conventional R-factors R are based on F, with F set to zero for negative F^2. The threshold expression of $F^2 > \sigma(F^2)$ is used only for calculating R-

factors(gt) *etc*. and is not relevant to the choice of reflections for refinement. *R*-factors based on F^2 are statistically about twice as large as those based on *F*, and *R*- factors based on ALL data will be even larger.

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å^2)

	x	*y*	*z*	U_{iso}*/U_{eq}
N1	0.91763 (18)	0.38037 (19)	0.21508 (14)	0.0364 (3)
O1	0.65275 (15)	0.22394 (15)	−0.01717 (12)	0.0446 (3)
O2	0.65944 (15)	0.04540 (16)	0.17602 (12)	0.0491 (3)
O3	0.65792 (17)	−0.01967 (18)	0.35525 (13)	0.0611 (4)
O4	0.59187 (15)	0.62901 (16)	−0.17000 (12)	0.0459 (3)
O5	0.68483 (19)	0.0450 (2)	0.63223 (16)	0.0715 (5)
C1	0.8648 (2)	0.5485 (2)	0.10069 (16)	0.0356 (4)
C2	0.7092 (2)	0.3956 (2)	−0.00735 (16)	0.0341 (4)
C3	0.6248 (2)	0.4303 (2)	−0.09650 (16)	0.0364 (4)
H3	0.5244	0.3306	−0.1682	0.044*
C4	0.6884 (2)	0.6120 (2)	−0.07994 (16)	0.0371 (4)
C5	0.8428 (2)	0.7642 (2)	0.02468 (18)	0.0431 (4)
H5	0.8866	0.8859	0.0346	0.052*
C6	0.9272 (2)	0.7302 (2)	0.11142 (18)	0.0430 (4)
H6	1.0301	0.8309	0.1805	0.052*
C7	0.9597 (2)	0.5313 (2)	0.19950 (17)	0.0377 (4)
H7	1.0645	0.6404	0.2605	0.045*
C8	1.0163 (2)	0.3714 (2)	0.31829 (16)	0.0371 (4)
C9	0.9308 (2)	0.2225 (2)	0.35416 (16)	0.0381 (4)
C10	1.0311 (2)	0.2180 (3)	0.45585 (19)	0.0486 (5)
H10	0.9764	0.1205	0.4813	0.058*
C11	1.2094 (3)	0.3539 (3)	0.5200 (2)	0.0542 (5)
H11	1.2743	0.3465	0.5865	0.065*
C12	1.2902 (2)	0.5003 (3)	0.48467 (19)	0.0520 (5)
H12	1.4098	0.5937	0.5289	0.062*
C13	1.1959 (2)	0.5100 (2)	0.38442 (18)	0.0449 (4)
H13	1.2520	0.6092	0.3608	0.054*
C14	0.7341 (2)	0.0706 (2)	0.29112 (17)	0.0408 (4)
C15	0.6600 (3)	0.8098 (3)	−0.1699 (2)	0.0545 (5)
H15A	0.6832	0.9017	−0.0787	0.082*
H15B	0.5730	0.8035	−0.2330	0.082*
H15C	0.7693	0.8447	−0.1978	0.082*
H5B	0.675 (3)	0.022 (3)	0.5468 (12)	0.080*
H5A	0.591 (2)	0.046 (3)	0.648 (2)	0.080*
H1	0.8112 (18)	0.2707 (19)	0.166 (2)	0.080*
H1A	0.5504 (18)	0.145 (3)	−0.0780 (19)	0.080*

Atomic displacement parameters (Å^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
N1	0.0349 (8)	0.0350 (8)	0.0348 (7)	0.0161 (6)	0.0043 (6)	0.0143 (6)
O1	0.0436 (7)	0.0320 (6)	0.0458 (7)	0.0131 (5)	−0.0044 (5)	0.0157 (5)

O2	0.0443 (7)	0.0412 (7)	0.0466 (7)	0.0112 (5)	−0.0061 (6)	0.0213 (6)
O3	0.0562 (8)	0.0592 (8)	0.0482 (8)	0.0121 (7)	0.0074 (6)	0.0288 (7)
O4	0.0474 (7)	0.0416 (7)	0.0490 (7)	0.0213 (6)	0.0037 (6)	0.0238 (6)
O5	0.0548 (9)	0.0918 (11)	0.0524 (9)	0.0265 (9)	0.0044 (7)	0.0331 (9)
C1	0.0335 (8)	0.0346 (9)	0.0336 (8)	0.0154 (7)	0.0053 (7)	0.0135 (7)
C2	0.0337 (8)	0.0306 (8)	0.0361 (9)	0.0151 (7)	0.0096 (7)	0.0148 (7)
C3	0.0325 (8)	0.0326 (8)	0.0355 (9)	0.0127 (7)	0.0043 (7)	0.0127 (7)
C4	0.0375 (9)	0.0389 (9)	0.0383 (9)	0.0203 (8)	0.0106 (7)	0.0196 (8)
C5	0.0433 (10)	0.0328 (9)	0.0494 (10)	0.0155 (8)	0.0090 (8)	0.0202 (8)
C6	0.0397 (9)	0.0320 (9)	0.0419 (10)	0.0098 (7)	0.0028 (7)	0.0137 (7)
C7	0.0339 (9)	0.0342 (9)	0.0366 (9)	0.0135 (7)	0.0056 (7)	0.0131 (7)
C8	0.0375 (9)	0.0398 (9)	0.0324 (8)	0.0225 (8)	0.0060 (7)	0.0114 (7)
C9	0.0403 (9)	0.0407 (9)	0.0338 (9)	0.0239 (8)	0.0072 (7)	0.0133 (7)
C10	0.0517 (11)	0.0553 (11)	0.0456 (10)	0.0313 (10)	0.0098 (8)	0.0246 (9)
C11	0.0513 (11)	0.0727 (13)	0.0441 (11)	0.0381 (11)	0.0041 (9)	0.0241 (10)
C12	0.0379 (10)	0.0631 (12)	0.0454 (11)	0.0255 (9)	0.0019 (8)	0.0164 (10)
C13	0.0374 (9)	0.0456 (10)	0.0439 (10)	0.0192 (8)	0.0061 (8)	0.0157 (8)
C14	0.0441 (10)	0.0373 (9)	0.0395 (9)	0.0207 (8)	0.0068 (8)	0.0163 (8)
C15	0.0688 (13)	0.0461 (11)	0.0553 (12)	0.0315 (10)	0.0085 (10)	0.0275 (9)

Geometric parameters (Å, °)

N1—C7	1.301 (2)	C5—C6	1.360 (2)
N1—C8	1.420 (2)	C5—H5	0.9300
N1—H1	0.912 (9)	C6—H6	0.9300
O1—C2	1.3346 (18)	C7—H7	0.9300
O1—H1A	0.863 (10)	C8—C13	1.393 (2)
O2—C14	1.2625 (19)	C8—C9	1.400 (2)
O3—C14	1.237 (2)	C9—C10	1.391 (2)
O4—C4	1.3474 (18)	C9—C14	1.517 (2)
O4—C15	1.438 (2)	C10—C11	1.379 (3)
O5—H5B	0.858 (9)	C10—H10	0.9300
O5—H5A	0.851 (9)	C11—C12	1.375 (3)
C1—C6	1.408 (2)	C11—H11	0.9300
C1—C7	1.410 (2)	C12—C13	1.377 (2)
C1—C2	1.424 (2)	C12—H12	0.9300
C2—C3	1.384 (2)	C13—H13	0.9300
C3—C4	1.384 (2)	C15—H15A	0.9600
C3—H3	0.9300	C15—H15B	0.9600
C4—C5	1.403 (2)	C15—H15C	0.9600
C7—N1—C8	125.26 (14)	C13—C8—C9	120.22 (15)
C7—N1—H1	121.8 (13)	C13—C8—N1	120.48 (15)
C8—N1—H1	112.5 (13)	C9—C8—N1	119.29 (14)
C2—O1—H1A	109.4 (15)	C10—C9—C8	117.87 (16)
C4—O4—C15	118.67 (13)	C10—C9—C14	118.71 (16)
H5B—O5—H5A	105.0 (17)	C8—C9—C14	123.39 (15)
C6—C1—C7	117.43 (14)	C11—C10—C9	121.89 (18)
C6—C1—C2	117.96 (14)	C11—C10—H10	119.1
C7—C1—C2	124.60 (14)	C9—C10—H10	119.1

O1—C2—C3	123.29 (14)	C12—C11—C10	119.34 (17)
O1—C2—C1	117.29 (14)	C12—C11—H11	120.3
C3—C2—C1	119.42 (14)	C10—C11—H11	120.3
C2—C3—C4	120.63 (14)	C11—C12—C13	120.63 (17)
C2—C3—H3	119.7	C11—C12—H12	119.7
C4—C3—H3	119.7	C13—C12—H12	119.7
O4—C4—C3	115.29 (14)	C12—C13—C8	120.03 (17)
O4—C4—C5	123.87 (14)	C12—C13—H13	120.0
C3—C4—C5	120.83 (14)	C8—C13—H13	120.0
C6—C5—C4	118.62 (15)	O3—C14—O2	124.52 (16)
C6—C5—H5	120.7	O3—C14—C9	118.27 (15)
C4—C5—H5	120.7	O2—C14—C9	117.21 (15)
C5—C6—C1	122.51 (15)	O4—C15—H15A	109.5
C5—C6—H6	118.7	O4—C15—H15B	109.5
C1—C6—H6	118.7	H15A—C15—H15B	109.5
N1—C7—C1	127.47 (15)	O4—C15—H15C	109.5
N1—C7—H7	116.3	H15A—C15—H15C	109.5
C1—C7—H7	116.3	H15B—C15—H15C	109.5

Hydrogen-bond geometry (Å, °)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
N1—H1···O1	0.91 (1)	2.14 (2)	2.7257 (17)	121 (2)
N1—H1···O2	0.91 (1)	1.88 (2)	2.6366 (17)	139 (2)
O1—H1A···O2^{i}	0.86 (1)	1.72 (1)	2.5675 (16)	165 (2)
O5—H5A···O3^{ii}	0.85 (1)	2.07 (1)	2.907 (2)	169 (2)
O5—H5B···O3	0.86 (1)	1.95 (1)	2.806 (2)	178 (2)

Symmetry codes: (i) −*x*+1, −*y*, −*z*; (ii) −*x*+1, −*y*, −*z*+1.

Fig. 1

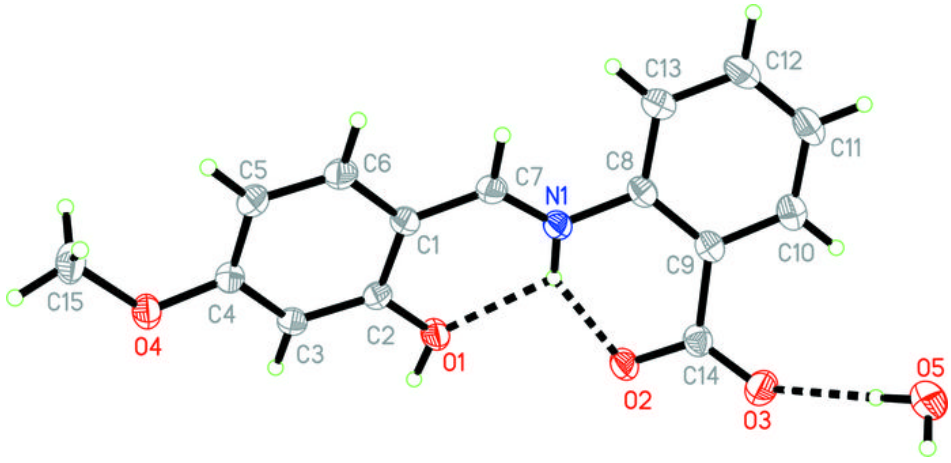
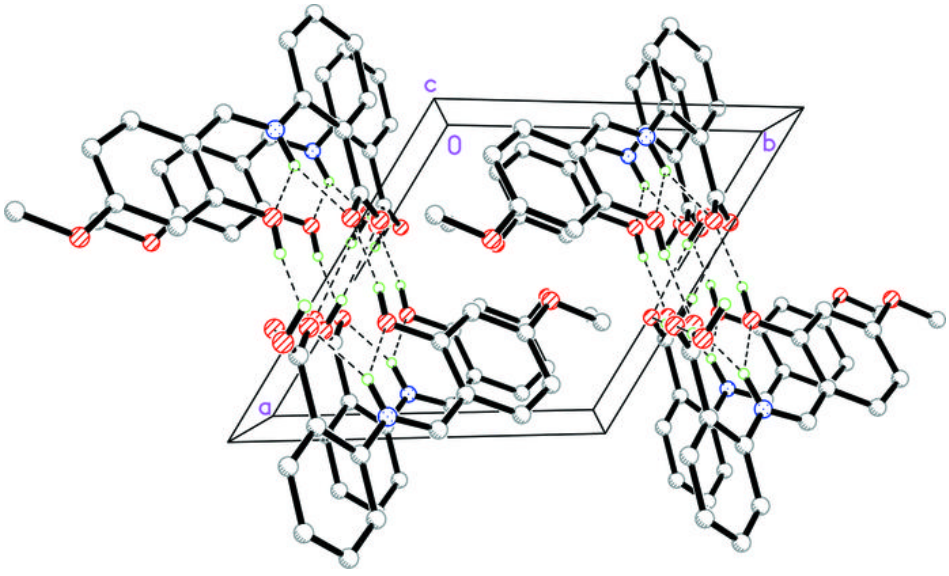


Fig. 2



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2,2,4-Trimethyl-7-nitro-2,3-dihydro-1*H*-1,5-benzodiazepin-5-ium perchlorate

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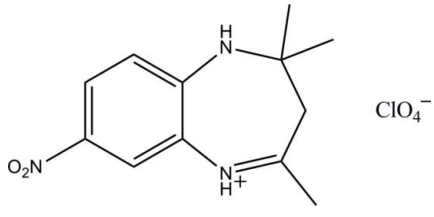
Key indicators: single-crystal X-ray study; T = 100 K; mean σ(C–C) = 0.004 Å; R factor = 0.046; wR factor = 0.138; data-to-parameter ratio = 15.8.

In the title molecular salt, $C_{12}H_{16}N_3O_2^+\cdot ClO_4^-$, the nitro group is close to being coplanar with the benzene ring [dihedral angle = 8.1 (3)°]. The seven-membered ring has a maximum deviation of 0.502 (3) Å at the C atom between the dimethyl- and methyl-substituted C atoms. In the crystal, the components are linked into infinite sheets lying parallel to the *bc* plane by N—H···O and C—H···O hydrogen bonds. A short O···N contact of 2.896 (4) Å occurs within the sheets and a short O···O contact of 2.608 (4) Å occurs between the sheets.

Related literature

For general background and applications of benzimidazole derivatives, see: Landquist (1984); Insuasty *et al.* (2010); Balakrishna & Kaboudin (2001); Ballo *et al.* (2010). For the preparation of the title compound, see: Grech *et al.* (1994). For ring conformations, see Cremer & Pople (1975). For the stability of the temperature controller used for the data collection, see: Cosier & Glazer (1986).



Experimental

Crystal data

$C_{12}H_{16}N_3O_2^+\cdot ClO_4^-$ M_r = 333.73
Monoclinic, $C2/c$
a = 21.046 (7) Å
b = 11.818 (3) Å
c = 15.636 (6) Å
β = 132.176 (9)°
V = 2882.0 (16) Å^3
Z = 8
Mo $K\alpha$ radiation
μ = 0.30 mm^{-1}
T = 100 K
0.30 × 0.17 × 0.08 mm

Data collection

Bruker APEXII DUO CCD diffractometer
Absorption correction: multi-scan (*SADABS*; Bruker, 2009)
T_{min} = 0.915, T_{max} = 0.976
24582 measured reflections
3323 independent reflections
2816 reflections with $I > 2\sigma(I)$
R_{int} = 0.066

Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.046
$wR(F^2)$ = 0.138
S = 1.05
3323 reflections
210 parameters
H atoms treated by a mixture of independent and constrained refinement
$\Delta\rho_{max}$ = 0.69 e Å^{-3}
$\Delta\rho_{min}$ = −0.69 e Å^{-3}

Table 1
Hydrogen-bond geometry (Å, °).

D—H···A	D—H	H···A	D···A	D—H···A
N1—H1*N*1···O6^{i}	0.80 (3)	2.15 (3)	2.941 (3)	173 (3)
N2—H1*N*2···O4	0.82 (5)	2.09 (4)	2.864 (4)	156 (4)
N2—H1*N*2···O4^{ii}	0.82 (5)	2.46 (5)	3.000 (4)	124 (3)
C3—H3*A*···O1^{i}	0.93	2.51	3.373 (3)	155
C11—H11*A*···O5^{i}	0.96	2.58	3.524 (3)	169
C11—H11*B*···O3^{iii}	0.96	2.45	3.396 (3)	168

Symmetry codes: (i) $x, -y+2, z-\frac{1}{2}$; (ii) $-x, y, -z+\frac{1}{2}$; (iii) $x, -y+1, z-\frac{1}{2}$.

Data collection: *APEX2* (Bruker, 2009); cell refinement: *SAINT* (Bruker, 2009); data reduction: *SAINT*; program(s) used to solve structure: *SHELXTL* (Sheldrick, 2008); program(s) used to refine structure: *SHELXTL*; molecular graphics: *SHELXTL*; software used to prepare material for publication: *SHELXTL* and *PLATON* (Spek, 2009).

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Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: HB5507).

References

Balakrishna, M. S. & Kaboudin, B. (2001). *Tetrahedron Lett.* **42**, 1127–1129.
Ballo, D., Ahabchane, N. H., Zouihri, H., Essassi, E. M. & Ng, S. W. (2010). *Acta Cryst.* E**66**, o1277.
Bruker (2009). *APEX2*, *SAINT* and *SADABS*. Bruker AXS Inc., Madison, Wisconsin, USA.
Cremer, D. & Pople, J. A. (1975). *J. Am. Chem. Soc.* **97**, 1354–1358.
Cosier, J. & Glazer, A. M. (1986). *J. Appl. Cryst.* **19**, 105–107.
Grech, O., Sakellariou, R. & Speziale, V. (1994). *J. Heterocycl. Chem.* **31**, 509–511.
Insuasty, B., Garcia, A., Abonia, R., Nogueras, M. & Cobo, J. (2010). *Molbank*, **2010**, M664.
Landquist, J. K. (1984). *Comprehensive Heterocyclic Chemistry*, edited by A. R. Katritzky & C. W. Rees, p. 166. Oxford: Pergamon.
Sheldrick, G. M. (2008). *Acta Cryst.* A**64**, 112–122.
Spek, A. L. (2009). *Acta Cryst.* D**65**, 148–155.

‡ Thomson Reuters ResearcherID: A-5523-2009.
§ Thomson Reuters ResearcherID: A-3561-2009.

supplementary materials

Acta Cryst. (2010). E**66**, o1845 [**doi:10.1107/S1600536810024475**]

2,2,4-Trimethyl-7-nitro-2,3-dihydro-1*H*-1,5-benzodiazepin-5-ium perchlorate

S. H. Mehdi, O. Sulaiman, R. M. Ghalib, C. S. Yeap and H.-K. Fun

Comment

Benzodiazepines are interesting compounds due to their wide range of biological activities (Landquist, 1984). Recently many methods have been employed for the synthesis of benzodiazepines derivatives (Insuasty *et al.*, 2010; Balakrishna & Kaboudin, 2001; Ballo *et al.*, 2010). Here we report the synthesis and the crystal structure of title compound.

The asymmetric unit of title compound (Fig. 1) consists of one the benzodiazepinium cation and one perchlorate anion. The nitro group is coplanar with the benzene ring with the dihedral angle of 8.1 (3)°. The seven-membered ring (N1/C1/C6/N2/C7–C9) have a maximum deviation of 0.502 (3) Å at atom C8. In the crystal structure, the molecules are linked into infinite two-dimensional planes parallel to *bc* plane by the intermolecular N—H···O, C—H···O hydrogen bonds (Table 1) and short O6···N3 interaction of 2.896 (4) Å. Short O2···O3 interaction of 2.608 (4) Å linked these planes into a three-dimensional framewrok (Fig. 2).

Experimental

A mixture of 4-nitro *o*-phenylenediamine (0.153 g m) and 4-hydroxy coumarin (0.162 g m) in molar ratio 1:1 was refluxed in a mixture of acetic acid-ethanol (1:1 *v*/*v*) for 3 h (Grech *et al.*, 1994). The solid settled in the reaction mixture was filtered and crystallized from ethanol to furnish brownish plates of the unexpected title compound, (I) (55%, m.p. 458 K).

Refinement

The N-bound hydrogen atoms were located from the difference Fourier map and were refined freely. The rest of hydrogen atoms were positioned geometrically [C–H = 0.93–0.97 Å] and refined using a riding model, with U_{iso}(H) = 1.2 or 1.5U_{eq}(C). Rotating-group model was applied for methyl groups.

Figures

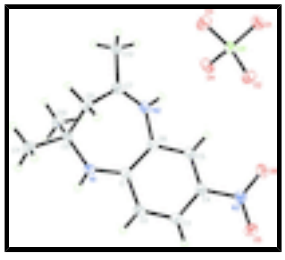


Fig. 1. The molecular structure of (I) with 50% probability ellipsoids for non-H atoms.

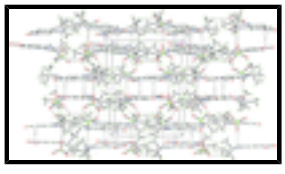


Fig. 2. The crystal packing of (I), viewed down the *c* axis, showing the components linked into a 3-D network. Intermolecular hydrogen bonds are shown as dashed lines.

2,2,4-Trimethyl-7-nitro-2,3-dihydro-1*H*-1,5-benzodiazepin-5-ium perchlorate

Crystal data

$C_{12}H_{16}N_3O_2^+ \cdot ClO_4^-$	$F(000) = 1392$
$M_r = 333.73$	$D_x = 1.538$ Mg m^{-3}
Monoclinic, *C*2/*c*	Mo *K*α radiation, λ = 0.71073 Å
Hall symbol: -C 2yc	Cell parameters from 7331 reflections
a = 21.046 (7) Å	θ = 2.2–29.8°
b = 11.818 (3) Å	μ = 0.30 mm^{-1}
c = 15.636 (6) Å	*T* = 100 K
β = 132.176 (9)°	Plate, brown
V = 2882.0 (16) Å^3	0.30 × 0.17 × 0.08 mm
Z = 8	

Data collection

Bruker APEXII DUO CCD diffractometer	3323 independent reflections
Radiation source: fine-focus sealed tube	2816 reflections with $I > 2\sigma(I)$
graphite	$R_{int} = 0.066$
φ and ω scans	$\theta_{max} = 27.5°$, $\theta_{min} = 2.2°$
Absorption correction: multi-scan (*SADABS*; Bruker, 2009)	$h = -27 \rightarrow 27$
$T_{min} = 0.915$, $T_{max} = 0.976$	$k = -15 \rightarrow 15$
24582 measured reflections	$l = -20 \rightarrow 20$

Refinement

Refinement on F^2	Primary atom site location: structure-invariant direct methods
Least-squares matrix: full	Secondary atom site location: difference Fourier map
$R[F^2 > 2\sigma(F^2)] = 0.046$	Hydrogen site location: inferred from neighbouring sites
$wR(F^2) = 0.138$	H atoms treated by a mixture of independent and constrained refinement
$S = 1.05$	$w = 1/[\sigma^2(F_o^2) + (0.0714P)^2 + 7.0069P]$ where $P = (F_o^2 + 2F_c^2)/3$
3323 reflections	$(\Delta/\sigma)_{max} < 0.001$
210 parameters	$\Delta\rho_{max} = 0.69$ e Å^{-3}
0 restraints	$\Delta\rho_{min} = -0.69$ e Å^{-3}

Special details

Experimental. The crystal was placed in the cold stream of an Oxford Cryosystems Cobra open-flow nitrogen cryostat (Cosier & Glazer, 1986) operating at 100.0 (1) K.

Geometry. All e.s.d.'s (except the e.s.d. in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell e.s.d.'s are taken into account individually in the estimation of e.s.d.'s in distances, angles and torsion angles; correlations between e.s.d.'s in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell e.s.d.'s is used for estimating e.s.d.'s involving l.s. planes.

Refinement. Refinement of F^2 against ALL reflections. The weighted *R*-factor *wR* and goodness of fit *S* are based on F^2, conventional *R*-factors *R* are based on *F*, with *F* set to zero for negative F^2. The threshold expression of $F^2 > \sigma(F^2)$ is used only for calculating *R*-factors(gt) *etc*. and is not relevant to the choice of reflections for refinement. *R*-factors based on F^2 are statistically about twice as large as those based on *F*, and *R*- factors based on ALL data will be even larger.

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å^2)

	x	*y*	*z*	U_{iso}*/U_{eq}
Cl1	0.15021 (3)	0.71202 (4)	0.49658 (4)	0.01923 (16)
O1	0.13150 (11)	0.68718 (14)	0.56727 (14)	0.0259 (4)
O2	0.19403 (11)	0.82394 (13)	0.52807 (14)	0.0245 (4)
O3	0.21587 (10)	0.62367 (14)	0.52533 (14)	0.0256 (4)
O4	0.07604 (10)	0.70691 (14)	0.37336 (13)	0.0234 (4)
O5	0.08273 (11)	1.21240 (13)	0.25797 (14)	0.0249 (4)
O6	0.09384 (11)	1.07773 (14)	0.36195 (13)	0.0246 (4)
N1	0.11724 (12)	0.79665 (15)	0.04379 (16)	0.0183 (4)
N2	0.10204 (12)	0.72103 (15)	0.21588 (15)	0.0176 (4)
N3	0.08881 (11)	1.11171 (16)	0.28211 (15)	0.0194 (4)
C1	0.10956 (12)	0.86625 (17)	0.10449 (16)	0.0152 (4)
C2	0.10763 (13)	0.98440 (18)	0.08478 (17)	0.0166 (4)
H2A	0.1127	1.0079	0.0328	0.020*
C3	0.09866 (12)	1.06450 (17)	0.13882 (17)	0.0166 (4)
H3A	0.0967	1.1410	0.1232	0.020*
C4	0.09241 (12)	1.02892 (18)	0.21822 (17)	0.0172 (4)
C5	0.09300 (13)	0.91616 (18)	0.24014 (17)	0.0172 (4)
H5A	0.0872	0.8945	0.2918	0.021*
C6	0.10220 (12)	0.83451 (17)	0.18541 (17)	0.0155 (4)
C7	0.14051 (13)	0.63366 (18)	0.21973 (17)	0.0180 (4)
C8	0.19130 (13)	0.64237 (19)	0.18564 (18)	0.0191 (4)
H8A	0.2184	0.5700	0.1991	0.023*
H8B	0.2364	0.6978	0.2347	0.023*
C9	0.13798 (13)	0.67632 (17)	0.05830 (17)	0.0165 (4)
C10	0.05645 (14)	0.60604 (19)	−0.02308 (18)	0.0216 (4)
H10A	0.0269	0.6260	−0.1015	0.032*
H10B	0.0200	0.6207	−0.0077	0.032*
H10C	0.0710	0.5271	−0.0113	0.032*
C11	0.19389 (15)	0.6604 (2)	0.0295 (2)	0.0234 (5)
H11A	0.1627	0.6841	−0.0485	0.035*
H11B	0.2091	0.5821	0.0377	0.035*
H11C	0.2450	0.7051	0.0813	0.035*
C12	0.13540 (15)	0.52362 (18)	0.26078 (19)	0.0222 (4)
H12A	0.0970	0.5305	0.2738	0.033*
H12B	0.1914	0.5028	0.3315	0.033*

H12C	0.1145	0.4665	0.2035	0.033*
H1N1	0.1130 (16)	0.826 (2)	−0.006 (2)	0.016 (6)*
H1N2	0.0798 (19)	0.715 (2)	0.243 (3)	0.030 (8)*

Atomic displacement parameters (Å^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Cl1	0.0193 (3)	0.0214 (3)	0.0170 (3)	−0.00116 (18)	0.0122 (2)	−0.00003 (18)
O1	0.0328 (9)	0.0283 (9)	0.0249 (8)	−0.0029 (7)	0.0228 (8)	0.0002 (7)
O2	0.0298 (8)	0.0167 (8)	0.0277 (8)	−0.0057 (6)	0.0195 (7)	−0.0039 (6)
O3	0.0230 (8)	0.0219 (8)	0.0289 (9)	0.0046 (6)	0.0162 (7)	0.0013 (7)
O4	0.0169 (7)	0.0350 (9)	0.0147 (8)	−0.0018 (6)	0.0091 (7)	−0.0003 (6)
O5	0.0305 (9)	0.0176 (8)	0.0253 (8)	0.0029 (6)	0.0183 (7)	0.0006 (6)
O6	0.0319 (9)	0.0267 (8)	0.0192 (8)	0.0026 (7)	0.0188 (7)	0.0002 (6)
N1	0.0239 (9)	0.0180 (9)	0.0167 (9)	0.0012 (7)	0.0152 (8)	0.0019 (7)
N2	0.0186 (8)	0.0192 (9)	0.0156 (8)	−0.0018 (7)	0.0118 (7)	0.0008 (7)
N3	0.0185 (8)	0.0213 (9)	0.0169 (8)	0.0015 (7)	0.0113 (7)	−0.0003 (7)
C1	0.0108 (8)	0.0192 (10)	0.0122 (9)	−0.0005 (7)	0.0064 (7)	−0.0002 (7)
C2	0.0147 (9)	0.0202 (10)	0.0134 (9)	−0.0019 (8)	0.0088 (8)	0.0006 (7)
C3	0.0132 (9)	0.0174 (10)	0.0136 (9)	−0.0013 (7)	0.0067 (8)	0.0001 (7)
C4	0.0146 (9)	0.0204 (10)	0.0141 (9)	0.0014 (8)	0.0087 (8)	−0.0008 (8)
C5	0.0144 (9)	0.0234 (10)	0.0127 (9)	0.0004 (8)	0.0086 (8)	0.0012 (8)
C6	0.0128 (9)	0.0179 (10)	0.0138 (9)	−0.0011 (7)	0.0082 (8)	0.0003 (7)
C7	0.0164 (9)	0.0205 (10)	0.0113 (9)	−0.0025 (8)	0.0069 (8)	0.0003 (7)
C8	0.0159 (9)	0.0220 (10)	0.0172 (10)	0.0016 (8)	0.0102 (8)	0.0027 (8)
C9	0.0162 (9)	0.0164 (9)	0.0174 (10)	0.0013 (8)	0.0115 (8)	0.0018 (8)
C10	0.0209 (10)	0.0231 (11)	0.0182 (10)	−0.0032 (8)	0.0121 (9)	−0.0019 (8)
C11	0.0254 (11)	0.0241 (11)	0.0289 (12)	0.0026 (9)	0.0215 (10)	0.0029 (9)
C12	0.0278 (11)	0.0181 (10)	0.0207 (10)	−0.0013 (9)	0.0163 (9)	0.0017 (8)

Geometric parameters (Å, °)

Cl1—O1	1.4310 (16)	C4—C5	1.374 (3)
Cl1—O4	1.4538 (16)	C5—C6	1.387 (3)
Cl1—O2	1.4941 (16)	C5—H5A	0.9300
Cl1—O3	1.5388 (17)	C7—C8	1.484 (3)
O5—N3	1.229 (2)	C7—C12	1.486 (3)
O6—N3	1.246 (2)	C8—C9	1.544 (3)
N1—C1	1.345 (3)	C8—H8A	0.9700
N1—C9	1.460 (3)	C8—H8B	0.9700
N1—H1N1	0.79 (3)	C9—C10	1.524 (3)
N2—C7	1.288 (3)	C9—C11	1.528 (3)
N2—C6	1.424 (3)	C10—H10A	0.9600
N2—H1N2	0.81 (3)	C10—H10B	0.9600
N3—C4	1.436 (3)	C10—H10C	0.9600
C1—C6	1.425 (3)	C11—H11A	0.9600
C1—C2	1.425 (3)	C11—H11B	0.9600
C2—C3	1.364 (3)	C11—H11C	0.9600
C2—H2A	0.9300	C12—H12A	0.9600

C3—C4	1.398 (3)	C12—H12B	0.9600
C3—H3A	0.9300	C12—H12C	0.9600
O1—Cl1—O4	114.06 (10)	N2—C7—C8	120.61 (19)
O1—Cl1—O2	110.86 (10)	N2—C7—C12	119.75 (19)
O4—Cl1—O2	110.46 (10)	C8—C7—C12	119.63 (19)
O1—Cl1—O3	107.10 (10)	C7—C8—C9	113.96 (17)
O4—Cl1—O3	108.27 (10)	C7—C8—H8A	108.8
O2—Cl1—O3	105.65 (10)	C9—C8—H8A	108.8
C1—N1—C9	130.62 (18)	C7—C8—H8B	108.8
C1—N1—H1N1	115.8 (19)	C9—C8—H8B	108.8
C9—N1—H1N1	113.4 (19)	H8A—C8—H8B	107.7
C7—N2—C6	128.90 (19)	N1—C9—C10	110.47 (17)
C7—N2—H1N2	118 (2)	N1—C9—C11	106.44 (17)
C6—N2—H1N2	113 (2)	C10—C9—C11	110.21 (18)
O5—N3—O6	122.75 (18)	N1—C9—C8	109.64 (17)
O5—N3—C4	119.30 (18)	C10—C9—C8	111.79 (17)
O6—N3—C4	117.94 (18)	C11—C9—C8	108.13 (17)
N1—C1—C6	127.01 (19)	C9—C10—H10A	109.5
N1—C1—C2	116.50 (18)	C9—C10—H10B	109.5
C6—C1—C2	116.48 (18)	H10A—C10—H10B	109.5
C3—C2—C1	122.82 (19)	C9—C10—H10C	109.5
C3—C2—H2A	118.6	H10A—C10—H10C	109.5
C1—C2—H2A	118.6	H10B—C10—H10C	109.5
C2—C3—C4	118.43 (19)	C9—C11—H11A	109.5
C2—C3—H3A	120.8	C9—C11—H11B	109.5
C4—C3—H3A	120.8	H11A—C11—H11B	109.5
C5—C4—C3	121.52 (19)	C9—C11—H11C	109.5
C5—C4—N3	118.88 (18)	H11A—C11—H11C	109.5
C3—C4—N3	119.55 (19)	H11B—C11—H11C	109.5
C4—C5—C6	120.17 (19)	C7—C12—H12A	109.5
C4—C5—H5A	119.9	C7—C12—H12B	109.5
C6—C5—H5A	119.9	H12A—C12—H12B	109.5
C5—C6—N2	114.60 (18)	C7—C12—H12C	109.5
C5—C6—C1	120.55 (19)	H12A—C12—H12C	109.5
N2—C6—C1	124.83 (18)	H12B—C12—H12C	109.5
C9—N1—C1—C6	−14.5 (3)	C7—N2—C6—C1	31.3 (3)
C9—N1—C1—C2	166.30 (19)	N1—C1—C6—C5	−178.74 (19)
N1—C1—C2—C3	178.87 (18)	C2—C1—C6—C5	0.5 (3)
C6—C1—C2—C3	−0.5 (3)	N1—C1—C6—N2	0.2 (3)
C1—C2—C3—C4	1.0 (3)	C2—C1—C6—N2	179.44 (18)
C2—C3—C4—C5	−1.6 (3)	C6—N2—C7—C8	−2.4 (3)
C2—C3—C4—N3	175.77 (18)	C6—N2—C7—C12	176.47 (19)
O5—N3—C4—C5	−175.37 (19)	N2—C7—C8—C9	−62.3 (3)
O6—N3—C4—C5	6.1 (3)	C12—C7—C8—C9	118.8 (2)
O5—N3—C4—C3	7.1 (3)	C1—N1—C9—C10	97.6 (2)
O6—N3—C4—C3	−171.40 (18)	C1—N1—C9—C11	−142.8 (2)
C3—C4—C5—C6	1.7 (3)	C1—N1—C9—C8	−26.1 (3)
N3—C4—C5—C6	−175.70 (18)	C7—C8—C9—N1	74.8 (2)

C4—C5—C6—N2	179.81 (18)	C7—C8—C9—C10	−48.0 (2)
C4—C5—C6—C1	−1.2 (3)	C7—C8—C9—C11	−169.51 (18)
C7—N2—C6—C5	−149.7 (2)		

Hydrogen-bond geometry (Å, °)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
N1—H1N1···O6^{i}	0.80 (3)	2.15 (3)	2.941 (3)	173 (3)
N2—H1N2···O4	0.82 (5)	2.09 (4)	2.864 (4)	156 (4)
N2—H1N2···O4^{ii}	0.82 (5)	2.46 (5)	3.000 (4)	124 (3)
C3—H3A···O1^{i}	0.93	2.51	3.373 (3)	155
C11—H11A···O5^{i}	0.96	2.58	3.524 (3)	169
C11—H11B···O3^{iii}	0.96	2.45	3.396 (3)	168

Symmetry codes: (i) *x*, −*y*+2, *z*−1/2; (ii) −*x*, *y*, −*z*+1/2; (iii) *x*, −*y*+1, *z*−1/2.

Fig. 1

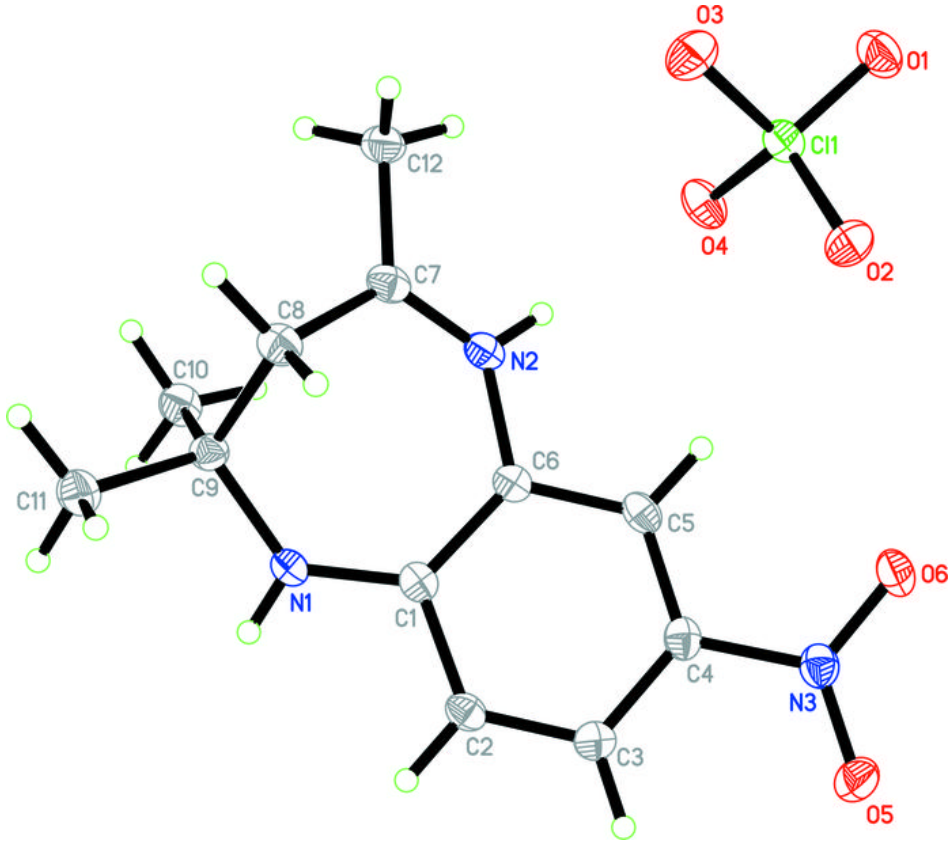
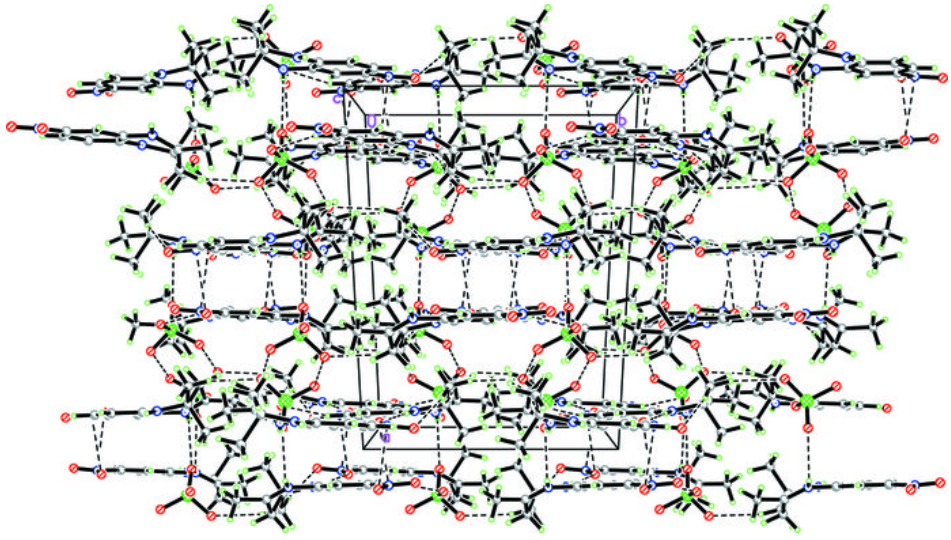


Fig. 2



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1,3,3-Trimethyl-1,2,3,4-tetrahydropyrido[1,2-*a*]benzimidazol-1-ol

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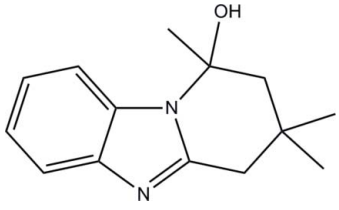
Key indicators: single-crystal X-ray study; T = 100 K; mean σ(C–C) = 0.002 Å; R factor = 0.046; wR factor = 0.117; data-to-parameter ratio = 15.9.

In the title compound, $C_{14}H_{18}N_2O$, the benzimidazole grouping is close to planar, with a maximum deviation of 0.042 Å; the six-membered non-aromatic ring adopts an envelope conformation. In the crystal structure, molecules are linked into infinite sheets lying parallel to the *bc* plane by O—H···N and C—H···O hydrogen bonds.

Related literature

For applications of benzimidazole derivatives, see: Horton *et al.* (2003); Insuasty *et al.* (2008*a*,*b*). For the preparation of the title compound, see: Grech *et al.* (1994). For ring conformations, see Cremer & Pople (1975). For the stability of the temperature controller used for the data collection, see: Cosier & Glazer (1986).



Experimental

Crystal data

$C_{14}H_{18}N_2O$
M_r = 230.30
Monoclinic, $P2_1/c$
a = 9.615 (5) Å
b = 8.194 (4) Å
c = 15.965 (8) Å
β = 99.601 (12)°
V = 1240.2 (11) Å^3
Z = 4
Mo $K\alpha$ radiation
μ = 0.08 mm^{-1}
T = 100 K
0.38 × 0.12 × 0.07 mm

Data collection

Bruker APEXII DUO CCD diffractometer
Absorption correction: multi-scan (*SADABS*; Bruker, 2009)
T_{min} = 0.971, T_{max} = 0.995
13460 measured reflections
3597 independent reflections
2612 reflections with $I > 2\sigma(I)$
R_{int} = 0.052

Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.046
$wR(F^2)$ = 0.117
S = 1.02
3597 reflections
226 parameters
All H-atom parameters refined
$\Delta\rho_{max}$ = 0.33 e Å^{-3}
$\Delta\rho_{min}$ = −0.25 e Å^{-3}

Table 1
Hydrogen-bond geometry (Å, °).

D—H···A	D—H	H···A	D···A	D—H···A
O1—H1*O*1···N1^{i}	0.97 (2)	1.84 (2)	2.803 (2)	174 (2)
C5—H5*A*···O1^{ii}	0.962 (15)	2.499 (15)	3.216 (2)	131.3 (11)

Symmetry codes: (i) $-x+1, y+\frac{1}{2}, -z+\frac{1}{2}$; (ii) $-x+1, -y+1, -z$.

Data collection: *APEX2* (Bruker, 2009); cell refinement: *SAINT* (Bruker, 2009); data reduction: *SAINT*; program(s) used to solve structure: *SHELXTL* (Sheldrick, 2008); program(s) used to refine structure: *SHELXTL*; molecular graphics: *SHELXTL*; software used to prepare material for publication: *SHELXTL* and *PLATON* (Spek, 2009).

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Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: HB5508).

References

Bruker (2009). *APEX2*, *SAINT* and *SADABS*. Bruker AXS Inc., Madison, Wisconsin, USA.
Cosier, J. & Glazer, A. M. (1986). *J. Appl. Cryst.* **19**, 105–107.
Cremer, D. & Pople, J. A. (1975). *J. Am. Chem. Soc.* **97**, 1354–1358.
Grech, O., Sakellariou, R. & Speziale, V. (1994). *J. Heterocycl. Chem.* **31**, 509–511.
Horton, D. A., Bourne, G. T. & Smythe, M. L. (2003). *Chem. Rev.* **103**, 893–930.
Insuasty, B., Orozco, F., Lizarazo, C., Quiroga, J., Abonía, R., Hursthouse, M., Nogueras, M. & Cobo, J. (2008*a*). *Bioorg. Med. Chem.* **16**, 8492–8500.
Insuasty, B., Orozco, F., Quiroga, J., Abonía, R., Nogueras, M. & Cobo, J. (2008*b*). *Eur. J. Med. Chem.* **43**, 1955–1962.
Sheldrick, G. M. (2008). *Acta Cryst.* A**64**, 112–122.
Spek, A. L. (2009). *Acta Cryst.* D**65**, 148–155.

‡ Thomson Reuters ResearcherID: A-5523-2009.
§ Thomson Reuters ResearcherID: A-3561-2009.

supplementary materials

Acta Cryst. (2010). E**66**, o1832 [**doi:10.1107/S1600536810024487**]

1,3,3-Trimethyl-1,2,3,4-tetrahydropyrido[1,2-*a*]benzimidazol-1-ol

S. H. Mehdi, R. Hashim, R. M. Ghalib, C. S. Yeap and H.-K. Fun

Comment

Benzimidazole derivatives are an important class of bioactive molecules and are well known due to their wide range of pharmacological activities as an anti-ulcers, anti-hypertensive, anti-viral, anti-fungal, anti-cancer, and anti-histaminic (Horton *et al.*, 2003; Insuasty *et al.*, 2008*a*, *b*) agents. Here we report the synthesis and the crystal structure of title compound.

In the title compound (Fig. 1), the benzimidazole group is essentially coplanar (N1/C1–C6/N2/C11) with the maximum deviation of 0.042 Å at atom C6. The N2/C7–C11 ring adopts an envelope conformation with Q=0.4933 (14) Å, θ=52.81 (15)° and φ=182.3 (2)° (Cremer & Pople, 1975).

In the crystal structure, the molecules are linked into infinite two-dimensional planes parallel to *bc* plane by the intermolecular O1—H1O1···N1 and C5—H5A···O1 hydrogen bonds (Fig. 2, Table 1).

Experimental

A mixture of *o*-phenylenediamine (0.108 g m) and dimedone (0.140 g m) in molar ratio 1:1 was refluxed in a mixture of acetic acid-ethanol (1:1 *v*/*v*) for 3 h (Grech *et al.*, 1994). The reaction mixture was dried on rotavapor at low pressure and further fractionated successively with diethyl ether, chloroform and ethanol. The ethanol fraction was dried on rotavapor and the dry mass so obtained was crystallized in methanol:chloroform (1:1) mixture to give yellow needles of (I) (55%, m.p. 451 K).

Refinement

All hydrogen atoms were located from the difference Fourier map and was refined freely.

Figures

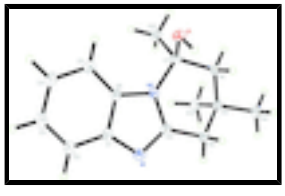


Fig. 1. The molecular structure of (I) with 50% probability ellipsoids for non-H atoms.

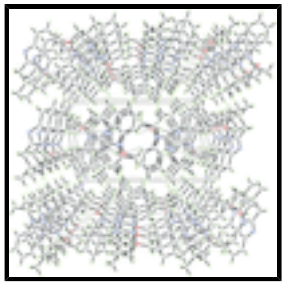


Fig. 2. The crystal packing of (I), viewed down the *b* axis, showing the molecules linked into sheets lying parallel to *bc*. Intermolecular hydrogen bonds are shown as dashed lines.

1,3,3-Trimethyl-1,2,3,4-tetrahydropyrido[1,2-*a*]benzimidazol-1-ol

Crystal data

$C_{14}H_{18}N_2O$	$F(000) = 496$
$M_r = 230.30$	$D_x = 1.233$ Mg m^{-3}
Monoclinic, $P2_1/c$	Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å
Hall symbol: -P 2ybc	Cell parameters from 2162 reflections
$a = 9.615$ (5) Å	$\theta = 3.1$–$29.6°$
$b = 8.194$ (4) Å	$\mu = 0.08$ mm^{-1}
$c = 15.965$ (8) Å	$T = 100$ K
$\beta = 99.601$ (12)°	Needle, yellow
$V = 1240.2$ (11) Å^3	0.38 × 0.12 × 0.07 mm
$Z = 4$	

Data collection

Bruker APEXII DUO CCD diffractometer	3597 independent reflections
Radiation source: fine-focus sealed tube	2612 reflections with $I > 2\sigma(I)$
graphite	$R_{int} = 0.052$
φ and ω scans	$\theta_{max} = 30.0°$, $\theta_{min} = 2.6°$
Absorption correction: multi-scan (*SADABS*; Bruker, 2009)	$h = -13 \rightarrow 13$
$T_{min} = 0.971$, $T_{max} = 0.995$	$k = -11 \rightarrow 10$
13460 measured reflections	$l = -22 \rightarrow 18$

Refinement

Refinement on F^2	Primary atom site location: structure-invariant direct methods
Least-squares matrix: full	Secondary atom site location: difference Fourier map
$R[F^2 > 2\sigma(F^2)] = 0.046$	Hydrogen site location: inferred from neighbouring sites
$wR(F^2) = 0.117$	All H-atom parameters refined
$S = 1.02$	$w = 1/[\sigma^2(F_o^2) + (0.0528P)^2 + 0.2357P]$ where $P = (F_o^2 + 2F_c^2)/3$
3597 reflections	$(\Delta/\sigma)_{max} < 0.001$

226 parameters	$\Delta\rho_{max} = 0.33$ e Å^{-3}
0 restraints	$\Delta\rho_{min} = -0.25$ e Å^{-3}

Special details

Experimental. The crystal was placed in the cold stream of an Oxford Cryosystems Cobra open-flow nitrogen cryostat (Cosier & Glazer, 1986) operating at 100.0 (1) K.

Geometry. All e.s.d.'s (except the e.s.d. in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell e.s.d.'s are taken into account individually in the estimation of e.s.d.'s in distances, angles and torsion angles; correlations between e.s.d.'s in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell e.s.d.'s is used for estimating e.s.d.'s involving l.s. planes.

Refinement. Refinement of F^2 against ALL reflections. The weighted *R*-factor *wR* and goodness of fit *S* are based on F^2, conventional *R*-factors *R* are based on *F*, with *F* set to zero for negative F^2. The threshold expression of $F^2 > \sigma(F^2)$ is used only for calculating *R*-factors(gt) *etc*. and is not relevant to the choice of reflections for refinement. *R*-factors based on F^2 are statistically about twice as large as those based on *F*, and *R*- factors based on ALL data will be even larger.

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å^2)

	x	*y*	*z*	U_{iso}*/U_{eq}
O1	0.65445 (9)	0.44319 (11)	0.12156 (6)	0.0178 (2)
N1	0.40305 (10)	0.05504 (14)	0.22183 (7)	0.0176 (2)
N2	0.54560 (10)	0.19700 (13)	0.15038 (6)	0.0148 (2)
C1	0.32424 (12)	0.11377 (16)	0.14618 (8)	0.0160 (3)
C2	0.17999 (13)	0.09810 (17)	0.11474 (9)	0.0199 (3)
C3	0.12707 (13)	0.17745 (18)	0.03945 (9)	0.0215 (3)
C4	0.21420 (13)	0.27314 (18)	−0.00320 (8)	0.0199 (3)
C5	0.35783 (13)	0.28830 (17)	0.02639 (8)	0.0179 (3)
C6	0.41136 (12)	0.20479 (15)	0.10110 (8)	0.0152 (2)
C7	0.67647 (12)	0.27365 (16)	0.13019 (8)	0.0153 (3)
C8	0.79944 (12)	0.23815 (16)	0.20337 (8)	0.0164 (3)
C9	0.79390 (12)	0.07980 (16)	0.25468 (8)	0.0165 (3)
C10	0.65512 (13)	0.08393 (18)	0.29055 (8)	0.0186 (3)
C11	0.53240 (12)	0.10891 (16)	0.22157 (8)	0.0157 (3)
C12	0.70543 (14)	0.21133 (19)	0.04460 (9)	0.0208 (3)
C13	0.80018 (14)	−0.07437 (18)	0.20160 (9)	0.0218 (3)
C14	0.91813 (13)	0.08019 (19)	0.32872 (9)	0.0224 (3)
H1A	0.0269 (15)	0.1672 (18)	0.0155 (9)	0.020 (4)*
H2A	0.1203 (16)	0.033 (2)	0.1467 (10)	0.026 (4)*
H4A	0.1727 (15)	0.3345 (18)	−0.0553 (9)	0.016 (4)*
H5A	0.4140 (15)	0.3569 (19)	−0.0037 (9)	0.017 (4)*
H8A	0.8923 (16)	0.241 (2)	0.1794 (10)	0.025 (4)*
H8B	0.8028 (15)	0.334 (2)	0.2438 (10)	0.025 (4)*
H10A	0.6384 (15)	−0.0185 (19)	0.3209 (9)	0.018 (4)*
H10B	0.6583 (16)	0.177 (2)	0.3319 (10)	0.024 (4)*
H12A	0.7260 (17)	0.095 (2)	0.0457 (11)	0.030 (4)*
H12B	0.7853 (17)	0.279 (2)	0.0300 (11)	0.032 (4)*
H12C	0.6228 (18)	0.233 (2)	−0.0008 (11)	0.034 (5)*

H13A	0.7168 (16)	−0.0878 (19)	0.1571 (10)	0.024 (4)*
H13B	0.8059 (15)	−0.171 (2)	0.2371 (10)	0.024 (4)*
H13C	0.8856 (17)	−0.074 (2)	0.1725 (11)	0.032 (4)*
H14A	0.9187 (16)	0.180 (2)	0.3648 (10)	0.028 (4)*
H14B	0.9107 (17)	−0.017 (2)	0.3658 (11)	0.034 (5)*
H14C	1.0108 (18)	0.082 (2)	0.3068 (11)	0.036 (5)*
H1O1	0.640 (2)	0.487 (3)	0.1756 (13)	0.050 (6)*

Atomic displacement parameters (Å^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
O1	0.0215 (4)	0.0149 (5)	0.0175 (5)	0.0005 (3)	0.0047 (3)	0.0024 (4)
N1	0.0167 (5)	0.0195 (6)	0.0166 (5)	−0.0010 (4)	0.0028 (4)	0.0018 (4)
N2	0.0138 (4)	0.0170 (5)	0.0130 (5)	−0.0010 (4)	0.0009 (4)	0.0014 (4)
C1	0.0169 (5)	0.0153 (6)	0.0158 (6)	0.0004 (4)	0.0024 (4)	−0.0007 (5)
C2	0.0155 (5)	0.0206 (7)	0.0232 (7)	−0.0010 (5)	0.0020 (5)	−0.0017 (6)
C3	0.0171 (6)	0.0229 (7)	0.0229 (7)	0.0009 (5)	−0.0014 (5)	−0.0041 (6)
C4	0.0208 (6)	0.0210 (7)	0.0164 (6)	0.0036 (5)	−0.0018 (5)	−0.0009 (5)
C5	0.0202 (6)	0.0173 (7)	0.0157 (6)	0.0013 (5)	0.0014 (5)	0.0001 (5)
C6	0.0148 (5)	0.0160 (6)	0.0144 (6)	0.0001 (4)	0.0010 (4)	−0.0019 (5)
C7	0.0154 (5)	0.0150 (6)	0.0157 (6)	−0.0013 (4)	0.0036 (4)	0.0021 (5)
C8	0.0157 (5)	0.0162 (6)	0.0167 (6)	−0.0007 (4)	0.0007 (4)	0.0004 (5)
C9	0.0145 (5)	0.0169 (6)	0.0170 (6)	0.0002 (4)	0.0000 (4)	0.0018 (5)
C10	0.0176 (5)	0.0229 (7)	0.0147 (6)	−0.0007 (5)	0.0012 (4)	0.0041 (6)
C11	0.0168 (5)	0.0153 (6)	0.0150 (6)	0.0006 (4)	0.0030 (4)	0.0017 (5)
C12	0.0223 (6)	0.0249 (8)	0.0164 (6)	0.0014 (5)	0.0067 (5)	−0.0008 (6)
C13	0.0230 (6)	0.0177 (7)	0.0241 (7)	0.0018 (5)	0.0017 (5)	0.0002 (6)
C14	0.0185 (6)	0.0244 (8)	0.0220 (7)	0.0007 (5)	−0.0030 (5)	0.0038 (6)

Geometric parameters (Å, °)

O1—C7	1.4085 (17)	C8—C9	1.5400 (19)
O1—H1O1	0.96 (2)	C8—H8A	1.029 (15)
N1—C11	1.3203 (16)	C8—H8B	1.012 (16)
N1—C1	1.3997 (17)	C9—C13	1.528 (2)
N2—C11	1.3700 (17)	C9—C14	1.5340 (18)
N2—C6	1.3965 (16)	C9—C10	1.5378 (18)
N2—C7	1.4890 (16)	C10—C11	1.4878 (18)
C1—C2	1.4000 (18)	C10—H10A	0.995 (16)
C1—C6	1.4060 (18)	C10—H10B	1.004 (16)
C2—C3	1.387 (2)	C12—H12A	0.976 (18)
C2—H2A	0.988 (16)	C12—H12B	1.006 (17)
C3—C4	1.404 (2)	C12—H12C	0.998 (17)
C3—H1A	0.979 (14)	C13—H13A	0.984 (16)
C4—C5	1.3886 (18)	C13—H13B	0.967 (17)
C4—H4A	0.997 (15)	C13—H13C	1.009 (17)
C5—C6	1.3968 (18)	C14—H14A	1.000 (17)
C5—H5A	0.961 (15)	C14—H14B	1.001 (18)
C7—C12	1.5271 (19)	C14—H14C	1.010 (17)

C7—C8	1.5450 (18)		
C7—O1—H1O1	108.6 (12)	H8A—C8—H8B	106.5 (12)
C11—N1—C1	104.90 (11)	C13—C9—C14	109.35 (11)
C11—N2—C6	106.65 (10)	C13—C9—C10	109.98 (11)
C11—N2—C7	126.90 (10)	C14—C9—C10	109.00 (11)
C6—N2—C7	126.43 (10)	C13—C9—C8	113.17 (11)
N1—C1—C2	129.74 (12)	C14—C9—C8	108.46 (11)
N1—C1—C6	109.93 (11)	C10—C9—C8	106.78 (10)
C2—C1—C6	120.29 (12)	C11—C10—C9	110.96 (11)
C3—C2—C1	117.79 (12)	C11—C10—H10A	107.7 (8)
C3—C2—H2A	122.8 (9)	C9—C10—H10A	112.6 (8)
C1—C2—H2A	119.4 (9)	C11—C10—H10B	108.4 (9)
C2—C3—C4	121.33 (12)	C9—C10—H10B	109.2 (9)
C2—C3—H1A	119.5 (9)	H10A—C10—H10B	108.0 (12)
C4—C3—H1A	119.1 (9)	N1—C11—N2	113.35 (11)
C5—C4—C3	121.67 (13)	N1—C11—C10	125.66 (12)
C5—C4—H4A	118.4 (8)	N2—C11—C10	120.98 (11)
C3—C4—H4A	119.9 (8)	C7—C12—H12A	112.3 (10)
C4—C5—C6	116.79 (12)	C7—C12—H12B	106.4 (10)
C4—C5—H5A	119.5 (9)	H12A—C12—H12B	112.6 (14)
C6—C5—H5A	123.7 (9)	C7—C12—H12C	110.3 (10)
N2—C6—C5	132.67 (11)	H12A—C12—H12C	108.8 (14)
N2—C6—C1	105.13 (11)	H12B—C12—H12C	106.2 (14)
C5—C6—C1	122.06 (11)	C9—C13—H13A	112.9 (9)
O1—C7—N2	108.58 (10)	C9—C13—H13B	110.6 (9)
O1—C7—C12	106.80 (10)	H13A—C13—H13B	106.9 (13)
N2—C7—C12	109.84 (10)	C9—C13—H13C	111.5 (10)
O1—C7—C8	110.08 (10)	H13A—C13—H13C	107.1 (13)
N2—C7—C8	108.95 (10)	H13B—C13—H13C	107.4 (13)
C12—C7—C8	112.51 (11)	C9—C14—H14A	111.9 (9)
C9—C8—C7	118.09 (10)	C9—C14—H14B	109.3 (10)
C9—C8—H8A	108.9 (9)	H14A—C14—H14B	107.6 (13)
C7—C8—H8A	108.5 (9)	C9—C14—H14C	110.6 (10)
C9—C8—H8B	108.3 (9)	H14A—C14—H14C	105.5 (13)
C7—C8—H8B	106.0 (9)	H14B—C14—H14C	111.8 (14)
C11—N1—C1—C2	−177.80 (14)	C6—N2—C7—C12	−58.00 (16)
C11—N1—C1—C6	−0.14 (15)	C11—N2—C7—C8	0.12 (17)
N1—C1—C2—C3	176.20 (13)	C6—N2—C7—C8	178.34 (11)
C6—C1—C2—C3	−1.2 (2)	O1—C7—C8—C9	148.09 (11)
C1—C2—C3—C4	−1.3 (2)	N2—C7—C8—C9	29.14 (15)
C2—C3—C4—C5	2.2 (2)	C12—C7—C8—C9	−92.92 (14)
C3—C4—C5—C6	−0.5 (2)	C7—C8—C9—C13	64.20 (14)
C11—N2—C6—C5	173.80 (14)	C7—C8—C9—C14	−174.28 (11)
C7—N2—C6—C5	−4.7 (2)	C7—C8—C9—C10	−56.95 (15)
C11—N2—C6—C1	−1.75 (14)	C13—C9—C10—C11	−68.67 (15)
C7—N2—C6—C1	179.73 (11)	C14—C9—C10—C11	171.46 (11)
C4—C5—C6—N2	−176.96 (13)	C8—C9—C10—C11	54.49 (14)
C4—C5—C6—C1	−2.03 (19)	C1—N1—C11—N2	−1.04 (15)

N1—C1—C6—N2	1.20 (14)	C1—N1—C11—C10	177.57 (12)
C2—C1—C6—N2	179.11 (11)	C6—N2—C11—N1	1.82 (15)
N1—C1—C6—C5	−174.94 (11)	C7—N2—C11—N1	−179.67 (11)
C2—C1—C6—C5	3.0 (2)	C6—N2—C11—C10	−176.86 (12)
C11—N2—C7—O1	−119.77 (13)	C7—N2—C11—C10	1.64 (19)
C6—N2—C7—O1	58.45 (16)	C9—C10—C11—N1	150.69 (13)
C11—N2—C7—C12	123.78 (14)	C9—C10—C11—N2	−30.80 (17)

Hydrogen-bond geometry (Å, °)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
O1—H1O1···N1^{i}	0.97 (2)	1.84 (2)	2.803 (2)	174 (2)
C5—H5A···O1^{ii}	0.962 (15)	2.499 (15)	3.216 (2)	131.3 (11)

Symmetry codes: (i) −*x*+1, *y*+1/2, −*z*+1/2; (ii) −*x*+1, −*y*+1, −*z*.

Fig. 1

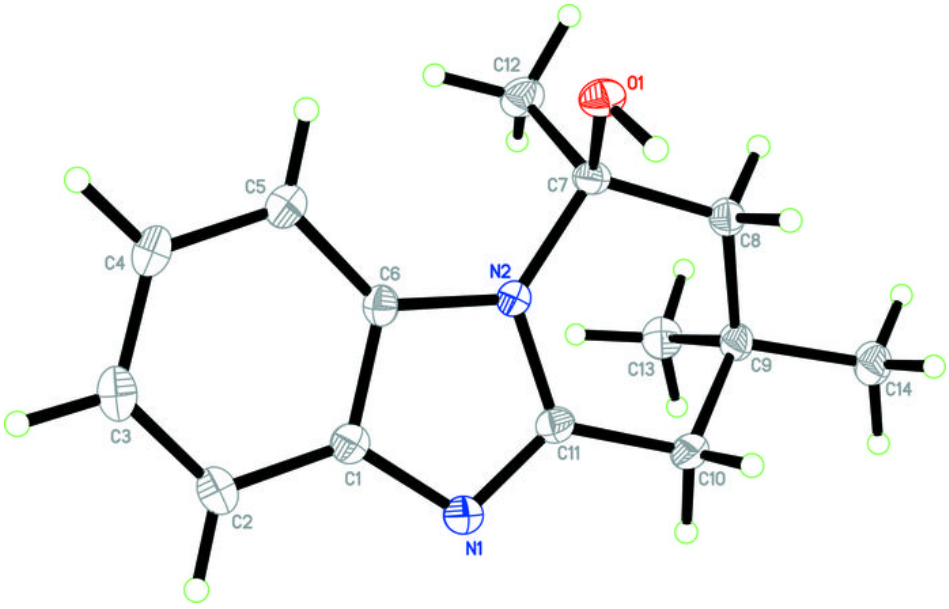
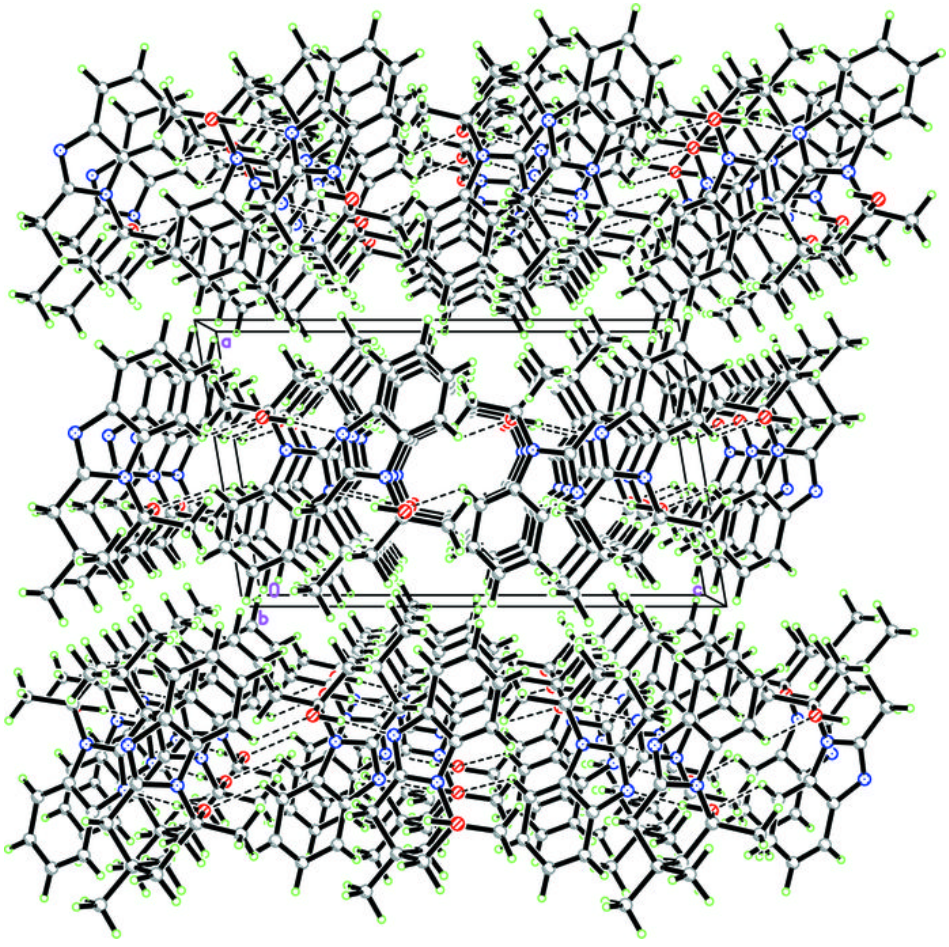


Fig. 2



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(2*E*)-1-(6-Chloro-2-methyl-4-phenylquinolin-3-yl)-3-phenylprop-2-en-1-one

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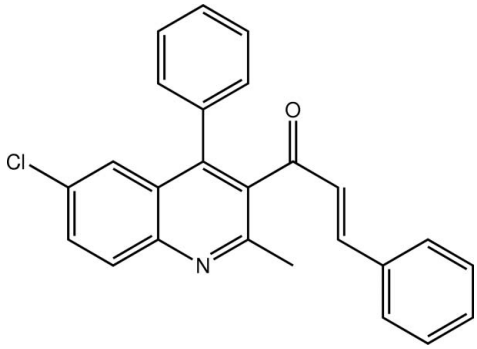
Key indicators: single-crystal X-ray study; T = 100 K; mean σ(C–C) = 0.004 Å; R factor = 0.065; wR factor = 0.188; data-to-parameter ratio = 15.5.

In the title compound, $C_{25}H_{18}ClNO$, the conformation about the C=C double bond is *E*. Significant twists are evident in the molecule, with the benzene ring forming a dihedral angle of 53.92 (11)° with the quinolinyl residue. Further, the chalcone residue is approximately perpendicular to the quinolinyl residue [$C_q-C_q-C_c-O_c$ torsion angle = −104.5 (3)°, where q = quinolinyl and c = chalcone]. In the crystal, the presence of C—H···O and C—H···π interactions leads to supramolecular layers lying parallel to ($\bar{1}$02).

Related literature

For the biological activity of quinoline derivatives, see: Campbell *et al.* (1998). For the biological activity of chalcone derivatives, see: Chen *et al.* (2001); Zi & Simoneau (2005). For a related structure, see: Prasath *et al.* (2010).



Experimental

Crystal data

$C_{25}H_{18}ClNO$ M_r = 383.85
Monoclinic, $P2_1/c$
a = 9.9250 (9) Å
b = 11.1001 (9) Å
c = 17.4651 (15) Å
β = 97.250 (1)°
V = 1908.7 (3) Å^3
Z = 4
Mo $K\alpha$ radiation
μ = 0.22 mm^{-1}
T = 100 K
0.46 × 0.30 × 0.26 mm

Data collection

Bruker SMART APEX CCD diffractometer
Absorption correction: multi-scan (*SADABS*; Sheldrick, 1996)
T_{min} = 0.536, T_{max} = 1.000
16152 measured reflections
3948 independent reflections
3030 reflections with $I > 2\sigma(I)$
R_{int} = 0.079

Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.065
$wR(F^2)$ = 0.188
S = 1.09
3948 reflections
254 parameters
H-atom parameters constrained
$\Delta\rho_{max}$ = 0.85 e Å^{-3}
$\Delta\rho_{min}$ = −0.49 e Å^{-3}

Table 1
Hydrogen-bond geometry (Å, °).

*Cg*1 is the centroid of the N1,C10–C12,C17,C18 ring.

D—H···A	D—H	H···A	D···A	D—H···A
C5—H5···O1^{i}	0.95	2.48	3.315 (3)	146
C21—H21···*Cg*1^{ii}	0.95	2.71	3.459 (3)	137

Symmetry codes: (i) $-x+1, y-\frac{1}{2}, -z+\frac{3}{2}$; (ii) $-x, -y+1, -z+1$.

Data collection: *APEX2* (Bruker, 2008); cell refinement: *SAINT* (Bruker, 2008); data reduction: *SAINT*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *ORTEP-3* (Farrugia, 1997) and *DIAMOND* (Brandenburg, 2006); software used to prepare material for publication: *publCIF* (Westrip, 2010).

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Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: HB5510).

References

Brandenburg, K. (2006). *DIAMOND*. Crystal Impact GbR, Bonn, Germany.
Bruker (2008). *APEX2* and *SAINT*. Bruker AXS Inc., Madison, Wisconsin, USA.
Campbell, S. F., Hardstone, J. D. & Palmer, M. J. (1998). *J. Med. Chem.* **31**, 1031–1035.
Chen, Y.-L., Fang, K.-C., Sheu, J.-Y., Hsu, S.-L. & Tzeng, C.-C. (2001). *J. Med. Chem.* **44**, 2374–2377.
Farrugia, L. J. (1997). *J. Appl. Cryst.* **30**, 565.
Prasath, R., Sarveswari, S., Vijayakumar, V., Narasimhamurthy, T. & Tiekink, E. R. T. (2010). *Acta Cryst.* E**66**, o1110.
Sheldrick, G. M. (1996). *SADABS*. University of Göttingen, Germany.
Sheldrick, G. M. (2008). *Acta Cryst.* A**64**, 112–122.
Westrip, S. P. (2010). *J. Appl. Cryst.* **43**. Submitted.
Zi, X. & Simoneau, A. R. (2005). *Cancer Res.* **65**, 3479–3486.

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supplementary materials

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(2*E*)-1-(6-Chloro-2-methyl-4-phenylquinolin-3-yl)-3-phenylprop-2-en-1-one

A. J. Viji, S. Sarveswari, V. Vijayakumar, K. W. Tan and E. R. T. Tiekink

Comment

Both quinolines (Campbell *et al.*, 1998) and open chain flavonoids, *i.e.* chalcones (Chen *et al.*, 2001; Zi & Simoneau, 2005), are known to possess a wide range of biological activities. Herein, in continuation of previous studies (Prasath *et al.*, 2010), we describe the crystal structure of a molecule containing both quinoline and chalcone residues, namely, the title compound, (I).

In (I), Fig. 1, the quinolinyl residue is planar [r.m.s. = 0.041 Å] with both the benzene ring and chalcone residue being twisted out of the plane. The dihedral angle formed between the quinolinyl and benzene (C20–C25) rings is 53.92 (11) °. In the case of the chalcone residue, the twist is best illustrated by the O1–C9–C10–C11 torsion angle of -104.5 (3) °. There are also twists within the chalcone residues as exemplified by the C7–C8–C9–O1 and C7–C8–C9–C10 torsion angles of -163.7 (3) and 14.7 (4) °, respectively. The conformation about the C7═C8 bond [1.340 (4) Å] is E.

Supramolecular layers parallel to ($\bar{1}$ 0 2) are evident in the crystal structure. These, Fig. 2 and Table 1, are stabilized by C–H···O contacts and C–H···π interactions where the π-system is the NC_5 ring of the quinolinyl residue.

Experimental

A mixture of 3-acetyl-6-chloro-2-methyl-4-phenylquinoline (0.01 *M*), benzaldehyde (0.0 1*M*) and a catalytic amount of KOH in distilled ethanol (50 ml) was stirred for about 12 h. The resulting mixture was concentrated to remove ethanol, poured on to ice and neutralized with dilute acetic acid. The solid that formed was filtered, dried, purified by column chromatography using a 1:1 mixture of ethyl acetate and petroleum ether, and recrystallized using ethyl acetate to produce colourless blocks of (I); Yield: 65% and m.pt: 400 K.

Refinement

The C-bound H atoms were geometrically placed (C–H = 0.95–0.98 Å) and refined as riding with U_{iso}(H) = 1.2–1.5U_{eq}(C).

Figures

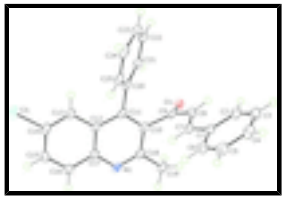


Fig. 1. The molecular structure of (I) showing displacement ellipsoids at the 50% probability level.

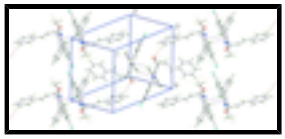


Fig. 2. A view of the supramolecular array in (I) highlighting the C–H···O and C–H···π interactions as orange and purple dashed lines, respectively.

(2*E*)-1-(6-Chloro-2-methyl-4-phenylquinolin-3-yl)-3-phenylprop-2-en-1-one

Crystal data

$C_{25}H_{18}ClNO$	$F(000) = 800$
$M_r = 383.85$	$D_x = 1.336$ Mg m^{-3}
Monoclinic, $P2_1/c$	Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å
Hall symbol: -P 2ybc	Cell parameters from 4382 reflections
$a = 9.9250$ (9) Å	$\theta = 2.2$–$28.1°$
$b = 11.1001$ (9) Å	$\mu = 0.22$ mm^{-1}
$c = 17.4651$ (15) Å	$T = 100$ K
$\beta = 97.250$ (1)°	Block, colourless
$V = 1908.7$ (3) Å^3	0.46 × 0.30 × 0.26 mm
$Z = 4$	

Data collection

Bruker SMART APEX CCD diffractometer	3948 independent reflections
Radiation source: fine-focus sealed tube	3030 reflections with $I > 2\sigma(I)$
graphite	$R_{int} = 0.079$
ω scans	$\theta_{max} = 26.5°$, $\theta_{min} = 2.1°$
Absorption correction: multi-scan (*SADABS*; Sheldrick, 1996)	$h = -12 \rightarrow 12$
$T_{min} = 0.536$, $T_{max} = 1.000$	$k = -13 \rightarrow 13$
16152 measured reflections	$l = -21 \rightarrow 21$

Refinement

Refinement on F^2	Primary atom site location: structure-invariant direct methods
Least-squares matrix: full	Secondary atom site location: difference Fourier map
$R[F^2 > 2\sigma(F^2)] = 0.065$	Hydrogen site location: inferred from neighbouring sites
$wR(F^2) = 0.188$	H-atom parameters constrained
$S = 1.09$	$w = 1/[\sigma^2(F_o^2) + (0.0925P)^2 + 1.6015P]$ where $P = (F_o^2 + 2F_c^2)/3$
3948 reflections	$(\Delta/\sigma)_{max} < 0.001$
254 parameters	$\Delta\rho_{max} = 0.85$ e Å^{-3}
0 restraints	$\Delta\rho_{min} = -0.49$ e Å^{-3}

Special details

Geometry. All s.u.'s (except the s.u. in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell s.u.'s are taken into account individually in the estimation of s.u.'s in distances, angles and torsion angles; correlations between s.u.'s in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell s.u.'s is used for estimating s.u.'s involving l.s. planes.

Refinement. Refinement of F^2 against ALL reflections. The weighted *R*-factor *wR* and goodness of fit *S* are based on F^2, conventional *R*-factors *R* are based on *F*, with *F* set to zero for negative F^2. The threshold expression of $F^2 > 2\sigma(F^2)$ is used only for calculating *R*-factors(gt) *etc*. and is not relevant to the choice of reflections for refinement. *R*-factors based on F^2 are statistically about twice as large as those based on *F*, and *R*- factors based on ALL data will be even larger.

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters ($Å^2$)

	x	*y*	*z*	U_{iso}*/U_{eq}
Cl1	0.10119 (8)	−0.00729 (6)	0.39598 (4)	0.0310 (2)
O1	0.13396 (19)	0.68284 (16)	0.58922 (12)	0.0270 (5)
N1	0.3459 (2)	0.4751 (2)	0.42881 (14)	0.0225 (5)
C1	0.4920 (3)	0.5159 (2)	0.77131 (17)	0.0218 (6)
C2	0.4665 (3)	0.5785 (2)	0.83726 (17)	0.0254 (6)
H2	0.3927	0.6335	0.8343	0.031*
C3	0.5471 (3)	0.5616 (2)	0.90671 (18)	0.0275 (6)
H3	0.5278	0.6040	0.9513	0.033*
C4	0.6565 (3)	0.4825 (2)	0.91160 (18)	0.0284 (7)
H4	0.7118	0.4706	0.9595	0.034*
C5	0.6847 (3)	0.4212 (2)	0.84662 (18)	0.0291 (7)
H5	0.7599	0.3677	0.8497	0.035*
C6	0.6033 (3)	0.4376 (2)	0.77700 (17)	0.0254 (6)
H6	0.6233	0.3952	0.7325	0.030*
C7	0.4062 (3)	0.5249 (2)	0.69742 (17)	0.0219 (6)
H7	0.4326	0.4781	0.6562	0.026*
C8	0.2941 (3)	0.5922 (2)	0.68141 (17)	0.0232 (6)
H8	0.2633	0.6365	0.7224	0.028*
C9	0.2165 (3)	0.6014 (2)	0.60506 (17)	0.0218 (6)
C10	0.2406 (3)	0.5114 (2)	0.54359 (16)	0.0196 (6)
C11	0.1878 (2)	0.3965 (2)	0.54427 (16)	0.0196 (6)
C12	0.2102 (2)	0.3183 (2)	0.48211 (16)	0.0192 (6)
C13	0.1502 (3)	0.2022 (2)	0.47167 (16)	0.0211 (6)
H13	0.0911	0.1735	0.5063	0.025*
C14	0.1783 (3)	0.1328 (2)	0.41150 (17)	0.0237 (6)
C15	0.2654 (3)	0.1713 (2)	0.35909 (17)	0.0255 (6)
H15	0.2848	0.1199	0.3184	0.031*
C16	0.3223 (3)	0.2835 (2)	0.36714 (17)	0.0242 (6)
H16	0.3817	0.3100	0.3320	0.029*
C17	0.2931 (3)	0.3600 (2)	0.42726 (16)	0.0206 (6)
C18	0.3167 (3)	0.5479 (2)	0.48365 (17)	0.0215 (6)
C19	0.3681 (3)	0.6752 (2)	0.48052 (18)	0.0269 (6)
H19A	0.4366	0.6794	0.4448	0.040*

H19B	0.4088	0.7001	0.5321	0.040*
H19C	0.2923	0.7290	0.4626	0.040*
C20	0.1112 (3)	0.3561 (2)	0.60680 (16)	0.0210 (6)
C21	−0.0006 (3)	0.4208 (2)	0.62611 (17)	0.0238 (6)
H21	−0.0310	0.4900	0.5969	0.029*
C22	−0.0675 (3)	0.3855 (3)	0.68711 (18)	0.0288 (7)
H22	−0.1427	0.4308	0.6999	0.035*
C23	−0.0251 (3)	0.2841 (3)	0.72961 (18)	0.0306 (7)
H23	−0.0697	0.2607	0.7723	0.037*
C24	0.0828 (3)	0.2169 (2)	0.70960 (18)	0.0293 (7)
H24	0.1099	0.1458	0.7377	0.035*
C25	0.1511 (3)	0.2522 (2)	0.64943 (17)	0.0250 (6)
H25	0.2256	0.2059	0.6367	0.030*

Atomic displacement parameters (Å^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Cl1	0.0373 (4)	0.0150 (3)	0.0400 (5)	−0.0062 (3)	0.0013 (3)	−0.0048 (3)
O1	0.0212 (10)	0.0136 (9)	0.0452 (13)	0.0019 (7)	0.0001 (9)	−0.0028 (8)
N1	0.0180 (11)	0.0158 (11)	0.0339 (14)	0.0000 (9)	0.0036 (9)	0.0010 (9)
C1	0.0213 (13)	0.0120 (12)	0.0325 (16)	−0.0028 (10)	0.0048 (11)	0.0020 (10)
C2	0.0247 (14)	0.0163 (13)	0.0354 (17)	0.0002 (10)	0.0042 (12)	−0.0017 (11)
C3	0.0313 (16)	0.0166 (13)	0.0342 (17)	−0.0025 (11)	0.0026 (12)	−0.0023 (11)
C4	0.0320 (16)	0.0165 (13)	0.0348 (17)	−0.0024 (11)	−0.0034 (13)	0.0032 (11)
C5	0.0248 (15)	0.0170 (13)	0.0442 (19)	0.0037 (11)	−0.0011 (13)	0.0019 (12)
C6	0.0255 (14)	0.0172 (13)	0.0340 (17)	0.0015 (11)	0.0060 (12)	−0.0009 (11)
C7	0.0221 (14)	0.0118 (11)	0.0326 (16)	−0.0023 (10)	0.0070 (11)	−0.0002 (11)
C8	0.0245 (14)	0.0155 (12)	0.0302 (16)	0.0010 (10)	0.0056 (11)	−0.0036 (11)
C9	0.0162 (13)	0.0122 (12)	0.0371 (16)	−0.0043 (10)	0.0038 (11)	−0.0005 (11)
C10	0.0153 (12)	0.0151 (12)	0.0279 (15)	0.0016 (10)	0.0004 (10)	0.0016 (10)
C11	0.0126 (12)	0.0154 (12)	0.0298 (15)	0.0007 (9)	−0.0014 (10)	0.0019 (10)
C12	0.0115 (12)	0.0158 (12)	0.0298 (15)	0.0020 (9)	0.0005 (10)	0.0012 (10)
C13	0.0156 (12)	0.0153 (12)	0.0320 (16)	0.0011 (10)	0.0018 (11)	0.0017 (11)
C14	0.0237 (14)	0.0134 (12)	0.0326 (16)	0.0009 (10)	−0.0023 (11)	0.0009 (11)
C15	0.0283 (15)	0.0171 (13)	0.0310 (16)	0.0054 (11)	0.0035 (12)	−0.0025 (11)
C16	0.0196 (13)	0.0209 (13)	0.0324 (16)	0.0011 (11)	0.0039 (11)	0.0009 (11)
C17	0.0139 (12)	0.0148 (12)	0.0329 (16)	0.0013 (9)	0.0017 (10)	0.0014 (11)
C18	0.0163 (13)	0.0143 (12)	0.0332 (16)	−0.0002 (10)	0.0002 (11)	0.0014 (11)
C19	0.0246 (14)	0.0149 (13)	0.0416 (18)	−0.0036 (11)	0.0059 (12)	0.0009 (12)
C20	0.0191 (13)	0.0138 (12)	0.0294 (15)	−0.0042 (9)	0.0003 (11)	−0.0011 (10)
C21	0.0182 (13)	0.0177 (13)	0.0348 (17)	−0.0018 (10)	0.0013 (11)	−0.0017 (11)
C22	0.0206 (14)	0.0254 (14)	0.0409 (18)	−0.0062 (11)	0.0066 (12)	−0.0082 (13)
C23	0.0322 (16)	0.0280 (15)	0.0329 (17)	−0.0155 (13)	0.0085 (13)	−0.0038 (12)
C24	0.0374 (17)	0.0172 (13)	0.0319 (17)	−0.0087 (12)	−0.0007 (13)	0.0029 (12)
C25	0.0273 (14)	0.0134 (12)	0.0334 (17)	−0.0018 (10)	0.0000 (12)	−0.0012 (11)

Geometric parameters (Å, °)

Cl1—C14	1.739 (3)	C12—C17	1.417 (4)

O1—C9	1.228 (3)	C12—C13	1.422 (3)
N1—C18	1.314 (4)	C13—C14	1.360 (4)
N1—C17	1.379 (3)	C13—H13	0.9500
C1—C2	1.396 (4)	C14—C15	1.403 (4)
C1—C6	1.399 (4)	C15—C16	1.368 (4)
C1—C7	1.457 (4)	C15—H15	0.9500
C2—C3	1.379 (4)	C16—C17	1.409 (4)
C2—H2	0.9500	C16—H16	0.9500
C3—C4	1.391 (4)	C18—C19	1.506 (3)
C3—H3	0.9500	C19—H19A	0.9800
C4—C5	1.382 (4)	C19—H19B	0.9800
C4—H4	0.9500	C19—H19C	0.9800
C5—C6	1.384 (4)	C20—C21	1.399 (4)
C5—H5	0.9500	C20—C25	1.402 (4)
C6—H6	0.9500	C21—C22	1.381 (4)
C7—C8	1.340 (4)	C21—H21	0.9500
C7—H7	0.9500	C22—C23	1.384 (4)
C8—C9	1.457 (4)	C22—H22	0.9500
C8—H8	0.9500	C23—C24	1.385 (4)
C9—C10	1.508 (4)	C23—H23	0.9500
C10—C11	1.380 (3)	C24—C25	1.377 (4)
C10—C18	1.425 (4)	C24—H24	0.9500
C11—C12	1.429 (4)	C25—H25	0.9500
C11—C20	1.477 (4)		
C18—N1—C17	117.8 (2)	C13—C14—C15	122.3 (2)
C2—C1—C6	118.3 (3)	C13—C14—Cl1	119.8 (2)
C2—C1—C7	123.4 (2)	C15—C14—Cl1	117.8 (2)
C6—C1—C7	118.3 (3)	C16—C15—C14	119.4 (3)
C3—C2—C1	120.9 (3)	C16—C15—H15	120.3
C3—C2—H2	119.6	C14—C15—H15	120.3
C1—C2—H2	119.6	C15—C16—C17	120.3 (3)
C2—C3—C4	120.1 (3)	C15—C16—H16	119.8
C2—C3—H3	119.9	C17—C16—H16	119.8
C4—C3—H3	119.9	N1—C17—C16	117.3 (2)
C5—C4—C3	119.9 (3)	N1—C17—C12	122.7 (2)
C5—C4—H4	120.1	C16—C17—C12	119.9 (2)
C3—C4—H4	120.1	N1—C18—C10	123.1 (2)
C4—C5—C6	120.0 (3)	N1—C18—C19	116.4 (3)
C4—C5—H5	120.0	C10—C18—C19	120.5 (2)
C6—C5—H5	120.0	C18—C19—H19A	109.5
C5—C6—C1	120.8 (3)	C18—C19—H19B	109.5
C5—C6—H6	119.6	H19A—C19—H19B	109.5
C1—C6—H6	119.6	C18—C19—H19C	109.5
C8—C7—C1	126.9 (3)	H19A—C19—H19C	109.5
C8—C7—H7	116.6	H19B—C19—H19C	109.5
C1—C7—H7	116.6	C21—C20—C25	118.3 (3)
C7—C8—C9	124.0 (3)	C21—C20—C11	121.4 (2)
C7—C8—H8	118.0	C25—C20—C11	120.4 (2)
C9—C8—H8	118.0	C22—C21—C20	120.9 (3)

O1—C9—C8	121.3 (2)	C22—C21—H21	119.6
O1—C9—C10	119.3 (3)	C20—C21—H21	119.6
C8—C9—C10	119.4 (2)	C21—C22—C23	120.1 (3)
C11—C10—C18	120.5 (2)	C21—C22—H22	120.0
C11—C10—C9	120.8 (2)	C23—C22—H22	120.0
C18—C10—C9	118.7 (2)	C22—C23—C24	119.7 (3)
C10—C11—C12	117.3 (2)	C22—C23—H23	120.2
C10—C11—C20	121.2 (2)	C24—C23—H23	120.2
C12—C11—C20	121.5 (2)	C25—C24—C23	120.7 (3)
C17—C12—C13	118.6 (2)	C25—C24—H24	119.7
C17—C12—C11	118.3 (2)	C23—C24—H24	119.7
C13—C12—C11	123.0 (2)	C24—C25—C20	120.4 (3)
C14—C13—C12	119.3 (3)	C24—C25—H25	119.8
C14—C13—H13	120.4	C20—C25—H25	119.8
C12—C13—H13	120.4		
C6—C1—C2—C3	−1.5 (4)	C13—C14—C15—C16	−1.5 (4)
C7—C1—C2—C3	176.5 (3)	Cl1—C14—C15—C16	176.6 (2)
C1—C2—C3—C4	0.8 (4)	C14—C15—C16—C17	−0.3 (4)
C2—C3—C4—C5	0.2 (4)	C18—N1—C17—C16	178.5 (2)
C3—C4—C5—C6	−0.6 (4)	C18—N1—C17—C12	−0.3 (4)
C4—C5—C6—C1	−0.1 (4)	C15—C16—C17—N1	−175.5 (2)
C2—C1—C6—C5	1.1 (4)	C15—C16—C17—C12	3.3 (4)
C7—C1—C6—C5	−177.0 (3)	C13—C12—C17—N1	174.2 (2)
C2—C1—C7—C8	0.2 (4)	C11—C12—C17—N1	−4.0 (4)
C6—C1—C7—C8	178.2 (3)	C13—C12—C17—C16	−4.5 (4)
C1—C7—C8—C9	176.9 (2)	C11—C12—C17—C16	177.2 (2)
C7—C8—C9—O1	−163.7 (3)	C17—N1—C18—C10	4.0 (4)
C7—C8—C9—C10	14.7 (4)	C17—N1—C18—C19	−176.0 (2)
O1—C9—C10—C11	−104.5 (3)	C11—C10—C18—N1	−3.2 (4)
C8—C9—C10—C11	77.1 (3)	C9—C10—C18—N1	178.2 (2)
O1—C9—C10—C18	74.1 (3)	C11—C10—C18—C19	176.8 (2)
C8—C9—C10—C18	−104.3 (3)	C9—C10—C18—C19	−1.9 (4)
C18—C10—C11—C12	−1.3 (4)	C10—C11—C20—C21	54.1 (4)
C9—C10—C11—C12	177.3 (2)	C12—C11—C20—C21	−126.0 (3)
C18—C10—C11—C20	178.7 (2)	C10—C11—C20—C25	−124.8 (3)
C9—C10—C11—C20	−2.7 (4)	C12—C11—C20—C25	55.2 (3)
C10—C11—C12—C17	4.6 (3)	C25—C20—C21—C22	2.0 (4)
C20—C11—C12—C17	−175.4 (2)	C11—C20—C21—C22	−176.9 (2)
C10—C11—C12—C13	−173.6 (2)	C20—C21—C22—C23	−0.7 (4)
C20—C11—C12—C13	6.5 (4)	C21—C22—C23—C24	−1.4 (4)
C17—C12—C13—C14	2.7 (4)	C22—C23—C24—C25	2.1 (4)
C11—C12—C13—C14	−179.1 (2)	C23—C24—C25—C20	−0.8 (4)
C12—C13—C14—C15	0.3 (4)	C21—C20—C25—C24	−1.2 (4)
C12—C13—C14—Cl1	−177.80 (19)	C11—C20—C25—C24	177.6 (2)

Hydrogen-bond geometry (Å, °)

Cg1 is the centroid of the N1,C10–C12,C17,C18 ring.

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*

C5—H5···O1^{i}	0.95	2.48	3.315 (3)	146
C21—H21···Cg1^{ii}	0.95	2.71	3.459 (3)	137

Symmetry codes: (i) −*x*+1, *y*−1/2, −*z*+3/2; (ii) −*x*, −*y*+1, −*z*+1.

Fig. 1

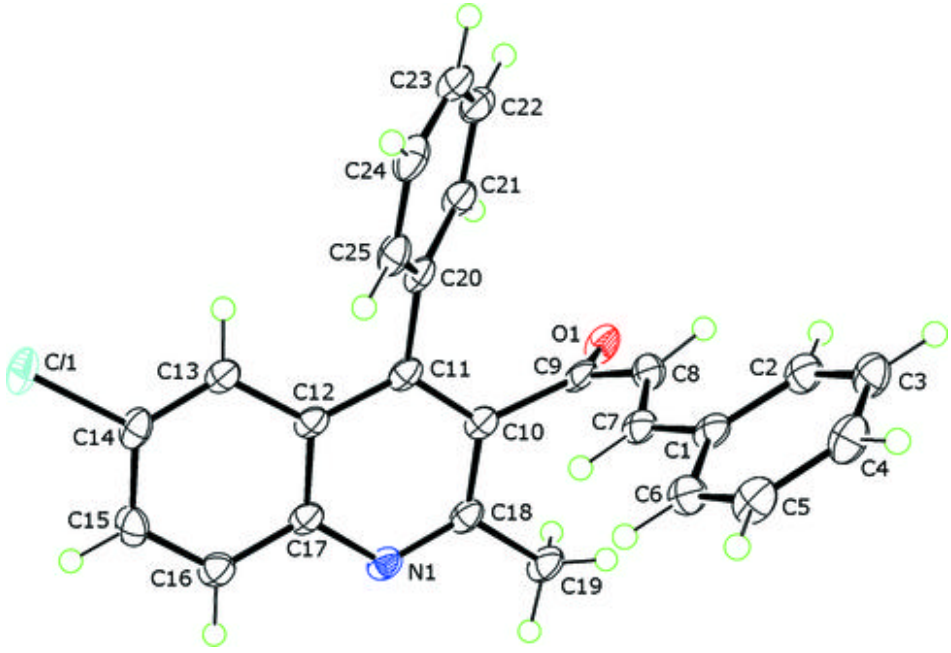
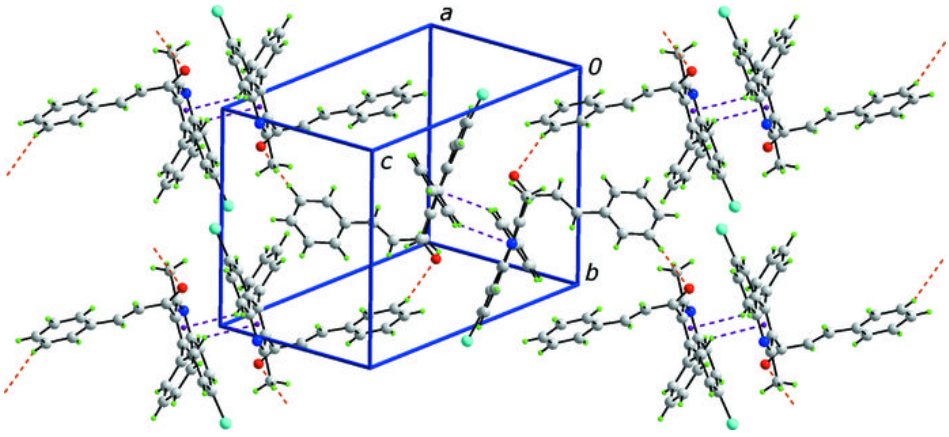

C23
C22
C24
C21
C25
C20
O1
C/1
C13
C11
C9
C8
C2
C3
C12
C14
C10
C7
C1
C4
C6
C15
C18
C5
C17
C16
N1
C19

Fig. 2



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3,3-Bis[(4-chlorophenyl)sulfanyl]-1-methylpiperidin-2-one

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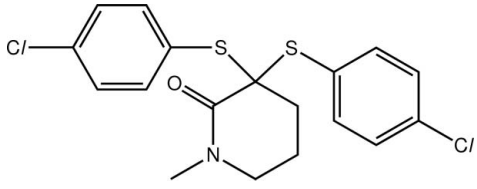
Key indicators: single-crystal X-ray study; T = 290 K; mean σ(C–C) = 0.004 Å; R factor = 0.043; wR factor = 0.121; data-to-parameter ratio = 15.1.

The piperidone ring in the title compound, $C_{18}H_{17}Cl_2NOS_2$, has a distorted half-chair conformation. The S-bound benzene rings are approximately perpendicular to and splayed out of the mean plane through the piperidone ring [dihedral angles = 71.86 (13) and 46.94 (11)°]. In the crystal, C—H···O interactions link the molecules into [010] supramolecular chains with a helical topology. C—H···Cl and C—H···π interactions are also present.

Related literature

For background to β-thiocarbonyl compounds, see: Vinhato (2007); Olivato *et al.* (2009). For related structures, see: Zukerman-Schpector *et al.* (2006, 2008). For ring conformational analysis, see: Cremer & Pople (1975). For further synthetic details, see: Hashmat & McDermott (2002); Zoretic & Soja (1976).



Experimental

Crystal data

$C_{18}H_{17}Cl_2NOS_2$
M_r = 398.37
Monoclinic, $P2_1/n$
a = 8.0313 (2) Å
b = 9.7460 (2) Å
c = 24.2623 (7) Å
β = 94.0767 (12)°
V = 1894.28 (8) Å^3
Z = 4
Mo $K\alpha$ radiation
μ = 0.57 mm^{-1}
T = 290 K
0.33 × 0.30 × 0.29 mm

Data collection

Nonius KappaCCD diffractometer
Absorption correction: multi-scan (*SADABS*; Sheldrick, 1996)
T_{min} = 0.82, T_{max} = 0.85
12888 measured reflections
3288 independent reflections
2778 reflections with $I > 2\sigma(I)$
R_{int} = 0.049

Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.043
$wR(F^2)$ = 0.121
S = 1.05
3288 reflections
218 parameters
H-atom parameters constrained
$\Delta\rho_{max}$ = 0.37 e Å^{-3}
$\Delta\rho_{min}$ = −0.38 e Å^{-3}

Table 1
Hydrogen-bond geometry (Å, °).

*Cg*1 is the centroid of the C7–C12.

D—H···A	D—H	H···A	D···A	D—H···A
C9—H9···O1^{i}	0.93	2.32	3.218 (3)	164
C11—H11···Cl2^{ii}	0.93	2.83	3.708 (3)	157
C19—H19a···*Cg*1^{iii}	0.96	2.95	3.676 (3)	133

Symmetry codes: (i) $-x+\frac{3}{2}, y-\frac{1}{2}, -z+\frac{3}{2}$; (ii) $-x+\frac{1}{2}, y+\frac{1}{2}, -z+\frac{3}{2}$; (iii) $-x+\frac{1}{2}, y-\frac{1}{2}, -z+\frac{3}{2}$.

Data collection: *COLLECT* (Nonius, 1999); cell refinement: *SCALEPACK* (Otwinowski & Minor, 1997); data reduction: *DENZO* (Otwinowski & Minor, 1997) and *SCALEPACK*; program(s) used to solve structure: *SIR97* (Altomare *et al.*, 1999); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *ORTEP-3* (Farrugia, 1997) and *DIAMOND* (Brandenburg, 2006); software used to prepare material for publication: *WinGX* (Farrugia, 1999).

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Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: HB5512).

References

Altomare, A., Burla, M. C., Camalli, M., Cascarano, G. L., Giacovazzo, C., Guagliardi, A., Moliterni, A. G. G., Polidori, G. & Spagna, R. (1999). *J. Appl. Cryst.* **32**, 115–119.
Brandenburg, K. (2006). *DIAMOND*. Crystal Impact GbR, Bonn, Germany.
Cremer, D. & Pople, J. A. (1975). *J. Am. Chem. Soc.* **97**, 1354–1358.
Farrugia, L. J. (1997). *J. Appl. Cryst.* **30**, 565.
Farrugia, L. J. (1999). *J. Appl. Cryst.* **32**, 837–838.
Hashmat, A. M. & McDermott, M. (2002). *Tetrahedron Lett.* **43**, 6271–6273.
Nonius (1999). *COLLECT*. Nonius BV, Delft, The Netherlands.
Olivato, P. R., Domingues, N. L. C., Mondino, M. G., Tormena, C. F., Rittner, R. & Dal Colle, M. (2009). *J. Mol. Struct.* **920**, 393–400.
Otwinowski, Z. & Minor, W. (1997). *Methods in Enzymology*, Vol. 276, *Macromolecular Crystallography*, Part A, edited by C. W. Carter Jr & R. M. Sweet, pp. 307–326. New York: Academic Press.
Sheldrick, G. M. (1996). *SADABS*. University of Göttingen, Germany.
Sheldrick, G. M. (2008). *Acta Cryst.* A**64**, 112–122.
Vinhato, E. (2007). PhD Thesis, University of São Paulo, Brazil.
Zoretic, P. A. & Soja, P. (1976). *J. Org. Chem.* **41**, 3587–3589.
Zukerman-Schpector, J., Maganhi, S., Olivato, P. R., Vinhato, E. & Cerqueira, C. R. (2006). *Z. Kristallogr. New Cryst. Struct.* **221**, 165–166.
Zukerman-Schpector, J., Olivato, P. R., Cerqueira, C. R. Jr, Vinhato, E. & Tiekink, E. R. T. (2008). *Acta Cryst.* E**64**, o835–o836.

supplementary materials

Acta Cryst. (2010). E**66**, o1863 [**doi:10.1107/S1600536810024347**]

3,3-Bis[(4-chlorophenyl)sulfanyl]-1-methylpiperidin-2-one

J. Zukerman-Schpector, C. A. De Simone, P. R. Olivato, C. R. Cerqueira Jr, J. M. M. Santos and E. R. T. Tiekink

Comment

As part of our on-going research on the conformational and electronic interactions in β-thio-carbonyl compounds, *e.g.* *N*,*N*-diethyl-2-[(4'-substituted) phenylthio]acetamides, *N*-methoxy-*N*-methyl-2-[(4'-substituted) phenylthio]propanamides, and 1-methyl-3-phenylsulfonyl-2-piperidone, utilizing spectroscopic, theoretical and X-ray diffraction methods (Vinhato, 2007; Olivato *et al.*, 2009; Zukerman-Schpector *et al.* 2008), the title compound, (I), was synthesized and its crystal structure determined.

In (I), Fig. 1, the piperidone ring has a distorted half-chair conformation: the ring-puckering parameters are q_2 = 0.453 (2) Å, q_3 = -0.271 (2) Å, QT = 0.528 (3) Å, φ_2 = 37.4 (3) ° (Cremer & Pople, 1975). While the S2-bound benzene ring is orientated to be almost perpendicular to the plane through the piperidone ring [dihedral angle = 71.86 (13) °], the S1-bond benzene ring is somewhat splayed with respect to the other rings, forming dihedral angles of 46.94 (11) and 61.68 (13) ° with those through the piperidone and S2-bound benzene rings, respectively.

Supramolecular helical chains aligned along the *b* axis dominate the crystal packing, Fig. 2 and Table 1, and these are sustained in the crystal structure by C–H···Cl and C–H···π interactions, Table 1.

Experimental

Firstly, 4-chlorothiophenol (5.8 g, 40 mmol) was reacted with bromine (1.1 ml, 40 mmol) in dichloromethane (250 ml) on hydrated silica gel support (25 g of SiO_2 and 12 ml of water) to give 4-chlorophenyl disulfide (5.3 g, yield = 93%). A yellow solid was obtained after filtration and evaporation without further purification (Hashmat & McDermott, 2002). 1-Methyl-2-piperidinone (2.0 g, 18 mmol) was added dropwise to a cooled (195 K) solution of hexamethylphosphoramide (HMPA) (3.3 ml, 18 mmol), diisopropylamine (2.6 ml, 18 mmol) and butyllithium (11.5 ml, 18 mmol) in THF (60 ml). After 20 minutes, 4-chlorophenyl disulfide (5.3 g, 18 mmol) dissolved in THF (10 ml) was added dropwise to the enolate solution (Zoretic & Soja, 1976). After stirring for 3 h at 195 K, water (80 ml) was added at room temperature and extraction with chloroform was performed. The organic layer was dried over anhydrous sodium sulfate. After evaporation of solvent, a crude solid was obtained. Purification through flash chromatography with a solution of hexane and ethyl acetate in a 7:3 ratio give the pure product (2.8 g, yield = 35%). Irregular lumps of (I) were obtained by vapour diffusion of *n*-hexane into a chloroform solution held at 283 K; m.p. 372–373 K. IR (cm^{-1}): ν(C=O) 1663. NMR ($CDCl_3$, p.p.m.): δ 1.93–1.95 (2*H*, m), 1.97–1.99 (2*H*, m), 2.91 (3*H*, s), 3.21 (2*H*, triplet, J = 6.0 Hz), 7.31–7.33 (4*H*, m, Aryl-H), 7.55–7.57 (4*H*, m, Aryl-H). Analysis found: C 54.33, H 4.30, N 3.39%. $C_{18}H_{17}OCl_2NS_2$ requires: C 54.27, H 4.30, N 3.52%.

Refinement

The H atoms were geometrically placed (C–H = 0.93–0.97 Å) and refined as riding with U_{iso}(H) = 1.2–1.5U_{eq}(C).

Figures

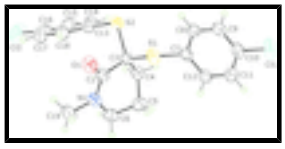


Fig. 1. The molecular structure of (I) showing displacement ellipsoids at the 35% probability level (arbitrary spheres for the H atoms).

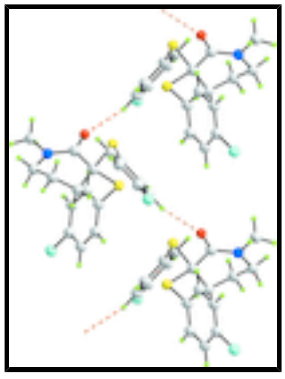


Fig. 2. Supramolecular chain in (I) mediated by C–H···O interactions (orange dashed lines). The chain with helical topology is aligned along the *b* axis.

3,3-Bis[(4-chlorophenyl)sulfanyl]-1-methylpiperidin-2-one

Crystal data

$C_{18}H_{17}Cl_2NOS_2$	$F(000) = 824$
$M_r = 398.37$	$D_x = 1.397$ Mg m^{-3}
Monoclinic, $P2_1/n$	Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å
Hall symbol: -P 2yn	Cell parameters from 10679 reflections
$a = 8.0313$ (2) Å	$\theta = 2.9$–$27.5°$
$b = 9.7460$ (2) Å	$\mu = 0.57$ mm^{-1}
$c = 24.2623$ (7) Å	$T = 290$ K
$\beta = 94.0767$ (12)°	Irregular, colourless
$V = 1894.28$ (8) Å^3	0.33 × 0.30 × 0.29 mm
$Z = 4$	

Data collection

Nonius KappaCCD diffractometer	3288 independent reflections
Radiation source: sealed tube	2778 reflections with $I > 2\sigma(I)$
graphite	$R_{int} = 0.049$
CCD rotation images scans	$\theta_{max} = 25.0°$, $\theta_{min} = 3.3°$
Absorption correction: multi-scan (*SADABS*; Sheldrick, 1996)	$h = -9 \rightarrow 8$
$T_{min} = 0.82$, $T_{max} = 0.85$	$k = -11 \rightarrow 11$
12888 measured reflections	$l = -28 \rightarrow 26$

Refinement

Refinement on F^2	Primary atom site location: structure-invariant direct methods
Least-squares matrix: full	Secondary atom site location: difference Fourier map
$R[F^2 > 2\sigma(F^2)] = 0.043$	Hydrogen site location: inferred from neighbouring sites
$wR(F^2) = 0.121$	H-atom parameters constrained
$S = 1.05$	$w = 1/[\sigma^2(F_o^2) + (0.0558P)^2 + 0.758P]$ where $P = (F_o^2 + 2F_c^2)/3$
3288 reflections	$(\Delta/\sigma)_{max} < 0.001$
218 parameters	$\Delta\rho_{max} = 0.37$ e Å^{-3}
0 restraints	$\Delta\rho_{min} = -0.38$ e Å^{-3}

Special details

Geometry. All s.u.'s (except the s.u. in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell s.u.'s are taken into account individually in the estimation of s.u.'s in distances, angles and torsion angles; correlations between s.u.'s in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell s.u.'s is used for estimating s.u.'s involving l.s. planes.

Refinement. Refinement of F^2 against ALL reflections. The weighted *R*-factor *wR* and goodness of fit *S* are based on F^2, conventional *R*-factors *R* are based on *F*, with *F* set to zero for negative F^2. The threshold expression of $F^2 > \sigma(F^2)$ is used only for calculating *R*-factors(gt) *etc*. and is not relevant to the choice of reflections for refinement. *R*-factors based on F^2 are statistically about twice as large as those based on *F*, and *R*- factors based on ALL data will be even larger.

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å^2)

	x	*y*	*z*	U_{iso}*/U_{eq}
C2	0.3322 (3)	0.3195 (2)	0.66893 (9)	0.0514 (5)
C3	0.4451 (2)	0.2265 (2)	0.70636 (9)	0.0490 (5)
C4	0.3506 (3)	0.1218 (2)	0.73838 (9)	0.0527 (5)
H4A	0.3189	0.0448	0.7145	0.063*
H4B	0.4223	0.0876	0.7692	0.063*
C5	0.1959 (3)	0.1856 (3)	0.75971 (10)	0.0629 (6)
H5A	0.1407	0.1199	0.7823	0.075*
H5B	0.2264	0.2650	0.7823	0.075*
C6	0.0808 (3)	0.2277 (3)	0.71127 (11)	0.0697 (7)
H6A	0.0309	0.1464	0.6940	0.084*
H6B	−0.0085	0.2835	0.7243	0.084*
C7	0.6208 (2)	0.2649 (2)	0.81264 (9)	0.0520 (5)
C8	0.7382 (3)	0.1601 (2)	0.81591 (10)	0.0557 (5)
H8	0.7841	0.1296	0.7840	0.067*
C9	0.7876 (3)	0.1008 (2)	0.86615 (11)	0.0632 (6)
H9	0.8659	0.0303	0.8681	0.076*
C10	0.7204 (3)	0.1464 (3)	0.91293 (11)	0.0678 (7)
C11	0.6026 (3)	0.2500 (3)	0.91080 (11)	0.0756 (7)

H11	0.5572	0.2800	0.9429	0.091*
C12	0.5534 (3)	0.3082 (3)	0.86065 (10)	0.0673 (7)
H12	0.4737	0.3776	0.8589	0.081*
C13	0.4783 (3)	0.0506 (2)	0.61552 (9)	0.0572 (5)
C14	0.4608 (3)	−0.0901 (3)	0.61981 (11)	0.0687 (6)
H14	0.5093	−0.1360	0.6505	0.082*
C15	0.3712 (4)	−0.1629 (3)	0.57846 (13)	0.0814 (8)
H15	0.3600	−0.2576	0.5811	0.098*
C16	0.2998 (3)	−0.0938 (4)	0.53379 (12)	0.0798 (8)
C17	0.3157 (4)	0.0450 (4)	0.52858 (12)	0.0869 (9)
H17	0.2660	0.0900	0.4979	0.104*
C18	0.4061 (4)	0.1180 (3)	0.56924 (11)	0.0744 (7)
H18	0.4188	0.2123	0.5657	0.089*
C19	0.0614 (4)	0.3812 (3)	0.62912 (13)	0.0835 (8)
H19A	0.0725	0.4778	0.6362	0.125*
H19B	−0.0530	0.3545	0.6314	0.125*
H19C	0.0954	0.3612	0.5928	0.125*
O1	0.3934 (2)	0.40242 (17)	0.63843 (7)	0.0719 (5)
Cl1	0.78388 (14)	0.07472 (10)	0.97627 (4)	0.1129 (3)
Cl2	0.19021 (13)	−0.18374 (14)	0.48074 (4)	0.1289 (4)
S1	0.56494 (8)	0.35278 (6)	0.75025 (3)	0.0615 (2)
S2	0.60276 (7)	0.14457 (7)	0.66590 (3)	0.0638 (2)
N1	0.1666 (2)	0.3052 (2)	0.67012 (8)	0.0589 (5)

Atomic displacement parameters (Å^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
C2	0.0504 (12)	0.0463 (11)	0.0566 (12)	−0.0034 (9)	−0.0033 (9)	−0.0035 (9)
C3	0.0412 (11)	0.0466 (11)	0.0588 (12)	−0.0035 (8)	−0.0002 (9)	−0.0038 (9)
C4	0.0553 (12)	0.0434 (11)	0.0585 (13)	−0.0066 (9)	−0.0020 (10)	−0.0008 (9)
C5	0.0609 (14)	0.0606 (13)	0.0688 (15)	−0.0116 (11)	0.0150 (11)	−0.0024 (11)
C6	0.0474 (13)	0.0693 (15)	0.0928 (19)	−0.0050 (11)	0.0079 (12)	−0.0031 (13)
C7	0.0425 (11)	0.0500 (11)	0.0621 (12)	−0.0023 (9)	−0.0056 (9)	−0.0108 (10)
C8	0.0446 (11)	0.0576 (12)	0.0646 (14)	0.0018 (9)	0.0013 (10)	−0.0100 (10)
C9	0.0493 (12)	0.0538 (13)	0.0846 (17)	0.0044 (10)	−0.0083 (11)	−0.0089 (12)
C10	0.0654 (15)	0.0707 (15)	0.0645 (15)	−0.0047 (12)	−0.0161 (12)	−0.0043 (12)
C11	0.0682 (16)	0.0962 (19)	0.0615 (15)	0.0109 (14)	−0.0027 (12)	−0.0207 (14)
C12	0.0574 (14)	0.0725 (15)	0.0699 (16)	0.0178 (12)	−0.0097 (11)	−0.0204 (12)
C13	0.0451 (11)	0.0698 (14)	0.0566 (13)	0.0102 (10)	0.0043 (9)	−0.0087 (10)
C14	0.0633 (15)	0.0689 (16)	0.0735 (16)	0.0100 (12)	0.0019 (12)	−0.0054 (12)
C15	0.0790 (19)	0.0766 (17)	0.090 (2)	−0.0058 (14)	0.0131 (15)	−0.0209 (15)
C16	0.0612 (16)	0.109 (2)	0.0690 (17)	−0.0075 (15)	0.0079 (13)	−0.0283 (16)
C17	0.086 (2)	0.112 (2)	0.0606 (16)	0.0151 (17)	−0.0100 (14)	−0.0096 (16)
C18	0.0828 (18)	0.0781 (17)	0.0609 (15)	0.0126 (14)	−0.0043 (13)	−0.0028 (12)
C19	0.0666 (17)	0.0893 (19)	0.0905 (19)	0.0192 (14)	−0.0237 (14)	−0.0028 (15)
O1	0.0693 (11)	0.0663 (10)	0.0790 (11)	−0.0096 (8)	−0.0020 (9)	0.0199 (9)
Cl1	0.1408 (8)	0.1145 (7)	0.0781 (5)	0.0100 (6)	−0.0305 (5)	0.0123 (5)
Cl2	0.1044 (7)	0.1885 (11)	0.0944 (6)	−0.0460 (7)	0.0104 (5)	−0.0639 (7)

S1	0.0640 (4)	0.0479 (3)	0.0702 (4)	−0.0118 (2)	−0.0113 (3)	−0.0013 (2)
S2	0.0407 (3)	0.0814 (4)	0.0688 (4)	0.0036 (3)	−0.0002 (3)	−0.0123 (3)
N1	0.0470 (10)	0.0599 (11)	0.0686 (12)	0.0035 (8)	−0.0055 (8)	−0.0025 (9)

Geometric parameters (Å, °)

C2—O1	1.222 (3)	C10—C11	1.382 (4)
C2—N1	1.340 (3)	C10—Cl1	1.731 (3)
C2—C3	1.533 (3)	C11—C12	1.375 (4)
C3—C4	1.518 (3)	C11—H11	0.9300
C3—S2	1.839 (2)	C12—H12	0.9300
C3—S1	1.851 (2)	C13—C14	1.383 (4)
C4—C5	1.513 (3)	C13—C18	1.391 (3)
C4—H4A	0.9700	C13—S2	1.777 (2)
C4—H4B	0.9700	C14—C15	1.388 (4)
C5—C6	1.500 (3)	C14—H14	0.9300
C5—H5A	0.9700	C15—C16	1.367 (4)
C5—H5B	0.9700	C15—H15	0.9300
C6—N1	1.463 (3)	C16—C17	1.366 (4)
C6—H6A	0.9700	C16—Cl2	1.743 (3)
C6—H6B	0.9700	C17—C18	1.380 (4)
C7—C12	1.385 (3)	C17—H17	0.9300
C7—C8	1.388 (3)	C18—H18	0.9300
C7—S1	1.769 (2)	C19—N1	1.460 (3)
C8—C9	1.381 (3)	C19—H19A	0.9600
C8—H8	0.9300	C19—H19B	0.9600
C9—C10	1.365 (4)	C19—H19C	0.9600
C9—H9	0.9300		
O1—C2—N1	121.6 (2)	C9—C10—Cl1	119.9 (2)
O1—C2—C3	120.21 (19)	C11—C10—Cl1	119.0 (2)
N1—C2—C3	118.18 (19)	C12—C11—C10	119.2 (2)
C4—C3—C2	113.84 (17)	C12—C11—H11	120.4
C4—C3—S2	111.66 (14)	C10—C11—H11	120.4
C2—C3—S2	109.95 (14)	C11—C12—C7	120.9 (2)
C4—C3—S1	114.26 (15)	C11—C12—H12	119.5
C2—C3—S1	102.08 (13)	C7—C12—H12	119.5
S2—C3—S1	104.26 (10)	C14—C13—C18	119.3 (2)
C5—C4—C3	110.55 (17)	C14—C13—S2	120.93 (19)
C5—C4—H4A	109.5	C18—C13—S2	119.6 (2)
C3—C4—H4A	109.5	C13—C14—C15	120.2 (3)
C5—C4—H4B	109.5	C13—C14—H14	119.9
C3—C4—H4B	109.5	C15—C14—H14	119.9
H4A—C4—H4B	108.1	C16—C15—C14	119.2 (3)
C6—C5—C4	108.67 (19)	C16—C15—H15	120.4
C6—C5—H5A	110.0	C14—C15—H15	120.4
C4—C5—H5A	110.0	C17—C16—C15	121.6 (3)
C6—C5—H5B	110.0	C17—C16—Cl2	118.4 (3)
C4—C5—H5B	110.0	C15—C16—Cl2	119.9 (3)
H5A—C5—H5B	108.3	C16—C17—C18	119.5 (3)

N1—C6—C5	112.44 (19)	C16—C17—H17	120.2
N1—C6—H6A	109.1	C18—C17—H17	120.2
C5—C6—H6A	109.1	C17—C18—C13	120.1 (3)
N1—C6—H6B	109.1	C17—C18—H18	119.9
C5—C6—H6B	109.1	C13—C18—H18	119.9
H6A—C6—H6B	107.8	N1—C19—H19A	109.5
C12—C7—C8	118.7 (2)	N1—C19—H19B	109.5
C12—C7—S1	118.79 (17)	H19A—C19—H19B	109.5
C8—C7—S1	122.34 (17)	N1—C19—H19C	109.5
C9—C8—C7	120.6 (2)	H19A—C19—H19C	109.5
C9—C8—H8	119.7	H19B—C19—H19C	109.5
C7—C8—H8	119.7	C7—S1—C3	105.06 (10)
C10—C9—C8	119.5 (2)	C13—S2—C3	102.48 (9)
C10—C9—H9	120.3	C2—N1—C19	117.4 (2)
C8—C9—H9	120.3	C2—N1—C6	125.80 (19)
C9—C10—C11	121.1 (2)	C19—N1—C6	116.7 (2)
O1—C2—C3—C4	−175.5 (2)	C14—C15—C16—C17	0.6 (4)
N1—C2—C3—C4	3.4 (3)	C14—C15—C16—Cl2	178.7 (2)
O1—C2—C3—S2	−49.4 (2)	C15—C16—C17—C18	0.0 (5)
N1—C2—C3—S2	129.55 (18)	Cl2—C16—C17—C18	−178.1 (2)
O1—C2—C3—S1	60.9 (2)	C16—C17—C18—C13	−0.9 (4)
N1—C2—C3—S1	−120.22 (18)	C14—C13—C18—C17	1.1 (4)
C2—C3—C4—C5	−40.9 (2)	S2—C13—C18—C17	177.0 (2)
S2—C3—C4—C5	−166.11 (15)	C12—C7—S1—C3	−113.91 (19)
S1—C3—C4—C5	75.9 (2)	C8—C7—S1—C3	70.55 (19)
C3—C4—C5—C6	63.6 (2)	C4—C3—S1—C7	29.71 (18)
C4—C5—C6—N1	−48.4 (3)	C2—C3—S1—C7	153.07 (14)
C12—C7—C8—C9	−0.4 (3)	S2—C3—S1—C7	−92.45 (12)
S1—C7—C8—C9	175.18 (17)	C14—C13—S2—C3	−104.0 (2)
C7—C8—C9—C10	−0.3 (3)	C18—C13—S2—C3	80.2 (2)
C8—C9—C10—C11	0.6 (4)	C4—C3—S2—C13	67.21 (17)
C8—C9—C10—Cl1	−178.95 (18)	C2—C3—S2—C13	−60.15 (16)
C9—C10—C11—C12	−0.3 (4)	S1—C3—S2—C13	−168.93 (11)
Cl1—C10—C11—C12	179.3 (2)	O1—C2—N1—C19	6.9 (3)
C10—C11—C12—C7	−0.3 (4)	C3—C2—N1—C19	−172.0 (2)
C8—C7—C12—C11	0.7 (4)	O1—C2—N1—C6	−168.6 (2)
S1—C7—C12—C11	−175.0 (2)	C3—C2—N1—C6	12.5 (3)
C18—C13—C14—C15	−0.4 (4)	C5—C6—N1—C2	11.0 (3)
S2—C13—C14—C15	−176.2 (2)	C5—C6—N1—C19	−164.5 (2)
C13—C14—C15—C16	−0.5 (4)		

Hydrogen-bond geometry (Å, °)

Cg1 is the centroid of the C7–C12.

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
C9—H9···O1^{i}	0.93	2.32	3.218 (3)	164
C11—H11···Cl2^{ii}	0.93	2.83	3.708 (3)	157
C19—H19a···Cg1^{iii}	0.96	2.95	3.676 (3)	133

Symmetry codes: (i) −*x*+3/2, *y*−1/2, −*z*+3/2; (ii) −*x*+1/2, *y*+1/2, −*z*+3/2; (iii) −*x*+1/2, *y*−1/2, −*z*+3/2.

Fig. 1

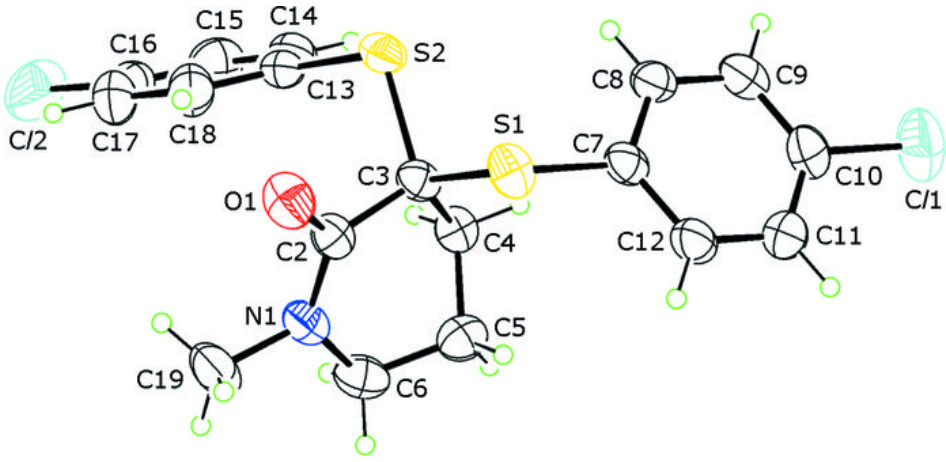
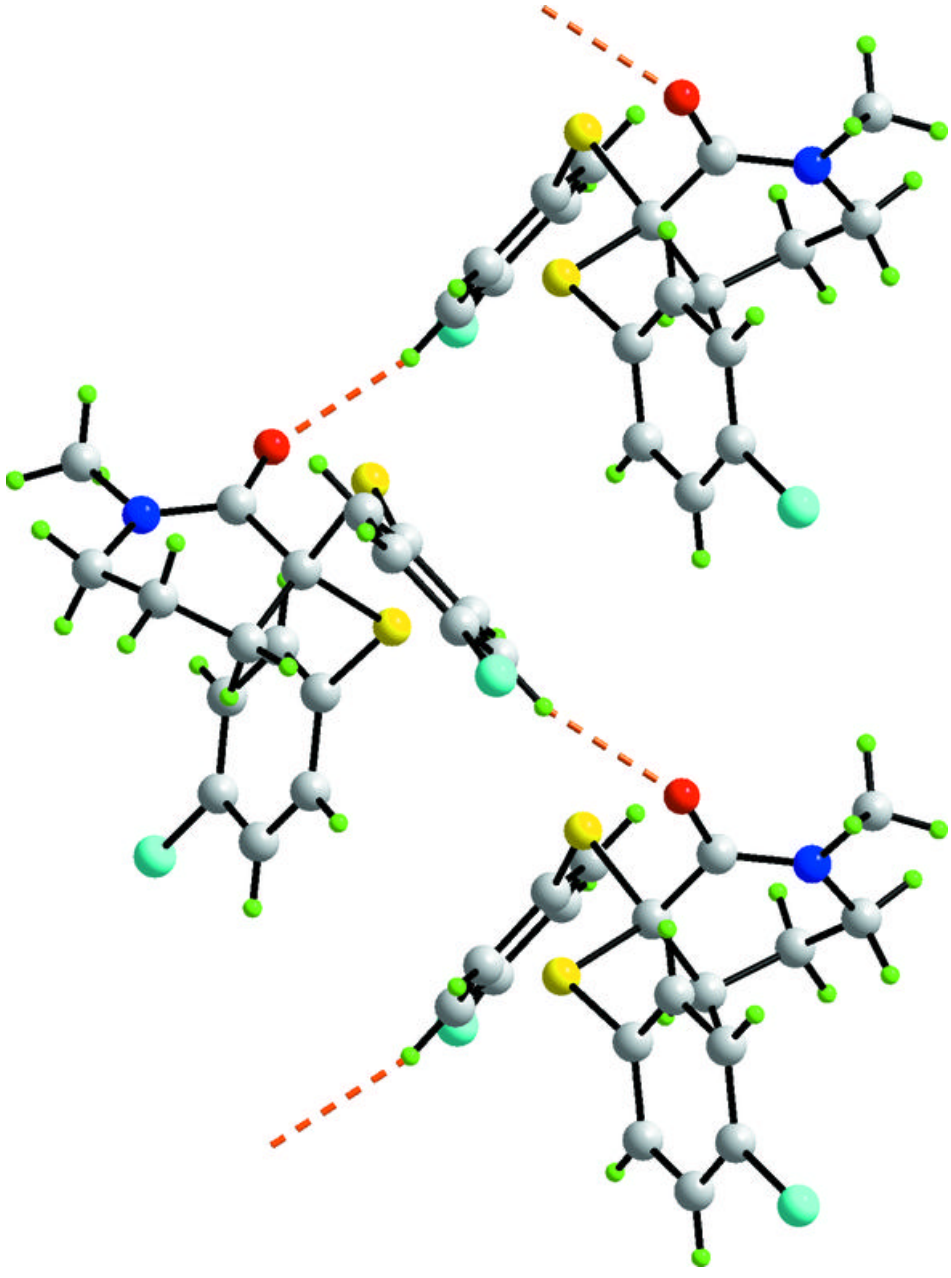


Fig. 2



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Methyl 2,6-bis[(5-bromo-4,6-dimethoxypyrimidin-2-yl)oxy]benzoate

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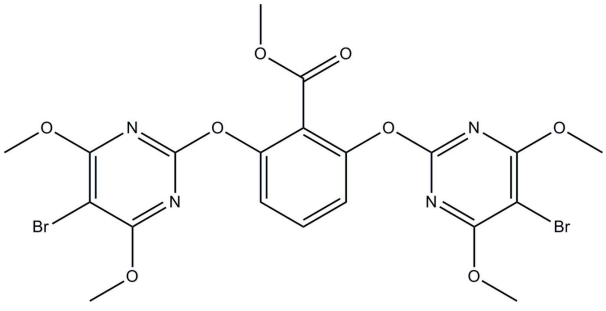
Key indicators: single-crystal X-ray study; T = 293 K; mean σ(C–C) = 0.007 Å; R factor = 0.064; wR factor = 0.254; data-to-parameter ratio = 27.6.

In the title compound, $C_{20}H_{18}Br_2N_4O_8$, the interplanar angle of the pyrimidine rings is 75.1 (2)°. The central benzene ring is inclined at interplanar angles of 66.5 (2) and 71.9 (2)° with respect to the two pyrimidine rings. In the crystal structure, adjacent molecules are connected into two-molecule-thick arrays parallel to the *bc* plane *via* short Br···Br [3.5328 (12) Å] and Br···O [3.206 (3) and 3.301 (4) Å] interactions. A weak intermolecular π–π aromatic stacking interaction [centroid–centroid distance = 3.526 (3) Å] is also observed.

Related literature

For general background to and applications of the title compound, see: Koichiro *et al.* (1988); He *et al.* (2007); Li *et al.* (2006); Gerorge (1983). For closely related structures, see: Fun *et al.* (2010); Li & Luo (2006).



Experimental

Crystal data

$C_{20}H_{18}Br_2N_4O_8$
M_r = 602.20
Monoclinic, $C2/c$
a = 29.972 (5) Å
b = 8.1392 (12) Å
c = 23.061 (3) Å
β = 123.120 (3)°
V = 4711.8 (12) Å^3
Z = 8
Mo $K\alpha$ radiation
μ = 3.49 mm^{-1}
T = 293 K
0.20 × 0.18 × 0.14 mm

Data collection

Bruker APEXII DUO CCD diffractometer
Absorption correction: multi-scan (*SADABS*; Bruker, 2009)
T_{min} = 0.549, T_{max} = 0.640
25204 measured reflections
8438 independent reflections
4458 reflections with $I > 2\sigma(I)$
R_{int} = 0.066

Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.064
$wR(F^2)$ = 0.254
S = 1.02
8438 reflections
306 parameters
H-atom parameters constrained
$\Delta\rho_{max}$ = 1.32 e Å^{-3}
$\Delta\rho_{min}$ = −1.56 e Å^{-3}

Data collection: *APEX2* (Bruker, 2009); cell refinement: *SAINT* (Bruker, 2009); data reduction: *SAINT*; program(s) used to solve structure: *SHELXTL* (Sheldrick, 2008); program(s) used to refine structure: *SHELXTL*; molecular graphics: *SHELXTL*; software used to prepare material for publication: *SHELXTL* and *PLATON* (Spek, 2009).

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Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: HB5519).

References

Bruker (2009). *APEX2*, *SAINT* and *SADABS*. Bruker AXS Inc., Madison, Wisconsin, USA.
Fun, H.-K., Goh, J. H., Rai, S., Isloor, A. M. & Shetty, P. (2010). *Acta Cryst.* E**66**, **ci5115**.
Gerorge, L. (1983). US Patent No. 4 394 506.
He, Y.-Z., Li, Y.-X., Zhu, X.-L., Xi, Z., Niu, C., Wan, J., Zhang, L. & Yang, G.-F. (2007). *J. Chem. Inf. Model.* **47**, 2335–2344.
Koichiro, S., Shoji, K., Yasubumi, T., Takeshige, M. & Ryo, Y. (1988). Japan Patent 88-132167 (CA112:216956, 1998).
Li, Y.-X. & Luo, Y.-P. (2006). *Acta Cryst.* E**62**, o1323–o1325.
Li, Y.-X., Luo, Y.-P., Xi, Z., Niu, C., He, Y.-Z. & Yang, G.-F. (2006). *J. Agric. Food Chem.* **54**, 9135–9139.
Sheldrick, G. M. (2008). *Acta Cryst.* A**64**, 112–122.
Spek, A. L. (2009). *Acta Cryst.* D**65**, 148–155.

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§ Thomson Reuters ResearcherID: C-7576-2009.

supplementary materials

Acta Cryst. (2010). E**66**, o1871 [**doi:10.1107/S1600536810024724**]

Methyl 2,6-bis[(5-bromo-4,6-dimethoxypyrimidin-2-yl)oxy]benzoate

H.-K. Fun, J. H. Goh, S. Rai, A. M. Isloor and P. Shetty

Comment

Methyl-2,6-bis[(5-bromo-4,6-dimethoxypyrimidin-2-yl)oxy]benzoate is a derivative of herbicide showing excellent herbicidal effects on annual and perennial weeds and high-safety crops, especially rice and wheat and is applied to paddy fields, ploughed fields and non-agricultural land (Koichiro *et al.*, 1988). Most sulphonylurea herbicides and all pyrimidinylbenzoate herbicides (He *et al.*, 2007) such as nicofulfuron, amidosulfuron, halopyrazosulfuron, ethoxysulfuron, pyriminobac-methyl and pyriftalid, possess 4,6-dimethoxypyrimidin-2-yl groups (Li *et al.*, 2006), while sulfometuron-methyl, a kind of sulfonylurea, contains 4,6-dimethylpyrimidin-2-yl groups, which suggests that the two disubstituted pyrimidin-2-yl groups possess high biological activity (Gerorge, 1983).

In the title compound (Fig. 1), the two pyrimidine rings with atom sequences N1/C1/C2/C3/N2/C4 and C11/N3/C12/C13/C14/N4 are essentially planar, with maximum deviations of -0.028 (6) and 0.010 (5) Å, respectively, at atoms C1 and N4. An interplanar angle of 75.1 (2)° is formed between these two pyrimidine rings. The central phenyl ring (C5-C10) is inclined at interplanar angles of 66.5 (2) and 71.9 (2)°, respectively, with respect to the N1/C1/C2/C3/N2/C4 and C11/N3/C12/C13/C14/N4 pyrimidine rings. The geometric parameters agree well with those observed in closely related structures (Fun *et al.*, 2010; Li & Luo, 2006).

In the crystal structure, no classical hydrogen bond is observed. The interesting features of the crystal structure are the intermolecular short Br···Br [Br1···Br2^{i} = 3.5328 (12) Å; (i) -x+1/2, y-1/2, -z+1/2] and Br···O [Br1···O8^{i} = 3.301 (4) and Br2···O1^{ii} = 3.206 (3) Å; (ii) x, -y+2, z+1/2] interactions, which are shorter than the sum of the Van der Waals radii of the relevant atoms, interconnecting adjacent molecules into two-molecule-thick arrays parallel to the *bc* plane. Weak intermolecular π–π aromatic stacking interactions [*Cg*1···*Cg*1^{iii} = 3.526 (3) Å; (iii): -x, y, -z+1/2] involving the C11/N3/C12/C13/C14/N4 pyrimidine ring further stabilize the crystal structure.

Experimental

To a stirred solution of methyl-2,6-dihydroxybenzoate (0.50 g, 0.0026 mol) in acetonitrile (10 ml) was added potassium carbonate (1.00 g, 0.0070 mol) and 5-bromo-4,6-dimethoxy-2-(methylsulfonyl)pyrimidine (1.78 g, 0.0050 mol). The reaction mixture was heated to reflux for 4 h. Mass analysis showed completion of the reaction. The reaction mixture was filtered and filtrate was concentrated. The residue was recrystallized using dichloromethane to obtain brown blocks of (I) (Yield: 67 %, *M.p.* 440–443 K).

Refinement

All H atoms were placed in their calculated positions, with C—H = 0.93 – 0.96 Å, and refined using a riding model with U_{iso} = 1.2 or 1.5 U_{eq}(C). The rotating group model was used for the methyl groups.

Figures

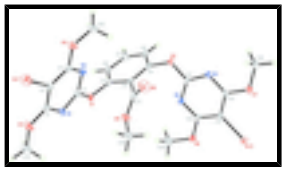


Fig. 1. The molecular structure of (I), showing 20 % probability displacement ellipsoids for non-H atoms.

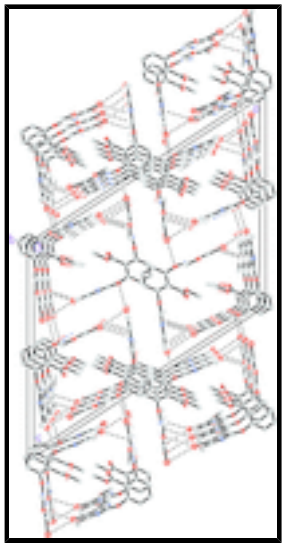


Fig. 2. The crystal structure of (I), viewed along the *b* axis, showing two-molecule-wide arrays parallel to the *bc* plane. H atoms not involved in intermolecular interactions (dashed lines) have been omitted for clarity.

Methyl 2,6-bis[(5-bromo-4,6-dimethoxypyrimidin-2-yl)oxy]benzoate

Crystal data

$C_{20}H_{18}Br_2N_4O_8$	$F(000) = 2400$
$M_r = 602.20$	$D_x = 1.698$ Mg m^{-3}
Monoclinic, *C*2/*c*	Mo *K*α radiation, λ = 0.71073 Å
Hall symbol: -C 2yc	Cell parameters from 2909 reflections
a = 29.972 (5) Å	θ = 2.7–25.5°
b = 8.1392 (12) Å	μ = 3.49 mm^{-1}
c = 23.061 (3) Å	*T* = 293 K
β = 123.120 (3)°	Block, brown
V = 4711.8 (12) Å^3	0.20 × 0.18 × 0.14 mm
Z = 8	

Data collection

Bruker APEXII DUO CCD diffractometer	8438 independent reflections
Radiation source: fine-focus sealed tube	4458 reflections with $I > 2\sigma(I)$
graphite	$R_{int} = 0.066$
φ and ω scans	$\theta_{max} = 32.5°$, $\theta_{min} = 2.7°$
Absorption correction: multi-scan (*SADABS*; Bruker, 2009)	*h* = −45→45

T_{min} = 0.549, T_{max} = 0.640	k = −12→12
25204 measured reflections	l = −34→34

Refinement

Refinement on F^2	Primary atom site location: structure-invariant direct methods
Least-squares matrix: full	Secondary atom site location: difference Fourier map
$R[F^2 > 2\sigma(F^2)]$ = 0.064	Hydrogen site location: inferred from neighbouring sites
$wR(F^2)$ = 0.254	H-atom parameters constrained
S = 1.02	$w = 1/[\sigma^2(F_o^2) + (0.1449P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
8438 reflections	$(\Delta/\sigma)_{max}$ = 0.001
306 parameters	$\Delta\rho_{max}$ = 1.32 e Å^{-3}
0 restraints	$\Delta\rho_{min}$ = −1.56 e Å^{-3}

Special details

Geometry. All esds (except the esd in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell esds are taken into account individually in the estimation of esds in distances, angles and torsion angles; correlations between esds in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell esds is used for estimating esds involving l.s. planes.

Refinement. Refinement of F^2 against ALL reflections. The weighted R-factor wR and goodness of fit S are based on F^2, conventional R-factors R are based on F, with F set to zero for negative F^2. The threshold expression of $F^2 > 2\text{sigma}(F^2)$ is used only for calculating R-factors(gt) etc. and is not relevant to the choice of reflections for refinement. R-factors based on F^2 are statistically about twice as large as those based on F, and R- factors based on ALL data will be even larger.

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å^2)

	x	y	z	U_{iso}*/U_{eq}
Br1	0.30639 (2)	0.57188 (7)	0.09822 (4)	0.0594 (2)
Br2	0.08330 (2)	0.91910 (6)	0.40182 (3)	0.04252 (17)
O1	0.11548 (12)	0.9112 (3)	0.04513 (18)	0.0337 (7)
O2	0.05069 (15)	0.5753 (3)	0.15875 (19)	0.0372 (7)
O3	0.28301 (15)	0.9322 (4)	0.0904 (3)	0.0563 (11)
O4	0.20456 (14)	0.4280 (4)	0.0769 (2)	0.0459 (9)
O5	0.16295 (15)	0.8884 (5)	0.1855 (2)	0.0568 (10)
O6	0.16019 (17)	0.6258 (6)	0.2086 (3)	0.0729 (14)
O7	0.07542 (16)	0.5580 (4)	0.3707 (2)	0.0422 (8)
O8	0.06803 (15)	1.0608 (4)	0.27029 (19)	0.0409 (8)
N1	0.19889 (16)	0.9262 (4)	0.0691 (2)	0.0377 (9)
N2	0.15798 (13)	0.6659 (4)	0.0595 (2)	0.0324 (8)
N3	0.06285 (16)	0.5635 (4)	0.2625 (2)	0.0334 (8)
N4	0.05992 (14)	0.8206 (4)	0.21251 (19)	0.0320 (7)
C1	0.24118 (18)	0.8474 (6)	0.0787 (3)	0.0378 (10)
C2	0.24567 (18)	0.6781 (6)	0.0836 (3)	0.0389 (10)

C3	0.20209 (17)	0.5919 (5)	0.0728 (3)	0.0352 (9)
C4	0.15971 (16)	0.8269 (5)	0.0587 (2)	0.0311 (9)
C5	0.07637 (16)	0.8238 (5)	0.0466 (2)	0.0314 (9)
C6	0.02573 (18)	0.8241 (6)	−0.0133 (3)	0.0410 (11)
H6A	0.0198	0.8777	−0.0526	0.049*
C7	−0.01538 (19)	0.7465 (6)	−0.0153 (3)	0.0472 (12)
H7A	−0.0494	0.7494	−0.0554	0.057*
C8	−0.00662 (19)	0.6642 (6)	0.0420 (3)	0.0410 (11)
H8A	−0.0343	0.6082	0.0405	0.049*
C9	0.04382 (18)	0.6656 (5)	0.1021 (2)	0.0337 (9)
C10	0.08581 (17)	0.7468 (5)	0.1067 (2)	0.0314 (8)
C11	0.05805 (17)	0.6583 (5)	0.2136 (2)	0.0310 (8)
C12	0.06957 (17)	0.6433 (5)	0.3175 (2)	0.0315 (8)
C13	0.07150 (16)	0.8121 (5)	0.3220 (2)	0.0318 (9)
C14	0.06590 (16)	0.8963 (5)	0.2677 (2)	0.0300 (8)
C15	0.2797 (3)	1.1092 (7)	0.0878 (5)	0.068 (2)
H15A	0.3105	1.1541	0.0909	0.101*
H15B	0.2780	1.1486	0.1259	0.101*
H15C	0.2482	1.1428	0.0450	0.101*
C16	0.1604 (2)	0.3438 (6)	0.0691 (4)	0.0586 (17)
H16A	0.1653	0.2277	0.0675	0.088*
H16B	0.1285	0.3779	0.0269	0.088*
H16C	0.1575	0.3686	0.1076	0.088*
C17	0.1402 (2)	0.7456 (6)	0.1719 (3)	0.0437 (11)
C18	0.2141 (3)	0.9103 (8)	0.2484 (4)	0.0720 (14)
H18A	0.2214	1.0256	0.2574	0.108*
H18B	0.2409	0.8602	0.2438	0.108*
H18C	0.2141	0.8600	0.2860	0.108*
C19	0.0734 (3)	0.3785 (6)	0.3658 (4)	0.0590 (16)
H19A	0.0695	0.3336	0.4013	0.089*
H19B	0.1057	0.3382	0.3717	0.089*
H19C	0.0436	0.3459	0.3212	0.089*
C20	0.0691 (3)	1.1479 (9)	0.2166 (4)	0.0720 (14)
H20A	0.0732	1.2634	0.2267	0.108*
H20B	0.0364	1.1289	0.1729	0.108*
H20C	0.0985	1.1093	0.2145	0.108*

Atomic displacement parameters (Å^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Br1	0.0381 (3)	0.0527 (3)	0.0907 (5)	0.0122 (2)	0.0374 (3)	0.0068 (3)
Br2	0.0570 (3)	0.0430 (3)	0.0376 (3)	−0.0108 (2)	0.0324 (2)	−0.0123 (2)
O1	0.0330 (14)	0.0321 (15)	0.0452 (19)	0.0082 (11)	0.0272 (14)	0.0116 (13)
O2	0.058 (2)	0.0298 (15)	0.0372 (18)	−0.0026 (13)	0.0347 (17)	−0.0028 (13)
O3	0.0390 (18)	0.0438 (19)	0.096 (3)	−0.0040 (14)	0.043 (2)	−0.0001 (19)
O4	0.0391 (17)	0.0321 (16)	0.068 (3)	0.0026 (12)	0.0305 (18)	−0.0035 (16)
O5	0.048 (2)	0.067 (2)	0.040 (2)	−0.0182 (17)	0.0144 (18)	0.0008 (19)
O6	0.057 (2)	0.075 (3)	0.057 (3)	0.013 (2)	0.012 (2)	0.024 (2)

O7	0.062 (2)	0.0343 (17)	0.040 (2)	−0.0001 (14)	0.0346 (18)	0.0038 (14)
O8	0.056 (2)	0.0282 (15)	0.038 (2)	0.0019 (13)	0.0257 (17)	−0.0022 (14)
N1	0.0375 (19)	0.0338 (19)	0.048 (2)	0.0027 (14)	0.0270 (19)	0.0063 (17)
N2	0.0304 (16)	0.0305 (17)	0.036 (2)	0.0020 (13)	0.0180 (15)	−0.0021 (15)
N3	0.0444 (19)	0.0308 (18)	0.035 (2)	−0.0017 (14)	0.0279 (18)	−0.0015 (15)
N4	0.0391 (18)	0.0312 (17)	0.0285 (19)	0.0000 (14)	0.0202 (16)	0.0004 (15)
C1	0.035 (2)	0.038 (2)	0.042 (3)	0.0017 (17)	0.022 (2)	0.000 (2)
C2	0.035 (2)	0.037 (2)	0.046 (3)	0.0058 (17)	0.023 (2)	−0.001 (2)
C3	0.034 (2)	0.031 (2)	0.040 (3)	0.0046 (15)	0.0196 (19)	0.0021 (18)
C4	0.0302 (18)	0.037 (2)	0.028 (2)	0.0081 (15)	0.0168 (17)	0.0035 (18)
C5	0.0341 (19)	0.035 (2)	0.032 (2)	0.0063 (16)	0.0225 (18)	0.0031 (18)
C6	0.037 (2)	0.052 (3)	0.037 (3)	0.0065 (19)	0.022 (2)	0.011 (2)
C7	0.033 (2)	0.060 (3)	0.040 (3)	0.002 (2)	0.015 (2)	0.000 (2)
C8	0.038 (2)	0.049 (3)	0.038 (3)	−0.0044 (19)	0.022 (2)	−0.006 (2)
C9	0.044 (2)	0.031 (2)	0.036 (2)	0.0029 (16)	0.028 (2)	−0.0070 (18)
C10	0.038 (2)	0.031 (2)	0.029 (2)	0.0024 (16)	0.0204 (18)	−0.0012 (17)
C11	0.039 (2)	0.0274 (19)	0.033 (2)	−0.0021 (15)	0.0233 (19)	−0.0040 (17)
C12	0.0352 (19)	0.035 (2)	0.030 (2)	−0.0022 (16)	0.0214 (18)	0.0028 (18)
C13	0.0311 (18)	0.037 (2)	0.032 (2)	−0.0015 (15)	0.0199 (18)	−0.0054 (18)
C14	0.0306 (18)	0.0305 (19)	0.030 (2)	−0.0004 (14)	0.0169 (17)	−0.0062 (17)
C15	0.065 (4)	0.039 (3)	0.109 (6)	−0.011 (2)	0.055 (4)	−0.006 (3)
C16	0.045 (3)	0.037 (3)	0.093 (5)	−0.001 (2)	0.037 (3)	−0.002 (3)
C17	0.042 (2)	0.055 (3)	0.033 (3)	0.000 (2)	0.020 (2)	−0.004 (2)
C18	0.073 (3)	0.073 (3)	0.053 (3)	−0.018 (2)	0.023 (2)	0.003 (2)
C19	0.104 (5)	0.032 (2)	0.054 (4)	0.000 (3)	0.052 (4)	0.006 (2)
C20	0.073 (3)	0.073 (3)	0.053 (3)	−0.018 (2)	0.023 (2)	0.003 (2)

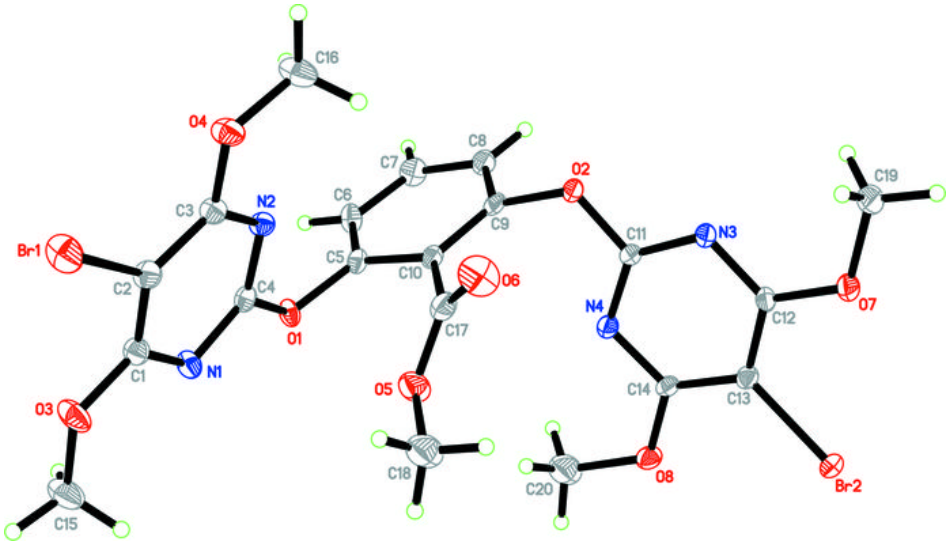
Geometric parameters (Å, °)

Br1—C2	1.872 (4)	C5—C6	1.386 (7)
Br2—C13	1.887 (4)	C5—C10	1.401 (6)
O1—C4	1.368 (5)	C6—C7	1.363 (7)
O1—C5	1.388 (5)	C6—H6A	0.9300
O2—C11	1.342 (5)	C7—C8	1.373 (8)
O2—C9	1.412 (6)	C7—H7A	0.9300
O3—C1	1.324 (6)	C8—C9	1.384 (7)
O3—C15	1.443 (6)	C8—H8A	0.9300
O4—C3	1.337 (5)	C9—C10	1.374 (6)
O4—C16	1.411 (6)	C10—C17	1.496 (7)
O5—C17	1.297 (6)	C12—C13	1.376 (6)
O5—C18	1.433 (8)	C13—C14	1.356 (6)
O6—C17	1.213 (7)	C15—H15A	0.9600
O7—C12	1.336 (5)	C15—H15B	0.9600
O7—C19	1.464 (6)	C15—H15C	0.9600
O8—C14	1.341 (5)	C16—H16A	0.9600
O8—C20	1.442 (8)	C16—H16B	0.9600
N1—C1	1.327 (6)	C16—H16C	0.9600
N1—C4	1.335 (6)	C18—H18A	0.9600
N2—C4	1.312 (6)	C18—H18B	0.9600

N2—C3	1.328 (5)	C18—H18C	0.9600
N3—C11	1.308 (6)	C19—H19A	0.9600
N3—C12	1.339 (6)	C19—H19B	0.9600
N4—C11	1.323 (5)	C19—H19C	0.9600
N4—C14	1.334 (6)	C20—H20A	0.9600
C1—C2	1.383 (6)	C20—H20B	0.9600
C2—C3	1.380 (6)	C20—H20C	0.9600
C4—O1—C5	117.6 (3)	N4—C11—O2	118.2 (4)
C11—O2—C9	118.4 (3)	O7—C12—N3	119.6 (4)
C1—O3—C15	118.4 (4)	O7—C12—C13	118.1 (4)
C3—O4—C16	117.6 (4)	N3—C12—C13	122.3 (4)
C17—O5—C18	119.2 (5)	C14—C13—C12	117.1 (4)
C12—O7—C19	118.0 (4)	C14—C13—Br2	122.1 (3)
C14—O8—C20	118.4 (5)	C12—C13—Br2	120.8 (4)
C1—N1—C4	113.8 (4)	N4—C14—O8	118.8 (4)
C4—N2—C3	114.4 (4)	N4—C14—C13	122.2 (4)
C11—N3—C12	114.7 (4)	O8—C14—C13	119.0 (4)
C11—N4—C14	115.3 (4)	O3—C15—H15A	109.5
O3—C1—N1	119.6 (4)	O3—C15—H15B	109.5
O3—C1—C2	117.7 (4)	H15A—C15—H15B	109.5
N1—C1—C2	122.4 (4)	O3—C15—H15C	109.5
C3—C2—C1	116.9 (4)	H15A—C15—H15C	109.5
C3—C2—Br1	121.9 (3)	H15B—C15—H15C	109.5
C1—C2—Br1	121.1 (3)	O4—C16—H16A	109.5
N2—C3—O4	118.6 (4)	O4—C16—H16B	109.5
N2—C3—C2	122.4 (4)	H16A—C16—H16B	109.5
O4—C3—C2	119.0 (4)	O4—C16—H16C	109.5
N2—C4—N1	129.8 (4)	H16A—C16—H16C	109.5
N2—C4—O1	117.6 (4)	H16B—C16—H16C	109.5
N1—C4—O1	112.6 (4)	O6—C17—O5	123.8 (5)
C6—C5—O1	117.0 (4)	O6—C17—C10	124.0 (5)
C6—C5—C10	120.5 (4)	O5—C17—C10	112.2 (4)
O1—C5—C10	122.5 (4)	O5—C18—H18A	109.5
C7—C6—C5	120.6 (5)	O5—C18—H18B	109.5
C7—C6—H6A	119.7	H18A—C18—H18B	109.5
C5—C6—H6A	119.7	O5—C18—H18C	109.5
C6—C7—C8	120.0 (5)	H18A—C18—H18C	109.5
C6—C7—H7A	120.0	H18B—C18—H18C	109.5
C8—C7—H7A	120.0	O7—C19—H19A	109.5
C7—C8—C9	119.3 (4)	O7—C19—H19B	109.5
C7—C8—H8A	120.3	H19A—C19—H19B	109.5
C9—C8—H8A	120.3	O7—C19—H19C	109.5
C10—C9—C8	122.3 (4)	H19A—C19—H19C	109.5
C10—C9—O2	121.0 (4)	H19B—C19—H19C	109.5
C8—C9—O2	116.7 (4)	O8—C20—H20A	109.5
C9—C10—C5	117.2 (4)	O8—C20—H20B	109.5
C9—C10—C17	121.5 (4)	H20A—C20—H20B	109.5
C5—C10—C17	121.2 (4)	O8—C20—H20C	109.5
N3—C11—N4	128.3 (4)	H20A—C20—H20C	109.5

N3—C11—O2	113.5 (3)	H20B—C20—H20C	109.5
C15—O3—C1—N1	−4.0 (8)	C8—C9—C10—C17	−179.4 (4)
C15—O3—C1—C2	−177.8 (6)	O2—C9—C10—C17	−1.0 (6)
C4—N1—C1—O3	−179.2 (5)	C6—C5—C10—C9	3.4 (6)
C4—N1—C1—C2	−5.6 (7)	O1—C5—C10—C9	179.2 (4)
O3—C1—C2—C3	178.6 (5)	C6—C5—C10—C17	−179.9 (4)
N1—C1—C2—C3	4.9 (8)	O1—C5—C10—C17	−4.1 (6)
O3—C1—C2—Br1	−5.6 (7)	C12—N3—C11—N4	1.2 (7)
N1—C1—C2—Br1	−179.2 (4)	C12—N3—C11—O2	−179.2 (4)
C4—N2—C3—O4	177.9 (5)	C14—N4—C11—N3	−2.2 (7)
C4—N2—C3—C2	−1.0 (7)	C14—N4—C11—O2	178.3 (4)
C16—O4—C3—N2	−2.1 (7)	C9—O2—C11—N3	178.6 (4)
C16—O4—C3—C2	176.8 (5)	C9—O2—C11—N4	−1.8 (6)
C1—C2—C3—N2	−1.4 (8)	C19—O7—C12—N3	−0.9 (7)
Br1—C2—C3—N2	−177.1 (4)	C19—O7—C12—C13	−180.0 (5)
C1—C2—C3—O4	179.8 (5)	C11—N3—C12—O7	−179.3 (4)
Br1—C2—C3—O4	4.0 (7)	C11—N3—C12—C13	−0.3 (6)
C3—N2—C4—N1	0.0 (7)	O7—C12—C13—C14	179.5 (4)
C3—N2—C4—O1	179.8 (4)	N3—C12—C13—C14	0.4 (6)
C1—N1—C4—N2	3.2 (8)	O7—C12—C13—Br2	1.1 (5)
C1—N1—C4—O1	−176.5 (4)	N3—C12—C13—Br2	−178.0 (3)
C5—O1—C4—N2	12.3 (6)	C11—N4—C14—O8	−179.9 (4)
C5—O1—C4—N1	−167.9 (4)	C11—N4—C14—C13	2.2 (6)
C4—O1—C5—C6	−121.7 (5)	C20—O8—C14—N4	−6.1 (6)
C4—O1—C5—C10	62.4 (5)	C20—O8—C14—C13	171.9 (5)
O1—C5—C6—C7	−177.4 (4)	C12—C13—C14—N4	−1.4 (6)
C10—C5—C6—C7	−1.4 (7)	Br2—C13—C14—N4	177.0 (3)
C5—C6—C7—C8	−1.4 (8)	C12—C13—C14—O8	−179.4 (4)
C6—C7—C8—C9	2.1 (8)	Br2—C13—C14—O8	−1.0 (5)
C7—C8—C9—C10	0.1 (7)	C18—O5—C17—O6	−2.0 (9)
C7—C8—C9—O2	−178.4 (4)	C18—O5—C17—C10	176.5 (5)
C11—O2—C9—C10	72.1 (5)	C9—C10—C17—O6	39.9 (7)
C11—O2—C9—C8	−109.4 (5)	C5—C10—C17—O6	−136.6 (6)
C8—C9—C10—C5	−2.8 (6)	C9—C10—C17—O5	−138.5 (5)
O2—C9—C10—C5	175.7 (4)	C5—C10—C17—O5	44.9 (6)

Fig. 1


C16
O4
C3
N2
Br1
C2
C4
O1
C1
N1
O3
C15
C6
C7
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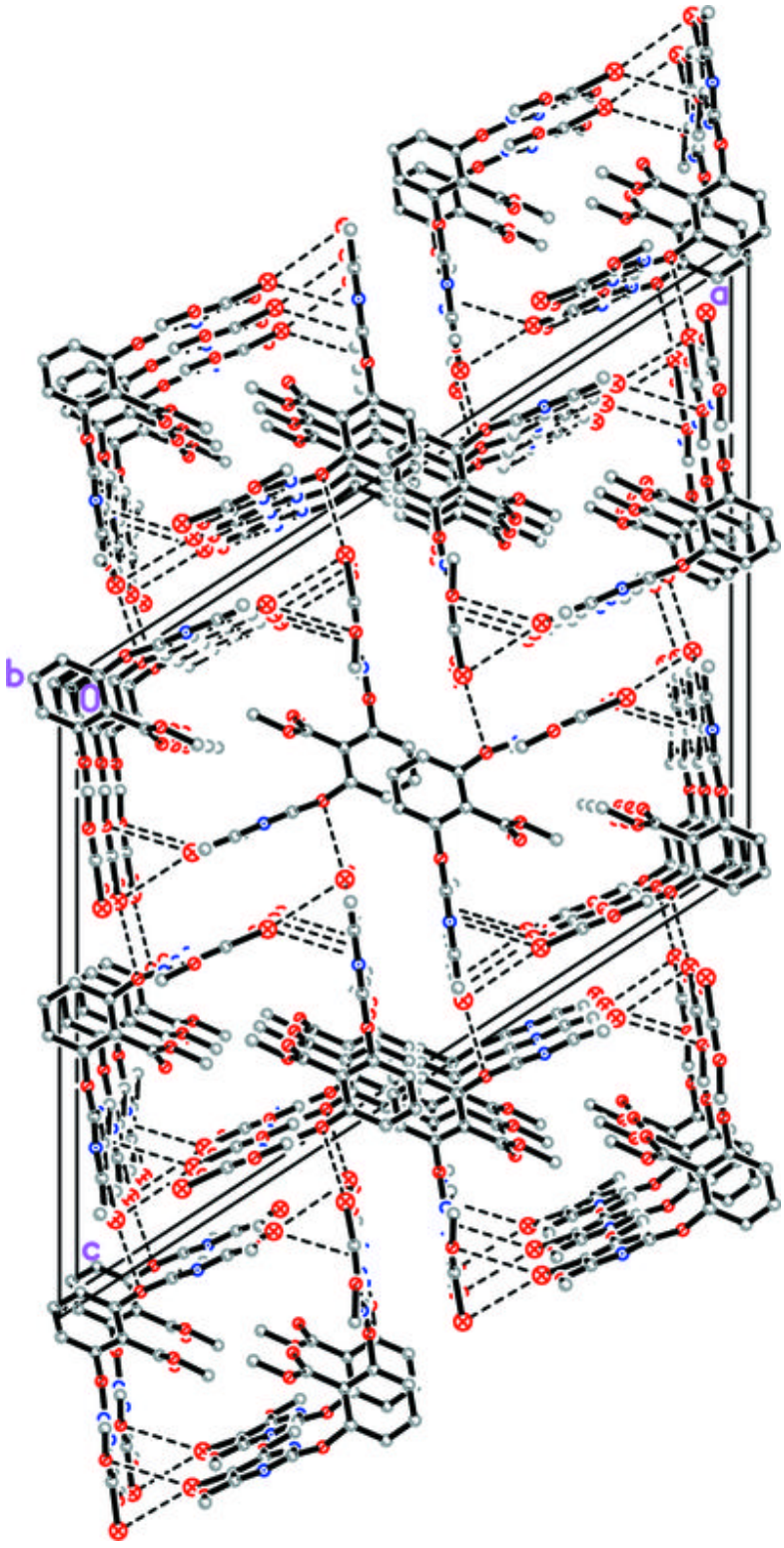
C5
C10
C9
O2
O6
C17
O5
C18
C11
N3
C19
N4
C12
O7
C14
C13
O8
C20
Br2

Fig. 2



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N′-[(*E*)-1-(5-Chloro-2-hydroxyphenyl)-ethylidene]pyridine-3-carbohydrazide monohydrate

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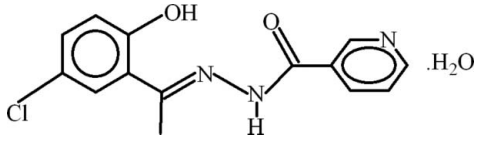
Key indicators: single-crystal X-ray study; T = 296 K; mean σ(C–C) = 0.004 Å; R factor = 0.047; wR factor = 0.135; data-to-parameter ratio = 12.6.

In the title compound, $C_{14}H_{12}ClN_3O_2\cdot H_2O$, the benzene ring and the pyridine rings are oriented at a dihedral angle of 57.73 (12)° and an intramolecular O—H···N hydrogen bond generates an S(6) ring. In the crystal, the water molecule forms O—H···O and O—H···N hydrogen bonds to the organic molecule, leading to chains containing $R_4^4(16)$ loops. In addition, weak aromatic π–π stacking interactions between the centroids of pyridine rings [at distance of 3.864 (2) and 4.013 (2) Å] and C—H···π interactions occur.

Related literature

For background to Schiff bases and for related structures, see: Shafiq *et al.* (2009*a*,*b*): For graph-set notation, see: Bernstein *et al.* (1995).



Experimental

Crystal data

$C_{14}H_{12}ClN_3O_2\cdot H_2O$
M_r = 307.73
Triclinic, $P\overline{1}$
a = 7.1693 (5) Å
b = 7.4964 (4) Å
c = 14.5966 (9) Å
α = 90.138 (2)°
β = 95.835 (1)°
γ = 115.755 (2)°
V = 701.94 (8) Å^3
Z = 2
Mo $K\alpha$ radiation
μ = 0.29 mm^{-1}
T = 296 K
0.28 × 0.18 × 0.14 mm

Data collection

Bruker Kappa APEXII CCD diffractometer
Absorption correction: multi-scan (*SADABS*; Bruker, 2005)
T_{min} = 0.942, T_{max} = 0.959
10105 measured reflections
2491 independent reflections
2151 reflections with $I > 2\sigma(I)$
R_{int} = 0.027

Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.047
$wR(F^2)$ = 0.135
S = 1.17
2491 reflections
198 parameters
H atoms treated by a mixture of independent and constrained refinement
$\Delta\rho_{max}$ = 0.24 e Å^{-3}
$\Delta\rho_{min}$ = −0.35 e Å^{-3}

Table 1
Hydrogen-bond geometry (Å, °).

*Cg*2 is the centroid of the C1–C6 phenyl ring.

D—H···A	D—H	H···A	D···A	D—H···A
O1—H1···N1	0.82	1.84	2.555 (3)	144
N2—H2···O3^{i}	0.86	2.06	2.898 (4)	166
O3—H3*A*···O2	0.89 (5)	1.88 (5)	2.760 (4)	171 (3)
O3—H3*B*···N3^{ii}	0.91 (4)	2.01 (4)	2.885 (4)	161 (4)
C8—H8*A*···*Cg*2^{iii}	0.96	2.99	3.763 (4)	139

Symmetry codes: (i) $x-1, y, z$; (ii) $-x+1, -y, -z+1$; (iii) $-x, -y+1, -z$.

Data collection: *APEX2* (Bruker, 2009); cell refinement: *SAINT* (Bruker, 2009); data reduction: *SAINT*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *ORTEP-3* (Farrugia, 1997) and *PLATON* (Spek, 2009); software used to prepare material for publication: *WinGX* (Farrugia, 1999) and *PLATON*.

The authors acknowledge the provision of funds for the purchase of diffractometer and encouragement by Dr Muhammad Akram Chaudhary, Vice Chancellor, University of Sargodha, Pakistan.

Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: HB5528).

References

Bernstein, J., Davis, R. E., Shimoni, L. & Chang, N.-L. (1995). *Angew. Chem. Int. Ed. Engl.* **34**, 1555–1573.
Bruker (2005). *SADABS*. Bruker AXS Inc., Madison, Wisconsin, USA.
Bruker (2009). *APEX2* and *SAINT*. Bruker AXS Inc., Madison, Wisconsin, USA.
Farrugia, L. J. (1997). *J. Appl. Cryst.* **30**, 565.
Farrugia, L. J. (1999). *J. Appl. Cryst.* **32**, 837–838.
Shafiq, Z., Yaqub, M., Tahir, M. N., Hussain, A. & Iqbal, M. S. (2009*a*). *Acta Cryst.* E**65**, o2496.
Shafiq, Z., Yaqub, M., Tahir, M. N., Hussain, A. & Iqbal, M. S. (2009*b*). *Acta Cryst.* E**65**, o2899.
Sheldrick, G. M. (2008). *Acta Cryst.* A**64**, 112–122.
Spek, A. L. (2009). *Acta Cryst.* D**65**, 148–155.

supplementary materials

Acta Cryst. (2010). E**66**, o1880 [**doi:10.1107/S1600536810025213**]

N'-[(*E*)-1-(5-Chloro-2-hydroxyphenyl)ethylidene]pyridine-3-carbohydrazide monohydrate

A. Hussain, Z. Shafiq, M. N. Tahir and M. Yaqub

Comment

We have reported crystal structures of Schiff bases containing pyridne (Shafiq *et al.*, 2009*a*, 2009*b*) and as a part of this project, we report herein the structure and synthesis of the title compound (I, Fig. 1).

In (I) the group A (C1–C8/O1/CL1) of 5-chloro-2-hydroxyacetophenone, the central group B (N1/N2/C9/O2) and the pyridine ring C (C10—C14/N3) are planar with r. m. s. deviation of 0.0330, 0.0182 and 0.0082 Å, respectively. The dihedral angle between A/B, A/C and B/C is 6.62 (11), 58.08 (10) and 52.98 (14)°, respectively. There exist intramolecular H-bonding of O—H···N type forming an S(6) ring motif (Bernstein *et al.*, 1995). The water molecule acts as donar as well as accepter and therefore interconnects three molecules. Due to intra as well as intermolecular H-bondings of O—H···O and O—H···N types (Table 1, Fig. 2), the title compound is stabilized in infinite one dimensional polymeric chains. In the polymeric chains $R_4^4(16)$ ring motifs are formed. The π–π interactions exist between the centroids of pyridine rings at distance of 3.864 (2) Å [symmetry: -*x*, -*y*, 1 - *z*] and at 4.013 (2) Å [symmetry: 1 - *x*, 1 - *y*, 1 - *z*]. The C—H···π interaction (Table 1) also plays an important role in stabilizing the structure.

Experimental

To a hot stirred solution of 5-chloro-2-hydroxyacetophenone (1.71 g, 0.01 mole) in ethanol, 25 ml nicotinic acid hydrazide (1.37 g, 0.01 mol) was added. The resultant mixture was then heated under reflux for 7–8 h. The reaction was monitored through TLC. The precipitate were formed were collected by suction filteration. The resultant crude material was dried and recrystalized in 1,4-dioxan:ethanol(1:2) to affoard light brown needles of (I).

Refinement

The coordinates of H-atoms of water molecule were refined. The H-atoms were positioned geometrically (O–H = 0.82, N–H = 0.86, C–H = 0.93–0.96 Å) and refined as riding with U_{iso}(H) = xU_{eq}(C, N, O), where x = 1.5 for methyl and x = 1.2 for all other H-atoms.

Figures

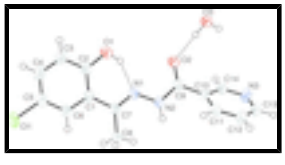


Fig. 1. View of the title compound with displacement ellipsoids drawn at the 50% probability level. The dotted line shows the intramolecular H-bond.

Fig. 2. The partial packing of (I), which shows that molecules form infinite one dimensional polymeric chains with different ring motifs.

N'-[(*E*)-1-(5-Chloro-2-hydroxyphenyl)ethylidene]pyridine-3- carbohydrazide monohydrate

Crystal data

$C_{14}H_{12}ClN_3O_2 \cdot H_2O$	$Z = 2$
$M_r = 307.73$	$F(000) = 320$
Triclinic, $P\overline{1}$	$D_x = 1.456$ Mg m^{-3}
Hall symbol: -P 1	Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å
$a = 7.1693$ (5) Å	Cell parameters from 1770 reflections
$b = 7.4964$ (4) Å	$\theta = 2.6$–$28.4°$
$c = 14.5966$ (9) Å	$\mu = 0.29$ mm^{-1}
$\alpha = 90.138$ (2)°	$T = 296$ K
$\beta = 95.835$ (1)°	Needle, light brown
$\gamma = 115.755$ (2)°	0.28 × 0.18 × 0.14 mm
$V = 701.94$ (8) Å^3	

Data collection

Bruker Kappa APEXII CCD diffractometer	2491 independent reflections
Radiation source: fine-focus sealed tube	2151 reflections with $I > 2\sigma(I)$
graphite	$R_{int} = 0.027$
Detector resolution: 8.20 pixels mm^{-1}	$\theta_{max} = 25.3°$, $\theta_{min} = 2.8°$
ω scans	$h = -8 \rightarrow 8$
Absorption correction: multi-scan (*SADABS*; Bruker, 2005)	$k = -8 \rightarrow 8$
$T_{min} = 0.942$, $T_{max} = 0.959$	$l = -16 \rightarrow 17$
10105 measured reflections	

Refinement

Refinement on F^2	Primary atom site location: structure-invariant direct methods
Least-squares matrix: full	Secondary atom site location: difference Fourier map
$R[F^2 > 2\sigma(F^2)] = 0.047$	Hydrogen site location: inferred from neighbouring sites
$wR(F^2) = 0.135$	H atoms treated by a mixture of independent and constrained refinement
$S = 1.17$	$w = 1/[\sigma^2(F_o^2) + (0.0375P)^2 + 0.8617P]$ where $P = (F_o^2 + 2F_c^2)/3$
2491 reflections	$(\Delta/\sigma)_{max} < 0.001$

198 parameters

0 restraints

$\Delta\rho_{max} = 0.24$ e Å^{-3}

$\Delta\rho_{min} = -0.35$ e Å^{-3}

Special details

Geometry. Bond distances, angles *etc*. have been calculated using the rounded fractional coordinates. All su's are estimated from the variances of the (full) variance-covariance matrix. The cell e.s.d.'s are taken into account in the estimation of distances, angles and torsion angles

Refinement. Refinement of F^2 against ALL reflections. The weighted *R*-factor *wR* and goodness of fit *S* are based on F^2, conventional *R*-factors *R* are based on *F*, with *F* set to zero for negative F^2. The threshold expression of $F^2 > \sigma(F^2)$ is used only for calculating *R*-factors(gt) *etc*. and is not relevant to the choice of reflections for refinement. *R*-factors based on F^2 are statistically about twice as large as those based on *F*, and *R*- factors based on ALL data will be even larger.

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å^2)

	x	*y*	*z*	U_{iso}*/U_{eq}
Cl1	−0.33027 (14)	0.26260 (13)	−0.24936 (5)	0.0523 (3)
O1	0.3445 (3)	0.2717 (4)	0.01706 (15)	0.0491 (8)
O2	0.4191 (3)	0.2364 (4)	0.25756 (15)	0.0544 (8)
N1	0.1131 (3)	0.2425 (3)	0.14368 (15)	0.0338 (7)
N2	0.0986 (4)	0.2273 (4)	0.23701 (15)	0.0347 (7)
N3	0.2974 (4)	0.0892 (5)	0.53373 (18)	0.0523 (10)
C1	−0.0064 (4)	0.2462 (4)	−0.01053 (18)	0.0311 (8)
C2	0.1854 (4)	0.2739 (4)	−0.04006 (19)	0.0365 (9)
C3	0.2156 (5)	0.3040 (5)	−0.1323 (2)	0.0505 (11)
C4	0.0595 (6)	0.3026 (5)	−0.1958 (2)	0.0502 (11)
C5	−0.1289 (5)	0.2703 (4)	−0.16794 (19)	0.0391 (9)
C6	−0.1630 (4)	0.2451 (4)	−0.07681 (19)	0.0347 (8)
C7	−0.0461 (4)	0.2199 (4)	0.08716 (18)	0.0306 (8)
C8	−0.2576 (5)	0.1709 (6)	0.1141 (2)	0.0476 (10)
C9	0.2671 (4)	0.2336 (4)	0.28988 (19)	0.0343 (9)
C10	0.2551 (4)	0.2337 (4)	0.39173 (18)	0.0341 (9)
C11	0.2132 (4)	0.3709 (5)	0.4384 (2)	0.0398 (9)
C12	0.2188 (5)	0.3679 (5)	0.5328 (2)	0.0500 (11)
C13	0.2599 (5)	0.2246 (6)	0.5769 (2)	0.0537 (13)
C14	0.2966 (5)	0.0971 (5)	0.4425 (2)	0.0421 (10)
O3	0.7770 (3)	0.2277 (4)	0.34221 (16)	0.0478 (8)
H1	0.31433	0.26059	0.07012	0.0736*
H2	−0.01187	0.21446	0.26025	0.0416*
H3	0.34320	0.32529	−0.15140	0.0608*
H4	0.08174	0.32343	−0.25733	0.0605*
H6	−0.29067	0.22721	−0.05904	0.0416*
H8A	−0.27145	0.29111	0.12362	0.0715*
H8B	−0.27573	0.10118	0.17002	0.0715*
H8C	−0.36158	0.08889	0.06588	0.0715*
H11	0.18180	0.46339	0.40644	0.0478*
H12	0.19538	0.46062	0.56616	0.0598*

H13	0.26161	0.22236	0.64064	0.0645*
H14	0.32550	0.00545	0.41125	0.0505*
H3A	0.657 (6)	0.217 (5)	0.314 (3)	0.0574*
H3B	0.735 (6)	0.139 (5)	0.387 (3)	0.0574*

Atomic displacement parameters (Å^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Cl1	0.0600 (5)	0.0632 (5)	0.0309 (4)	0.0269 (4)	−0.0066 (3)	0.0055 (3)
O1	0.0391 (12)	0.0743 (16)	0.0436 (12)	0.0329 (12)	0.0093 (10)	0.0112 (12)
O2	0.0426 (12)	0.1011 (19)	0.0355 (12)	0.0456 (13)	0.0069 (10)	0.0129 (12)
N1	0.0346 (12)	0.0435 (14)	0.0252 (12)	0.0192 (11)	0.0011 (9)	0.0024 (10)
N2	0.0313 (12)	0.0509 (14)	0.0248 (12)	0.0209 (11)	0.0026 (9)	0.0032 (10)
N3	0.0568 (17)	0.079 (2)	0.0347 (14)	0.0416 (16)	0.0083 (12)	0.0156 (14)
C1	0.0344 (14)	0.0286 (14)	0.0287 (14)	0.0127 (12)	0.0015 (11)	0.0001 (11)
C2	0.0393 (16)	0.0394 (16)	0.0347 (15)	0.0204 (13)	0.0056 (12)	0.0032 (12)
C3	0.0509 (19)	0.069 (2)	0.0438 (18)	0.0342 (18)	0.0205 (15)	0.0110 (16)
C4	0.067 (2)	0.063 (2)	0.0297 (16)	0.0352 (19)	0.0135 (15)	0.0081 (14)
C5	0.0493 (18)	0.0391 (16)	0.0281 (14)	0.0199 (14)	−0.0012 (12)	0.0013 (12)
C6	0.0338 (14)	0.0366 (15)	0.0316 (15)	0.0141 (12)	0.0012 (11)	0.0001 (12)
C7	0.0314 (14)	0.0326 (14)	0.0282 (14)	0.0148 (12)	0.0015 (11)	0.0004 (11)
C8	0.0356 (16)	0.079 (2)	0.0296 (15)	0.0264 (16)	0.0031 (12)	0.0055 (15)
C9	0.0307 (14)	0.0450 (17)	0.0301 (14)	0.0197 (13)	0.0014 (11)	0.0039 (12)
C10	0.0270 (13)	0.0469 (17)	0.0267 (14)	0.0153 (12)	−0.0004 (11)	0.0020 (12)
C11	0.0356 (15)	0.0473 (17)	0.0368 (16)	0.0192 (14)	0.0000 (12)	0.0014 (13)
C12	0.0470 (18)	0.068 (2)	0.0382 (17)	0.0284 (17)	0.0032 (14)	−0.0074 (16)
C13	0.053 (2)	0.092 (3)	0.0261 (16)	0.041 (2)	0.0038 (14)	0.0042 (16)
C14	0.0458 (17)	0.057 (2)	0.0322 (16)	0.0302 (16)	0.0057 (13)	0.0064 (14)
O3	0.0364 (12)	0.0757 (17)	0.0380 (12)	0.0304 (12)	0.0052 (9)	0.0118 (11)

Geometric parameters (Å, °)

Cl1—C5	1.755 (4)	C5—C6	1.376 (4)
O1—C2	1.349 (4)	C7—C8	1.492 (5)
O2—C9	1.223 (4)	C9—C10	1.498 (4)
O1—H1	0.8200	C10—C11	1.385 (4)
O3—H3A	0.89 (5)	C10—C14	1.382 (4)
O3—H3B	0.91 (4)	C11—C12	1.375 (4)
N1—N2	1.378 (3)	C12—C13	1.377 (5)
N1—C7	1.285 (4)	C3—H3	0.9300
N2—C9	1.348 (4)	C4—H4	0.9300
N3—C14	1.333 (4)	C6—H6	0.9300
N3—C13	1.330 (5)	C8—H8C	0.9600
N2—H2	0.8600	C8—H8A	0.9600
C1—C7	1.479 (4)	C8—H8B	0.9600
C1—C6	1.403 (4)	C11—H11	0.9300
C1—C2	1.412 (4)	C12—H12	0.9300
C2—C3	1.389 (4)	C13—H13	0.9300
C3—C4	1.375 (5)	C14—H14	0.9300

C4—C5	1.370 (6)		
C2—O1—H1	109.00	C9—C10—C14	119.0 (3)
H3A—O3—H3B	102 (4)	C9—C10—C11	122.9 (3)
N2—N1—C7	120.6 (3)	C10—C11—C12	118.8 (3)
N1—N2—C9	116.3 (3)	C11—C12—C13	118.5 (3)
C13—N3—C14	116.9 (3)	N3—C13—C12	123.9 (3)
N1—N2—H2	122.00	N3—C14—C10	123.7 (3)
C9—N2—H2	122.00	C2—C3—H3	120.00
C2—C1—C6	118.2 (2)	C4—C3—H3	120.00
C2—C1—C7	122.3 (3)	C5—C4—H4	120.00
C6—C1—C7	119.5 (3)	C3—C4—H4	120.00
C1—C2—C3	119.6 (3)	C1—C6—H6	120.00
O1—C2—C3	117.1 (3)	C5—C6—H6	120.00
O1—C2—C1	123.3 (3)	C7—C8—H8B	109.00
C2—C3—C4	120.9 (3)	C7—C8—H8C	109.00
C3—C4—C5	119.7 (3)	H8A—C8—H8B	110.00
Cl1—C5—C6	119.2 (3)	H8A—C8—H8C	109.00
Cl1—C5—C4	119.7 (2)	H8B—C8—H8C	109.00
C4—C5—C6	121.1 (3)	C7—C8—H8A	109.00
C1—C6—C5	120.4 (3)	C10—C11—H11	121.00
N1—C7—C8	124.7 (2)	C12—C11—H11	121.00
C1—C7—C8	120.6 (3)	C13—C12—H12	121.00
N1—C7—C1	114.7 (3)	C11—C12—H12	121.00
O2—C9—N2	122.8 (3)	N3—C13—H13	118.00
O2—C9—C10	121.7 (3)	C12—C13—H13	118.00
N2—C9—C10	115.5 (3)	N3—C14—H14	118.00
C11—C10—C14	118.1 (3)	C10—C14—H14	118.00
C7—N1—N2—C9	173.6 (3)	O1—C2—C3—C4	178.1 (3)
N2—N1—C7—C1	178.2 (2)	C1—C2—C3—C4	−1.5 (5)
N2—N1—C7—C8	−1.8 (4)	C2—C3—C4—C5	−0.3 (5)
N1—N2—C9—O2	−5.8 (4)	C3—C4—C5—Cl1	−178.5 (3)
N1—N2—C9—C10	175.2 (2)	C3—C4—C5—C6	2.0 (5)
C14—N3—C13—C12	0.8 (6)	Cl1—C5—C6—C1	178.6 (2)
C13—N3—C14—C10	−1.4 (6)	C4—C5—C6—C1	−1.9 (4)
C6—C1—C2—O1	−178.0 (3)	O2—C9—C10—C11	126.3 (3)
C6—C1—C2—C3	1.6 (4)	O2—C9—C10—C14	−50.7 (4)
C7—C1—C2—O1	2.4 (4)	N2—C9—C10—C11	−54.6 (4)
C7—C1—C2—C3	−178.0 (3)	N2—C9—C10—C14	128.4 (3)
C2—C1—C6—C5	0.1 (4)	C9—C10—C11—C12	−175.7 (3)
C7—C1—C6—C5	179.7 (3)	C14—C10—C11—C12	1.3 (5)
C2—C1—C7—N1	6.1 (4)	C9—C10—C14—N3	177.6 (3)
C2—C1—C7—C8	−173.9 (3)	C11—C10—C14—N3	0.4 (5)
C6—C1—C7—N1	−173.5 (2)	C10—C11—C12—C13	−1.9 (5)
C6—C1—C7—C8	6.6 (4)	C11—C12—C13—N3	0.9 (6)

Hydrogen-bond geometry (Å, °)

Cg2 is the centroid of the C1–C6 phenyl ring.

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
O1—H1···N1	0.82	1.84	2.555 (3)	144
N2—H2···O3^{i}	0.86	2.06	2.898 (4)	166
O3—H3A···O2	0.89 (5)	1.88 (5)	2.760 (4)	171 (3)
O3—H3B···N3^{ii}	0.91 (4)	2.01 (4)	2.885 (4)	161 (4)
C8—H8A···Cg2^{iii}	0.96	2.99	3.763 (4)	139

Symmetry codes: (i) *x*−1, *y*, *z*; (ii) −*x*+1, −*y*, −*z*+1; (iii) −*x*, −*y*+1, −*z*.

Fig. 1

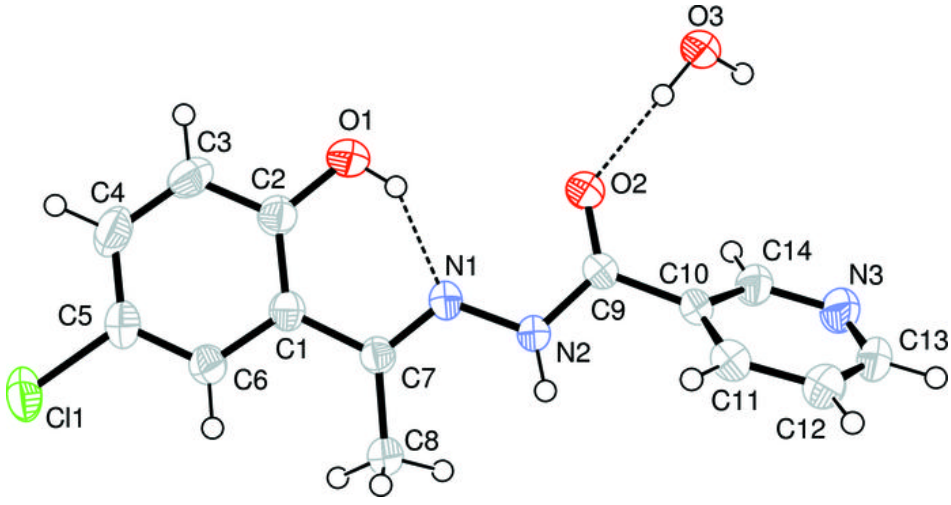
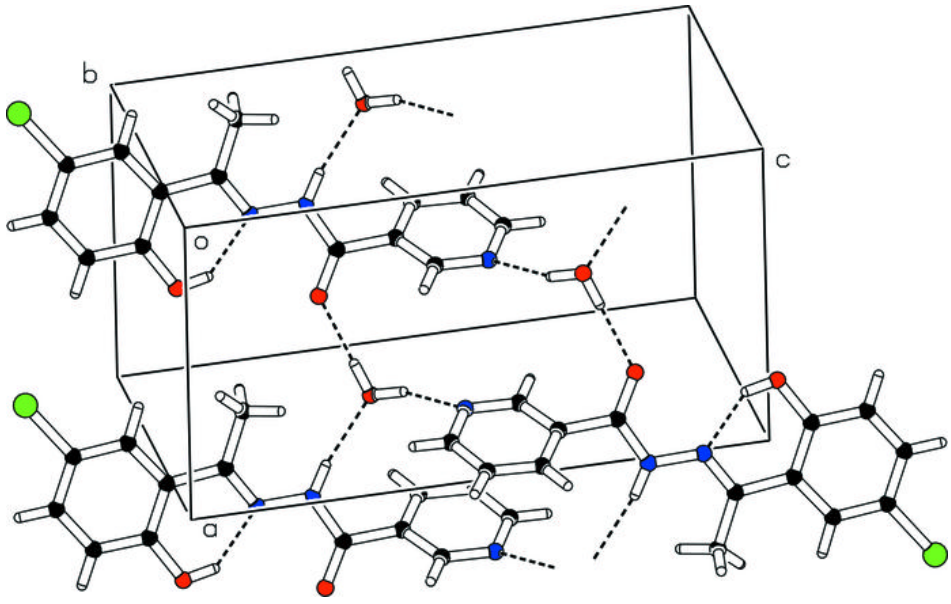


Fig. 2



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N′-[(*E*)-(1-Methyl-1*H*-pyrrol-2-yl)methylidene]pyridine-4-carbohydrazide. Corrigendum

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The name of one of the authors in the paper by Hussain *et al.* [*Acta Cryst.* (2010), E**66**, o1881] is corrected.

In the paper by Hussain *et al.* (2010), the last author is incorrectly given as 'Muhammad Mazhar'. The correct name of the last author should be 'Mazhar Hussain' as above.

References

Hussain, A., Tahir, M. N., Shafiq, Z., Yaqub, M. & Mazhar, M. (2010). *Acta Cryst.* E**66**, o1881.

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N′-[(*E*)-(1-Methyl-1*H*-pyrrol-2-yl)methylidene]pyridine-4-carbohydrazide

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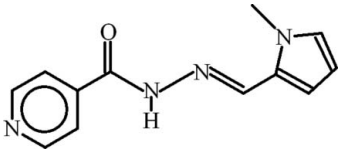
Key indicators: single-crystal X-ray study; T = 296 K; mean σ(C–C) = 0.002 Å; R factor = 0.045; wR factor = 0.127; data-to-parameter ratio = 18.1.

In the title compound, $C_{12}H_{12}N_4O$, the pyridine and pyrrole rings are inclined at an angle of 29.22 (8)° and an intramolecular C—H···N interaction geneates an S(6) ring. In the crystal, molecules are linked by N—H···N hydrogen bonds, forming (010) C(7) chains. The chains are cross-linked by weak C—H···O interactions, which generate $R_2^2(18)$ ring motifs within an infinite sheet. Finally, two C—H···π interactions are present, where the C—H groups are from the pyridine ring and π is the pyrrole ring.

Related literature

For background information on Schiff bases containing heterocyclic rings and for related structures, see: Shafiq *et al.*,(2009*a*,*b*); Hussain *et al.* (2010) For graph-set notation, see: Bernstein *et al.* (1995).



Experimental

Crystal data

$C_{12}H_{12}N_4O$
M_r = 228.26
Monoclinic, $P2_1/n$
a = 8.2134 (3) Å
b = 10.6740 (4) Å
c = 13.1332 (4) Å
β = 96.938 (2)°
V = 1142.95 (7) Å^3
Z = 4
Mo $K\alpha$ radiation
μ = 0.09 mm^{-1}
T = 296 K
0.24 × 0.18 × 0.15 mm

Data collection

Bruker Kappa APEXII CCD diffractometer
Absorption correction: multi-scan (*SADABS*; Bruker, 2005)
T_{min} = 0.980, T_{max} = 0.985
12030 measured reflections
2803 independent reflections
2023 reflections with $I > 2\sigma(I)$
R_{int} = 0.029

Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.045
$wR(F^2)$ = 0.127
S = 1.04
2803 reflections
155 parameters
H-atom parameters constrained
$\Delta\rho_{max}$ = 0.28 e Å^{-3}
$\Delta\rho_{min}$ = −0.21 e Å^{-3}

Table 1
Hydrogen-bond geometry (Å, °).

*Cg*1 is the centroid of the C8—C11/N4 ring.

D—H···A	D—H	H···A	D···A	D—H···A
N2—H2···N1^{i}	0.86	2.19	3.0205 (18)	163
C4—H4···O1^{ii}	0.93	2.54	3.3821 (19)	150
C12—H12*B*···O1^{iii}	0.96	2.55	3.450 (2)	156
C12—H12*C*···N3	0.96	2.36	3.025 (2)	126
C2—H2*A*···*Cg*1^{iv}	0.93	2.83	3.3258 (16)	114
C5—H5···*Cg*1^{v}	0.93	2.71	3.4669 (17)	139

Symmetry codes: (i) $-x+\frac{1}{2}, y+\frac{1}{2}, -z+\frac{1}{2}$; (ii) $x-\frac{1}{2}, -y+\frac{1}{2}, z-\frac{1}{2}$; (iii) $-x+2, -y+1, -z+1$; (iv) $-x+1, -y+1, -z+1$; (v) $-x+\frac{3}{2}, y-\frac{1}{2}, -z+\frac{1}{2}$.

Data collection: *APEX2* (Bruker, 2009); cell refinement: *SAINT* (Bruker, 2009); data reduction: *SAINT*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *ORTEP-3 for Windows* (Farrugia, 1997) and *PLATON* (Spek, 2009); software used to prepare material for publication: *WinGX* (Farrugia, 1999) and *PLATON*.

The authors acknowledge the provision of funds for the purchase of diffractometer and encouragement by Dr Muhammad Akram Chaudhary, Vice Chancellor, University of Sargodha, Pakistan.

Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: HB5530).

References

Bernstein, J., Davis, R. E., Shimoni, L. & Chang, N.-L. (1995). *Angew. Chem. Int. Ed. Engl.* **34**, 1555–1573.
Bruker (2005). *SADABS*. Bruker AXS Inc., Madison, Wisconsin, USA.
Bruker (2009). *APEX2* and *SAINT*. Bruker AXS Inc., Madison, Wisconsin, USA.
Farrugia, L. J. (1997). *J. Appl. Cryst.* **30**, 565.
Farrugia, L. J. (1999). *J. Appl. Cryst.* **32**, 837–838.
Hussain, A., Shafiq, Z., Tahir, M. N. & Yaqub, M. (2010). *Acta. Cryst.* E**66**, o1880.
Shafiq, Z., Yaqub, M., Tahir, M. N., Hussain, A. & Iqbal, M. S. (2009*a*). *Acta Cryst.* E**65**, o2496.
Shafiq, Z., Yaqub, M., Tahir, M. N., Hussain, A. & Iqbal, M. S. (2009*b*). *Acta Cryst.* E**65**, o2899.
Sheldrick, G. M. (2008). *Acta Cryst.* A**64**, 112–122.
Spek, A. L. (2009). *Acta Cryst.* D**65**, 148–155.

supplementary materials

Acta Cryst. (2010). E**66**, o1881 [**doi:10.1107/S1600536810025341**]

N'-[(*E*)-(1-Methyl-1*H*-pyrrol-2-yl)methylidene]pyridine-4-carbohydrazide

A. Hussain, M. N. Tahir, Z. Shafiq, M. Yaqub and M. Mazhar

Comment

We have reported crystal structures of Schiff bases with N-containing aromatic ring (Shafiq *et al.*, 2009*a*, 2009*b*), (Hussain *et al.*, 2010) and as a part of this project, we report herein the structure and synthesis of the title compound (I, Fig. 1).

In (I) the pyridine ring A (C1–C5/N1), the central moiety B (O1/C6/N2/N3/C7) and the pyrrol moiety C (C8—C11/N4/C12) are planar with r. m. s. deviations of 0.0345, 0.0285 and 0.0276 Å, respectively. The dihedral angle between A/B, A/C and B/C is 38.32 (8)°, 29.22 (8)° and 9.44 (13)°, respectively. In title molecule, there exist intra as well inter-molecular H-bondings (Table 1). The molecules form infinite one dimensional polymeric chains extending along the *b* axis (Fig. 2), if only strong H-bondings are considered. If the strong as well as weak H-bondings are considered then the molecules form two-dimensional polymeric chains with $R_2^2(18)$ (Bernstein *et al.*, 1995) ring motifs (Fig. 3). The C—H···π interactions (Table 1) also play important role in stabilizing the molecules.

Experimental

To a hot stirred solution of isoniazid (1.37 g, 0.01 mole) in ethanol 15 ml was added *N*-methylpyrrol-2-carboxaldehyde (1.1 ml, 0.01 mol). The resultant mixture was then heated under reflux. The reaction was monitored through TLC. After an hour, the precipitate were formed. The reaction mixture was further heated for 30 min. The resultant crude material was recrystalized in 1,4-dioxane:ethanol (1:4) to affoard red prisms of (I).

Refinement

The H-atoms were positioned geometrically (N–H = 0.86 Å, `C–H = 0.93–0.96 Å) and refined as riding with U_{iso}(H) = xU_{eq}(C, N), where x = 1.5 for methyl and x = 1.2 for all other H-atoms.

Figures

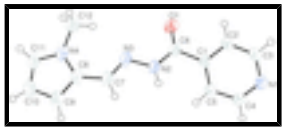


Fig. 1. View of (I) with displacement ellipsoids drawn at the 50% probability level. H-atoms are shown by small circles of arbitrary radius.

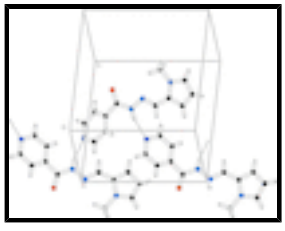


Fig. 2. The partial packing of (I), which shows that molecules form infinite one dimensional polymeric chains extending along *b* axis.

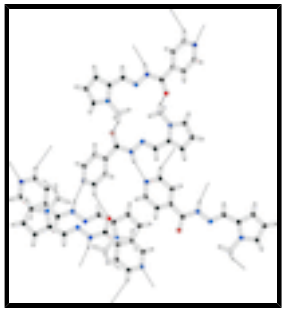


Fig. 3. The partial packing (*PLATON*; Spek, 2009) which shows that molecules form $R_2^2(18)$ ring motifs in the infinite polymeric chains.

N'-[(*E*)-(1-Methyl-1*H*-pyrrol-2-yl)methylidene]pyridine- 4-carbohydrazide

Crystal data

$C_{12}H_{12}N_4O$	$F(000) = 480$
$M_r = 228.26$	$D_x = 1.326$ Mg m^{-3}
Monoclinic, $P2_1/n$	Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å
Hall symbol: -P 2yn	Cell parameters from 1770 reflections
$a = 8.2134$ (3) Å	$\theta = 2.6–28.4°$
$b = 10.6740$ (4) Å	$\mu = 0.09$ mm^{-1}
$c = 13.1332$ (4) Å	$T = 296$ K
$\beta = 96.938$ (2)°	Prism, red
$V = 1142.95$ (7) Å^3	0.24 × 0.18 × 0.15 mm
$Z = 4$	

Data collection

Bruker Kappa APEXII CCD diffractometer	2803 independent reflections
Radiation source: fine-focus sealed tube	2023 reflections with $I > 2\sigma(I)$
graphite	$R_{int} = 0.029$
Detector resolution: 7.50 pixels mm^{-1}	$\theta_{max} = 28.3°$, $\theta_{min} = 2.5°$
ω scans	$h = -10\rightarrow10$
Absorption correction: multi-scan (*SADABS*; Bruker, 2005)	$k = -14\rightarrow14$
$T_{min} = 0.980$, $T_{max} = 0.985$	$l = -17\rightarrow17$
12030 measured reflections	

Refinement

Refinement on F^2	Primary atom site location: structure-invariant direct methods
Least-squares matrix: full	Secondary atom site location: difference Fourier map
$R[F^2 > 2\sigma(F^2)] = 0.045$	Hydrogen site location: inferred from neighbouring sites
$wR(F^2) = 0.127$	H-atom parameters constrained
$S = 1.04$	$w = 1/[\sigma^2(F_o^2) + (0.0618P)^2 + 0.235P]$ where $P = (F_o^2 + 2F_c^2)/3$

2803 reflections	$(\Delta/\sigma)_{max} < 0.001$
155 parameters	$\Delta\rho_{max} = 0.28$ e Å^{-3}
0 restraints	$\Delta\rho_{min} = -0.21$ e Å^{-3}

Special details

Geometry. Bond distances, angles *etc*. have been calculated using the rounded fractional coordinates. All su's are estimated from the variances of the (full) variance-covariance matrix. The cell e.s.d.'s are taken into account in the estimation of distances, angles and torsion angles

Refinement. Refinement of F^2 against ALL reflections. The weighted *R*-factor *wR* and goodness of fit *S* are based on F^2, conventional *R*-factors *R* are based on *F*, with *F* set to zero for negative F^2. The threshold expression of $F^2 > \sigma(F^2)$ is used only for calculating *R*-factors(gt) *etc*. and is not relevant to the choice of reflections for refinement. *R*-factors based on F^2 are statistically about twice as large as those based on *F*, and *R*- factors based on ALL data will be even larger.

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å^2)

	x	*y*	*z*	U_{iso}*/U_{eq}
O1	0.68517 (16)	0.25900 (11)	0.46989 (10)	0.0596 (4)
N1	0.25031 (16)	0.01556 (12)	0.25463 (10)	0.0424 (4)
N2	0.55170 (15)	0.41010 (11)	0.37015 (10)	0.0388 (4)
N3	0.65784 (16)	0.50489 (12)	0.40795 (10)	0.0417 (4)
N4	0.85194 (16)	0.74061 (12)	0.46127 (10)	0.0411 (4)
C1	0.46019 (16)	0.19827 (12)	0.34909 (10)	0.0315 (4)
C2	0.40449 (19)	0.10059 (13)	0.40461 (11)	0.0374 (4)
C3	0.30152 (19)	0.01259 (14)	0.35500 (12)	0.0414 (5)
C4	0.3056 (2)	0.11012 (14)	0.20128 (11)	0.0421 (5)
C5	0.40918 (19)	0.20229 (14)	0.24441 (11)	0.0378 (4)
C6	0.57736 (18)	0.29160 (14)	0.40312 (11)	0.0371 (4)
C7	0.62947 (19)	0.61063 (14)	0.36395 (12)	0.0416 (5)
C8	0.72195 (19)	0.72388 (14)	0.38651 (12)	0.0404 (5)
C9	0.6991 (2)	0.83500 (15)	0.33312 (13)	0.0497 (5)
C10	0.8163 (2)	0.92006 (16)	0.37628 (13)	0.0539 (6)
C11	0.9081 (2)	0.85957 (15)	0.45424 (13)	0.0496 (6)
C12	0.9127 (2)	0.65484 (17)	0.54194 (14)	0.0574 (6)
H2	0.46924	0.42717	0.32551	0.0466*
H2A	0.43635	0.09445	0.47482	0.0449*
H3	0.26551	−0.05268	0.39352	0.0497*
H4	0.27213	0.11375	0.13112	0.0505*
H5	0.44438	0.26614	0.20412	0.0454*
H7	0.54104	0.61488	0.31268	0.0500*
H9	0.61937	0.85044	0.27801	0.0597*
H10	0.82924	1.00246	0.35569	0.0646*
H11	0.99575	0.89429	0.49628	0.0595*
H12A	0.86108	0.67234	0.60217	0.0860*
H12B	1.02928	0.66469	0.55737	0.0860*
H12C	0.88828	0.57043	0.51995	0.0860*

Atomic displacement parameters (Å^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
O1	0.0566 (8)	0.0471 (7)	0.0666 (8)	−0.0071 (6)	−0.0275 (6)	0.0054 (6)
N1	0.0438 (8)	0.0334 (7)	0.0475 (7)	−0.0070 (6)	−0.0048 (5)	−0.0019 (5)
N2	0.0359 (7)	0.0296 (6)	0.0480 (7)	−0.0057 (5)	−0.0070 (5)	−0.0040 (5)
N3	0.0389 (7)	0.0336 (7)	0.0511 (7)	−0.0081 (5)	−0.0010 (5)	−0.0087 (5)
N4	0.0427 (7)	0.0335 (7)	0.0474 (7)	−0.0083 (5)	0.0062 (6)	−0.0074 (5)
C1	0.0297 (7)	0.0266 (7)	0.0374 (7)	0.0006 (5)	0.0003 (5)	−0.0018 (5)
C2	0.0437 (8)	0.0331 (8)	0.0340 (7)	−0.0001 (6)	−0.0012 (6)	0.0025 (6)
C3	0.0458 (9)	0.0331 (8)	0.0449 (8)	−0.0071 (7)	0.0035 (6)	0.0052 (6)
C4	0.0509 (9)	0.0385 (8)	0.0341 (7)	−0.0045 (7)	−0.0061 (6)	−0.0011 (6)
C5	0.0453 (9)	0.0318 (7)	0.0359 (7)	−0.0047 (6)	0.0030 (6)	0.0032 (6)
C6	0.0348 (8)	0.0343 (8)	0.0406 (7)	−0.0037 (6)	−0.0022 (6)	−0.0022 (6)
C7	0.0380 (8)	0.0344 (8)	0.0509 (9)	−0.0047 (7)	−0.0012 (7)	−0.0074 (7)
C8	0.0396 (8)	0.0351 (8)	0.0470 (8)	−0.0051 (6)	0.0069 (7)	−0.0087 (6)
C9	0.0580 (10)	0.0381 (9)	0.0529 (9)	−0.0047 (8)	0.0064 (8)	−0.0029 (7)
C10	0.0729 (12)	0.0331 (8)	0.0580 (10)	−0.0118 (8)	0.0178 (9)	−0.0040 (7)
C11	0.0560 (10)	0.0380 (9)	0.0570 (10)	−0.0198 (8)	0.0162 (8)	−0.0155 (8)
C12	0.0538 (11)	0.0461 (10)	0.0680 (11)	−0.0058 (8)	−0.0098 (8)	0.0025 (9)

Geometric parameters (Å, °)

O1—C6	1.219 (2)	C7—C8	1.439 (2)
N1—C3	1.335 (2)	C8—C9	1.379 (2)
N1—C4	1.339 (2)	C9—C10	1.393 (2)
N2—N3	1.3877 (18)	C10—C11	1.359 (2)
N2—C6	1.3453 (19)	C2—H2A	0.9300
N3—C7	1.277 (2)	C3—H3	0.9300
N4—C8	1.372 (2)	C4—H4	0.9300
N4—C11	1.358 (2)	C5—H5	0.9300
N4—C12	1.443 (2)	C7—H7	0.9300
N2—H2	0.8600	C9—H9	0.9300
C1—C2	1.3815 (19)	C10—H10	0.9300
C1—C5	1.3886 (19)	C11—H11	0.9300
C1—C6	1.502 (2)	C12—H12A	0.9600
C2—C3	1.374 (2)	C12—H12B	0.9600
C4—C5	1.377 (2)	C12—H12C	0.9600
C3—N1—C4	116.64 (13)	N4—C11—C10	109.47 (15)
N3—N2—C6	120.21 (12)	C1—C2—H2A	120.00
N2—N3—C7	114.22 (13)	C3—C2—H2A	120.00
C8—N4—C11	108.33 (13)	N1—C3—H3	118.00
C8—N4—C12	127.81 (13)	C2—C3—H3	118.00
C11—N4—C12	123.58 (14)	N1—C4—H4	118.00
C6—N2—H2	120.00	C5—C4—H4	118.00
N3—N2—H2	120.00	C1—C5—H5	121.00
C2—C1—C6	119.03 (12)	C4—C5—H5	121.00

C2—C1—C5	117.80 (13)	N3—C7—H7	117.00
C5—C1—C6	123.13 (12)	C8—C7—H7	117.00
C1—C2—C3	119.32 (13)	C8—C9—H9	126.00
N1—C3—C2	123.67 (14)	C10—C9—H9	126.00
N1—C4—C5	123.72 (14)	C9—C10—H10	127.00
C1—C5—C4	118.86 (13)	C11—C10—H10	127.00
N2—C6—C1	113.89 (12)	N4—C11—H11	125.00
O1—C6—N2	124.87 (14)	C10—C11—H11	125.00
O1—C6—C1	121.24 (13)	N4—C12—H12A	109.00
N3—C7—C8	125.91 (15)	N4—C12—H12B	109.00
N4—C8—C9	107.35 (13)	N4—C12—H12C	109.00
C7—C8—C9	125.57 (15)	H12A—C12—H12B	109.00
N4—C8—C7	127.04 (14)	H12A—C12—H12C	109.00
C8—C9—C10	107.99 (15)	H12B—C12—H12C	109.00
C9—C10—C11	106.87 (15)		
C4—N1—C3—C2	0.6 (2)	C2—C1—C5—C4	0.4 (2)
C3—N1—C4—C5	−0.5 (2)	C6—C1—C5—C4	177.90 (14)
C6—N2—N3—C7	173.81 (14)	C2—C1—C6—O1	38.1 (2)
N3—N2—C6—O1	4.1 (2)	C2—C1—C6—N2	−142.47 (14)
N3—N2—C6—C1	−175.38 (12)	C5—C1—C6—O1	−139.38 (16)
N2—N3—C7—C8	−178.82 (14)	C5—C1—C6—N2	40.08 (19)
C11—N4—C8—C7	177.64 (15)	C1—C2—C3—N1	−0.2 (2)
C11—N4—C8—C9	0.04 (17)	N1—C4—C5—C1	0.0 (2)
C12—N4—C8—C7	−8.4 (3)	N3—C7—C8—N4	−2.9 (3)
C12—N4—C8—C9	174.00 (15)	N3—C7—C8—C9	174.33 (16)
C8—N4—C11—C10	0.12 (19)	N4—C8—C9—C10	−0.18 (18)
C12—N4—C11—C10	−174.15 (15)	C7—C8—C9—C10	−177.82 (15)
C5—C1—C2—C3	−0.3 (2)	C8—C9—C10—C11	0.25 (19)
C6—C1—C2—C3	−177.89 (14)	C9—C10—C11—N4	−0.23 (19)

Hydrogen-bond geometry (Å, °)

Cg1 is the centroid of the C8—C11/N4 ring.

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
N2—H2···N1^{i}	0.86	2.19	3.0205 (18)	163
C4—H4···O1^{ii}	0.93	2.54	3.3821 (19)	150
C12—H12B···O1^{iii}	0.96	2.55	3.450 (2)	156
C12—H12C···N3	0.96	2.36	3.025 (2)	126
C2—H2A···Cg1^{iv}	0.93	2.83	3.3258 (16)	114
C5—H5···Cg1^{v}	0.93	2.71	3.4669 (17)	139

Symmetry codes: (i) −*x*+1/2, *y*+1/2, −*z*+1/2; (ii) *x*−1/2, −*y*+1/2, *z*−1/2; (iii) −*x*+2, −*y*+1, −*z*+1; (iv) −*x*+1, −*y*+1, −*z*+1; (v) −*x*+3/2, *y*−1/2, −*z*+1/2.

Fig. 1

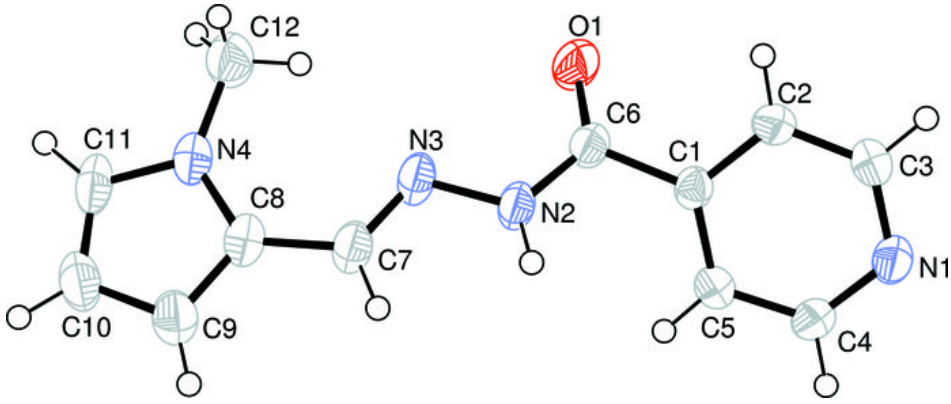


Fig. 2

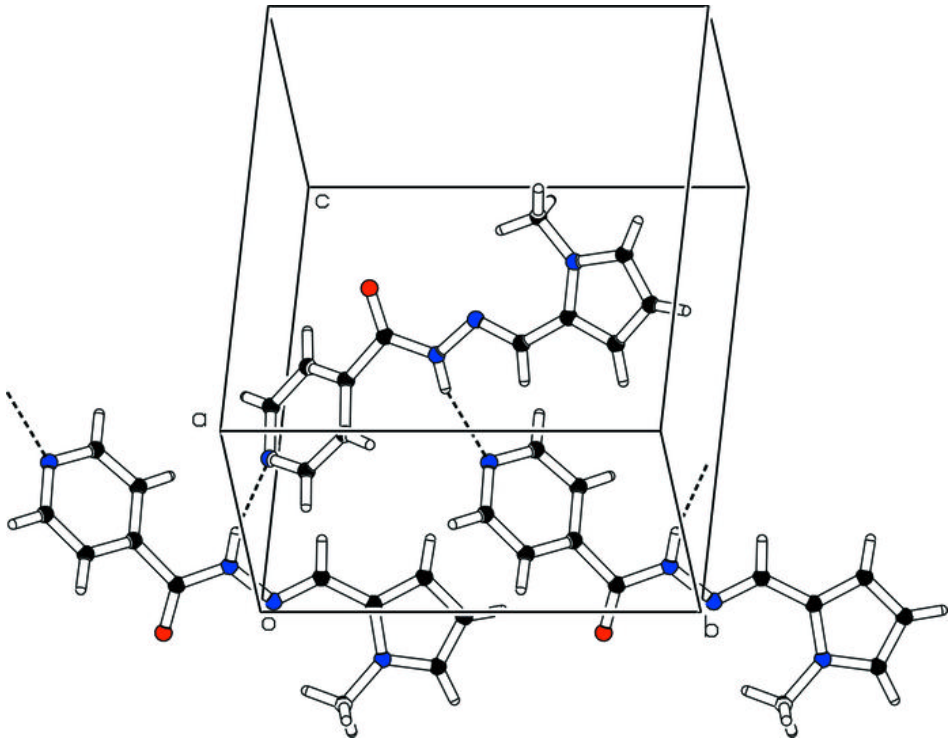
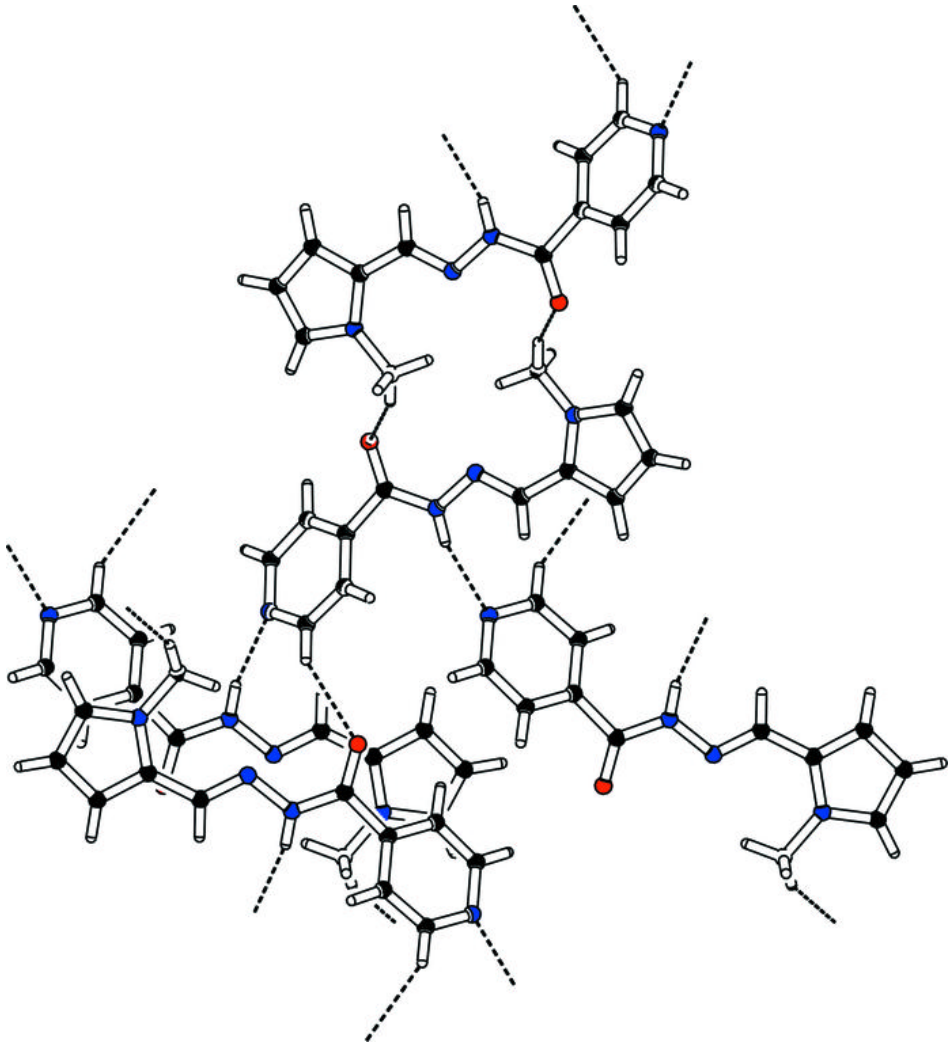


Fig. 3



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4,4′-[(2,7-Dibromofluorene-9,9-diyl)-dimethylene]dipyridinium bis(perchlorate)

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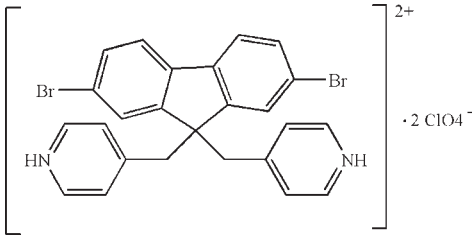
Key indicators: single-crystal X-ray study; T = 295 K; mean σ(C–C) = 0.003 Å; R factor = 0.039; wR factor = 0.103; data-to-parameter ratio = 16.5.

In the crystal of the title compound, $C_{25}H_{20}Br_2N_2^{2+}\cdot 2ClO_4^-$, intermolecular N—H···O and C—H···O hydrogen bonds, along with C—H···π interactions, stabilize the crystal structure.

Related literature

A variety of ligands of different molecular dimensions and functional properties have been utilized in the preparation of numerous supramolecular assemblies with exotic architectures, see: Applegarth *et al.*, (2005). For related structures, see: Meerssche *et al.* (1979, 1980).



Experimental

Crystal data

$C_{25}H_{20}Br_2N_2^{2+}\cdot 2ClO_4^-$
M_r = 707.15
Monoclinic, $C2/c$
a = 15.605 (3) Å
b = 11.267 (2) Å
c = 16.318 (3) Å
β = 117.60 (3)°
V = 2542.6 (11) Å^3
Z = 4
Mo $K\alpha$ radiation
μ = 3.45 mm^{-1}
T = 295 K
0.25 × 0.20 × 0.18 mm

Data collection

Enraf–Nonius CAD-4 diffractometer
Absorption correction: ψ scan (North *et al.*, 1968)
T_{min} = 0.441, T_{max} = 0.537
11835 measured reflections
2915 independent reflections
2611 reflections with $I > 2\sigma(I)$
R_{int} = 0.062
3 standard reflections every 100 reflections
intensity decay: none

Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.039
$wR(F^2)$ = 0.103
S = 1.06
2915 reflections
177 parameters
H-atom parameters constrained
$\Delta\rho_{max}$ = 1.01 e Å^{-3}
$\Delta\rho_{min}$ = −0.79 e Å^{-3}

Table 1
Hydrogen-bond geometry (Å, °).

*Cg*3 is the centroid of the C1–C6 ring.

D—H···A	D—H	H···A	D···A	D—H···A
N1—H1A···O3	0.86	2.24	2.997 (3)	148
C11—H11A···O1	0.93	2.57	3.196 (3)	125
C12—H12A···O4^{i}	0.93	2.44	3.193 (3)	138
C13—H13A···O1^{ii}	0.93	2.47	3.376 (3)	164
C10—H10A···Cg3	0.93	2.93	3.688 (2)	140

Symmetry codes: (i) $-x+1, y, -z+\frac{1}{2}$; (ii) $x, -y+1, z+\frac{1}{2}$.

Data collection: *CAD-4 Software* (Enraf–Nonius, 1989); cell refinement: *CAD-4 Software*; data reduction: *NRCVAX* (Gabe *et al.*, 1989); program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *SHELXTL/PC* (Sheldrick, 2008); software used to prepare material for publication: *WinGX* (Farrugia, 1999).

The authors would like to thank the Natural Science Foundation of Shandong Province (No. Y2007B14).

Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: HG2685).

References

Applegarth, L., Goetra, A. E. & Steed, J. W. (2005). *Chem. Commun.* **18**, 2405–2406.
Enraf–Nonius (1989). *CAD-4 Software.* Enraf–Nonius, Delft, The Netherlands.
Farrugia, L. J. (1999). *J. Appl. Cryst.* **32**, 837–838.
Gabe, E. J., Le Page, Y., Charland, J.-P., Lee, F. L. & White, P. S. (1989). *J. Appl. Cryst.* **22**, 384–387.
Meerssche, M., Germain, G., Declercq, J. P. & Touillaux, R. (1979). *Cryst. Struct. Commun.* **8**, 119–122.
Meerssche, M., Germain, G., Declercq, J. P., Touillaux, R., Roberfroid, M. & Razzouk, C. (1980). *Cryst. Struct. Commun.* **9**, 515–518.
North, A. C. T., Phillips, D. C. & Mathews, F. S. (1968). *Acta Cryst.* A**24**, 351–359.
Sheldrick, G. M. (2008). *Acta Cryst.* A**64**, 112–122.

supplementary materials

Acta Cryst. (2010). E**66**, o1718 [**doi:10.1107/S1600536810021859**]

4,4'-[(2,7-Dibromofluorene-9,9-diyl)dimethylene]dipyridinium bis(perchlorate)

Z. Xuan, S. Zhao, L. Lu, X. Wang and X. Yang

Comment

A variety of ligands of different molecular dimensions and functional properties were utilized for the preparation of numerous supramolecular assemblies of exotic architectures as reported in the recent literature (Applegarth *et al.*, 2005). Herein, we report a new bipyridine derivative of 2,7-dibromo-9,9-(4-pyridyl-methyl) fluorene [DBPMF].

scheme I

The structure of the title compound contains a protonated 2,7-dibromo-9,9-bis(4-pyridinium-methyl) fluorene dications $DBPMFH_2^{2+}$ and two perchlorate anions ClO_4^-. All the bond lengths and bond angles in the phenyl ring and five-membered ring are corresponding with those observed in 2-acetylaminofluorene (Meerssche *et al.*, 1980) and 4-acetylamino-fluorene (Meerssche *et al.*, 1979). Two bromine atoms along with the thirteen atoms of fluorenyl ring are coplanar (P1) and the biggest deviation is 0.038Å for C6 atom. The dihedral angle between the plane P1 and the pyridyl ring containing N1 atom is 72.11 (2)°.

In the crystal lattice, there are four types of supramolecular interactions (Table 1), including N—H···O hydrogen bonds, C—H···O potential hydrogen bonds, C—H···π supramolecular interaction and π–π stacking interactions. Among these supramolecular interactions, the two types N—H···O hydrogen bonds link two $DBPMFH_2^{2+}$ cations with two ClO_4^- anions to construct one-dimensional chains, then the other supramolecular interactions help the 1D chains to form three-dimensional net-works, which stabilize the crystal structure.

Experimental

DBPMF was synthesized by the reaction of 2,7-dibromofluorene (3.24 g, 0.01 mol) and 4-chloromethyl pyridine hydrochloride (1.64 g, 0.02 mol) in DMSO (70 ml). The title compound was obtained by the reaction of DBPMF (2.55 g, 5.0 mmol) and $HClO_4$ (0.26 ml, 5.0 mmol) in EtOH (50 ml). Single crystals suitable for x-ray measurements were obtained by recrystallization at room temperature.

Refinement

H atoms were fixed geometrically and allowed to ride on their attached atoms, with C—H distances=0.93-0.97 Å, N—H distance=0.86Å and with U_{iso}=1.2-1.5U_{eq}.

Figures

Fig. 1. The structure of the title compound showing 30% probability displacement ellipsoids and the atom-numbering scheme.

4,4'-[(2,7-Dibromofluorene-9,9-diyl)dimethylene]dipyridinium bis(perchlorate)

Crystal data

$C_{25}H_{20}Br_2N_2^{2+}\cdot 2ClO_4^-$	$F(000) = 1408$
$M_r = 707.15$	$D_x = 1.847$ Mg m^{-3}
Monoclinic, $C2/c$	Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å
Hall symbol: -C 2yc	Cell parameters from 25 reflections
$a = 15.605$ (3) Å	$\theta = 4$–$14°$
$b = 11.267$ (2) Å	$\mu = 3.45$ mm^{-1}
$c = 16.318$ (3) Å	$T = 295$ K
$\beta = 117.60$ (3)°	Block, yellow
$V = 2542.6$ (11) Å^3	0.25 × 0.20 × 0.18 mm
$Z = 4$	

Data collection

Enraf–Nonius CAD-4 diffractometer	2611 reflections with $I > 2\sigma(I)$
Radiation source: fine-focus sealed tube	$R_{int} = 0.062$
graphite	$\theta_{max} = 27.5°$, $\theta_{min} = 3.1°$
ω/2θ scans	$h = -20\rightarrow 20$
Absorption correction: ψ scan (North *et al.*, 1968)	$k = -14\rightarrow 14$
$T_{min} = 0.441$, $T_{max} = 0.537$	$l = -21\rightarrow 21$
11835 measured reflections	3 standard reflections every 100 reflections
2915 independent reflections	intensity decay: none

Refinement

Refinement on F^2	Primary atom site location: structure-invariant direct methods
Least-squares matrix: full	Secondary atom site location: difference Fourier map
$R[F^2 > 2\sigma(F^2)] = 0.039$	Hydrogen site location: inferred from neighbouring sites
$wR(F^2) = 0.103$	H-atom parameters constrained
$S = 1.06$	$w = 1/[\sigma^2(F_o^2) + (0.0681P)^2 + 0.5103P]$ where $P = (F_o^2 + 2F_c^2)/3$
2915 reflections	$(\Delta/\sigma)_{max} = 0.001$
177 parameters	$\Delta\rho_{max} = 1.01$ e Å^{-3}

0 restraints $\Delta\rho_{min} = -0.79$ e Å^{-3}

Special details

Geometry. All esds (except the esd in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell esds are taken into account individually in the estimation of esds in distances, angles and torsion angles; correlations between esds in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell esds is used for estimating esds involving l.s. planes.

Refinement. Refinement of F^2 against ALL reflections. The weighted *R*-factor wR and goodness of fit *S* are based on F^2, conventional *R*-factors *R* are based on *F*, with *F* set to zero for negative F^2. The threshold expression of $F^2 > \sigma(F^2)$ is used only for calculating *R*-factors(gt) etc. and is not relevant to the choice of reflections for refinement. *R*-factors based on F^2 are statistically about twice as large as those based on *F*, and *R*- factors based on ALL data will be even larger.

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å^2)

	x	*y*	*z*	U_{iso}*/U_{eq}
Br1	−0.201221 (15)	0.319251 (18)	−0.114789 (15)	0.01844 (12)
N1	0.33006 (13)	0.39368 (16)	0.24329 (14)	0.0178 (4)
H1A	0.3819	0.3707	0.2418	0.021*
C1	−0.13197 (15)	0.2901 (2)	0.01439 (16)	0.0153 (4)
C2	−0.11455 (16)	0.17300 (17)	0.04368 (17)	0.0162 (5)
H2A	−0.1377	0.1115	0.0009	0.019*
C3	−0.06207 (15)	0.14838 (19)	0.13788 (15)	0.0154 (4)
H3A	−0.0500	0.0704	0.1589	0.019*
C4	−0.02836 (14)	0.24228 (18)	0.19940 (15)	0.0140 (4)
C5	−0.04692 (14)	0.36049 (18)	0.16834 (16)	0.0141 (4)
C6	−0.09989 (14)	0.38606 (18)	0.07490 (15)	0.0146 (4)
H6A	−0.1134	0.4638	0.0536	0.017*
C7	0.0000	0.4457 (2)	0.2500	0.0123 (5)
C8	0.07543 (14)	0.52981 (17)	0.24235 (15)	0.0136 (4)
H8A	0.0429	0.5737	0.1849	0.016*
H8B	0.0965	0.5870	0.2924	0.016*
C9	0.16421 (14)	0.47237 (18)	0.24518 (15)	0.0133 (4)
C10	0.16000 (15)	0.39694 (18)	0.17545 (15)	0.0157 (4)
H10A	0.1004	0.3722	0.1290	0.019*
C11	0.24415 (15)	0.35912 (19)	0.17540 (16)	0.0175 (4)
H11A	0.2413	0.3098	0.1285	0.021*
C12	0.33797 (15)	0.46320 (19)	0.31370 (16)	0.0183 (4)
H12A	0.3986	0.4841	0.3605	0.022*
C13	0.25553 (15)	0.50303 (18)	0.31584 (15)	0.0152 (4)
H13A	0.2606	0.5505	0.3645	0.018*
Cl1	0.41022 (4)	0.31707 (4)	0.05644 (4)	0.01488 (15)
O1	0.31184 (11)	0.35890 (17)	0.01812 (12)	0.0258 (4)
O2	0.41264 (16)	0.19359 (15)	0.03767 (15)	0.0321 (5)
O3	0.45717 (12)	0.33505 (14)	0.15648 (12)	0.0213 (4)
O4	0.46088 (12)	0.38494 (16)	0.01772 (12)	0.0286 (4)

Atomic displacement parameters (Å^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Br1	0.02330 (17)	0.01761 (16)	0.01334 (17)	−0.00066 (7)	0.00760 (12)	−0.00009 (7)
N1	0.0150 (8)	0.0174 (9)	0.0236 (10)	0.0018 (7)	0.0112 (8)	0.0021 (8)
C1	0.0146 (9)	0.0182 (9)	0.0130 (10)	−0.0009 (8)	0.0064 (8)	0.0001 (9)
C2	0.0211 (11)	0.0122 (10)	0.0171 (12)	−0.0033 (7)	0.0105 (10)	−0.0052 (8)
C3	0.0200 (10)	0.0111 (9)	0.0167 (11)	0.0006 (8)	0.0097 (9)	0.0000 (9)
C4	0.0152 (9)	0.0124 (9)	0.0165 (11)	0.0002 (7)	0.0090 (8)	0.0018 (8)
C5	0.0144 (9)	0.0106 (9)	0.0196 (11)	−0.0009 (7)	0.0097 (8)	−0.0020 (9)
C6	0.0158 (9)	0.0119 (9)	0.0171 (10)	−0.0002 (7)	0.0086 (8)	0.0008 (8)
C7	0.0125 (12)	0.0115 (13)	0.0135 (14)	0.000	0.0064 (11)	0.000
C8	0.0160 (9)	0.0095 (8)	0.0167 (10)	−0.0007 (7)	0.0088 (8)	0.0001 (8)
C9	0.0162 (9)	0.0108 (9)	0.0152 (10)	−0.0005 (7)	0.0091 (8)	0.0032 (8)
C10	0.0165 (9)	0.0158 (10)	0.0154 (10)	−0.0007 (8)	0.0079 (8)	0.0000 (8)
C11	0.0207 (10)	0.0148 (10)	0.0201 (12)	0.0005 (8)	0.0121 (9)	0.0000 (9)
C12	0.0153 (9)	0.0183 (10)	0.0184 (11)	−0.0014 (8)	0.0054 (8)	0.0019 (9)
C13	0.0181 (10)	0.0134 (9)	0.0135 (10)	−0.0010 (8)	0.0068 (8)	0.0017 (8)
Cl1	0.0145 (3)	0.0161 (3)	0.0132 (3)	−0.00181 (16)	0.0057 (2)	−0.00099 (17)
O1	0.0162 (8)	0.0345 (9)	0.0247 (9)	0.0037 (7)	0.0077 (7)	0.0074 (8)
O2	0.0390 (10)	0.0178 (9)	0.0283 (11)	−0.0006 (7)	0.0061 (9)	−0.0061 (7)
O3	0.0210 (8)	0.0273 (8)	0.0128 (8)	−0.0003 (6)	0.0055 (7)	−0.0034 (7)
O4	0.0253 (8)	0.0390 (10)	0.0264 (9)	−0.0070 (7)	0.0161 (7)	0.0037 (8)

Geometric parameters (Å, °)

Br1—C1	1.900 (2)	C7—C8	1.561 (2)
N1—C11	1.342 (3)	C8—C9	1.510 (3)
N1—C12	1.348 (3)	C8—H8A	0.9700
N1—H1A	0.8600	C8—H8B	0.9700
C1—C2	1.387 (3)	C9—C10	1.397 (3)
C1—C6	1.392 (3)	C9—C13	1.399 (3)
C2—C3	1.394 (3)	C10—C11	1.381 (3)
C2—H2A	0.9300	C10—H10A	0.9300
C3—C4	1.384 (3)	C11—H11A	0.9300
C3—H3A	0.9300	C12—C13	1.378 (3)
C4—C5	1.407 (3)	C12—H12A	0.9300
C4—C4^{i}	1.468 (4)	C13—H13A	0.9300
C5—C6	1.387 (3)	Cl1—O2	1.4289 (18)
C5—C7	1.526 (3)	Cl1—O4	1.4395 (17)
C6—H6A	0.9300	Cl1—O1	1.4423 (16)
C7—C5^{i}	1.526 (3)	Cl1—O3	1.4609 (19)
C7—C8^{i}	1.561 (2)		
C11—N1—C12	122.30 (19)	C9—C8—C7	116.89 (17)
C11—N1—H1A	118.9	C9—C8—H8A	108.1
C12—N1—H1A	118.9	C7—C8—H8A	108.1
C2—C1—C6	123.1 (2)	C9—C8—H8B	108.1

C2—C1—Br1	117.84 (18)	C7—C8—H8B	108.1
C6—C1—Br1	119.06 (17)	H8A—C8—H8B	107.3
C1—C2—C3	119.4 (2)	C10—C9—C13	117.85 (19)
C1—C2—H2A	120.3	C10—C9—C8	122.64 (18)
C3—C2—H2A	120.3	C13—C9—C8	119.28 (19)
C4—C3—C2	118.7 (2)	C11—C10—C9	120.1 (2)
C4—C3—H3A	120.7	C11—C10—H10A	119.9
C2—C3—H3A	120.7	C9—C10—H10A	119.9
C3—C4—C5	121.1 (2)	N1—C11—C10	119.8 (2)
C3—C4—C4^{i}	130.12 (13)	N1—C11—H11A	120.1
C5—C4—C4^{i}	108.75 (13)	C10—C11—H11A	120.1
C6—C5—C4	120.7 (2)	N1—C12—C13	119.5 (2)
C6—C5—C7	129.05 (19)	N1—C12—H12A	120.2
C4—C5—C7	110.21 (19)	C13—C12—H12A	120.2
C5—C6—C1	117.00 (19)	C12—C13—C9	120.3 (2)
C5—C6—H6A	121.5	C12—C13—H13A	119.8
C1—C6—H6A	121.5	C9—C13—H13A	119.8
C5—C7—C5^{i}	102.1 (2)	O2—Cl1—O4	110.40 (13)
C5—C7—C8^{i}	112.17 (11)	O2—Cl1—O1	110.72 (12)
C5^{i}—C7—C8^{i}	112.75 (11)	O4—Cl1—O1	109.07 (11)
C5—C7—C8	112.75 (11)	O2—Cl1—O3	108.98 (11)
C5^{i}—C7—C8	112.17 (11)	O4—Cl1—O3	108.89 (10)
C8^{i}—C7—C8	105.2 (2)	O1—Cl1—O3	108.74 (11)

Symmetry codes: (i) −*x*, *y*, −*z*+1/2.

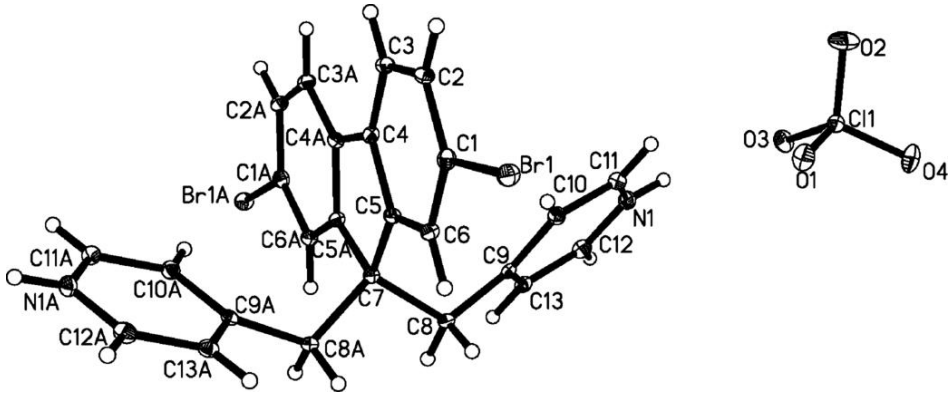
Hydrogen-bond geometry (Å, °)

Cg3 is the centroid of the C1–C6 ring.

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
N1—H1A···O3	0.86	2.24	2.997 (3)	148.
C11—H11A···O1	0.93	2.57	3.196 (3)	125.
C12—H12A···O4^{ii}	0.93	2.44	3.193 (3)	138.
C13—H13A···O1^{iii}	0.93	2.47	3.376 (3)	164.
C10—H10A···Cg3	0.93	2.93	3.688 (2)	140.

Symmetry codes: (ii) −*x*+1, *y*, −*z*+1/2; (iii) *x*, −*y*+1, *z*+1/2.

Fig. 1


C3
C3A
C2
C2A
C4A
C4
C1
Br1
C1A
Br1A
C5
C6A
C5A
C6
C11
C10
N1
C12
C9
C13
C11A
N1A
C10A
C9A
C7
C8
C12A
C13A
C8A
O2
Cl1
O3
O1
O4

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2,4,6-Triphenylaniline

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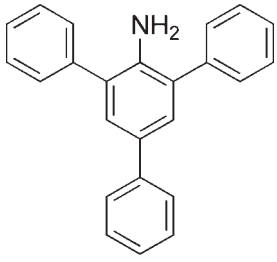
Received 14 May 2010; accepted 16 June 2010

Key indicators: single-crystal X-ray study; T = 100 K; mean σ(C–C) = 0.001 Å; R factor = 0.043; wR factor = 0.125; data-to-parameter ratio = 29.6.

Individual molecules of the title compound, $C_{24}H_{19}N$, do not participate in hydrogen-bonding interactions due to the steric bulk of the phenyl rings *ortho* to the amine. The dihedral angles between the central ring and the pendant rings are 68.26 (10), 55.28 (10) and 30.61 (11)°.

Related literature

The reaction of equimolar amounts of pyrazole-3,5-dicarboxylic acid (HPzDCA) and primary amines have yielded ammonium carboxylate salts that adopt layered architectures, see: Ugono *et al.* (2009); Beatty *et al.* (2002*a*,*b*). For other amines that do not exhibit intermolecular hydrogen bonding due to the bulky *ortho* phenyl groups, see: Cherian *et al.* (2005); Lonkin & Marshal (2004). For the preparation of 2,4,6-triphenylaniline, see: Basu *et al.* (2003); Paul & Clark (2003).



Experimental

Crystal data

$C_{24}H_{19}N$
M_r = 321.40
Monoclinic, $P2_1/c$
a = 10.735 (2) Å
b = 14.792 (3) Å
c = 11.911 (2) Å
β = 113.02 (3)°
V = 1740.7 (6) Å^3
Z = 4
Mo $K\alpha$ radiation
μ = 0.07 mm^{-1}
T = 100 K
0.50 × 0.50 × 0.25 mm

Data collection

Bruker SMART APEXII diffractometer
Absorption correction: multi-scan (*SADABS*; Sheldrick, 1996)
T_{min} = 0.966, T_{max} = 0.983
44061 measured reflections
6695 independent reflections
5813 reflections with $I > 2\sigma(I)$
R_{int} = 0.027

Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.043
$wR(F^2)$ = 0.125
S = 1.02
6695 reflections
226 parameters
H-atom parameters constrained
$\Delta\rho_{max}$ = 0.48 e Å^{-3}
$\Delta\rho_{min}$ = −0.23 e Å^{-3}

Data collection: *APEX2* (Bruker, 2007); cell refinement: *SAINT* (Bruker, 2007); data reduction: *SAINT*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *X-SEED* (Barbour, 2001); software used to prepare material for publication: *SHELXL97* and *PLATON* (Spek, 2009).

The authors are grateful to the Center for Nanoscience at the University of Missouri-St Louis for access to the single-crystal X-ray facility.

Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: HG2686).

References

Barbour, L. J. (2001). *J. Supramol. Chem.* **1**, 189–191.
Basu, B., Das, P., Bhuiyan, M. M. H. & Jha, S. (2003). *Tetrahedron Lett.* **44**, 3817–3820.
Beatty, A. M., Grange, K. E. & Simpson, S. E. (2002*a*). *Chem. Eur. J.* **8**, 3254–3259.
Beatty, A. M., Schneider, C. L., Simpson, A. E. & Zaher, J. L. (2002*b*). *CrystEngComm*, **4**, 282–287.
Bruker (2007). *APEX2* and *SAINT*. Bruker AXS Inc., Madison, Wisconsin, USA.
Cherian, A. E., Domski, G. J., Rose, J. M., Lobkovsky, E. B. & Coates, G. W. (2005). *Org. Lett.* **7**, 5135–5137.
Lonkin, A. S. & Marshal, W. J. (2004). *Organometallics*, **23**, 3276–3283.
Paul, S. & Clark, J. H. (2003). *Green Chem.* **5**, 635–638.
Sheldrick, G. M. (1996). *SADABS*. University of Göttingen, Germany.
Sheldrick, G. M. (2008). *Acta Cryst.* A**64**, 112–122.
Spek, A. L. (2009). *Acta Cryst.* D**65**, 148–155.
Ugono, O., Rath, N. P. & Beatty, A. M. (2009). *Cryst. Growth Des.* **9**, 4595–4598.

supplementary materials

Acta Cryst. (2010). E**66**, o1777 [**doi:10.1107/S160053681002338X**]

2,4,6-Triphenylaniline

O. Ugono, S. Cowin and A. M. Beatty

Comment

The reactions of equimolar amounts of pyrazole-3,5-dicarboxylic acid (HPzDCA) and primary amines have yielded ammonium carboxylate salts that adopt layered architectures (Ugono *et al.*, 2009; Beatty *et al.*, 2002a,b). The level of structural fidelity for these organic salts allows, from a crystal engineering point of view, for the tuning of material properties by changing the identity of the organic group for the amines employed in the reaction. The reaction of pyrazole-3,5-dicarboxylic acid and 2,4,6-triphenylaniline (TPA) does not produce appreciable amounts of the desired ammonium carboxylate salt. However, large colorless single crystals of the aniline were obtained and structurally characterized.

The title compound packs in the monoclinic space group $P\,2_1/c$, with one molecule in the asymmetric unit. TPA does not self aggregate *via* intermolecular hydrogen bonds in the solid state. This lack of significant intermolecular hydrogen bonds appears to be due to the bulky *ortho* phenyl groups. These groups ensure that the distance requirements for hydrogen bond interactions are not satisfied, as potential participating hydrogen bonding donors and acceptors can not approach each other. This is not uncommon, as other amines, namely 2,6-bis(Benzofuran-2-yl)phenylamine (Lonkin *et al.*, 2004) and (*R*,*R*)-2,6-bis(1-Phenylethyl)4-methylaniline (Cherian *et al.*, 2005) among others, exhibit this characteristic for identical reasons.

Experimental

Into a 20 ml scintillation vial was placed 65 mg (37 mmol s) of pyrazole-3,5-dicarboxylic acid, 120 mg (37 mmol s) of 2,4,6-triphenylaniline (Basu *et al.*, 2003; Paul & Clark, 2003) and 5 ml of a 3:2 ethanol:water mixture. The mixture was warmed gently until the solution became clear and then filtered. The filtrate was placed in another scintillation vial, and colorless single crystals of the title compound were obtained in 48 h.

Refinement

All non hydrogen atoms were refined anisotropically. Phenyl hydrogen atoms were placed in calculated positions and treated with a riding model C–H= 0.95 Å, $U_{iso}(H_{aryl})= 1.2U_{eq}(C)$ for aromatic carbons. Amine hydrogen atoms were also placed in calulated positions and treated with a riding model N–H= 0.88 Å, $U_{iso}(H_{amine})= 1.2U_{eq}(N)$.

Figures

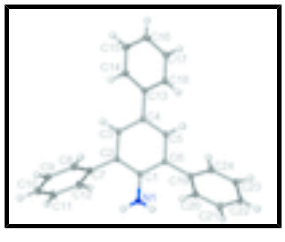


Fig. 1. Thermal ellipsoid plot of 2,4,6-triphenylaniline at 50% probability.

2,4,6-Triphenylaniline

Crystal data

$C_{24}H_{19}N$	$F(000) = 680$
$M_r = 321.40$	$D_x = 1.226$ Mg m^{-3}
Monoclinic, $P2_1/c$	Melting point = 395–398 K
Hall symbol: -P 2ybc	Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å
$a = 10.735$ (2) Å	Cell parameters from 6695 reflections
$b = 14.792$ (3) Å	$\theta = 2.1$–$33.9°$
$c = 11.911$ (2) Å	$\mu = 0.07$ mm^{-1}
$\beta = 113.02$ (3)°	$T = 100$ K
$V = 1740.7$ (6) Å^3	Prism, colorless
$Z = 4$	0.50 × 0.50 × 0.25 mm

Data collection

Bruker SMART APEXII diffractometer	6695 independent reflections
Radiation source: fine-focus sealed tube	5813 reflections with $I > 2\sigma(I)$
graphite	$R_{int} = 0.027$
ω scans	$\theta_{max} = 33.9°$, $\theta_{min} = 2.1°$
Absorption correction: multi-scan (*SADABS*; Sheldrick, 1996)	$h = -16 \rightarrow 16$
$T_{min} = 0.966$, $T_{max} = 0.983$	$k = -23 \rightarrow 23$
44061 measured reflections	$l = -18 \rightarrow 18$

Refinement

Refinement on F^2	Primary atom site location: structure-invariant direct methods
Least-squares matrix: full	Secondary atom site location: difference Fourier map
$R[F^2 > 2\sigma(F^2)] = 0.043$	Hydrogen site location: inferred from neighbouring sites
$wR(F^2) = 0.125$	H-atom parameters constrained
$S = 1.02$	$w = 1/[\sigma^2(F_o^2) + (0.0697P)^2 + 0.5511P]$ where $P = (F_o^2 + 2F_c^2)/3$
6695 reflections	$(\Delta/\sigma)_{max} = 0.001$
226 parameters	$\Delta\rho_{max} = 0.48$ e Å^{-3}
0 restraints	$\Delta\rho_{min} = -0.23$ e Å^{-3}

Special details

Geometry. All e.s.d.'s (except the e.s.d. in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell e.s.d.'s are taken into account individually in the estimation of e.s.d.'s in distances, angles and torsion angles; correlations

between e.s.d.'s in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell e.s.d.'s is used for estimating e.s.d.'s involving l.s. planes.

Refinement. Refinement of F^2 against ALL reflections. The weighted *R*-factor *wR* and goodness of fit *S* are based on F^2. Conventional *R*-factors *R* are based on *F*, with *F* set to zero for negative F^2. The threshold expression of $F^2 > \sigma(F^2)$ is used only for calculating *R*-factors (gt) *etc*. and is not relevant to the choice of reflections for refinement. *R*-factors based on F^2 are statistically about twice as large as those based on *F*, and *R*- factors based on ALL data will be even larger.

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å^2)

	x	*y*	*z*	U_{iso}*/U_{eq}
N1	−0.03946 (8)	0.31892 (6)	0.10628 (7)	0.02312 (15)
H1A	−0.0309	0.3532	0.1693	0.028*
H1B	−0.1086	0.2817	0.0760	0.028*
C1	0.05584 (7)	0.32362 (5)	0.05479 (6)	0.01365 (13)
C2	0.16729 (8)	0.38320 (5)	0.10276 (7)	0.01385 (13)
C3	0.26324 (8)	0.38694 (5)	0.05077 (7)	0.01493 (13)
H3	0.3376	0.4272	0.0842	0.018*
C4	0.25338 (7)	0.33322 (5)	−0.04924 (7)	0.01409 (13)
C5	0.14616 (7)	0.27160 (5)	−0.09177 (7)	0.01405 (13)
H5	0.1399	0.2322	−0.1567	0.017*
C6	0.04796 (7)	0.26577 (5)	−0.04244 (6)	0.01310 (13)
C7	0.18451 (8)	0.44422 (5)	0.20775 (7)	0.01407 (13)
C8	0.29191 (8)	0.43079 (5)	0.32071 (7)	0.01645 (14)
H8	0.3517	0.3812	0.3314	0.020*
C9	0.31156 (8)	0.48981 (6)	0.41751 (7)	0.01874 (15)
H9	0.3837	0.4796	0.4941	0.022*
C10	0.22601 (9)	0.56362 (6)	0.40238 (7)	0.01889 (15)
H10	0.2404	0.6042	0.4681	0.023*
C11	0.11933 (9)	0.57760 (6)	0.29049 (7)	0.01905 (15)
H11	0.0609	0.6280	0.2797	0.023*
C12	0.09793 (9)	0.51788 (5)	0.19407 (7)	0.01751 (14)
H12	0.0239	0.5273	0.1184	0.021*
C13	0.34837 (8)	0.34425 (5)	−0.11131 (7)	0.01444 (13)
C14	0.48238 (8)	0.37311 (6)	−0.04755 (7)	0.01809 (14)
H14	0.5146	0.3829	0.0380	0.022*
C15	0.56863 (8)	0.38749 (6)	−0.10796 (8)	0.02019 (15)
H15	0.6589	0.4071	−0.0633	0.024*
C16	0.52351 (9)	0.37333 (6)	−0.23338 (8)	0.02020 (15)
H16	0.5819	0.3842	−0.2747	0.024*
C17	0.39142 (9)	0.34296 (6)	−0.29744 (8)	0.01904 (15)
H17	0.3603	0.3318	−0.3826	0.023*
C18	0.30489 (8)	0.32897 (5)	−0.23725 (7)	0.01613 (14)
H18	0.2150	0.3088	−0.2821	0.019*
C19	−0.06390 (7)	0.19929 (5)	−0.09729 (6)	0.01294 (12)
C20	−0.19933 (8)	0.22763 (5)	−0.14897 (7)	0.01598 (14)
H20	−0.2206	0.2894	−0.1433	0.019*
C21	−0.30318 (8)	0.16641 (5)	−0.20861 (7)	0.01793 (14)
H21	−0.3944	0.1866	−0.2431	0.022*

C22	−0.27334 (8)	0.07567 (5)	−0.21765 (7)	0.01761 (14)
H22	−0.3438	0.0339	−0.2587	0.021*
C23	−0.13918 (8)	0.04676 (5)	−0.16595 (7)	0.01747 (14)
H23	−0.1184	−0.0151	−0.1715	0.021*
C24	−0.03506 (8)	0.10781 (5)	−0.10612 (7)	0.01537 (13)
H24	0.0559	0.0872	−0.0712	0.018*

Atomic displacement parameters (Å^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
N1	0.0255 (3)	0.0285 (4)	0.0204 (3)	−0.0110 (3)	0.0144 (3)	−0.0100 (3)
C1	0.0160 (3)	0.0130 (3)	0.0116 (3)	−0.0006 (2)	0.0051 (2)	0.0004 (2)
C2	0.0169 (3)	0.0120 (3)	0.0117 (3)	−0.0010 (2)	0.0047 (2)	−0.0007 (2)
C3	0.0165 (3)	0.0133 (3)	0.0141 (3)	−0.0019 (2)	0.0050 (2)	−0.0016 (2)
C4	0.0147 (3)	0.0134 (3)	0.0139 (3)	−0.0009 (2)	0.0053 (2)	−0.0010 (2)
C5	0.0153 (3)	0.0124 (3)	0.0139 (3)	−0.0006 (2)	0.0052 (2)	−0.0015 (2)
C6	0.0146 (3)	0.0112 (3)	0.0123 (3)	−0.0006 (2)	0.0040 (2)	−0.0001 (2)
C7	0.0177 (3)	0.0130 (3)	0.0113 (3)	−0.0022 (2)	0.0054 (2)	−0.0006 (2)
C8	0.0166 (3)	0.0180 (3)	0.0134 (3)	−0.0012 (2)	0.0045 (2)	−0.0003 (2)
C9	0.0196 (3)	0.0231 (4)	0.0123 (3)	−0.0046 (3)	0.0049 (3)	−0.0016 (3)
C10	0.0253 (4)	0.0192 (3)	0.0140 (3)	−0.0058 (3)	0.0095 (3)	−0.0039 (3)
C11	0.0268 (4)	0.0151 (3)	0.0165 (3)	0.0002 (3)	0.0098 (3)	−0.0012 (2)
C12	0.0229 (3)	0.0148 (3)	0.0132 (3)	0.0011 (3)	0.0052 (3)	0.0004 (2)
C13	0.0153 (3)	0.0125 (3)	0.0155 (3)	−0.0007 (2)	0.0060 (2)	−0.0011 (2)
C14	0.0154 (3)	0.0195 (3)	0.0182 (3)	−0.0013 (2)	0.0054 (3)	−0.0018 (3)
C15	0.0159 (3)	0.0192 (3)	0.0262 (4)	−0.0002 (3)	0.0090 (3)	−0.0002 (3)
C16	0.0214 (4)	0.0173 (3)	0.0264 (4)	0.0023 (3)	0.0142 (3)	0.0026 (3)
C17	0.0245 (4)	0.0166 (3)	0.0186 (3)	0.0012 (3)	0.0112 (3)	0.0001 (3)
C18	0.0181 (3)	0.0144 (3)	0.0158 (3)	−0.0012 (2)	0.0065 (3)	−0.0017 (2)
C19	0.0153 (3)	0.0117 (3)	0.0117 (3)	−0.0009 (2)	0.0052 (2)	0.0001 (2)
C20	0.0162 (3)	0.0129 (3)	0.0166 (3)	0.0004 (2)	0.0041 (2)	0.0001 (2)
C21	0.0162 (3)	0.0162 (3)	0.0178 (3)	−0.0010 (2)	0.0028 (3)	0.0006 (2)
C22	0.0189 (3)	0.0152 (3)	0.0167 (3)	−0.0041 (2)	0.0048 (3)	−0.0012 (2)
C23	0.0204 (3)	0.0123 (3)	0.0204 (3)	−0.0017 (2)	0.0088 (3)	−0.0018 (2)
C24	0.0168 (3)	0.0124 (3)	0.0176 (3)	−0.0007 (2)	0.0075 (3)	−0.0006 (2)

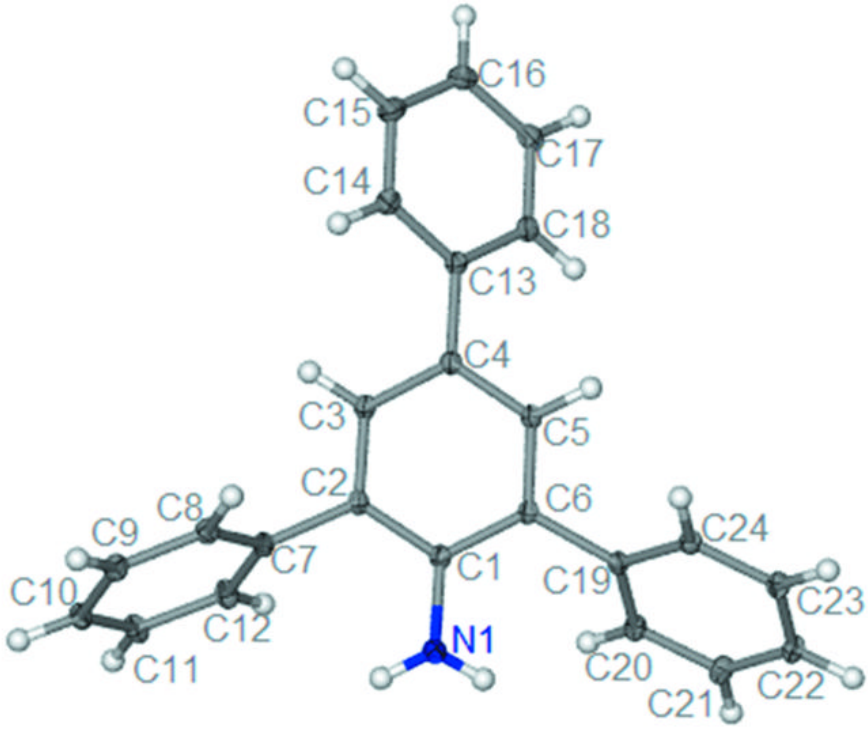
Geometric parameters (Å, °)

N1—C1	1.3850 (11)	C12—H12	0.9500
N1—H1A	0.8800	C13—C18	1.4040 (11)
N1—H1B	0.8800	C13—C14	1.4050 (11)
C1—C2	1.4142 (11)	C14—C15	1.3933 (12)
C1—C6	1.4156 (10)	C14—H14	0.9500
C2—C3	1.3951 (11)	C15—C16	1.3944 (13)
C2—C7	1.4939 (11)	C15—H15	0.9500
C3—C4	1.4010 (11)	C16—C17	1.3960 (13)
C3—H3	0.9500	C16—H16	0.9500
C4—C5	1.3987 (10)	C17—C18	1.3930 (12)
C4—C13	1.4841 (11)	C17—H17	0.9500

C5—C6	1.3959 (11)	C18—H18	0.9500
C5—H5	0.9500	C19—C24	1.4012 (11)
C6—C19	1.4907 (10)	C19—C20	1.4030 (11)
C7—C12	1.3997 (11)	C20—C21	1.3958 (11)
C7—C8	1.4020 (12)	C20—H20	0.9500
C8—C9	1.3950 (11)	C21—C22	1.3939 (12)
C8—H8	0.9500	C21—H21	0.9500
C9—C10	1.3923 (13)	C22—C23	1.3938 (12)
C9—H9	0.9500	C22—H22	0.9500
C10—C11	1.3916 (13)	C23—C24	1.3962 (11)
C10—H10	0.9500	C23—H23	0.9500
C11—C12	1.3949 (11)	C24—H24	0.9500
C11—H11	0.9500		
C1—N1—H1A	120.0	C7—C12—H12	119.7
C1—N1—H1B	120.0	C18—C13—C14	117.95 (8)
H1A—N1—H1B	120.0	C18—C13—C4	120.56 (7)
N1—C1—C2	120.47 (7)	C14—C13—C4	121.46 (7)
N1—C1—C6	120.92 (7)	C15—C14—C13	120.93 (8)
C2—C1—C6	118.53 (7)	C15—C14—H14	119.5
C3—C2—C1	120.01 (7)	C13—C14—H14	119.5
C3—C2—C7	118.45 (7)	C14—C15—C16	120.51 (8)
C1—C2—C7	121.53 (7)	C14—C15—H15	119.7
C2—C3—C4	122.11 (7)	C16—C15—H15	119.7
C2—C3—H3	118.9	C15—C16—C17	119.14 (8)
C4—C3—H3	118.9	C15—C16—H16	120.4
C5—C4—C3	117.09 (7)	C17—C16—H16	120.4
C5—C4—C13	121.31 (7)	C18—C17—C16	120.38 (8)
C3—C4—C13	121.54 (7)	C18—C17—H17	119.8
C6—C5—C4	122.53 (7)	C16—C17—H17	119.8
C6—C5—H5	118.7	C17—C18—C13	121.06 (8)
C4—C5—H5	118.7	C17—C18—H18	119.5
C5—C6—C1	119.59 (7)	C13—C18—H18	119.5
C5—C6—C19	117.89 (6)	C24—C19—C20	118.49 (7)
C1—C6—C19	122.51 (7)	C24—C19—C6	120.41 (7)
C12—C7—C8	118.77 (7)	C20—C19—C6	120.94 (7)
C12—C7—C2	120.91 (7)	C21—C20—C19	120.92 (7)
C8—C7—C2	120.26 (7)	C21—C20—H20	119.5
C9—C8—C7	120.42 (8)	C19—C20—H20	119.5
C9—C8—H8	119.8	C22—C21—C20	120.14 (7)
C7—C8—H8	119.8	C22—C21—H21	119.9
C10—C9—C8	120.33 (8)	C20—C21—H21	119.9
C10—C9—H9	119.8	C23—C22—C21	119.36 (7)
C8—C9—H9	119.8	C23—C22—H22	120.3
C11—C10—C9	119.64 (7)	C21—C22—H22	120.3
C11—C10—H10	120.2	C22—C23—C24	120.65 (7)
C9—C10—H10	120.2	C22—C23—H23	119.7
C10—C11—C12	120.22 (8)	C24—C23—H23	119.7
C10—C11—H11	119.9	C23—C24—C19	120.44 (7)
C12—C11—H11	119.9	C23—C24—H24	119.8

C11—C12—C7	120.61 (8)	C19—C24—H24	119.8
C11—C12—H12	119.7		

Fig. 1



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4-[(*E*)-({4-[Bis(2-hydroxyethyl)amino]-phenyl}imino)methyl]phenol

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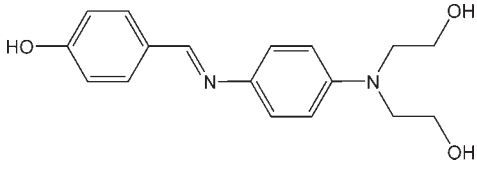
Key indicators: single-crystal X-ray study; T = 296 K; mean σ(C–C) = 0.002 Å; R factor = 0.047; wR factor = 0.109; data-to-parameter ratio = 25.4.

In the title compound, $C_{17}H_{20}N_2O_3$, the amino N atom is in a planar environment (sum of angles = 360.0°). All hydroxy H atoms are involved in hydrogen bonding. In the crystal structure, two O—H···O and an O—H···N_{imino} hydrogen bond result in the formation of a three-dimensional network. The latter hydrogen bonding causes distortion of the planarity of the 4-HO–C_6H_4–CH=N–C_6H_4– fragment by rotation around the =N—C_{Ph} bond. The crystal studied was a non-merohedral twin [refined BASF parameter for the major component = 0.5293 (7)].

Related literature

For Schiff bases of the general type p-R'–C_6H_4–CH=N–C_6H_4–R''-p, see: von König *et al.* (1982); Haldavanekar *et al.* (2009); Ferlin *et al.* (2004); Lewis *et al.* (2009). For the only two structurally characterized compounds of the type with R'' = N(alkyl)$_2$, see: Nagao *et al.* (2002); Nakai *et al.* (1976). For the structure of 2,2′-(4-{[(1*E*)-(4-methoxyphenyl)methylene]-amino}phenylimino) bisethanol, see: Liu *et al.* (2010). For the preparation, see: Cho & Park (1997); Ferlin *et al.* (2004); von König *et al.* (1982). For a description of the Cambridge Structural Database, see: Allen (2002).



Experimental

Crystal data

$C_{17}H_{20}N_2O_3$
M_r = 300.35
Monoclinic, $P2_1/n$
a = 10.1426 (9) Å
b = 9.5192 (9) Å
c = 15.8600 (14) Å
β = 92.679 (1)°
V = 1529.6 (2) Å^3
Z = 4
Mo $K\alpha$ radiation
μ = 0.09 mm^{-1}
T = 296 K
0.36 × 0.27 × 0.13 mm

Data collection

Bruker SMART APEXII diffractometer
Absorption correction: multi-scan (*TWINABS*; Sheldrick, 1996)
T_{min} = 0.968, T_{max} = 0.988
5506 measured reflections
5506 independent reflections
2959 reflections with $I > 2\sigma(I)$

Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.047
$wR(F^2)$ = 0.109
S = 0.84
5506 reflections
217 parameters
H atoms treated by a mixture of independent and constrained refinement
$\Delta\rho_{max}$ = 0.16 e Å^{-3}
$\Delta\rho_{min}$ = −0.18 e Å^{-3}

Table 1
Hydrogen-bond geometry (Å, °).

D—H···A	D—H	H···A	D···A	D—H···A
O1—H1···O3^{i}	0.89 (2)	1.82 (2)	2.669 (2)	160 (2)
O2—H2···N1^{ii}	0.95 (2)	1.82 (2)	2.771 (2)	172 (2)
O3—H3···O2^{iii}	0.89 (2)	1.79 (2)	2.674 (2)	174 (2)

Symmetry codes: (i) $x, y, z+1$; (ii) $x-\frac{1}{2}, -y+\frac{1}{2}, z-\frac{1}{2}$; (iii) $-x+\frac{3}{2}, y+\frac{1}{2}, -z+\frac{1}{2}$.

Data collection: *APEX2* (Bruker, 2007); cell refinement: *SAINT* (Bruker, 2007); data reduction: *SAINT*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *SHELXTL* (Sheldrick, 2008) and *OLEX2* (Dolomanov *et al.*, 2009); software used to prepare material for publication: *SHELXL97* and *OLEX2*.

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Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: HG2687).

References

Allen, F. H. (2002). *Acta Cryst.* B**58**, 380–388.
Bruker (2007). *APEX2* and *SAINT*. Bruker AXS Inc., Madison, Wisconsin, USA.
Cho, Y. H. & Park, J. C. (1997). *Tetrahedron Lett.* **38**, 8331–8334.
Dolomanov, O. V., Bourhis, L. J., Gildea, R. J., Howard, J. A. K. & Puschmann, H. (2009). *J. Appl. Cryst.* **42**, 339–341.
Ferlin, M. G., Dalla Via, L. & Gia, O. M. (2004). *Bioorg. Med. Chem.* **12**, 771–777.
Haldavanekar, V., Prabhu, M., Dharmaraj, R. & Kankan, R. N. (2009). WO Patent 2009147383 A1.
König, A. von, Moll, F. & Rosenhahn, L. (1982). US Patent 4358531.
Lewis, J., Matteucci, M., Chen, T. & Jiao, H. (2009). WO Patent 2009140553 A2.
Liu, X., Yang, B., Wang, M. & Borzov, M. V. (2010). *Acta Cryst.* E**66**. Submitted.
Nagao, Y., Kimura, F., Kozawa, K. & Uchida, T. (2002). *Shikizai Kyokaishi*, **75**, 415–420.
Nakai, H., Shiro, M., Emuzi, K., Sakata, S. & Kubota, T. (1976). *Acta Cryst.* B**32**, 1827–1833.
Sheldrick, G. M. (1996). *TWINABS*. University of Göttingen, Germany.
Sheldrick, G. M. (2008). *Acta Cryst.* A**64**, 112–122.

supplementary materials

Acta Cryst. (2010). E**66**, o1646 [**doi:10.1107/S1600536810021926**]

4-[(*E*)-({4-[Bis(2-hydroxyethyl)amino]phenyl}imino)methyl]phenol

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Comment

Schiff bases of general type *p*-R'–C_6H_4–CH=N–C_6H_4–R"-*p* are well-known objects that find their practical application in various areas [photography (for instance, see von König *et al.*, 1982), medicinal and pharmaceutical chemistry (for instance, see Haldavanekar *et al.*, 2009; Ferlin *et al.*, 2004; Lewis *et al.*, 2009)]. Recently we were interested in preparation of a series of 2,2'-(4-{[(1*E*)-phenylmethylene]amino}phenylimino)bisethanols as semi-products for their further conversion into paracyclophanes. This way, 4-[(*E*)-({4-[bis(2-hydroxyethyl)amino]phenyl}imino)methyl]phenol, $C_{17}H_{20}N_2O_3$, (I), and 2,2'-(4-{[(1*E*)-(4-methoxyphenyl)methylene]amino}phenylimino)bisethanol, $C_{18}H_{22}N_2O_3$, [II; Liu *et al.* (2010)], were prepared by a condensation reaction between 2,2'-[(4-aminophenyl)imino]bisethanol and 4-methoxy- or 4-hydroxybenzaldehyde, respectively (see Scheme).

Despite of the fact that structurally characterized Schiff bases of general type *p*-R'–C_6H_4–CH=N–C_6H_4–R"-*p* are well presented in the Cambridge Structural Database [CSD; Version 5.27, release February 2009; Allen, 2002; 128 entries, 173 fragments], among them there are only two compounds with R" = *N*(alkyl)$_2$ [namely: R' = H, R" = NEt_2 (Nagao *et al.*, 2002) and R' = NO_2, R" = NMe_2 (Nakai *et al.*, 1976)]. From this viewpoint, X-ray single crystal study of (I) presents a certain descriptive interest.

The asymmetric unit of (I) is shown in Fig. 1. Except of dihedral angle C7–N1–C8–C9, asymmetric units of (I) and [II; Liu *et al.* (2010)] have nearly identical geometries (Supplementary materials). Bond lengths, valency angles and C4–C7–N1–C8 torsion angle values for C4/C7/N1/C8 fragment match well the reported median values for *p*-R'–C_6H_4–CH=N–C_6H_4–R"-*p* [analysis of the Cambridge Structural Database (CSD); Version 5.27, release February 2009; Allen, 2002; 128 entries, 173 fragments]. Fragments O1/C1—C7/N1 and C8—C13/N2/C14/C16 are nearly planar [within 0.04 and 0.07 Å for (I)]. Atom N2 is also in a planar environment [sum of the valent angles 360.0 (6)°] what presents the most frequent case for aryldialkylamines (range from 317.6 to 360.0°, median value 359.0°)..

All hydroxy H-atoms in (I) are involved into hydrogen bonding [for the H-bonds lengths and angles values see the Table 1]. This way, O1—H1···O3 H-bonds assemble the molecules in chains stretched along the *c*-axis of the crystal lattice [linked molecules are connected by a simple (0,0,±1) translation]. These chains, in their turn, assemble into "foldered" zigzag layers parallel to the *a*0*b* face due to O2—H2···N1 bonds (see Fig. 2). Finally, O3—H3···O2 bonds join the adjacent layers what completes the entire 3D-framework (see Fig. 3). Involving of the N1 imino-atom into H-binding, evidently, causes a considerable distortion of the 4-HO–C_6H_4–CH=N–C_6H_4– fragment planarity by rotation around the ═N—C_{Ph} bond.

Experimental

1-Chloro-4-nitrobenzene, 4-methoxy- and 4-hydroxybenzaldehydes, 2,2'-iminobisethanol, ammonium formate, 10% Pd/C catalyst and solvents were purchased from Sinopharm Chemical Reagent and Tianjin Fuyu Chemical companies. 2,2'-[(4-nitrophenyl)imino]bisethanol was prepared as described by Cho & Park (1997) and Ferlin *et al.* (2004). Reduction of the

nitro-group was carried out as described by Lewis *et al.* (2009). Schiff-base preparation was done closely to what described by von König *et al.* (1982). – ^{1}H NMR spectra were recorded on a Varian INOVA-400 instrument in CD_3OD at 298 K using the resonance of the residual solvent protons as an internal reference [δ(H) = 3.30 ppm]. Procedure: 1-chloro-4-nitrobenzene (15.76 g, 0.10 mol) was dissolved in 2,2'-iminobisethanol (50 ml). The reaction mixture was heated at 393 K for 10 h, cooled down to room temperature, the precipitated crude 2,2'-[(4-nitrophenyl)imino]bisethanol filtered off, dried in vacuum and recrystallized from minimal amount of hot ethanol. Yield 11.54 g (51%). 2,2'-[(4-nitrophenyl)imino]bisethanol (8.15 g, 0.036 mol) was dissolved in MeOH (50 ml). To this solution, $HCOONH_4$ (0.216 mol) and 10% Pd/C (0.6 g) were added and the slurry was stirred at 293 K for 30 min. On removal of the catalyst by filtration, the filtrate was placed into a N_2-flushed flask containing 1 ml of acetic acid and an equimolar (0.036 mol) amount of 4-hydroxybenzaldehyde (0.036 mol) was added dropwise at 333 K during 30 min. The reaction mixture was kept at the same temperature for additional 30 min, cooled down to 273 K and ice-cold water (200 ml) was added. The precipitated light-green (I) solid was collected by filtration, washed with water, dried under reduced pressure and, finally, re-crystallized by a slow evaporation of their methanol solutions in air at 293 K. Yield 92%, m.p. 476 K. ^{1}H NMR for (I) δ: 8.45 (s, 1H, CH═N), 6.78–7.73 (m, 8H, C_6H_4), 3.30, 3.74 (both t, 4 H and 4 H, $^3J_{HH}$ = 7.2 Hz, CH_2). Single crystal of (I) suitable for X-ray diffraction analysis was picked up directly from the obtained materials.

Refinement

All non-H atoms were refined anisotropically. H atoms except of H7 and OH group ones were treated as riding atoms with distances C—H = 0.97 (CH_2), 0.93 Å ($C_{Ar}H$), and U_{iso}(H) = 1.2U_{eq}(C). Atoms H7 and OH group H atoms were found from difference Fourier syntheses and refined isotropically.

Figures

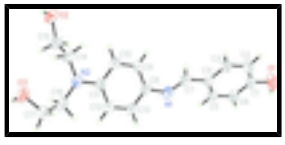


Fig. 1. Asymmetric unit of the compound (I) with labelling and thermal ellipsoids at the 50% probability level.

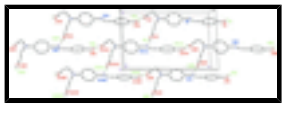


Fig. 2. Assembling of the molecules of (I) into a "foldered" zigzag layer. Hydrogen atoms except of the OH ones are omitted for clarity. Labelling is provided only for atoms involved in H-bonding. H-bonds are depicted as dashed lines.

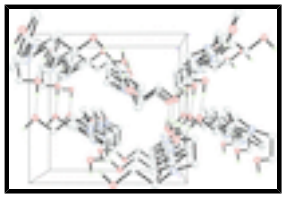


Fig. 3. Inter-layer assembling of the molecules of (I) into a 3D-network. Hydrogen atoms except of the OH ones are omitted for clarity. Only O3—H3···O2^{iii} [symmetry code: (iii) –x + 1.5, y + 0.5, –z + 0.5] bonds and their symmetry equivalents are depicted (dashed lines).

4-[(*E*)-({4-[bis(2-hydroxyethyl)amino]phenyl}imino)methyl]phenol

Crystal data

$C_{17}H_{20}N_2O_3$	$F(000)$ = 640
M_r = 300.35	D_x = 1.304 Mg m^{-3}

Monoclinic, $P2_1/n$	Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å
Hall symbol: -P 2yn	Cell parameters from 4620 reflections
$a = 10.1426$ (9) Å	$\theta = 2.3–27.0°$
$b = 9.5192$ (9) Å	$\mu = 0.09$ mm^{-1}
$c = 15.8600$ (14) Å	$T = 296$ K
$\beta = 92.679$ (1)°	Block, green
$V = 1529.6$ (2) Å^3	0.36 × 0.27 × 0.13 mm
$Z = 4$	

Data collection

Bruker SMART APEXII diffractometer	5506 measured reflections
Radiation source: fine-focus sealed tube	5506 independent reflections
graphite	2959 reflections with $I > 2\sigma(I)$
Detector resolution: 8.333 pixels mm^{-1}	$\theta_{max} = 25.1°$, $\theta_{min} = 2.3°$
phi and ω scans	$h = -12\rightarrow12$
Absorption correction: multi-scan (*TWINABS*; Sheldrick, 1996)	$k = 0\rightarrow11$
$T_{min} = 0.968$, $T_{max} = 0.988$	$l = 0\rightarrow18$

Refinement

Refinement on F^2	Secondary atom site location: difference Fourier map
Least-squares matrix: full	Hydrogen site location: inferred from neighbouring sites
$R[F^2 > 2\sigma(F^2)] = 0.047$	H atoms treated by a mixture of independent and constrained refinement
$wR(F^2) = 0.109$	$w = 1/[\sigma^2(F_o^2) + (0.0702P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
$S = 0.84$	$(\Delta/\sigma)_{max} < 0.001$
5506 reflections	$\Delta\rho_{max} = 0.16$ e Å^{-3}
217 parameters	$\Delta\rho_{min} = -0.18$ e Å^{-3}
0 restraints	Extinction correction: *SHELXL97* (Sheldrick, 2008), $Fc^*=kFc[1+0.001xFc^2\lambda^3/\sin(2\theta)]^{-1/4}$
Primary atom site location: structure-invariant direct methods	Extinction coefficient: 0.0107 (15)

Special details

Experimental. Sample of (I) was a two-component non-merohedral twin with approximately equal component contribution. Thus, the structure of (I) was solved and pre-refined for one of the components (HKLF 4 format) and finally refined for the full set of reflexions (HKLF 5 file format). The refined BASF parameter for the prevailing component equals 0.5293 (7).

Geometry. All esds (except the esd in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell esds are taken into account individually in the estimation of esds in distances, angles and torsion angles; correlations between esds in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell esds is used for estimating esds involving l.s. planes.

Refinement. Refinement of F^2 against ALL reflections. The weighted *R*-factor wR and goodness of fit *S* are based on F^2, conventional *R*-factors *R* are based on *F*, with *F* set to zero for negative F^2. The threshold expression of $F^2 > 2\sigma(F^2)$ is used only for calculating *R*-factors(gt) etc. and is not relevant to the choice of reflections for refinement. *R*-factors based on F^2 are statistically about twice as large as those based on *F*, and *R*- factors based on ALL data will be even larger.

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å^2)

	x	*y*	*z*	U_{iso}*/U_{eq}
O1	0.84481 (15)	0.10572 (15)	1.16972 (7)	0.0735 (5)
O2	0.56639 (11)	0.06213 (12)	0.32409 (7)	0.0477 (3)
O3	0.90811 (13)	0.32742 (15)	0.26638 (8)	0.0649 (4)
N1	0.89456 (12)	0.22592 (15)	0.77116 (8)	0.0438 (4)
N2	0.89798 (12)	0.13765 (13)	0.41928 (7)	0.0423 (4)
C1	0.84745 (17)	0.11819 (19)	1.08463 (10)	0.0479 (5)
C2	0.80262 (17)	0.00647 (18)	1.03658 (10)	0.0551 (5)
H2A	0.7703	−0.0730	1.0628	0.066*
C3	0.80526 (16)	0.01135 (18)	0.94979 (10)	0.0505 (5)
H3A	0.7768	−0.0661	0.9181	0.061*
C4	0.84966 (15)	0.12981 (17)	0.90899 (9)	0.0394 (4)
C5	0.89081 (15)	0.24390 (17)	0.95828 (9)	0.0434 (4)
H5	0.9183	0.3256	0.9322	0.052*
C6	0.89162 (15)	0.23798 (17)	1.04515 (9)	0.0443 (4)
H6	0.9218	0.3143	1.0772	0.053*
C7	0.85321 (16)	0.1266 (2)	0.81716 (10)	0.0442 (4)
C8	0.88878 (15)	0.20652 (16)	0.68171 (9)	0.0401 (4)
C9	0.78712 (16)	0.13679 (17)	0.63799 (9)	0.0444 (4)
H9	0.7167	0.1025	0.6673	0.053*
C10	0.78819 (16)	0.11715 (17)	0.55179 (9)	0.0452 (4)
H10	0.7175	0.0715	0.5242	0.054*
C11	0.89302 (15)	0.16422 (16)	0.50488 (9)	0.0385 (4)
C12	0.99168 (16)	0.24157 (17)	0.54925 (9)	0.0449 (4)
H12	1.0603	0.2802	0.5201	0.054*
C13	0.98867 (16)	0.26125 (17)	0.63517 (9)	0.0450 (4)
H13	1.0557	0.3128	0.6627	0.054*
C14	0.79307 (15)	0.05868 (17)	0.37522 (9)	0.0433 (4)
H14B	0.7674	−0.0192	0.4103	0.052*
H14A	0.8258	0.0202	0.3236	0.052*
C15	0.67400 (15)	0.14873 (17)	0.35403 (10)	0.0442 (4)
H15B	0.6494	0.1998	0.4038	0.053*
H15A	0.6948	0.2166	0.3110	0.053*
C16	1.01067 (15)	0.17981 (18)	0.37224 (10)	0.0479 (5)
H16A	1.0211	0.1130	0.3269	0.057*
H16B	1.0892	0.1743	0.4094	0.057*
C17	1.00283 (17)	0.32486 (19)	0.33494 (10)	0.0536 (5)
H17A	0.9782	0.3916	0.3777	0.064*
H17B	1.0885	0.3519	0.3155	0.064*
H1	0.880 (2)	0.183 (2)	1.1930 (13)	0.107 (9)*
H2	0.5011 (18)	0.130 (2)	0.3071 (11)	0.086 (7)*

H3	0.913 (2)	0.408 (2)	0.2387 (13)	0.117 (9)*
H7	0.8211 (14)	0.0378 (16)	0.7921 (9)	0.050 (5)*

Atomic displacement parameters (Å^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
O1	0.1199 (13)	0.0705 (11)	0.0296 (8)	−0.0099 (9)	−0.0027 (7)	0.0057 (7)
O2	0.0524 (8)	0.0448 (8)	0.0442 (7)	0.0026 (7)	−0.0141 (6)	−0.0081 (6)
O3	0.0834 (10)	0.0586 (9)	0.0499 (8)	−0.0142 (8)	−0.0269 (7)	0.0155 (7)
N1	0.0480 (9)	0.0525 (10)	0.0303 (8)	−0.0016 (7)	−0.0057 (6)	0.0003 (7)
N2	0.0449 (8)	0.0523 (9)	0.0290 (8)	−0.0043 (7)	−0.0030 (7)	0.0018 (6)
C1	0.0604 (12)	0.0515 (12)	0.0314 (10)	0.0057 (10)	−0.0029 (9)	0.0022 (8)
C2	0.0775 (13)	0.0447 (12)	0.0430 (11)	−0.0039 (10)	0.0006 (10)	0.0081 (9)
C3	0.0674 (13)	0.0429 (11)	0.0406 (11)	−0.0041 (9)	−0.0050 (9)	−0.0011 (8)
C4	0.0432 (10)	0.0426 (10)	0.0319 (9)	0.0031 (8)	−0.0042 (8)	0.0015 (8)
C5	0.0492 (11)	0.0445 (11)	0.0365 (10)	−0.0023 (9)	0.0010 (8)	0.0039 (8)
C6	0.0508 (11)	0.0455 (11)	0.0364 (10)	−0.0008 (9)	−0.0017 (8)	−0.0056 (8)
C7	0.0466 (11)	0.0480 (12)	0.0373 (11)	0.0008 (9)	−0.0057 (8)	−0.0017 (9)
C8	0.0452 (10)	0.0437 (10)	0.0307 (9)	0.0000 (8)	−0.0061 (8)	0.0004 (8)
C9	0.0448 (10)	0.0548 (11)	0.0333 (10)	−0.0069 (9)	−0.0025 (8)	0.0042 (8)
C10	0.0473 (10)	0.0521 (11)	0.0352 (10)	−0.0096 (9)	−0.0087 (8)	0.0014 (8)
C11	0.0440 (10)	0.0404 (10)	0.0303 (9)	0.0020 (8)	−0.0073 (8)	0.0050 (7)
C12	0.0445 (10)	0.0555 (12)	0.0343 (10)	−0.0052 (9)	−0.0036 (8)	0.0060 (8)
C13	0.0456 (10)	0.0515 (12)	0.0370 (10)	−0.0068 (9)	−0.0092 (8)	0.0010 (8)
C14	0.0521 (10)	0.0451 (11)	0.0318 (9)	0.0012 (9)	−0.0067 (8)	−0.0011 (8)
C15	0.0486 (10)	0.0451 (11)	0.0383 (10)	−0.0015 (9)	−0.0066 (8)	−0.0017 (8)
C16	0.0472 (10)	0.0608 (12)	0.0351 (10)	0.0070 (9)	−0.0035 (8)	0.0014 (8)
C17	0.0553 (11)	0.0654 (13)	0.0392 (10)	−0.0113 (10)	−0.0088 (9)	0.0078 (9)

Geometric parameters (Å, °)

O1—C1	1.3563 (18)	C7—H7	0.984 (15)
O1—H1	0.89 (2)	C8—C13	1.383 (2)
O2—C15	1.4310 (17)	C8—C9	1.385 (2)
O2—H2	0.952 (19)	C9—C10	1.3805 (19)
O3—C17	1.4172 (18)	C9—H9	0.9300
O3—H3	0.89 (2)	C10—C11	1.400 (2)
N1—C7	1.277 (2)	C10—H10	0.9300
N1—C8	1.4292 (18)	C11—C12	1.405 (2)
N2—C11	1.3843 (18)	C12—C13	1.3773 (19)
N2—C16	1.4504 (18)	C12—H12	0.9300
N2—C14	1.4546 (18)	C13—H13	0.9300
C1—C2	1.373 (2)	C14—C15	1.506 (2)
C1—C6	1.385 (2)	C14—H14B	0.9700
C2—C3	1.379 (2)	C14—H14A	0.9700
C2—H2A	0.9300	C15—H15B	0.9700
C3—C4	1.386 (2)	C15—H15A	0.9700
C3—H3A	0.9300	C16—C17	1.503 (2)
C4—C5	1.391 (2)	C16—H16A	0.9700

C4—C7	1.459 (2)	C16—H16B	0.9700
C5—C6	1.3786 (19)	C17—H17A	0.9700
C5—H5	0.9300	C17—H17B	0.9700
C6—H6	0.9300		
C1—O1—H1	108.4 (14)	C9—C10—H10	119.2
C15—O2—H2	102.4 (11)	C11—C10—H10	119.2
C17—O3—H3	110.1 (14)	N2—C11—C10	121.75 (14)
C7—N1—C8	118.17 (14)	N2—C11—C12	121.97 (14)
C11—N2—C16	121.30 (13)	C10—C11—C12	116.28 (14)
C11—N2—C14	120.41 (13)	C13—C12—C11	121.25 (15)
C16—N2—C14	118.18 (12)	C13—C12—H12	119.4
O1—C1—C2	117.58 (16)	C11—C12—H12	119.4
O1—C1—C6	122.93 (16)	C12—C13—C8	121.84 (15)
C2—C1—C6	119.49 (15)	C12—C13—H13	119.1
C1—C2—C3	120.43 (16)	C8—C13—H13	119.1
C1—C2—H2A	119.8	N2—C14—C15	111.96 (13)
C3—C2—H2A	119.8	N2—C14—H14B	109.2
C2—C3—C4	121.04 (16)	C15—C14—H14B	109.2
C2—C3—H3A	119.5	N2—C14—H14A	109.2
C4—C3—H3A	119.5	C15—C14—H14A	109.2
C3—C4—C5	117.93 (14)	H14B—C14—H14A	107.9
C3—C4—C7	118.23 (16)	O2—C15—C14	109.72 (13)
C5—C4—C7	123.83 (15)	O2—C15—H15B	109.7
C6—C5—C4	121.16 (15)	C14—C15—H15B	109.7
C6—C5—H5	119.4	O2—C15—H15A	109.7
C4—C5—H5	119.4	C14—C15—H15A	109.7
C5—C6—C1	119.89 (15)	H15B—C15—H15A	108.2
C5—C6—H6	120.1	N2—C16—C17	115.35 (14)
C1—C6—H6	120.1	N2—C16—H16A	108.4
N1—C7—C4	125.38 (17)	C17—C16—H16A	108.4
N1—C7—H7	121.1 (8)	N2—C16—H16B	108.4
C4—C7—H7	113.5 (8)	C17—C16—H16B	108.4
C13—C8—C9	117.40 (14)	H16A—C16—H16B	107.5
C13—C8—N1	118.95 (14)	O3—C17—C16	109.84 (14)
C9—C8—N1	123.64 (14)	O3—C17—H17A	109.7
C10—C9—C8	121.38 (15)	C16—C17—H17A	109.7
C10—C9—H9	119.3	O3—C17—H17B	109.7
C8—C9—H9	119.3	C16—C17—H17B	109.7
C9—C10—C11	121.62 (15)	H17A—C17—H17B	108.2
O1—C1—C2—C3	−178.64 (16)	C16—N2—C11—C10	−176.39 (14)
C6—C1—C2—C3	2.0 (3)	C14—N2—C11—C10	−0.2 (2)
C1—C2—C3—C4	−1.7 (3)	C16—N2—C11—C12	4.6 (2)
C2—C3—C4—C5	−0.3 (2)	C14—N2—C11—C12	−179.19 (14)
C2—C3—C4—C7	178.38 (16)	C9—C10—C11—N2	176.24 (14)
C3—C4—C5—C6	2.1 (2)	C9—C10—C11—C12	−4.7 (2)
C7—C4—C5—C6	−176.54 (15)	N2—C11—C12—C13	−176.78 (14)
C4—C5—C6—C1	−1.8 (2)	C10—C11—C12—C13	4.1 (2)
O1—C1—C6—C5	−179.58 (16)	C11—C12—C13—C8	−0.2 (2)

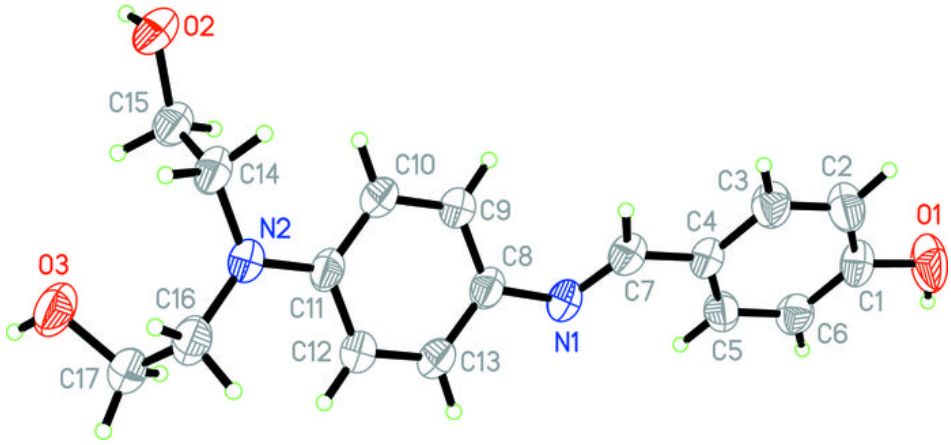
C2—C1—C6—C5	−0.3 (2)	C9—C8—C13—C12	−3.3 (2)
C8—N1—C7—C4	−178.79 (15)	N1—C8—C13—C12	177.43 (14)
C3—C4—C7—N1	−178.17 (16)	C11—N2—C14—C15	79.93 (17)
C5—C4—C7—N1	0.5 (3)	C16—N2—C14—C15	−103.73 (15)
C7—N1—C8—C13	−143.95 (16)	N2—C14—C15—O2	−170.21 (11)
C7—N1—C8—C9	36.9 (2)	C11—N2—C16—C17	−89.41 (17)
C13—C8—C9—C10	2.8 (2)	C14—N2—C16—C17	94.28 (17)
N1—C8—C9—C10	−178.01 (14)	N2—C16—C17—O3	−71.61 (18)
C8—C9—C10—C11	1.3 (2)		

Hydrogen-bond geometry (Å, °)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
O1—H1···O3^{i}	0.89 (2)	1.82 (2)	2.669 (2)	160 (2)
O2—H2···N1^{ii}	0.95 (2)	1.82 (2)	2.771 (2)	172 (2)
O3—H3···O2^{iii}	0.89 (2)	1.79 (2)	2.674 (2)	174 (2)

Symmetry codes: (i) *x*, *y*, *z*+1; (ii) *x*−1/2, −*y*+1/2, *z*−1/2; (iii) −*x*+3/2, *y*+1/2, −*z*+1/2.

Fig. 1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C14
N2
O3
C16
C17
C10
C9
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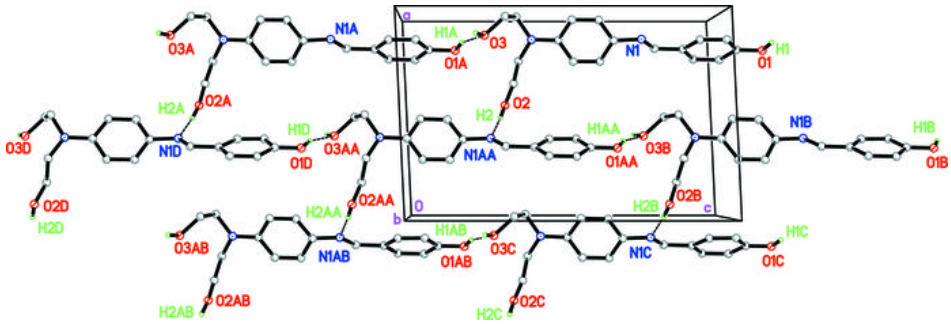
N1
C7
C4
C3
C2
O1
C1
C6
C5

Fig. 2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H1
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N1D
H1D
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O3AA
H2
O2
N1AA
H1AA
O1AA
O3B
N1B
H1B
O1B
O2D
H2D
H2AA
O2AA
H2B
O2B
O3AB
N1AB
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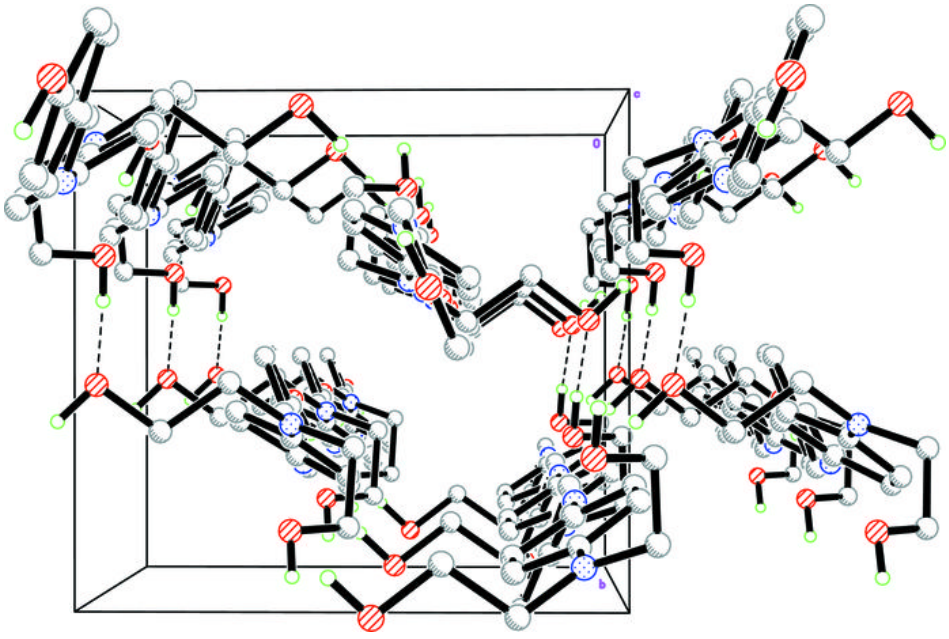
H1C
O1C
H2AB
O2AB
H2C
O2C

Fig. 3



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2′,3,4,4′-Tetramethoxychalcone

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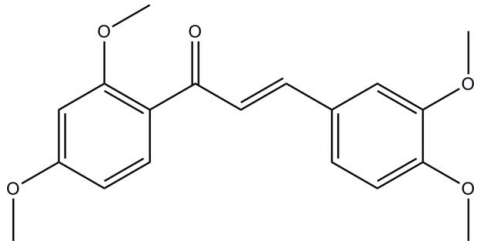
Key indicators: single-crystal X-ray study; T = 100 K; mean σ(C–C) = 0.003 Å; R factor = 0.044; wR factor = 0.188; data-to-parameter ratio = 18.7.

In the title compound [systematic name: 1-(2,4-dimethoxyphenyl)-3-(3,4-dimethoxyphenyl)prop-2-en-1-one], $C_{19}H_{20}O_5$, the dihedral angle between the benzene rings is 26.88 (5)°. One of the methoxy groups is twisted slightly away from the plane [C—O—C—C torsion angle = −12.8 (3)°] while the others are almost co-planer [C—O—C—C torsion angles = −3.2 (3), 2.6 (3) and −3.6 (3)°]. The crystal packing is stabilized by intermolecular C—H···O interactions. A weak intramolecular C—H···O interaction occurs.

Related literature

For properties and uses of chalcones, see: Marais *et al.* (2005); Fichou *et al.* (1988); Uchida *et al.* (1998). For the biological activity of flavenoids, see: Pietta *et al.* (2003). For related structures, see: Patil *et al.* (2006*a*,*b*,*c*); Teh *et al.* (2006*a*,*b*,*c*); Rosli *et al.* (2006). For the synthesis of the title compound, see: Kraus *et al.* (2008). For bond-length data, see: Allen *et al.* (1987).



Experimental

Crystal data

$C_{19}H_{20}O_5$
M_r = 328.35
Monoclinic, $P2_1/c$
a = 12.5839 (7) Å
b = 11.7204 (7) Å
c = 12.1339 (6) Å
β = 109.489 (2)°
V = 1687.07 (16) Å^3
Z = 4
Mo $K\alpha$ radiation
μ = 0.09 mm^{-1}
T = 100 K
0.49 × 0.22 × 0.07 mm

Data collection

Bruker APEXII diffractometer
Absorption correction: multi-scan (*SADABS*; Bruker, 2008)
T_{min} = 0.976, T_{max} = 0.994
32681 measured reflections
4205 independent reflections
2539 reflections with $I > 2\sigma(I)$
R_{int} = 0.039

Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.044
$wR(F^2)$ = 0.188
S = 1.12
4205 reflections
225 parameters
H atoms treated by a mixture of independent and constrained refinement
$\Delta\rho_{max}$ = 0.21 e Å^{-3}
$\Delta\rho_{min}$ = −0.20 e Å^{-3}

Table 1
Hydrogen-bond geometry (Å, °).

D—H···A	D—H	H···A	D···A	D—H···A
C8—H8···O1	0.96 (2)	2.29 (2)	2.813 (3)	113.6 (15)
C18—H18B···O3^{i}	0.96	2.46	3.253 (3)	140

Symmetry code: (i) $x, -y+\frac{1}{2}, z+\frac{1}{2}$.

Data collection: *APEX2* (Bruker, 2008); cell refinement: *SAINT-Plus* (Bruker, 2008); data reduction: *SAINT-Plus* and *XPREP* (Bruker, 2008); program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *DIAMOND* (Brandenberg & Putz, 2005); software used to prepare material for publication: WingGX (Farrugia, 1999).

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Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: HG2688).

References

Allen, F. H., Kennard, O., Watson, D. G., Brammer, L., Orpen, A. G. & Taylor, R. (1987). *J. Chem. Soc. Perkin Trans. 2* pp. S1–19.
Brandenberg, K. & Putz, H. (2005). *DIAMOND*. Crystal Impact GbR, Bonn, Germany.
Bruker (2008). *APEX2*, *SAINT-Plus*, *XPREP* and *SADABS*. Bruker AXS Inc., Madison, Wisconsin, USA.
Farrugia, L. J. (1999). *J. Appl. Cryst.*) **32**, 837-838.
Fichou, D., Watanabe, T., Takenda, T., Miyata, S., Goto, Y. & Nakayama, M. (1988). *Jpn.J. Appl. Phys.* **27**, L429–L430.
Kraus, G. & Roy, S. (2008). *J. Nat. Prod.* **71**, 1961–1962.
Marais, J. P. J., Ferreira, D. & Slade, D. (2005). *Phytochemistry*, **66**, 2145–2176.
Patil, P. S., Ng, S.-L., Razak, I. A., Fun, H.-K. & Dharmaprakash, S. M. (2006*c*). *Acta Cryst.* E**62**, o4448–o4449.
Patil, P. S., Teh, J. B.-J., Fun, H.-K., Razak, I. A. & Dharmaprakash, S. M. (2006*a*). *Acta Cryst.* E**62**, o896–o898.
Patil, P. S., Teh, J. B.-J., Fun, H.-K., Razak, I. A. & Dharmaprakash, S. M. (2006*b*). *Acta Cryst.* E**62**, o1710–o1712.
Pietta, P., Gardana, C. & Pietta, A. (2003). *Flavonoids in Health and Disease*. 2nd ed. edited by C. A. Rice-Evans & L.Packer. New York: Marcel Dekker, Inc.
Rosli, M. M., Patil, P. S., Fun, H.-K., Razak, I. A. & Dharmaprakash, S. M. (2006). *Acta Cryst.* E**62**, o4228–o4230.
Sheldrick, G. M. (2008). *Acta Cryst.* A**64**, 112–122.
Teh, J. B.-J., Patil, P. S., Fun, H.-K., Razak, I. A. & Dharmaprakash, S. M. (2006*a*). *Acta Cryst.* E**62**, o890–o892.

Teh, J. B.-J., Patil, P. S., Fun, H.-K., Razak, I. A. & Dharmaprakash, S. M. (2006*b*). *Acta Cryst.* E**62**, o2399–o2400.
Teh, J. B.-J., Patil, P. S., Fun, H.-K., Razak, I. A. & Dharmaprakash, S. M. (2006*c*). *Acta Cryst.* E**62**, o2991–o2992.
Uchida, T., Kozawa, K., Sakai, T., Aoki, M., Yoguchi, H., Abdureyim, A. & Watanabe, Y. (1998). *Mol. Cryst. Liq. Cryst.* **62**, 135–140.

supplementary materials

Acta Cryst. (2010). E**66**, o1798-o1799 [**doi:10.1107/S1600536810022142**]

2',3,4,4'-Tetramethoxychalcone

J. H. van Tonder, T. J. Muller and B. C. B. Bezuidenhoudt

Comment

Flavonoids are a prominent class of secondary plant metabolites known for their wide range of biological active compounds that exibit antibacterial, antifugal, antitumor and anti-inflammatory properties (Pietta *et al.*, 2003). Chalcones are an important subclass of these compounds and are often utilized as intermediates in the synthesis of a variety of cyclic flavonoids (Marais *et al.*, 2005). Furthermore, many chalcone derivatives are known to have excellent non-linear optical (NLO) properties (Fichou *et al.*, 1988; Uchida *et al.*, 1998; Patil *et al.*, 2006*a*,b). We report here a new chalcone which we have successfully synthesized (the title compound, (I)). Bond distances in (I) have normal values (Allen *et al.*, 1987) and bond angles and distances are comparable to those in related structures (Teh *et al.*, 2006*a*,b,c; Patil *et al.*, 2006*a*,b,c; Rosli *et al.* 2006). The least squares plane through the enone group (C7, C8, C9 and O3) exhibit dihedral angles of 29.2 (1)° and 4.5 (1)° with the C1—C6 and C10—C15 benzene rings, respectively. The dihedral angle between the two benzene rings is 26.88 (5)°. The methoxy group attached at C1 is slightly twisted away from the C1—C6 benzene ring plane, with a C16—O1—C1—C2 torsion angle of -12.8 (3)°. The methoxy groups at C3, C12 and C13 are almost co-planar with the C1—C6 and C10—C15 benzene rings with C17—O2—C3—C2, C18—O4—C12—C11 and C19—O5—C13—C14 torsion angels of -3.2 (3)°, 2.6 (3)° and -3.6 (3)°, respectively. An intramolecular C8—H8···O1 hydrogen bond is observed in the molecular structure of (I), while the molecules form chains through intermolecular C18—H18B···O3^{i} hydrogen bonds (Table 1).

Experimental

The title compoud was synthesized according to the procedure by Kraus *et al.* (2008) Freshly ground KOH (1.55 g; 27.80 mmol; 5 eq.) was added to a cold (ice bath) stirring solution of 2',4'-dimethoxyacetophenone (1.00 g; 5.56 mmol) and 3,4-dimethoxybenzaldehyde (1.13 g; 7.12 mmol; 1.2 eq.) in EtOH (40 ml). The reaction mixture was allowed to heat to room temperature and stirred to completion (TLC). Ice was added to the reaction mixture prior to acidification with concentrated HCl (litmus). Extraction was performed with EtOAc (3 *x* 100 ml) and the organic fractions combined. The organic phase was neutralized with a saturated solution of $NaHCO_3$ (litmus), washed with water, dried (Na_2SO_4) and evaporated *in vacuo* at *ca* 40 °C. Crystallization from EtOH afforded the desired chalcone (1.55 g; 84.7%) as yellow needles. R_f 0.16 (H:A; 8:2); Mp 88.3 °C; ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.69 (1*H*, d, *J* = 8.61 Hz, H-6'), 7.58 (1*H*, d, *J* = 15.71 Hz, H-β), 7.33 (1*H*, d, *J* = 15.71 Hz, H-α), 7.14 (1*H*, dd, *J* = 1.92, 8.32 Hz, H-5), 7.08 (1*H*, d, *J* = 1.92 Hz, H-2), 6.84 (1*H*, d, *J* = 8.32 Hz, H-6), 6.52 (1*H*, dd, *J* = 2.25, 8.61 Hz, H-5'), 6.46 (1*H*, d, *J* = 2.25 Hz, H– 3'), 3.88 (3*H*, s, –OCH_3), 3.87 (3*H*, s, –OCH_3), 3.85 (3*H*, s, –OCH_3), 3.82 (3*H*, s, –OCH_3); ^{13}C NMR (151 MHz, $CDCl_3$) δ 190.58, 163.96, 160.21, 150.95, 149.11, 142.34 (C-β), 132.63 (C-6'), 128.39, 125.28 (C-α), 122.60 (C-5), 122.36, 111.13 (C-6), 110.24 (C-2), 105.14 (C-5'), 98.66 (C-3'), 55.94 (–OCH_3), 55.86 (–OCH_3), 55.71 (–OCH_3), 55.50 (–OCH_3).

Refinement

The aromatic H atoms were placed in geometrically idealized positions and constrained to ride on its parent atoms with U_{iso} (H) = 1.2U_{eq}(C) and at a distance of 0.93 Å. The hydrogen atoms of the methine (H8 and H9) group were determined from a difference Fourier map and their positional parameters freely refined (C8—H8 = 0.96 (2)Å and C9—H9 = 1.01 (2) Å). The methyl H atoms were placed in geometrically idealized positions and constrained to ride on its parent atoms with U_{iso}(H) = 1.5U_{eq}(C) and at a distance of 0.96 Å.

Figures

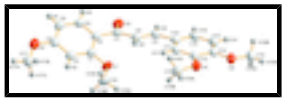


Fig. 1. Representation of the title compound, showing the numbering scheme and displacement ellipsoids (50% probability).

1-(2,4-dimethoxyphenyl)-3-(3,4-dimethoxyphenyl)prop-2-en-1-one

Crystal data

$C_{19}H_{20}O_5$	$F(000) = 696$
$M_r = 328.35$	$D_x = 1.293$ Mg m^{-3}
Monoclinic, $P2_1/c$	Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å
Hall symbol: -P 2ybc	Cell parameters from 7154 reflections
$a = 12.5839$ (7) Å	$\theta = 2.4$–$23.6°$
$b = 11.7204$ (7) Å	$\mu = 0.09$ mm^{-1}
$c = 12.1339$ (6) Å	$T = 100$ K
$\beta = 109.489$ (2)°	Plate, colourless
$V = 1687.07$ (16) Å^3	0.49 × 0.22 × 0.07 mm
$Z = 4$	

Data collection

Bruker APEXII diffractometer	2539 reflections with $I > 2\sigma(I)$
graphite	$R_{int} = 0.039$
phi and ω scans	$\theta_{max} = 28.4°$, $\theta_{min} = 1.7°$
Absorption correction: multi-scan (*SADABS*; Bruker, 2008)	$h = -16 \rightarrow 16$
$T_{min} = 0.976$, $T_{max} = 0.994$	$k = -15 \rightarrow 15$
32681 measured reflections	$l = -11 \rightarrow 16$
4205 independent reflections	

Refinement

Refinement on F^2	Primary atom site location: structure-invariant direct methods
Least-squares matrix: full	Secondary atom site location: difference Fourier map

$R[F^2 > 2\sigma(F^2)] = 0.044$	Hydrogen site location: inferred from neighbouring sites
$wR(F^2) = 0.188$	H atoms treated by a mixture of independent and constrained refinement
$S = 1.12$	$w = 1/[\sigma^2(F_o^2) + (0.0998P)^2 + 0.0628P]$ where $P = (F_o^2 + 2F_c^2)/3$
4205 reflections	$(\Delta/\sigma)_{max} = 0.001$
225 parameters	$\Delta\rho_{max} = 0.21$ e Å^{-3}
0 restraints	$\Delta\rho_{min} = -0.20$ e Å^{-3}

Special details

Geometry. All s.u.'s (except the s.u. in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell s.u.'s are taken into account individually in the estimation of s.u.'s in distances, angles and torsion angles; correlations between s.u.'s in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell s.u.'s is used for estimating s.u.'s involving l.s. planes.

Refinement. Refinement of F^2 against ALL reflections. The weighted *R*-factor *wR* and goodness of fit *S* are based on F^2, conventional *R*-factors *R* are based on *F*, with *F* set to zero for negative F^2. The threshold expression of $F^2 > 2\sigma(F^2)$ is used only for calculating *R*-factors(gt) *etc*. and is not relevant to the choice of reflections for refinement. *R*-factors based on F^2 are statistically about twice as large as those based on *F*, and *R*- factors based on ALL data will be even larger.

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å^2)

	x	*y*	*z*	U_{iso}*/U_{eq}
C1	0.57536 (15)	0.12721 (14)	0.10767 (13)	0.0572 (4)
C2	0.66866 (16)	0.07753 (15)	0.09002 (15)	0.0635 (5)
H2	0.7138	0.027	0.1449	0.076*
C3	0.69406 (17)	0.10359 (16)	−0.00938 (16)	0.0665 (5)
C4	0.62632 (18)	0.17787 (18)	−0.09154 (16)	0.0724 (5)
H4	0.6422	0.1941	−0.1594	0.087*
C5	0.53595 (17)	0.22720 (17)	−0.07222 (14)	0.0654 (5)
H5	0.4918	0.2781	−0.1274	0.079*
C6	0.50707 (15)	0.20426 (14)	0.02731 (13)	0.0555 (4)
C7	0.40909 (15)	0.26733 (15)	0.04011 (13)	0.0582 (4)
C8	0.33980 (16)	0.21568 (16)	0.10368 (15)	0.0603 (5)
C9	0.25176 (15)	0.26831 (16)	0.11757 (14)	0.0596 (5)
C10	0.18227 (14)	0.22631 (15)	0.18413 (14)	0.0570 (4)
C11	0.20392 (14)	0.12066 (15)	0.24240 (14)	0.0571 (4)
H11	0.2627	0.0756	0.2367	0.068*
C12	0.14066 (14)	0.08267 (15)	0.30728 (14)	0.0574 (4)
C13	0.05259 (14)	0.15026 (17)	0.31711 (15)	0.0614 (5)
C14	0.02979 (16)	0.25345 (18)	0.26000 (16)	0.0692 (5)
H14	−0.0292	0.2982	0.2656	0.083*
C15	0.09404 (16)	0.29117 (17)	0.19425 (16)	0.0676 (5)
H15	0.0777	0.3612	0.1563	0.081*
C16	0.60374 (18)	0.01862 (18)	0.28377 (17)	0.0782 (6)
H16A	0.5762	0.0164	0.3486	0.117*

H16B	0.6836	0.0318	0.312	0.117*
H16C	0.5882	−0.0529	0.2429	0.117*
C17	0.86153 (19)	−0.0100 (2)	0.0519 (2)	0.0954 (7)
H17A	0.9212	−0.0335	0.0241	0.143*
H17B	0.8224	−0.0761	0.0653	0.143*
H17C	0.8927	0.0315	0.1237	0.143*
C18	0.24973 (17)	−0.08614 (17)	0.36379 (18)	0.0710 (5)
H18A	0.2528	−0.1544	0.4085	0.107*
H18B	0.3184	−0.0439	0.3967	0.107*
H18C	0.2405	−0.1061	0.2844	0.107*
C19	−0.09188 (18)	0.1716 (2)	0.4026 (2)	0.0927 (7)
H19A	−0.1252	0.1302	0.451	0.139*
H19B	−0.1484	0.1879	0.3286	0.139*
H19C	−0.0607	0.2418	0.4403	0.139*
O1	0.54938 (13)	0.10796 (12)	0.20672 (10)	0.0780 (4)
O2	0.78452 (13)	0.06147 (14)	−0.03354 (13)	0.0874 (5)
O3	0.38578 (12)	0.36122 (11)	−0.00560 (11)	0.0767 (4)
O4	0.15725 (11)	−0.01826 (11)	0.36644 (12)	0.0717 (4)
O5	−0.00515 (11)	0.10484 (13)	0.38441 (12)	0.0785 (4)
H8	0.3591 (17)	0.1401 (19)	0.1332 (17)	0.075 (6)*
H9	0.2294 (16)	0.3460 (17)	0.0808 (16)	0.071 (5)*

Atomic displacement parameters (Å^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
C1	0.0751 (11)	0.0504 (9)	0.0446 (8)	−0.0050 (8)	0.0182 (8)	−0.0034 (7)
C2	0.0785 (12)	0.0527 (10)	0.0560 (9)	−0.0032 (9)	0.0180 (9)	−0.0043 (8)
C3	0.0762 (12)	0.0620 (12)	0.0645 (10)	−0.0128 (9)	0.0279 (9)	−0.0147 (9)
C4	0.0920 (14)	0.0757 (13)	0.0567 (10)	−0.0123 (11)	0.0342 (10)	−0.0027 (9)
C5	0.0802 (13)	0.0633 (11)	0.0498 (9)	−0.0111 (9)	0.0176 (8)	0.0044 (8)
C6	0.0685 (10)	0.0508 (9)	0.0431 (8)	−0.0099 (8)	0.0132 (7)	−0.0021 (7)
C7	0.0725 (11)	0.0511 (10)	0.0446 (8)	−0.0058 (8)	0.0110 (7)	0.0012 (7)
C8	0.0714 (12)	0.0497 (10)	0.0566 (9)	−0.0034 (9)	0.0171 (8)	0.0030 (8)
C9	0.0670 (11)	0.0513 (10)	0.0526 (9)	−0.0035 (9)	0.0094 (8)	−0.0001 (8)
C10	0.0586 (10)	0.0538 (10)	0.0518 (8)	−0.0006 (8)	0.0092 (7)	−0.0036 (7)
C11	0.0563 (9)	0.0538 (10)	0.0592 (9)	0.0007 (8)	0.0167 (8)	−0.0018 (8)
C12	0.0565 (10)	0.0527 (10)	0.0593 (9)	−0.0041 (8)	0.0143 (8)	−0.0027 (8)
C13	0.0541 (9)	0.0673 (12)	0.0610 (9)	−0.0043 (8)	0.0168 (8)	−0.0096 (9)
C14	0.0586 (11)	0.0715 (13)	0.0739 (11)	0.0105 (9)	0.0172 (9)	−0.0051 (10)
C15	0.0668 (11)	0.0596 (11)	0.0677 (11)	0.0070 (9)	0.0110 (9)	0.0027 (9)
C16	0.0932 (14)	0.0743 (13)	0.0629 (10)	0.0076 (11)	0.0204 (10)	0.0213 (10)
C17	0.0753 (14)	0.1100 (19)	0.0954 (16)	0.0027 (13)	0.0213 (12)	−0.0291 (14)
C18	0.0812 (13)	0.0533 (11)	0.0818 (12)	0.0052 (9)	0.0316 (10)	0.0076 (9)
C19	0.0673 (12)	0.125 (2)	0.0908 (14)	0.0056 (13)	0.0336 (11)	−0.0140 (14)
O1	0.1039 (10)	0.0834 (10)	0.0517 (7)	0.0266 (8)	0.0326 (7)	0.0199 (6)
O2	0.0914 (10)	0.0909 (11)	0.0904 (10)	−0.0003 (8)	0.0444 (8)	−0.0111 (8)
O3	0.0972 (10)	0.0607 (8)	0.0724 (8)	0.0086 (7)	0.0284 (7)	0.0193 (7)
O4	0.0769 (9)	0.0598 (8)	0.0869 (9)	0.0028 (6)	0.0385 (7)	0.0107 (6)

O5	0.0707 (8)	0.0858 (10)	0.0877 (9)	−0.0012 (7)	0.0378 (7)	−0.0051 (7)

Geometric parameters (Å, °)

C1—O1	1.3654 (19)	C12—C13	1.399 (2)
C1—C2	1.390 (3)	C13—O5	1.369 (2)
C1—C6	1.395 (2)	C13—C14	1.376 (3)
C2—C3	1.381 (3)	C14—C15	1.384 (3)
C2—H2	0.93	C14—H14	0.93
C3—O2	1.359 (2)	C15—H15	0.93
C3—C4	1.382 (3)	C16—O1	1.418 (2)
C4—C5	1.364 (3)	C16—H16A	0.96
C4—H4	0.93	C16—H16B	0.96
C5—C6	1.398 (2)	C16—H16C	0.96
C5—H5	0.93	C17—O2	1.430 (3)
C6—C7	1.489 (3)	C17—H17A	0.96
C7—O3	1.223 (2)	C17—H17B	0.96
C7—C8	1.473 (3)	C17—H17C	0.96
C8—C9	1.327 (3)	C18—O4	1.419 (2)
C8—H8	0.96 (2)	C18—H18A	0.96
C9—C10	1.460 (3)	C18—H18B	0.96
C9—H9	1.01 (2)	C18—H18C	0.96
C10—C15	1.384 (3)	C19—O5	1.418 (3)
C10—C11	1.407 (2)	C19—H19A	0.96
C11—C12	1.367 (2)	C19—H19B	0.96
C11—H11	0.93	C19—H19C	0.96
C12—O4	1.363 (2)		
O1—C1—C2	121.95 (15)	O5—C13—C12	115.08 (17)
O1—C1—C6	116.73 (16)	C14—C13—C12	119.51 (17)
C2—C1—C6	121.24 (15)	C13—C14—C15	120.49 (17)
C3—C2—C1	119.70 (17)	C13—C14—H14	119.8
C3—C2—H2	120.1	C15—C14—H14	119.8
C1—C2—H2	120.1	C14—C15—C10	121.04 (18)
O2—C3—C2	124.22 (19)	C14—C15—H15	119.5
O2—C3—C4	115.62 (17)	C10—C15—H15	119.5
C2—C3—C4	120.16 (18)	O1—C16—H16A	109.5
C5—C4—C3	119.46 (17)	O1—C16—H16B	109.5
C5—C4—H4	120.3	H16A—C16—H16B	109.5
C3—C4—H4	120.3	O1—C16—H16C	109.5
C4—C5—C6	122.60 (18)	H16A—C16—H16C	109.5
C4—C5—H5	118.7	H16B—C16—H16C	109.5
C6—C5—H5	118.7	O2—C17—H17A	109.5
C1—C6—C5	116.82 (17)	O2—C17—H17B	109.5
C1—C6—C7	125.93 (15)	H17A—C17—H17B	109.5
C5—C6—C7	117.21 (15)	O2—C17—H17C	109.5
O3—C7—C8	120.85 (17)	H17A—C17—H17C	109.5
O3—C7—C6	118.74 (16)	H17B—C17—H17C	109.5
C8—C7—C6	120.39 (15)	O4—C18—H18A	109.5
C9—C8—C7	122.73 (18)	O4—C18—H18B	109.5

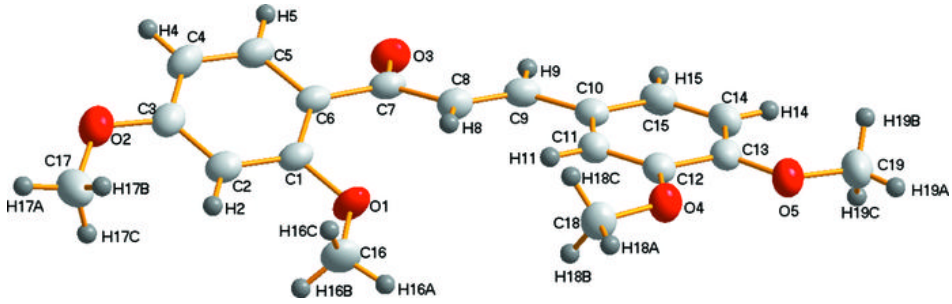
C9—C8—H8	120.1 (12)	H18A—C18—H18B	109.5
C7—C8—H8	117.1 (12)	O4—C18—H18C	109.5
C8—C9—C10	126.39 (18)	H18A—C18—H18C	109.5
C8—C9—H9	118.9 (11)	H18B—C18—H18C	109.5
C10—C9—H9	114.7 (11)	O5—C19—H19A	109.5
C15—C10—C11	117.73 (17)	O5—C19—H19B	109.5
C15—C10—C9	120.67 (17)	H19A—C19—H19B	109.5
C11—C10—C9	121.57 (16)	O5—C19—H19C	109.5
C12—C11—C10	121.57 (16)	H19A—C19—H19C	109.5
C12—C11—H11	119.2	H19B—C19—H19C	109.5
C10—C11—H11	119.2	C1—O1—C16	119.85 (15)
O4—C12—C11	124.71 (16)	C3—O2—C17	118.05 (17)
O4—C12—C13	115.65 (15)	C12—O4—C18	117.21 (14)
C11—C12—C13	119.64 (17)	C13—O5—C19	117.86 (18)
O5—C13—C14	125.41 (17)		
O1—C1—C2—C3	−177.22 (16)	C15—C10—C11—C12	−0.2 (2)
C6—C1—C2—C3	−0.7 (3)	C9—C10—C11—C12	178.26 (15)
C1—C2—C3—O2	178.59 (16)	C10—C11—C12—O4	−179.63 (15)
C1—C2—C3—C4	−0.7 (3)	C10—C11—C12—C13	−0.4 (2)
O2—C3—C4—C5	−177.74 (17)	O4—C12—C13—O5	−0.4 (2)
C2—C3—C4—C5	1.6 (3)	C11—C12—C13—O5	−179.68 (14)
C3—C4—C5—C6	−1.2 (3)	O4—C12—C13—C14	−179.86 (15)
O1—C1—C6—C5	177.78 (15)	C11—C12—C13—C14	0.9 (3)
C2—C1—C6—C5	1.1 (2)	O5—C13—C14—C15	179.90 (17)
O1—C1—C6—C7	0.2 (2)	C12—C13—C14—C15	−0.7 (3)
C2—C1—C6—C7	−176.47 (15)	C13—C14—C15—C10	0.1 (3)
C4—C5—C6—C1	−0.2 (3)	C11—C10—C15—C14	0.3 (3)
C4—C5—C6—C7	177.62 (16)	C9—C10—C15—C14	−178.11 (16)
C1—C6—C7—O3	150.16 (17)	C2—C1—O1—C16	−12.8 (3)
C5—C6—C7—O3	−27.4 (2)	C6—C1—O1—C16	170.51 (17)
C1—C6—C7—C8	−31.7 (2)	C2—C3—O2—C17	−3.2 (3)
C5—C6—C7—C8	150.79 (16)	C4—C3—O2—C17	176.09 (18)
O3—C7—C8—C9	−1.9 (3)	C11—C12—O4—C18	2.6 (2)
C6—C7—C8—C9	179.96 (15)	C13—C12—O4—C18	−176.60 (15)
C7—C8—C9—C10	−176.58 (15)	C14—C13—O5—C19	−3.6 (3)
C8—C9—C10—C15	178.36 (17)	C12—C13—O5—C19	176.98 (16)
C8—C9—C10—C11	0.0 (3)		

Hydrogen-bond geometry (Å, °)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
C8—H8···O1	0.96 (2)	2.29 (2)	2.813 (3)	113.6 (15)
C18—H18B···O3^{i}	0.96	2.46	3.253 (3)	140

Symmetry codes: (i) *x*, −*y*+1/2, *z*+1/2.

Fig. 1


H5
H4
C4
C5
O3
C8
H9
C10
H15
C14
H14
H19B
C3
C6
C7
C9
C15
O2
H8
C11
H11
C13
C19
C17
H18C
C12
H19A
H17B
C2
C1
O1
O4
O5
H17A
H2
H16C
C18
H19C
H17C
C16
H18A
H18B
H16B
H16A

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μ_3-Oxido-tris{dichlorido[1,3-bis(1,3,5-trimethylphenyl)imidazol-2-ylidene]-gold(III)} bis(trifluoromethanesulfonyl)imide–[bis(trifluoromethanesulfonyl)imide]silver(I) (1/2)

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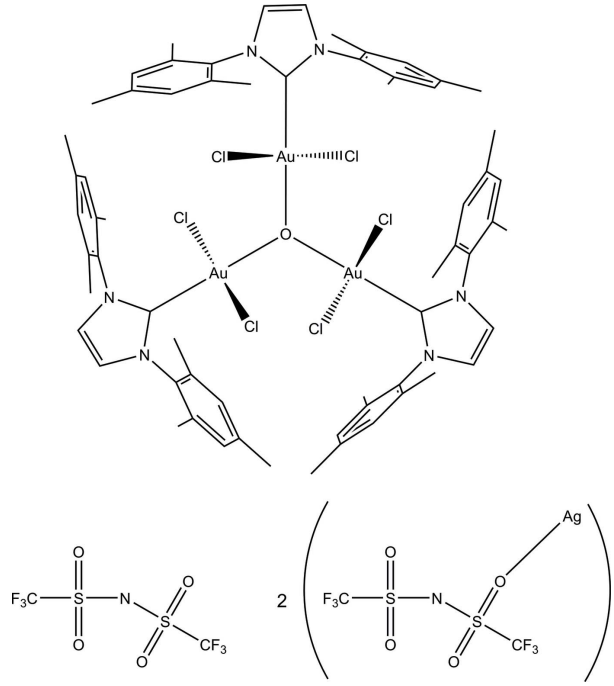
Key indicators: single-crystal X-ray study; T = 200 K; mean σ(C–C) = 0.015 Å; disorder in main residue; R factor = 0.050; wR factor = 0.094; data-to-parameter ratio = 19.1.

The unusual trinuclear Au^{III} oxide title complex, $[Au_3Cl_6O(C_{21}H_{24}N_2)_3](C_2F_6NO_4S_2)\cdot 2[Ag(C_2F_6NO_4S_2)]$, is the side product of the reaction of [1,3-bis(1,3,5-trimethylphenyl)-imidazol-2-ylidene]dichloridophenylgold(III) with silver bis(trifluoromethanesulfonyl)imide in the presence of traces of water. In contrast to corresponding Au^{I} complexes, the core structure of the title compound is planar. Two silver(I) bis(trifluoromethanesulfonyl)imide units are loosely bound to the complex cation. Here the silver atoms, disordered over two positions in a 0.870 (2):0.130 (2) ratio, interact either with the lone pairs of three chlorine ligands or two chlorine ligands and one edge of the mesityl π-system. The crystal under investigation was a partial racemic twin.

Related literature

Tris[(phosphane)gold(I)]oxonium ions are a convenient source for (phosphane)gold cations see: Nesmeyanov *et al.* (1980). For the trigonal-pyramidal structure of these trinuclear complexes, see, for example: Yang *et al.* (1993); Schmidbaur *et al.* (1993); Angermaier & Schmidbaur (1994, 1995). For the silver coordination of the bis(trifluoromethanesulfonyl)imide anion *via* oxygen, see: Nockemann *et al.* (2008). For details of the preparation, see: Pažický *et al.* (2010).



Experimental

Crystal data

$[Au_3Cl_6O(C_{21}H_{24}N_2)_3](C_2F_6NO_4S_2)\cdot 2[Ag(C_2F_6NO_4S_2)]$
M_r = 2789.06
Tetragonal, $P4_32_12$
a = 13.9472 (9) Å
c = 45.724 (3) Å
V = 8894.5 (10) Å^3
Z = 4
Mo $K\alpha$ radiation
μ = 5.79 mm^{-1}
T = 200 K
0.25 × 0.17 × 0.11 mm

Data collection

Bruker SMART APEX diffractometer
Absorption correction: multi-scan (*SADABS*; Sheldrick, 2008*a*)
T_{min} = 0.326, T_{max} = 0.569
93947 measured reflections
11087 independent reflections
10564 reflections with $I > 2\sigma(I)$
R_{int} = 0.068

Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.050
$wR(F^2)$ = 0.094
S = 1.27
11087 reflections
581 parameters
12 restraints
H-atom parameters constrained
$\Delta\rho_{max}$ = 1.65 e Å^{-3}
$\Delta\rho_{min}$ = −1.45 e Å^{-3}
Absolute structure: Flack (1983), 4737 Friedel pairs
Flack parameter: 0.396 (7)

Data collection: *SMART* (Bruker, 2001); cell refinement: *SAINT* (Bruker, 2001); data reduction: *SAINT*; program(s) used to solve structure: *SHELXTL* (Sheldrick, 2008*b*); program(s) used to refine structure: *SHELXTL*; molecular graphics: *SHELXTL*; software used to prepare material for publication: *SHELXTL*.

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Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: HG2690).

References

Angermaier, K. & Schmidbaur, H. (1994). *Inorg. Chem.* **33**, 2069–2070.
Angermaier, K. & Schmidbaur, H. (1995). *Acta Cryst.* C**51**, 1793–1795.
Bruker (2001). *SAINT* and *SMART*. Bruker AXS Inc., Madison, Wisconsin, USA.
Flack, H. D. (1983). *Acta Cryst.* A**39**, 876–881.
Nesmeyanov, A. N., Perevalova, E. G., Struchkov, Y. T., Antipin, M. Y., Grandberg, K. I. & Dyadchenko, V. P. (1980). *J. Organomet. Chem.* **201**, 343–351.
Nockemann, P., Thijs, B., Van Hecke, K., Van Meervelt, L. & Binnemans, K. (2008). *Cryst. Growth Des.* **8**, 1353–1363.
Pažický, M., Loos, A., Ferreira, M. J., Rominger, F., Jäkel, C., Hashmi, A. S. K. & Limbach, M. (2010). Personal communication.
Schmidbaur, H., Kolb, A., Zeller, E., Schier, A. & Beruda, H. (1993). *Z. Anorg. Allg. Chem.* **619**, 1575–1581.
Sheldrick, G. M. (2008*a*). *SADABS*. University of Göttingen, Germany.
Sheldrick, G. M. (2008*b*). *Acta Cryst.* A**64**, 112–122.
Yang, Y., Ramamoorthy, V. & Sharp, P. R. (1993). *Inorg. Chem.* **32**, 1946–1951.

supplementary materials

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μ_3-Oxido-tris{dichlorido[1,3-bis(1,3,5-trimethylphenyl)imidazol-2-ylidene]gold(III)} bis(trifluoromethanesulfonyl)imide-[bis(trifluoromethanesulfonyl)imide]silver(I) (1/2)

M. Pazický, F. Rominger and M. Limbach

Comment

The structure of the title compound consists of a trinuclear complex cation around a central oxygen atom with a trigonal planar Au^{III} environment. Loosley bound to this cation are two silver bis(trifluoromethanesulfonyl)imide moieties with a twofold disordered silver position. Finally there is another free bis(trifluoromethanesulfonyl)imide anion to compensate the charge of the cation. Although tris[(phosphane)gold(I)]oxonium ions are a well known source for LAu+ as shown by Nesmeyanov *et al.* (1980), to the best of our knowledge there have been no reports on trimeric $[Au_3O]^+$ complexes with N-heterocyclic carbenes or generally $[Au^{III}O]^+$ complexes in the literature before.

Both, the trinuclear cation and the free imide anion reside at a special position on a crystallographic twofold axis. The non-crystallographic symmetry of the cation is D_3. Thus, in contrast to corresponding $[(LAu^I)_3O]^+$ complexes with pyramidal geometry (*e.g.* Yang *et al.*, 1993; Schmidbaur *et al.*, 1993; Angermaier & Schmidbaur, 1994, 1995), the structure of the $Au^{III}{}_3O$ core of the title compound is flat. Therefore the Au···Au distances are with 3.4655 (5) and 3.5688 (6) Å necessarily much longer than in the Au^I complexes and we assume no aurophilic interactions. The Au—O distances amount to 2.046 (7) and 2.010 (3) Å, the Au—C_{NHC} distances to 2.018 (12) and 1.982 (7) Å. The Cl—Au—Cl axes are inclined with respect to the Au_3O plane by about 37.0° and 42.0°, which leads to a octahedral chlorine environment for the central oxygen atom with Cl···O distances between 2.986 (5) and 2.996 (5) Å, which is clearly below the van der Waals distance (3.27 Å). As already mentioned two $Ag[N(SO_2CF_3)_2]$ units are loosley bound to this cation. Remarkably there are two alternative positions for the silver center which are occupied by 87% and 13% resp. At the main position the silver is in contact with three chlorine atoms of the cation (Ag···Cl between 2.644 (2) and 2.769 (3) Å), at the alternative position among two chlorine atoms (Ag···Cl 2.302 (8) and 2.754 (8) Å) the silver contacts one edge of the mesityl π-system (Ag···C 2.544 (12) and 2.587 (13) Å). The distorted tetrahedral environment of the silver centers is completed in both cases remarkably with an oxygen atom of the bis(trifluoromethanesulfonyl)imide anion (Ag···O 2.340 (7) and 2.342 (10) Å) rather than the nitrogen. This unexpected coordination mode of the bis(trifluoromethanesulfonyl)imide anion has been observed before by Nockemann *et al.* (2008).

Experimental

To a solution of phenyldichloro-1,3-bis(1,3,5-trimethylphenyl)imidazol-2-ylidene gold(III) (20 mg, 30.8 µmol) in dry d2-dichloromethane, as described by Pažický *et al.* (2010), silver bis(trifluoromethanesulfonyl)imide (12 mg, 30.8 µmol) was added at room temperature. The solution was stirred for five minutes and filtered over celite. Yellow crystals of the title compound besides white crystals of dichloro-1,3-bis(1,3,5-trimethylphenyl)imidazol-2-ylidene gold(III) bis(trifluoromethanesulfonyl)imide were obtained by slow diffusion of the concentrated filtrate of the crude product into pentane at 8 °C.

Refinement

Rigid bond restraints were applied to the U^{ij} values of the nitrogen atom N2 and its surrounding carbon atoms C1, C3, and C11 as well as an isotropic restraint (ISOR) to N2. These prevents atom N2 from going non positive definite. The rest of the adps of the structure was not restrained, as these looked rather reasonable. We can give no convincing explanation for the unsatisfying behavior of N2 and its environment. But in return there is also no plausible possibilty for misinterpretation or atom misassignment here. Obviously the data just results in unrealistic adps in this part of the structure for some reason.

Hydrogen atoms were placed in calculated positions (C–H 0.95– 0.98 Å) and were included in the refinement in the riding model approximation with U_{iso}(H) set to 1.2–1.5 U_{eq}(C). A model with staggered conformation with respect to the closest substituent was used for the phenyl-bound methyl groups, which may lead to some ambiguity.

The nature of the disordered silver atom was not clear at first. There were several reasons that led us to the present interpretation. First of all silver bis(trifluoromethanesulfonyl)imide was present in the solution as the only species with an electrophilic atom besides of gold. Furthermore the coordination behaviour to the aromatic π-system and/or to the chlorine ligands as well as to the anion fits fine to the well known geometry of other silver complexes. And finally the refinement of a model with two alternative and partially occupied silver positions converged very well with completely reasonable occupation and displacement parameters.

The refinement of the Flack parameter (Flack, 1983) resulted in a value of 0.396 (7), indicating partial racemic twinning of the crystal.

Figures

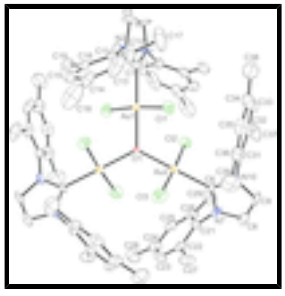


Fig. 1. Thermal ellipsoid representation of the trinuclear oxo cation of the title compound. Displacement ellipsoids were plotted at 50% probability level. Hydrogen atoms, the anion and the silver moiety are omitted for the sake of clarity.

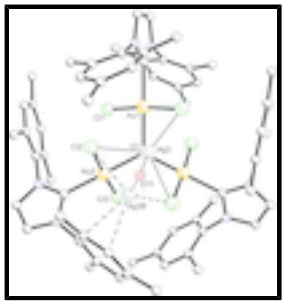


Fig. 2. Both alternative silver positions (87% Ag3:13% Ag3B) and their coordination modes to the trinuclear oxo cation in a simple ball and stick representation. From the bis(trifluoromethanesulfonyl)imide anion coordinated to the silver only the coordinating oxygen atom (O11) is shown for clarity. Due to the 2-fold symmetry the same pattern is found at the reverse side of the cation, which is omitted for the sake of clarity as well.

μ3-Oxido-tris{dichlorido[1,3-bis(1,3,5-trimethylphenyl)imidazol-2-\ ylidene]gold(III)} bis(trifluoromethanesulfonyl)imide–\ [bis(trifluoromethanesulfonyl)imide]silver(I) (1/2)

Crystal data

$[Au_3Cl_6O(C_{21}H_{24}N_2)_3](C_2F_6NO_4S_2)\cdot[Ag(C_2F_6NO_4S_2)_2]$	D_x = 2.083 Mg m^{-3}
M_r = 2789.06	Mo $K\alpha$ radiation, λ = 0.71073 Å
Tetragonal, $P4_32_12$	Cell parameters from 7947 reflections
Hall symbol: P 4nw 2abw	θ = 2.3–26.5°
a = 13.9472 (9) Å	μ = 5.79 mm^{-1}
c = 45.724 (3) Å	T = 200 K
V = 8894.5 (10) Å^3	Polyhedron, orange
Z = 4	0.25 × 0.17 × 0.11 mm
F(000) = 5376	

Data collection

Bruker SMART APEX diffractometer	11087 independent reflections
Radiation source: fine-focus sealed tube	10564 reflections with $I > 2\sigma(I)$
graphite	R_{int} = 0.068
ω scans	θ_{max} = 28.3°, θ_{min} = 2.0°
Absorption correction: multi-scan (*SADABS*; Sheldrick, 2008a)	h = −18→18
T_{min} = 0.326, T_{max} = 0.569	k = −18→18
93947 measured reflections	l = −61→59

Refinement

Refinement on F^2	Secondary atom site location: difference Fourier map
Least-squares matrix: full	Hydrogen site location: inferred from neighbouring sites
$R[F^2 > 2\sigma(F^2)]$ = 0.050	H-atom parameters constrained
$wR(F^2)$ = 0.094	$w = 1/[\sigma^2(F_o^2) + (0.0179P)^2 + 57.4255P]$ where $P = (F_o^2 + 2F_c^2)/3$
S = 1.27	$(\Delta/\sigma)_{max}$ = 0.001
11087 reflections	$\Delta\rho_{max}$ = 1.65 e Å^{-3}
581 parameters	$\Delta\rho_{min}$ = −1.45 e Å^{-3}
12 restraints	Absolute structure: Flack (1983), 4737 Friedel pairs
Primary atom site location: structure-invariant direct methods	Flack parameter: 0.396 (7)

Special details

Geometry. All e.s.d.'s (except the e.s.d. in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell e.s.d.'s are taken into account individually in the estimation of e.s.d.'s in distances, angles and torsion angles; correlations

between e.s.d.'s in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell e.s.d.'s is used for estimating e.s.d.'s involving l.s. planes.

Refinement. Refinement of F^2 against ALL reflections. The weighted *R*-factor *wR* and goodness of fit *S* are based on F^2, conventional *R*-factors *R* are based on *F*, with *F* set to zero for negative F^2. The threshold expression of $F^2 > \sigma(F^2)$ is used only for calculating *R*-factors(gt) *etc*. and is not relevant to the choice of reflections for refinement. *R*-factors based on F^2 are statistically about twice as large as those based on *F*, and *R*- factors based on ALL data will be even larger.

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å^2)

	x	*y*	*z*	U_{iso}*/U_{eq}	Occ. (<1)
Au1	0.47994 (2)	0.47994 (2)	0.0000	0.01855 (9)	
Cl1	0.49234 (17)	0.47738 (18)	0.04966 (4)	0.0362 (5)	
Au2	0.56741 (2)	0.69371 (2)	0.027945 (7)	0.01900 (7)	
Cl2	0.41769 (15)	0.71618 (17)	0.00937 (5)	0.0337 (5)	
Cl3	0.71719 (17)	0.6628 (2)	0.04497 (7)	0.0477 (7)	
O1	0.5837 (3)	0.5837 (3)	0.0000	0.0284 (19)	
Ag3	0.46707 (8)	0.68405 (8)	−0.04559 (2)	0.0536 (3)	0.870 (2)
Ag3B	0.5271 (5)	0.8028 (6)	−0.03324 (15)	0.058 (2)	0.130 (2)
C1	0.3776 (6)	0.3776 (6)	0.0000	0.037 (3)	
N2	0.3920 (5)	0.2874 (5)	0.00768 (19)	0.037 (2)	
C3	0.3046 (7)	0.2407 (7)	0.0040 (3)	0.062 (4)	
H3	0.2933	0.1741	0.0067	0.074*	
C6	0.5503 (6)	0.8017 (6)	0.05561 (17)	0.0222 (16)	
N7	0.5764 (6)	0.8943 (5)	0.05029 (17)	0.0308 (17)	
C8	0.5536 (8)	0.9498 (7)	0.0742 (2)	0.044 (3)	
H8	0.5645	1.0166	0.0763	0.053*	
C9	0.5128 (9)	0.8909 (7)	0.0937 (2)	0.047 (3)	
H9	0.4893	0.9089	0.1124	0.056*	
N10	0.5109 (6)	0.8000 (5)	0.08202 (15)	0.0286 (16)	
C11	0.4835 (7)	0.2484 (6)	0.0171 (2)	0.0332 (19)	
C12	0.4957 (11)	0.2391 (7)	0.0473 (2)	0.058 (4)	
C13	0.5888 (12)	0.2127 (7)	0.0558 (2)	0.062 (4)	
H13	0.6021	0.2046	0.0760	0.075*	
C14	0.6622 (9)	0.1978 (7)	0.0358 (2)	0.045 (3)	
C15	0.6394 (8)	0.1980 (7)	0.0071 (2)	0.037 (2)	
H15	0.6862	0.1773	−0.0066	0.045*	
C16	0.5505 (7)	0.2271 (6)	−0.0033 (2)	0.033 (2)	
C17	0.4194 (14)	0.2516 (10)	0.0696 (3)	0.101 (7)	
H17A	0.3590	0.2686	0.0599	0.152*	
H17B	0.4377	0.3029	0.0832	0.152*	
H17C	0.4110	0.1917	0.0805	0.152*	
C18	0.7632 (11)	0.1742 (9)	0.0464 (3)	0.074 (5)	
H18A	0.8061	0.1674	0.0296	0.112*	
H18B	0.7620	0.1140	0.0575	0.112*	
H18C	0.7864	0.2260	0.0591	0.112*	
C19	0.5314 (7)	0.2320 (7)	−0.0354 (2)	0.037 (2)	
H19A	0.5889	0.2121	−0.0461	0.056*	
H19B	0.5147	0.2978	−0.0409	0.056*	

H19C	0.4781	0.1891	−0.0404	0.056*
C21	0.6180 (6)	0.9258 (6)	0.02272 (19)	0.0237 (17)
C22	0.7164 (7)	0.9273 (6)	0.0204 (2)	0.032 (2)
C23	0.7551 (6)	0.9507 (7)	−0.0071 (2)	0.035 (2)
H23	0.8228	0.9537	−0.0094	0.042*
C24	0.6973 (7)	0.9695 (7)	−0.0308 (2)	0.036 (2)
C25	0.5982 (7)	0.9694 (6)	−0.0267 (2)	0.037 (2)
H25	0.5579	0.9835	−0.0429	0.044*
C26	0.5560 (6)	0.9495 (6)	0.0003 (2)	0.0314 (19)
C27	0.7821 (7)	0.9102 (8)	0.0458 (2)	0.043 (2)
H27A	0.8488	0.9161	0.0394	0.064*
H27B	0.7712	0.8456	0.0536	0.064*
H27C	0.7691	0.9577	0.0611	0.064*
C28	0.7370 (8)	0.9888 (8)	−0.0611 (2)	0.049 (3)
H28A	0.6840	1.0019	−0.0746	0.073*
H28B	0.7727	0.9325	−0.0679	0.073*
H28C	0.7799	1.0444	−0.0604	0.073*
C29	0.4533 (8)	0.9624 (8)	0.0046 (3)	0.052 (3)
H29A	0.4227	0.9762	−0.0143	0.078*
H29B	0.4423	1.0160	0.0180	0.078*
H29C	0.4258	0.9037	0.0129	0.078*
C31	0.4692 (7)	0.7163 (6)	0.09582 (18)	0.0275 (18)
C32	0.3718 (7)	0.6983 (8)	0.0923 (2)	0.036 (2)
C33	0.3346 (8)	0.6165 (8)	0.1046 (2)	0.044 (3)
H33	0.2683	0.6029	0.1023	0.053*
C34	0.3913 (8)	0.5534 (8)	0.1202 (2)	0.044 (3)
C35	0.4871 (8)	0.5756 (7)	0.1245 (2)	0.040 (2)
H35	0.5254	0.5342	0.1362	0.049*
C36	0.5283 (8)	0.6565 (7)	0.11232 (18)	0.037 (2)
C37	0.3100 (8)	0.7712 (9)	0.0770 (3)	0.054 (3)
H37A	0.3500	0.8245	0.0702	0.082*
H37B	0.2615	0.7954	0.0906	0.082*
H37C	0.2783	0.7412	0.0602	0.082*
C38	0.3493 (11)	0.4622 (9)	0.1320 (3)	0.064 (4)
H38A	0.3986	0.4271	0.1429	0.096*
H38B	0.3264	0.4226	0.1157	0.096*
H38C	0.2956	0.4773	0.1450	0.096*
C39	0.6317 (8)	0.6810 (10)	0.1185 (2)	0.058 (3)
H39A	0.6606	0.6304	0.1305	0.087*
H39B	0.6350	0.7421	0.1290	0.087*
H39C	0.6668	0.6865	0.1000	0.087*
N11	0.3867 (6)	0.9291 (7)	−0.11355 (19)	0.041 (2)
S1	0.44103 (18)	0.84305 (18)	−0.09968 (5)	0.0356 (5)
O11	0.4141 (6)	0.8202 (6)	−0.07076 (16)	0.054 (2)
O12	0.5421 (5)	0.8391 (6)	−0.10565 (19)	0.056 (2)
C41	0.3857 (10)	0.7501 (9)	−0.1216 (3)	0.050 (3)
F1	0.4146 (7)	0.6650 (5)	−0.11142 (19)	0.086 (3)
F2	0.2925 (6)	0.7518 (5)	−0.12012 (18)	0.070 (2)
F3	0.4097 (7)	0.7548 (6)	−0.14891 (17)	0.085 (3)

S2	0.40339 (16)	1.03734 (17)	−0.10456 (5)	0.0305 (5)
O21	0.4876 (5)	1.0540 (6)	−0.08791 (16)	0.0469 (18)
O22	0.3869 (6)	1.0968 (5)	−0.12919 (14)	0.0466 (19)
C42	0.3037 (8)	1.0632 (9)	−0.0801 (2)	0.046 (3)
F4	0.3092 (6)	1.0118 (6)	−0.05641 (14)	0.085 (3)
F5	0.2218 (5)	1.0482 (6)	−0.09288 (16)	0.067 (2)
F6	0.3077 (6)	1.1556 (6)	−0.07284 (16)	0.072 (2)
N31	0.0200 (6)	0.0200 (6)	0.0000	0.036 (2)
S3	0.07670 (17)	0.04173 (16)	0.02944 (5)	0.0366 (5)
O31	0.1221 (6)	0.1333 (5)	0.03190 (16)	0.0480 (18)
O32	0.0217 (6)	0.0065 (6)	0.05325 (16)	0.059 (2)
C43	0.1783 (9)	−0.0397 (9)	0.0274 (3)	0.060 (3)
F7	0.2316 (7)	−0.0298 (7)	0.0511 (2)	0.107 (3)
F8	0.2302 (5)	−0.0250 (6)	0.00419 (18)	0.078 (2)
F9	0.1494 (6)	−0.1304 (5)	0.0266 (2)	0.078 (2)

Atomic displacement parameters (Å^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Au1	0.01652 (12)	0.01652 (12)	0.02262 (19)	−0.00444 (16)	0.00103 (12)	−0.00103 (12)
Cl1	0.0411 (13)	0.0417 (12)	0.0257 (9)	−0.0049 (10)	0.0032 (9)	0.0017 (9)
Au2	0.01676 (14)	0.01689 (14)	0.02334 (13)	−0.00161 (11)	0.00300 (12)	−0.00450 (12)
Cl2	0.0203 (10)	0.0392 (13)	0.0416 (12)	0.0038 (8)	−0.0038 (9)	−0.0035 (9)
Cl3	0.0249 (12)	0.0474 (15)	0.0707 (18)	0.0065 (10)	−0.0177 (12)	−0.0156 (13)
O1	0.022 (3)	0.022 (3)	0.042 (5)	−0.015 (3)	0.019 (3)	−0.019 (3)
Ag3	0.0658 (7)	0.0547 (6)	0.0404 (5)	0.0226 (5)	−0.0012 (5)	0.0145 (5)
Ag3B	0.045 (4)	0.078 (5)	0.051 (4)	0.016 (4)	0.004 (3)	0.012 (4)
C1	0.023 (3)	0.023 (3)	0.064 (9)	−0.009 (4)	0.007 (4)	−0.007 (4)
N2	0.026 (3)	0.022 (4)	0.065 (5)	−0.021 (3)	0.014 (3)	0.002 (3)
C3	0.013 (4)	0.032 (5)	0.141 (12)	−0.013 (4)	0.020 (6)	−0.013 (7)
C6	0.026 (4)	0.015 (4)	0.026 (4)	0.004 (3)	−0.001 (3)	−0.010 (3)
N7	0.044 (5)	0.012 (3)	0.036 (4)	−0.008 (3)	0.008 (4)	−0.006 (3)
C8	0.058 (7)	0.023 (5)	0.052 (6)	−0.002 (4)	0.018 (5)	−0.016 (4)
C9	0.070 (8)	0.027 (5)	0.044 (6)	−0.005 (5)	0.023 (6)	−0.024 (4)
N10	0.040 (4)	0.019 (3)	0.027 (3)	0.004 (3)	0.006 (3)	−0.008 (3)
C11	0.045 (5)	0.012 (4)	0.042 (5)	−0.003 (3)	0.024 (4)	0.000 (3)
C12	0.112 (11)	0.021 (5)	0.043 (6)	0.019 (6)	0.044 (7)	0.012 (4)
C13	0.137 (13)	0.014 (5)	0.036 (6)	0.018 (6)	0.005 (7)	0.011 (4)
C14	0.072 (8)	0.015 (4)	0.048 (6)	0.011 (5)	−0.009 (5)	0.001 (4)
C15	0.053 (6)	0.025 (5)	0.033 (5)	−0.010 (5)	0.003 (4)	0.007 (4)
C16	0.047 (6)	0.015 (4)	0.037 (5)	−0.007 (4)	0.010 (4)	−0.001 (4)
C17	0.167 (17)	0.055 (9)	0.081 (10)	0.026 (10)	0.090 (11)	0.022 (7)
C18	0.108 (12)	0.050 (8)	0.065 (8)	0.033 (8)	−0.039 (8)	−0.005 (6)
C19	0.035 (5)	0.027 (5)	0.050 (6)	0.001 (4)	−0.007 (4)	−0.009 (4)
C21	0.018 (4)	0.018 (4)	0.035 (5)	0.005 (3)	0.002 (3)	0.001 (4)
C22	0.039 (5)	0.016 (4)	0.042 (5)	−0.001 (4)	−0.003 (4)	−0.006 (4)
C23	0.019 (4)	0.036 (5)	0.050 (6)	−0.003 (4)	0.003 (4)	0.008 (4)
C24	0.040 (5)	0.029 (5)	0.039 (5)	−0.005 (4)	−0.002 (4)	0.007 (4)

C25	0.044 (6)	0.020 (4)	0.045 (5)	−0.004 (4)	−0.009 (5)	−0.002 (4)
C26	0.026 (4)	0.021 (4)	0.047 (5)	−0.006 (3)	−0.010 (4)	0.001 (4)
C27	0.034 (6)	0.048 (7)	0.046 (6)	−0.012 (4)	−0.010 (5)	0.001 (5)
C28	0.052 (7)	0.046 (7)	0.048 (6)	−0.001 (5)	0.005 (5)	0.019 (5)
C29	0.043 (6)	0.052 (7)	0.062 (7)	0.019 (5)	0.004 (5)	0.014 (6)
C31	0.036 (5)	0.025 (4)	0.022 (4)	0.003 (4)	0.007 (4)	−0.004 (3)
C32	0.030 (5)	0.048 (6)	0.029 (5)	0.014 (4)	0.002 (4)	−0.006 (4)
C33	0.035 (6)	0.066 (8)	0.030 (5)	0.004 (5)	0.014 (4)	0.004 (5)
C34	0.052 (7)	0.051 (7)	0.029 (5)	−0.001 (5)	0.006 (4)	0.000 (4)
C35	0.054 (6)	0.040 (5)	0.027 (5)	0.015 (5)	−0.006 (4)	0.002 (4)
C36	0.049 (6)	0.046 (6)	0.017 (4)	0.002 (5)	−0.001 (4)	−0.003 (4)
C37	0.042 (6)	0.062 (8)	0.060 (7)	0.022 (6)	0.017 (6)	0.007 (6)
C38	0.102 (11)	0.042 (7)	0.047 (7)	−0.006 (7)	0.019 (7)	0.006 (5)
C39	0.053 (7)	0.083 (10)	0.039 (6)	−0.012 (7)	−0.018 (5)	0.004 (6)
N11	0.045 (5)	0.035 (5)	0.044 (5)	0.008 (4)	−0.012 (4)	0.000 (4)
S1	0.0315 (12)	0.0343 (12)	0.0409 (13)	0.0072 (10)	−0.0020 (10)	0.0067 (10)
O11	0.061 (5)	0.056 (5)	0.045 (4)	0.016 (4)	0.000 (4)	0.016 (4)
O12	0.033 (4)	0.058 (5)	0.077 (6)	0.018 (4)	0.009 (4)	0.019 (4)
C41	0.059 (8)	0.043 (7)	0.048 (7)	0.008 (6)	−0.012 (6)	−0.001 (5)
F1	0.116 (7)	0.032 (4)	0.109 (6)	0.016 (4)	−0.023 (6)	0.002 (4)
F2	0.062 (5)	0.058 (5)	0.091 (6)	−0.010 (4)	−0.016 (4)	−0.006 (4)
F3	0.115 (8)	0.086 (6)	0.055 (5)	0.019 (5)	0.004 (5)	−0.017 (4)
S2	0.0290 (11)	0.0361 (13)	0.0264 (11)	0.0080 (9)	0.0001 (9)	0.0017 (9)
O21	0.034 (4)	0.055 (5)	0.052 (4)	0.007 (4)	−0.014 (3)	−0.002 (4)
O22	0.064 (5)	0.049 (5)	0.027 (4)	0.007 (4)	0.003 (3)	0.005 (3)
C42	0.042 (6)	0.064 (7)	0.031 (5)	0.014 (6)	0.004 (5)	0.001 (5)
F4	0.096 (6)	0.115 (7)	0.044 (4)	0.052 (5)	0.033 (4)	0.033 (4)
F5	0.033 (4)	0.086 (6)	0.083 (5)	0.008 (3)	0.008 (3)	0.003 (4)
F6	0.071 (5)	0.069 (5)	0.075 (5)	0.017 (4)	0.012 (4)	−0.025 (4)
N31	0.027 (3)	0.027 (3)	0.055 (7)	0.001 (5)	−0.006 (4)	0.006 (4)
S3	0.0335 (12)	0.0326 (12)	0.0437 (12)	−0.0024 (9)	0.0002 (11)	0.0019 (10)
O31	0.058 (5)	0.033 (4)	0.054 (4)	−0.012 (3)	0.001 (4)	−0.012 (3)
O32	0.064 (5)	0.063 (6)	0.050 (4)	−0.011 (4)	0.021 (4)	0.005 (4)
C43	0.056 (8)	0.053 (8)	0.070 (8)	0.004 (6)	−0.017 (7)	−0.005 (7)
F7	0.101 (7)	0.098 (7)	0.121 (7)	0.028 (6)	−0.078 (6)	−0.002 (6)
F8	0.037 (4)	0.105 (6)	0.091 (6)	0.025 (4)	0.019 (4)	0.019 (5)
F9	0.072 (5)	0.036 (4)	0.124 (7)	0.016 (3)	−0.017 (5)	−0.002 (4)

Geometric parameters (Å, °)

Au1—C1	2.018 (12)	C22—C27	1.500 (13)
Au1—O1	2.046 (7)	C23—C24	1.376 (13)
Au1—Cl1^{i}	2.277 (2)	C23—H23	0.9500
Au1—Cl1	2.278 (2)	C24—C25	1.394 (14)
Cl1—Ag3^{i}	2.684 (3)	C24—C28	1.516 (13)
Au2—C6	1.982 (7)	C25—C26	1.394 (14)
Au2—O1	2.010 (3)	C25—H25	0.9500
Au2—Cl3	2.271 (2)	C26—C29	1.457 (14)
Au2—Cl2	2.276 (2)	C27—H27A	0.9800

Au2—Ag3B	3.234 (7)	C27—H27B	0.9800
Cl2—Ag3	2.644 (2)	C27—H27C	0.9800
Cl2—Ag3B	2.754 (8)	C28—H28A	0.9800
Cl3—Ag3B^{i}	2.302 (8)	C28—H28B	0.9800
Cl3—Ag3^{i}	2.769 (3)	C28—H28C	0.9800
O1—Au2^{i}	2.010 (3)	C29—H29A	0.9800
Ag3—O11	2.340 (7)	C29—H29B	0.9800
Ag3—Cl1^{i}	2.684 (3)	C29—H29C	0.9800
Ag3—Cl3^{i}	2.769 (3)	C31—C32	1.390 (13)
Ag3B—Cl3^{i}	2.302 (8)	C31—C36	1.395 (13)
Ag3B—O11	2.342 (10)	C32—C33	1.374 (15)
Ag3B—C25	2.544 (12)	C32—C37	1.504 (14)
Ag3B—C26	2.587 (13)	C33—C34	1.382 (15)
C1—N2	1.322 (10)	C33—H33	0.9500
C1—N2^{i}	1.322 (10)	C34—C35	1.385 (15)
N2—C3	1.392 (11)	C34—C38	1.500 (15)
N2—C11	1.452 (13)	C35—C36	1.385 (14)
C3—C3^{i}	1.31 (2)	C35—H35	0.9500
C3—H3	0.9500	C36—C39	1.508 (15)
C6—N10	1.327 (10)	C37—H37A	0.9800
C6—N7	1.364 (10)	C37—H37B	0.9800
N7—C8	1.375 (11)	C37—H37C	0.9800
N7—C21	1.455 (11)	C38—H38A	0.9800
C8—C9	1.340 (14)	C38—H38B	0.9800
C8—H8	0.9500	C38—H38C	0.9800
C9—N10	1.376 (11)	C39—H39A	0.9800
C9—H9	0.9500	C39—H39B	0.9800
N10—C31	1.450 (11)	C39—H39C	0.9800
C11—C16	1.352 (12)	N11—S1	1.555 (9)
C11—C12	1.400 (14)	N11—S2	1.582 (9)
C12—C13	1.40 (2)	S1—O11	1.411 (8)
C12—C17	1.484 (16)	S1—O12	1.437 (8)
C13—C14	1.390 (17)	S1—C41	1.812 (13)
C13—H13	0.9500	C41—F3	1.294 (14)
C14—C15	1.349 (14)	C41—F2	1.303 (14)
C14—C18	1.526 (17)	C41—F1	1.338 (13)
C15—C16	1.389 (14)	S2—O22	1.418 (7)
C15—H15	0.9500	S2—O21	1.419 (7)
C16—C19	1.495 (13)	S2—C42	1.821 (10)
C17—H17A	0.9800	C42—F4	1.301 (12)
C17—H17B	0.9800	C42—F5	1.301 (13)
C17—H17C	0.9800	C42—F6	1.332 (14)
C18—H18A	0.9800	N31—S3^{i}	1.590 (6)
C18—H18B	0.9800	N31—S3	1.590 (6)
C18—H18C	0.9800	S3—O32	1.420 (7)
C19—H19A	0.9800	S3—O31	1.431 (7)
C19—H19B	0.9800	S3—C43	1.818 (12)

C19—H19C	0.9800	C43—F8	1.302 (15)
C21—C22	1.376 (12)	C43—F7	1.318 (14)
C21—C26	1.383 (12)	C43—F9	1.328 (14)
C22—C23	1.406 (13)		
C1—Au1—O1	180.0 (3)	C24—C23—C22	121.5 (9)
C1—Au1—Cl1^{i}	92.44 (6)	C24—C23—H23	119.2
O1—Au1—Cl1^{i}	87.56 (6)	C22—C23—H23	119.2
C1—Au1—Cl1	92.44 (6)	C23—C24—C25	118.3 (9)
O1—Au1—Cl1	87.56 (6)	C23—C24—C28	122.6 (9)
Cl1^{i}—Au1—Cl1	175.12 (12)	C25—C24—C28	119.0 (9)
Au1—Cl1—Ag3^{i}	90.42 (7)	C24—C25—C26	122.5 (9)
C6—Au2—O1	179.5 (3)	C24—C25—Ag3B	111.8 (6)
C6—Au2—Cl3	92.1 (2)	C26—C25—Ag3B	76.0 (5)
O1—Au2—Cl3	88.25 (13)	C24—C25—H25	118.7
C6—Au2—Cl2	91.3 (2)	C26—C25—H25	118.7
O1—Au2—Cl2	88.36 (12)	Ag3B—C25—H25	82.3
Cl3—Au2—Cl2	176.55 (9)	C21—C26—C25	116.1 (8)
C6—Au2—Ag3B	100.0 (3)	C21—C26—C29	122.9 (10)
O1—Au2—Ag3B	80.16 (16)	C25—C26—C29	120.7 (9)
Cl3—Au2—Ag3B	123.08 (16)	C21—C26—Ag3B	110.3 (6)
Cl2—Au2—Ag3B	56.83 (15)	C25—C26—Ag3B	72.5 (5)
Au2—Cl2—Ag3	95.30 (8)	C29—C26—Ag3B	91.4 (7)
Au2—Cl2—Ag3B	79.40 (16)	C22—C27—H27A	109.5
Ag3—Cl2—Ag3B	42.07 (18)	C22—C27—H27B	109.5
Au2—Cl3—Ag3B^{i}	123.6 (2)	H27A—C27—H27B	109.5
Au2—Cl3—Ag3^{i}	92.12 (9)	C22—C27—H27C	109.5
Ag3B^{i}—Cl3—Ag3^{i}	43.8 (2)	H27A—C27—H27C	109.5
Au2—O1—Au2^{i}	125.2 (3)	H27B—C27—H27C	109.5
Au2—O1—Au1	117.41 (17)	C24—C28—H28A	109.5
Au2^{i}—O1—Au1	117.41 (17)	C24—C28—H28B	109.5
O11—Ag3—Cl2	104.3 (2)	H28A—C28—H28B	109.5
O11—Ag3—Cl1^{i}	142.3 (2)	C24—C28—H28C	109.5
Cl2—Ag3—Cl1^{i}	104.40 (8)	H28A—C28—H28C	109.5
O11—Ag3—Cl3^{i}	100.4 (2)	H28B—C28—H28C	109.5
Cl2—Ag3—Cl3^{i}	102.64 (9)	C26—C29—H29A	109.5
Cl1^{i}—Ag3—Cl3^{i}	96.55 (8)	C26—C29—H29B	109.5
Cl3^{i}—Ag3B—O11	115.9 (4)	H29A—C29—H29B	109.5
Cl3^{i}—Ag3B—C25	100.4 (4)	C26—C29—H29C	109.5
O11—Ag3B—C25	104.7 (4)	H29A—C29—H29C	109.5
Cl3^{i}—Ag3B—C26	114.8 (4)	H29B—C29—H29C	109.5
O11—Ag3B—C26	117.2 (4)	C32—C31—C36	122.2 (9)
C25—Ag3B—C26	31.5 (3)	C32—C31—N10	119.1 (8)
Cl3^{i}—Ag3B—Cl2	113.1 (3)	C36—C31—N10	118.7 (8)
O11—Ag3B—Cl2	101.0 (3)	C33—C32—C31	118.1 (9)
C25—Ag3B—Cl2	122.3 (4)	C33—C32—C37	122.3 (10)

C26—Ag3B—Cl2	90.8 (3)	C31—C32—C37	119.5 (10)
Cl3^{i}—Ag3B—Au2	79.3 (2)	C32—C33—C34	121.6 (10)
O11—Ag3B—Au2	143.1 (4)	C32—C33—H33	119.2
C25—Ag3B—Au2	105.1 (3)	C34—C33—H33	119.2
C26—Ag3B—Au2	80.4 (3)	C33—C34—C35	118.9 (10)
Cl2—Ag3B—Au2	43.77 (11)	C33—C34—C38	120.2 (11)
N2—C1—N2^{i}	111.0 (11)	C35—C34—C38	120.9 (11)
N2—C1—Au1	124.5 (5)	C36—C35—C34	121.7 (9)
N2^{i}—C1—Au1	124.5 (5)	C36—C35—H35	119.2
C1—N2—C3	106.3 (9)	C34—C35—H35	119.2
C1—N2—C11	124.7 (7)	C35—C36—C31	117.4 (10)
C3—N2—C11	129.0 (8)	C35—C36—C39	120.5 (10)
C3^{i}—C3—N2	108.1 (6)	C31—C36—C39	122.1 (10)
C3^{i}—C3—H3	126.0	C32—C37—H37A	109.5
N2—C3—H3	126.0	C32—C37—H37B	109.5
N10—C6—N7	106.8 (7)	H37A—C37—H37B	109.5
N10—C6—Au2	128.1 (6)	C32—C37—H37C	109.5
N7—C6—Au2	125.0 (6)	H37A—C37—H37C	109.5
C6—N7—C8	109.2 (7)	H37B—C37—H37C	109.5
C6—N7—C21	123.1 (7)	C34—C38—H38A	109.5
C8—N7—C21	127.6 (7)	C34—C38—H38B	109.5
C9—C8—N7	106.5 (8)	H38A—C38—H38B	109.5
C9—C8—H8	126.8	C34—C38—H38C	109.5
N7—C8—H8	126.8	H38A—C38—H38C	109.5
C8—C9—N10	108.3 (8)	H38B—C38—H38C	109.5
C8—C9—H9	125.9	C36—C39—H39A	109.5
N10—C9—H9	125.9	C36—C39—H39B	109.5
C6—N10—C9	109.2 (8)	H39A—C39—H39B	109.5
C6—N10—C31	125.2 (7)	C36—C39—H39C	109.5
C9—N10—C31	125.5 (7)	H39A—C39—H39C	109.5
C16—C11—C12	125.2 (11)	H39B—C39—H39C	109.5
C16—C11—N2	119.0 (9)	S1—N11—S2	124.0 (6)
C12—C11—N2	115.7 (9)	O11—S1—O12	115.5 (5)
C11—C12—C13	114.1 (10)	O11—S1—N11	115.3 (5)
C11—C12—C17	125.5 (14)	O12—S1—N11	115.5 (5)
C13—C12—C17	120.3 (12)	O11—S1—C41	104.1 (6)
C14—C13—C12	122.6 (10)	O12—S1—C41	106.5 (6)
C14—C13—H13	118.7	N11—S1—C41	96.8 (5)
C12—C13—H13	118.7	S1—O11—Ag3	124.1 (5)
C15—C14—C13	117.8 (11)	S1—O11—Ag3B	122.1 (5)
C15—C14—C18	121.9 (11)	Ag3—O11—Ag3B	49.0 (3)
C13—C14—C18	120.1 (11)	F3—C41—F2	108.0 (10)
C14—C15—C16	123.0 (10)	F3—C41—F1	107.7 (10)
C14—C15—H15	118.5	F2—C41—F1	107.4 (11)
C16—C15—H15	118.5	F3—C41—S1	112.8 (10)
C11—C16—C15	116.4 (9)	F2—C41—S1	112.5 (8)
C11—C16—C19	123.0 (10)	F1—C41—S1	108.3 (8)
C15—C16—C19	120.6 (9)	O22—S2—O21	117.7 (5)

C12—C17—H17A	109.5	O22—S2—N11	109.2 (5)
C12—C17—H17B	109.5	O21—S2—N11	114.7 (5)
H17A—C17—H17B	109.5	O22—S2—C42	104.4 (5)
C12—C17—H17C	109.5	O21—S2—C42	105.7 (5)
H17A—C17—H17C	109.5	N11—S2—C42	103.7 (5)
H17B—C17—H17C	109.5	F4—C42—F5	109.7 (11)
C14—C18—H18A	109.5	F4—C42—F6	108.9 (9)
C14—C18—H18B	109.5	F5—C42—F6	107.7 (10)
H18A—C18—H18B	109.5	F4—C42—S2	111.0 (8)
C14—C18—H18C	109.5	F5—C42—S2	111.3 (7)
H18A—C18—H18C	109.5	F6—C42—S2	108.2 (8)
H18B—C18—H18C	109.5	S3^{i}—N31—S3	121.8 (7)
C16—C19—H19A	109.5	O32—S3—O31	119.2 (5)
C16—C19—H19B	109.5	O32—S3—N31	108.3 (5)
H19A—C19—H19B	109.5	O31—S3—N31	117.2 (5)
C16—C19—H19C	109.5	O32—S3—C43	104.1 (6)
H19A—C19—H19C	109.5	O31—S3—C43	102.5 (6)
H19B—C19—H19C	109.5	N31—S3—C43	103.0 (4)
C22—C21—C26	124.1 (8)	F8—C43—F7	109.8 (11)
C22—C21—N7	118.1 (8)	F8—C43—F9	107.2 (11)
C26—C21—N7	117.8 (8)	F7—C43—F9	107.1 (11)
C21—C22—C23	117.2 (8)	F8—C43—S3	112.1 (9)
C21—C22—C27	123.0 (9)	F7—C43—S3	109.4 (9)
C23—C22—C27	119.7 (9)	F9—C43—S3	111.1 (9)
C1—Au1—Cl1—Ag3^{i}	131.82 (6)	N7—C21—C22—C23	175.2 (8)
O1—Au1—Cl1—Ag3^{i}	−48.18 (6)	C26—C21—C22—C27	174.1 (9)
Cl1^{i}—Au1—Cl1—Ag3^{i}	−48.18 (6)	N7—C21—C22—C27	−7.9 (13)
C6—Au2—Cl2—Ag3	140.2 (2)	C21—C22—C23—C24	−1.3 (14)
O1—Au2—Cl2—Ag3	−40.19 (15)	C27—C22—C23—C24	−178.3 (9)
Cl3—Au2—Cl2—Ag3	−50.6 (18)	C22—C23—C24—C25	3.1 (14)
Ag3B—Au2—Cl2—Ag3	39.12 (19)	C22—C23—C24—C28	−176.1 (9)
C6—Au2—Cl2—Ag3B	101.1 (3)	C23—C24—C25—C26	−1.2 (14)
O1—Au2—Cl2—Ag3B	−79.3 (2)	C28—C24—C25—C26	178.1 (9)
Cl3—Au2—Cl2—Ag3B	−89.7 (18)	C23—C24—C25—Ag3B	−88.0 (10)
C6—Au2—Cl3—Ag3B^{i}	168.8 (4)	C28—C24—C25—Ag3B	91.2 (10)
O1—Au2—Cl3—Ag3B^{i}	−10.8 (3)	Cl3^{i}—Ag3B—C25—C24	−1.4 (8)
Cl2—Au2—Cl3—Ag3B^{i}	−0.4 (19)	O11—Ag3B—C25—C24	−121.8 (7)
Ag3B—Au2—Cl3—Ag3B^{i}	−87.8 (2)	C26—Ag3B—C25—C24	119.8 (10)
C6—Au2—Cl3—Ag3^{i}	136.3 (2)	Cl2—Ag3B—C25—C24	124.7 (7)
O1—Au2—Cl3—Ag3^{i}	−43.33 (16)	Au2—Ag3B—C25—C24	80.2 (8)
Cl2—Au2—Cl3—Ag3^{i}	−32.9 (18)	Cl3^{i}—Ag3B—C25—C26	−121.2 (6)
Ag3B—Au2—Cl3—Ag3^{i}	−120.4 (2)	O11—Ag3B—C25—C26	118.4 (6)
C6—Au2—O1—Au2^{i}	179 (100)	Cl2—Ag3B—C25—C26	4.9 (7)
Cl3—Au2—O1—Au2^{i}	−53.29 (8)	Au2—Ag3B—C25—C26	−39.5 (6)
Cl2—Au2—O1—Au2^{i}	127.34 (6)	C22—C21—C26—C25	4.6 (13)

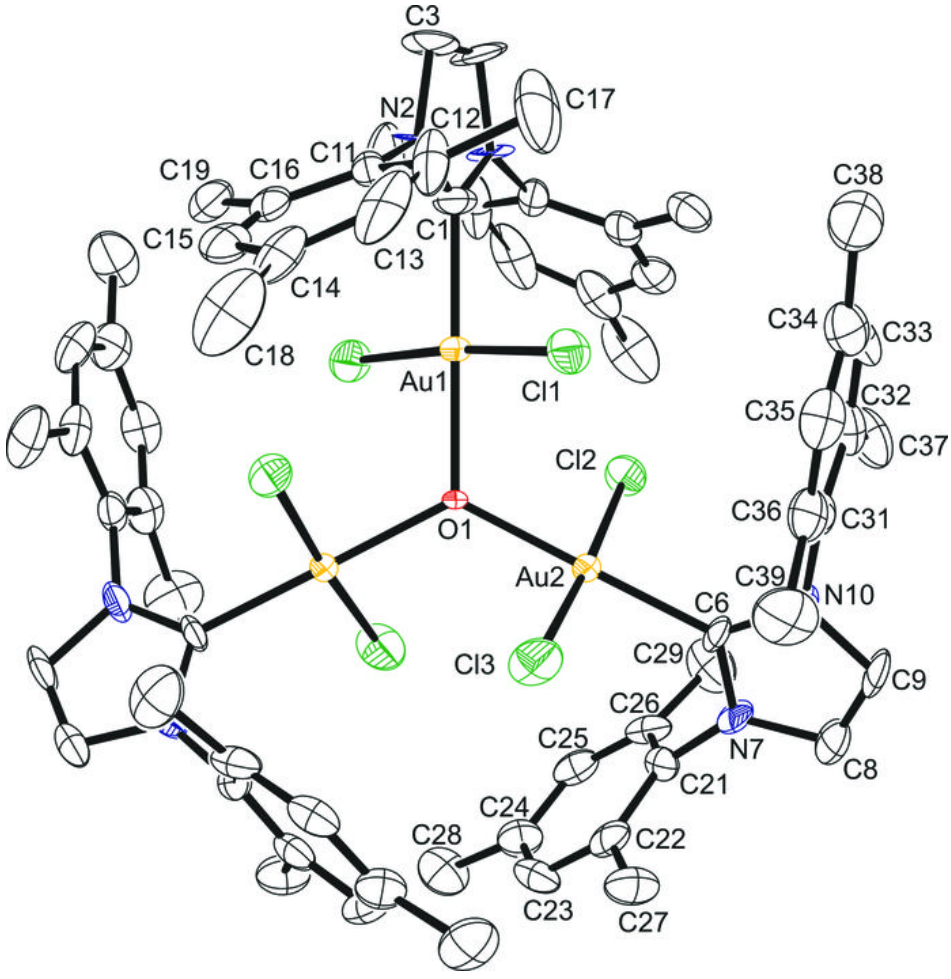
Ag3B—Au2—O1—Au2^{i}	70.74 (14)	N7—C21—C26—C25	−173.4 (7)
C6—Au2—O1—Au1	−1(30)	C22—C21—C26—C29	−169.7 (9)
Cl3—Au2—O1—Au1	126.71 (8)	N7—C21—C26—C29	12.3 (13)
Cl2—Au2—O1—Au1	−52.66 (6)	C22—C21—C26—Ag3B	84.5 (10)
Ag3B—Au2—O1—Au1	−109.26 (14)	N7—C21—C26—Ag3B	−93.5 (8)
C1—Au1—O1—Au2	45.730 (10)	C24—C25—C26—C21	−2.5 (13)
Cl1^{i}—Au1—O1—Au2	132.01 (6)	Ag3B—C25—C26—C21	104.6 (8)
Cl1—Au1—O1—Au2	−47.99 (6)	C24—C25—C26—C29	171.9 (9)
C1—Au1—O1—Au2^{i}	−134.270 (10)	Ag3B—C25—C26—C29	−81.0 (9)
Cl1^{i}—Au1—O1—Au2^{i}	−47.99 (6)	C24—C25—C26—Ag3B	−107.1 (9)
Cl1—Au1—O1—Au2^{i}	132.01 (6)	Cl3^{i}—Ag3B—C26—C21	−44.0 (8)
Au2—Cl2—Ag3—O11	−125.6 (2)	O11—Ag3B—C26—C21	174.9 (6)
Ag3B—Cl2—Ag3—O11	−57.9 (3)	C25—Ag3B—C26—C21	−112.1 (9)
Au2—Cl2—Ag3—Cl1^{i}	79.04 (10)	Cl2—Ag3B—C26—C21	72.0 (6)
Ag3B—Cl2—Ag3—Cl1^{i}	146.8 (2)	Au2—Ag3B—C26—C21	29.4 (6)
Au2—Cl2—Ag3—Cl3^{i}	−21.24 (9)	Cl3^{i}—Ag3B—C26—C25	68.0 (6)
Ag3B—Cl2—Ag3—Cl3^{i}	46.5 (2)	O11—Ag3B—C26—C25	−73.1 (7)
Au2—Cl2—Ag3B—Cl3^{i}	42.5 (3)	Cl2—Ag3B—C26—C25	−175.9 (6)
Ag3—Cl2—Ag3B—Cl3^{i}	−67.9 (3)	Au2—Ag3B—C26—C25	141.4 (6)
Au2—Cl2—Ag3B—O11	167.0 (3)	Cl3^{i}—Ag3B—C26—C29	−170.1 (6)
Ag3—Cl2—Ag3B—O11	56.6 (3)	O11—Ag3B—C26—C29	48.8 (8)
Au2—Cl2—Ag3B—C25	−77.7 (4)	C25—Ag3B—C26—C29	121.8 (9)
Ag3—Cl2—Ag3B—C25	172.0 (5)	Cl2—Ag3B—C26—C29	−54.1 (6)
Au2—Cl2—Ag3B—C26	−75.1 (3)	Au2—Ag3B—C26—C29	−96.8 (6)
Ag3—Cl2—Ag3B—C26	174.5 (4)	C6—N10—C31—C32	−91.8 (11)
Ag3—Cl2—Ag3B—Au2	−110.34 (19)	C9—N10—C31—C32	85.8 (12)
C6—Au2—Ag3B—Cl3^{i}	134.2 (3)	C6—N10—C31—C36	88.5 (11)
O1—Au2—Ag3B—Cl3^{i}	−46.3 (3)	C9—N10—C31—C36	−94.0 (12)
Cl3—Au2—Ag3B—Cl3^{i}	35.1 (3)	C36—C31—C32—C33	−2.8 (14)
Cl2—Au2—Ag3B—Cl3^{i}	−140.8 (3)	N10—C31—C32—C33	177.5 (8)
C6—Au2—Ag3B—O11	−106.6 (7)	C36—C31—C32—C37	173.3 (9)
O1—Au2—Ag3B—O11	72.9 (6)	N10—C31—C32—C37	−6.5 (13)
Cl3—Au2—Ag3B—O11	154.3 (5)	C31—C32—C33—C34	0.4 (15)
Cl2—Au2—Ag3B—O11	−21.6 (5)	C37—C32—C33—C34	−175.6 (10)
C6—Au2—Ag3B—C25	36.2 (4)	C32—C33—C34—C35	2.6 (15)
O1—Au2—Ag3B—C25	−144.3 (4)	C32—C33—C34—C38	−176.7 (10)
Cl3—Au2—Ag3B—C25	−62.9 (4)	C33—C34—C35—C36	−3.4 (15)
Cl2—Au2—Ag3B—C25	121.2 (4)	C38—C34—C35—C36	175.9 (9)
C6—Au2—Ag3B—C26	16.4 (3)	C34—C35—C36—C31	1.1 (14)
O1—Au2—Ag3B—C26	−164.1 (3)	C34—C35—C36—C39	177.3 (10)
Cl3—Au2—Ag3B—C26	−82.7 (3)	C32—C31—C36—C35	2.0 (13)
Cl2—Au2—Ag3B—C26	101.4 (3)	N10—C31—C36—C35	−178.2 (8)
C6—Au2—Ag3B—Cl2	−85.0 (3)	C32—C31—C36—C39	−174.1 (9)
O1—Au2—Ag3B—Cl2	94.5 (2)	N10—C31—C36—C39	5.7 (13)
Cl3—Au2—Ag3B—Cl2	175.88 (11)	S2—N11—S1—O11	72.3 (8)
O1—Au1—C1—N2	−161.2 (4)	S2—N11—S1—O12	−66.5 (8)

Cl1^{i}—Au1—C1—N2	112.5 (5)	S2—N11—S1—C41	−178.5 (7)
Cl1—Au1—C1—N2	−67.5 (5)	O12—S1—O11—Ag3	−49.2 (8)
O1—Au1—C1—N2^{i}	18.8 (4)	N11—S1—O11—Ag3	172.0 (5)
Cl1^{i}—Au1—C1—N2^{i}	−67.5 (5)	C41—S1—O11—Ag3	67.2 (7)
Cl1—Au1—C1—N2^{i}	112.5 (5)	O12—S1—O11—Ag3B	10.0 (8)
N2^{i}—C1—N2—C3	1.4 (7)	N11—S1—O11—Ag3B	−128.8 (6)
Au1—C1—N2—C3	−178.7 (7)	C41—S1—O11—Ag3B	126.5 (6)
N2^{i}—C1—N2—C11	179.6 (10)	Cl2—Ag3—O11—S1	167.3 (5)
Au1—C1—N2—C11	−0.4 (10)	Cl1^{i}—Ag3—O11—S1	−54.0 (8)
C1—N2—C3—C3^{i}	−3.7 (19)	Cl3^{i}—Ag3—O11—S1	61.3 (6)
C11—N2—C3—C3^{i}	178.1 (13)	Cl2—Ag3—O11—Ag3B	62.2 (3)
O1—Au2—C6—N10	35 (31)	Cl1^{i}—Ag3—O11—Ag3B	−159.2 (3)
Cl3—Au2—C6—N10	−93.2 (8)	Cl3^{i}—Ag3—O11—Ag3B	−43.9 (3)
Cl2—Au2—C6—N10	86.2 (8)	Cl3^{i}—Ag3B—O11—S1	−43.7 (8)
Ag3B—Au2—C6—N10	142.7 (7)	C25—Ag3B—O11—S1	65.9 (7)
O1—Au2—C6—N7	−144 (30)	C26—Ag3B—O11—S1	97.0 (6)
Cl3—Au2—C6—N7	88.2 (7)	Cl2—Ag3B—O11—S1	−166.3 (5)
Cl2—Au2—C6—N7	−92.4 (7)	Au2—Ag3B—O11—S1	−151.2 (5)
Ag3B—Au2—C6—N7	−35.9 (8)	Cl3^{i}—Ag3B—O11—Ag3	65.7 (4)
N10—C6—N7—C8	0.9 (11)	C25—Ag3B—O11—Ag3	175.2 (4)
Au2—C6—N7—C8	179.7 (7)	C26—Ag3B—O11—Ag3	−153.6 (5)
N10—C6—N7—C21	−176.8 (8)	Cl2—Ag3B—O11—Ag3	−56.9 (2)
Au2—C6—N7—C21	2.0 (12)	Au2—Ag3B—O11—Ag3	−41.9 (5)
C6—N7—C8—C9	−0.6 (13)	O11—S1—C41—F3	−174.4 (8)
C21—N7—C8—C9	176.9 (10)	O12—S1—C41—F3	−51.9 (10)
N7—C8—C9—N10	0.2 (14)	N11—S1—C41—F3	67.3 (9)
N7—C6—N10—C9	−0.8 (11)	O11—S1—C41—F2	63.2 (10)
Au2—C6—N10—C9	−179.6 (7)	O12—S1—C41—F2	−174.3 (8)
N7—C6—N10—C31	177.1 (8)	N11—S1—C41—F2	−55.1 (10)
Au2—C6—N10—C31	−1.7 (13)	O11—S1—C41—F1	−55.3 (10)
C8—C9—N10—C6	0.4 (13)	O12—S1—C41—F1	67.2 (10)
C8—C9—N10—C31	−177.5 (9)	N11—S1—C41—F1	−173.6 (9)
C1—N2—C11—C16	−78.3 (11)	S1—N11—S2—O22	149.0 (7)
C3—N2—C11—C16	99.6 (13)	S1—N11—S2—O21	14.5 (9)
C1—N2—C11—C12	99.5 (10)	S1—N11—S2—C42	−100.2 (7)
C3—N2—C11—C12	−82.6 (14)	O22—S2—C42—F4	179.2 (9)
C16—C11—C12—C13	5.3 (15)	O21—S2—C42—F4	−56.1 (10)
N2—C11—C12—C13	−172.4 (8)	N11—S2—C42—F4	64.9 (10)
C16—C11—C12—C17	−172.7 (11)	O22—S2—C42—F5	56.7 (10)
N2—C11—C12—C17	9.7 (16)	O21—S2—C42—F5	−178.6 (8)
C11—C12—C13—C14	0.4 (16)	N11—S2—C42—F5	−57.6 (9)
C17—C12—C13—C14	178.5 (11)	O22—S2—C42—F6	−61.5 (8)
C12—C13—C14—C15	−8.0 (16)	O21—S2—C42—F6	63.3 (8)
C12—C13—C14—C18	176.9 (10)	N11—S2—C42—F6	−175.7 (7)
C13—C14—C15—C16	10.6 (15)	S3^{i}—N31—S3—O32	160.1 (4)
C18—C14—C15—C16	−174.3 (10)	S3^{i}—N31—S3—O31	21.6 (4)

C12—C11—C16—C15	−3.0 (14)	S3^{i}—N31—S3—C43	−90.0 (5)
N2—C11—C16—C15	174.5 (7)	O32—S3—C43—F8	171.7 (9)
C12—C11—C16—C19	175.6 (9)	O31—S3—C43—F8	−63.4 (10)
N2—C11—C16—C19	−6.8 (13)	N31—S3—C43—F8	58.7 (10)
C14—C15—C16—C11	−5.3 (14)	O32—S3—C43—F7	−66.3 (11)
C14—C15—C16—C19	175.9 (9)	O31—S3—C43—F7	58.6 (11)
C6—N7—C21—C22	−93.0 (11)	N31—S3—C43—F7	−179.3 (10)
C8—N7—C21—C22	89.8 (12)	O32—S3—C43—F9	51.8 (11)
C6—N7—C21—C26	85.2 (11)	O31—S3—C43—F9	176.6 (9)
C8—N7—C21—C26	−92.1 (12)	N31—S3—C43—F9	−61.2 (11)
C26—C21—C22—C23	−2.8 (14)		

Symmetry codes: (i) *y*, *x*, −*z*.

Fig. 1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C17
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Cl1
C35
C32
C37
Cl2
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C36
C31
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C39
N10
C6
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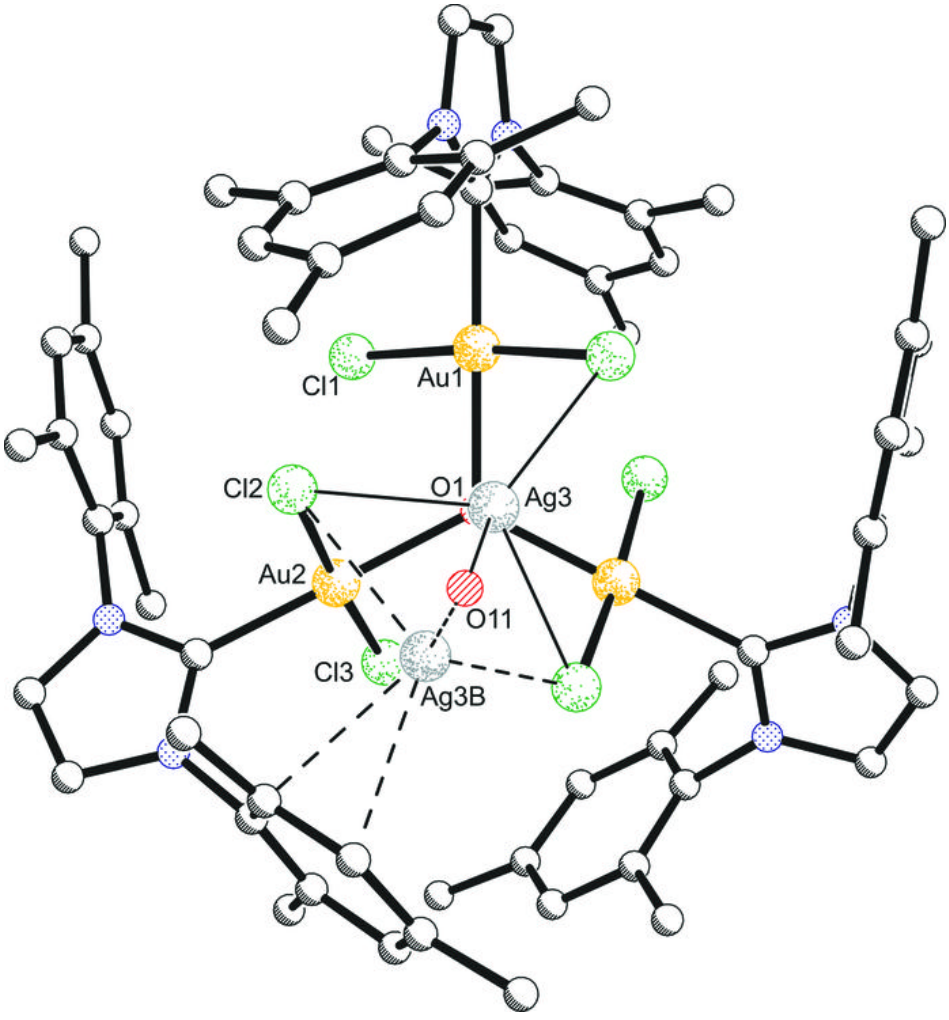
C21
C24
C28
C22
C23
C27

Fig. 2



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2-(4-Fluorobenzylidene)-*N*-(4-methoxybenzylidene)-1,3,4-thiadiazol-2-amine

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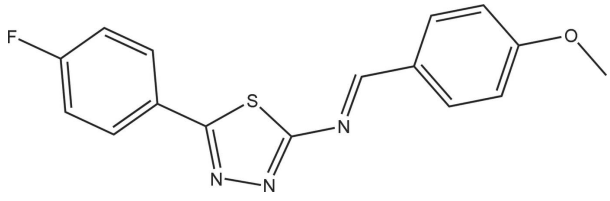
Key indicators: single-crystal X-ray study; T = 293 K; mean σ(C–C) = 0.006 Å; R factor = 0.048; wR factor = 0.132; data-to-parameter ratio = 13.2.

The title compound, $C_{16}H_{12}FN_3OS$, was synthesized by the reaction of 5-(4-methoxyphenyl)-1,3,4-thiadiazol-2-amine and 4-fluorobenzaldehyde. An intramolecular C—H···S hydrogen bond results in the formation of two five-membered rings. In the crystal structure, intermolecular C—H···N hydrogen bonding links the molecules, forming a two-dimensional network.

Related literature

For the biological activity of 1,3,4-thiadiazole derivatives, see: Nakagawa *et al.* (1996); Wang *et al.* (1999).



Experimental

Crystal data

$C_{16}H_{12}FN_3OS$
M_r = 313.35
Orthorhombic, $Pca2_1$
a = 7.4580 (15) Å
b = 17.821 (4) Å
c = 10.891 (2) Å
V = 1447.5 (5) Å^3
Z = 4
Mo $K\alpha$ radiation
μ = 0.24 mm^{-1}
T = 293 K
0.30 × 0.30 × 0.10 mm

Data collection

Enraf–Nonius CAD-4 diffractometer
Absorption correction: ψ scan (North *et al.*, 1968)
T_{min} = 0.932, T_{max} = 0.977
2617 measured reflections
2617 independent reflections
1965 reflections with $I > 2\sigma(I)$
R_{int} = 0.045
3 standard reflections every 200 reflections
intensity decay: 1%

Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.048
$wR(F^2)$ = 0.132
S = 1.01
2617 reflections
199 parameters
1 restraint
H-atom parameters constrained
$\Delta\rho_{max}$ = 0.33 e Å^{-3}
$\Delta\rho_{min}$ = −0.17 e Å^{-3}
Absolute structure: Flack (1983), 1062 Friedel pairs
Flack parameter: −0.11 (13)

Table 1
Hydrogen-bond geometry (Å, °).

D—H···A	D—H	H···A	D···A	D—H···A
C8—H8A···S	0.93	2.59	3.043 (5)	110
C12—H12A···S	0.93	2.75	3.138 (4)	106
C12—H12A···N3^{i}	0.93	2.62	3.451 (6)	148

Symmetry code: (i) $-x+2, -y+1, z-\frac{1}{2}$.

Data collection: *CAD-4 EXPRESS* (Enraf–Nonius, 1989); cell refinement: *CAD-4 EXPRESS*; data reduction: *XCAD4* (Harms & Wocadlo, 1995); program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *SHELXTL* (Sheldrick, 2008); software used to prepare material for publication: *SHELXL97*.

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Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: HG2691).

References

Enraf–Nonius (1989). *CAD-4 EXPRESS*. Enraf–Nonius, Delft, The Netherlands.
Flack, H. D. (1983). *Acta Cryst.* A**39**, 876–881.
Harms, K. & Wocadlo, S. (1995). *XCAD4*. University of Marburg, Germany.
Nakagawa, Y., Nishimura, K., Izumi, K., Kinoshita, K., Kimura, T. & Kurihara, N. (1996). *J. Pestic. Sci.* **21**, 195–201.
North, A. C. T., Phillips, D. C. & Mathews, F. S. (1968). *Acta Cryst.* A**24**, 351–359.
Sheldrick, G. M. (2008). *Acta Cryst.* A**64**, 112–122.
Wang, Y. G., Cao, L., Yan, J., Ye, W. F., Zhou, Q. C. & Lu, B. X. (1999). *Chem. J. Chin. Univ.* **20**, 1903–1905.

supplementary materials

Acta Cryst. (2010). E**66**, o1716 [**doi:10.1107/S160053681002221X**]

2-(4-Fluorobenzylidene)-*N*-(4-methoxybenzylidene)-1,3,4-thiadiazol-2-amine

Q. He, K. An, P. Wang, P. Yu and R. Wan

Comment

1,3,4-Thiadiazole derivatives represent an interesting class of compounds possessing broad spectrum biological activities (Nakagawa *et al.*, 1996; Wang *et al.*, 1999). These compounds are known to exhibit diverse biological effects, such as insecticidal, fungicidal activities (Wang *et al.*, 1999).

We report herein the crystal structure of the title compound,(I). In the molecule of the title compound (Fig. 1), bond lengths are within normal ranges. Rings A(C2—C7), B(S/C9/N2/N3/C10) and C(C11—C16) are planar. The dihedral angle between them is A/B = 21.4 (1) Å, A/C=29.6 (3)Å and B/C= 10.7 (4) Å. The intramolecular C—H···S hydrogen bonds (Table 1) result in the formation of two planar five-membered rings D(H8A/C8/N1/C9/S) and E(S/H12A/C12/C11/C10). They are oriented with respect to the adjacent rings at dihedral angles of A/D= 11.6 (4) Å, B/D= 14.1 (4) Å, C/D= 24.5 (1) Å, A/E= 27.4 (1) Å, B/E= 6.1 (1) Å, C/E= 8.2 (1)Å and D/E= 19.5 (1) Å. In the crystal structure, intermolecular C—H···S hydrogen bond (Table 1) links the molecules to form a two-dimensional network (Fig. 2), in which they may be effective in the stabilization of the structure.

Experimental

5-(4-methoxyphenyl)-1,3,4-thiadiazol-2-amine(5 mmol) and 4-fluorobenzaldehyde(5 mmol) were added in toluene (50 ml). The water was removed by distillation for 5 h. The reaction mixture was left to cool to room temperature, filtered, and the filter cake was crystallized from acetone to give pure compound (I) (m.p. 412–414 K). Crystals of (I) suitable for X-ray diffraction were obtained by slow evaporation of an acetone solution.

Refinement

All H atoms bonded to the C atoms were placed geometrically at the distances of 0.93–0.97 Å and included in the refinement in riding motion approximation with $U_{iso}(H) = 1.2_{eq}$ of the carrier atom.

Figures

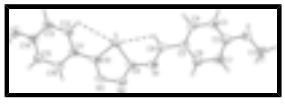


Fig. 1. The molecular structure of the title molecule, with the atom-numbering scheme. Displacement ellipsoids are drawn at the 50% probability level. Hydrogen bonds are shown as dashed line.

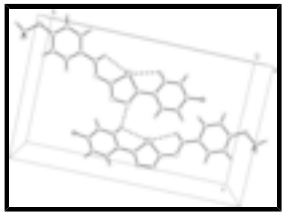


Fig. 2. A partial packing diagram of(I). Hydrogen bonds are shown as dashed lines.

2-(4-Fluorobenzylidene)-*N*-(4-methoxybenzylidene)-1,3,4-thiadiazol-2-amine

Crystal data

$C_{16}H_{12}FN_3OS$	$D_x = 1.438$ Mg m^{-3}
$M_r = 313.35$	Melting point = 412–414 K
Orthorhombic, $Pca2_1$	Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å
Hall symbol: P 2ac -2ac	Cell parameters from 25 reflections
$a = 7.4580$ (15) Å	$\theta = 9$–$13°$
$b = 17.821$ (4) Å	$\mu = 0.24$ mm^{-1}
$c = 10.891$ (2) Å	$T = 293$ K
$V = 1447.5$ (5) Å^3	Block, colourless
$Z = 4$	0.30 × 0.30 × 0.10 mm
$F(000) = 648$	

Data collection

Enraf–Nonius CAD-4 diffractometer	1965 reflections with $I > 2\sigma(I)$
Radiation source: fine-focus sealed tube	$R_{int} = 0.045$
graphite	$\theta_{max} = 25.3°$, $\theta_{min} = 1.1°$
$\omega/2\theta$ scans	$h = -8\rightarrow0$
Absorption correction: ψ scan (North *et al.*, 1968)	$k = 0\rightarrow21$
$T_{min} = 0.932$, $T_{max} = 0.977$	$l = -13\rightarrow13$
2617 measured reflections	3 standard reflections every 200 reflections
2617 independent reflections	intensity decay: 1%

Refinement

Refinement on F^2	Secondary atom site location: difference Fourier map
Least-squares matrix: full	Hydrogen site location: inferred from neighbouring sites
$R[F^2 > 2\sigma(F^2)] = 0.048$	H-atom parameters constrained
$wR(F^2) = 0.132$	$w = 1/[\sigma^2(F_o^2) + (0.078P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
$S = 1.01$	$(\Delta/\sigma)_{max} < 0.001$
2617 reflections	$\Delta\rho_{max} = 0.33$ e Å^{-3}
199 parameters	$\Delta\rho_{min} = -0.17$ e Å^{-3}
1 restraint	Absolute structure: Flack (1983), 1062 Friedel pairs
Primary atom site location: structure-invariant direct methods	Flack parameter: −0.11 (13)

Special details

Geometry. All e.s.d.'s (except the e.s.d. in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell e.s.d.'s are taken into account individually in the estimation of e.s.d.'s in distances, angles and torsion angles; correlations between e.s.d.'s in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell e.s.d.'s is used for estimating e.s.d.'s involving l.s. planes.

Refinement. Refinement of F^2 against ALL reflections. The weighted *R*-factor *wR* and goodness of fit *S* are based on F^2, conventional *R*-factors *R* are based on *F*, with *F* set to zero for negative F^2. The threshold expression of $F^2 > \sigma(F^2)$ is used only for calculating *R*-factors(gt) *etc*. and is not relevant to the choice of reflections for refinement. *R*-factors based on F^2 are statistically about twice as large as those based on *F*, and *R*- factors based on ALL data will be even larger.

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å^2)

	x	*y*	*z*	U_{iso}*/U_{eq}
S	0.92308 (13)	0.41730 (5)	0.79211 (10)	0.0604 (3)
O	0.9032 (5)	−0.04222 (18)	0.5620 (3)	0.0858 (10)
F	0.8635 (5)	0.78682 (14)	0.8637 (3)	0.0990 (9)
N1	0.8911 (5)	0.2684 (2)	0.8632 (3)	0.0645 (10)
N2	0.8471 (5)	0.3651 (2)	1.0054 (3)	0.0687 (9)
N3	0.8461 (5)	0.4421 (2)	1.0171 (3)	0.0654 (9)
C1	0.9071 (7)	−0.1065 (3)	0.6422 (6)	0.0918 (16)
H1B	0.9074	−0.1516	0.5940	0.138*
H1C	0.8031	−0.1060	0.6942	0.138*
H1D	1.0132	−0.1048	0.6920	0.138*
C2	0.9047 (6)	0.0268 (3)	0.6164 (4)	0.0678 (12)
C3	0.8810 (6)	0.0860 (2)	0.5372 (4)	0.0739 (12)
H3B	0.8684	0.0770	0.4535	0.089*
C4	0.8755 (6)	0.1585 (3)	0.5806 (4)	0.0687 (11)
H4A	0.8579	0.1981	0.5262	0.082*
C5	0.8963 (5)	0.1733 (2)	0.7064 (4)	0.0603 (10)
C6	0.9228 (5)	0.1129 (2)	0.7838 (5)	0.0657 (10)
H6A	0.9388	0.1217	0.8673	0.079*
C7	0.9261 (6)	0.0401 (3)	0.7411 (4)	0.0715 (13)
H7A	0.9425	0.0003	0.7952	0.086*
C8	0.8852 (6)	0.2493 (3)	0.7494 (4)	0.0643 (11)
H8A	0.8730	0.2871	0.6912	0.077*
C9	0.8836 (5)	0.3439 (2)	0.8931 (4)	0.0574 (10)
C10	0.8857 (5)	0.4763 (2)	0.9128 (3)	0.0542 (9)
C11	0.8879 (5)	0.5579 (2)	0.9023 (3)	0.0512 (9)
C12	0.9457 (5)	0.5931 (2)	0.7942 (5)	0.0611 (9)
H12A	0.9893	0.5640	0.7298	0.073*
C13	0.9392 (5)	0.6695 (2)	0.7818 (5)	0.0661 (10)
H13A	0.9787	0.6924	0.7099	0.079*
C14	0.8735 (6)	0.7118 (2)	0.8768 (4)	0.0673 (11)
C15	0.8172 (6)	0.6802 (3)	0.9853 (4)	0.0709 (12)
H15A	0.7758	0.7101	1.0492	0.085*
C16	0.8234 (5)	0.6033 (2)	0.9975 (3)	0.0606 (10)

H16A	0.7841	0.5813	1.0701	0.073*

Atomic displacement parameters (Å^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
S	0.0706 (6)	0.0737 (6)	0.0370 (4)	−0.0041 (5)	0.0021 (5)	0.0022 (6)
O	0.120 (3)	0.064 (2)	0.073 (2)	0.0014 (18)	0.0043 (19)	0.0027 (16)
F	0.140 (2)	0.0664 (16)	0.091 (2)	−0.0069 (16)	−0.0093 (18)	0.0074 (14)
N1	0.064 (2)	0.077 (3)	0.052 (2)	−0.0011 (18)	−0.0054 (17)	0.0085 (18)
N2	0.082 (2)	0.084 (2)	0.0407 (18)	−0.0013 (19)	−0.0027 (17)	0.0109 (16)
N3	0.086 (2)	0.076 (2)	0.0349 (17)	−0.0007 (19)	0.0027 (16)	0.0037 (15)
C1	0.106 (4)	0.065 (3)	0.104 (4)	−0.001 (3)	0.014 (3)	0.013 (3)
C2	0.071 (3)	0.074 (3)	0.059 (3)	0.002 (2)	0.002 (2)	0.004 (2)
C3	0.094 (3)	0.079 (3)	0.049 (2)	0.005 (2)	−0.002 (2)	0.005 (2)
C4	0.085 (3)	0.070 (3)	0.051 (2)	0.002 (2)	0.000 (2)	0.0147 (19)
C5	0.061 (2)	0.070 (3)	0.050 (2)	−0.003 (2)	0.0007 (18)	0.0064 (19)
C6	0.075 (2)	0.074 (2)	0.048 (2)	0.0045 (19)	0.003 (2)	0.009 (3)
C7	0.080 (3)	0.071 (3)	0.063 (3)	0.012 (2)	0.000 (2)	0.014 (2)
C8	0.067 (2)	0.077 (3)	0.050 (2)	0.000 (2)	0.0010 (18)	0.0091 (19)
C9	0.057 (2)	0.073 (3)	0.0419 (19)	−0.0012 (19)	−0.0034 (16)	0.0054 (18)
C10	0.0435 (18)	0.085 (3)	0.0337 (18)	0.0011 (18)	−0.0032 (14)	0.0043 (17)
C11	0.0456 (19)	0.075 (3)	0.0328 (17)	−0.0029 (17)	−0.0051 (13)	0.0045 (18)
C12	0.059 (2)	0.086 (3)	0.0384 (16)	−0.0027 (18)	−0.003 (2)	0.003 (3)
C13	0.065 (2)	0.085 (3)	0.049 (2)	−0.010 (2)	−0.0044 (19)	0.006 (2)
C14	0.075 (3)	0.070 (3)	0.057 (3)	−0.004 (2)	−0.009 (2)	0.007 (2)
C15	0.081 (3)	0.082 (3)	0.049 (2)	0.005 (2)	−0.003 (2)	−0.007 (2)
C16	0.060 (2)	0.083 (3)	0.0388 (18)	0.001 (2)	0.0008 (18)	−0.0020 (18)

Geometric parameters (Å, °)

S—C10	1.706 (4)	C4—H4A	0.9300
S—C9	1.734 (4)	C5—C6	1.381 (5)
O—C2	1.365 (6)	C5—C8	1.436 (6)
O—C1	1.441 (6)	C6—C7	1.379 (6)
F—C14	1.347 (5)	C6—H6A	0.9300
N1—C8	1.287 (6)	C7—H7A	0.9300
N1—C9	1.385 (5)	C8—H8A	0.9300
N2—C9	1.309 (5)	C10—C11	1.459 (6)
N2—N3	1.379 (5)	C11—C16	1.401 (5)
N3—C10	1.323 (5)	C11—C12	1.402 (7)
C1—H1B	0.9600	C12—C13	1.370 (5)
C1—H1C	0.9600	C12—H12A	0.9300
C1—H1D	0.9600	C13—C14	1.370 (7)
C2—C3	1.374 (6)	C13—H13A	0.9300
C2—C7	1.388 (6)	C14—C15	1.375 (6)
C3—C4	1.377 (6)	C15—C16	1.376 (6)
C3—H3B	0.9300	C15—H15A	0.9300
C4—C5	1.403 (6)	C16—H16A	0.9300

C10—S—C9	87.1 (2)	C2—C7—H7A	120.4
C2—O—C1	117.0 (4)	N1—C8—C5	124.2 (4)
C8—N1—C9	118.8 (4)	N1—C8—H8A	117.9
C9—N2—N3	112.0 (3)	C5—C8—H8A	117.9
C10—N3—N2	112.2 (3)	N2—C9—N1	120.5 (4)
O—C1—H1B	109.5	N2—C9—S	114.3 (3)
O—C1—H1C	109.5	N1—C9—S	125.2 (3)
H1B—C1—H1C	109.5	N3—C10—C11	122.0 (4)
O—C1—H1D	109.5	N3—C10—S	114.4 (3)
H1B—C1—H1D	109.5	C11—C10—S	123.5 (3)
H1C—C1—H1D	109.5	C16—C11—C12	118.0 (4)
O—C2—C3	114.8 (4)	C16—C11—C10	121.0 (3)
O—C2—C7	125.4 (4)	C12—C11—C10	121.0 (4)
C3—C2—C7	119.9 (4)	C13—C12—C11	121.1 (5)
C2—C3—C4	120.6 (4)	C13—C12—H12A	119.5
C2—C3—H3B	119.7	C11—C12—H12A	119.5
C4—C3—H3B	119.7	C14—C13—C12	119.0 (5)
C3—C4—C5	120.5 (4)	C14—C13—H13A	120.5
C3—C4—H4A	119.7	C12—C13—H13A	120.5
C5—C4—H4A	119.7	F—C14—C13	119.0 (4)
C6—C5—C4	117.8 (4)	F—C14—C15	118.8 (4)
C6—C5—C8	123.0 (4)	C13—C14—C15	122.2 (4)
C4—C5—C8	119.2 (4)	C14—C15—C16	118.7 (4)
C7—C6—C5	122.0 (4)	C14—C15—H15A	120.6
C7—C6—H6A	119.0	C16—C15—H15A	120.6
C5—C6—H6A	119.0	C15—C16—C11	121.0 (4)
C6—C7—C2	119.3 (4)	C15—C16—H16A	119.5
C6—C7—H7A	120.4	C11—C16—H16A	119.5
C9—N2—N3—C10	−1.3 (5)	C10—S—C9—N2	−0.2 (3)
C1—O—C2—C3	−173.1 (4)	C10—S—C9—N1	−179.1 (4)
C1—O—C2—C7	6.2 (7)	N2—N3—C10—C11	178.3 (3)
O—C2—C3—C4	178.5 (4)	N2—N3—C10—S	1.1 (4)
C7—C2—C3—C4	−0.9 (7)	C9—S—C10—N3	−0.5 (3)
C2—C3—C4—C5	0.8 (7)	C9—S—C10—C11	−177.7 (3)
C3—C4—C5—C6	0.2 (6)	N3—C10—C11—C16	−9.2 (6)
C3—C4—C5—C8	−178.3 (4)	S—C10—C11—C16	167.7 (3)
C4—C5—C6—C7	−1.1 (6)	N3—C10—C11—C12	174.2 (4)
C8—C5—C6—C7	177.5 (4)	S—C10—C11—C12	−8.8 (5)
C5—C6—C7—C2	0.9 (7)	C16—C11—C12—C13	−0.1 (6)
O—C2—C7—C6	−179.2 (4)	C10—C11—C12—C13	176.6 (3)
C3—C2—C7—C6	0.1 (7)	C11—C12—C13—C14	−0.5 (6)
C9—N1—C8—C5	178.4 (3)	C12—C13—C14—F	−178.6 (3)
C6—C5—C8—N1	−3.1 (7)	C12—C13—C14—C15	1.4 (7)
C4—C5—C8—N1	175.4 (4)	F—C14—C15—C16	178.5 (4)
N3—N2—C9—N1	179.8 (3)	C13—C14—C15—C16	−1.5 (7)
N3—N2—C9—S	0.9 (5)	C14—C15—C16—C11	0.9 (6)
C8—N1—C9—N2	164.0 (4)	C12—C11—C16—C15	−0.1 (6)
C8—N1—C9—S	−17.2 (6)	C10—C11—C16—C15	−176.7 (4)

Hydrogen-bond geometry (Å, °)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
C8—H8A···S	0.93	2.59	3.043 (5)	110.
C12—H12A···S	0.93	2.75	3.138 (4)	106.
C12—H12A···N3^{i}	0.93	2.62	3.451 (6)	148.

Symmetry codes: (i) −*x*+2, −*y*+1, *z*−1/2.

Fig. 1

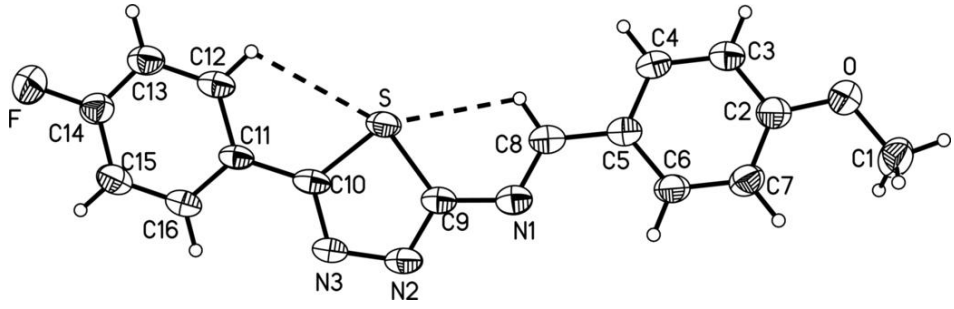
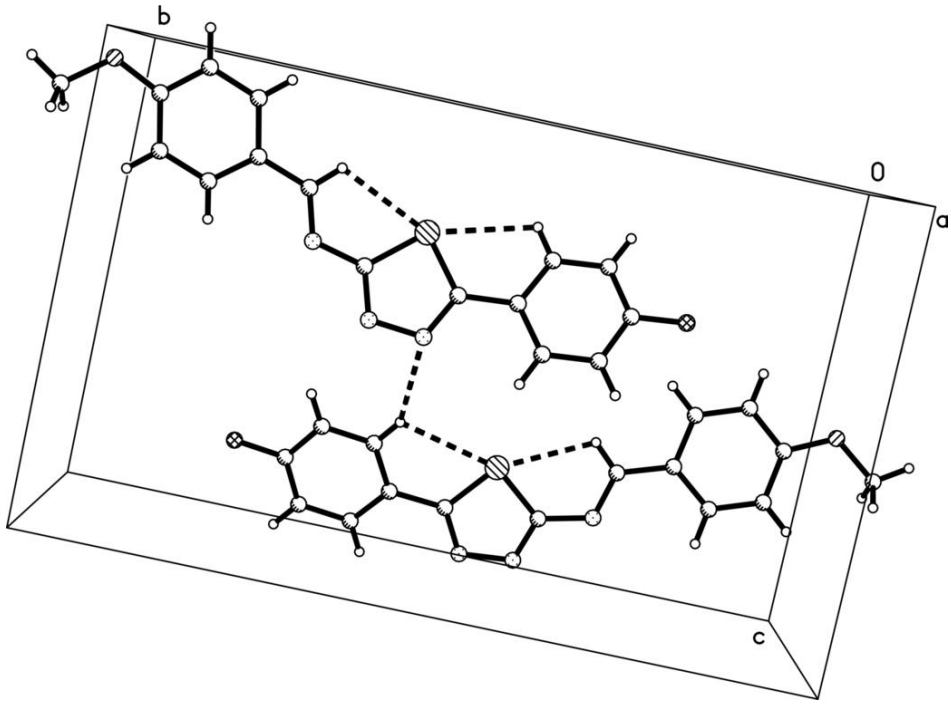


Fig. 2



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Dibutyl{*N*′-[1-(5-chloro-2-oxidophenyl-κ*O*)ethylidene]-3-hydroxy-2-naphthohydrazidato-κ^2*N*′,*O*^{2}}tin(IV)

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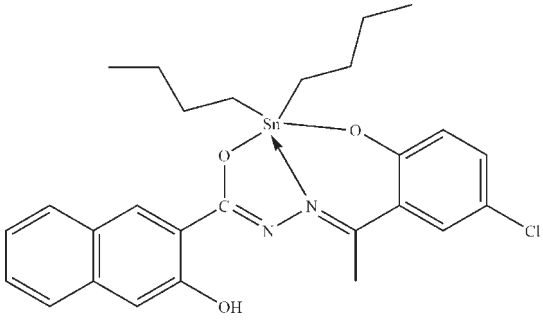
Key indicators: single-crystal X-ray study; T = 100 K; mean σ(C–C) = 0.007 Å; R factor = 0.050; wR factor = 0.101; data-to-parameter ratio = 14.3.

The five-coordinate Sn^{IV} atoms in the two crystallographically independent molecules of the title compound, [Sn(C$_4$H$_9$)$_2$(C$_{19}$H$_{13}$ClN$_2$O$_3$)], are in distorted *cis*-C$_2$NO$_2$Sn trigonal-bipyramidal coordination environments. The tridentate dianion of the Schiff base, *N*′-[1-(5-chloro-2-oxidophenyl)-ethylidene]-3-hydroxy-2-naphthohydrazide, displays intermolecular O—H···N hydrogen bonding, which stabilizes the overall compound.

Related literature

For a related structure, see: Lee *et al.* (2009). For the specific biological activity of metal complexes with hydrazone ligands, see: Bernhardt *et al.* (2006); Ainscough *et al.* (1999); Mohd Ali *et al.* (2004).



Experimental

Crystal data

[Sn(C$_4$H$_9$)$_2$(C$_{19}$H$_{13}$ClN$_2$O$_3$)]
M_r = 585.67
Monoclinic, $P2_1/n$
a = 24.8256 (13) Å
b = 7.1994 (4) Å
c = 28.3649 (15) Å
β = 96.376 (1)°
V = 5038.3 (5) Å^3
Z = 8
Mo $K\alpha$ radiation
μ = 1.15 mm^{-1}
T = 100 K
0.25 × 0.25 × 0.15 mm

Data collection

Bruker APEXII CCD area-detector diffractometer
Absorption correction: multi-scan (*SADABS*; Bruker, 2009)
T_{min} = 0.762, T_{max} = 0.846
37459 measured reflections
8881 independent reflections
8369 reflections with $I > 2\sigma(I)$
R_{int} = 0.032

Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.050
$wR(F^2)$ = 0.101
S = 1.32
8881 reflections
621 parameters
H-atom parameters constrained
$\Delta\rho_{max}$ = 0.82 e Å^{-3}
$\Delta\rho_{min}$ = −1.50 e Å^{-3}

Table 1
Hydrogen-bond geometry (Å, °).

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
O3—H3*A*···N2	0.84	1.85	2.602 (5)	147
O6—H6*A*···N4	0.84	1.88	2.617 (5)	146

Data collection: *APEX2* (Bruker, 2009); cell refinement: *SAINT* (Bruker, 2009); data reduction: *SAINT*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *X-SEED* (Barbour, 2001); software used to prepare material for publication: *publCIF* (Westrip, 2010).

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Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: HG2693).

References

Ainscough, E. W., Brodie, A. M., Denny, W. A., Finlay, G. J., Gothe, S. A. & Ranford, J. D. (1999). *J. Inorg. Biochem.* **77**, 125–133
Barbour, L. J. (2001). *J. Supramol. Chem.* **1**, 189–191.
Bernhardt, P. V., Mattsson, J. & Richardson, D. R. (2006). *Inorg. Chem.* **45**, 752–760.
Bruker (2009). *APEX2*, *SAINT* and *SADABS*. Bruker AXS Inc., Madison, Wisconsin, USA.
Lee, S. M., Lo, K. M., Ali, H. M. & Ng, S. W. (2009). *Acta Cryst.* E**65**, m1689.
Mohd Ali, H. M., Zain, S., Basirun, W. J., Rahuma, S. M., Sharifah Rohaiza, S. O., Abdullah, N. & Teoh, H. L. (2004). *Malays. J. Sci.* **23**, 119–127.
Sheldrick, G. M. (2008). *Acta Cryst.* A**64**, 112–122.
Westrip, S. P. (2010). *publCIF*. In preparation.

supplementary materials

Acta Cryst. (2010). E**66**, m803 [**doi:10.1107/S1600536810021896**]

Dibutyl{*N*'-[1-(5-chloro-2-oxidophenyl-κ*O*)ethylidene]-3-hydroxy-2-naphthohydrazidato-κ^2N',O^2}tin(IV)

S. M. Lee, H. Mohd Ali and K. M. Lo

Comment

Schiff bases derived from substituted salicylaldehydes have been widely used as polydentate ligands in the preparation of metal complexes. The metal complexes of these hydrazones with substituted salicylaldehydes are known to possess potential biological activities such as antifungal, anticancer and many others [Bernhardt *et al.* (2006), Ainscough *et al.* (1999), Mohd Ali *et al.* (2004)]. We have earlier reported the synthesis and molecular structure of a diphenyltin complex of the Schiff base derived from the reaction of 3-hydroxy-2-naphthoic hydrazide with 5-chlorobenzaldehyde [Lee *et al.* (2009)]. The crystal structure of this complex consists of discrete molecules in which the tin atom is *O,N, O'*-chelated by the deprotonated Schiff base ligand. As an extension of our work in structural characterization of organotin with hydrazones, we report here the molecular structure of a dibutyltin complex of a Schiff base derived from the reaction of 3-hydroxy-2-naphthoic hydrazide with 5-chloro-2-hydroxyacetophenone. The unit cell of the title complex consists of two crystallographically independent molecules. In both molecules, the Schiff base ligand, *N'*-[1-(5-chloro-2-oxidophenyl)ethylidene-3-hydroxy-2-naphthohydrazone] forms a tridentate dianion which coordinated to the dibutyltin fragment in a distorted *cis*-C_2NO_2Sn trigonal bipyramidal configuration; the axial O—Sn—O angle are 153.03 (13)^o and 152.41 (13)^o.

Experimental

The Schiff base ligand was prepared by the condensation reaction of 3-hydroxy-2-naphthoic hydrazide with 5-chloro-2-hydroxyacetophenone. The prepared Schiff base (0.74 g, 2.0 mmol), dibutyltin dichloride (0.61 g, 2 mmol) and triethylamine (0.6 ml) were refluxed in 50 ml of ethanol for 5 h. The solution was left for crystallizaton at room temperature during which yellow crystals were obtained.

Refinement

Hydrogen atoms were placed at calculated positions (C–H 0.95 to 0.98 Å) and were treated as riding on their parent carbon atoms, with *U*(H) set to 1.2–1.5 times U_{eq}(C). The hydroxy-H was refined with a restraint of 0.84 ± 0.01 Å.

Figures

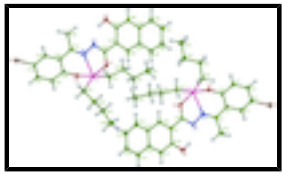


Fig. 1. The molecular structure of {*N*'-[1-(5-chloro-2-oxidophenyl-κ*O*)ethylidene]-3-hydroxy-2- naphthohydrazidato-κ^2N',O}dibutyltin(IV) showing 50% probability displacement ellipsoids and the atom numbering. Hydrogen atoms are drawn as spheres of arbitrary radius.

Dibutyl{*N*'-[1-(5-chloro-2-oxidophenyl-κ*O*)ethylidene]- 3-hydroxy-2-naphthohydrazidato-κ^2*N*',*O*^{2}}tin(IV)

Crystal data

$[Sn(C_4H_9)_2(C_{19}H_{13}ClN_2O_3)]$	$F(000) = 2384$
$M_r = 585.67$	$D_x = 1.544$ Mg m^{-3}
Monoclinic, $P2_1/n$	Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å
Hall symbol: -P 2yn	Cell parameters from 9440 reflections
$a = 24.8256$ (13) Å	$\theta = 3.0–28.3°$
$b = 7.1994$ (4) Å	$\mu = 1.15$ mm^{-1}
$c = 28.3649$ (15) Å	$T = 100$ K
$\beta = 96.376$ (1)°	Prism, yellow
$V = 5038.3$ (5) Å^3	0.25 × 0.25 × 0.15 mm
$Z = 8$	

Data collection

Bruker APEXII CCD area-detector diffractometer	8881 independent reflections
Radiation source: fine-focus sealed tube	8369 reflections with $I > 2\sigma(I)$
graphite	$R_{int} = 0.032$
ω scans	$\theta_{max} = 25.0°$, $\theta_{min} = 1.0°$
Absorption correction: multi-scan (*SADABS*; Bruker, 2009)	$h = -29\rightarrow29$
$T_{min} = 0.762$, $T_{max} = 0.846$	$k = -8\rightarrow8$
37459 measured reflections	$l = -33\rightarrow33$

Refinement

Refinement on F^2	Primary atom site location: structure-invariant direct methods
Least-squares matrix: full	Secondary atom site location: difference Fourier map
$R[F^2 > 2\sigma(F^2)] = 0.050$	Hydrogen site location: inferred from neighbouring sites
$wR(F^2) = 0.101$	H-atom parameters constrained
$S = 1.32$	$w = 1/[\sigma^2(F_o^2) + (0.0158P)^2 + 27.1939P]$ where $P = (F_o^2 + 2F_c^2)/3$
8881 reflections	$(\Delta/\sigma)_{max} = 0.002$
621 parameters	$\Delta\rho_{max} = 0.82$ e Å^{-3}
0 restraints	$\Delta\rho_{min} = -1.50$ e Å^{-3}

Special details

Geometry. All e.s.d.'s (except the e.s.d. in the dihedral angle between two l.s. planes)

are estimated using the full covariance matrix. The cell e.s.d.'s are taken

into account individually in the estimation of e.s.d.'s in distances, angles and torsion angles; correlations between e.s.d.'s in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell e.s.d.'s is used for estimating e.s.d.'s involving l.s. planes.

Refinement. Refinement of F^2 against ALL reflections. The weighted *R*-factor *wR* and goodness of fit *S* are based on F^2, conventional *R*-factors *R* are based on *F*, with *F* set to zero for negative F^2. The threshold expression of $F^2 > \sigma(F^2)$ is used only for calculating *R*-factors(gt) *etc*. and is not relevant to the choice of reflections for refinement. *R*-factors based on F^2 are statistically about twice as large as those based on *F*, and *R*-factors based on ALL data will be even larger.

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å^2)

	x	*y*	*z*	U_{iso}*/U_{eq}
Sn1	0.339899 (13)	0.57545 (4)	0.642199 (11)	0.01339 (9)
Sn2	0.663321 (13)	0.45272 (4)	0.866500 (11)	0.01362 (9)
Cl1	0.09889 (5)	0.79045 (19)	0.48251 (5)	0.0265 (3)
Cl2	0.90500 (5)	0.15766 (18)	1.01382 (4)	0.0222 (3)
N1	0.26021 (16)	0.6163 (5)	0.66655 (13)	0.0155 (9)
N2	0.26107 (16)	0.6250 (5)	0.71576 (13)	0.0156 (9)
N3	0.73912 (16)	0.3783 (5)	0.83779 (13)	0.0143 (8)
N4	0.73331 (17)	0.3608 (5)	0.78836 (13)	0.0154 (9)
O1	0.29315 (13)	0.4587 (5)	0.58494 (11)	0.0181 (7)
O2	0.35201 (13)	0.6827 (5)	0.71334 (11)	0.0169 (7)
O3	0.22477 (14)	0.5987 (6)	0.79810 (12)	0.0249 (8)
H3A	0.2236	0.5980	0.7684	0.037*
O4	0.71848 (14)	0.5613 (5)	0.91961 (11)	0.0190 (7)
O5	0.64255 (13)	0.3284 (5)	0.79779 (11)	0.0172 (7)
O6	0.76138 (14)	0.3611 (6)	0.70211 (12)	0.0240 (8)
H6A	0.7662	0.3611	0.7319	0.036*
C1	0.2097 (2)	0.6282 (6)	0.58896 (17)	0.0161 (10)
C2	0.24893 (19)	0.5410 (6)	0.56375 (17)	0.0158 (10)
C3	0.2405 (2)	0.5362 (7)	0.51393 (17)	0.0180 (10)
H3	0.2668	0.4781	0.4970	0.022*
C4	0.1953 (2)	0.6129 (7)	0.48898 (17)	0.0175 (10)
H4	0.1905	0.6096	0.4553	0.021*
C5	0.1570 (2)	0.6953 (7)	0.51414 (18)	0.0191 (11)
C6	0.1634 (2)	0.7064 (7)	0.56248 (17)	0.0185 (11)
H6	0.1367	0.7670	0.5785	0.022*

C7	0.2130 (2)	0.6357 (6)	0.64094 (17)	0.0157 (10)
C8	0.3104 (2)	0.6565 (6)	0.73630 (16)	0.0144 (10)
C9	0.3190 (2)	0.6643 (6)	0.78861 (17)	0.0157 (10)
C10	0.27594 (19)	0.6359 (7)	0.81743 (17)	0.0167 (10)
C11	0.2865 (2)	0.6438 (7)	0.86580 (17)	0.0188 (11)
H11	0.2580	0.6214	0.8847	0.023*
C12	0.3386 (2)	0.6845 (7)	0.88818 (17)	0.0174 (10)
C13	0.3501 (2)	0.7017 (7)	0.93840 (18)	0.0221 (11)
H13	0.3221	0.6813	0.9581	0.027*
C14	0.4011 (2)	0.7474 (7)	0.95847 (18)	0.0253 (12)
H14	0.4079	0.7604	0.9919	0.030*
C15	0.4434 (2)	0.7753 (8)	0.93039 (18)	0.0258 (12)
H15	0.4786	0.8063	0.9450	0.031*
C16	0.4345 (2)	0.7584 (7)	0.88228 (18)	0.0231 (11)
H16	0.4636	0.7767	0.8636	0.028*
C17	0.3820 (2)	0.7133 (6)	0.85986 (17)	0.0164 (10)
C18	0.3703 (2)	0.7002 (6)	0.81034 (17)	0.0164 (10)
H18	0.3989	0.7169	0.7911	0.020*
C19	0.1629 (2)	0.6682 (7)	0.66458 (18)	0.0198 (11)
H19A	0.1657	0.6011	0.6948	0.030*
H19B	0.1313	0.6234	0.6440	0.030*
H19C	0.1589	0.8014	0.6704	0.030*
C20	0.3635 (2)	0.8241 (7)	0.60966 (17)	0.0181 (10)
H20A	0.3316	0.8751	0.5898	0.022*
H20B	0.3745	0.9162	0.6348	0.022*
C21	0.4097 (2)	0.8011 (7)	0.57894 (17)	0.0196 (11)
H21A	0.3985	0.7128	0.5529	0.024*
H21B	0.4172	0.9222	0.5645	0.024*
C22	0.4611 (2)	0.7306 (8)	0.60696 (19)	0.0261 (12)
H22A	0.4533	0.6115	0.6222	0.031*
H22B	0.4729	0.8208	0.6324	0.031*
C23	0.5069 (2)	0.7017 (8)	0.5766 (2)	0.0341 (14)
H23A	0.5391	0.6569	0.5965	0.051*
H23B	0.5153	0.8196	0.5618	0.051*
H23C	0.4960	0.6098	0.5519	0.051*
C24	0.3781 (2)	0.3161 (6)	0.66053 (16)	0.0158 (10)
H24A	0.3497	0.2197	0.6606	0.019*
H24B	0.4013	0.2827	0.6356	0.019*
C25	0.4127 (2)	0.3118 (7)	0.70831 (18)	0.0218 (11)
H25A	0.3916	0.3649	0.7327	0.026*
H25B	0.4449	0.3916	0.7066	0.026*
C26	0.4315 (2)	0.1172 (7)	0.72372 (18)	0.0233 (12)
H26A	0.4526	0.0628	0.6995	0.028*
H26B	0.3996	0.0371	0.7263	0.028*
C27	0.4666 (2)	0.1227 (9)	0.7715 (2)	0.0330 (14)
H27A	0.4744	−0.0044	0.7826	0.050*
H27B	0.4472	0.1888	0.7947	0.050*
H27C	0.5007	0.1873	0.7679	0.050*
C28	0.79522 (19)	0.3650 (6)	0.91222 (16)	0.0143 (10)

C29	0.76097 (18)	0.4648 (6)	0.93933 (16)	0.0133 (9)
C30	0.7725 (2)	0.4687 (7)	0.98883 (17)	0.0168 (10)
H30	0.7496	0.5376	1.0071	0.020*
C31	0.8163 (2)	0.3747 (7)	1.01155 (17)	0.0167 (10)
H31	0.8234	0.3775	1.0451	0.020*
C32	0.84958 (19)	0.2763 (6)	0.98459 (17)	0.0150 (10)
C33	0.84028 (19)	0.2696 (6)	0.93631 (17)	0.0138 (10)
H33	0.8640	0.2010	0.9188	0.017*
C34	0.7875 (2)	0.3568 (6)	0.86017 (17)	0.0156 (10)
C35	0.68199 (19)	0.3368 (6)	0.77180 (17)	0.0153 (10)
C36	0.66883 (19)	0.3165 (6)	0.71995 (16)	0.0148 (10)
C37	0.70804 (19)	0.3304 (7)	0.68733 (17)	0.0165 (10)
C38	0.69298 (19)	0.3140 (7)	0.63940 (17)	0.0172 (10)
H38	0.7196	0.3257	0.6180	0.021*
C39	0.6383 (2)	0.2799 (6)	0.62151 (17)	0.0159 (10)
C40	0.6216 (2)	0.2574 (7)	0.57239 (18)	0.0221 (11)
H40	0.6475	0.2685	0.5503	0.027*
C41	0.5690 (2)	0.2201 (7)	0.55652 (18)	0.0236 (12)
H41	0.5587	0.2024	0.5236	0.028*
C42	0.5290 (2)	0.2073 (7)	0.58903 (18)	0.0237 (12)
H42	0.4923	0.1828	0.5776	0.028*
C43	0.5438 (2)	0.2303 (7)	0.63622 (18)	0.0223 (11)
H43	0.5172	0.2222	0.6577	0.027*
C44	0.5990 (2)	0.2664 (6)	0.65380 (17)	0.0164 (10)
C45	0.6156 (2)	0.2860 (7)	0.70265 (17)	0.0169 (10)
H45	0.5892	0.2777	0.7244	0.020*
C46	0.8346 (2)	0.3182 (7)	0.83287 (17)	0.0183 (11)
H46A	0.8328	0.4006	0.8052	0.028*
H46B	0.8332	0.1886	0.8222	0.028*
H46C	0.8685	0.3401	0.8533	0.028*
C47	0.6361 (2)	0.2234 (7)	0.90457 (18)	0.0217 (11)
H47A	0.6578	0.1134	0.8975	0.026*
H47B	0.6443	0.2498	0.9389	0.026*
C48	0.5764 (2)	0.1718 (7)	0.89511 (19)	0.0246 (12)
H48A	0.5690	0.0651	0.9154	0.029*
H48B	0.5684	0.1324	0.8616	0.029*
C49	0.5389 (2)	0.3319 (7)	0.90469 (19)	0.0229 (11)
H49A	0.5518	0.3891	0.9356	0.028*
H49B	0.5404	0.4277	0.8798	0.028*
C50	0.4805 (2)	0.2693 (8)	0.9054 (2)	0.0328 (14)
H50A	0.4576	0.3775	0.9097	0.049*
H50B	0.4783	0.1822	0.9316	0.049*
H50C	0.4680	0.2079	0.8753	0.049*
C51	0.6336 (2)	0.7244 (7)	0.84806 (17)	0.0185 (11)
H51A	0.6049	0.7546	0.8684	0.022*
H51B	0.6636	0.8138	0.8560	0.022*
C52	0.61069 (19)	0.7563 (7)	0.79624 (17)	0.0182 (11)
H52A	0.6091	0.8918	0.7902	0.022*
H52B	0.6361	0.7021	0.7755	0.022*

C53	0.5552 (2)	0.6757 (7)	0.78225 (18)	0.0220 (11)
H53A	0.5294	0.7298	0.8027	0.026*
H53B	0.5564	0.5399	0.7878	0.026*
C54	0.5348 (2)	0.7132 (8)	0.73038 (19)	0.0292 (13)
H54A	0.4967	0.6758	0.7242	0.044*
H54B	0.5565	0.6418	0.7099	0.044*
H54C	0.5381	0.8460	0.7237	0.044*

Atomic displacement parameters (Å^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Sn1	0.01504 (18)	0.01007 (16)	0.01526 (16)	0.00157 (13)	0.00262 (12)	0.00071 (12)
Sn2	0.01455 (18)	0.01240 (16)	0.01387 (16)	0.00251 (13)	0.00139 (12)	−0.00070 (13)
Cl1	0.0267 (7)	0.0260 (7)	0.0248 (7)	0.0067 (6)	−0.0070 (5)	0.0001 (5)
Cl2	0.0198 (6)	0.0236 (6)	0.0222 (6)	0.0062 (5)	−0.0030 (5)	0.0017 (5)
N1	0.020 (2)	0.012 (2)	0.015 (2)	0.0007 (17)	0.0031 (17)	−0.0005 (16)
N2	0.018 (2)	0.014 (2)	0.014 (2)	0.0022 (17)	0.0020 (16)	0.0017 (16)
N3	0.018 (2)	0.0119 (19)	0.0124 (19)	0.0017 (16)	0.0003 (16)	−0.0001 (15)
N4	0.021 (2)	0.012 (2)	0.013 (2)	0.0044 (17)	0.0009 (16)	−0.0008 (16)
O1	0.0158 (18)	0.0165 (17)	0.0218 (17)	0.0034 (14)	0.0014 (14)	−0.0027 (14)
O2	0.0186 (18)	0.0145 (17)	0.0179 (17)	0.0014 (14)	0.0039 (14)	−0.0009 (14)
O3	0.0180 (19)	0.037 (2)	0.0202 (18)	−0.0022 (17)	0.0053 (15)	−0.0045 (17)
O4	0.0200 (18)	0.0168 (17)	0.0195 (17)	0.0036 (15)	−0.0007 (14)	−0.0050 (14)
O5	0.0149 (18)	0.0212 (18)	0.0158 (16)	−0.0008 (14)	0.0034 (14)	−0.0036 (14)
O6	0.0142 (19)	0.038 (2)	0.0196 (18)	0.0012 (16)	0.0028 (14)	−0.0021 (17)
C1	0.018 (3)	0.008 (2)	0.022 (2)	−0.0023 (19)	0.001 (2)	0.0013 (19)
C2	0.015 (2)	0.009 (2)	0.023 (2)	0.0003 (19)	0.0003 (19)	0.001 (2)
C3	0.023 (3)	0.010 (2)	0.021 (2)	0.000 (2)	0.004 (2)	−0.001 (2)
C4	0.022 (3)	0.014 (2)	0.016 (2)	−0.002 (2)	0.000 (2)	−0.0022 (19)
C5	0.021 (3)	0.012 (2)	0.023 (3)	0.000 (2)	−0.003 (2)	0.001 (2)
C6	0.021 (3)	0.011 (2)	0.023 (3)	0.001 (2)	0.002 (2)	−0.002 (2)
C7	0.021 (3)	0.004 (2)	0.022 (3)	−0.0004 (19)	0.003 (2)	−0.0012 (18)
C8	0.020 (3)	0.008 (2)	0.016 (2)	0.0071 (19)	0.005 (2)	−0.0004 (18)
C9	0.018 (3)	0.009 (2)	0.021 (2)	0.0017 (19)	0.003 (2)	0.0001 (19)
C10	0.011 (2)	0.015 (2)	0.025 (3)	0.0046 (19)	0.007 (2)	−0.001 (2)
C11	0.017 (3)	0.017 (3)	0.024 (3)	0.004 (2)	0.010 (2)	0.002 (2)
C12	0.022 (3)	0.011 (2)	0.021 (2)	0.005 (2)	0.005 (2)	0.0002 (19)
C13	0.031 (3)	0.014 (2)	0.022 (3)	0.003 (2)	0.006 (2)	0.002 (2)
C14	0.042 (3)	0.018 (3)	0.015 (2)	0.007 (2)	0.000 (2)	0.000 (2)
C15	0.029 (3)	0.023 (3)	0.023 (3)	0.000 (2)	−0.006 (2)	0.001 (2)
C16	0.025 (3)	0.022 (3)	0.022 (3)	0.000 (2)	0.002 (2)	0.002 (2)
C17	0.020 (3)	0.010 (2)	0.020 (2)	0.004 (2)	0.003 (2)	0.0007 (19)
C18	0.019 (3)	0.011 (2)	0.020 (2)	0.003 (2)	0.007 (2)	−0.0010 (19)
C19	0.020 (3)	0.016 (2)	0.023 (3)	0.000 (2)	0.002 (2)	0.000 (2)
C20	0.019 (3)	0.013 (2)	0.023 (3)	0.004 (2)	0.006 (2)	0.002 (2)
C21	0.023 (3)	0.017 (2)	0.019 (2)	−0.002 (2)	0.003 (2)	0.002 (2)
C22	0.027 (3)	0.022 (3)	0.029 (3)	−0.002 (2)	0.004 (2)	0.007 (2)
C23	0.029 (3)	0.017 (3)	0.058 (4)	−0.002 (2)	0.011 (3)	0.004 (3)

C24	0.020 (3)	0.009 (2)	0.019 (2)	0.006 (2)	0.004 (2)	0.0058 (19)
C25	0.018 (3)	0.023 (3)	0.024 (3)	0.006 (2)	0.001 (2)	0.004 (2)
C26	0.022 (3)	0.025 (3)	0.022 (3)	0.008 (2)	0.004 (2)	0.007 (2)
C27	0.036 (3)	0.034 (3)	0.029 (3)	0.014 (3)	0.003 (3)	0.009 (3)
C28	0.015 (2)	0.011 (2)	0.017 (2)	−0.0028 (19)	0.0004 (19)	−0.0012 (18)
C29	0.009 (2)	0.012 (2)	0.019 (2)	−0.0032 (19)	0.0009 (18)	−0.0004 (19)
C30	0.017 (3)	0.013 (2)	0.021 (2)	−0.004 (2)	0.006 (2)	−0.004 (2)
C31	0.018 (3)	0.013 (2)	0.019 (2)	−0.003 (2)	0.001 (2)	−0.0006 (19)
C32	0.010 (2)	0.012 (2)	0.022 (3)	0.0022 (19)	−0.0038 (19)	−0.0013 (19)
C33	0.011 (2)	0.009 (2)	0.022 (2)	−0.0018 (18)	0.0026 (19)	−0.0027 (19)
C34	0.019 (3)	0.009 (2)	0.019 (2)	−0.0020 (19)	0.002 (2)	−0.0008 (19)
C35	0.014 (3)	0.010 (2)	0.022 (2)	0.0049 (19)	0.002 (2)	−0.0015 (19)
C36	0.017 (3)	0.010 (2)	0.017 (2)	0.0046 (19)	0.0026 (19)	0.0000 (19)
C37	0.010 (2)	0.014 (2)	0.025 (3)	0.0009 (19)	0.004 (2)	−0.003 (2)
C38	0.013 (2)	0.021 (3)	0.019 (2)	0.004 (2)	0.0044 (19)	0.000 (2)
C39	0.017 (3)	0.012 (2)	0.018 (2)	0.007 (2)	0.0003 (19)	0.0004 (19)
C40	0.029 (3)	0.017 (3)	0.020 (3)	0.005 (2)	0.000 (2)	0.000 (2)
C41	0.030 (3)	0.020 (3)	0.019 (3)	0.003 (2)	−0.004 (2)	−0.003 (2)
C42	0.025 (3)	0.018 (3)	0.026 (3)	−0.003 (2)	−0.006 (2)	0.002 (2)
C43	0.023 (3)	0.020 (3)	0.024 (3)	−0.002 (2)	0.002 (2)	0.000 (2)
C44	0.017 (3)	0.012 (2)	0.020 (2)	0.003 (2)	−0.001 (2)	0.0004 (19)
C45	0.016 (3)	0.014 (2)	0.021 (2)	0.005 (2)	0.003 (2)	−0.001 (2)
C46	0.023 (3)	0.015 (2)	0.017 (2)	0.001 (2)	0.001 (2)	−0.001 (2)
C47	0.027 (3)	0.015 (2)	0.024 (3)	0.002 (2)	0.006 (2)	0.004 (2)
C48	0.034 (3)	0.017 (3)	0.024 (3)	−0.007 (2)	0.008 (2)	0.000 (2)
C49	0.023 (3)	0.017 (3)	0.029 (3)	0.002 (2)	−0.001 (2)	0.004 (2)
C50	0.023 (3)	0.025 (3)	0.052 (4)	−0.006 (2)	0.011 (3)	−0.007 (3)
C51	0.019 (3)	0.019 (3)	0.018 (2)	0.003 (2)	0.005 (2)	0.001 (2)
C52	0.011 (2)	0.020 (3)	0.024 (3)	0.004 (2)	0.003 (2)	0.004 (2)
C53	0.013 (3)	0.021 (3)	0.032 (3)	0.003 (2)	0.002 (2)	0.005 (2)
C54	0.030 (3)	0.027 (3)	0.029 (3)	0.001 (3)	−0.007 (2)	0.000 (2)

Geometric parameters (Å, °)

Sn1—O1	2.067 (3)	C23—H23C	0.9800
Sn1—C20	2.126 (5)	C24—C25	1.522 (7)
Sn1—C24	2.132 (4)	C24—H24A	0.9900
Sn1—O2	2.150 (3)	C24—H24B	0.9900
Sn1—N1	2.186 (4)	C25—C26	1.526 (7)
Sn2—O4	2.073 (3)	C25—H25A	0.9900
Sn2—C47	2.123 (5)	C25—H25B	0.9900
Sn2—C51	2.135 (5)	C26—C27	1.528 (7)
Sn2—O5	2.155 (3)	C26—H26A	0.9900
Sn2—N3	2.198 (4)	C26—H26B	0.9900
Cl1—C5	1.751 (5)	C27—H27A	0.9800
Cl2—C32	1.748 (5)	C27—H27B	0.9800
N1—C7	1.316 (6)	C27—H27C	0.9800
N1—N2	1.395 (5)	C28—C29	1.406 (7)
N2—C8	1.316 (6)	C28—C33	1.421 (7)

N3—C34	1.304 (6)	C28—C34	1.469 (6)
N3—N4	1.399 (5)	C29—C30	1.402 (6)
N4—C35	1.319 (6)	C30—C31	1.378 (7)
O1—C2	1.331 (6)	C30—H30	0.9500
O2—C8	1.294 (6)	C31—C32	1.383 (7)
O3—C10	1.353 (6)	C31—H31	0.9500
O3—H3A	0.8400	C32—C33	1.364 (7)
O4—C29	1.333 (6)	C33—H33	0.9500
O5—C35	1.291 (6)	C34—C46	1.498 (7)
O6—C37	1.362 (6)	C35—C36	1.478 (6)
O6—H6A	0.8400	C36—C45	1.375 (7)
C1—C2	1.417 (7)	C36—C37	1.419 (7)
C1—C6	1.418 (7)	C37—C38	1.375 (7)
C1—C7	1.469 (7)	C38—C39	1.418 (7)
C2—C3	1.406 (7)	C38—H38	0.9500
C3—C4	1.374 (7)	C39—C44	1.414 (7)
C3—H3	0.9500	C39—C40	1.418 (7)
C4—C5	1.385 (7)	C40—C41	1.359 (8)
C4—H4	0.9500	C40—H40	0.9500
C5—C6	1.365 (7)	C41—C42	1.431 (8)
C6—H6	0.9500	C41—H41	0.9500
C7—C19	1.496 (7)	C42—C43	1.358 (7)
C8—C9	1.476 (6)	C42—H42	0.9500
C9—C18	1.377 (7)	C43—C44	1.427 (7)
C9—C10	1.431 (7)	C43—H43	0.9500
C10—C11	1.369 (7)	C44—C45	1.408 (7)
C11—C12	1.407 (7)	C45—H45	0.9500
C11—H11	0.9500	C46—H46A	0.9800
C12—C13	1.427 (7)	C46—H46B	0.9800
C12—C17	1.427 (7)	C46—H46C	0.9800
C13—C14	1.370 (8)	C47—C48	1.524 (7)
C13—H13	0.9500	C47—H47A	0.9900
C14—C15	1.402 (8)	C47—H47B	0.9900
C14—H14	0.9500	C48—C49	1.525 (7)
C15—C16	1.363 (7)	C48—H48A	0.9900
C15—H15	0.9500	C48—H48B	0.9900
C16—C17	1.424 (7)	C49—C50	1.519 (7)
C16—H16	0.9500	C49—H49A	0.9900
C17—C18	1.405 (7)	C49—H49B	0.9900
C18—H18	0.9500	C50—H50A	0.9800
C19—H19A	0.9800	C50—H50B	0.9800
C19—H19B	0.9800	C50—H50C	0.9800
C19—H19C	0.9800	C51—C52	1.533 (7)
C20—C21	1.525 (7)	C51—H51A	0.9900
C20—H20A	0.9900	C51—H51B	0.9900
C20—H20B	0.9900	C52—C53	1.507 (7)
C21—C22	1.514 (7)	C52—H52A	0.9900
C21—H21A	0.9900	C52—H52B	0.9900
C21—H21B	0.9900	C53—C54	1.526 (7)

C22—C23	1.514 (8)	C53—H53A	0.9900
C22—H22A	0.9900	C53—H53B	0.9900
C22—H22B	0.9900	C54—H54A	0.9800
C23—H23A	0.9800	C54—H54B	0.9800
C23—H23B	0.9800	C54—H54C	0.9800
O1—Sn1—C20	99.15 (17)	C24—C25—H25A	108.9
O1—Sn1—C24	91.79 (16)	C26—C25—H25A	108.9
C20—Sn1—C24	134.95 (19)	C24—C25—H25B	108.9
O1—Sn1—O2	153.02 (13)	C26—C25—H25B	108.9
C20—Sn1—O2	95.08 (16)	H25A—C25—H25B	107.7
C24—Sn1—O2	94.22 (15)	C25—C26—C27	110.9 (5)
O1—Sn1—N1	81.61 (14)	C25—C26—H26A	109.5
C20—Sn1—N1	109.07 (16)	C27—C26—H26A	109.5
C24—Sn1—N1	115.74 (17)	C25—C26—H26B	109.5
O2—Sn1—N1	72.08 (13)	C27—C26—H26B	109.5
O4—Sn2—C47	98.34 (17)	H26A—C26—H26B	108.1
O4—Sn2—C51	90.85 (17)	C26—C27—H27A	109.5
C47—Sn2—C51	135.8 (2)	C26—C27—H27B	109.5
O4—Sn2—O5	152.42 (13)	H27A—C27—H27B	109.5
C47—Sn2—O5	94.55 (17)	C26—C27—H27C	109.5
C51—Sn2—O5	96.75 (16)	H27A—C27—H27C	109.5
O4—Sn2—N3	80.65 (14)	H27B—C27—H27C	109.5
C47—Sn2—N3	109.41 (17)	C29—C28—C33	118.4 (4)
C51—Sn2—N3	114.78 (17)	C29—C28—C34	123.4 (4)
O5—Sn2—N3	72.08 (13)	C33—C28—C34	118.2 (4)
C7—N1—N2	117.5 (4)	O4—C29—C30	118.3 (4)
C7—N1—Sn1	128.4 (3)	O4—C29—C28	122.4 (4)
N2—N1—Sn1	114.1 (3)	C30—C29—C28	119.3 (4)
C8—N2—N1	111.1 (4)	C31—C30—C29	121.4 (4)
C34—N3—N4	117.7 (4)	C31—C30—H30	119.3
C34—N3—Sn2	129.0 (3)	C29—C30—H30	119.3
N4—N3—Sn2	113.3 (3)	C30—C31—C32	118.8 (4)
C35—N4—N3	110.9 (4)	C30—C31—H31	120.6
C2—O1—Sn1	122.5 (3)	C32—C31—H31	120.6
C8—O2—Sn1	112.6 (3)	C33—C32—C31	121.9 (4)
C10—O3—H3A	109.5	C33—C32—Cl2	119.7 (4)
C29—O4—Sn2	122.5 (3)	C31—C32—Cl2	118.4 (4)
C35—O5—Sn2	112.1 (3)	C32—C33—C28	120.1 (4)
C37—O6—H6A	109.5	C32—C33—H33	119.9
C2—C1—C6	118.1 (4)	C28—C33—H33	119.9
C2—C1—C7	123.9 (4)	N3—C34—C28	119.7 (4)
C6—C1—C7	118.0 (4)	N3—C34—C46	120.0 (4)
O1—C2—C3	117.8 (4)	C28—C34—C46	120.3 (4)
O1—C2—C1	123.2 (4)	O5—C35—N4	124.5 (4)
C3—C2—C1	118.9 (4)	O5—C35—C36	117.8 (4)
C4—C3—C2	122.0 (5)	N4—C35—C36	117.7 (4)
C4—C3—H3	119.0	C45—C36—C37	118.7 (4)
C2—C3—H3	119.0	C45—C36—C35	117.9 (4)
C3—C4—C5	118.4 (5)	C37—C36—C35	123.4 (4)

C3—C4—H4	120.8	O6—C37—C38	117.8 (4)
C5—C4—H4	120.8	O6—C37—C36	121.6 (4)
C6—C5—C4	122.1 (5)	C38—C37—C36	120.5 (4)
C6—C5—Cl1	119.3 (4)	C37—C38—C39	120.9 (4)
C4—C5—Cl1	118.5 (4)	C37—C38—H38	119.6
C5—C6—C1	120.5 (5)	C39—C38—H38	119.6
C5—C6—H6	119.8	C44—C39—C38	118.9 (4)
C1—C6—H6	119.8	C44—C39—C40	118.8 (5)
N1—C7—C1	119.9 (4)	C38—C39—C40	122.4 (5)
N1—C7—C19	120.2 (4)	C41—C40—C39	120.9 (5)
C1—C7—C19	119.9 (4)	C41—C40—H40	119.6
O2—C8—N2	123.9 (4)	C39—C40—H40	119.6
O2—C8—C9	117.8 (4)	C40—C41—C42	120.6 (5)
N2—C8—C9	118.3 (4)	C40—C41—H41	119.7
C18—C9—C10	118.9 (4)	C42—C41—H41	119.7
C18—C9—C8	118.7 (4)	C43—C42—C41	119.8 (5)
C10—C9—C8	122.4 (4)	C43—C42—H42	120.1
O3—C10—C11	118.8 (4)	C41—C42—H42	120.1
O3—C10—C9	121.6 (4)	C42—C43—C44	120.7 (5)
C11—C10—C9	119.6 (5)	C42—C43—H43	119.7
C10—C11—C12	121.7 (5)	C44—C43—H43	119.7
C10—C11—H11	119.2	C45—C44—C39	118.8 (4)
C12—C11—H11	119.2	C45—C44—C43	121.8 (5)
C11—C12—C13	122.6 (5)	C39—C44—C43	119.3 (4)
C11—C12—C17	119.3 (4)	C36—C45—C44	122.2 (5)
C13—C12—C17	118.1 (5)	C36—C45—H45	118.9
C14—C13—C12	120.5 (5)	C44—C45—H45	118.9
C14—C13—H13	119.7	C34—C46—H46A	109.5
C12—C13—H13	119.7	C34—C46—H46B	109.5
C13—C14—C15	121.0 (5)	H46A—C46—H46B	109.5
C13—C14—H14	119.5	C34—C46—H46C	109.5
C15—C14—H14	119.5	H46A—C46—H46C	109.5
C16—C15—C14	120.5 (5)	H46B—C46—H46C	109.5
C16—C15—H15	119.7	C48—C47—Sn2	117.3 (3)
C14—C15—H15	119.7	C48—C47—H47A	108.0
C15—C16—C17	120.4 (5)	Sn2—C47—H47A	108.0
C15—C16—H16	119.8	C48—C47—H47B	108.0
C17—C16—H16	119.8	Sn2—C47—H47B	108.0
C18—C17—C16	122.6 (5)	H47A—C47—H47B	107.2
C18—C17—C12	117.9 (5)	C47—C48—C49	112.7 (4)
C16—C17—C12	119.5 (5)	C47—C48—H48A	109.0
C9—C18—C17	122.5 (5)	C49—C48—H48A	109.0
C9—C18—H18	118.7	C47—C48—H48B	109.0
C17—C18—H18	118.7	C49—C48—H48B	109.0
C7—C19—H19A	109.5	H48A—C48—H48B	107.8
C7—C19—H19B	109.5	C50—C49—C48	112.4 (4)
H19A—C19—H19B	109.5	C50—C49—H49A	109.1
C7—C19—H19C	109.5	C48—C49—H49A	109.1
H19A—C19—H19C	109.5	C50—C49—H49B	109.1

H19B—C19—H19C	109.5	C48—C49—H49B	109.1
C21—C20—Sn1	114.7 (3)	H49A—C49—H49B	107.9
C21—C20—H20A	108.6	C49—C50—H50A	109.5
Sn1—C20—H20A	108.6	C49—C50—H50B	109.5
C21—C20—H20B	108.6	H50A—C50—H50B	109.5
Sn1—C20—H20B	108.6	C49—C50—H50C	109.5
H20A—C20—H20B	107.6	H50A—C50—H50C	109.5
C22—C21—C20	112.4 (4)	H50B—C50—H50C	109.5
C22—C21—H21A	109.1	C52—C51—Sn2	117.0 (3)
C20—C21—H21A	109.1	C52—C51—H51A	108.1
C22—C21—H21B	109.1	Sn2—C51—H51A	108.1
C20—C21—H21B	109.1	C52—C51—H51B	108.1
H21A—C21—H21B	107.9	Sn2—C51—H51B	108.1
C21—C22—C23	112.9 (5)	H51A—C51—H51B	107.3
C21—C22—H22A	109.0	C53—C52—C51	115.2 (4)
C23—C22—H22A	109.0	C53—C52—H52A	108.5
C21—C22—H22B	109.0	C51—C52—H52A	108.5
C23—C22—H22B	109.0	C53—C52—H52B	108.5
H22A—C22—H22B	107.8	C51—C52—H52B	108.5
C22—C23—H23A	109.5	H52A—C52—H52B	107.5
C22—C23—H23B	109.5	C52—C53—C54	112.4 (4)
H23A—C23—H23B	109.5	C52—C53—H53A	109.1
C22—C23—H23C	109.5	C54—C53—H53A	109.1
H23A—C23—H23C	109.5	C52—C53—H53B	109.1
H23B—C23—H23C	109.5	C54—C53—H53B	109.1
C25—C24—Sn1	115.3 (3)	H53A—C53—H53B	107.8
C25—C24—H24A	108.5	C53—C54—H54A	109.5
Sn1—C24—H24A	108.5	C53—C54—H54B	109.5
C25—C24—H24B	108.5	H54A—C54—H54B	109.5
Sn1—C24—H24B	108.5	C53—C54—H54C	109.5
H24A—C24—H24B	107.5	H54A—C54—H54C	109.5
C24—C25—C26	113.5 (4)	H54B—C54—H54C	109.5
O1—Sn1—N1—C7	−27.5 (4)	C11—C12—C17—C16	178.7 (5)
C20—Sn1—N1—C7	69.4 (4)	C13—C12—C17—C16	−0.2 (7)
C24—Sn1—N1—C7	−115.4 (4)	C10—C9—C18—C17	−1.1 (7)
O2—Sn1—N1—C7	158.6 (4)	C8—C9—C18—C17	178.9 (4)
O1—Sn1—N1—N2	153.6 (3)	C16—C17—C18—C9	−177.2 (5)
C20—Sn1—N1—N2	−109.6 (3)	C12—C17—C18—C9	1.2 (7)
C24—Sn1—N1—N2	65.7 (3)	O1—Sn1—C20—C21	−79.3 (4)
O2—Sn1—N1—N2	−20.3 (3)	C24—Sn1—C20—C21	22.6 (5)
C7—N1—N2—C8	−162.1 (4)	O2—Sn1—C20—C21	123.7 (4)
Sn1—N1—N2—C8	17.0 (5)	N1—Sn1—C20—C21	−163.5 (3)
O4—Sn2—N3—C34	23.2 (4)	Sn1—C20—C21—C22	−60.6 (5)
C47—Sn2—N3—C34	−72.5 (4)	C20—C21—C22—C23	178.3 (4)
C51—Sn2—N3—C34	109.8 (4)	O1—Sn1—C24—C25	−169.9 (4)
O5—Sn2—N3—C34	−161.0 (4)	C20—Sn1—C24—C25	85.2 (4)
O4—Sn2—N3—N4	−153.8 (3)	O2—Sn1—C24—C25	−16.3 (4)
C47—Sn2—N3—N4	110.6 (3)	N1—Sn1—C24—C25	−88.4 (4)
C51—Sn2—N3—N4	−67.2 (3)	Sn1—C24—C25—C26	170.4 (3)

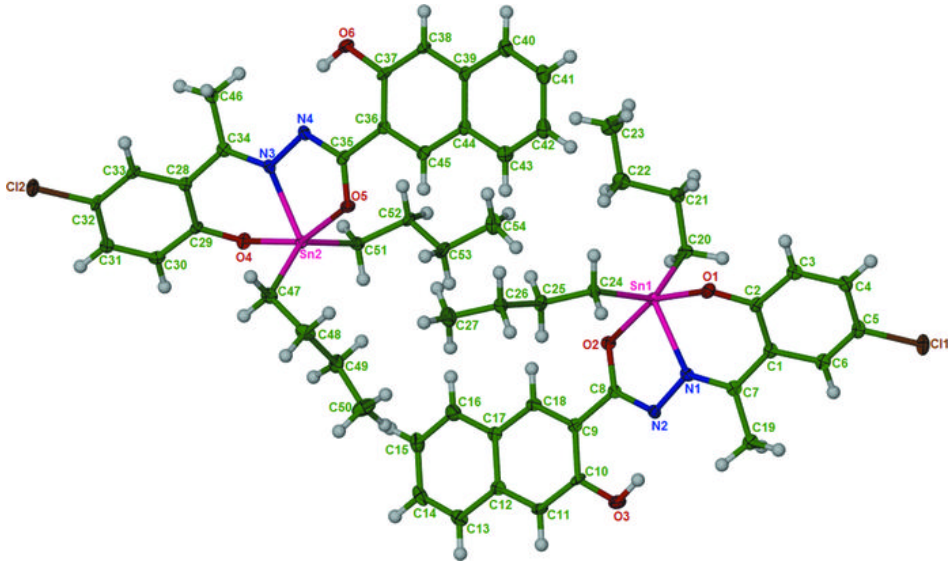
O5—Sn2—N3—N4	22.1 (3)	C24—C25—C26—C27	179.2 (4)
C34—N3—N4—C35	163.4 (4)	Sn2—O4—C29—C30	−135.1 (4)
Sn2—N3—N4—C35	−19.3 (4)	Sn2—O4—C29—C28	46.9 (6)
C20—Sn1—O1—C2	−61.1 (4)	C33—C28—C29—O4	178.6 (4)
C24—Sn1—O1—C2	162.8 (4)	C34—C28—C29—O4	−0.2 (7)
O2—Sn1—O1—C2	59.9 (5)	C33—C28—C29—C30	0.6 (7)
N1—Sn1—O1—C2	47.0 (4)	C34—C28—C29—C30	−178.2 (4)
O1—Sn1—O2—C8	7.4 (5)	O4—C29—C30—C31	−178.9 (4)
C20—Sn1—O2—C8	129.2 (3)	C28—C29—C30—C31	−0.9 (7)
C24—Sn1—O2—C8	−95.0 (3)	C29—C30—C31—C32	0.6 (7)
N1—Sn1—O2—C8	20.7 (3)	C30—C31—C32—C33	−0.1 (7)
C47—Sn2—O4—C29	60.2 (4)	C30—C31—C32—Cl2	180.0 (4)
C51—Sn2—O4—C29	−163.2 (4)	C31—C32—C33—C28	−0.2 (7)
O5—Sn2—O4—C29	−56.8 (5)	Cl2—C32—C33—C28	179.8 (4)
N3—Sn2—O4—C29	−48.2 (3)	C29—C28—C33—C32	−0.1 (7)
O4—Sn2—O5—C35	−12.8 (5)	C34—C28—C33—C32	178.8 (4)
C47—Sn2—O5—C35	−130.6 (3)	N4—N3—C34—C28	−177.1 (4)
C51—Sn2—O5—C35	92.2 (3)	Sn2—N3—C34—C28	6.1 (6)
N3—Sn2—O5—C35	−21.7 (3)	N4—N3—C34—C46	1.0 (6)
Sn1—O1—C2—C3	138.3 (4)	Sn2—N3—C34—C46	−175.8 (3)
Sn1—O1—C2—C1	−43.3 (6)	C29—C28—C34—N3	−26.8 (7)
C6—C1—C2—O1	−178.1 (4)	C33—C28—C34—N3	154.4 (4)
C7—C1—C2—O1	−0.7 (7)	C29—C28—C34—C46	155.1 (5)
C6—C1—C2—C3	0.2 (7)	C33—C28—C34—C46	−23.7 (6)
C7—C1—C2—C3	177.6 (4)	Sn2—O5—C35—N4	20.6 (6)
O1—C2—C3—C4	178.2 (4)	Sn2—O5—C35—C36	−159.9 (3)
C1—C2—C3—C4	−0.2 (7)	N3—N4—C35—O5	−0.7 (6)
C2—C3—C4—C5	−0.7 (7)	N3—N4—C35—C36	179.8 (4)
C3—C4—C5—C6	1.7 (8)	O5—C35—C36—C45	−1.4 (7)
C3—C4—C5—Cl1	−179.2 (4)	N4—C35—C36—C45	178.1 (4)
C4—C5—C6—C1	−1.8 (8)	O5—C35—C36—C37	177.4 (4)
Cl1—C5—C6—C1	179.1 (4)	N4—C35—C36—C37	−3.1 (7)
C2—C1—C6—C5	0.8 (7)	C45—C36—C37—O6	179.8 (4)
C7—C1—C6—C5	−176.8 (4)	C35—C36—C37—O6	1.0 (7)
N2—N1—C7—C1	179.9 (4)	C45—C36—C37—C38	0.2 (7)
Sn1—N1—C7—C1	0.9 (6)	C35—C36—C37—C38	−178.6 (4)
N2—N1—C7—C19	0.8 (6)	O6—C37—C38—C39	179.3 (4)
Sn1—N1—C7—C19	−178.2 (3)	C36—C37—C38—C39	−1.1 (7)
C2—C1—C7—N1	22.4 (7)	C37—C38—C39—C44	1.2 (7)
C6—C1—C7—N1	−160.2 (4)	C37—C38—C39—C40	−178.3 (5)
C2—C1—C7—C19	−158.6 (5)	C44—C39—C40—C41	−1.2 (7)
C6—C1—C7—C19	18.8 (6)	C38—C39—C40—C41	178.3 (5)
Sn1—O2—C8—N2	−20.6 (6)	C39—C40—C41—C42	1.6 (8)
Sn1—O2—C8—C9	159.9 (3)	C40—C41—C42—C43	−0.8 (8)
N1—N2—C8—O2	2.4 (6)	C41—C42—C43—C44	−0.2 (8)
N1—N2—C8—C9	−178.2 (4)	C38—C39—C44—C45	−0.5 (7)
O2—C8—C9—C18	0.5 (6)	C40—C39—C44—C45	179.0 (4)
N2—C8—C9—C18	−179.0 (4)	C38—C39—C44—C43	−179.4 (5)
O2—C8—C9—C10	−179.5 (4)	C40—C39—C44—C43	0.2 (7)

N2—C8—C9—C10	1.1 (7)	C42—C43—C44—C45	−178.3 (5)
C18—C9—C10—O3	−179.5 (4)	C42—C43—C44—C39	0.6 (7)
C8—C9—C10—O3	0.5 (7)	C37—C36—C45—C44	0.6 (7)
C18—C9—C10—C11	−0.3 (7)	C35—C36—C45—C44	179.4 (4)
C8—C9—C10—C11	179.6 (4)	C39—C44—C45—C36	−0.4 (7)
O3—C10—C11—C12	−179.1 (4)	C43—C44—C45—C36	178.5 (5)
C9—C10—C11—C12	1.7 (7)	O4—Sn2—C47—C48	143.3 (4)
C10—C11—C12—C13	177.1 (5)	C51—Sn2—C47—C48	43.4 (5)
C10—C11—C12—C17	−1.7 (7)	O5—Sn2—C47—C48	−61.2 (4)
C11—C12—C13—C14	−177.9 (5)	N3—Sn2—C47—C48	−133.7 (4)
C17—C12—C13—C14	1.0 (7)	Sn2—C47—C48—C49	−57.6 (5)
C12—C13—C14—C15	−1.0 (8)	C47—C48—C49—C50	−167.9 (5)
C13—C14—C15—C16	0.3 (8)	O4—Sn2—C51—C52	150.9 (4)
C14—C15—C16—C17	0.4 (8)	C47—Sn2—C51—C52	−106.2 (4)
C15—C16—C17—C18	177.9 (5)	O5—Sn2—C51—C52	−2.6 (4)
C15—C16—C17—C12	−0.5 (7)	N3—Sn2—C51—C52	70.8 (4)
C11—C12—C17—C18	0.2 (7)	Sn2—C51—C52—C53	75.6 (5)
C13—C12—C17—C18	−178.6 (4)	C51—C52—C53—C54	179.8 (4)

Hydrogen-bond geometry (Å, °)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
O3—H3A···N2	0.84	1.85	2.602 (5)	147.
O6—H6A···N4	0.84	1.88	2.617 (5)	146.

Fig. 1


O6
C38
C40
C37
C39
C41
C46
C23
N4
C36
C34
N3
C35
C44
C42
C45
C43
C22
C33
C28
Cl2
O5
C21
C52
C32
C54
C20
C29
O4
Sn2
C51
C53
C3
O1
C24
Sn1
C4
C31
C30
C47
C26
C25
C2
C27
C5
O2
Cl1
C48
C1
C6
C49
N1
C8
C7
C50
C16
C17
C18
N2
C19
C9
C15
C10
C14
C12
C11
O3
C13

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(*R*)-4-Phenyl-2-[(*S*)-1,2,3,4-tetrahydroisoquinolin-3-yl]-4,5-dihydro-1,3-oxazole

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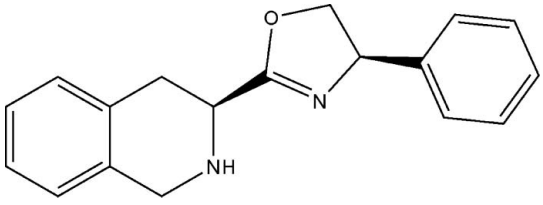
Key indicators: single-crystal X-ray study; T = 173 K; mean σ(C–C) = 0.003 Å; R factor = 0.030; wR factor = 0.076; data-to-parameter ratio = 8.0.

The asymmetric unit cell of the title compound, $C_{18}H_{18}N_2O$, contains four molecules. In the crystal structure, an intermolecular N—H···N hydrogen bond helps to establish the packing.

Related literature

For the assymetric synthetic applications of oxazoline, see: Hargaden *et al.* (2009). For tetraisoquinolines and their biological significance, see: Scott *et al.* (2002). For ligand catalysis activity, see: Chakka *et al.* (2010).



Experimental

Crystal data

$C_{18}H_{18}N_2O$
M_r = 278.34
Orthorhombic, $P2_12_12_1$
a = 5.4023 (3) Å
b = 10.0999 (6) Å
c = 26.2205 (17) Å
V = 1430.66 (15) Å^3
Z = 4
Cu $K\alpha$ radiation
μ = 0.64 mm^{-1}
T = 173 K
0.22 × 0.21 × 0.10 mm

Data collection

Bruker Kappa DUO APEXII diffractometer
Absorption correction: multi-scan (*SADABS*; Sheldrick, 1997)
T_{min} = 0.682, T_{max} = 0.753
6634 measured reflections
1552 independent reflections
1479 reflections with $I > 2\sigma(I)$
R_{int} = 0.036

Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.030
$wR(F^2)$ = 0.076
S = 1.05
1552 reflections
195 parameters
1 restraint
H atoms treated by a mixture of independent and constrained refinement
$\Delta\rho_{max}$ = 0.14 e Å^{-3}
$\Delta\rho_{min}$ = −0.12 e Å^{-3}

Table 1
Hydrogen-bond geometry (Å, °).

D—H···A	D—H	H···A	D···A	D—H···A
N1—H1*N*···N2^{i}	0.96 (1)	2.20 (1)	3.139 (2)	165 (2)

Symmetry code: (i) $x+1, y, z$.

Data collection: *SAINT* (Bruker, 2006); cell refinement: *DENZO-SMN* (Otwinowski & Minor, 1997); data reduction: *DENZO-SMN*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *X-SEED* (Barbour, 2001); software used to prepare material for publication: *SHELXL97*.

The authors would like to thank Dr Hong Su (University of Cape Town) for the data collection and structure refinement.

Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: HG2694).

References

Barbour, L. J. (2001). *J. Supramol. Chem.* **1**, 189–191.
Bruker (2006). *SAINT*. Bruker AXS Inc., Madison, Wisconsin, USA.
Chakka, S. K., Andersson, P. G., Maguire, G. E. M., Kruger, H. G. & Govender, T. (2010). *Eur. J. Org. Chem.* pp. 972–980.
Hargaden, G. C. & Guiry, P. J. (2009). *Chem. Rev.* **109**, 2505–2550.
Otwinowski, Z. & Minor, W. (1997). *Methods in Enzymology*, Vol. 276, *Macromolecular Crystallography*, Part A, edited by C. W. Carter Jr & R. M. Sweet, pp. 307–326. New York: Academic Press.
Scott, J. D. & Williams, R. M. (2002). *Chem. Rev.* **102**, 1669–1730.
Sheldrick, G. M. (1997). *SADABS*. University of Göttingen, Germany.
Sheldrick, G. M. (2008). *Acta Cryst.* A**64**, 112–122.

supplementary materials

Acta Cryst. (2010). E**66**, o1818 [**doi:10.1107/S1600536810022130**]

(*R*)-4-Phenyl-2-[(*S*)-1,2,3,4-tetrahydroisoquinolin-3-yl]-4,5-dihydro-1,3-oxazole

S. K. Chakka, T. Govender, H. G. Kruger and G. E. M. Maguire

Comment

Heterocyclic rings play roles in a number of key areas of organic and inorganic chemistry. As part of an ongoing study into the asymmetric hydrogen transfer reactions we made a series of ligands (Chakka *et al.*, 2010). The title compound (**I**) is one such molecule (Fig 1). It combines for the first time two important heterocyclic rings into a single structure, namely oxazoline (Hargaden *et al.*, 2009) and tetraisoquinoline (TIQ), (Scott *et al.*, 2002). The asymmetric unit cell contains four molecules. There are inter-molecular N(1)—H···N(1) bond interactions (2.212 Å) that hold the structure in two dimensional planes. The intermolecular distance value between ring centroids in the *b* axis direction (5.402 Å), suggests that there is no π-stacking interaction between parallel molecules (Fig 2).

Experimental

A solution of Cbz-protected TIQ–oxazoline (1.0 g, 2.89 mmol) in methanol (30 ml) was added to a suspension of 10 wt.% Pd/C (0.5 g) in methanol (10 ml). The reaction mixture was connected to an H_2 source at atmospheric pressure and stirred at room temperature for 3 h. Completion of the reaction was monitored by TLC using hexane/ethyl acetate (7:3) with the R_f = 0.6. The Pd/C was filtered off over a celite pad and the filtrate was concentrated under reduced pressure to afford crude (**I**). The title compound was purified on a deactivated silica gel column packed with a suspension of silica gel in 20% Et_3N/CH_2Cl_2. The silica was washed with 1% Et_3N/CH_2Cl_2. The chromatography was then performed using 0–2% MeOH/1%Et_3N/CH_2Cl_2 as the eluent to afford TIQ-oxazoline product. *M*.p: 304 – 306 K.

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.37–7.23 (m, 3H), 7.23–7.10 (m, 5H), 7.05 (m, 1H), 5.23 (t, J = 18.21 Hz, 1H), 4.68 (q, J = 10.10, 8.26 Hz, 1H), 4.16 (m, 3H), 3.92 (m, 1H), 3.10–3.05 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 168.9, 142.0, 135.0, 133.3, 129.2, 128.7, 127.6, 126.5, 126.2, 126.1, 126.0, 69.4, 51.5, 47.6, 32.4.

IR (neat): 3225, 1663, 1493, 1108, 957, 907, 916, 740, 749, 697 cm^{-1}.

HR ESI MS: 279.1492 $[M + H]^+$ (calcd. for $C_{18}H_{19}N_2O$ 279.1512).

Refinement

All hydrogen atoms, except H1N on N1, were positioned geometrically with C—H = 0.95 - 1.00 Å and refined as riding on their parent atoms with U_{iso} (H) = 1.2 - 1.5 U_{eq} (C). The hydrogen atoms H1N were located in the difference electron density maps and refined with simple bond length constraint.

Figures

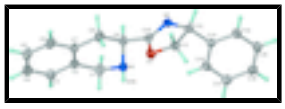


Fig. 1. Molecular structure of (**I**) showing numbering scheme. All non-hydrogen atoms are shown as ellipsoids with probability level of 50%.

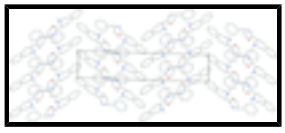


Fig. 2. Projection viewed along [010]. All hydrogen atoms except the hydrogen H1N on N1 are omitted. The hydrogen bonds are shown as dotted lines.

(*R*)-4-Phenyl-2-[(*S*)-1,2,3,4-tetrahydroisoquinolin-3-yl]-4,5- dihydro-1,3-oxazole

Crystal data

$C_{18}H_{18}N_2O$	$F(000) = 592$
$M_r = 278.34$	$D_x = 1.292$ Mg m^{-3}
Orthorhombic, $P2_12_12_1$	Cu $K\alpha$ radiation, $\lambda = 1.54178$ Å
Hall symbol: P 2ac 2ab	Cell parameters from 6634 reflections
$a = 5.4023$ (3) Å	$\theta = 4.7$–$69.2°$
$b = 10.0999$ (6) Å	$\mu = 0.64$ mm^{-1}
$c = 26.2205$ (17) Å	$T = 173$ K
$V = 1430.66$ (15) Å^3	Needle, colourless
$Z = 4$	0.22 × 0.21 × 0.10 mm

Data collection

Bruker Kappa DUO APEXII diffractometer	1552 independent reflections
Radiation source: fine-focus sealed tube	1479 reflections with $I > 2\sigma(I)$
graphite	$R_{int} = 0.036$
Detector resolution: n/a pixels mm^{-1}	$\theta_{max} = 69.2°$, $\theta_{min} = 4.7°$
0.5° φ scans and ω scans	$h = -6 \rightarrow 6$
Absorption correction: multi-scan (*SADABS*; Sheldrick, 1997)	$k = -11 \rightarrow 12$
$T_{min} = 0.682$, $T_{max} = 0.753$	$l = -15 \rightarrow 30$
6634 measured reflections	

Refinement

Refinement on F^2	Secondary atom site location: difference Fourier map
Least-squares matrix: full	Hydrogen site location: inferred from neighbouring sites
$R[F^2 > 2\sigma(F^2)] = 0.030$	H atoms treated by a mixture of independent and constrained refinement
$wR(F^2) = 0.076$	$w = 1/[\sigma^2(F_o^2) + (0.0436P)^2 + 0.1838P]$ where $P = (F_o^2 + 2F_c^2)/3$
$S = 1.05$	$(\Delta/\sigma)_{max} < 0.001$

1552 reflections	$\Delta\rho_{max}$ = 0.14 e Å^{-3}
195 parameters	$\Delta\rho_{min}$ = −0.12 e Å^{-3}
1 restraint	Extinction correction: *SHELXL97* (Sheldrick, 2008), $Fc^*=kFc[1+0.001xFc^2\lambda^3/\sin(2\theta)]^{-1/4}$
Primary atom site location: structure-invariant direct methods	Extinction coefficient: 0.0039 (5)

Special details

Experimental. Half sphere of data collected using *SAINT* strategy (Bruker, 2006). Crystal to detector distance = 50 mm; combination of φ and ω scans of 0.5°, 30 s per °, 2 iterations.

Geometry. All e.s.d.'s (except the e.s.d. in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell e.s.d.'s are taken into account individually in the estimation of e.s.d.'s in distances, angles and torsion angles; correlations between e.s.d.'s in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell e.s.d.'s is used for estimating e.s.d.'s involving l.s. planes.

Refinement. Refinement of F^2 against ALL reflections. The weighted *R*-factor *wR* and goodness of fit *S* are based on F^2, conventional *R*-factors *R* are based on *F*, with *F* set to zero for negative F^2. The threshold expression of $F^2 > \sigma(F^2)$ is used only for calculating *R*-factors(gt) *etc*. and is not relevant to the choice of reflections for refinement. *R*-factors based on F^2 are statistically about twice as large as those based on *F*, and *R*- factors based on ALL data will be even larger.

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å^2)

	x	*y*	*z*	U_{iso}*/U_{eq}
O1	0.4184 (2)	0.79986 (13)	0.19408 (5)	0.0306 (3)
N1	0.5780 (3)	1.06125 (15)	0.15598 (6)	0.0272 (3)
H1N	0.702 (3)	1.0028 (18)	0.1694 (7)	0.033 (6)*
N2	0.0533 (3)	0.90911 (15)	0.19216 (6)	0.0285 (4)
C1	0.6813 (4)	1.15005 (18)	0.11756 (7)	0.0324 (4)
H1A	0.8214	1.1991	0.1329	0.039*
H1B	0.5533	1.2157	0.1080	0.039*
C2	0.7714 (3)	1.08180 (18)	0.06969 (7)	0.0269 (4)
C3	0.9535 (4)	1.13952 (18)	0.03901 (7)	0.0322 (4)
H3	1.0184	1.2238	0.0480	0.039*
C4	1.0408 (4)	1.0762 (2)	−0.00419 (7)	0.0363 (5)
H4	1.1656	1.1162	−0.0245	0.044*
C5	0.9444 (4)	0.9538 (2)	−0.01748 (7)	0.0382 (5)
H5	1.0025	0.9096	−0.0471	0.046*
C6	0.7634 (4)	0.89605 (19)	0.01249 (7)	0.0356 (5)
H6	0.6978	0.8123	0.0031	0.043*
C7	0.6755 (4)	0.95876 (18)	0.05633 (7)	0.0285 (4)
C8	0.4854 (4)	0.89025 (19)	0.08944 (7)	0.0350 (5)
H8A	0.5606	0.8097	0.1043	0.042*
H8B	0.3448	0.8621	0.0678	0.042*
C9	0.3869 (3)	0.97793 (18)	0.13282 (7)	0.0272 (4)
H9	0.2567	1.0374	0.1183	0.033*
C10	0.2691 (3)	0.89535 (18)	0.17416 (7)	0.0260 (4)
C11	0.2612 (3)	0.72424 (17)	0.22836 (7)	0.0279 (4)

H11A	0.3444	0.7089	0.2615	0.033*
H11B	0.2159	0.6378	0.2132	0.033*
C12	0.0312 (3)	0.81315 (17)	0.23493 (7)	0.0258 (4)
H12	−0.1226	0.7592	0.2308	0.031*
C13	0.0251 (3)	0.88531 (17)	0.28547 (6)	0.0247 (4)
C14	−0.1619 (3)	0.86228 (18)	0.32043 (7)	0.0288 (4)
H14	−0.2902	0.8014	0.3124	0.035*
C15	−0.1639 (4)	0.92738 (19)	0.36719 (7)	0.0327 (4)
H15	−0.2932	0.9106	0.3909	0.039*
C16	0.0209 (4)	1.01606 (19)	0.37932 (7)	0.0329 (4)
H16	0.0188	1.0608	0.4112	0.040*
C17	0.2105 (4)	1.03964 (19)	0.34458 (7)	0.0330 (4)
H17	0.3394	1.0999	0.3528	0.040*
C18	0.2114 (3)	0.97527 (18)	0.29802 (7)	0.0290 (4)
H18	0.3403	0.9925	0.2743	0.035*

Atomic displacement parameters (Å^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
O1	0.0268 (6)	0.0313 (6)	0.0336 (7)	0.0056 (6)	0.0025 (5)	0.0064 (5)
N1	0.0279 (7)	0.0272 (7)	0.0267 (7)	0.0012 (7)	0.0002 (6)	−0.0021 (6)
N2	0.0249 (7)	0.0349 (8)	0.0257 (7)	0.0035 (7)	−0.0025 (6)	0.0027 (7)
C1	0.0363 (11)	0.0260 (8)	0.0349 (10)	−0.0015 (8)	0.0026 (8)	−0.0034 (8)
C2	0.0281 (9)	0.0266 (8)	0.0260 (8)	0.0031 (8)	−0.0035 (7)	0.0029 (7)
C3	0.0335 (10)	0.0292 (9)	0.0338 (10)	−0.0020 (8)	−0.0014 (8)	0.0045 (8)
C4	0.0385 (10)	0.0396 (10)	0.0309 (9)	0.0013 (10)	0.0044 (8)	0.0087 (8)
C5	0.0493 (12)	0.0387 (10)	0.0267 (9)	0.0046 (10)	0.0070 (9)	0.0009 (8)
C6	0.0488 (12)	0.0302 (9)	0.0279 (9)	−0.0025 (9)	0.0006 (8)	−0.0024 (7)
C7	0.0326 (9)	0.0291 (9)	0.0237 (8)	0.0016 (8)	−0.0018 (7)	0.0029 (7)
C8	0.0437 (12)	0.0335 (9)	0.0277 (9)	−0.0099 (9)	0.0030 (8)	−0.0035 (8)
C9	0.0253 (9)	0.0310 (9)	0.0252 (9)	0.0017 (8)	−0.0027 (7)	0.0016 (7)
C10	0.0260 (9)	0.0272 (8)	0.0247 (8)	0.0024 (8)	−0.0050 (7)	−0.0001 (7)
C11	0.0297 (9)	0.0262 (8)	0.0278 (9)	0.0022 (8)	0.0005 (7)	0.0006 (7)
C12	0.0227 (8)	0.0284 (8)	0.0262 (8)	0.0007 (7)	−0.0006 (7)	−0.0002 (8)
C13	0.0232 (8)	0.0245 (8)	0.0264 (8)	0.0045 (7)	−0.0024 (7)	0.0029 (7)
C14	0.0254 (9)	0.0281 (9)	0.0329 (10)	−0.0005 (8)	0.0017 (8)	0.0027 (7)
C15	0.0311 (10)	0.0358 (10)	0.0313 (9)	0.0013 (9)	0.0059 (8)	0.0021 (8)
C16	0.0360 (11)	0.0361 (9)	0.0267 (8)	0.0044 (9)	−0.0025 (8)	−0.0049 (8)
C17	0.0320 (9)	0.0301 (9)	0.0368 (10)	−0.0044 (8)	−0.0050 (8)	−0.0035 (8)
C18	0.0244 (9)	0.0310 (9)	0.0316 (9)	−0.0010 (8)	0.0011 (7)	0.0030 (8)

Geometric parameters (Å, °)

O1—C10	1.362 (2)	C8—C9	1.537 (2)
O1—C11	1.454 (2)	C8—H8A	0.9900
N1—C1	1.460 (2)	C8—H8B	0.9900
N1—C9	1.464 (2)	C9—C10	1.508 (2)
N1—H1N	0.960 (10)	C9—H9	1.0000
N2—C10	1.265 (2)	C11—C12	1.542 (3)

N2—C12	1.487 (2)	C11—H11A	0.9900
C1—C2	1.513 (2)	C11—H11B	0.9900
C1—H1A	0.9900	C12—C13	1.513 (2)
C1—H1B	0.9900	C12—H12	1.0000
C2—C7	1.391 (3)	C13—C14	1.384 (2)
C2—C3	1.398 (3)	C13—C18	1.395 (3)
C3—C4	1.384 (3)	C14—C15	1.391 (3)
C3—H3	0.9500	C14—H14	0.9500
C4—C5	1.386 (3)	C15—C16	1.378 (3)
C4—H4	0.9500	C15—H15	0.9500
C5—C6	1.383 (3)	C16—C17	1.391 (3)
C5—H5	0.9500	C16—H16	0.9500
C6—C7	1.396 (3)	C17—C18	1.383 (3)
C6—H6	0.9500	C17—H17	0.9500
C7—C8	1.512 (3)	C18—H18	0.9500
C10—O1—C11	105.26 (13)	C10—C9—C8	111.06 (15)
C1—N1—C9	109.66 (14)	N1—C9—H9	108.0
C1—N1—H1N	111.3 (13)	C10—C9—H9	108.0
C9—N1—H1N	106.9 (13)	C8—C9—H9	108.0
C10—N2—C12	106.47 (15)	N2—C10—O1	118.72 (17)
N1—C1—C2	114.56 (14)	N2—C10—C9	126.58 (17)
N1—C1—H1A	108.6	O1—C10—C9	114.67 (15)
C2—C1—H1A	108.6	O1—C11—C12	103.52 (14)
N1—C1—H1B	108.6	O1—C11—H11A	111.1
C2—C1—H1B	108.6	C12—C11—H11A	111.1
H1A—C1—H1B	107.6	O1—C11—H11B	111.1
C7—C2—C3	119.32 (17)	C12—C11—H11B	111.1
C7—C2—C1	119.75 (16)	H11A—C11—H11B	109.0
C3—C2—C1	120.92 (17)	N2—C12—C13	110.39 (13)
C4—C3—C2	121.21 (18)	N2—C12—C11	103.33 (14)
C4—C3—H3	119.4	C13—C12—C11	113.32 (14)
C2—C3—H3	119.4	N2—C12—H12	109.9
C3—C4—C5	119.33 (19)	C13—C12—H12	109.9
C3—C4—H4	120.3	C11—C12—H12	109.9
C5—C4—H4	120.3	C14—C13—C18	118.68 (17)
C6—C5—C4	119.93 (19)	C14—C13—C12	121.02 (16)
C6—C5—H5	120.0	C18—C13—C12	120.29 (15)
C4—C5—H5	120.0	C13—C14—C15	120.66 (17)
C5—C6—C7	121.13 (19)	C13—C14—H14	119.7
C5—C6—H6	119.4	C15—C14—H14	119.7
C7—C6—H6	119.4	C16—C15—C14	120.32 (18)
C2—C7—C6	119.08 (18)	C16—C15—H15	119.8
C2—C7—C8	121.13 (16)	C14—C15—H15	119.8
C6—C7—C8	119.76 (17)	C15—C16—C17	119.57 (17)
C7—C8—C9	113.36 (15)	C15—C16—H16	120.2
C7—C8—H8A	108.9	C17—C16—H16	120.2
C9—C8—H8A	108.9	C18—C17—C16	119.98 (18)
C7—C8—H8B	108.9	C18—C17—H17	120.0
C9—C8—H8B	108.9	C16—C17—H17	120.0

H8A—C8—H8B	107.7	C17—C18—C13	120.78 (17)
N1—C9—C10	108.50 (14)	C17—C18—H18	119.6
N1—C9—C8	113.21 (15)	C13—C18—H18	119.6
C9—N1—C1—C2	−52.7 (2)	C11—O1—C10—C9	−173.78 (14)
N1—C1—C2—C7	23.6 (3)	N1—C9—C10—N2	108.6 (2)
N1—C1—C2—C3	−155.27 (17)	C8—C9—C10—N2	−126.4 (2)
C7—C2—C3—C4	−0.4 (3)	N1—C9—C10—O1	−69.47 (19)
C1—C2—C3—C4	178.49 (18)	C8—C9—C10—O1	55.6 (2)
C2—C3—C4—C5	0.5 (3)	C10—O1—C11—C12	−14.48 (17)
C3—C4—C5—C6	−0.3 (3)	C10—N2—C12—C13	109.57 (16)
C4—C5—C6—C7	−0.2 (3)	C10—N2—C12—C11	−11.91 (18)
C3—C2—C7—C6	−0.1 (3)	O1—C11—C12—N2	15.96 (17)
C1—C2—C7—C6	−178.97 (17)	O1—C11—C12—C13	−103.52 (16)
C3—C2—C7—C8	177.66 (17)	N2—C12—C13—C14	127.42 (17)
C1—C2—C7—C8	−1.2 (3)	C11—C12—C13—C14	−117.22 (18)
C5—C6—C7—C2	0.4 (3)	N2—C12—C13—C18	−53.6 (2)
C5—C6—C7—C8	−177.41 (18)	C11—C12—C13—C18	61.8 (2)
C2—C7—C8—C9	8.5 (3)	C18—C13—C14—C15	−0.1 (3)
C6—C7—C8—C9	−173.72 (17)	C12—C13—C14—C15	178.90 (16)
C1—N1—C9—C10	−175.40 (15)	C13—C14—C15—C16	0.1 (3)
C1—N1—C9—C8	60.83 (19)	C14—C15—C16—C17	−0.3 (3)
C7—C8—C9—N1	−38.5 (2)	C15—C16—C17—C18	0.7 (3)
C7—C8—C9—C10	−160.89 (15)	C16—C17—C18—C13	−0.7 (3)
C12—N2—C10—O1	3.0 (2)	C14—C13—C18—C17	0.4 (3)
C12—N2—C10—C9	−174.98 (16)	C12—C13—C18—C17	−178.58 (17)
C11—O1—C10—N2	8.0 (2)		

Hydrogen-bond geometry (Å, °)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
N1—H1N···N2^{i}	0.96 (1)	2.20 (1)	3.139 (2)	165 (2)

Symmetry codes: (i) *x*+1, *y*, *z*.

Fig. 1

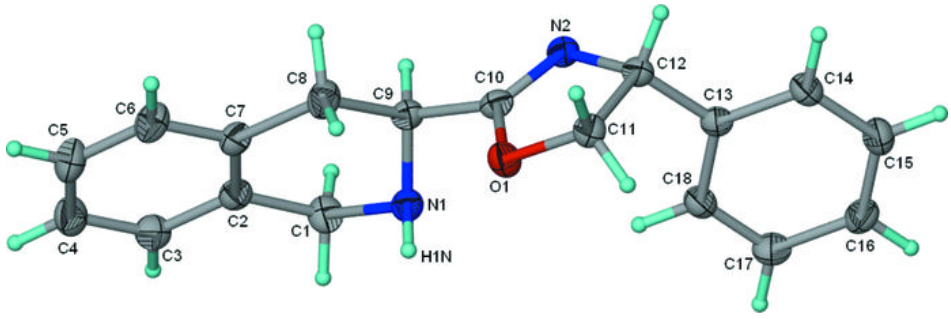
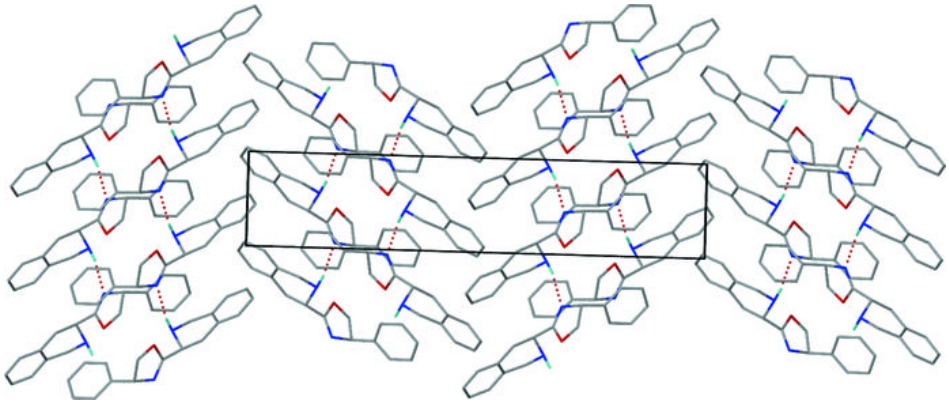

N2
C12
C14
C8
C9
C10
C13
C6
C7
C11
C5
C15
O1
C18
N1
C2
C1
C4
C3
H1N
C16
C17

Fig. 2



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Structure Reports Online
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Bis(μ-3,5-dinitro-2-oxidobenzoato)-$\kappa^3O^1,O^2:O^1$;$\kappa^3O^1:O^1,O^2$-bis[aqua(2-phenyl-1,3,7,8-tetraazacyclopenta[*l*]-phenanthrene-κ^2N^7,N^8)cobalt(II)]

Xiang-Cheng Wang, Jing Chen, Chun-Jie Wang and Chun-Xiang Li*

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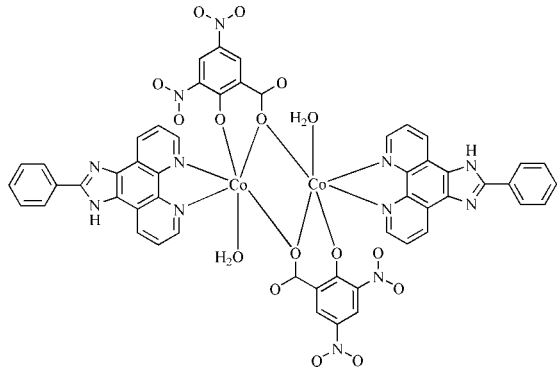
Received 27 April 2010; accepted 13 May 2010

Key indicators: single-crystal X-ray study; T = 292 K; mean σ(C–C) = 0.006 Å; R factor = 0.044; wR factor = 0.111; data-to-parameter ratio = 10.7.

In the title compound, $[Co_2(C_7H_2N_2O_7)_2(C_{19}H_{12}N_4)_2(H_2O)_2]$, the Co^{II} atom is six-coordinated by two N atoms from a 2-phenyl-1*H*-1,3,7,8,-tetraazacyclopenta[*l*]phenanthrene (*L*) ligand, three O atoms from two 3,5-dinitro-2-oxidobenzoate (3,5-dinitrosalicylate or DNSA) ligands and one O atom from a water molecule in a distorted octahedral geometry. The Co^{II} atoms are bridged by two carboxylate O atoms from two DNSA ligands, forming a centrosymmetric dinuclear structure. Neighbouring dinuclear units interact with each other through two types of π–π interactions between the *L* ligands [shortest centroid–centroid distance = 3.646 (3) Å] and between the *L* and DNSA ligands [shortest atom-to-centroid distance = 3.794 (3) Å]. N—H···O, O—H···N and O—H···O hydrogen bonds are observed, which lead to a three-dimensional structure.

Related literature

For general background to metal–organic coordination polymers, see: Che *et al.* (2008). For a related structure, see: Liu *et al.* (2009). For the ligand synthesis, see: Steck & Day (1943).



Experimental

Crystal data

$[Co_2(C_7H_2N_2O_7)_2(C_{19}H_{12}N_4)_2(H_2O)_2]$
M_r = 1198.76
Triclinic, $P\overline{1}$
a = 8.2943 (4) Å
b = 11.0232 (5) Å
c = 13.6139 (7) Å
α = 102.690 (4)°
β = 107.282 (4)°
γ = 90.459 (4)°
V = 1155.9 (1) Å^3
Z = 1
Mo $K\alpha$ radiation
μ = 0.81 mm^{-1}
T = 292 K
0.32 × 0.27 × 0.23 mm

Data collection

Oxford Diffraction Gemini R Ultra CCD diffractometer
Absorption correction: multi-scan (*CrysAlis RED*; Oxford Diffraction, 2006)
T_{min} = 0.771, T_{max} = 0.829
7153 measured reflections
4041 independent reflections
2933 reflections with $I > 2\sigma(I)$
R_{int} = 0.028

Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.044
$wR(F^2)$ = 0.111
S = 1.00
4041 reflections
378 parameters
168 restraints
H atoms treated by a mixture of independent and constrained refinement
$\Delta\rho_{max}$ = 0.97 e Å^{-3}
$\Delta\rho_{min}$ = −1.00 e Å^{-3}

Table 1
Selected bond lengths (Å).

Co—N1	2.102 (3)	Co—O1^{i}	2.216 (3)
Co—N2	2.095 (3)	Co—O3	1.991 (3)
Co—O1	2.050 (2)	Co—O*W*1	2.139 (3)

Symmetry code: (i) $-x, -y, -z+1$.

Table 2
Hydrogen-bond geometry (Å, °).

D—H···A	D—H	H···A	D···A	D—H···A
N4—H4···O6^{ii}	0.86	2.17	2.948 (5)	150
O*W*1—H1*WA*···N3^{iii}	0.81 (6)	2.03 (6)	2.831 (5)	172 (5)
O*W*1—H1*WB*···O2^{iv}	0.80 (5)	1.88 (5)	2.662 (4)	165 (5)

Symmetry codes: (ii) $x-1, y, z-1$; (iii) $-x, -y+1, -z+1$; (iv) $-x+1, -y, -z+1$.

Data collection: *CrysAlis CCD* (Oxford Diffraction, 2006); cell refinement: *CrysAlis RED* (Oxford Diffraction, 2006); data reduction: *CrysAlis RED*; program(s) used to solve structure: *SHELXTL*

(Sheldrick, 2008); program(s) used to refine structure: *SHELXTL*; molecular graphics: *SHELXTL* and *DIAMOND* (Brandenburg, 1999); software used to prepare material for publication: *SHELXTL*.

The authors thank Jiangsu University for supporting this work.

Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: HY2303).

References

Brandenburg, K. (1999). *DIAMOND*. Crystal Impact GbR, Bonn, Germany.
Che, G.-B., Liu, C.-B., Liu, B., Wang, Q.-W. & Xu, Z.-L. (2008). *CrystEngComm*, **10**, 184–191.
Liu, D.-M., Li, X.-Y., Wang, X.-C., Li, C.-X. & Liu, C.-B. (2009). *Acta Cryst.* E**65**, o1308.
Oxford Diffraction (2006). *CrysAlis CCD* and *CrysAlis RED*. Oxford Diffraction Ltd, Abingdon, Oxfordshire, England.
Sheldrick, G. M. (2008). *Acta Cryst.* A**64**, 112–122.
Steck, E. A. & Day, A. R. (1943). *J. Am. Chem. Soc.* **65**, 452–456.

supplementary materials

Acta Cryst. (2010). E**66**, m751-m752 [**doi:10.1107/S1600536810017629**]

Bis(μ-3,5-dinitro-2-oxidobenzoato)-$\kappa^3O^1,O^2:O^1;\kappa^3O^1:O^1,O^2$-bis[aqua(2-phenyl-1,3,7,8-tetraazacyclopenta[*l*]phenanthrene-κ^2N^7,N^8)cobalt(II)]

X.-C. Wang, J. Chen, C.-J. Wang and C.-X. Li

Comment

Metal-organic coordination polymers have attracted increasing interest over the past decade because of their intriguing structures and tremendous potential applications in catalysis, molecular adsorption, nonlinear optics, magnetism, and so on (Che *et al.*, 2008). 1,10-Phenanthroline (phen) has been widely used to build supramolecular architectures owing to its excellent coordinating ability and large conjugated system. However, building blocks derived from the appropriate modification of phen, such as 2-phenyl-1*H*-1,3,7,8-tetra-azacyclopenta[l]phenanthrene (*L*) have received considerably less attention (Liu *et al.*, 2009). Hereby, we have prepared the title compound based on *L* and 3,5-dinitrosalicylic acid (H_2DNSA) ligands.

In the title compound, the Co^{II} atom is six-coordinated by two N atoms from one *L* ligand, four O atoms from two DNSA ligands and one water molecule (Fig. 1). The Co—O distances range from 1.991 (3) to 2.216 (3) Å and the Co—N lengths are 2.095 (3) and 2.102 (3) Å (Table 1). The N1, N2, O1, O3 atoms comprise the equatorial plane, while the $O1^i$ and OW1 atoms occupy the axial position [symmetry code: (i) -x, -y, 1-z]. A carboxylate O atom and the hydroxy O atom of the DNSA ligand coordinate to one Co atom, and this carboxylate O atom bridges the other Co atom, forming a dinuclear structure. The two nitro groups are uncoordinated.

It is noteworthy that various hydrogen bonds interactions are observed in the title compound. (a) An N—H···O hydrogen bond between the imidazole ring donor and the nitro group of the DNSA ligand (Table 2). (b) O—H···N or O—H···O hydrogen bonds involving the coordinated water molecule OW1 and the imidazole N3 and carboxylate O2 atoms (Table 2). In addition, two types of π–π stacking interactions further intensify the architectures. One is the offset face-to-face π–π interactions between the *L* ligands with the shortest centroid–centroid distance of 3.646 (3) Å, while the other exists between the *L* and DNSA ligands [shortest atom-to-centroid distance = 3.794 (3) Å] (Fig. 2), which lead to a three-dimensional supramolecular structure (Fig. 3).

Experimental

The *L* ligand was synthesized according to the literature method (Steck & Day, 1943). The title compound was synthesized under hydrothermal conditions. A mixture of *L* (0.06 g, 0.2 mmol), H_2DNSA (0.048 g, 0.2 mmol), $Co(NO_3)_2$ (0.036 g, 0.2 mmol) and water (10 ml) in a mole ratio 1:1:1:5000 was placed in a 25 ml Teflon-lined autoclave and heated for 3 d at 433 K under autogenous pressure. Upon cooling and opening the bomb, yellow block-shaped crystals were obtained, washed with H_2O and dried in air (yield 45% based on Co).

Refinement

H atoms on C and N atoms were positioned geometrically and refined as riding atoms, with C—H = 0.93 and N—H = 0.86 Å and with U_{iso}(H) = 1.2U_{eq}(C,N). H atoms of water molecule were located from a difference Fourier map and their positions and U_{iso} values were refined freely.

Figures

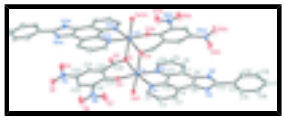


Fig. 1. Molecular structure of the title compound. Displacement ellipsoids are drawn at the 30% probability level. H atoms have been omitted for clarity. [Symmetry code: (A) -x, -y, -z+1.]

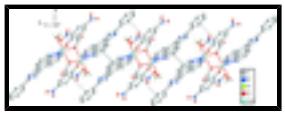


Fig. 2. View of the one-dimensional supramolecular chain generated by π–π interactions (dashed lines). H atoms except those of water molecules have been omitted for clarity.

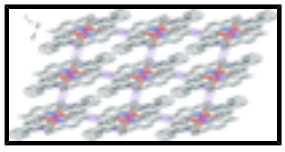


Fig. 3. View of a three-dimensional supramolecular structure with hydrogen bonds indicated by dotted lines. Most H atoms have been omitted.

Bis(μ-3,5-dinitro-2-oxidobenzoato)-$\kappa^3O^1,O^2:O^1$;$\kappa^3O^1:O^1,O^2$- bis[aqua(2-phenyl-1,3,7,8-tetraazacyclopenta[*l*]phenanthrene- κ^2N^7,N^8)cobalt(II)]

Crystal data

$[Co_2(C_7H_2N_2O_7)_2(C_{19}H_{12}N_4)_2(H_2O)_2]$	$Z = 1$
$M_r = 1198.76$	$F(000) = 610$
	$D_x = 1.722$ Mg m^{-3}
Triclinic, $P\overline{1}$	$D_m = 1.722$ Mg m^{-3}
	D_m measured by not measured
Hall symbol: -P 1	Mo $K\alpha$ radiation, λ = 0.71073 Å
$a = 8.2943$ (4) Å	Cell parameters from 3653 reflections
$b = 11.0232$ (5) Å	θ = 4.4–25°
$c = 13.6139$ (7) Å	μ = 0.81 mm^{-1}
α = 102.690 (4)°	$T = 292$ K
β = 107.282 (4)°	Block, yellow
γ = 90.459 (4)°	0.32 × 0.27 × 0.23 mm
$V = 1155.9$ (1) Å^3	

Data collection

Oxford Diffraction Gemini R Ultra CCD diffractometer	4041 independent reflections
Radiation source: fine-focus sealed tube	2933 reflections with $I > 2\sigma(I)$
graphite	$R_{int} = 0.028$

ω scans	θ_{max} = 25.0°, θ_{min} = 4.4°
Absorption correction: multi-scan (*CrysAlis RED*; Oxford Diffraction, 2006)	h = −9→9
T_{min} = 0.771, T_{max} = 0.829	k = −13→11
7153 measured reflections	l = −14→16

Refinement

Refinement on F^2	Primary atom site location: structure-invariant direct methods
Least-squares matrix: full	Secondary atom site location: difference Fourier map
$R[F^2 > 2\sigma(F^2)]$ = 0.044	Hydrogen site location: inferred from neighbouring sites
$wR(F^2)$ = 0.111	H atoms treated by a mixture of independent and constrained refinement
S = 1.00	$w = 1/[\sigma^2(F_o^2) + (0.0638P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
4041 reflections	$(\Delta/\sigma)_{max}$ = 0.002
378 parameters	$\Delta\rho_{max}$ = 0.97 e Å^{-3}
168 restraints	$\Delta\rho_{min}$ = −1.00 e Å^{-3}

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å^2)

	x	*y*	*z*	U_{iso}*/U_{eq}
C1	−0.0231 (5)	0.3815 (4)	0.6428 (3)	0.0304 (9)
H1	0.0452	0.3635	0.7049	0.037*
C2	−0.1233 (6)	0.4828 (4)	0.6499 (3)	0.0346 (10)
H2	−0.1214	0.5307	0.7157	0.041*
C3	−0.2237 (5)	0.5105 (4)	0.5595 (3)	0.0336 (9)
H3	−0.2911	0.5774	0.5631	0.040*
C4	−0.2245 (5)	0.4375 (4)	0.4614 (3)	0.0286 (8)
C5	−0.3250 (5)	0.4543 (4)	0.3592 (3)	0.0299 (8)
C6	−0.3182 (5)	0.3757 (4)	0.2679 (3)	0.0311 (9)
C7	−0.2138 (5)	0.2745 (4)	0.2631 (3)	0.0277 (8)
C8	−0.1991 (5)	0.1923 (4)	0.1726 (3)	0.0344 (9)
H8	−0.2600	0.2020	0.1058	0.041*
C9	−0.0946 (6)	0.0974 (4)	0.1829 (3)	0.0369 (10)
H9	−0.0838	0.0422	0.1233	0.044*
C10	−0.0049 (5)	0.0841 (4)	0.2834 (3)	0.0325 (9)
H10	0.0650	0.0189	0.2895	0.039*
C11	−0.1165 (5)	0.2559 (4)	0.3627 (3)	0.0247 (8)
C12	−0.1215 (5)	0.3373 (3)	0.4607 (3)	0.0249 (8)
C13	−0.4998 (5)	0.5157 (4)	0.2329 (3)	0.0322 (9)
C14	−0.6334 (5)	0.5801 (4)	0.1703 (3)	0.0356 (9)
C15	−0.6963 (6)	0.6831 (4)	0.2208 (4)	0.0438 (11)
H15	−0.6518	0.7137	0.2935	0.053*
C16	−0.8264 (7)	0.7403 (5)	0.1618 (4)	0.0546 (13)
H16	−0.8696	0.8091	0.1957	0.066*

C17	−0.8916 (7)	0.6973 (5)	0.0553 (4)	0.0606 (14)
H17	−0.9787	0.7365	0.0167	0.073*
C18	−0.8286 (7)	0.5960 (6)	0.0052 (4)	0.0619 (15)
H18	−0.8723	0.5671	−0.0677	0.074*
C19	−0.7008 (7)	0.5364 (5)	0.0621 (4)	0.0511 (13)
H19	−0.6599	0.4668	0.0276	0.061*
C20	0.3815 (5)	−0.0284 (4)	0.6442 (3)	0.0269 (8)
C21	0.5087 (5)	−0.0973 (4)	0.6896 (3)	0.0328 (9)
H21	0.5419	−0.1637	0.6466	0.039*
C22	0.5884 (5)	−0.0697 (4)	0.7980 (3)	0.0368 (9)
C23	0.5475 (5)	0.0299 (4)	0.8637 (3)	0.0360 (9)
H23	0.6050	0.0499	0.9358	0.043*
C24	0.4202 (5)	0.0997 (4)	0.8213 (3)	0.0323 (9)
C25	0.3257 (5)	0.0739 (4)	0.7106 (3)	0.0265 (8)
C26	0.2996 (5)	−0.0712 (4)	0.5268 (3)	0.0271 (8)
N1	−0.0218 (4)	0.3109 (3)	0.5517 (2)	0.0254 (7)
N2	−0.0149 (4)	0.1606 (3)	0.3706 (2)	0.0250 (6)
N3	−0.4378 (4)	0.5429 (3)	0.3369 (3)	0.0324 (8)
N4	−0.4312 (4)	0.4167 (3)	0.1875 (3)	0.0321 (8)
H4	−0.4538	0.3850	0.1209	0.039*
N5	0.7161 (5)	−0.1487 (4)	0.8424 (3)	0.0484 (9)
N6	0.3854 (5)	0.2056 (4)	0.8942 (3)	0.0446 (9)
O1	0.1485 (3)	−0.0397 (2)	0.4865 (2)	0.0305 (5)
O2	0.3743 (4)	−0.1379 (3)	0.4735 (2)	0.0459 (8)
O3	0.2036 (4)	0.1369 (3)	0.6762 (2)	0.0339 (5)
O4	0.7338 (5)	−0.2469 (4)	0.7867 (3)	0.0650 (9)
O5	0.8033 (5)	−0.1117 (4)	0.9352 (3)	0.0691 (10)
O6	0.4661 (6)	0.2254 (4)	0.9869 (3)	0.0813 (11)
O7	0.2851 (6)	0.2779 (4)	0.8644 (3)	0.0857 (10)
OW1	0.3241 (4)	0.2215 (3)	0.5222 (3)	0.0345 (5)
Co	0.09090 (7)	0.14151 (5)	0.52610 (4)	0.0264 (2)
H1WA	0.362 (7)	0.285 (6)	0.566 (5)	0.064 (18)*
H1WB	0.407 (7)	0.184 (5)	0.523 (4)	0.058 (16)*

Atomic displacement parameters (Å^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
C1	0.034 (2)	0.031 (2)	0.0251 (15)	0.0072 (17)	0.0071 (17)	0.0072 (14)
C2	0.041 (3)	0.031 (2)	0.0312 (16)	0.0091 (18)	0.0129 (18)	0.0042 (17)
C3	0.032 (2)	0.031 (2)	0.0381 (15)	0.0114 (19)	0.0118 (18)	0.0079 (15)
C4	0.027 (2)	0.0249 (19)	0.0326 (12)	0.0062 (16)	0.0055 (16)	0.0089 (14)
C5	0.026 (2)	0.027 (2)	0.0351 (13)	0.0054 (16)	0.0042 (16)	0.0115 (14)
C6	0.027 (2)	0.035 (2)	0.0308 (14)	0.0071 (17)	0.0025 (16)	0.0133 (14)
C7	0.024 (2)	0.0286 (19)	0.0279 (13)	0.0026 (15)	0.0021 (15)	0.0094 (14)
C8	0.036 (3)	0.040 (2)	0.0254 (16)	0.0039 (18)	0.0045 (18)	0.0088 (15)
C9	0.040 (3)	0.041 (2)	0.0267 (14)	0.0078 (19)	0.0101 (18)	0.0022 (17)
C10	0.029 (2)	0.037 (2)	0.0295 (13)	0.0080 (19)	0.0082 (17)	0.0038 (15)
C11	0.020 (2)	0.0269 (19)	0.0264 (12)	0.0036 (15)	0.0042 (15)	0.0091 (13)

C12	0.021 (2)	0.0230 (18)	0.0279 (12)	0.0032 (15)	0.0026 (15)	0.0069 (13)
C13	0.031 (2)	0.030 (2)	0.0349 (14)	0.0058 (16)	0.0057 (16)	0.0121 (16)
C14	0.030 (2)	0.036 (2)	0.0398 (16)	0.0072 (17)	0.0048 (16)	0.0158 (16)
C15	0.044 (3)	0.036 (2)	0.049 (2)	0.011 (2)	0.008 (2)	0.0137 (18)
C16	0.048 (3)	0.047 (3)	0.072 (2)	0.021 (2)	0.014 (2)	0.025 (2)
C17	0.046 (3)	0.070 (3)	0.069 (2)	0.023 (3)	0.005 (2)	0.041 (2)
C18	0.058 (4)	0.074 (4)	0.045 (2)	0.015 (3)	−0.005 (2)	0.024 (2)
C19	0.050 (3)	0.059 (3)	0.0401 (16)	0.018 (2)	0.005 (2)	0.0139 (19)
C20	0.019 (2)	0.029 (2)	0.0318 (13)	0.0034 (15)	0.0040 (13)	0.0095 (14)
C21	0.025 (2)	0.035 (2)	0.0384 (15)	0.0094 (17)	0.0063 (16)	0.0134 (16)
C22	0.024 (2)	0.047 (2)	0.0400 (16)	0.0079 (18)	0.0040 (16)	0.0203 (16)
C23	0.027 (2)	0.051 (2)	0.0278 (19)	0.0026 (18)	−0.0005 (17)	0.0160 (16)
C24	0.025 (2)	0.042 (2)	0.0263 (13)	0.0014 (17)	0.0010 (14)	0.0089 (14)
C25	0.022 (2)	0.031 (2)	0.0252 (13)	0.0047 (15)	0.0029 (14)	0.0104 (13)
C26	0.0219 (17)	0.0223 (19)	0.0328 (14)	0.0051 (15)	0.0040 (12)	0.0035 (14)
N1	0.0257 (17)	0.0237 (14)	0.0258 (11)	0.0052 (13)	0.0052 (13)	0.0070 (11)
N2	0.0223 (16)	0.0260 (15)	0.0258 (10)	0.0044 (12)	0.0052 (12)	0.0071 (11)
N3	0.032 (2)	0.0288 (17)	0.0350 (13)	0.0090 (15)	0.0051 (15)	0.0109 (13)
N4	0.033 (2)	0.0336 (18)	0.0272 (14)	0.0092 (15)	0.0014 (14)	0.0112 (13)
N5	0.034 (2)	0.062 (2)	0.0523 (18)	0.0166 (19)	0.0058 (15)	0.0300 (15)
N6	0.041 (2)	0.057 (2)	0.0267 (13)	0.0099 (17)	0.0015 (15)	0.0037 (14)
O1	0.0280 (10)	0.0323 (9)	0.0278 (9)	0.0142 (9)	0.0037 (8)	0.0059 (8)
O2	0.0315 (15)	0.0534 (16)	0.0404 (14)	0.0173 (13)	0.0048 (12)	−0.0062 (12)
O3	0.0321 (11)	0.0361 (11)	0.0274 (8)	0.0156 (9)	0.0014 (8)	0.0050 (8)
O4	0.055 (2)	0.0667 (19)	0.0686 (19)	0.0307 (17)	0.0039 (16)	0.0270 (15)
O5	0.059 (2)	0.084 (2)	0.0569 (17)	0.0309 (18)	−0.0046 (14)	0.0289 (16)
O6	0.092 (2)	0.092 (2)	0.0308 (12)	0.0423 (19)	−0.0108 (15)	−0.0076 (15)
O7	0.0906 (19)	0.0901 (18)	0.0420 (14)	0.0503 (15)	−0.0127 (14)	−0.0113 (14)
OW1	0.0268 (11)	0.0354 (13)	0.0367 (13)	0.0091 (10)	0.0058 (10)	0.0039 (11)
Co	0.0251 (3)	0.0267 (3)	0.0236 (3)	0.0104 (2)	0.0015 (2)	0.0059 (2)

Geometric parameters (Å, °)

C1—N1	1.314 (5)	C17—C18	1.369 (8)
C1—C2	1.401 (5)	C17—H17	0.9300
C1—H1	0.9300	C18—C19	1.379 (6)
C2—C3	1.365 (6)	C18—H18	0.9300
C2—H2	0.9300	C19—H19	0.9300
C3—C4	1.398 (6)	C20—C21	1.379 (5)
C3—H3	0.9300	C20—C25	1.453 (5)
C4—C12	1.402 (5)	C20—C26	1.503 (6)
C4—C5	1.446 (5)	C21—C22	1.389 (6)
C5—C6	1.366 (6)	C21—H21	0.9300
C5—N3	1.377 (5)	C22—C23	1.368 (6)
C6—N4	1.376 (5)	C22—N5	1.454 (5)
C6—C7	1.420 (5)	C23—C24	1.373 (5)
C7—C8	1.398 (6)	C23—H23	0.9300
C7—C11	1.416 (5)	C24—C25	1.440 (5)
C8—C9	1.368 (6)	C24—N6	1.448 (5)

C8—H8	0.9300	C25—O3	1.265 (4)
C9—C10	1.389 (6)	C26—O2	1.220 (5)
C9—H9	0.9300	C26—O1	1.294 (4)
C10—N2	1.322 (5)	N4—H4	0.8600
C10—H10	0.9300	N5—O4	1.215 (5)
C11—N2	1.356 (5)	N5—O5	1.229 (5)
C11—C12	1.447 (5)	N6—O7	1.202 (5)
C12—N1	1.363 (5)	N6—O6	1.209 (5)
C13—N3	1.319 (5)	OW1—H1WA	0.81 (6)
C13—N4	1.349 (5)	OW1—H1WB	0.80 (5)
C13—C14	1.475 (5)	Co—N1	2.102 (3)
C14—C19	1.383 (6)	Co—N2	2.095 (3)
C14—C15	1.383 (6)	Co—O1	2.050 (2)
C15—C16	1.388 (6)	Co—O1^{i}	2.216 (3)
C15—H15	0.9300	Co—O3	1.991 (3)
C16—C17	1.359 (8)	Co—OW1	2.139 (3)
C16—H16	0.9300		
N1—C1—C2	122.5 (4)	C21—C20—C26	116.4 (3)
N1—C1—H1	118.8	C25—C20—C26	123.5 (3)
C2—C1—H1	118.8	C20—C21—C22	121.5 (4)
C3—C2—C1	119.4 (4)	C20—C21—H21	119.3
C3—C2—H2	120.3	C22—C21—H21	119.3
C1—C2—H2	120.3	C23—C22—C21	121.1 (4)
C2—C3—C4	119.4 (4)	C23—C22—N5	119.6 (4)
C2—C3—H3	120.3	C21—C22—N5	119.3 (4)
C4—C3—H3	120.3	C22—C23—C24	118.9 (4)
C3—C4—C12	117.8 (3)	C22—C23—H23	120.6
C3—C4—C5	125.9 (3)	C24—C23—H23	120.6
C12—C4—C5	116.3 (3)	C23—C24—C25	123.5 (4)
C6—C5—N3	110.5 (3)	C23—C24—N6	116.4 (4)
C6—C5—C4	121.0 (3)	C25—C24—N6	120.0 (3)
N3—C5—C4	128.5 (4)	O3—C25—C24	121.1 (3)
C5—C6—N4	105.3 (3)	O3—C25—C20	124.0 (3)
C5—C6—C7	124.8 (3)	C24—C25—C20	114.9 (3)
N4—C6—C7	129.9 (4)	O2—C26—O1	122.3 (4)
C8—C7—C11	117.7 (3)	O2—C26—C20	119.4 (3)
C8—C7—C6	127.5 (4)	O1—C26—C20	118.2 (3)
C11—C7—C6	114.8 (3)	C1—N1—C12	118.8 (3)
C9—C8—C7	119.6 (4)	C1—N1—Co	127.4 (2)
C9—C8—H8	120.2	C12—N1—Co	113.2 (2)
C7—C8—H8	120.2	C10—N2—C11	119.2 (3)
C8—C9—C10	119.4 (4)	C10—N2—Co	127.0 (2)
C8—C9—H9	120.3	C11—N2—Co	113.5 (2)
C10—C9—H9	120.3	C13—N3—C5	104.8 (3)
N2—C10—C9	122.7 (4)	C13—N4—C6	107.2 (3)
N2—C10—H10	118.7	C13—N4—H4	126.4
C9—C10—H10	118.7	C6—N4—H4	126.4
N2—C11—C7	121.5 (3)	O4—N5—O5	123.0 (4)

N2—C11—C12	116.9 (3)	O4—N5—C22	119.2 (4)
C7—C11—C12	121.7 (3)	O5—N5—C22	117.9 (4)
N1—C12—C4	122.0 (3)	O7—N6—O6	119.1 (4)
N1—C12—C11	116.5 (3)	O7—N6—C24	121.8 (4)
C4—C12—C11	121.5 (3)	O6—N6—C24	118.9 (3)
N3—C13—N4	112.1 (3)	C26—O1—Co	120.4 (3)
N3—C13—C14	125.6 (4)	C26—O1—Co^{i}	125.8 (2)
N4—C13—C14	122.2 (4)	Co—O1—Co^{i}	100.87 (10)
C19—C14—C15	119.4 (4)	C25—O3—Co	127.0 (2)
C19—C14—C13	120.8 (4)	Co—OW1—H1WA	116 (4)
C15—C14—C13	119.8 (4)	Co—OW1—H1WB	124 (4)
C14—C15—C16	119.4 (5)	H1WA—OW1—H1WB	102 (5)
C14—C15—H15	120.3	O3—Co—O1	87.05 (10)
C16—C15—H15	120.3	O3—Co—N2	175.08 (14)
C17—C16—C15	120.9 (5)	O1—Co—N2	96.09 (11)
C17—C16—H16	119.5	O3—Co—N1	98.70 (11)
C15—C16—H16	119.5	O1—Co—N1	167.77 (12)
C16—C17—C18	119.7 (4)	N2—Co—N1	78.95 (12)
C16—C17—H17	120.1	O3—Co—OW1	88.76 (12)
C18—C17—H17	120.1	O1—Co—OW1	95.00 (13)
C17—C18—C19	120.5 (5)	N2—Co—OW1	87.20 (12)
C17—C18—H18	119.7	N1—Co—OW1	95.91 (13)
C19—C18—H18	119.7	O3—Co—O1^{i}	95.02 (11)
C18—C19—C14	120.0 (5)	O1—Co—O1^{i}	79.13 (10)
C18—C19—H19	120.0	N2—Co—O1^{i}	89.30 (11)
C14—C19—H19	120.0	N1—Co—O1^{i}	89.56 (11)
C21—C20—C25	119.9 (4)	OW1—Co—O1^{i}	172.82 (12)

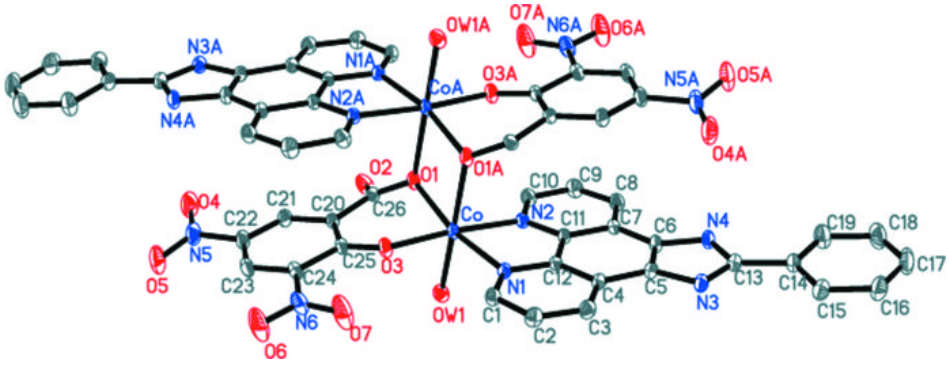
Symmetry codes: (i) −*x*, −*y*, −*z*+1.

Hydrogen-bond geometry (Å, °)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
N4—H4···O6^{ii}	0.86	2.17	2.948 (5)	150
OW1—H1WA···N3^{iii}	0.81 (6)	2.03 (6)	2.831 (5)	172 (5)
OW1—H1WB···O2^{iv}	0.80 (5)	1.88 (5)	2.662 (4)	165 (5)

Symmetry codes: (ii) *x*−1, *y*, *z*−1; (iii) −*x*, −*y*+1, −*z*+1; (iv) −*x*+1, −*y*, −*z*+1.

Fig. 1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O7A
N6A
O6A
N3A
N1A
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O3A
N5A
O5A
N4A
N2A
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O2
O1
O1A
C10
C9
C8
O4
C21
C20
C26
Co
N2
C11
C7
C6
N4
C19
C18
C22
N5
C25
O3
C17
O5
C23
C24
N1
C12
C4
C5
C13
N3
C14
N6
OW1
C1
C3
C15
C16
O6
O7
C2

Fig. 2

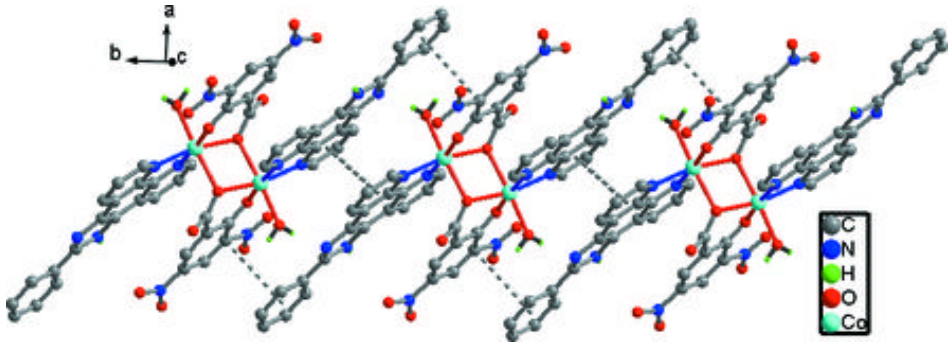
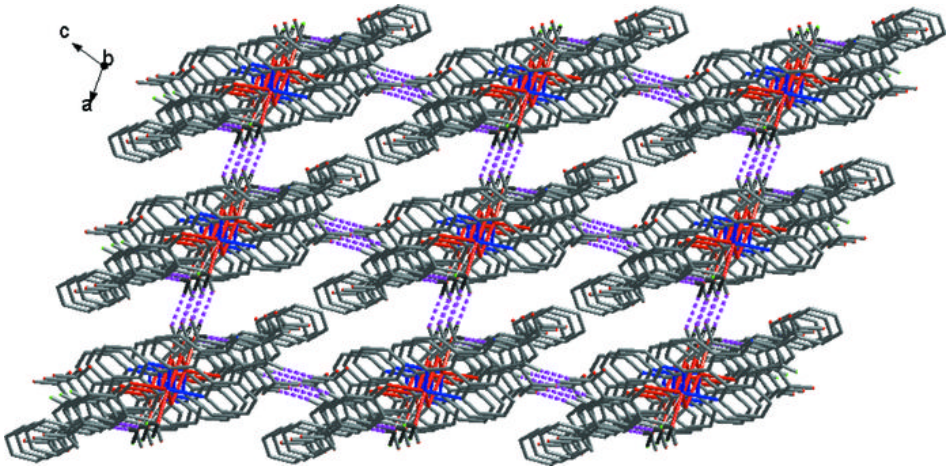


Fig. 3



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Azido(benzonitrile-κN)[hydridotris(pyrazol-1-yl-κN^2)borato](triphenylphosphine-κP)ruthenium(II)

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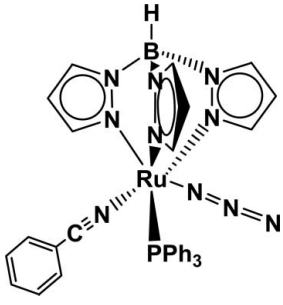
Key indicators: single-crystal X-ray study; T = 200 K; mean σ(C–C) = 0.006 Å; R factor = 0.041; wR factor = 0.093; data-to-parameter ratio = 13.6.

Facile ligand substitution is observed when the ruthenium–azide complex, $[RuN_3(Tp)(PPh_3)_2]$ [Tp,$HB(pz)_3$, pz = pyrazolyl, PPh_3 = triphenylphosphine] is treated with benzonitrile, yielding the title compound, $[Ru(C_9H_{10}BN_6)(N_3)(C_7H_5N)(C_{18}H_{15}P)]$. The asymmetric unit contains two crystallographically independent molecules. In each one, the Ru^{II} atom is six-coordinated in a distorted octahedral geometry by five N atoms from an htpb ligand, an azide ligand and a benzonitrile ligand and one P atom from a triphenylphosphine (tpp) ligand. The azide group is almost linear and is coordinated to Ru with an average Ru—N—N angle of 124.9 (3)°.

Related literature

For general background to azide and triazole compounds, see: Dori & Ziolo (1973); Huynh *et al.* (2003); Krivopalov & Shkurko (2005); Meyer *et al.* (1998); Padwa (1976).



Experimental

Crystal data

$[Ru(C_9H_{10}BN_6)(N_3)(C_7H_5N)(C_{18}H_{15}P)]$
M_r = 721.53
Triclinic, $P\overline{1}$
a = 11.1888 (2) Å
b = 16.2588 (3) Å
c = 18.9944 (4) Å
α = 109.588 (1)°
β = 91.930 (1)°
γ = 90.823 (1)°
V = 3252.37 (11) Å^3
Z = 4
Mo $K\alpha$ radiation
μ = 0.57 mm^{-1}
T = 200 K
0.20 × 0.08 × 0.03 mm

Data collection

Nonius KappaCCD diffractometer
Absorption correction: multi-scan (*DENZO/SCALEPACK*; Otwinowski & Minor, 1997)
T_{min} = 0.894, T_{max} = 0.983
28844 measured reflections
11501 independent reflections
8347 reflections with $I > 2\sigma(I)$
R_{int} = 0.049

Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.041
$wR(F^2)$ = 0.093
S = 1.01
11501 reflections
847 parameters
H-atom parameters constrained
$\Delta\rho_{max}$ = 0.56 e Å^{-3}
$\Delta\rho_{min}$ = −0.48 e Å^{-3}

Table 1
Selected bond lengths (Å).

Ru1—N1	2.122 (3)	Ru2—N11	2.109 (3)
Ru1—N3	2.075 (3)	Ru2—N13	2.083 (3)
Ru1—N5	2.086 (3)	Ru2—N15	2.077 (3)
Ru1—N7	1.984 (3)	Ru2—N17	1.983 (3)
Ru1—N8	2.119 (3)	Ru2—N18	2.108 (3)
Ru1—P1	2.3068 (11)	Ru2—P2	2.3204 (10)

Data collection: *COLLECT* (Nonius, 1998); cell refinement: *DENZO/SCALEPACK* (Otwinowski & Minor, 1997); data reduction: *DENZO/SCALEPACK*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *ORTEP-3* (Farrugia, 1997); software used to prepare material for publication: *WinGX* (Farrugia, 1999).

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Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: HY2311).

References

Dori, Z. & Ziolo, R. F. (1973). *Chem. Rev.* **73**, 247–254.
Farrugia, L. J. (1997). *J. Appl. Cryst.* **30**, 565.
Farrugia, L. J. (1999). *J. Appl. Cryst.* **32**, 837–838.
Huynh, M. H. V., Meyer, T. J., Labouriau, A., Morris, D. E. & White, P. S. (2003). *J. Am. Chem. Soc.* **125**, 2828–2829.
Krivopalov, V. P. & Shkurko, O. P. (2005). *Russ. Chem. Rev.* **74**, 339–379.
Meyer, K., Bendix, J., Metzler-Nolte, N., Weyhermüller, T. & Wieghardt, K. (1998). *J. Am. Chem. Soc.* **120**, 7260–7270.
Nonius (1998). *COLLECT*. Nonius BV, Delft, The Netherlands.
Otwinowski, Z. & Minor, W. (1997). *Methods in Enzymology*, Vol. 276, *Macromolecular Crystallography*, Part A, edited by C. W. Carter Jr & R. M. Sweet, pp. 307–326. New York: Academic Press.
Padwa, A. (1976). *Angew. Chem. Int. Ed. Engl.* **15**, 123–136.
Sheldrick, G. M. (2008). *Acta Cryst.* A**64**, 112–122.

supplementary materials

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Azido(benzonitrile-κN)[hydridotris(pyrazol-1-yl-κN^2)borato](triphenylphosphine-κP)ruthenium(II)

C.-C. Huang, H.-G. Chen, Y. H. Lo, W.-R. Lai and C.-H. Lin

Comment

Organic azides are synthetically helpful reagents. Amongst many transformations, perhaps the most important one is the 1,3-dipolar cycloaddition reactions with alkynes to synthesize triazoles (Padwa, 1976). Triazoles are nitrogen heteroarenes, which have found a range of significant applications in pharmaceutical and agricultural industries (Krivopalov & Shkurko, 2005). On the other hand, the azide anion, N_3^- , is a versatile ligand because it shows a variety of coordination modes, e.g. end-on monodentate, one-end bridging and end-to-end bridging modes, and also because its complexes exhibit interesting thermal and photochemical reactivities (Dori & Ziolo, 1973; Huynh *et al.*, 2003; Meyer *et al.*, 1998).

The title compound contains two crystallographically distinct molecules (Fig. 1, Table 1). The azide groups are almost linear [N8—N9—N10 = 176.8 (4), N18—N19—N20 = 175.7 (4)°] and are coordinated to Ru with Ru—N—N angles of 123.8 (3) and 125.9 (3)°. There is a small difference between the N—N distances [1.172 (4), 1.188 (4) and 1.173 (4), 1.172 (4) Å]. The Ru1—N7 and N7—C28 bond lengths of 1.983 (3) and 1.150 (4) Å correspond to a single Ru—N bond and a C≡N bond. The N7—C28—C29 of angle 179.0 (4)° indicates an *sp* hybridization as expected.

Experimental

To a solution of $[RuN_3(htpb)(tpp)_2]$ (htpb = hydridotripyrazolylborate, tpp = triphenylphosphine) in 30 ml of THF was added 10 ml of PhCN. The solution was stirred for 22 h, with color changed from yellow to orange-yellow, and then the solution was filtered through Celite. The solvent of the filtrate was removed under vacuum, and the residue was washed with *n*-hexane to give the title compound. The bright-yellow crystals of the title compound for X-ray structure analysis were obtained by slow diffusion of diethyl ether into a CH_2Cl_2 solution of the title compound at 0°C for 3 d.

Refinement

H atoms were placed in idealized positions and constrained to ride on their parent atoms, with C—H = 0.95 and B—H = 1.00 Å and $U_{iso}(H) = 1.2U_{eq}(C, B)$.

Figures

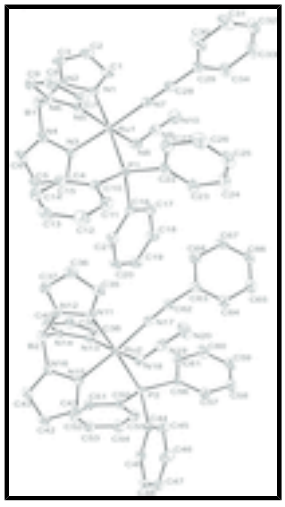


Fig. 1. Molecular structure of the title compound. Displacement ellipsoids are drawn at the 30% probability level.

Azido(benzonitrile-κ*N*)[hydridotris(pyrazol-1-yl- κN^2)borato](triphenylphosphine-κ*P*)ruthenium(II)

Crystal data

$[Ru(C_9H_{10}BN_6)(N_3)(C_7H_5N)(C_{18}H_{15}P)]$	$Z = 4$
$M_r = 721.53$	$F(000) = 1472$
Triclinic, $P\overline{1}$	$D_x = 1.474$ Mg m^{-3}
Hall symbol: -P 1	Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å
$a = 11.1888$ (2) Å	Cell parameters from 5430 reflections
$b = 16.2588$ (3) Å	$\theta = 2.7–25.0°$
$c = 18.9944$ (4) Å	$\mu = 0.57$ mm^{-1}
$\alpha = 109.588$ (1)°	$T = 200$ K
$\beta = 91.930$ (1)°	Prism, yellow
$\gamma = 90.823$ (1)°	0.20 × 0.08 × 0.03 mm
$V = 3252.37$ (11) Å^3	

Data collection

Nonius KappaCCD diffractometer	11501 independent reflections
Radiation source: fine-focus sealed tube	8347 reflections with $I > 2\sigma(I)$
graphite	$R_{int} = 0.049$
Detector resolution: 9 pixels mm^{-1}	$\theta_{max} = 25.0°$, $\theta_{min} = 1.1°$
ω and φ scans	$h = -13\rightarrow13$
Absorption correction: multi-scan (*DENZO*/*SCALEPACK*; Otwinowski & Minor, 1997)	$k = -14\rightarrow19$
$T_{min} = 0.894$, $T_{max} = 0.983$	$l = -22\rightarrow22$
28844 measured reflections	

Refinement

Refinement on F^2	Primary atom site location: structure-invariant direct methods
Least-squares matrix: full	Secondary atom site location: difference Fourier map
$R[F^2 > 2\sigma(F^2)] = 0.041$	Hydrogen site location: inferred from neighbouring sites
$wR(F^2) = 0.093$	H-atom parameters constrained
$S = 1.01$	$w = 1/[\sigma^2(F_o^2) + (0.0383P)^2 + 0.0352P]$ where $P = (F_o^2 + 2F_c^2)/3$
11501 reflections	$(\Delta/\sigma)_{max} = 0.001$
847 parameters	$\Delta\rho_{max} = 0.56$ e Å^{-3}
0 restraints	$\Delta\rho_{min} = -0.48$ e Å^{-3}

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å^2)

	x	*y*	*z*	U_{iso}*/U_{eq}
B1	0.6242 (4)	0.5295 (3)	0.2622 (3)	0.0396 (12)
H1'	0.5758	0.4750	0.2356	0.048*
B2	0.8881 (4)	0.5283 (3)	0.7621 (3)	0.0353 (11)
H2'	0.9355	0.4754	0.7376	0.042*
C1	0.8553 (3)	0.6230 (3)	0.1793 (2)	0.0350 (10)
H1	0.9165	0.6654	0.1825	0.042*
C2	0.8230 (4)	0.5530 (3)	0.1152 (2)	0.0454 (11)
H2	0.8558	0.5387	0.0672	0.054*
C3	0.7325 (4)	0.5088 (3)	0.1369 (2)	0.0428 (11)
H3	0.6909	0.4575	0.1057	0.051*
C4	0.8330 (4)	0.5572 (3)	0.4207 (2)	0.0406 (11)
H4	0.8924	0.5893	0.4568	0.049*
C5	0.7939 (4)	0.4732 (3)	0.4112 (2)	0.0495 (12)
H5	0.8201	0.4376	0.4391	0.059*
C6	0.7100 (4)	0.4515 (3)	0.3535 (2)	0.0460 (11)
H6	0.6672	0.3972	0.3336	0.055*
C7	0.5004 (3)	0.7446 (3)	0.3399 (2)	0.0356 (10)
H7	0.5072	0.8060	0.3643	0.043*
C8	0.3939 (3)	0.6988 (3)	0.3114 (2)	0.0453 (12)
H8	0.3163	0.7219	0.3124	0.054*
C9	0.4244 (3)	0.6135 (3)	0.2816 (2)	0.0439 (11)
H9	0.3709	0.5655	0.2578	0.053*
C10	0.6223 (3)	0.7708 (2)	0.5168 (2)	0.0276 (9)
C11	0.5806 (3)	0.8369 (3)	0.5780 (2)	0.0407 (10)
H11	0.6194	0.8928	0.5943	0.049*
C12	0.4826 (4)	0.8216 (3)	0.6155 (3)	0.0484 (12)
H12	0.4551	0.8670	0.6574	0.058*
C13	0.4256 (3)	0.7412 (3)	0.5921 (3)	0.0473 (12)
H13	0.3590	0.7308	0.6179	0.057*
C14	0.4647 (3)	0.6759 (3)	0.5314 (2)	0.0448 (11)

H14	0.4242	0.6206	0.5149	0.054*
C15	0.5639 (3)	0.6901 (3)	0.4936 (2)	0.0368 (10)
H15	0.5911	0.6442	0.4520	0.044*
C16	0.8749 (3)	0.7677 (2)	0.5389 (2)	0.0255 (8)
C17	0.9956 (3)	0.7738 (3)	0.5255 (2)	0.0375 (10)
H17	1.0184	0.7898	0.4840	0.045*
C18	1.0829 (3)	0.7568 (3)	0.5716 (2)	0.0444 (11)
H18	1.1650	0.7633	0.5628	0.053*
C19	1.0514 (3)	0.7305 (3)	0.6305 (2)	0.0423 (11)
H19	1.1114	0.7182	0.6618	0.051*
C20	0.9336 (3)	0.7222 (3)	0.6434 (2)	0.0389 (10)
H20	0.9117	0.7033	0.6835	0.047*
C21	0.8452 (3)	0.7411 (2)	0.5985 (2)	0.0329 (9)
H21	0.7635	0.7358	0.6087	0.039*
C22	0.7704 (3)	0.9056 (2)	0.4965 (2)	0.0312 (9)
C23	0.8647 (3)	0.9581 (3)	0.5366 (2)	0.0403 (10)
H23	0.9298	0.9327	0.5545	0.048*
C24	0.8653 (4)	1.0487 (3)	0.5513 (3)	0.0512 (12)
H24	0.9314	1.0838	0.5783	0.061*
C25	0.7734 (4)	1.0862 (3)	0.5275 (3)	0.0564 (13)
H25	0.7741	1.1477	0.5384	0.068*
C26	0.6797 (5)	1.0362 (3)	0.4877 (3)	0.0626 (15)
H26	0.6152	1.0630	0.4706	0.075*
C27	0.6769 (4)	0.9461 (3)	0.4717 (3)	0.0546 (13)
H27	0.6107	0.9120	0.4437	0.066*
C28	0.7948 (3)	0.8687 (3)	0.2999 (2)	0.0340 (9)
C29	0.8049 (3)	0.9435 (3)	0.2768 (2)	0.0352 (10)
C30	0.7032 (4)	0.9777 (3)	0.2551 (3)	0.0586 (14)
H30	0.6270	0.9522	0.2571	0.070*
C31	0.7110 (5)	1.0477 (3)	0.2310 (3)	0.0637 (15)
H31	0.6405	1.0703	0.2159	0.076*
C32	0.8192 (5)	1.0851 (3)	0.2286 (3)	0.0668 (15)
H32	0.8241	1.1340	0.2119	0.080*
C33	0.9201 (5)	1.0533 (3)	0.2497 (3)	0.0781 (17)
H33	0.9955	1.0797	0.2475	0.094*
C34	0.9145 (4)	0.9819 (3)	0.2750 (3)	0.0575 (13)
H34	0.9853	0.9602	0.2906	0.069*
C35	0.6565 (3)	0.6144 (3)	0.6709 (2)	0.0355 (10)
H35	0.5964	0.6553	0.6717	0.043*
C36	0.6849 (4)	0.5451 (3)	0.6086 (2)	0.0480 (11)
H36	0.6500	0.5302	0.5595	0.058*
C37	0.7734 (4)	0.5024 (3)	0.6324 (2)	0.0459 (11)
H37	0.8112	0.4513	0.6024	0.055*
C38	1.0176 (3)	0.7460 (3)	0.8471 (2)	0.0349 (10)
H38	1.0124	0.8069	0.8727	0.042*
C39	1.1234 (3)	0.7041 (3)	0.8214 (2)	0.0413 (11)
H39	1.2015	0.7294	0.8256	0.050*
C40	1.0891 (3)	0.6182 (3)	0.7887 (2)	0.0397 (11)
H40	1.1411	0.5719	0.7657	0.048*

C41	0.6899 (3)	0.5506 (2)	0.9147 (2)	0.0310 (9)
H41	0.6315	0.5807	0.9483	0.037*
C42	0.7323 (3)	0.4688 (3)	0.9094 (2)	0.0378 (10)
H42	0.7111	0.4338	0.9384	0.045*
C43	0.8113 (3)	0.4499 (3)	0.8530 (2)	0.0370 (10)
H43	0.8548	0.3977	0.8353	0.044*
C44	0.6426 (3)	0.7564 (2)	1.0298 (2)	0.0268 (8)
C45	0.5213 (3)	0.7460 (3)	1.0065 (2)	0.0384 (10)
H45	0.4959	0.7569	0.9623	0.046*
C46	0.4381 (3)	0.7198 (3)	1.0481 (2)	0.0469 (12)
H46	0.3563	0.7118	1.0316	0.056*
C47	0.4734 (4)	0.7054 (3)	1.1133 (2)	0.0436 (11)
H47	0.4164	0.6872	1.1414	0.052*
C48	0.5904 (3)	0.7175 (3)	1.1369 (2)	0.0416 (11)
H48	0.6148	0.7084	1.1821	0.050*
C49	0.6745 (3)	0.7428 (3)	1.0960 (2)	0.0352 (10)
H49	0.7557	0.7510	1.1136	0.042*
C50	0.8942 (3)	0.7713 (2)	1.0188 (2)	0.0282 (9)
C51	0.9526 (3)	0.6919 (2)	0.9966 (2)	0.0313 (9)
H51	0.9222	0.6448	0.9546	0.038*
C52	1.0545 (3)	0.6817 (3)	1.0357 (2)	0.0394 (10)
H52	1.0936	0.6274	1.0203	0.047*
C53	1.1003 (3)	0.7491 (3)	1.0967 (2)	0.0434 (11)
H53	1.1707	0.7417	1.1231	0.052*
C54	1.0427 (4)	0.8275 (3)	1.1190 (2)	0.0483 (12)
H54	1.0734	0.8743	1.1611	0.058*
C55	0.9406 (3)	0.8385 (3)	1.0806 (2)	0.0381 (10)
H55	0.9016	0.8928	1.0967	0.046*
C56	0.7436 (3)	0.8994 (2)	0.9921 (2)	0.0271 (8)
C57	0.6509 (4)	0.9475 (3)	1.0291 (2)	0.0450 (11)
H57	0.5875	0.9187	1.0443	0.054*
C58	0.6477 (4)	1.0375 (3)	1.0450 (3)	0.0584 (14)
H58	0.5831	1.0693	1.0715	0.070*
C59	0.7375 (4)	1.0806 (3)	1.0225 (2)	0.0468 (11)
H59	0.7353	1.1419	1.0329	0.056*
C60	0.8305 (4)	1.0334 (3)	0.9845 (3)	0.0518 (13)
H60	0.8935	1.0621	0.9688	0.062*
C61	0.8321 (3)	0.9440 (3)	0.9694 (3)	0.0441 (11)
H61	0.8962	0.9121	0.9425	0.053*
C62	0.7215 (3)	0.8628 (3)	0.7954 (2)	0.0313 (9)
C63	0.6984 (3)	0.9433 (3)	0.7822 (2)	0.0338 (9)
C64	0.6199 (4)	0.9992 (3)	0.8289 (3)	0.0504 (12)
H64	0.5836	0.9836	0.8673	0.060*
C65	0.5950 (4)	1.0775 (3)	0.8194 (3)	0.0603 (14)
H65	0.5392	1.1152	0.8502	0.072*
C66	0.6503 (4)	1.1015 (3)	0.7655 (3)	0.0512 (12)
H66	0.6338	1.1562	0.7598	0.061*
C67	0.7275 (4)	1.0481 (3)	0.7207 (2)	0.0464 (11)
H67	0.7644	1.0650	0.6832	0.056*

C68	0.7543 (4)	0.9678 (3)	0.7286 (2)	0.0434 (11)
H68	0.8102	0.9307	0.6974	0.052*
N1	0.7875 (3)	0.6218 (2)	0.23571 (17)	0.0298 (7)
N2	0.7132 (3)	0.5507 (2)	0.20954 (18)	0.0345 (8)
N3	0.7748 (3)	0.5870 (2)	0.37157 (17)	0.0307 (8)
N4	0.6987 (3)	0.5207 (2)	0.32976 (18)	0.0361 (8)
N5	0.5921 (2)	0.6903 (2)	0.32828 (17)	0.0295 (7)
N6	0.5438 (3)	0.6089 (2)	0.29169 (18)	0.0356 (8)
N7	0.7850 (2)	0.8086 (2)	0.31847 (17)	0.0285 (7)
N8	0.9664 (3)	0.7047 (2)	0.35704 (19)	0.0387 (9)
N9	1.0281 (3)	0.7336 (2)	0.3220 (2)	0.0391 (8)
N10	1.0951 (3)	0.7611 (3)	0.2875 (2)	0.0607 (11)
N11	0.7258 (2)	0.6156 (2)	0.73002 (17)	0.0291 (7)
N12	0.7979 (3)	0.5453 (2)	0.70548 (18)	0.0324 (8)
N13	0.9242 (2)	0.6894 (2)	0.83116 (17)	0.0279 (7)
N14	0.9701 (2)	0.6093 (2)	0.79404 (17)	0.0300 (7)
N15	0.7429 (2)	0.58089 (19)	0.86601 (16)	0.0270 (7)
N16	0.8175 (2)	0.5169 (2)	0.82667 (18)	0.0307 (7)
N17	0.7334 (2)	0.8024 (2)	0.81263 (17)	0.0288 (7)
N18	0.5513 (3)	0.6914 (2)	0.83975 (18)	0.0355 (8)
N19	0.4879 (3)	0.7312 (2)	0.81356 (19)	0.0370 (8)
N20	0.4184 (3)	0.7681 (3)	0.7884 (3)	0.0688 (13)
P1	0.76176 (8)	0.78578 (6)	0.47329 (5)	0.0251 (2)
P2	0.75346 (8)	0.78065 (6)	0.96896 (5)	0.0242 (2)
Ru1	0.77697 (2)	0.703233 (19)	0.348879 (17)	0.02482 (9)
Ru2	0.73983 (2)	0.697064 (19)	0.842995 (16)	0.02291 (9)

Atomic displacement parameters (Å^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
B1	0.049 (3)	0.036 (3)	0.032 (3)	−0.006 (2)	0.001 (2)	0.011 (2)
B2	0.039 (2)	0.030 (3)	0.038 (3)	0.007 (2)	0.003 (2)	0.013 (2)
C1	0.037 (2)	0.043 (3)	0.030 (2)	0.0103 (19)	0.0069 (18)	0.017 (2)
C2	0.055 (3)	0.056 (3)	0.026 (3)	0.016 (2)	0.009 (2)	0.014 (2)
C3	0.060 (3)	0.035 (3)	0.029 (3)	0.009 (2)	−0.006 (2)	0.006 (2)
C4	0.058 (3)	0.038 (3)	0.031 (3)	0.022 (2)	0.007 (2)	0.017 (2)
C5	0.086 (3)	0.029 (3)	0.041 (3)	0.016 (2)	0.010 (3)	0.020 (2)
C6	0.071 (3)	0.031 (3)	0.046 (3)	0.008 (2)	0.018 (2)	0.022 (2)
C7	0.037 (2)	0.040 (3)	0.032 (2)	0.0067 (19)	−0.0003 (18)	0.015 (2)
C8	0.029 (2)	0.068 (3)	0.046 (3)	0.004 (2)	0.0015 (19)	0.029 (3)
C9	0.034 (2)	0.057 (3)	0.044 (3)	−0.018 (2)	−0.0098 (19)	0.023 (2)
C10	0.0270 (19)	0.032 (2)	0.025 (2)	0.0027 (17)	−0.0008 (16)	0.0111 (19)
C11	0.038 (2)	0.040 (3)	0.040 (3)	0.0025 (19)	0.0050 (19)	0.008 (2)
C12	0.044 (2)	0.058 (3)	0.045 (3)	0.015 (2)	0.020 (2)	0.018 (3)
C13	0.030 (2)	0.073 (4)	0.052 (3)	0.004 (2)	0.009 (2)	0.039 (3)
C14	0.041 (2)	0.054 (3)	0.043 (3)	−0.012 (2)	0.002 (2)	0.022 (3)
C15	0.040 (2)	0.041 (3)	0.031 (2)	−0.0008 (19)	0.0042 (18)	0.014 (2)
C16	0.0306 (19)	0.021 (2)	0.024 (2)	0.0014 (16)	−0.0003 (16)	0.0071 (17)

C17	0.035 (2)	0.048 (3)	0.036 (3)	0.0012 (19)	0.0014 (18)	0.022 (2)
C18	0.030 (2)	0.064 (3)	0.042 (3)	0.004 (2)	−0.0005 (19)	0.022 (3)
C19	0.044 (2)	0.046 (3)	0.040 (3)	0.010 (2)	−0.011 (2)	0.020 (2)
C20	0.044 (2)	0.046 (3)	0.037 (3)	0.004 (2)	−0.0021 (19)	0.028 (2)
C21	0.037 (2)	0.035 (2)	0.030 (2)	0.0058 (18)	0.0060 (17)	0.015 (2)
C22	0.035 (2)	0.029 (2)	0.030 (2)	0.0019 (18)	0.0069 (17)	0.0103 (19)
C23	0.039 (2)	0.039 (3)	0.043 (3)	−0.001 (2)	0.008 (2)	0.014 (2)
C24	0.055 (3)	0.033 (3)	0.065 (4)	−0.004 (2)	0.016 (2)	0.015 (3)
C25	0.075 (3)	0.032 (3)	0.068 (4)	0.007 (3)	0.025 (3)	0.022 (3)
C26	0.080 (4)	0.044 (3)	0.070 (4)	0.028 (3)	0.002 (3)	0.027 (3)
C27	0.063 (3)	0.032 (3)	0.063 (3)	0.008 (2)	−0.018 (2)	0.011 (2)
C28	0.035 (2)	0.035 (3)	0.034 (3)	0.0047 (18)	0.0022 (18)	0.014 (2)
C29	0.047 (2)	0.028 (2)	0.033 (2)	0.0030 (19)	0.0057 (19)	0.013 (2)
C30	0.053 (3)	0.066 (4)	0.079 (4)	0.015 (3)	0.014 (3)	0.053 (3)
C31	0.081 (4)	0.059 (4)	0.067 (4)	0.028 (3)	0.018 (3)	0.040 (3)
C32	0.097 (4)	0.042 (3)	0.073 (4)	−0.003 (3)	−0.005 (3)	0.035 (3)
C33	0.077 (4)	0.058 (4)	0.112 (5)	−0.030 (3)	−0.017 (3)	0.048 (4)
C34	0.054 (3)	0.051 (3)	0.077 (4)	−0.006 (2)	−0.014 (3)	0.036 (3)
C35	0.039 (2)	0.039 (3)	0.032 (2)	−0.0059 (19)	−0.0058 (18)	0.018 (2)
C36	0.067 (3)	0.046 (3)	0.028 (3)	−0.010 (2)	−0.008 (2)	0.010 (2)
C37	0.070 (3)	0.032 (3)	0.029 (3)	0.001 (2)	0.011 (2)	0.002 (2)
C38	0.039 (2)	0.036 (3)	0.034 (3)	−0.0002 (19)	0.0048 (18)	0.016 (2)
C39	0.025 (2)	0.058 (3)	0.048 (3)	0.000 (2)	0.0054 (19)	0.027 (3)
C40	0.030 (2)	0.054 (3)	0.045 (3)	0.013 (2)	0.0120 (19)	0.028 (2)
C41	0.036 (2)	0.030 (2)	0.028 (2)	−0.0052 (17)	0.0003 (17)	0.0122 (19)
C42	0.051 (2)	0.028 (2)	0.041 (3)	−0.0063 (19)	−0.004 (2)	0.022 (2)
C43	0.045 (2)	0.027 (2)	0.043 (3)	0.0004 (18)	−0.006 (2)	0.018 (2)
C44	0.0307 (19)	0.020 (2)	0.028 (2)	−0.0006 (16)	0.0045 (16)	0.0065 (18)
C45	0.032 (2)	0.051 (3)	0.033 (2)	−0.0027 (19)	0.0017 (18)	0.015 (2)
C46	0.033 (2)	0.064 (3)	0.041 (3)	−0.008 (2)	0.0066 (19)	0.013 (3)
C47	0.047 (3)	0.040 (3)	0.046 (3)	−0.005 (2)	0.018 (2)	0.016 (2)
C48	0.050 (3)	0.045 (3)	0.040 (3)	0.007 (2)	0.010 (2)	0.027 (2)
C49	0.034 (2)	0.037 (3)	0.040 (3)	0.0056 (18)	0.0035 (18)	0.020 (2)
C50	0.0230 (18)	0.037 (2)	0.028 (2)	−0.0030 (17)	−0.0002 (16)	0.016 (2)
C51	0.033 (2)	0.030 (2)	0.032 (2)	0.0012 (17)	−0.0052 (17)	0.0125 (19)
C52	0.035 (2)	0.043 (3)	0.044 (3)	0.012 (2)	−0.0019 (19)	0.019 (2)
C53	0.030 (2)	0.061 (3)	0.046 (3)	−0.001 (2)	−0.0085 (19)	0.028 (3)
C54	0.047 (3)	0.051 (3)	0.043 (3)	−0.003 (2)	−0.016 (2)	0.011 (2)
C55	0.037 (2)	0.034 (3)	0.039 (3)	0.0001 (19)	−0.0072 (19)	0.008 (2)
C56	0.034 (2)	0.023 (2)	0.023 (2)	−0.0001 (16)	−0.0029 (16)	0.0076 (18)
C57	0.055 (3)	0.034 (3)	0.052 (3)	0.010 (2)	0.022 (2)	0.021 (2)
C58	0.079 (3)	0.035 (3)	0.068 (4)	0.019 (3)	0.027 (3)	0.024 (3)
C59	0.067 (3)	0.023 (2)	0.049 (3)	0.002 (2)	−0.004 (2)	0.011 (2)
C60	0.046 (3)	0.038 (3)	0.080 (4)	−0.009 (2)	0.002 (2)	0.030 (3)
C61	0.033 (2)	0.029 (3)	0.069 (3)	−0.0016 (18)	0.004 (2)	0.015 (2)
C62	0.032 (2)	0.032 (2)	0.031 (2)	0.0018 (17)	−0.0019 (17)	0.013 (2)
C63	0.037 (2)	0.033 (2)	0.036 (3)	−0.0023 (18)	−0.0058 (18)	0.017 (2)
C64	0.062 (3)	0.042 (3)	0.055 (3)	0.013 (2)	0.014 (2)	0.025 (3)
C65	0.074 (3)	0.041 (3)	0.071 (4)	0.020 (3)	0.014 (3)	0.023 (3)

C66	0.073 (3)	0.036 (3)	0.051 (3)	0.009 (2)	−0.001 (2)	0.022 (3)
C67	0.066 (3)	0.040 (3)	0.041 (3)	−0.007 (2)	−0.001 (2)	0.025 (2)
C68	0.052 (3)	0.040 (3)	0.041 (3)	0.000 (2)	0.001 (2)	0.019 (2)
N1	0.0373 (17)	0.030 (2)	0.0233 (19)	0.0038 (15)	−0.0015 (14)	0.0109 (16)
N2	0.0454 (19)	0.030 (2)	0.029 (2)	0.0013 (16)	−0.0012 (15)	0.0106 (17)
N3	0.0379 (18)	0.028 (2)	0.0283 (19)	0.0074 (15)	0.0050 (14)	0.0109 (16)
N4	0.048 (2)	0.028 (2)	0.035 (2)	0.0013 (16)	0.0074 (16)	0.0126 (17)
N5	0.0274 (16)	0.035 (2)	0.0277 (19)	−0.0018 (14)	−0.0032 (13)	0.0125 (16)
N6	0.0351 (18)	0.039 (2)	0.033 (2)	−0.0065 (16)	−0.0018 (15)	0.0128 (18)
N7	0.0258 (16)	0.032 (2)	0.0283 (19)	0.0035 (14)	−0.0006 (13)	0.0117 (17)
N8	0.0350 (18)	0.052 (2)	0.033 (2)	0.0108 (17)	0.0060 (15)	0.0187 (19)
N9	0.0322 (18)	0.041 (2)	0.035 (2)	0.0069 (16)	−0.0022 (16)	0.0016 (19)
N10	0.043 (2)	0.078 (3)	0.062 (3)	−0.011 (2)	0.006 (2)	0.026 (3)
N11	0.0330 (17)	0.032 (2)	0.0250 (19)	−0.0014 (14)	−0.0004 (14)	0.0126 (16)
N12	0.0441 (19)	0.0240 (19)	0.029 (2)	0.0041 (15)	0.0069 (15)	0.0081 (16)
N13	0.0297 (16)	0.032 (2)	0.0269 (19)	0.0013 (14)	0.0017 (13)	0.0162 (16)
N14	0.0329 (17)	0.0288 (19)	0.0320 (19)	0.0071 (14)	0.0062 (14)	0.0142 (16)
N15	0.0336 (16)	0.0242 (18)	0.0240 (18)	−0.0008 (14)	−0.0011 (13)	0.0094 (15)
N16	0.0345 (17)	0.0252 (19)	0.035 (2)	0.0040 (14)	0.0007 (14)	0.0132 (16)
N17	0.0294 (16)	0.031 (2)	0.0283 (19)	0.0000 (14)	0.0002 (14)	0.0123 (16)
N18	0.0305 (17)	0.040 (2)	0.041 (2)	0.0000 (15)	0.0005 (15)	0.0198 (18)
N19	0.0298 (17)	0.042 (2)	0.039 (2)	−0.0004 (16)	0.0060 (15)	0.0128 (19)
N20	0.040 (2)	0.087 (3)	0.101 (4)	0.022 (2)	0.004 (2)	0.059 (3)
P1	0.0258 (5)	0.0255 (6)	0.0269 (6)	0.0018 (4)	0.0011 (4)	0.0124 (5)
P2	0.0241 (5)	0.0239 (6)	0.0259 (6)	0.0009 (4)	0.0003 (4)	0.0103 (5)
Ru1	0.02614 (16)	0.02651 (19)	0.02497 (19)	0.00370 (13)	0.00169 (12)	0.01262 (15)
Ru2	0.02437 (15)	0.02269 (18)	0.02441 (19)	0.00007 (12)	0.00033 (12)	0.01164 (15)

Geometric parameters (Å, °)

B1—N6	1.539 (5)	C38—N13	1.339 (5)
B1—N2	1.548 (5)	C38—C39	1.394 (5)
B1—N4	1.555 (5)	C38—H38	0.9500
B1—H1'	1.0000	C39—C40	1.368 (6)
B2—N14	1.528 (5)	C39—H39	0.9500
B2—N16	1.542 (5)	C40—N14	1.349 (4)
B2—N12	1.545 (5)	C40—H40	0.9500
B2—H2'	1.0000	C41—N15	1.336 (4)
C1—N1	1.339 (4)	C41—C42	1.390 (5)
C1—C2	1.392 (6)	C41—H41	0.9500
C1—H1	0.9500	C42—C43	1.368 (5)
C2—C3	1.386 (6)	C42—H42	0.9500
C2—H2	0.9500	C43—N16	1.344 (4)
C3—N2	1.345 (5)	C43—H43	0.9500
C3—H3	0.9500	C44—C49	1.384 (5)
C4—N3	1.341 (4)	C44—C45	1.404 (5)
C4—C5	1.379 (6)	C44—P2	1.849 (3)
C4—H4	0.9500	C45—C46	1.391 (5)
C5—C6	1.366 (6)	C45—H45	0.9500

C5—H5	0.9500	C46—C47	1.382 (6)
C6—N4	1.352 (4)	C46—H46	0.9500
C6—H6	0.9500	C47—C48	1.360 (6)
C7—N5	1.338 (4)	C47—H47	0.9500
C7—C8	1.389 (5)	C48—C49	1.382 (5)
C7—H7	0.9500	C48—H48	0.9500
C8—C9	1.364 (6)	C49—H49	0.9500
C8—H8	0.9500	C50—C55	1.387 (5)
C9—N6	1.350 (4)	C50—C51	1.396 (5)
C9—H9	0.9500	C50—P2	1.845 (3)
C10—C15	1.383 (5)	C51—C52	1.382 (5)
C10—C11	1.391 (5)	C51—H51	0.9500
C10—P1	1.840 (3)	C52—C53	1.378 (6)
C11—C12	1.391 (5)	C52—H52	0.9500
C11—H11	0.9500	C53—C54	1.378 (5)
C12—C13	1.372 (6)	C53—H53	0.9500
C12—H12	0.9500	C54—C55	1.381 (5)
C13—C14	1.368 (6)	C54—H54	0.9500
C13—H13	0.9500	C55—H55	0.9500
C14—C15	1.399 (5)	C56—C57	1.373 (5)
C14—H14	0.9500	C56—C61	1.381 (5)
C15—H15	0.9500	C56—P2	1.837 (4)
C16—C17	1.392 (5)	C57—C58	1.392 (5)
C16—C21	1.389 (5)	C57—H57	0.9500
C16—P1	1.842 (3)	C58—C59	1.376 (6)
C17—C18	1.383 (5)	C58—H58	0.9500
C17—H17	0.9500	C59—C60	1.376 (5)
C18—C19	1.378 (5)	C59—H59	0.9500
C18—H18	0.9500	C60—C61	1.385 (5)
C19—C20	1.361 (5)	C60—H60	0.9500
C19—H19	0.9500	C61—H61	0.9500
C20—C21	1.387 (5)	C62—N17	1.143 (4)
C20—H20	0.9500	C62—C63	1.438 (5)
C21—H21	0.9500	C63—C68	1.376 (5)
C22—C23	1.380 (5)	C63—C64	1.385 (5)
C22—C27	1.396 (5)	C64—C65	1.376 (5)
C22—P1	1.848 (4)	C64—H64	0.9500
C23—C24	1.404 (5)	C65—C66	1.374 (6)
C23—H23	0.9500	C65—H65	0.9500
C24—C25	1.345 (6)	C66—C67	1.341 (6)
C24—H24	0.9500	C66—H66	0.9500
C25—C26	1.358 (7)	C67—C68	1.398 (5)
C25—H25	0.9500	C67—H67	0.9500
C26—C27	1.392 (6)	C68—H68	0.9500
C26—H26	0.9500	N1—N2	1.355 (4)
C27—H27	0.9500	N3—N4	1.368 (4)
C28—N7	1.150 (4)	N5—N6	1.366 (4)
C28—C29	1.429 (5)	N8—N9	1.172 (4)
C29—C34	1.374 (5)	N9—N10	1.188 (4)

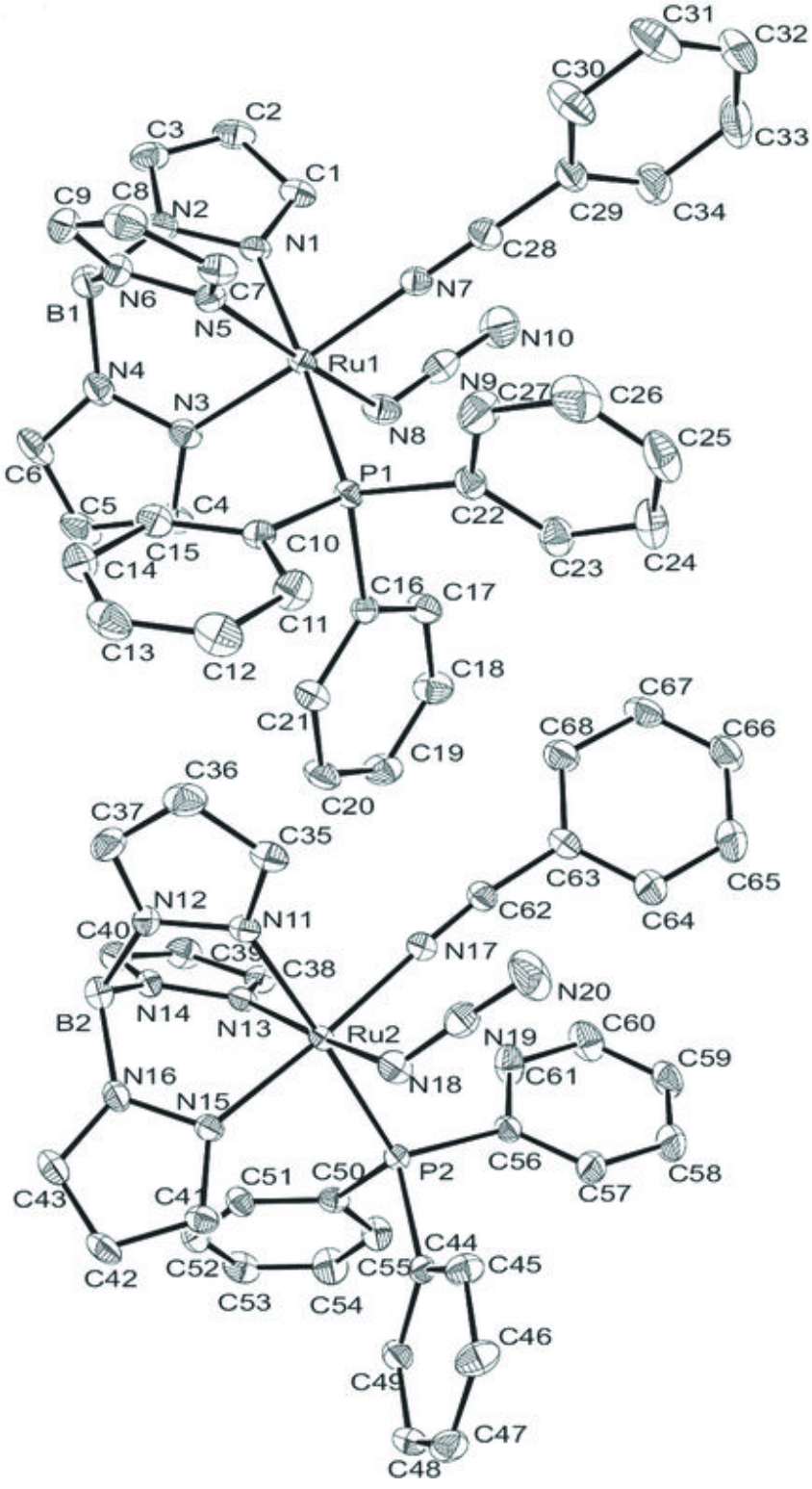
C29—C30	1.384 (5)	N11—N12	1.367 (4)
C30—C31	1.364 (6)	N13—N14	1.373 (4)
C30—H30	0.9500	N15—N16	1.372 (4)
C31—C32	1.356 (7)	N18—N19	1.173 (4)
C31—H31	0.9500	N19—N20	1.172 (4)
C32—C33	1.353 (7)	Ru1—N1	2.122 (3)
C32—H32	0.9500	Ru1—N3	2.075 (3)
C33—C34	1.398 (6)	Ru1—N5	2.086 (3)
C33—H33	0.9500	Ru1—N7	1.984 (3)
C34—H34	0.9500	Ru1—N8	2.119 (3)
C35—N11	1.337 (4)	Ru1—P1	2.3068 (11)
C35—C36	1.383 (5)	Ru2—N11	2.109 (3)
C35—H35	0.9500	Ru2—N13	2.083 (3)
C36—C37	1.366 (6)	Ru2—N15	2.077 (3)
C36—H36	0.9500	Ru2—N17	1.983 (3)
C37—N12	1.345 (5)	Ru2—N18	2.108 (3)
C37—H37	0.9500	Ru2—P2	2.3204 (10)
N6—B1—N2	107.2 (3)	C48—C47—C46	119.4 (4)
N6—B1—N4	107.9 (3)	C48—C47—H47	120.3
N2—B1—N4	107.3 (3)	C46—C47—H47	120.3
N6—B1—H1'	111.4	C47—C48—C49	120.8 (4)
N2—B1—H1'	111.4	C47—C48—H48	119.6
N4—B1—H1'	111.4	C49—C48—H48	119.6
N14—B2—N16	108.1 (3)	C48—C49—C44	121.3 (4)
N14—B2—N12	107.9 (3)	C48—C49—H49	119.3
N16—B2—N12	108.1 (3)	C44—C49—H49	119.3
N14—B2—H2'	110.9	C55—C50—C51	118.4 (3)
N16—B2—H2'	110.9	C55—C50—P2	122.5 (3)
N12—B2—H2'	110.9	C51—C50—P2	119.0 (3)
N1—C1—C2	110.0 (4)	C52—C51—C50	120.1 (4)
N1—C1—H1	125.0	C52—C51—H51	120.0
C2—C1—H1	125.0	C50—C51—H51	120.0
C3—C2—C1	104.7 (4)	C51—C52—C53	121.0 (4)
C3—C2—H2	127.7	C51—C52—H52	119.5
C1—C2—H2	127.7	C53—C52—H52	119.5
N2—C3—C2	108.6 (4)	C54—C53—C52	119.2 (4)
N2—C3—H3	125.7	C54—C53—H53	120.4
C2—C3—H3	125.7	C52—C53—H53	120.4
N3—C4—C5	110.0 (4)	C53—C54—C55	120.4 (4)
N3—C4—H4	125.0	C53—C54—H54	119.8
C5—C4—H4	125.0	C55—C54—H54	119.8
C6—C5—C4	106.2 (4)	C54—C55—C50	120.9 (4)
C6—C5—H5	126.9	C54—C55—H55	119.5
C4—C5—H5	126.9	C50—C55—H55	119.5
N4—C6—C5	108.0 (4)	C57—C56—C61	117.0 (3)
N4—C6—H6	126.0	C57—C56—P2	124.0 (3)
C5—C6—H6	126.0	C61—C56—P2	119.0 (3)
N5—C7—C8	110.7 (4)	C56—C57—C58	121.6 (4)
N5—C7—H7	124.7	C56—C57—H57	119.2

C8—C7—H7	124.7	C58—C57—H57	119.2
C9—C8—C7	105.4 (4)	C59—C58—C57	120.3 (4)
C9—C8—H8	127.3	C59—C58—H58	119.8
C7—C8—H8	127.3	C57—C58—H58	119.8
N6—C9—C8	108.2 (4)	C58—C59—C60	118.9 (4)
N6—C9—H9	125.9	C58—C59—H59	120.6
C8—C9—H9	125.9	C60—C59—H59	120.6
C15—C10—C11	118.7 (3)	C59—C60—C61	119.8 (4)
C15—C10—P1	119.9 (3)	C59—C60—H60	120.1
C11—C10—P1	121.1 (3)	C61—C60—H60	120.1
C12—C11—C10	120.6 (4)	C56—C61—C60	122.3 (4)
C12—C11—H11	119.7	C56—C61—H61	118.9
C10—C11—H11	119.7	C60—C61—H61	118.9
C13—C12—C11	120.1 (4)	N17—C62—C63	172.8 (4)
C13—C12—H12	119.9	C68—C63—C64	119.9 (4)
C11—C12—H12	119.9	C68—C63—C62	123.1 (4)
C14—C13—C12	120.0 (4)	C64—C63—C62	116.9 (3)
C14—C13—H13	120.0	C65—C64—C63	119.6 (4)
C12—C13—H13	120.0	C65—C64—H64	120.2
C13—C14—C15	120.5 (4)	C63—C64—H64	120.2
C13—C14—H14	119.8	C64—C65—C66	120.3 (4)
C15—C14—H14	119.8	C64—C65—H65	119.8
C10—C15—C14	120.1 (4)	C66—C65—H65	119.8
C10—C15—H15	119.9	C67—C66—C65	120.3 (4)
C14—C15—H15	119.9	C67—C66—H66	119.9
C17—C16—C21	117.8 (3)	C65—C66—H66	119.9
C17—C16—P1	119.3 (3)	C66—C67—C68	120.8 (4)
C21—C16—P1	122.8 (3)	C66—C67—H67	119.6
C18—C17—C16	120.9 (4)	C68—C67—H67	119.6
C18—C17—H17	119.6	C63—C68—C67	119.0 (4)
C16—C17—H17	119.6	C63—C68—H68	120.5
C19—C18—C17	120.3 (4)	C67—C68—H68	120.5
C19—C18—H18	119.8	C1—N1—N2	107.3 (3)
C17—C18—H18	119.8	C1—N1—Ru1	134.2 (3)
C20—C19—C18	119.5 (3)	N2—N1—Ru1	118.6 (2)
C20—C19—H19	120.2	C3—N2—N1	109.4 (3)
C18—C19—H19	120.2	C3—N2—B1	130.5 (4)
C19—C20—C21	120.7 (4)	N1—N2—B1	120.1 (3)
C19—C20—H20	119.7	C4—N3—N4	106.4 (3)
C21—C20—H20	119.7	C4—N3—Ru1	135.1 (3)
C20—C21—C16	120.8 (3)	N4—N3—Ru1	118.5 (2)
C20—C21—H21	119.6	C6—N4—N3	109.4 (3)
C16—C21—H21	119.6	C6—N4—B1	129.8 (4)
C23—C22—C27	117.5 (4)	N3—N4—B1	120.6 (3)
C23—C22—P1	124.0 (3)	C7—N5—N6	105.8 (3)
C27—C22—P1	118.5 (3)	C7—N5—Ru1	136.0 (3)
C22—C23—C24	120.6 (4)	N6—N5—Ru1	118.2 (2)
C22—C23—H23	119.7	C9—N6—N5	109.9 (3)
C24—C23—H23	119.7	C9—N6—B1	128.8 (4)

C25—C24—C23	120.7 (5)	N5—N6—B1	121.0 (3)
C25—C24—H24	119.6	C28—N7—Ru1	176.9 (3)
C23—C24—H24	119.6	N9—N8—Ru1	123.8 (3)
C24—C25—C26	119.9 (5)	N8—N9—N10	176.8 (4)
C24—C25—H25	120.1	C35—N11—N12	106.1 (3)
C26—C25—H25	120.1	C35—N11—Ru2	134.2 (3)
C25—C26—C27	120.7 (4)	N12—N11—Ru2	119.7 (2)
C25—C26—H26	119.6	C37—N12—N11	109.7 (3)
C27—C26—H26	119.6	C37—N12—B2	131.9 (3)
C26—C27—C22	120.5 (5)	N11—N12—B2	118.4 (3)
C26—C27—H27	119.8	C38—N13—N14	105.5 (3)
C22—C27—H27	119.8	C38—N13—Ru2	136.3 (3)
N7—C28—C29	179.0 (4)	N14—N13—Ru2	118.0 (2)
C34—C29—C30	119.1 (4)	C40—N14—N13	109.4 (3)
C34—C29—C28	121.1 (4)	C40—N14—B2	129.6 (3)
C30—C29—C28	119.7 (4)	N13—N14—B2	120.9 (3)
C31—C30—C29	120.8 (4)	C41—N15—N16	106.4 (3)
C31—C30—H30	119.6	C41—N15—Ru2	135.1 (3)
C29—C30—H30	119.6	N16—N15—Ru2	118.5 (2)
C32—C31—C30	120.1 (5)	C43—N16—N15	109.0 (3)
C32—C31—H31	119.9	C43—N16—B2	130.8 (3)
C30—C31—H31	119.9	N15—N16—B2	120.2 (3)
C33—C32—C31	120.4 (5)	C62—N17—Ru2	175.3 (3)
C33—C32—H32	119.8	N19—N18—Ru2	125.9 (3)
C31—C32—H32	119.8	N20—N19—N18	175.7 (4)
C32—C33—C34	120.6 (5)	C10—P1—C16	101.27 (15)
C32—C33—H33	119.7	C10—P1—C22	101.87 (16)
C34—C33—H33	119.7	C16—P1—C22	102.37 (17)
C29—C34—C33	119.0 (4)	C10—P1—Ru1	116.14 (13)
C29—C34—H34	120.5	C16—P1—Ru1	116.39 (11)
C33—C34—H34	120.5	C22—P1—Ru1	116.42 (12)
N11—C35—C36	110.3 (4)	C56—P2—C50	102.06 (17)
N11—C35—H35	124.9	C56—P2—C44	102.77 (16)
C36—C35—H35	124.9	C50—P2—C44	100.64 (16)
C37—C36—C35	105.7 (4)	C56—P2—Ru2	116.66 (12)
C37—C36—H36	127.2	C50—P2—Ru2	115.27 (12)
C35—C36—H36	127.2	C44—P2—Ru2	117.02 (13)
N12—C37—C36	108.2 (4)	N7—Ru1—N3	174.90 (12)
N12—C37—H37	125.9	N7—Ru1—N5	91.69 (11)
C36—C37—H37	125.9	N3—Ru1—N5	89.56 (12)
N13—C38—C39	111.4 (4)	N7—Ru1—N8	89.40 (12)
N13—C38—H38	124.3	N3—Ru1—N8	88.78 (12)
C39—C38—H38	124.3	N5—Ru1—N8	173.12 (13)
C40—C39—C38	104.2 (3)	N7—Ru1—N1	90.41 (12)
C40—C39—H39	127.9	N3—Ru1—N1	84.76 (12)
C38—C39—H39	127.9	N5—Ru1—N1	85.30 (12)
N14—C40—C39	109.4 (3)	N8—Ru1—N1	87.90 (12)
N14—C40—H40	125.3	N7—Ru1—P1	92.34 (9)
C39—C40—H40	125.3	N3—Ru1—P1	92.52 (9)

N15—C41—C42	110.5 (3)	N5—Ru1—P1	93.70 (9)
N15—C41—H41	124.8	N8—Ru1—P1	93.05 (10)
C42—C41—H41	124.8	N1—Ru1—P1	177.11 (9)
C43—C42—C41	104.9 (3)	N17—Ru2—N15	175.44 (12)
C43—C42—H42	127.5	N17—Ru2—N13	91.90 (11)
C41—C42—H42	127.5	N15—Ru2—N13	88.56 (11)
N16—C43—C42	109.2 (3)	N17—Ru2—N18	89.20 (12)
N16—C43—H43	125.4	N15—Ru2—N18	89.72 (11)
C42—C43—H43	125.4	N13—Ru2—N18	171.90 (13)
C49—C44—C45	117.8 (3)	N17—Ru2—N11	90.68 (12)
C49—C44—P2	122.8 (3)	N15—Ru2—N11	84.83 (11)
C45—C44—P2	119.3 (3)	N13—Ru2—N11	85.80 (11)
C46—C45—C44	120.1 (4)	N18—Ru2—N11	86.16 (12)
C46—C45—H45	119.9	N17—Ru2—P2	92.09 (9)
C44—C45—H45	119.9	N15—Ru2—P2	92.39 (9)
C47—C46—C45	120.5 (4)	N13—Ru2—P2	94.69 (9)
C47—C46—H46	119.7	N18—Ru2—P2	93.29 (9)
C45—C46—H46	119.7	N11—Ru2—P2	177.17 (8)

Fig. 1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N6
C7
N5
N10
Ru1
N4
N9
C27
C26
N3
N8
C25
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P1
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Ru2
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C58
C43
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P2
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catena-Poly[[bis(μ-3-aminopyrazine-2-carboxylato)-$\kappa^3N^1,O:O;\kappa^3O:N^1,O$)-dilithium]-di-μ-aqua]

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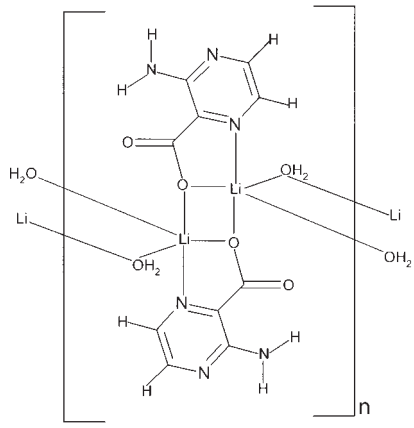
Key indicators: single-crystal X-ray study; T = 293 K; mean σ(C–C) = 0.002 Å; R factor = 0.049; wR factor = 0.147; data-to-parameter ratio = 16.6.

The title compound, $[Li(C_5H_4N_3O_2)(H_2O)]_n$, is composed of centrosymmetric dinuclear units, in which the Li^I ions are bridged by two carboxylate O atoms donated by two ligands. The dinuclear unit is nearly planar [r.m.s. deviation = 0.0125 (2) Å]. The Li^I ion is coordinated by an *N*,*O*-chelating ligand, a bridging carboxylate O atom from another ligand and two bridging water O atoms in a distorted trigonal-bipyramidal geometry. The water O atoms bridge the dinuclear units into a polymeric molecular column along [010]. The columns are held together by O—H···O and N—H···N hydrogen bonds. An intramolecular N—H···O interaction also occurs.

Related literature

For the structures of metal (*M*) complexes with the 3-aminopyrazine-2-carboxylate ligand, see: Leciejewicz *et al.* (1997 [*M* = Ca(II)], 1998 [*M* = Sr(II)]); Ptasiewicz-Bąk & Leciejewicz (1997 [*M* = Mg(II)], 1999 [*M* = Ni(II)]); Tayebee *et al.* (2008) [*M* = Na(I)]. For the structure of an Li(I) complex with pyrazine-2,3-dicarboxylate and aqua ligands, see: Tombul *et al.* (2008).



Experimental

Crystal data

$[Li(C_5H_4N_3O_2)(H_2O)]$
M_r = 163.07
Monoclinic, $P2_1/c$
a = 14.279 (3) Å
b = 3.6000 (7) Å
c = 13.300 (3) Å
β = 106.43 (3)°
V = 655.7 (2) Å^3
Z = 4
Mo $K\alpha$ radiation
μ = 0.13 mm^{-1}
T = 293 K
0.26 × 0.21 × 0.04 mm

Data collection

Kuma KM-4 four-circle diffractometer
Absorption correction: analytical (*CrysAlis RED*; Oxford Diffraction, 2006)
T_{min} = 0.980, T_{max} = 0.994
1997 measured reflections
1913 independent reflections
1297 reflections with $I > 2\sigma(I)$
R_{int} = 0.017
3 standard reflections every 200 reflections
intensity decay: 7.3%

Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.049
$wR(F^2)$ = 0.147
S = 1.04
1913 reflections
115 parameters
3 restraints
H atoms treated by a mixture of independent and constrained refinement
$\Delta\rho_{max}$ = 0.51 e Å^{-3}
$\Delta\rho_{min}$ = −0.39 e Å^{-3}

Table 1
Selected bond lengths (Å).

Li1—N1	2.118 (3)	Li1—O3	2.065 (3)
Li1—O1	1.999 (3)	Li1—O3^{ii}	2.201 (3)
Li1—O1^{i}	1.995 (3)		

Symmetry codes: (i) $-x+1, -y+1, -z+1$; (ii) $x, y-1, z$.

Table 2
Hydrogen-bond geometry (Å, °).

D—H···A	D—H	H···A	D···A	D—H···A
O3—H31···O2^{iii}	0.88 (1)	1.83 (1)	2.7028 (16)	175 (2)
O3—H32···O1^{iv}	0.84 (2)	2.54 (2)	2.9083 (17)	108 (2)
N3—H1···O2	0.86	2.08	2.7229 (17)	131
N3—H2···N2^{v}	0.86	2.30	3.1278 (19)	162

Symmetry codes: (iii) $x, -y+\frac{3}{2}, z+\frac{1}{2}$; (iv) $-x+1, -y+2, -z+1$; (v) $-x, y-\frac{1}{2}, -z+\frac{1}{2}$.

Data collection: *KM-4 Software* (Kuma, 1996); cell refinement: *KM-4 Software*; data reduction: *DATAPROC* (Kuma, 2001); program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *SHELXTL* (Sheldrick, 2008); software used to prepare material for publication: *SHELXTL*.

Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: HY2312).

References

Kuma (1996). *KM-4 Software*. Kuma Diffraction Ltd, Wrocław, Poland.
Kuma (2001). *DATAPROC*. Kuma Diffraction Ltd, Wrocław, Poland.
Leciejewicz, J., Ptasiewicz-Bąk, H. & Paluchowska, B. (1997). *Pol. J. Chem.* **71**, 1339–1364.
Leciejewicz,J., Ptasiewicz-Bąk, H. & Zachara, J. (1998). *Pol. J. Chem.* **72**, 1994–1998.
Oxford Diffraction (2006). *CrysAlis RED*. Oxford Diffraction Ltd, Abingdon, England.
Ptasiewicz-Bąk, H. & Leciejewicz, J. (1997). *Pol. J. Chem.* **71**, 1350–1358.
Ptasiewicz-Bąk, H. & Leciejewicz, J. (1999). *Pol. J. Chem.* **73**, 717–725.
Sheldrick, G. M. (2008). *Acta Cryst.* A**64**, 112–122.
Tayebee, R., Amani, V. & Khavasi, H. P. (2008). *Chin. J. Chem.* **26**, 500–504.
Tombul, M., Güven, K. & Büyükgüngör, O. (2008). *Acta Cryst.* E**64**, m491–m492.

supplementary materials

Acta Cryst. (2010). E**66**, m744-m745 [**doi:10.1107/S1600536810020647**]

catena-Poly[[bis(μ-3-aminopyrazine-2-carboxylato)-$\kappa^3N^1,O:O;\kappa^3O:N^1,O$)dilithium]-di-μ-aqua]

W. Starosta and J. Leciejewicz

Comment

Structural studies of divalent metal ion complexes with 3-aminopyrazine-2-carboxylate ligand have shown that the structures of Mg(II) and Ni(II) complexes consist of $ML_2(H_2O)_2$ monomers. In the Mg(II) comoplex, the ligand adopts a *cis* configuration (Ptasiewicz-Bąk & Leciejewicz, 1997), while in the Ni(II) complex, a *trans* configuration (Ptasiewicz-Bąk & Leciejewicz, 1999). Catenated polymeric molecular patterns have been reported in the structures of a Ca(II) complex (Leciejewicz *et al.*, 1997) and a Sr(II) complex (Leciejewicz *et al.*, 1998), in which metal ions are bridged by ligand carboxylate groups acting as bidentate. On the other hand, the structure of a Na(I) complex with the title ligand (Tayebee *et al.*,2008) is three-dimensional polymeric with Na(I) ions linked by an extended bridging system formed mainly by coordinated water O atoms.

The title compound is composed of centrosymmetric dinuclear units, in which each of the two Li^I ions is cheletated by a ligand *via* an N,O-bonding group. Its O atom acts as bidentate and bridges the other Li^I ion (Fig. 1). The dinuclear unit is nearly planar with r.m.s. of 0.0125 (2) Å. The Li^I ion is also coordinated by two water O atoms, which bridge the dinuclear units into molecular columns along two bridging pathways propagating in the *b*-axis direction (Fig. 2). The coordination geometry of the Li^I ion is trigonal bipyramidal, with the equatorial plane formed by O1, O3, $O3^{ii}$ and with N1 and $O1^{i}$ at the axial positions [symmetry codes: (i) 1-x, 1-y, 1-z; (ii) x, y-1, z]. The Li—O and Li—N bond distances (Table 1) and bond angles are typical for Li(I) complexes with carboxylate ligands (see, for example, Tombul *et al.*, 2008). The columns are linked by a network of hydrogen bonds, in which water O atoms are donors and the non-bonded carboxylate O atoms in adjacent columns act as acceptors. A weak hydrogen bond links an amino N atom with a hetero-ring N atom in the adjacent column. An intramolecular hydrogen bond which operates between the amino N3 atom and the non-bonding carboxylate O2 atom is also observed (Table 2).

Experimental

The title compound was synthesized by reacting 50 ml of boiling aqueous solutions, one containing 1 mmol of 3-aminopyrazine-2-carboxylic acid (Aldrich), the other containing 1 mmol of lithium hydroxide (Aldrich). The mixture was boiled under reflux for 3 h and after cooling to room temperature, filtered and left to crystallize. A few days later, colourless single crystals in the form of flat needles were found after evaporation to dryness. They were extracted, washed with cold ethanol and dried in air. A crystal used for X-ray data collection was cut to adopt the shape of a flat plate.

Refinement

Water H atoms were found from difference Fourier maps and their coordinates were refined with $U_{iso}(H) = 1.2U_{eq}(O)$. H atoms attached to C and N atoms were positioned geometrically and refined as riding, with C—H = 0.93 and N—H = 0.86 Å and $U_{iso}(H) = 1.2U_{eq}(C,N)$.

Figures

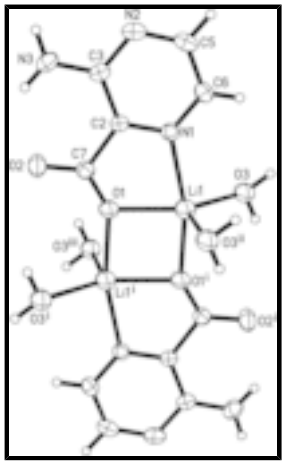


Fig. 1. The dinuclear unit of the title compound. Displacement ellipsoids are drawn at the 50% probability level. [Symmetry codes: (i) 1-x, 1-y, 1-z; (ii) x, -1+y, z; (iii) 1-x, 2-y, 1-z.]

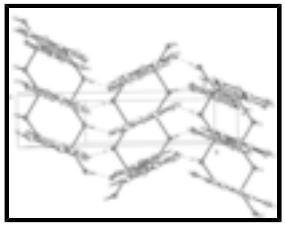


Fig. 2. Packing diagram of the title compound.

catena-Poly[[bis(μ-3-aminopyrazine-2-carboxylato)- $\kappa^3N^1,O:O;\kappa^3O:N^1,O$)dilithium]-di-μ-aqua]

Crystal data

$[Li(C_5H_4N_3O_2)(H_2O)]$	$F(000) = 336$
$M_r = 163.07$	$D_x = 1.652$ Mg m^{-3}
Monoclinic, $P2_1/c$	Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å
Hall symbol: -P 2ybc	Cell parameters from 25 reflections
$a = 14.279$ (3) Å	$\theta = 6–15°$
$b = 3.6000$ (7) Å	$\mu = 0.13$ mm^{-1}
$c = 13.300$ (3) Å	$T = 293$ K
$\beta = 106.43$ (3)°	Plate, colourless
$V = 655.7$ (2) Å^3	0.26 × 0.21 × 0.04 mm
$Z = 4$	

Data collection

Kuma KM-4 four-circle diffractometer	1297 reflections with $I > 2\sigma(I)$
Radiation source: fine-focus sealed tube	$R_{int} = 0.017$
graphite	$\theta_{max} = 30.1°$, $\theta_{min} = 1.5°$
profile data from ω–2θ scans	$h = -19\rightarrow19$
Absorption correction: analytical (*CrysAlis RED*; Oxford Diffraction, 2006)	$k = -5\rightarrow0$

T_{min} = 0.980, T_{max} = 0.994	l = 0→18
1997 measured reflections	3 standard reflections every 200 reflections
1913 independent reflections	intensity decay: 7.3%

Refinement

Refinement on F^2	Primary atom site location: structure-invariant direct methods
Least-squares matrix: full	Secondary atom site location: difference Fourier map
$R[F^2 > 2\sigma(F^2)]$ = 0.049	Hydrogen site location: inferred from neighbouring sites
$wR(F^2)$ = 0.147	H atoms treated by a mixture of independent and constrained refinement
S = 1.04	$w = 1/[\sigma^2(F_o^2) + (0.1051P)^2 + 0.022P]$ where $P = (F_o^2 + 2F_c^2)/3$
1913 reflections	$(\Delta/\sigma)_{max} < 0.001$
115 parameters	$\Delta\rho_{max}$ = 0.51 e Å^{-3}
3 restraints	$\Delta\rho_{min}$ = −0.39 e Å^{-3}

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å^2)

	x	y	z	U_{iso}*/U_{eq}
C2	0.25443 (8)	0.4711 (3)	0.39664 (9)	0.0184 (3)
O2	0.32090 (8)	0.2294 (4)	0.26435 (8)	0.0336 (3)
N1	0.27984 (8)	0.6065 (3)	0.49343 (8)	0.0216 (3)
N2	0.08397 (8)	0.5364 (4)	0.38343 (10)	0.0285 (3)
N3	0.12597 (9)	0.2931 (4)	0.24154 (10)	0.0320 (3)
H2	0.0649	0.2745	0.2090	0.038*
H1	0.1690	0.2235	0.2115	0.038*
O1	0.42229 (7)	0.4275 (4)	0.41421 (8)	0.0352 (3)
C7	0.33887 (9)	0.3657 (4)	0.35429 (10)	0.0218 (3)
C3	0.15415 (9)	0.4307 (4)	0.33936 (10)	0.0217 (3)
C6	0.20958 (10)	0.7070 (4)	0.53653 (11)	0.0254 (3)
H6	0.2262	0.8010	0.6044	0.030*
C5	0.11268 (10)	0.6720 (4)	0.48077 (12)	0.0284 (3)
H5	0.0653	0.7459	0.5123	0.034*
Li1	0.43334 (19)	0.6091 (9)	0.5591 (2)	0.0370 (6)
O3	0.44058 (8)	1.0866 (3)	0.64699 (9)	0.0338 (3)
H32	0.4986 (11)	1.117 (6)	0.6825 (15)	0.041*
H31	0.4047 (13)	1.146 (6)	0.6882 (14)	0.041*

Atomic displacement parameters (Å^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
C2	0.0170 (5)	0.0153 (5)	0.0223 (6)	−0.0007 (4)	0.0048 (4)	0.0018 (4)
O2	0.0301 (5)	0.0450 (7)	0.0277 (5)	−0.0089 (5)	0.0114 (4)	−0.0120 (5)
N1	0.0209 (5)	0.0192 (5)	0.0242 (5)	0.0012 (4)	0.0057 (4)	−0.0006 (4)
N2	0.0194 (5)	0.0264 (6)	0.0390 (6)	0.0012 (4)	0.0071 (4)	0.0025 (5)

N3	0.0227 (5)	0.0401 (7)	0.0290 (6)	−0.0056 (5)	0.0002 (4)	−0.0052 (5)
O1	0.0183 (5)	0.0522 (7)	0.0338 (5)	0.0004 (5)	0.0052 (4)	−0.0142 (5)
C7	0.0202 (6)	0.0209 (6)	0.0242 (5)	−0.0021 (4)	0.0064 (4)	−0.0015 (5)
C3	0.0199 (5)	0.0171 (5)	0.0262 (6)	−0.0019 (4)	0.0033 (4)	0.0034 (5)
C6	0.0282 (6)	0.0225 (7)	0.0273 (6)	0.0020 (5)	0.0108 (5)	−0.0020 (5)
C5	0.0238 (6)	0.0237 (7)	0.0408 (8)	0.0031 (5)	0.0140 (5)	0.0006 (6)
Li1	0.0256 (12)	0.0484 (17)	0.0355 (13)	0.0016 (11)	0.0060 (10)	−0.0120 (12)
O3	0.0256 (5)	0.0411 (7)	0.0352 (6)	−0.0012 (5)	0.0092 (4)	−0.0069 (5)

Geometric parameters (Å, °)

C2—N1	1.3274 (16)	C6—C5	1.378 (2)
C2—C3	1.4263 (17)	C6—H6	0.9300
C2—C7	1.5164 (17)	C5—H5	0.9300
O2—C7	1.2505 (17)	Li1—N1	2.118 (3)
N1—C6	1.3385 (17)	Li1—O1	1.999 (3)
N2—C5	1.335 (2)	Li1—O1^{i}	1.995 (3)
N2—C3	1.3510 (18)	Li1—O3	2.065 (3)
N3—C3	1.3431 (18)	Li1—O3^{ii}	2.201 (3)
N3—H2	0.8600	Li1—Li1^{i}	2.900 (5)
N3—H1	0.8600	O3—H32	0.837 (15)
O1—C7	1.2515 (17)	O3—H31	0.875 (14)
N1—C2—C3	120.87 (11)	N2—C5—H5	118.6
N1—C2—C7	115.10 (11)	C6—C5—H5	118.6
C3—C2—C7	124.03 (11)	O1^{i}—Li1—O1	86.88 (11)
C2—N1—C6	118.83 (11)	O1^{i}—Li1—O3	94.05 (12)
C2—N1—Li1	111.64 (11)	O1—Li1—O3	142.73 (18)
C6—N1—Li1	129.48 (11)	O1^{i}—Li1—N1	165.94 (15)
C5—N2—C3	117.50 (11)	O1—Li1—N1	79.08 (10)
C3—N3—H2	120.0	O3—Li1—N1	96.74 (12)
C3—N3—H1	120.0	O1^{i}—Li1—O3^{ii}	87.61 (12)
H2—N3—H1	120.0	O1—Li1—O3^{ii}	102.21 (14)
C7—O1—Li1^{i}	148.32 (12)	O3—Li1—O3^{ii}	115.07 (14)
C7—O1—Li1	118.26 (11)	N1—Li1—O3^{ii}	95.90 (13)
Li1^{i}—O1—Li1	93.13 (11)	O1^{i}—Li1—Li1^{i}	43.49 (8)
O2—C7—O1	125.43 (12)	O1—Li1—Li1^{i}	43.38 (8)
O2—C7—C2	118.94 (12)	O3—Li1—Li1^{i}	126.66 (18)
O1—C7—C2	115.63 (11)	N1—Li1—Li1^{i}	122.46 (16)
N3—C3—N2	117.93 (12)	O3^{ii}—Li1—Li1^{i}	96.72 (16)
N3—C3—C2	122.37 (12)	Li1—O3—Li1^{iii}	115.07 (14)
N2—C3—C2	119.69 (12)	Li1—O3—H32	108.2 (15)
N1—C6—C5	120.32 (12)	Li1^{iii}—O3—H32	94.4 (16)
N1—C6—H6	119.8	Li1—O3—H31	127.7 (15)
C5—C6—H6	119.8	Li1^{iii}—O3—H31	100.2 (15)
N2—C5—C6	122.78 (13)	H32—O3—H31	106.0 (15)

Symmetry codes: (i) −*x*+1, −*y*+1, −*z*+1; (ii) *x*, *y*−1, *z*; (iii) *x*, *y*+1, *z*.

Hydrogen-bond geometry (Å, °)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
O3—H31···O2^{iv}	0.88 (1)	1.83 (1)	2.7028 (16)	175.(2)
O3—H32···O1^{v}	0.84 (2)	2.54 (2)	2.9083 (17)	108.(2)
N3—H1···O2	0.86	2.08	2.7229 (17)	131
N3—H2···N2^{vi}	0.86	2.30	3.1278 (19)	162

Symmetry codes: (iv) *x*, −*y*+3/2, *z*+1/2; (v) −*x*+1, −*y*+2, −*z*+1; (vi) −*x*, *y*−1/2, −*z*+1/2.

Fig. 1

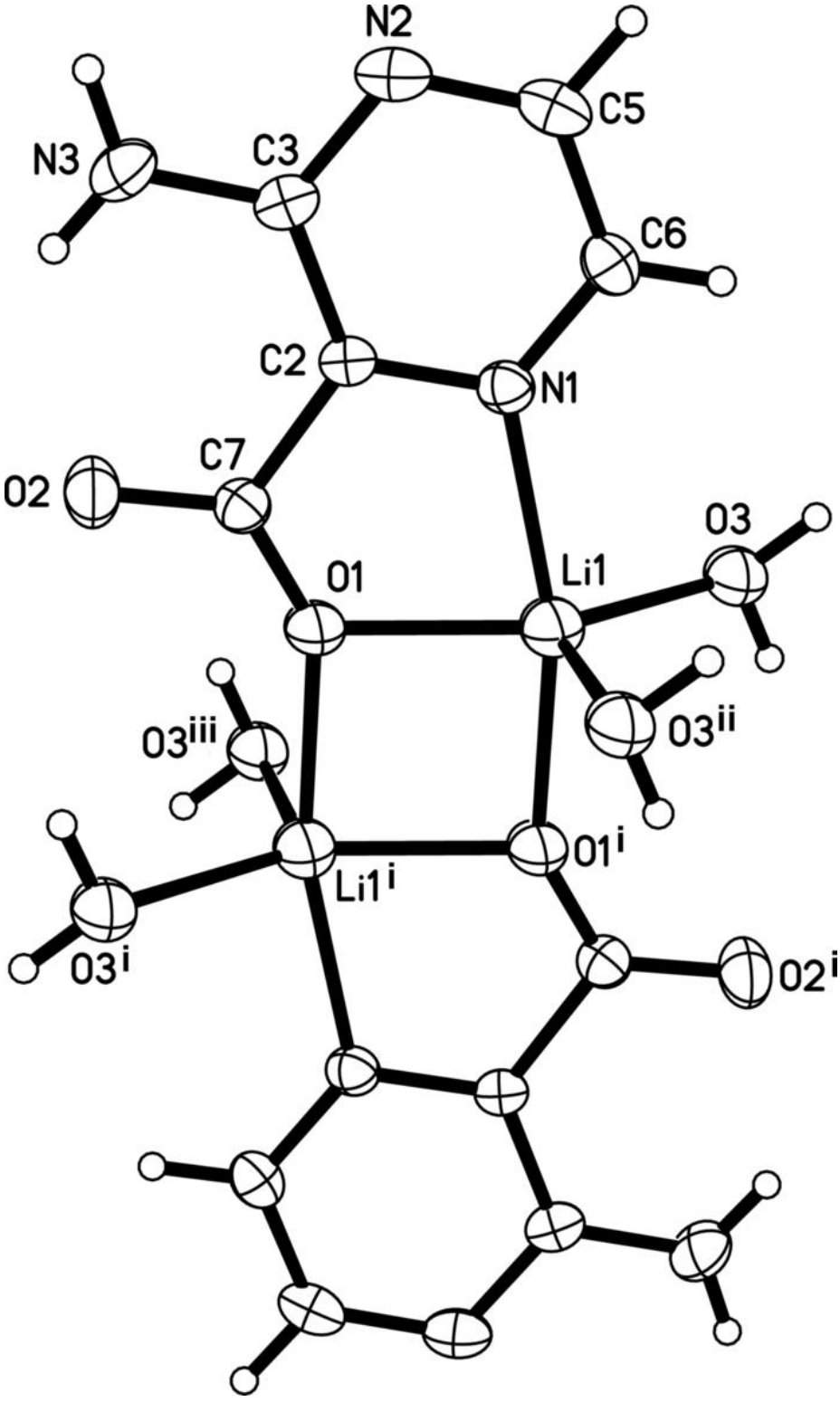
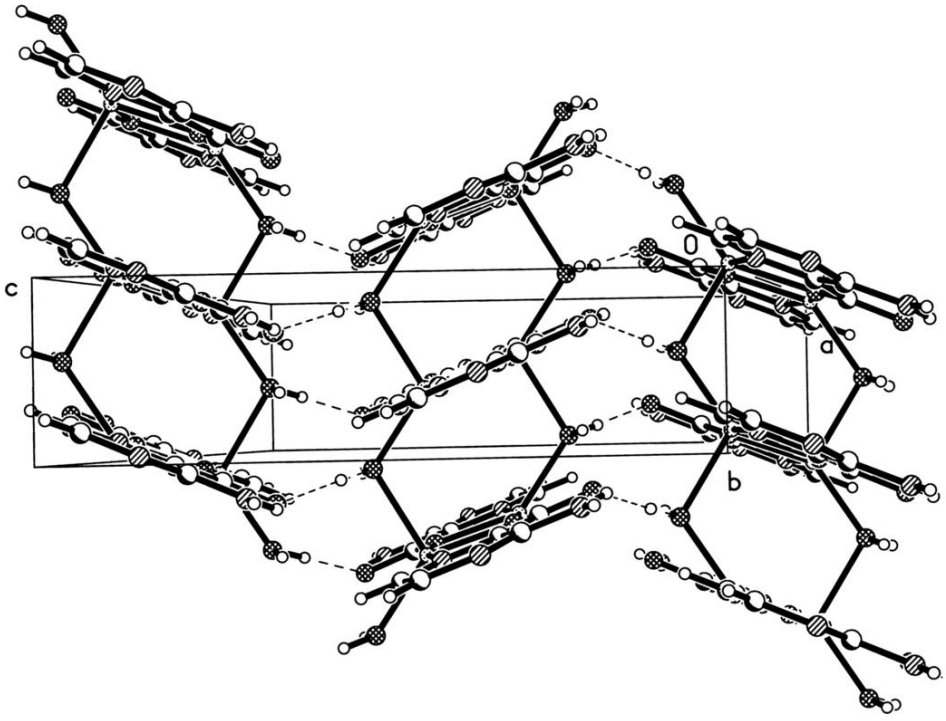


Fig. 2



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Poly[tetrakis(selenocyanato-κN)bis(methanol-κO)tris(μ-pyrimidine-$\kappa^2 N:N'$)-dicobalt(II)]

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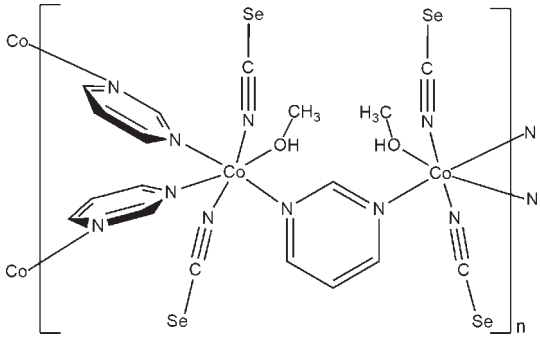
Key indicators: single-crystal X-ray study; T = 293 K; mean σ(C–C) = 0.006 Å; R factor = 0.038; wR factor = 0.069; data-to-parameter ratio = 20.7.

In the title compound, $[Co_2(NCSe)_4(C_4H_4N_2)_3(CH_3OH)_2]_n$, the Co^{II} ion is coordinated by three N-bonded pyrimidine ligands, two N-bonded selenocyanate anions and one O-bonded methanol molecule in an octahedral coordination mode. The asymmetric unit consists of one Co^{II} ion, one pyrimidine ligand, two selenocyanate anions and one methanol molecule in general positions as well as one pyrimidine ligand located around a twofold rotation axis. In the crystal structure, the pyrimidine ligands bridge $[Co(CNSe)_2(CH_3OH)]$ units into zigzag-like chains, which are further connected by pyrimidine ligands into layers parallel to (010).

Related literature

For general background, see: Wriedt & Näther (2009*a*,*b*); Wriedt, Sellmer & Näther (2009*a*,*b*). For the isotypic structure of a nickel thiocyanato complex, see: Wriedt *et al.* (2009).



Experimental

Crystal data

$[Co_2(CNSe)_4(C_4H_4N_2)_3(CH_4O)_2]$ M_r = 421.07
Orthorhombic, *Fdd*2
a = 20.4069 (8) Å
b = 33.0633 (15) Å
c = 8.3750 (3) Å
V = 5650.8 (4) Å^3
Z = 16
Mo $K\alpha$ radiation
μ = 6.36 mm^{-1}
T = 293 K
0.16 × 0.11 × 0.02 mm

Data collection

Stoe IPDS-2 diffractometer
Absorption correction: numerical (*X-SHAPE* and *X-RED32*; Stoe & Cie, 2002)
T_{min} = 0.431, T_{max} = 0.885
18545 measured reflections
3391 independent reflections
3067 reflections with $I > 2\sigma(I)$
R_{int} = 0.044

Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.038
$wR(F^2)$ = 0.069
S = 1.16
3391 reflections
164 parameters
1 restraint
H-atom parameters constrained
$\Delta\rho_{max}$ = 0.55 e Å^{-3}
$\Delta\rho_{min}$ = −0.35 e Å^{-3}
Absolute structure: Flack (1983), 1579 Friedel pairs
Flack parameter: 0.057 (13)

Table 1
Selected bond lengths (Å).

Co1—N1	2.191 (3)	Co1—N21	2.064 (4)
Co1—N2^{i}	2.188 (3)	Co1—N31	2.059 (4)
Co1—N11	2.184 (3)	Co1—O41	2.142 (3)

Symmetry code: (i) $-x+1, -y+\frac{1}{2}, z+\frac{1}{2}$.

Data collection: *X-AREA* (Stoe & Cie, 2002); cell refinement: *X-AREA*; data reduction: *X-AREA*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *SHELXTL* (Sheldrick, 2008); software used to prepare material for publication: *SHELXTL*.

MW thanks the Stiftung Stipendien-Fonds des Verbandes der Chemischen Industrie and the Studienstiftung des deutschen Volkes for a PhD scholarship. We gratefully acknowledge financial support by the State of Schleswig-Holstein and the Deutsche Forschungsgemeinschaft (Project 720/3-1). We thank Professor Dr Wolfgang Bensch for the opportunity to use of his experimental facilities.

Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: HY2313).

References

Flack, H. D. (1983). *Acta Cryst.* A**39**, 876–881.
Sheldrick, G. M. (2008). *Acta Cryst.* A**64**, 112–122.
Stoe & Cie (2002). *X-AREA*, *X-RED32* and *X-SHAPE*. Stoe & Cie, Darmstadt, Germany.
Wriedt, M. & Näther, C. (2009*a*). *Dalton Trans.* pp. 10192–10198.
Wriedt, M. & Näther, C. (2009*b*). *Z. Anorg. Allg. Chem.* **636**, 569–575.
Wriedt, M., Sellmer, S., Jess, I. & Näther, C. (2009). *Acta Cryst.* E**65**, m361–m362.
Wriedt, M., Sellmer, S. & Näther, C. (2009*a*). *Dalton Trans.* pp. 7975–7984.
Wriedt, M., Sellmer, S. & Näther, C. (2009*b*). *Inorg. Chem.* **48**, 6896–6903.

supplementary materials

Acta Cryst. (2010). E**66**, m742 [**doi:10.1107/S160053681002060X**]

Poly[tetrakis(selenocyanato-κN)bis(methanol-κO)tris(μ-pyrimidine-$\kappa^2 N:N'$)dicobalt(II)]

M. Wriedt, I. Jess and C. Näther

Comment

Recently, we have shown that thermal decomposition reactions are an elegante route for the discovering and preparation of new ligand-deficient coordination polymers with defined magnetic properties (Wriedt & Näther, 2009a,b; Wriedt, Sellmer & Näther, 2009a,b). In our ongoing investigation in this field, we have reacted cobalt(II) nitrate, potassium selenocyanate and pyrimidine in methanol. The crystals obtained were identified by single crystal X-ray determination.

The title compound (Fig. 1) represents a two-dimensional layered coordination polymer, which is isotypic to its corresponding nickel(II) thiocyanate analogue reproted recently (Wriedt *et al.*, 2009). The crystal structure consists of µ-1,3-(*N*,*N*) pyrimidine bridged zigzag-like cobalt(II) selenocynate chains, which are further linked by µ-1,3-(*N*,*N*) pyrimidine ligands into layers (Fig. 2). Within each layer the Co^{II} ions are bridged by three pyrimidine ligands and are further terminally coordinated by two *N*-bonded selenocyanate anions and one *O*-bonded methanol molecule in an octahedral coordination mode (Fig. 1). The layers are stacked in the direction of the crystallographic *b*-axis (Fig. 3). The CoN_5O octahedron is markedly distorted with three long Co—$N_{pyrimidine}$ distances in the range of 2.184 (3) to 2.191 (3) Å, one long Co—O_{MeOH} distance of 2.142 (3) Å and two short Co—NCSe distances of 2.059 (4) and 2.064 (4) Å (Table 1). The angles arround the metal centers range between 86.37 (13) to 96.00 (13) and 173.71 (13) to 177.16 (14)°. The shortest intra- and interlayer Co···Co distances amount to 6.0723 (6) and 8.5630 (9) Å, respectively.

Experimental

$Co(NO_3)_2.6H_2O$ (72.8 mg, 0.25 mmol), KNCSe (72.0 mg, 0.5 mmol) and pyrimidine (20.0 mg, 0.25 mmol) obtained from Alfa Aesar were transfered in a closed snap-vial with methanol (3 ml). After several days at room temperature without stirring, light pink block-shaped single crystals of the title compound were obtained in a mixture with unknown phases.

Refinement

The O-bound H atom was located in a difference Fourier map and its bond length set to a ideal value and finally refined using a riding model. All other H atoms were positioned with idealized geometry and refined using a riding model, with C—H = 0.93 (CH) and 0.96 (CH_3) Å and with U_{iso}(H) = 1.2(1.5 for methyl)U_{eq}(C). The absolute structure was determined on the basis of 1579 Friedel pairs.

Figures

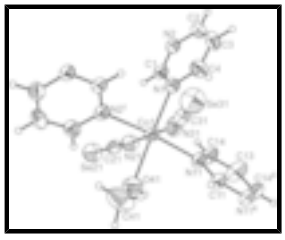


Fig. 1. Structure of the title compound with displacement ellipsoids drawn at the 50% probability level. [Symmetry codes: (i) -*x*+1, -*y*+1/2, *z*+1/2; (ii) -*x*+3/2, -*y*+1/2, *z*.]

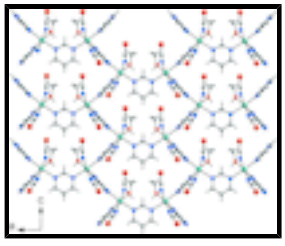


Fig. 2. A single layer in the title compound viewed along the *b* axis.

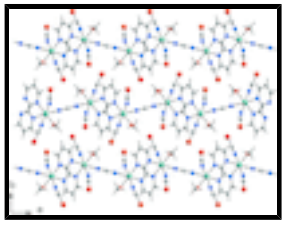


Fig. 3. Packing of the layers in the title compound viewed along the *c* axis.

Poly[tetrakis(selenocyanato-κ*N*)bis(methanol-κ*O*)tris(μ- pyrimidine-κ^2*N*:*N*')dicobalt(II)]

Crystal data

$[Co_2(CNSe)_4(C_4H_4N_2)_3(CH_4O)_2]$	$F(000) = 3232$
$M_r = 421.07$	$D_x = 1.980$ Mg m^{-3}
Orthorhombic, *Fdd*2	Mo *K*α radiation, λ = 0.71073 Å
Hall symbol: F 2 -2d	Cell parameters from 18545 reflections
a = 20.4069 (8) Å	θ = 2.4–28.0°
b = 33.0633 (15) Å	μ = 6.36 mm^{-1}
c = 8.3750 (3) Å	*T* = 293 K
V = 5650.8 (4) Å^3	Block, light pink
Z = 16	0.16 × 0.11 × 0.02 mm

Data collection

Stoe IPDS-2 diffractometer	3391 independent reflections
Radiation source: fine-focus sealed tube	3067 reflections with $I > 2\sigma(I)$
graphite	$R_{int} = 0.044$
ω scans	$\theta_{max} = 28.0°$, $\theta_{min} = 2.4°$
Absorption correction: numerical (*X-SHAPE* and *X-RED32*; Stoe & Cie, 2002)	$h = -26 \rightarrow 26$
$T_{min} = 0.431$, $T_{max} = 0.885$	$k = -43 \rightarrow 43$

18545 measured reflections

$l = -11 \rightarrow 10$

Refinement

Refinement on F^2

Least-squares matrix: full

$R[F^2 > 2\sigma(F^2)] = 0.038$

$wR(F^2) = 0.069$

$S = 1.16$

3391 reflections

164 parameters

1 restraint

Primary atom site location: structure-invariant direct methods

Secondary atom site location: difference Fourier map

Hydrogen site location: inferred from neighbouring sites

H-atom parameters constrained

$w = 1/[\sigma^2(F_o^2) + (0.0286P)^2 + 8.8704P]$ where $P = (F_o^2 + 2F_c^2)/3$

$(\Delta/\sigma)_{max} < 0.001$

$\Delta\rho_{max} = 0.55$ e Å^{-3}

$\Delta\rho_{min} = -0.35$ e Å^{-3}

Absolute structure: Flack (1983), 1579 Friedel pairs

Flack parameter: 0.057 (13)

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å^2)

	x	*y*	*z*	U_{iso}*/U_{eq}
Co1	0.60574 (2)	0.227474 (17)	0.78759 (6)	0.03270 (12)
N1	0.55104 (15)	0.27269 (10)	0.6504 (4)	0.0360 (8)
N2	0.47521 (15)	0.28919 (10)	0.4458 (5)	0.0382 (7)
C1	0.50711 (17)	0.26316 (13)	0.5388 (6)	0.0374 (9)
H1	0.4979	0.2358	0.5246	0.045*
C2	0.4883 (2)	0.32854 (13)	0.4677 (6)	0.0412 (9)
H2	0.4672	0.3477	0.4048	0.049*
C3	0.5320 (2)	0.34078 (14)	0.5813 (6)	0.0459 (11)
H3	0.5410	0.3681	0.5959	0.055*
C4	0.5623 (2)	0.31226 (13)	0.6730 (6)	0.0434 (10)
H4	0.5912	0.3204	0.7526	0.052*
N11	0.69371 (15)	0.24124 (11)	0.6493 (4)	0.0352 (8)
C11	0.7500	0.2500	0.7228 (7)	0.0372 (12)
H11	0.7500	0.2500	0.8339	0.045*
C13	0.7500	0.2500	0.4059 (8)	0.061 (2)
H13	0.7500	0.2500	0.2948	0.074*
C14	0.6944 (2)	0.24140 (17)	0.4914 (6)	0.0499 (12)
H14	0.6559	0.2355	0.4366	0.060*
N21	0.57994 (17)	0.18287 (12)	0.6270 (5)	0.0434 (8)
C21	0.56005 (17)	0.15562 (13)	0.5553 (5)	0.0381 (9)
Se21	0.53008 (3)	0.114405 (17)	0.44108 (7)	0.06121 (16)
N31	0.63231 (16)	0.26940 (12)	0.9575 (5)	0.0428 (8)
C31	0.63448 (17)	0.29139 (13)	1.0643 (5)	0.0373 (9)
Se31	0.63665 (3)	0.324181 (19)	1.23170 (7)	0.06461 (17)
O41	0.66187 (15)	0.18255 (10)	0.9111 (4)	0.0522 (8)
C41	0.6758 (4)	0.1790 (2)	1.0749 (8)	0.085 (2)
H41A	0.6359	0.1747	1.1328	0.127*
H41B	0.6964	0.2034	1.1118	0.127*

H41C	0.7048	0.1566	1.0918	0.127*
H1O4	0.6862	0.1792	0.8352	0.127*

Atomic displacement parameters (Å^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Co1	0.0252 (2)	0.0341 (3)	0.0388 (3)	−0.0009 (2)	−0.0010 (2)	−0.0043 (2)
N1	0.0287 (15)	0.0336 (18)	0.046 (2)	−0.0015 (13)	−0.0036 (13)	0.0000 (15)
N2	0.0294 (14)	0.0376 (17)	0.048 (2)	−0.0013 (14)	−0.0020 (14)	0.0017 (17)
C1	0.0270 (16)	0.036 (2)	0.049 (2)	0.0006 (15)	−0.0018 (18)	−0.0026 (19)
C2	0.045 (2)	0.033 (2)	0.045 (2)	0.0008 (17)	−0.0001 (19)	0.0031 (19)
C3	0.059 (3)	0.029 (2)	0.049 (3)	−0.0082 (19)	0.003 (2)	−0.0002 (19)
C4	0.048 (2)	0.039 (2)	0.043 (2)	−0.0022 (18)	−0.0087 (19)	−0.0029 (19)
N11	0.0268 (14)	0.0419 (19)	0.037 (2)	−0.0028 (13)	−0.0005 (13)	0.0017 (14)
C11	0.029 (2)	0.050 (3)	0.032 (3)	0.000 (2)	0.000	0.000
C13	0.046 (4)	0.108 (7)	0.030 (4)	−0.001 (4)	0.000	0.000
C14	0.0295 (19)	0.075 (3)	0.045 (3)	−0.005 (2)	−0.0032 (18)	−0.003 (2)
N21	0.0422 (18)	0.040 (2)	0.048 (2)	0.0000 (16)	−0.0047 (16)	−0.0091 (17)
C21	0.0304 (16)	0.043 (2)	0.042 (2)	0.0029 (16)	0.0016 (17)	0.002 (2)
Se21	0.0661 (3)	0.0505 (3)	0.0670 (4)	−0.0056 (2)	−0.0100 (3)	−0.0199 (3)
N31	0.0419 (18)	0.045 (2)	0.042 (2)	−0.0081 (16)	0.0024 (16)	−0.0071 (18)
C31	0.0276 (17)	0.039 (2)	0.046 (3)	−0.0020 (15)	0.0036 (16)	0.003 (2)
Se31	0.0715 (3)	0.0632 (4)	0.0592 (3)	−0.0041 (3)	0.0086 (3)	−0.0256 (3)
O41	0.0456 (16)	0.054 (2)	0.057 (2)	0.0146 (15)	−0.0044 (15)	0.0063 (16)
C41	0.101 (5)	0.071 (4)	0.082 (5)	0.002 (4)	−0.047 (4)	0.007 (3)

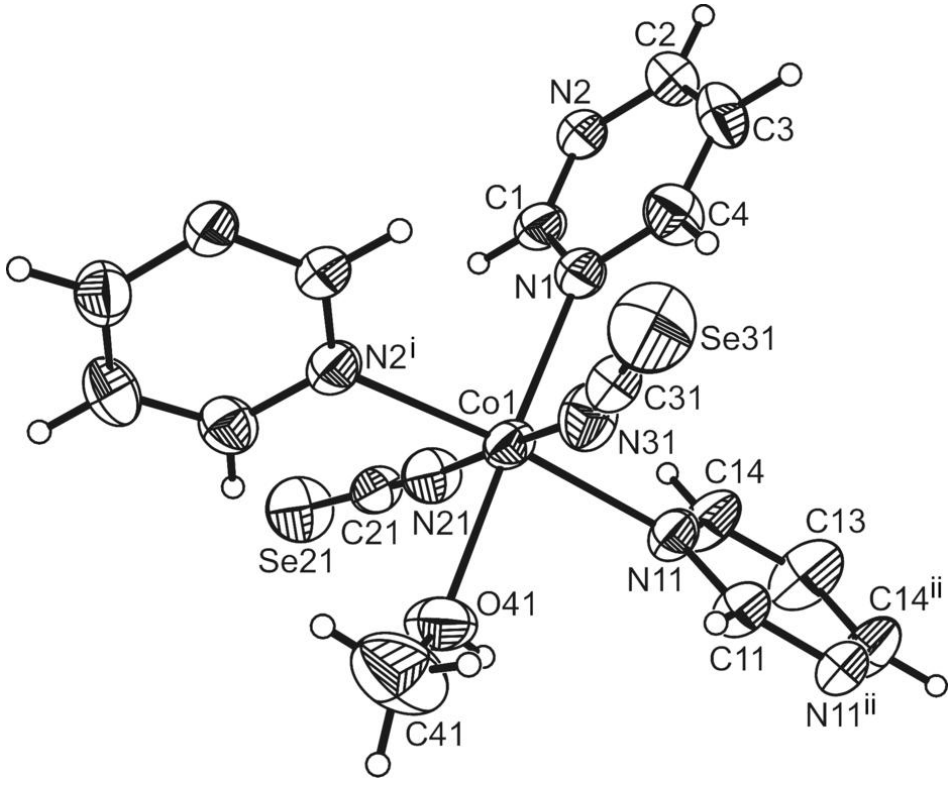
Geometric parameters (Å, °)

Co1—N1	2.191 (3)	N11—C11	1.335 (4)
Co1—N2^{i}	2.188 (3)	C11—N11^{ii}	1.335 (4)
Co1—N11	2.184 (3)	C11—H11	0.9300
Co1—N21	2.064 (4)	C13—C14	1.372 (6)
Co1—N31	2.059 (4)	C13—C14^{ii}	1.372 (6)
Co1—O41	2.142 (3)	C13—H13	0.9300
N1—C1	1.333 (5)	C14—H14	0.9300
N1—C4	1.342 (5)	N21—C21	1.157 (5)
N2—C1	1.331 (5)	C21—Se21	1.774 (5)
N2—C2	1.341 (5)	N31—C31	1.154 (5)
C1—H1	0.9300	C31—Se31	1.773 (4)
C2—C3	1.366 (6)	O41—C41	1.405 (7)
C2—H2	0.9300	O41—H1O4	0.8139
C3—C4	1.364 (7)	C41—H41A	0.9600
C3—H3	0.9300	C41—H41B	0.9600
C4—H4	0.9300	C41—H41C	0.9600
N11—C14	1.323 (6)		
N31—Co1—N21	176.69 (16)	C2—C3—H3	120.6
N31—Co1—O41	89.55 (15)	N1—C4—C3	121.2 (4)
N21—Co1—O41	87.46 (14)	N1—C4—H4	119.4

N31—Co1—N11	90.55 (13)	C3—C4—H4	119.4
N21—Co1—N11	90.75 (14)	C14—N11—C11	116.8 (4)
O41—Co1—N11	87.77 (13)	C14—N11—Co1	122.6 (3)
N31—Co1—N2^{i}	87.12 (14)	C11—N11—Co1	120.5 (3)
N21—Co1—N2^{i}	91.27 (14)	N11—C11—N11^{ii}	125.1 (5)
O41—Co1—N2^{i}	86.37 (13)	N11—C11—H11	117.5
N11—Co1—N2^{i}	173.71 (13)	N11^{ii}—C11—H11	117.5
N31—Co1—N1	92.13 (14)	C14—C13—C14^{ii}	117.1 (6)
N21—Co1—N1	90.91 (14)	C14—C13—H13	121.5
O41—Co1—N1	177.16 (14)	C14^{ii}—C13—H13	121.5
N11—Co1—N1	89.92 (12)	N11—C14—C13	122.1 (4)
N2^{i}—Co1—N1	96.00 (13)	N11—C14—H14	118.9
C1—N1—C4	116.4 (4)	C13—C14—H14	118.9
C1—N1—Co1	123.3 (3)	C21—N21—Co1	169.9 (4)
C4—N1—Co1	120.3 (3)	N21—C21—Se21	178.7 (4)
C1—N2—C2	116.8 (4)	C31—N31—Co1	166.0 (3)
C1—N2—Co1^{iii}	124.1 (3)	N31—C31—Se31	178.4 (4)
C2—N2—Co1^{iii}	118.5 (3)	C41—O41—Co1	129.6 (4)
N2—C1—N1	125.9 (4)	C41—O41—H1O4	128.9
N2—C1—H1	117.0	Co1—O41—H1O4	92.4
N1—C1—H1	117.0	O41—C41—H41A	109.5
N2—C2—C3	120.8 (4)	O41—C41—H41B	109.5
N2—C2—H2	119.6	H41A—C41—H41B	109.5
C3—C2—H2	119.6	O41—C41—H41C	109.5
C4—C3—C2	118.9 (4)	H41A—C41—H41C	109.5
C4—C3—H3	120.6	H41B—C41—H41C	109.5

Symmetry codes: (i) −*x*+1, −*y*+1/2, *z*+1/2; (ii) −*x*+3/2, −*y*+1/2, *z*; (iii) −*x*+1, −*y*+1/2, *z*−1/2.

Fig. 1


C2
N2
C3
C1
C4
N1
Se31
N2i
C31
Co1
N31
C14
C13
C21
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N11
C14ii
O41
C11
C41
N11ii

Fig. 2

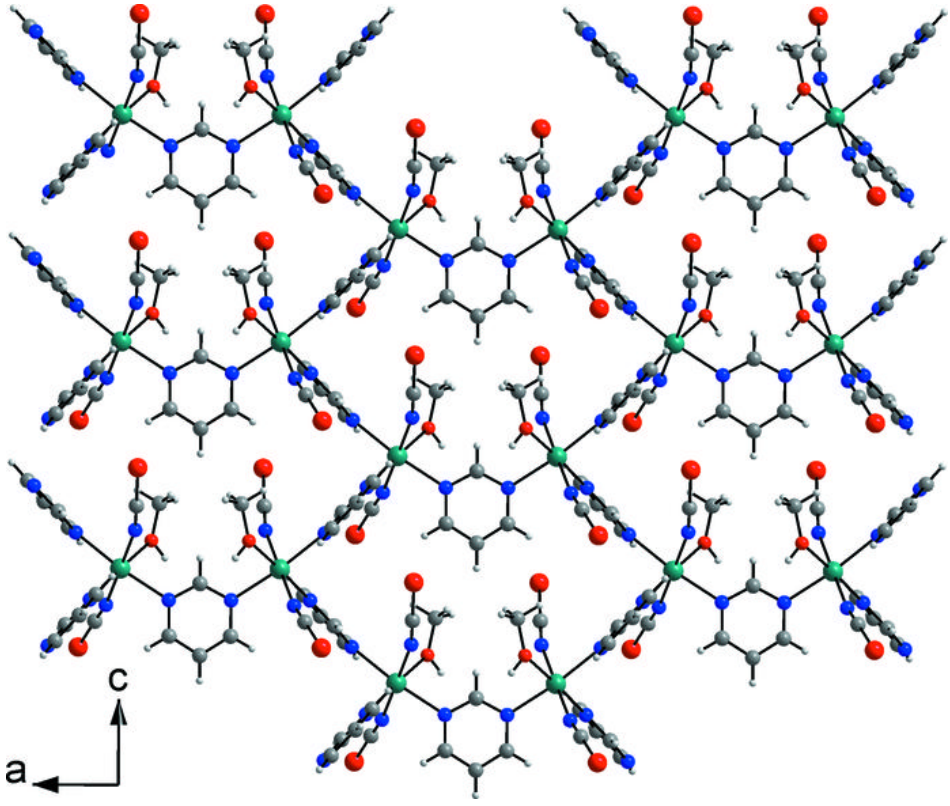
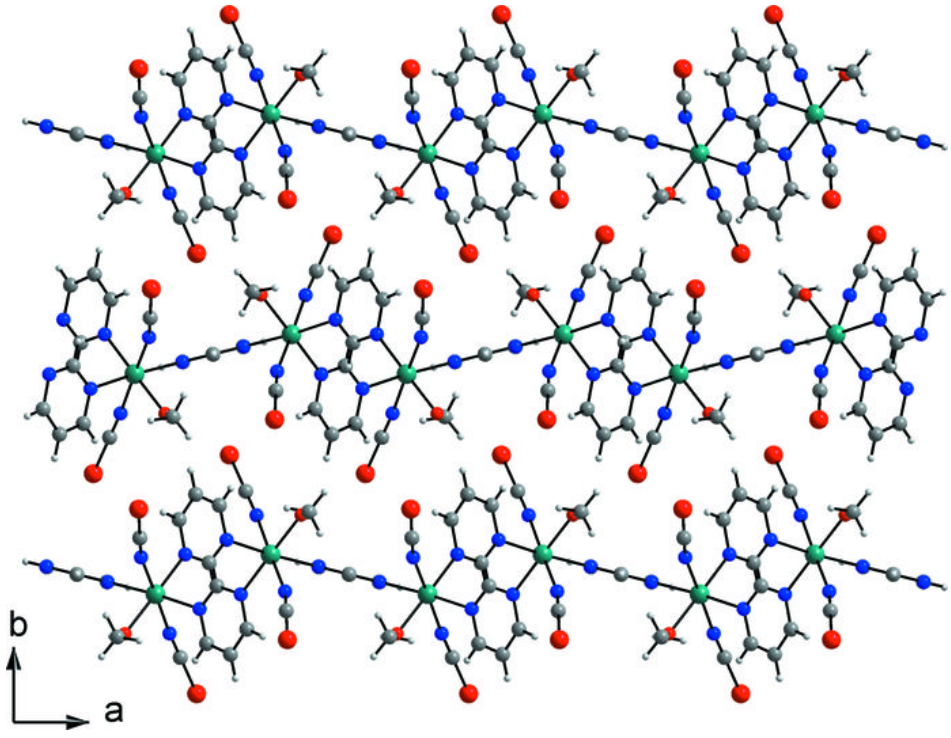


Fig. 3



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Poly[[bis(μ-4,4′-bipyridyl-κ²N:N′)bis(thiocyanato-κN)manganese(II)] diethyl ether disolvate]

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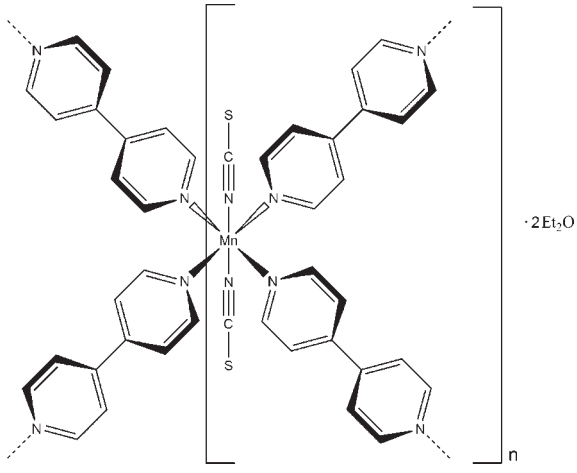
Key indicators: single-crystal X-ray study; T = 230 K; mean σ(C–C) = 0.008 Å; R factor = 0.073; wR factor = 0.206; data-to-parameter ratio = 15.5.

In the title compound, $\{[Mn(NCS)_2(C_{10}H_8N_2)_2]\cdot 2C_4H_{10}O\}_n$, the Mn^{II} ion is coordinated by four *N*-bonded 4,4′-bipyridine (bipy) ligands and two *N*-bonded thiocyanate anions in a distorted octahedral coordination geometry. The asymmetric unit consists of one Mn^{II} ion and two bipy ligands each located on a twofold rotation axis, as well as one thiocyanate anion and one diethyl ether molecule in general positions. In the crystal structure, the metal centers with terminally bonded thicyanate anions are bridged by the bipy ligands into layers parallel to (001). The diethyl ether solvent molecules occupy the voids of the structure.

Related literature

For general background to thermal decomposition reactions as an alternative tool for the discovery and preparation of new ligand-deficient coordination polymers with defined magnetic properties, see: Wriedt & Näther (2009*a*,*b*); Wriedt *et al.* (2009*a*,*b*). For the isotypic cobalt(II) structure, see: Lu *et al.* (1997).



Experimental

Crystal data

$[Mn(NCS)_2(C_{10}H_8N_2)_2]\cdot 2C_4H_{10}O$
M_r = 631.71
Monoclinic, $P2/c$
a = 11.702 (2) Å
b = 11.6391 (18) Å
c = 13.424 (2) Å
β = 106.75 (2)°
V = 1750.8 (5) Å^3
Z = 2
Mo $K\alpha$ radiation
μ = 0.53 mm^{-1}
T = 230 K
0.22 × 0.14 × 0.07 mm

Data collection

Stoe IPDS-1 diffractometer
Absorption correction: numerical (*X-SHAPE* and *X-RED32*; Stoe & Cie, 2002)
T_{min} = 0.912, T_{max} = 0.968
11086 measured reflections
2954 independent reflections
2446 reflections with $I > 2\sigma(I)$
R_{int} = 0.134

Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.073
$wR(F^2)$ = 0.206
S = 1.07
2954 reflections
191 parameters
H-atom parameters constrained
$\Delta\rho_{max}$ = 0.72 e Å^{-3}
$\Delta\rho_{min}$ = −1.37 e Å^{-3}

Table 1
Selected bond lengths (Å).

Mn1—N21	2.181 (4)	Mn1—N11	2.300 (4)
Mn1—N12^{i}	2.277 (4)	Mn1—N1	2.312 (3)

Symmetry code: (i) $x, y-1, z$.

Data collection: *X-AREA* (Stoe & Cie, 2002); cell refinement: *X-AREA*; data reduction: *X-AREA*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *SHELXTL* (Sheldrick, 2008); software used to prepare material for publication: *SHELXTL*.

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Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: HY2314).

References

Lu, J., Paliwala, T., Lim, S. C., Yu, C., Niu, T. & Jacobson, A. J. (1997). *Inorg. Chem.* **36**, 923–929.
Sheldrick, G. M. (2008). *Acta Cryst.* A**64**, 112–122.
Stoe & Cie (2002). *X-AREA*, *X-RED32* and *X-SHAPE*. Stoe & Cie, Darmstadt, Germany.
Wriedt, M. & Näther, C. (2009*a*). *Dalton Trans.* pp. 10192–10198.
Wriedt, M. & Näther, C. (2009*b*). *Z. Anorg. Allg. Chem.* **636**, 569–575.
Wriedt, M., Sellmer, S. & Näther, C. (2009*a*). *Dalton Trans.* pp. 7975–7984.
Wriedt, M., Sellmer, S. & Näther, C. (2009*b*). *Inorg. Chem.* **48**, 6896–6903.

supplementary materials

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Poly[[bis(*μ*-4,4'-bipyridyl-κ^2N:*N*')bis(thiocyanato-κN)manganese(II)] diethyl ether disolvate]

M. Wriedt, I. Jess and C. Näther

Comment

Recently, we are interested in thermal decomposition reactions as an alternative tool for the discovering and preparation of new ligand-deficient coordination polymers with defined magnetic properties (Wriedt & Näther, 2009a,b; Wriedt *et al.*, 2009a,b). In our ongoing investigation on the synthesis, structures and properties of such compounds we have reacted manganese(II) chloride, potassium thiocyanate and 4,4-bipyridine (bipy). In this reaction single crystals of the title compound were grown.

The title compound (Fig. 1) represents a two-dimensional layered coordination polymer, in which the Mn^{II} atom is coordinated by four bipy ligands and two thiocyanate anions in an octahedral coordination mode. The crystal structure is isotypic to its cobalt(II) analogue (Lu *et al.*, 1997). In the crystal structure the metal atoms are bridged by the bipy ligands into layers with terminally N-bonded thicyanate anions. The layers are stacked perpendicular to the crystallographic *c* axis in order that the metal atoms in one layer sit above or below the squares formed by the metal atoms of the adjacent layers. By this arrangement voids are formed in which the diethyl ether molecules are located (Fig. 2). The MnN_6 octahedron is markedly distorted with four long Mn—N_{bipy} distances in the range of 2.277 (4) to 2.312 (4) Å and two short Mn—NCS distances of 2.181 (4) Å (Table 1). The angles arround the metal atoms range between 88.27 (8) to 91.73 (8) and 176.54 (16) to 180°. The pyridyl rings of the bipy ligands form dihedral angles of 51.2 (1) and 52.6 (1)°, respectively. The shortest intra- and interlayer Mn···Mn distances amount to 11.6391 (6) and 8.3198 (11) Å, respectively.

Experimental

$MnCl_2$ (117.0 mg, 0.93 mmol) and KNCS (180.8 mg, 1.86 mmol) obtained from Alfa Aesar were dissolved in a mixture of 10 ml water and 15 ml ethanol. This mixture was layered with a solution of 4,4-bipyridine (306.3 mg, 2 mmol) in 10 ml diethyl ether. After one day colourless block-shaped single crystals of the title compound were grown at the phase interface.

Refinement

The H atoms were located in a difference Fourier map but were positioned with idealized geometry and refined using a riding model, with C—H = 0.94 (aromatic), 0.98 (methylene) and 0.97 (methyl) Å and with U_{iso}(H) = 1.2(1.5 for methyl)U_{eq}(C).

Figures

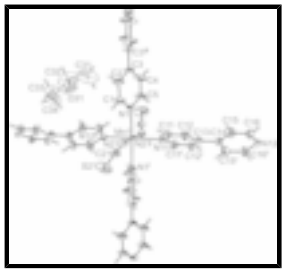


Fig. 1. Structure of the title compound with displacement ellipsoids drawn at the 50% probability level. [Symmetry codes: (i) -x+1, y, -z+3/2; (ii) x, y-1, z; (iii) -x, y, -z+3/2.]

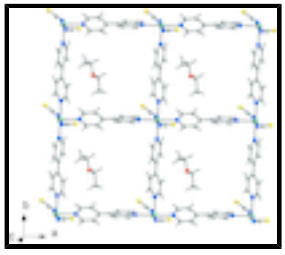


Fig. 2. A single layer in the title compound with view approximately along the crystallographic *c* axis.

Poly[[bis(μ-4,4'-bipyridyl-$\kappa^2N:N'$)bis(thiocyanato- κN)manganese(II)] diethyl ether disolvate]

Crystal data

$[Mn(NCS)_2(C_{10}H_8N_2)_2]\cdot 2C_4H_{10}O$	$F(000) = 662$
$M_r = 631.71$	$D_x = 1.198$ Mg m^{-3}
Monoclinic, $P2/c$	Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å
Hall symbol: -P 2yc	Cell parameters from 11086 reflections
$a = 11.702$ (2) Å	$\theta = 2.4$–$25.0°$
$b = 11.6391$ (18) Å	$\mu = 0.53$ mm^{-1}
$c = 13.424$ (2) Å	$T = 230$ K
$\beta = 106.75$ (2)°	Block, colourless
$V = 1750.8$ (5) Å^3	0.22 × 0.14 × 0.07 mm
$Z = 2$	

Data collection

Stoe IPDS-1 diffractometer	2954 independent reflections
Radiation source: fine-focus sealed tube	2446 reflections with $I > 2\sigma(I)$
graphite	$R_{int} = 0.134$
ω scans	$\theta_{max} = 25.0°$, $\theta_{min} = 2.4°$
Absorption correction: numerical (*X-SHAPE* and *X-RED32*; Stoe & Cie, 2002)	$h = -13\rightarrow13$
$T_{min} = 0.912$, $T_{max} = 0.968$	$k = -13\rightarrow13$
11086 measured reflections	$l = -15\rightarrow15$

Refinement

Refinement on F^2	Secondary atom site location: difference Fourier map
Least-squares matrix: full	Hydrogen site location: inferred from neighbouring sites
$R[F^2 > 2\sigma(F^2)] = 0.073$	H-atom parameters constrained
$wR(F^2) = 0.206$	$w = 1/[\sigma^2(F_o^2) + (0.1115P)^2 + 1.3719P]$ where $P = (F_o^2 + 2F_c^2)/3$
$S = 1.07$	$(\Delta/\sigma)_{max} < 0.001$
2954 reflections	$\Delta\rho_{max} = 0.72$ e Å^{-3}
191 parameters	$\Delta\rho_{min} = -1.37$ e Å^{-3}
0 restraints	Extinction correction: *SHELXL97* (Sheldrick, 2008), $Fc^*=kFc[1+0.001xFc^2\lambda^3/\sin(2\theta)]^{-1/4}$
Primary atom site location: structure-invariant direct methods	Extinction coefficient: 0.034 (7)

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å^2)

	x	*y*	*z*	U_{iso}*/U_{eq}
Mn1	0.5000	0.71119 (6)	0.7500	0.0284 (3)
N1	0.3018 (2)	0.7070 (3)	0.7479 (3)	0.0385 (8)
C1	0.2710 (3)	0.6632 (5)	0.8264 (4)	0.0557 (13)
H1	0.3317	0.6340	0.8829	0.067*
C2	0.1544 (4)	0.6575 (5)	0.8310 (4)	0.0617 (15)
H2	0.1373	0.6249	0.8892	0.074*
C3	0.0633 (3)	0.7003 (4)	0.7491 (4)	0.0408 (10)
C4	0.0940 (3)	0.7447 (5)	0.6646 (4)	0.0577 (13)
H4	0.0352	0.7725	0.6061	0.069*
C5	0.2141 (3)	0.7470 (5)	0.6684 (4)	0.0559 (13)
H5	0.2346	0.7788	0.6115	0.067*
N11	0.5000	0.9088 (4)	0.7500	0.0367 (11)
N12	0.5000	1.5156 (3)	0.7500	0.0354 (11)
C11	0.4781 (4)	0.9689 (3)	0.8272 (4)	0.0448 (10)
H11	0.4624	0.9285	0.8824	0.054*
C12	0.4775 (4)	1.0865 (4)	0.8300 (4)	0.0498 (11)
H12	0.4619	1.1249	0.8862	0.060*
C13	0.5000	1.1484 (4)	0.7500	0.0384 (13)
C16	0.4344 (4)	1.4556 (4)	0.6684 (4)	0.0488 (11)
H16	0.3880	1.4963	0.6104	0.059*
C15	0.4314 (4)	1.3368 (4)	0.6652 (4)	0.0509 (11)
H17	0.3837	1.2982	0.6063	0.061*
C14	0.5000	1.2758 (4)	0.7500	0.0390 (13)
N21	0.5534 (3)	0.7169 (3)	0.9196 (3)	0.0386 (8)
C21	0.6253 (3)	0.6927 (3)	0.9963 (4)	0.0412 (10)
S21	0.72754 (14)	0.65840 (19)	1.10210 (13)	0.0900 (6)
C31	0.0822 (10)	0.3656 (13)	0.6206 (10)	0.170 (6)
H31A	0.1479	0.4018	0.6020	0.255*

H31B	0.0756	0.3981	0.6853	0.255*
H31C	0.0086	0.3787	0.5659	0.255*
C32	0.1059 (12)	0.2324 (15)	0.6347 (9)	0.172 (6)
H32A	0.1679	0.2177	0.7002	0.206*
H32B	0.0329	0.1930	0.6375	0.206*
O31	0.1431 (5)	0.1896 (8)	0.5502 (5)	0.138 (3)
C33	0.1686 (9)	0.0670 (10)	0.5534 (11)	0.146 (5)
H33A	0.0974	0.0238	0.5554	0.175*
H33B	0.2328	0.0489	0.6166	0.175*
C34	0.2049 (11)	0.0329 (12)	0.4606 (12)	0.167 (5)
H34A	0.1368	0.0383	0.3991	0.251*
H34B	0.2341	−0.0456	0.4688	0.251*
H34C	0.2676	0.0837	0.4530	0.251*

Atomic displacement parameters (Å^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Mn1	0.0147 (4)	0.0265 (5)	0.0448 (6)	0.000	0.0100 (3)	0.000
N1	0.0135 (13)	0.0482 (19)	0.057 (2)	0.0019 (12)	0.0146 (14)	0.0072 (15)
C1	0.0196 (17)	0.087 (3)	0.060 (3)	0.0062 (19)	0.0109 (18)	0.025 (3)
C2	0.0233 (18)	0.101 (4)	0.064 (3)	0.005 (2)	0.0176 (19)	0.032 (3)
C3	0.0130 (17)	0.060 (2)	0.051 (3)	0.0018 (15)	0.0119 (15)	0.0015 (19)
C4	0.0209 (17)	0.103 (4)	0.050 (3)	0.012 (2)	0.0110 (17)	0.011 (3)
C5	0.0220 (18)	0.095 (4)	0.054 (3)	0.011 (2)	0.0174 (18)	0.019 (3)
N11	0.034 (2)	0.026 (2)	0.054 (3)	0.000	0.018 (2)	0.000
N12	0.0246 (19)	0.025 (2)	0.055 (3)	0.000	0.0101 (19)	0.000
C11	0.057 (2)	0.032 (2)	0.055 (3)	0.0032 (18)	0.030 (2)	0.0031 (18)
C12	0.065 (3)	0.036 (2)	0.058 (3)	0.004 (2)	0.032 (2)	−0.0027 (19)
C13	0.034 (2)	0.028 (3)	0.054 (4)	0.000	0.013 (2)	0.000
C16	0.050 (2)	0.032 (2)	0.055 (3)	−0.0014 (18)	0.0004 (19)	0.0048 (18)
C15	0.056 (2)	0.034 (2)	0.054 (3)	−0.0069 (19)	0.002 (2)	−0.0031 (19)
C14	0.036 (3)	0.028 (3)	0.056 (4)	0.000	0.018 (3)	0.000
N21	0.0276 (15)	0.0389 (18)	0.049 (2)	0.0025 (12)	0.0111 (15)	0.0026 (14)
C21	0.034 (2)	0.044 (2)	0.049 (3)	0.0014 (16)	0.0167 (19)	−0.0025 (18)
S21	0.0624 (9)	0.1362 (16)	0.0578 (12)	0.0265 (9)	−0.0047 (7)	0.0143 (9)
C31	0.111 (8)	0.246 (16)	0.144 (11)	0.028 (9)	0.022 (7)	−0.056 (11)
C32	0.136 (9)	0.308 (19)	0.079 (8)	−0.067 (11)	0.041 (7)	−0.028 (10)
O31	0.078 (3)	0.235 (9)	0.093 (5)	−0.005 (4)	0.010 (3)	0.028 (5)
C33	0.089 (6)	0.131 (8)	0.204 (14)	0.015 (6)	0.020 (7)	0.061 (8)
C34	0.134 (9)	0.179 (11)	0.198 (13)	0.057 (8)	0.062 (9)	0.020 (10)

Geometric parameters (Å, °)

Mn1—N21	2.181 (4)	C13—C12^{iii}	1.380 (5)
Mn1—N12^{i}	2.277 (4)	C13—C14	1.483 (7)
Mn1—N11	2.300 (4)	C16—C15	1.383 (6)
Mn1—N1	2.312 (3)	C16—H16	0.9400
N1—C1	1.311 (6)	C15—C14	1.385 (5)

N1—C5	1.333 (6)	C15—H17	0.9400
C1—C2	1.385 (5)	C14—C15^{iii}	1.385 (5)
C1—H1	0.9400	N21—C21	1.161 (6)
C2—C3	1.386 (6)	C21—S21	1.621 (5)
C2—H2	0.9400	C31—C32	1.577 (18)
C3—C4	1.384 (7)	C31—H31A	0.9700
C3—C3^{ii}	1.488 (6)	C31—H31B	0.9700
C4—C5	1.392 (5)	C31—H31C	0.9700
C4—H4	0.9400	C32—O31	1.418 (13)
C5—H5	0.9400	C32—H32A	0.9800
N11—C11	1.334 (5)	C32—H32B	0.9800
N11—C11^{iii}	1.334 (5)	O31—C33	1.455 (12)
N12—C16	1.338 (5)	C33—C34	1.482 (16)
N12—C16^{iii}	1.338 (5)	C33—H33A	0.9800
N12—Mn1^{iv}	2.277 (4)	C33—H33B	0.9800
C11—C12	1.370 (6)	C34—H34A	0.9700
C11—H11	0.9400	C34—H34B	0.9700
C12—C13	1.380 (5)	C34—H34C	0.9700
C12—H12	0.9400		
N21—Mn1—N21^{iii}	176.54 (16)	C11—C12—C13	119.8 (4)
N21—Mn1—N12^{i}	91.73 (8)	C11—C12—H12	120.1
N21^{iii}—Mn1—N12^{i}	91.73 (8)	C13—C12—H12	120.1
N21—Mn1—N11	88.27 (8)	C12—C13—C12^{iii}	117.0 (5)
N21^{iii}—Mn1—N11	88.27 (8)	C12—C13—C14	121.5 (3)
N12^{i}—Mn1—N11	180.0	C12^{iii}—C13—C14	121.5 (3)
N21—Mn1—N1	89.88 (12)	N12—C16—C15	123.4 (4)
N21^{iii}—Mn1—N1	90.19 (12)	N12—C16—H16	118.3
N12^{i}—Mn1—N1	88.79 (8)	C15—C16—H16	118.3
N11—Mn1—N1	91.21 (8)	C16—C15—C14	118.9 (4)
N21—Mn1—N1^{iii}	90.19 (12)	C16—C15—H17	120.6
N21^{iii}—Mn1—N1^{iii}	89.88 (12)	C14—C15—H17	120.6
N12^{i}—Mn1—N1^{iii}	88.79 (8)	C15^{iii}—C14—C15	118.3 (5)
N11—Mn1—N1^{iii}	91.21 (8)	C15^{iii}—C14—C13	120.8 (3)
N1—Mn1—N1^{iii}	177.58 (16)	C15—C14—C13	120.8 (3)
C1—N1—C5	116.9 (3)	C21—N21—Mn1	146.6 (3)
C1—N1—Mn1	120.3 (3)	N21—C21—S21	178.9 (4)
C5—N1—Mn1	122.7 (3)	C32—C31—H31A	109.5
N1—C1—C2	123.8 (4)	C32—C31—H31B	109.5
N1—C1—H1	118.1	H31A—C31—H31B	109.5
C2—C1—H1	118.1	C32—C31—H31C	109.5
C1—C2—C3	119.4 (4)	H31A—C31—H31C	109.5
C1—C2—H2	120.3	H31B—C31—H31C	109.5
C3—C2—H2	120.3	O31—C32—C31	109.5 (10)
C4—C3—C2	117.5 (3)	O31—C32—H32A	109.8
C4—C3—C3^{ii}	120.5 (4)	C31—C32—H32A	109.8

C2—C3—C3^{ii}	122.0 (5)	O31—C32—H32B	109.8
C3—C4—C5	118.4 (4)	C31—C32—H32B	109.8
C3—C4—H4	120.8	H32A—C32—H32B	108.2
C5—C4—H4	120.8	C32—O31—C33	115.3 (10)
N1—C5—C4	124.0 (4)	O31—C33—C34	110.1 (10)
N1—C5—H5	118.0	O31—C33—H33A	109.6
C4—C5—H5	118.0	C34—C33—H33A	109.6
C11—N11—C11^{iii}	116.8 (5)	O31—C33—H33B	109.6
C11—N11—Mn1	121.6 (2)	C34—C33—H33B	109.6
C11^{iii}—N11—Mn1	121.6 (2)	H33A—C33—H33B	108.2
C16—N12—C16^{iii}	117.1 (5)	C33—C34—H34A	109.5
C16—N12—Mn1^{iv}	121.4 (2)	C33—C34—H34B	109.5
C16^{iii}—N12—Mn1^{iv}	121.4 (2)	H34A—C34—H34B	109.5
N11—C11—C12	123.3 (4)	C33—C34—H34C	109.5
N11—C11—H11	118.4	H34A—C34—H34C	109.5
C12—C11—H11	118.4	H34B—C34—H34C	109.5

Symmetry codes: (i) *x*, *y*−1, *z*; (ii) −*x*, *y*, −*z*+3/2; (iii) −*x*+1, *y*, −*z*+3/2; (iv) *x*, *y*+1, *z*.

Fig. 1

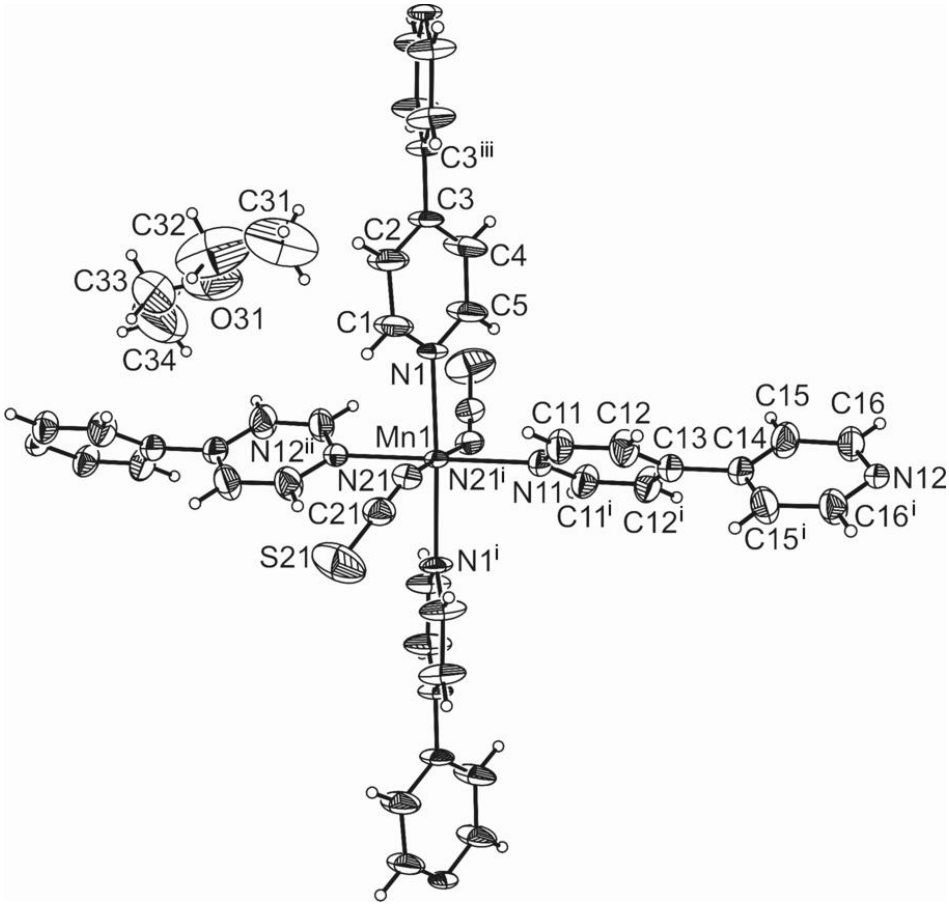
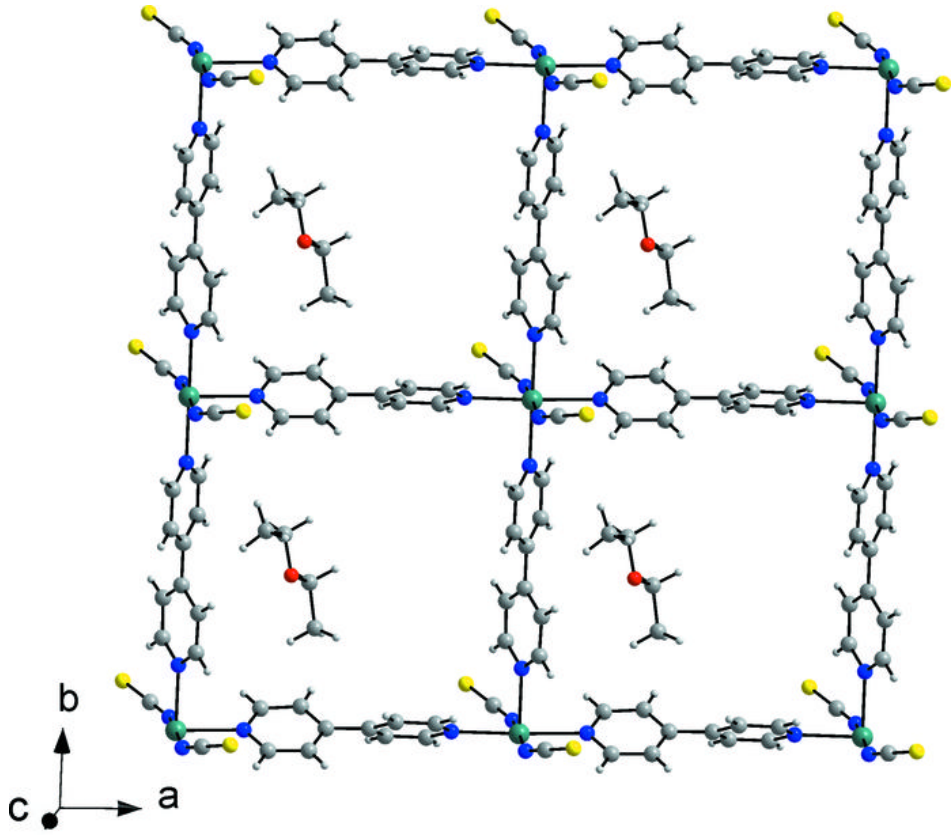

C3iii
C31
C32
C3
C2
C4
C33
O31
C5
C1
C34
N1
C15
C16
C11
C12
Mn1
C13
C14
N12ii
N21
N21i
N11
N12
C21
C11i
C12i
C16i
C15i
S21
N1i

Fig. 2



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Tetraaquabis(pyridine-κN)nickel(II) dinitrate

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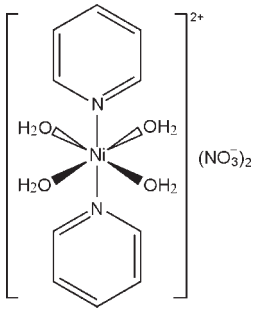
Key indicators: single-crystal X-ray study; T = 293 K; mean σ(C–C) = 0.005 Å; R factor = 0.049; wR factor = 0.129; data-to-parameter ratio = 21.1.

In the title compound, $[Ni(C_5H_5N)_2(H_2O)_4](NO_3)_2$, the Ni^{II} ion is coordinated by two *N*-bonded pyridine ligands and four water molecules in an octahedral coordination mode. The asymmetric unit consists of one Ni^{II} ion located on an inversion center, as well as one pyridine ligand, one nitrate anion and two water molecules in general positions. In the crystal structure, the discrete complex cations and nitrate anions are connected by O—H···O and C—H···O hydrogen bonds.

Related literature

For general background to thermal decomposition reactions as an alternative tool for the discovery and preparation of new ligand-deficient coordination polymers with defined magnetic properties, see: Wriedt & Näther (2009*a*,*b*); Wriedt *et al.* (2009*a*,*b*). For a related structure, see: Halut-Desportes (1981).



Experimental

Crystal data

$[Ni(C_5H_5N)_2(H_2O)_4](NO_3)_2$
M_r = 412.99
Monoclinic, $P2_1/n$
a = 7.3245 (4) Å
b = 11.3179 (6) Å
c = 10.9347 (5) Å
β = 96.436 (4)°
V = 900.75 (8) Å^3
Z = 2
Mo $K\alpha$ radiation
μ = 1.13 mm^{-1}
T = 293 K
0.28 × 0.16 × 0.07 mm

Data collection

Stoe IPDS-2 diffractometer
Absorption correction: numerical (*X-SHAPE* and *X-RED32*; Stoe & Cie, 2002)
T_{min} = 0.801, T_{max} = 0.927
12828 measured reflections
2427 independent reflections
2087 reflections with $I > 2\sigma(I)$
R_{int} = 0.040

Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.049
$wR(F^2)$ = 0.129
S = 1.15
2427 reflections
115 parameters
H-atom parameters constrained
$\Delta\rho_{max}$ = 0.32 e Å^{-3}
$\Delta\rho_{min}$ = −0.47 e Å^{-3}

Table 1
Selected bond lengths (Å).

Ni1—O4	2.113 (2)	Ni1—N1	2.140 (2)
Ni1—O5	2.128 (2)		

Table 2
Hydrogen-bond geometry (Å, °).

D—H···A	D—H	H···A	D···A	D—H···A
O4—H1*O4*···O2^{i}	0.82	2.39	3.209 (4)	174
O4—H2*O4*···O1^{ii}	0.82	2.26	3.077 (4)	179
O4—H3*O4*···O1	0.82	2.32	3.087 (3)	157
O5—H1*O5*···O3^{iii}	0.82	2.28	3.091 (4)	169
O5—H2*O5*···O1	0.82	2.43	3.191 (4)	155
C2—H2···O1^{iv}	0.93	2.50	3.310 (4)	145
C4—H4···O2^{v}	0.93	2.54	3.461 (4)	170

Symmetry codes: (i) $x-\frac{1}{2}, -y+\frac{3}{2}, z-\frac{1}{2}$; (ii) $-x+2, -y+1, -z+1$; (iii) $-x+\frac{3}{2}, y-\frac{1}{2}, -z+\frac{3}{2}$; (iv) $x-\frac{1}{2}, -y+\frac{1}{2}, z-\frac{1}{2}$; (v) $-x+\frac{5}{2}, y-\frac{1}{2}, -z+\frac{3}{2}$.

Data collection: *X-AREA* (Stoe & Cie, 2002); cell refinement: *X-AREA*; data reduction: *X-AREA*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *SHELXTL* (Sheldrick, 2008); software used to prepare material for publication: *SHELXTL*.

MW thanks the Stiftung Stipendien-Fonds des Verbandes der Chemischen Industrie and the Studienstiftung des deutschen Volkes for a PhD scholarship. We gratefully acknowledge financial support by the State of Schleswig-Holstein and the Deutsche Forschungsgemeinschaft (Project 720/3-1). We thank Professor Dr Wolfgang Bensch for the opportunity to use his experimental facilities.

Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: HY2315).

References

Halut-Desportes, S. (1981). *Rev. Chim. Miner.* **18**, 199.
Sheldrick, G. M. (2008). *Acta Cryst.* A**64**, 112–122.
Stoe & Cie (2002). *X-AREA*, *X-RED32* and *X-SHAPE*. Stoe & Cie, Darmstadt, Germany.
Wriedt, M. & Näther, C. (2009*a*). *Dalton Trans.* pp. 10192–10198.
Wriedt, M. & Näther, C. (2009*b*). *Z. Anorg. Allg. Chem.* **636**, 569–575.
Wriedt, M., Sellmer, S. & Näther, C. (2009*a*). *Dalton Trans.* pp. 7975–7984.
Wriedt, M., Sellmer, S. & Näther, C. (2009*b*). *Inorg. Chem.* **48**, 6896–6903.

supplementary materials

Acta Cryst. (2010). E**66**, m780 [**doi:10.1107/S1600536810021653**]

Tetraaquabis(pyridine-*κN*)nickel(II) dinitrate

M. Wriedt, I. Jess and C. Näther

Comment

Recently, we have shown that thermal decomposition reactions are an elegant route for the discovery and preparation of new ligand-deficient coordination polymers with defined magnetic properties (Wriedt & Näther, 2009a,b; Wriedt *et al.*, 2009a,b). In our ongoing investigation on the synthesis, structures and properties of such compounds based on paramagnetic transition metal pseudo-halides and N-donor ligands, we have reacted nickel(II) dinitrate hexahydrate, sodium dicyanamide and pyridine. In this reaction single crystals of the title compound were grown.

The title compound (Fig. 1) represents a discrete complex cation, in which the Ni^{II} atom, lying on an inversion center, is coordinated by two pyridine ligands and four water molecules in an octahedral coordination mode. The nitrate anions are not coordinated to the metal atoms (Fig. 2). The NiN_2O_4 octahedron is slightly distorted with Ni—$N_{pyridine}$ distances of 2.140 (2) Å and Ni—O_{water} distances of 2.113 (2) and 2.128 (2) Å (Table 1). The angles arround the metal atoms range between 85.71 (10) to 94.29 (10) and 180°. A similar coordination is found in a related structure (Halut-Desportes, 1981). The opposite pyridyl rings are coplanar due to symmetry. The shortest intermolecular Ni···Ni distance amounts to 7.3245 (4) Å.

Experimental

$Ni(NO_3)_2.6H_2O$ (72.7 mg, 0.25 mmol), sodium dicyanamide (44.5 mg, 0.5 mmol) and pyridine (0.5 ml) obtained from Alfa Aesar were reacted in a closed test-tube at 120°C for 3 d. On cooling light green block-shaped single crystals of the title compound were grown in a mixture with unknown phases.

Refinement

All H atoms were located in a difference Fourier map. H atoms bound to C atoms were positioned geometrically and refined as riding atoms, with C—H = 0.93 Å and with $U_{iso}(H) = 1.2U_{eq}(C)$. The water H atoms were disordered over three positions for each water molecule and were refined as riding, with O—H = 0.82 Å and $U_{iso}(H) = 1.5U_{eq}(O)$, using a split model with SOF = 0.6667 for each H atom.

Figures

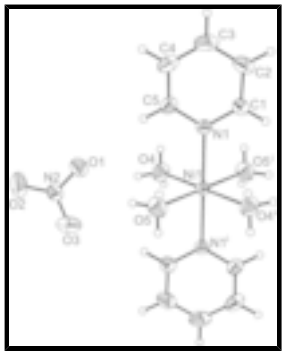


Fig. 1. The structure of the title compound with displacement ellipsoids drawn at the 30% probability level. Disordering of the H atoms is shown with full and open bonds. [Symmetry code: (i) -x+1, -y+1, -z+1.]

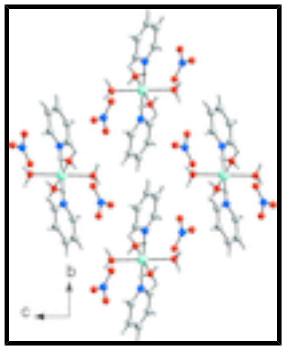


Fig. 2. Packing arrangement of the title compound with view along the *a* axis.

Tetraaquabis(pyridine-κ*N*)nickel(II) dinitrate

Crystal data

$[Ni(C_5H_5N)_2(H_2O)_4](NO_3)_2$	$F(000) = 428$
$M_r = 412.99$	$D_x = 1.523$ Mg m^{-3}
Monoclinic, $P2_1/n$	Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å
Hall symbol: -P 2yn	Cell parameters from 12828 reflections
$a = 7.3245$ (4) Å	$\theta = 2.6$–$29.2°$
$b = 11.3179$ (6) Å	$\mu = 1.13$ mm^{-1}
$c = 10.9347$ (5) Å	$T = 293$ K
$\beta = 96.436$ (4)°	Block, light green
$V = 900.75$ (8) Å^3	0.28 × 0.16 × 0.07 mm
$Z = 2$	

Data collection

Stoe IPDS-2 diffractometer	2427 independent reflections
Radiation source: fine-focus sealed tube	2087 reflections with $I > 2\sigma(I)$
graphite	$R_{int} = 0.040$
ω scans	$\theta_{max} = 29.2°$, $\theta_{min} = 2.6°$
Absorption correction: numerical (*X-SHAPE* and *X-RED32*; Stoe & Cie, 2002)	$h = -10 \rightarrow 9$

T_{min} = 0.801, T_{max} = 0.927	k = −15→15
12828 measured reflections	l = −15→14

Refinement

Refinement on F^2	Primary atom site location: structure-invariant direct methods
Least-squares matrix: full	Secondary atom site location: difference Fourier map
$R[F^2 > 2\sigma(F^2)]$ = 0.049	Hydrogen site location: inferred from neighbouring sites
$wR(F^2)$ = 0.129	H-atom parameters constrained
S = 1.15	$w = 1/[\sigma^2(F_o^2) + (0.0554P)^2 + 0.6589P]$ where $P = (F_o^2 + 2F_c^2)/3$
2427 reflections	$(\Delta/\sigma)_{max} < 0.001$
115 parameters	$\Delta\rho_{max}$ = 0.32 e Å^{-3}
0 restraints	$\Delta\rho_{min}$ = −0.47 e Å^{-3}

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å^2)

	x	*y*	*z*	U_{iso}*/U_{eq}	Occ. (<1)
Ni1	0.5000	0.5000	0.5000	0.03618 (15)	
N1	0.6201 (3)	0.32862 (19)	0.4879 (2)	0.0421 (5)	
C1	0.5276 (4)	0.2407 (3)	0.4281 (3)	0.0526 (7)	
H1	0.4095	0.2555	0.3908	0.063*	
C2	0.5994 (6)	0.1285 (3)	0.4191 (4)	0.0678 (9)	
H2	0.5305	0.0693	0.3770	0.081*	
C3	0.7731 (6)	0.1062 (3)	0.4729 (4)	0.0735 (10)	
H3	0.8250	0.0317	0.4676	0.088*	
C4	0.8695 (4)	0.1951 (3)	0.5348 (4)	0.0629 (8)	
H4	0.9881	0.1819	0.5722	0.076*	
C5	0.7896 (4)	0.3040 (3)	0.5412 (3)	0.0486 (6)	
H5	0.8560	0.3636	0.5844	0.058*	
N2	1.0498 (3)	0.6620 (2)	0.7423 (2)	0.0501 (5)	
O1	1.0070 (3)	0.5655 (2)	0.6942 (2)	0.0635 (6)	
O2	1.1995 (4)	0.6760 (3)	0.8009 (3)	0.0956 (10)	
O3	0.9347 (5)	0.7424 (3)	0.7281 (3)	0.0905 (9)	
O4	0.7425 (3)	0.5820 (2)	0.4544 (2)	0.0624 (6)	
H1O4	0.7224	0.6435	0.4154	0.094*	0.667
H2O4	0.8088	0.5431	0.4141	0.094*	0.667
H3O4	0.8104	0.5993	0.5166	0.094*	0.667
O5	0.5815 (4)	0.5041 (2)	0.6930 (2)	0.0670 (6)	
H1O5	0.5830	0.4380	0.7239	0.101*	0.667
H2O5	0.6849	0.5295	0.7147	0.101*	0.667
H3O5	0.5148	0.5457	0.7304	0.101*	0.667

Atomic displacement parameters (Å^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}

Ni1	0.0330 (2)	0.0335 (2)	0.0415 (2)	−0.00085 (16)	0.00174 (15)	−0.00095 (18)
N1	0.0411 (10)	0.0356 (10)	0.0498 (11)	0.0028 (8)	0.0065 (9)	−0.0007 (9)
C1	0.0526 (15)	0.0430 (14)	0.0613 (17)	−0.0008 (12)	0.0017 (13)	−0.0071 (12)
C2	0.083 (2)	0.0423 (16)	0.079 (2)	−0.0013 (15)	0.0110 (18)	−0.0126 (15)
C3	0.080 (2)	0.0451 (17)	0.099 (3)	0.0188 (16)	0.025 (2)	0.0026 (18)
C4	0.0477 (16)	0.0579 (18)	0.085 (2)	0.0131 (14)	0.0137 (15)	0.0159 (17)
C5	0.0403 (13)	0.0465 (14)	0.0595 (16)	0.0008 (11)	0.0069 (11)	0.0062 (12)
N2	0.0541 (13)	0.0526 (14)	0.0443 (11)	−0.0080 (11)	0.0088 (10)	−0.0055 (10)
O1	0.0690 (14)	0.0510 (13)	0.0687 (14)	−0.0078 (10)	−0.0002 (11)	−0.0095 (11)
O2	0.0725 (18)	0.123 (3)	0.0858 (19)	−0.0316 (17)	−0.0137 (15)	−0.0169 (18)
O3	0.104 (2)	0.0689 (17)	0.102 (2)	0.0254 (16)	0.0278 (18)	−0.0123 (15)
O4	0.0518 (12)	0.0568 (13)	0.0788 (15)	−0.0035 (10)	0.0088 (10)	0.0059 (11)
O5	0.0763 (16)	0.0655 (15)	0.0575 (13)	−0.0031 (11)	0.0000 (11)	−0.0016 (11)

Geometric parameters (Å, °)

Ni1—O4	2.113 (2)	C4—H4	0.9300
Ni1—O5	2.128 (2)	C5—H5	0.9300
Ni1—N1	2.140 (2)	N2—O2	1.216 (4)
N1—C1	1.333 (4)	N2—O1	1.238 (3)
N1—C5	1.340 (3)	N2—O3	1.238 (4)
C1—C2	1.381 (4)	O4—H1O4	0.8200
C1—H1	0.9300	O4—H2O4	0.8200
C2—C3	1.365 (5)	O4—H3O4	0.8200
C2—H2	0.9300	O5—H1O5	0.8200
C3—C4	1.364 (5)	O5—H2O5	0.8200
C3—H3	0.9300	O5—H3O5	0.8200
C4—C5	1.369 (4)		
O4—Ni1—O4^{i}	180.00 (11)	C4—C3—C2	118.9 (3)
O4—Ni1—O5^{i}	85.71 (10)	C4—C3—H3	120.6
O4^{i}—Ni1—O5^{i}	94.29 (10)	C2—C3—H3	120.6
O4—Ni1—O5	94.29 (10)	C3—C4—C5	119.3 (3)
O4^{i}—Ni1—O5	85.71 (10)	C3—C4—H4	120.4
O5^{i}—Ni1—O5	180.000 (1)	C5—C4—H4	120.4
O4—Ni1—N1	91.23 (9)	N1—C5—C4	123.1 (3)
O4^{i}—Ni1—N1	88.77 (9)	N1—C5—H5	118.5
O5^{i}—Ni1—N1	89.46 (9)	C4—C5—H5	118.5
O5—Ni1—N1	90.54 (9)	O2—N2—O1	120.5 (3)
O4—Ni1—N1^{i}	88.77 (9)	O2—N2—O3	122.1 (3)
O4^{i}—Ni1—N1^{i}	91.23 (9)	O1—N2—O3	117.3 (3)
O5^{i}—Ni1—N1^{i}	90.54 (9)	Ni1—O4—H1O4	112.9
O5—Ni1—N1^{i}	89.46 (9)	Ni1—O4—H2O4	117.0
N1—Ni1—N1^{i}	180.000 (1)	H1O4—O4—H2O4	105.0
C1—N1—C5	116.9 (2)	Ni1—O4—H3O4	110.9
C1—N1—Ni1	121.15 (19)	H1O4—O4—H3O4	106.6
C5—N1—Ni1	121.94 (19)	H2O4—O4—H3O4	103.5

N1—C1—C2	123.0 (3)	Ni1—O5—H1O5	112.2
N1—C1—H1	118.5	Ni1—O5—H2O5	116.2
C2—C1—H1	118.5	H1O5—O5—H2O5	103.3
C3—C2—C1	118.9 (3)	Ni1—O5—H3O5	113.0
C3—C2—H2	120.6	H1O5—O5—H3O5	107.4
C1—C2—H2	120.6	H2O5—O5—H3O5	103.7

Symmetry codes: (i) −*x*+1, −*y*+1, −*z*+1.

Hydrogen-bond geometry (Å, °)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
O4—H1O4···O2^{ii}	0.82	2.39	3.209 (4)	174
O4—H2O4···O1^{iii}	0.82	2.26	3.077 (4)	179
O4—H3O4···O1	0.82	2.32	3.087 (3)	157
O5—H1O5···O3^{iv}	0.82	2.28	3.091 (4)	169
O5—H2O5···O1	0.82	2.43	3.191 (4)	155
C2—H2···O1^{v}	0.93	2.50	3.310 (4)	145
C4—H4···O2^{vi}	0.93	2.54	3.461 (4)	170

Symmetry codes: (ii) *x*−1/2, −*y*+3/2, *z*−1/2; (iii) −*x*+2, −*y*+1, −*z*+1; (iv) −*x*+3/2, *y*−1/2, −*z*+3/2; (v) *x*−1/2, −*y*+1/2, *z*−1/2; (vi) −*x*+5/2, *y*−1/2, −*z*+3/2.

Fig. 1

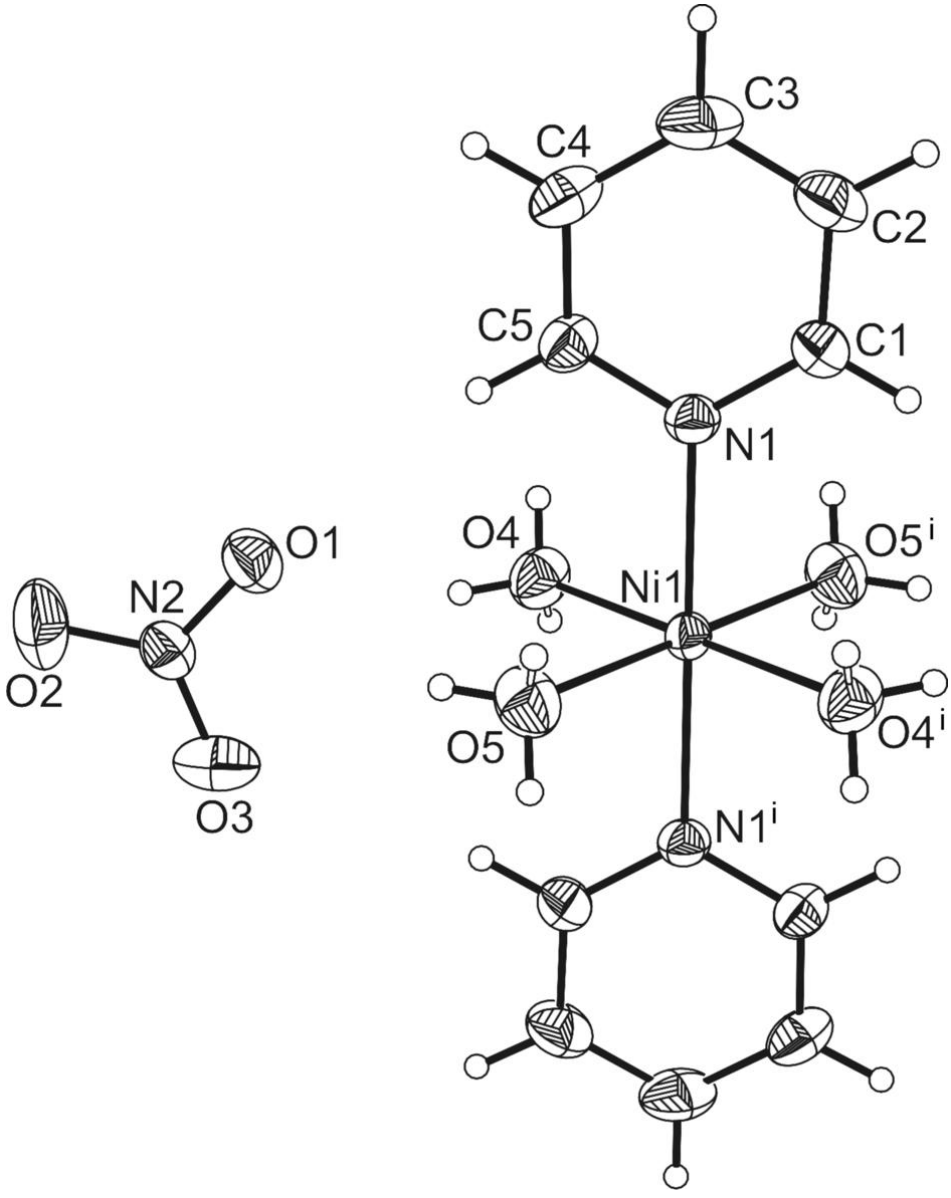
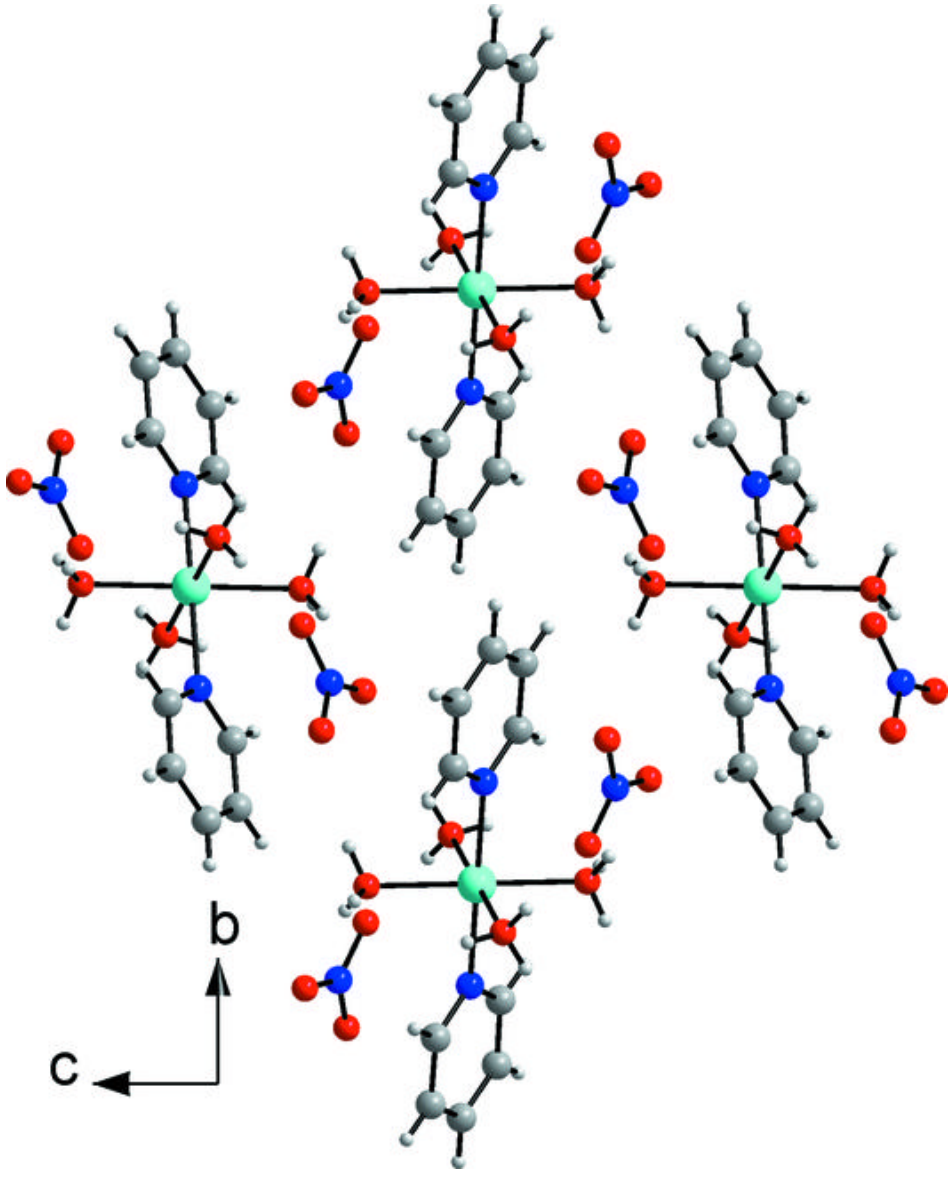


Fig. 2



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Bis(nitrato-κO)(5,7,12,14-tetramethyl-1,4,8,11-tetraazacyclotetradecane-6,13-diaminium-$\kappa^4N^1,N^4,N^8,N^{11}$)copper(II) dinitrate tetrahydrate

Xiang-Yun Liu[a]* and Hong-Ying Chu[b]

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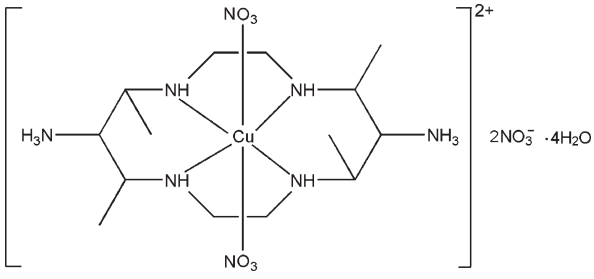
Key indicators: single-crystal X-ray study; T = 123 K; mean σ(C–C) = 0.004 Å; R factor = 0.046; wR factor = 0.133; data-to-parameter ratio = 15.0.

In the title compound, $[Cu(NO_3)_2(C_{14}H_{36}N_6)](NO_3)_2\cdot 4H_2O$, the Cu^{II} atom, lying on an inversion center, is six-coordinated in a distorted octahedral environment by four N atoms from a centrosymmetric 14-membered tetraazacyclotetradecane macrocyclic ligand and two O atoms from two nitrate anions. The supramolecular network is consolidated by extensive O—H···O and N—H···O hydrogen-bonding interactions.

Related literature

For Cu(II) complexes of related macrocyclic ligands, see: Bernhardt (1999); Bernhardt & Sharpe (1998).



Experimental

Crystal data

$[Cu(NO_3)_2(C_{14}H_{36}N_6)](NO_3)_2\cdot 4H_2O$
M_r = 672.14
Monoclinic, $P2_1/n$
a = 9.201 (2) Å
b = 16.576 (4) Å
c = 9.278 (2) Å
β = 98.788 (4)°
V = 1398.4 (5) Å^3
Z = 2
Mo $K\alpha$ radiation
μ = 0.87 mm^{-1}
T = 123 K
0.37 × 0.34 × 0.31 mm

Data collection

Bruker SMART 1000 CCD diffractometer
Absorption correction: multi-scan (*SADABS*; Bruker, 2001)
T_{min} = 0.739, T_{max} = 0.774
6071 measured reflections
3021 independent reflections
2269 reflections with $I > 2\sigma(I)$
R_{int} = 0.027

Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.046
$wR(F^2)$ = 0.133
S = 1.03
3021 reflections
202 parameters
6 restraints
H atoms treated by a mixture of independent and constrained refinement
$\Delta\rho_{max}$ = 1.24 e Å^{-3}
$\Delta\rho_{min}$ = −0.81 e Å^{-3}

Table 1
Hydrogen-bond geometry (Å, °).

D—H···A	D—H	H···A	D···A	D—H···A
N1—H1C···O3	0.93	2.43	3.155 (4)	134
N1—H1C···O2W^{i}	0.93	2.28	3.096 (4)	146
N2—H2A···O3	0.93	2.52	3.244 (4)	135
N2—H2A···O4^{ii}	0.93	2.47	3.249 (4)	141
N3—H3D···O4	0.91	2.08	2.924 (4)	155
N3—H3E···O1W^{iii}	0.91	1.86	2.748 (4)	164
N3—H3F···O2^{i}	0.91	2.06	2.902 (4)	154
N3—H3F···O3^{i}	0.91	2.32	3.108 (4)	145
O1W—H1WA···O2^{i}	0.84 (4)	2.01 (3)	2.823 (4)	160 (5)
O1W—H1WB···O5^{iv}	0.84 (2)	1.97 (2)	2.795 (4)	168 (5)
O2W—H2WA···O6^{ii}	0.93 (5)	2.00 (5)	2.913 (5)	166 (5)
O2W—H2WB···O6^{v}	0.92 (2)	2.18 (2)	3.084 (5)	167 (5)

Symmetry codes: (i) $-x+1, -y, -z+1$; (ii) $-x+\frac{3}{2}, y-\frac{1}{2}, -z+\frac{3}{2}$; (iii) $x+\frac{1}{2}, -y+\frac{1}{2}, z+\frac{1}{2}$; (iv) $x-1, y, z$; (v) $x-\frac{1}{2}, -y+\frac{1}{2}, z+\frac{1}{2}$.

Data collection: *SMART* (Bruker, 2007); cell refinement: *SAINT* (Bruker, 2007); data reduction: *SAINT*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *SHELXTL* (Sheldrick, 2008); software used to prepare material for publication: *SHELXTL*.

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Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: HY2316).

References

Bernhardt, P. V. (1999). *Inorg. Chem.* **38**, 3481–3483.
Bernhardt, P. V. & Sharpe, P. C. (1998). *Inorg. Chem.* **37**, 1629–1236.
Bruker (2001). *SADABS*. Bruker AXS Inc., Madison, Wisconsin, USA.
Bruker (2007). *SMART* and *SAINT*. Bruker AXS Inc., Madison, Wisconsin, USA.
Sheldrick, G. M. (2008). *Acta Cryst.* A**64**, 112–122.

supplementary materials

Acta Cryst. (2010). E**66**, m837 [**doi:10.1107/S1600536810023342**]

Bis(nitrato-κO)(5,7,12,14-tetramethyl-1,4,8,11-tetraazacyclotetradecane-6,13-diaminium-$\kappa^4N^1,N^4,N^8,N^{11}$)copper(II) dinitrate tetrahydrate

X.-Y. Liu and H.-Y. Chu

Comment

In the past, much attention has been given to the copper complexes of macrocyclic *trans*-5(*R*),7(*R*),12(*R*), 14(*R*)-tetramethyl-6, 13-dinitro-1,4,8,11-tetraazacyclotetradecane and related ligands (Bernhardt, 1999; Bernhardt & Sharpe, 1998). Recently, we have synthesized a Cu(II) complex based on 5,7,12,14-tetramethyl-6,13- diamino-1,4,8,11-tetraazacyclotetradecane and its structure is reported here.

The asymmetric unit of the title compound (Fig. 1) contains one Cu^{II} ion lying on an inversion center, one half of a 14-membered tetraazacyclotetradecane macrocyclic ligand, one coordinated nitrate anion, one uncoordinated nitrate anion and two solvent water molecules. The Cu^{II} ion has a slightly distorted octahedral coordination geometry, with two O atoms from two nitrate anions in the axial positions. The equatorial positions are occupied by four N atoms from the centrosymmetric 14-membered tetraazacyclotetradecane macrocyclic ligand [Cu1—N1 2.025 (2) and Cu1—N2 2.020 (2) Å]. The two uncoordinated nitrate anions are located above and below the 14-membered tetraazacyclotetradecane macrocycle and linked to the macrocycle *via* N—H···O hydrogen bonds (Table 1).

Experimental

An aqueous solution of 5,7,12,14-tetramethyl-6,13-diamino-1,4,8,11-tetraazacyclotetradecane (0.27 g, 1.0 mmol), $Cu(NO_3)_2$ (0.10 g, 0.5 mmol) and Na_2CO_3 (0.05 g, 0.5 mmol) was heated to reflux for 24 h. The reaction mixture was cooled to room temperature and red crystals of the title compound were obtained by slow evaporation of the solvent at room temperature.

Refinement

H atoms bound to C and N atoms were placed at calculated positions and were treated as riding on the parent atoms, with C—H = 1.00 (CH), 0.99 (CH_2) and 0.98 (CH_3) Å and N—H = 0.93 (NH) and 0.91 (NH_3) Å and with U_{iso}(H) = 1.2–1.5 U_{eq}(C, N). H atoms attached to water molecules were located in a difference Fourier map and refined with U_{iso}(H) = 1.2U_{eq}(O). The highest residual electron density was found 0.91 Å from O3 the deepest hole 0.52 Å from H2WA.

Figures

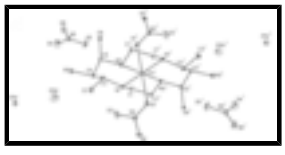


Fig. 1. The molecular structure of the title compound. Displacement ellipsoids are shown at the 30% probability level. H atoms have been omitted for clarity. [Symmetry code: (i) 2-x, -y, 1-z.]

Bis(nitrato-κ*O*)(5,7,12,14-tetramethyl-1,4,8,11- tetraazacyclotetradecane-6,13-diaminium-$\kappa^4N^1,N^4,N^8,N^{11}$)copper(II) dinitrate tetrahydrate

Crystal data

$[Cu(NO_3)_2(C_{14}H_{36}N_6)](NO_3)_2{\cdot}4H_2O$	$F(000) = 710$
$M_r = 672.14$	$D_x = 1.596$ Mg m^{-3}
Monoclinic, $P2_1/n$	Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å
Hall symbol: -P 2yn	Cell parameters from 2543 reflections
$a = 9.201$ (2) Å	$\theta = 2.5$–$27.0°$
$b = 16.576$ (4) Å	$\mu = 0.87$ mm^{-1}
$c = 9.278$ (2) Å	$T = 123$ K
$\beta = 98.788$ (4)°	Block, red
$V = 1398.4$ (5) Å^3	0.37 × 0.34 × 0.31 mm
$Z = 2$	

Data collection

Bruker SMART 1000 CCD diffractometer	3021 independent reflections
Radiation source: fine-focus sealed tube	2269 reflections with $I > 2\sigma(I)$
graphite	$R_{int} = 0.027$
φ and ω scans	$\theta_{max} = 27.1°$, $\theta_{min} = 2.5°$
Absorption correction: multi-scan (*SADABS*; Bruker, 2001)	$h = -11 \rightarrow 11$
$T_{min} = 0.739$, $T_{max} = 0.774$	$k = -21 \rightarrow 17$
6071 measured reflections	$l = -10 \rightarrow 11$

Refinement

Refinement on F^2	Primary atom site location: structure-invariant direct methods
Least-squares matrix: full	Secondary atom site location: difference Fourier map
$R[F^2 > 2\sigma(F^2)] = 0.046$	Hydrogen site location: inferred from neighbouring sites
$wR(F^2) = 0.133$	H atoms treated by a mixture of independent and constrained refinement
$S = 1.03$	$w = 1/[\sigma^2(F_o^2) + (0.0649P)^2 + 2.4391P]$ where $P = (F_o^2 + 2F_c^2)/3$
3021 reflections	$(\Delta/\sigma)_{max} = 0.036$
202 parameters	$\Delta\rho_{max} = 1.24$ e Å^{-3}
6 restraints	$\Delta\rho_{min} = -0.81$ e Å^{-3}

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å^2)

	x	*y*	*z*	U_{iso}*/U_{eq}

C1	0.8753 (4)	0.0883 (2)	0.2521 (3)	0.0169 (7)
H1A	0.9413	0.1356	0.2695	0.020*
H1B	0.7886	0.1039	0.1807	0.020*
C2	0.7676 (3)	0.13149 (18)	0.4684 (3)	0.0136 (6)
H2	0.8477	0.1722	0.4930	0.016*
C3	0.6400 (4)	0.1717 (2)	0.3687 (3)	0.0234 (8)
H3A	0.6749	0.1921	0.2809	0.035*
H3B	0.6019	0.2167	0.4205	0.035*
H3C	0.5616	0.1322	0.3408	0.035*
C4	0.7205 (3)	0.10160 (19)	0.6114 (3)	0.0129 (6)
H4	0.6574	0.0527	0.5888	0.016*
C5	0.8448 (3)	0.08013 (19)	0.7366 (3)	0.0137 (6)
H5	0.7973	0.0642	0.8224	0.016*
C6	0.9474 (3)	0.15076 (19)	0.7843 (3)	0.0167 (7)
H6A	1.0086	0.1378	0.8774	0.025*
H6B	0.8889	0.1991	0.7960	0.025*
H6C	1.0105	0.1608	0.7102	0.025*
C7	1.0453 (3)	−0.0192 (2)	0.8066 (3)	0.0170 (7)
H7A	1.0050	−0.0366	0.8947	0.020*
H7B	1.1144	0.0259	0.8342	0.020*
Cu1	1.0000	0.0000	0.5000	0.01124 (16)
N1	0.8274 (3)	0.06223 (16)	0.3922 (2)	0.0120 (5)
H1C	0.7509	0.0256	0.3683	0.014*
N2	0.9236 (3)	0.00785 (15)	0.6924 (3)	0.0128 (5)
H2A	0.8545	−0.0334	0.6882	0.015*
N3	0.6297 (3)	0.16570 (17)	0.6691 (3)	0.0173 (6)
H3D	0.6722	0.2147	0.6611	0.026*
H3E	0.6241	0.1555	0.7645	0.026*
H3F	0.5376	0.1657	0.6167	0.026*
N5	0.7860 (3)	0.36290 (18)	0.6169 (3)	0.0214 (6)
O4	0.6922 (3)	0.33861 (18)	0.6897 (3)	0.0377 (7)
O5	0.8513 (3)	0.31313 (17)	0.5511 (3)	0.0399 (7)
O6	0.8117 (3)	0.43623 (16)	0.6061 (4)	0.0402 (7)
O1W	0.1266 (3)	0.33514 (16)	0.4647 (3)	0.0236 (5)
O2W	0.4173 (4)	0.0272 (3)	0.8131 (4)	0.0592 (10)
H1WA	0.168 (5)	0.291 (2)	0.489 (6)	0.071*
H1WB	0.039 (3)	0.334 (3)	0.481 (6)	0.071*
H2WA	0.494 (5)	−0.008 (3)	0.846 (6)	0.071*
H2WB	0.396 (6)	0.045 (3)	0.901 (3)	0.071*
N4	0.7300 (3)	−0.14301 (18)	0.4733 (3)	0.0233 (6)
O1	0.8658 (2)	−0.13506 (15)	0.4843 (2)	0.0226 (5)
O2	0.6711 (3)	−0.21048 (15)	0.4441 (3)	0.0252 (6)
O3	0.6522 (3)	−0.08487 (18)	0.4963 (4)	0.0520 (9)

Atomic displacement parameters (Å^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
C1	0.0194 (16)	0.0188 (17)	0.0124 (14)	0.0044 (13)	0.0023 (11)	0.0043 (12)

C2	0.0175 (15)	0.0104 (15)	0.0122 (14)	0.0038 (12)	0.0004 (11)	0.0000 (11)
C3	0.0233 (18)	0.032 (2)	0.0150 (15)	0.0136 (15)	0.0039 (13)	0.0031 (14)
C4	0.0113 (14)	0.0153 (16)	0.0120 (13)	0.0026 (12)	0.0014 (11)	−0.0013 (11)
C5	0.0141 (15)	0.0155 (16)	0.0117 (13)	0.0025 (12)	0.0021 (11)	0.0011 (11)
C6	0.0171 (15)	0.0130 (16)	0.0192 (15)	0.0000 (12)	−0.0003 (12)	−0.0031 (12)
C7	0.0175 (15)	0.0232 (18)	0.0094 (13)	0.0068 (13)	−0.0009 (11)	0.0019 (11)
Cu1	0.0120 (3)	0.0135 (3)	0.0079 (2)	0.0030 (2)	0.00051 (17)	0.0002 (2)
N1	0.0121 (12)	0.0128 (13)	0.0112 (11)	0.0008 (10)	0.0022 (9)	−0.0003 (10)
N2	0.0123 (12)	0.0143 (14)	0.0113 (11)	0.0017 (10)	−0.0001 (9)	0.0009 (10)
N3	0.0161 (13)	0.0226 (16)	0.0134 (12)	0.0050 (11)	0.0030 (10)	−0.0006 (11)
N5	0.0167 (14)	0.0227 (16)	0.0244 (14)	0.0033 (12)	0.0021 (11)	0.0008 (12)
O4	0.0357 (16)	0.0389 (17)	0.0442 (16)	0.0024 (13)	0.0241 (13)	0.0093 (13)
O5	0.0442 (17)	0.0260 (15)	0.0558 (18)	−0.0001 (13)	0.0282 (14)	−0.0111 (13)
O6	0.0382 (16)	0.0149 (14)	0.071 (2)	−0.0009 (12)	0.0184 (14)	−0.0028 (13)
O1W	0.0252 (13)	0.0268 (14)	0.0192 (12)	−0.0001 (11)	0.0047 (10)	0.0005 (10)
O2W	0.051 (2)	0.068 (3)	0.056 (2)	0.0019 (19)	−0.0006 (17)	−0.0158 (19)
N4	0.0187 (14)	0.0206 (16)	0.0305 (16)	−0.0036 (12)	0.0031 (12)	−0.0016 (12)
O1	0.0153 (11)	0.0264 (14)	0.0268 (12)	−0.0057 (10)	0.0053 (9)	−0.0017 (10)
O2	0.0212 (12)	0.0197 (13)	0.0327 (13)	−0.0060 (10)	−0.0022 (10)	−0.0022 (10)
O3	0.0230 (15)	0.0230 (16)	0.111 (3)	0.0001 (12)	0.0151 (16)	−0.0074 (17)

Geometric parameters (Å, °)

C1—N1	1.499 (4)	C7—C1^{i}	1.505 (4)
C1—C7^{i}	1.505 (4)	C7—H7A	0.9900
C1—H1A	0.9900	C7—H7B	0.9900
C1—H1B	0.9900	Cu1—N2	2.020 (2)
C2—N1	1.496 (4)	Cu1—N1	2.025 (2)
C2—C3	1.532 (4)	Cu1—O1	2.550 (2)
C2—C4	1.539 (4)	N1—H1C	0.9300
C2—H2	1.0000	N2—H2A	0.9300
C3—H3A	0.9800	N3—H3D	0.9100
C3—H3B	0.9800	N3—H3E	0.9100
C3—H3C	0.9800	N3—H3F	0.9100
C4—N3	1.500 (4)	N5—O5	1.235 (4)
C4—C5	1.542 (4)	N5—O4	1.241 (4)
C4—H4	1.0000	N5—O6	1.245 (4)
C5—N2	1.491 (4)	O1W—H1WA	0.84 (4)
C5—C6	1.526 (4)	O1W—H1WB	0.84 (2)
C5—H5	1.0000	O2W—H2WA	0.93 (5)
C6—H6A	0.9800	O2W—H2WB	0.91 (2)
C6—H6B	0.9800	N4—O3	1.239 (4)
C6—H6C	0.9800	N4—O1	1.245 (4)
C7—N2	1.488 (3)	N4—O2	1.254 (4)
N1—C1—C7^{i}	108.5 (2)	N2—C7—H7A	109.9
N1—C1—H1A	110.0	C1^{i}—C7—H7A	109.9
C7^{i}—C1—H1A	110.0	N2—C7—H7B	109.9
N1—C1—H1B	110.0	C1^{i}—C7—H7B	109.9

C7^{i}—C1—H1B	110.0	H7A—C7—H7B	108.3
H1A—C1—H1B	108.4	N2^{i}—Cu1—N1	87.06 (10)
N1—C2—C3	110.6 (2)	N2—Cu1—N1	92.94 (10)
N1—C2—C4	109.4 (2)	O1—Cu1—N1	94.74 (9)
C3—C2—C4	111.7 (3)	O1—Cu1—N2	82.89 (8)
N1—C2—H2	108.3	O1—Cu1—N1^{i}	85.26 (9)
C3—C2—H2	108.3	O1—Cu1—N2^{i}	97.11 (8)
C4—C2—H2	108.3	C2—N1—C1	111.5 (2)
C2—C3—H3A	109.5	C2—N1—Cu1	118.36 (17)
C2—C3—H3B	109.5	C1—N1—Cu1	105.27 (18)
H3A—C3—H3B	109.5	C2—N1—H1C	107.1
C2—C3—H3C	109.5	C1—N1—H1C	107.1
H3A—C3—H3C	109.5	Cu1—N1—H1C	107.1
H3B—C3—H3C	109.5	C7—N2—C5	113.0 (2)
N3—C4—C2	109.0 (2)	C7—N2—Cu1	106.55 (18)
N3—C4—C5	106.5 (2)	C5—N2—Cu1	123.02 (18)
C2—C4—C5	116.8 (3)	C7—N2—H2A	104.1
N3—C4—H4	108.1	C5—N2—H2A	104.1
C2—C4—H4	108.1	Cu1—N2—H2A	104.1
C5—C4—H4	108.1	C4—N3—H3D	109.5
N2—C5—C6	113.0 (2)	C4—N3—H3E	109.5
N2—C5—C4	108.3 (2)	H3D—N3—H3E	109.5
C6—C5—C4	113.3 (3)	C4—N3—H3F	109.5
N2—C5—H5	107.3	H3D—N3—H3F	109.5
C6—C5—H5	107.3	H3E—N3—H3F	109.5
C4—C5—H5	107.3	O5—N5—O4	118.9 (3)
C5—C6—H6A	109.5	O5—N5—O6	120.0 (3)
C5—C6—H6B	109.5	O4—N5—O6	121.1 (3)
H6A—C6—H6B	109.5	H1WA—O1W—H1WB	109 (4)
C5—C6—H6C	109.5	H2WA—O2W—H2WB	99 (4)
H6A—C6—H6C	109.5	O3—N4—O1	120.2 (3)
H6B—C6—H6C	109.5	O3—N4—O2	119.3 (3)
N2—C7—C1^{i}	109.0 (2)	O1—N4—O2	120.5 (3)
N1—C2—C4—N3	−167.0 (2)	N2^{i}—Cu1—N1—C2	−142.1 (2)
C3—C2—C4—N3	−44.1 (3)	N2—Cu1—N1—C2	37.9 (2)
N1—C2—C4—C5	72.4 (3)	N2^{i}—Cu1—N1—C1	−16.78 (19)
C3—C2—C4—C5	−164.7 (3)	N2—Cu1—N1—C1	163.22 (19)
N3—C4—C5—N2	171.2 (2)	C1^{i}—C7—N2—C5	−175.9 (3)
C2—C4—C5—N2	−66.9 (3)	C1^{i}—C7—N2—Cu1	−37.9 (3)
N3—C4—C5—C6	−62.6 (3)	C6—C5—N2—C7	54.5 (3)
C2—C4—C5—C6	59.3 (3)	C4—C5—N2—C7	−179.2 (2)
C3—C2—N1—C1	56.7 (3)	C6—C5—N2—Cu1	−75.7 (3)
C4—C2—N1—C1	−179.9 (2)	C4—C5—N2—Cu1	50.7 (3)
C3—C2—N1—Cu1	178.9 (2)	N1^{i}—Cu1—N2—C7	11.4 (2)
C4—C2—N1—Cu1	−57.6 (3)	N1—Cu1—N2—C7	−168.6 (2)
C7^{i}—C1—N1—C2	171.5 (2)	N1^{i}—Cu1—N2—C5	144.2 (2)

C7^{i}—C1—N1—Cu1	42.0 (3)	N1—Cu1—N2—C5	−35.8 (2)

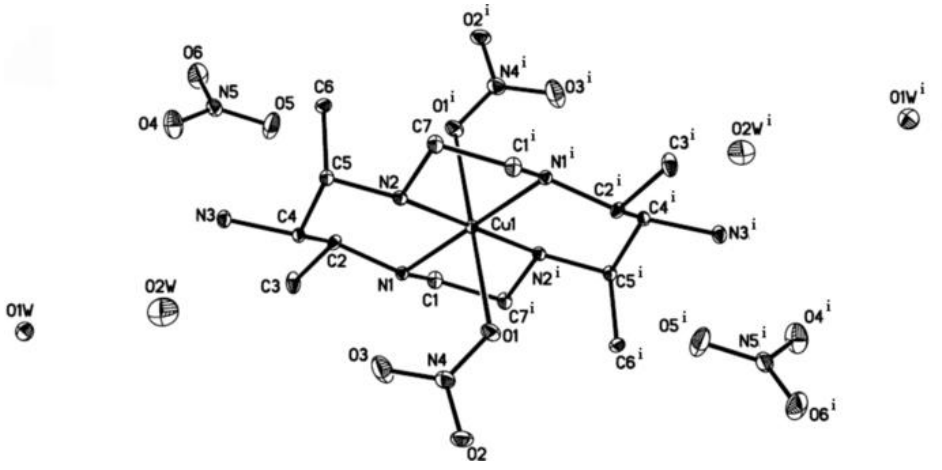
Symmetry codes: (i) −*x*+2, −*y*, −*z*+1.

Hydrogen-bond geometry (Å, °)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
N1—H1C···O3	0.93	2.43	3.155 (4)	134
N1—H1C···O2W^{ii}	0.93	2.28	3.096 (4)	146
N2—H2A···O3	0.93	2.52	3.244 (4)	135
N2—H2A···O4^{iii}	0.93	2.47	3.249 (4)	141
N3—H3D···O4	0.91	2.08	2.924 (4)	155
N3—H3E···O1W^{iv}	0.91	1.86	2.748 (4)	164
N3—H3F···O2^{ii}	0.91	2.06	2.902 (4)	154
N3—H3F···O3^{ii}	0.91	2.32	3.108 (4)	145
O1W—H1WA···O2^{ii}	0.84 (4)	2.01 (3)	2.823 (4)	160 (5)
O1W—H1WB···O5^{v}	0.84 (2)	1.97 (2)	2.795 (4)	168 (5)
O2W—H2WA···O6^{iii}	0.93 (5)	2.00 (5)	2.913 (5)	166 (5)
O2W—H2WB···O6^{vi}	0.92 (2)	2.18 (2)	3.084 (5)	167 (5)

Symmetry codes: (ii) −*x*+1, −*y*, −*z*+1; (iii) −*x*+3/2, *y*−1/2, −*z*+3/2; (iv) *x*+1/2, −*y*+1/2, *z*+1/2; (v) *x*−1, *y*, *z*; (vi) *x*−1/2, −*y*+1/2, *z*+1/2.

Fig. 1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O3i
O6
N5
O5
C6
O1i
C7
C1i
N1i
C3i
O2Wi
O1Wi
O4
C5
N2
C2i
C4i
N3
C4
Cu1
N3i
C2
C3
N1
C1
N2i
C5i
O2W
O1W
C7i
O1
O5i
N5i
O4i
O3
N4
C6i
O6i
O2

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Tricyclohexyl{2-[(3,5-di-*tert*-butyl-4-hydroxybenzyl)sulfanyl]acetato-κO}tin(IV)

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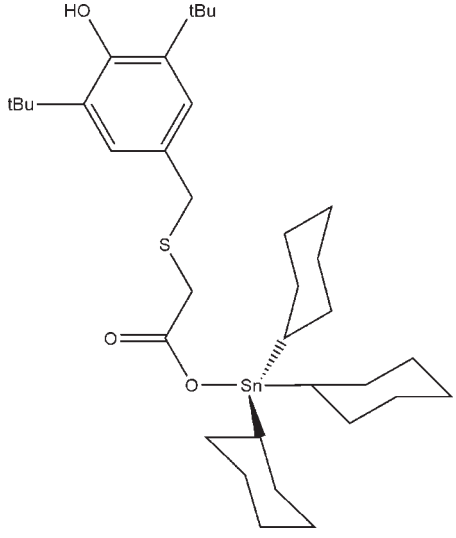
Key indicators: single-crystal X-ray study; T = 296 K; mean σ(C–C) = 0.007 Å; R factor = 0.050; wR factor = 0.117; data-to-parameter ratio = 22.0.

The title compound, $[Sn(C_6H_{11})_3(C_{17}H_{25}O_3S)]$, exists as a monomeric molecule with the Sn^{IV} atom in a distorted tetrahedral C_3O coordination geometry. The presence of two bulky *tert*-butyl groups on the carboxylate prevents any hydrogen-bonding interactions involving the hydroxy group.

Related literature

For tricyclohexyltin carboxylates, see: Tiekink (1991). For a triphenyltin analogue of the title compound, see: Lee *et al.* (2009). For other related structures, see: Alcock & Timms (1968); Keng *et al.* (2010); Ng & Kumar Das (1997); Thong *et al.* (2009); Zhang *et al.* (2007). For the preparation of the ligand, see: Yehye *et al.* (2009).



Experimental

Crystal data

$[Sn(C_6H_{11})_3(C_{17}H_{25}O_3S)]$
M_r = 677.56
Monoclinic, $P2_1/c$
a = 15.5048 (3) Å
b = 11.4261 (3) Å
c = 19.9794 (4) Å
β = 94.603 (2)°
V = 3528.12 (14) Å^3
Z = 4
Mo $K\alpha$ radiation
μ = 0.81 mm^{-1}
T = 296 K
0.23 × 0.16 × 0.12 mm

Data collection

Bruker APEXII CCD diffractometer
Absorption correction: multi-scan (*SADABS*; Bruker, 2001)
T_{min} = 0.835, T_{max} = 0.909
32619 measured reflections
8086 independent reflections
4695 reflections with $I > 2\sigma(I)$
R_{int} = 0.068

Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.050
$wR(F^2)$ = 0.117
S = 1.00
8086 reflections
368 parameters
H-atom parameters constrained
$\Delta\rho_{max}$ = 0.65 e Å^{-3}
$\Delta\rho_{min}$ = −0.37 e Å^{-3}

Table 1
Selected bond lengths (Å).

Sn1—O2	2.081 (3)	Sn1—C24	2.157 (5)
Sn1—C18	2.148 (4)	Sn1—C30	2.166 (4)

Data collection: *APEX2* (Bruker, 2007); cell refinement: *SAINT* (Bruker, 2007); data reduction: *SAINT*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *X-SEED* (Barbour, 2001); software used to prepare material for publication: *publCIF* (Westrip, 2010).

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Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: HY2317).

References

Alcock, N. W. & Timms, R. E. (1968). *J. Chem. Soc. A*, pp. 1876–1878.
Barbour, L. J. (2001). *J. Supramol. Chem.* **1**, 189–191.
Bruker (2001). *SADABS*. Bruker AXS Inc., Madison, Wisconsin, USA.
Bruker (2007). *APEX2* and *SAINT*. Bruker AXS Inc., Madison, Wisconsin, USA.
Keng, T. C., Lo, K. M. & Ng, S. W. (2010). *Acta Cryst.* E**66**, m307.
Lee, S. M., Lo, K. M., Mohd Ali, H. & Robinson, W. T. (2009). *Acta Cryst.* E**65**, m808.
Ng, S. W. & Kumar Das, V. G. (1997). *Acta Cryst.* C**53**, 548–549.
Sheldrick, G. M. (2008). *Acta Cryst.* A**64**, 112–122.
Thong, P. Y., Lo, K. M. & Ng, S. W. (2009). *Acta Cryst.* E**65**, m490.
Tiekink, E. R. T. (1991). *Appl. Org. Chem.* **5**, 1–23.
Westrip, S. P. (2010). *J. Appl. Cryst.* **43**. Submitted.
Yehye, W. A., Ariffin, A. & Ng, S. W. (2009). *Acta Cryst.* E**65**, o730.
Zhang, X., Song, H., Li, Q., Liu, X. & Tang, L. (2007). *Polyhedron*, **26**, 3743–3749.

supplementary materials

Acta Cryst. (2010). E**66**, m792 [**doi:10.1107/S1600536810021884**]

Tricyclohexyl{2-[(3,5-di-*tert*-butyl-4-hydroxybenzyl)sulfanyl]acetato-*κO*}tin(IV)

S. M. Lee, H. Mohd Ali and K. M. Lo

Comment

Triorganotin carboxylates are either monomeric or polymeric, depending primarily on the types of organic groups bonded to the tin atom. Triphenyltin carboxylates generally adopt a five-coordinated tin geometry with carboxylate bridges linking adjacent molecules into a polymeric chain, whereas tricyclohexyltin carboxylates have discrete four-coordinated tin structures (Tiekink, 1991).

The title compound is another example of a four-coordinated tricyclohexyltin carboxylate, in which the Sn^{IV} atom is in a distorted tetrahedral geometry. The close proximity of the carboxylate O3 towards the Sn atom [Sn1···O3 = 2.897 (3) Å] contributes to the distortion of the geometry (Alcock & Timms, 1968).

Experimental

The title compound was prepared by refluxing 2-(3,5-di-*tert*-4-hydroxybenzyl)sulfanylacetic acid (0.39 g, 1 mmol) with tricyclohexyltin hydroxide (0.39 g, 1 mmol) in absolute ethanol for 2 h. Colourless crystals were obtained by slow evaporation of the solution at room temperature.

Refinement

H atoms were placed at calculated positions and treated as riding on their parent atoms, with C—H = 0.93 (aromatic), 0.98 (CH), 0.97 (CH_2) and 0.96 (CH_3) Å and O—H = 0.82 Å and with U_{iso}(H) = 1.2(1.5 for methyl and hydroxyl)U_{eq}(C,O).

Figures

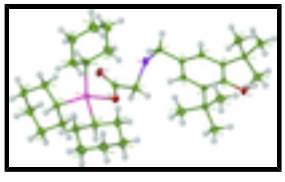


Fig. 1. The molecular structure of the title compound, showing the 30% probability displacement ellipsoids.

Tricyclohexyl{2-[(3,5-di-*tert*-butyl-4-hydroxybenzyl)sulfanyl]acetato- κ*O*}tin(IV)

Crystal data

$[Sn(C_6H_{11})_3(C_{17}H_{25}O_3S)]$	$F(000)$ = 1432
M_r = 677.56	D_x = 1.276 Mg m^{-3}
Monoclinic, $P2_1/c$	Mo $K\alpha$ radiation, λ = 0.71073 Å
Hall symbol: -P 2ybc	Cell parameters from 4134 reflections
a = 15.5048 (3) Å	θ = 2.2–20.5°

b = 11.4261 (3) Å	μ = 0.81 mm^{-1}
c = 19.9794 (4) Å	T = 296 K
β = 94.603 (2)°	Prism, colourless
V = 3528.12 (14) Å^3	0.23 × 0.16 × 0.12 mm
Z = 4	

Data collection

Bruker APEXII CCD diffractometer	8086 independent reflections
Radiation source: fine-focus sealed tube	4695 reflections with $I > 2\sigma(I)$
graphite	R_{int} = 0.068
φ and ω scans	θ_{max} = 27.5°, θ_{min} = 1.3°
Absorption correction: multi-scan (*SADABS*; Bruker, 2001)	h = −20→20
T_{min} = 0.835, T_{max} = 0.909	k = −14→14
32619 measured reflections	l = −25→25

Refinement

Refinement on F^2	Primary atom site location: structure-invariant direct methods
Least-squares matrix: full	Secondary atom site location: difference Fourier map
$R[F^2 > 2\sigma(F^2)]$ = 0.050	Hydrogen site location: inferred from neighbouring sites
$wR(F^2)$ = 0.117	H-atom parameters constrained
S = 1.00	$w = 1/[\sigma^2(F_o^2) + (0.0472P)^2 + 1.0822P]$ where $P = (F_o^2 + 2F_c^2)/3$
8086 reflections	$(\Delta/\sigma)_{max}$ = 0.002
368 parameters	$\Delta\rho_{max}$ = 0.65 e Å^{-3}
0 restraints	$\Delta\rho_{min}$ = −0.37 e Å^{-3}

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å^2)

	x	y	z	U_{iso}*/U_{eq}
Sn1	0.675022 (18)	0.68259 (2)	0.423505 (14)	0.05384 (11)
S1	0.91268 (8)	0.32747 (11)	0.47742 (6)	0.0688 (3)
O1	0.81458 (19)	0.1966 (3)	0.78627 (15)	0.0712 (9)
H1	0.8495	0.1485	0.8025	0.107*
O2	0.70824 (19)	0.5181 (3)	0.46211 (15)	0.0656 (8)
C1	0.7760 (3)	0.4750 (4)	0.4374 (2)	0.0571 (10)
O3	0.8166 (2)	0.5278 (3)	0.39778 (18)	0.0897 (11)
C2	0.7988 (3)	0.3518 (3)	0.4606 (2)	0.0570 (11)
H2A	0.7766	0.2970	0.4263	0.068*
H2B	0.7703	0.3355	0.5010	0.068*
C3	0.9325 (3)	0.4088 (4)	0.5546 (2)	0.0637 (12)
H3A	0.9943	0.4217	0.5628	0.076*
H3B	0.9050	0.4848	0.5491	0.076*

C4	0.9002 (3)	0.3496 (3)	0.6156 (2)	0.0512 (10)
C9	0.9478 (2)	0.2609 (4)	0.64754 (19)	0.0500 (9)
H9	0.9989	0.2374	0.6302	0.060*
C8	0.9223 (2)	0.2053 (3)	0.70464 (19)	0.0474 (9)
C7	0.8447 (3)	0.2435 (4)	0.72873 (19)	0.0503 (9)
C6	0.7929 (2)	0.3316 (3)	0.6972 (2)	0.0508 (10)
C5	0.8240 (3)	0.3836 (3)	0.6404 (2)	0.0527 (10)
H5	0.7920	0.4432	0.6187	0.063*
C10	0.7064 (3)	0.3702 (4)	0.7228 (2)	0.0593 (11)
C11	0.7205 (3)	0.4203 (4)	0.7944 (2)	0.0813 (15)
H11A	0.7474	0.3621	0.8238	0.122*
H11B	0.6658	0.4420	0.8099	0.122*
H11C	0.7572	0.4879	0.7940	0.122*
C13	0.6623 (3)	0.4652 (4)	0.6783 (3)	0.0890 (16)
H13A	0.7001	0.5315	0.6768	0.134*
H13B	0.6095	0.4886	0.6965	0.134*
H13C	0.6496	0.4351	0.6337	0.134*
C12	0.6446 (3)	0.2650 (5)	0.7238 (3)	0.0836 (15)
H12A	0.6377	0.2304	0.6799	0.125*
H12B	0.5893	0.2909	0.7366	0.125*
H12C	0.6681	0.2081	0.7556	0.125*
C14	0.9797 (3)	0.1098 (4)	0.7400 (2)	0.0549 (10)
C16	1.0166 (4)	0.1528 (5)	0.8085 (2)	0.0901 (16)
H16A	1.0515	0.0925	0.8303	0.135*
H16B	0.9700	0.1721	0.8355	0.135*
H16C	1.0514	0.2211	0.8030	0.135*
C15	0.9297 (3)	−0.0044 (4)	0.7481 (3)	0.0838 (15)
H15A	0.8964	−0.0224	0.7068	0.126*
H15B	0.8916	0.0045	0.7834	0.126*
H15C	0.9698	−0.0668	0.7592	0.126*
C17	1.0558 (3)	0.0774 (5)	0.6999 (3)	0.0928 (18)
H17A	1.0345	0.0500	0.6563	0.139*
H17B	1.0891	0.0167	0.7230	0.139*
H17C	1.0916	0.1449	0.6953	0.139*
C18	0.6470 (3)	0.6709 (4)	0.31668 (19)	0.0547 (10)
H18	0.6030	0.7304	0.3047	0.066*
C23	0.7229 (3)	0.6982 (4)	0.2761 (2)	0.0698 (12)
H23A	0.7700	0.6449	0.2891	0.084*
H23B	0.7428	0.7771	0.2863	0.084*
C22	0.6995 (4)	0.6874 (4)	0.2010 (2)	0.0835 (15)
H22A	0.6588	0.7488	0.1867	0.100*
H22B	0.7511	0.6980	0.1773	0.100*
C21	0.6598 (4)	0.5699 (5)	0.1829 (2)	0.0835 (15)
H21A	0.6426	0.5680	0.1351	0.100*
H21B	0.7027	0.5091	0.1925	0.100*
C20	0.5826 (3)	0.5459 (5)	0.2212 (2)	0.0797 (14)
H20A	0.5604	0.4684	0.2100	0.096*
H20B	0.5375	0.6023	0.2084	0.096*
C19	0.6063 (3)	0.5537 (4)	0.2967 (2)	0.0658 (12)

H19A	0.5547	0.5425	0.3203	0.079*
H19B	0.6466	0.4914	0.3101	0.079*
C30	0.5538 (3)	0.6957 (4)	0.4699 (2)	0.0628 (11)
H30	0.5175	0.6308	0.4523	0.075*
C35	0.5628 (3)	0.6826 (5)	0.5445 (2)	0.0833 (15)
H35A	0.6024	0.7418	0.5635	0.100*
H35B	0.5876	0.6066	0.5558	0.100*
C31	0.5065 (3)	0.8080 (4)	0.4489 (2)	0.0790 (14)
H31A	0.4963	0.8100	0.4004	0.095*
H31B	0.5423	0.8747	0.4628	0.095*
C24	0.7751 (3)	0.8051 (4)	0.4572 (3)	0.0741 (13)
H24	0.8144	0.8078	0.4212	0.089*
C25	0.7395 (4)	0.9250 (4)	0.4611 (3)	0.0963 (18)
H25A	0.6952	0.9252	0.4928	0.116*
H25B	0.7122	0.9464	0.4175	0.116*
C32	0.4200 (3)	0.8167 (6)	0.4804 (3)	0.104 (2)
H32A	0.3930	0.8910	0.4681	0.125*
H32B	0.3820	0.7549	0.4625	0.125*
C29	0.8294 (4)	0.7719 (5)	0.5180 (3)	0.1028 (19)
H29A	0.8588	0.6989	0.5099	0.123*
H29B	0.7928	0.7591	0.5545	0.123*
C28	0.8968 (4)	0.8659 (5)	0.5389 (4)	0.119 (2)
H28A	0.9251	0.8454	0.5823	0.142*
H28B	0.9405	0.8667	0.5067	0.142*
C27	0.8600 (4)	0.9832 (5)	0.5428 (3)	0.115 (2)
H27A	0.8249	0.9866	0.5808	0.138*
H27B	0.9066	1.0393	0.5506	0.138*
C26	0.8072 (4)	1.0163 (5)	0.4826 (4)	0.116 (2)
H26A	0.8444	1.0284	0.4465	0.139*
H26B	0.7785	1.0898	0.4906	0.139*
C33	0.4306 (3)	0.8070 (6)	0.5543 (3)	0.0961 (18)
H33A	0.3742	0.8091	0.5721	0.115*
H33B	0.4638	0.8731	0.5727	0.115*
C34	0.4763 (4)	0.6944 (5)	0.5756 (3)	0.0945 (17)
H34A	0.4396	0.6284	0.5620	0.113*
H34B	0.4862	0.6927	0.6242	0.113*

Atomic displacement parameters (Å^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Sn1	0.05522 (17)	0.05444 (18)	0.05190 (18)	0.00493 (15)	0.00459 (12)	−0.00436 (15)
S1	0.0727 (7)	0.0773 (8)	0.0591 (7)	0.0236 (7)	0.0228 (6)	0.0165 (6)
O1	0.0712 (19)	0.082 (2)	0.0642 (19)	0.0205 (16)	0.0254 (16)	0.0273 (16)
O2	0.0657 (18)	0.0605 (19)	0.072 (2)	0.0070 (15)	0.0132 (15)	−0.0017 (15)
C1	0.055 (3)	0.060 (3)	0.056 (3)	0.000 (2)	−0.005 (2)	0.002 (2)
O3	0.086 (2)	0.085 (2)	0.102 (3)	0.0218 (19)	0.031 (2)	0.043 (2)
C2	0.068 (3)	0.048 (2)	0.054 (3)	0.001 (2)	0.004 (2)	−0.0021 (19)
C3	0.056 (3)	0.071 (3)	0.064 (3)	−0.012 (2)	0.004 (2)	0.018 (2)

C4	0.054 (2)	0.047 (2)	0.052 (2)	−0.0078 (19)	0.0037 (19)	0.0063 (18)
C9	0.046 (2)	0.055 (2)	0.049 (2)	0.0007 (19)	0.0048 (18)	0.006 (2)
C8	0.048 (2)	0.048 (2)	0.046 (2)	−0.0017 (18)	−0.0007 (17)	0.0014 (18)
C7	0.053 (2)	0.051 (2)	0.047 (2)	0.000 (2)	0.0099 (18)	0.0037 (19)
C6	0.052 (2)	0.044 (2)	0.056 (2)	−0.0022 (19)	0.0043 (18)	0.0001 (19)
C5	0.057 (2)	0.043 (2)	0.056 (3)	0.001 (2)	−0.004 (2)	0.0075 (19)
C10	0.054 (2)	0.052 (2)	0.073 (3)	0.002 (2)	0.010 (2)	0.000 (2)
C11	0.072 (3)	0.089 (4)	0.085 (4)	0.006 (3)	0.021 (3)	−0.020 (3)
C13	0.070 (3)	0.080 (4)	0.117 (4)	0.025 (3)	0.009 (3)	0.019 (3)
C12	0.053 (3)	0.077 (3)	0.123 (4)	−0.007 (3)	0.015 (3)	−0.004 (3)
C14	0.054 (2)	0.057 (3)	0.054 (3)	0.007 (2)	0.0040 (19)	0.011 (2)
C16	0.104 (4)	0.099 (4)	0.063 (3)	0.010 (3)	−0.022 (3)	0.013 (3)
C15	0.088 (4)	0.059 (3)	0.104 (4)	0.008 (3)	0.004 (3)	0.017 (3)
C17	0.065 (3)	0.116 (5)	0.099 (4)	0.038 (3)	0.020 (3)	0.033 (3)
C18	0.058 (2)	0.056 (3)	0.050 (2)	0.009 (2)	0.0044 (18)	−0.003 (2)
C23	0.081 (3)	0.067 (3)	0.063 (3)	−0.007 (2)	0.009 (2)	0.001 (2)
C22	0.112 (4)	0.081 (4)	0.059 (3)	−0.007 (3)	0.016 (3)	0.011 (3)
C21	0.116 (4)	0.082 (4)	0.053 (3)	0.014 (3)	0.010 (3)	−0.007 (3)
C20	0.089 (4)	0.080 (3)	0.067 (3)	0.006 (3)	−0.012 (3)	−0.018 (3)
C19	0.064 (3)	0.072 (3)	0.062 (3)	−0.005 (2)	0.005 (2)	−0.002 (2)
C30	0.061 (3)	0.070 (3)	0.059 (3)	0.007 (2)	0.011 (2)	−0.005 (2)
C35	0.085 (3)	0.099 (4)	0.066 (3)	0.020 (3)	0.013 (3)	0.016 (3)
C31	0.068 (3)	0.096 (4)	0.073 (3)	0.020 (3)	0.010 (2)	0.010 (3)
C24	0.073 (3)	0.068 (3)	0.078 (3)	−0.001 (3)	−0.009 (2)	−0.008 (3)
C25	0.096 (4)	0.056 (3)	0.129 (5)	−0.008 (3)	−0.039 (3)	0.017 (3)
C32	0.073 (3)	0.136 (6)	0.105 (5)	0.034 (4)	0.017 (3)	−0.007 (4)
C29	0.110 (4)	0.062 (3)	0.127 (5)	0.010 (3)	−0.044 (4)	−0.002 (3)
C28	0.094 (4)	0.085 (4)	0.164 (6)	0.008 (4)	−0.066 (4)	−0.015 (4)
C27	0.133 (5)	0.082 (4)	0.121 (5)	−0.014 (4)	−0.036 (4)	−0.018 (4)
C26	0.113 (5)	0.060 (3)	0.164 (6)	−0.015 (3)	−0.045 (4)	0.011 (4)
C33	0.076 (3)	0.121 (5)	0.095 (4)	0.009 (3)	0.026 (3)	−0.023 (4)
C34	0.097 (4)	0.113 (5)	0.077 (4)	−0.015 (4)	0.037 (3)	0.002 (3)

Geometric parameters (Å, °)

Sn1—O2	2.081 (3)	C18—C19	1.520 (6)
Sn1—C18	2.148 (4)	C18—H18	0.9800
Sn1—C24	2.157 (5)	C23—C22	1.521 (6)
Sn1—C30	2.166 (4)	C23—H23A	0.9700
S1—C2	1.792 (4)	C23—H23B	0.9700
S1—C3	1.806 (5)	C22—C21	1.509 (6)
O1—C7	1.383 (4)	C22—H22A	0.9700
O1—H1	0.8200	C22—H22B	0.9700
O2—C1	1.294 (5)	C21—C20	1.497 (7)
C1—O3	1.211 (5)	C21—H21A	0.9700
C1—C2	1.515 (6)	C21—H21B	0.9700
C2—H2A	0.9700	C20—C19	1.526 (6)
C2—H2B	0.9700	C20—H20A	0.9700
C3—C4	1.514 (5)	C20—H20B	0.9700

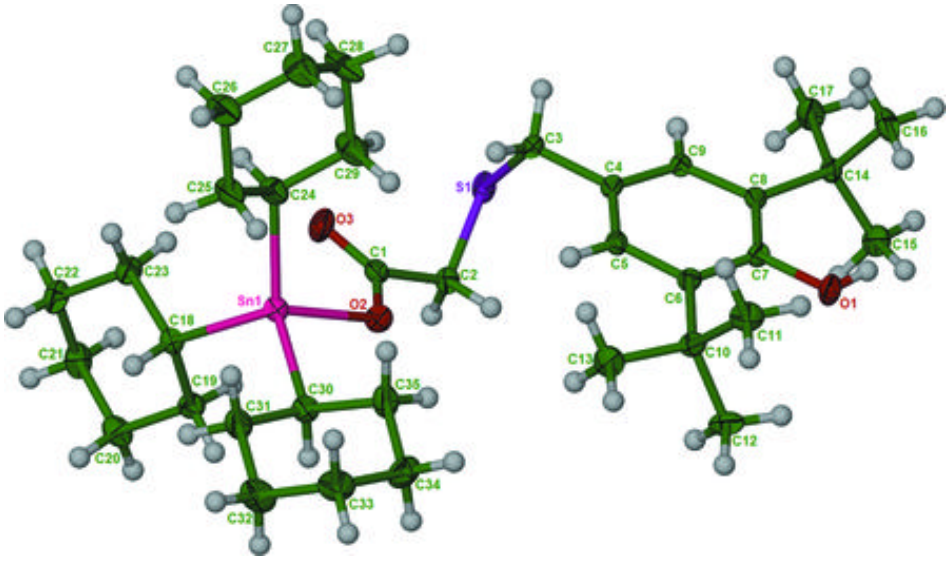
C3—H3A	0.9700	C19—H19A	0.9700
C3—H3B	0.9700	C19—H19B	0.9700
C4—C5	1.373 (5)	C30—C35	1.493 (6)
C4—C9	1.380 (5)	C30—C31	1.520 (6)
C9—C8	1.390 (5)	C30—H30	0.9800
C9—H9	0.9300	C35—C34	1.530 (7)
C8—C7	1.401 (5)	C35—H35A	0.9700
C8—C14	1.542 (5)	C35—H35B	0.9700
C7—C6	1.405 (5)	C31—C32	1.529 (6)
C6—C5	1.400 (5)	C31—H31A	0.9700
C6—C10	1.538 (5)	C31—H31B	0.9700
C5—H5	0.9300	C24—C29	1.471 (7)
C10—C13	1.529 (6)	C24—C25	1.481 (6)
C10—C12	1.538 (6)	C24—H24	0.9800
C10—C11	1.540 (6)	C25—C26	1.517 (7)
C11—H11A	0.9600	C25—H25A	0.9700
C11—H11B	0.9600	C25—H25B	0.9700
C11—H11C	0.9600	C32—C33	1.478 (7)
C13—H13A	0.9600	C32—H32A	0.9700
C13—H13B	0.9600	C32—H32B	0.9700
C13—H13C	0.9600	C29—C28	1.533 (8)
C12—H12A	0.9600	C29—H29A	0.9700
C12—H12B	0.9600	C29—H29B	0.9700
C12—H12C	0.9600	C28—C27	1.461 (8)
C14—C16	1.521 (6)	C28—H28A	0.9700
C14—C17	1.524 (6)	C28—H28B	0.9700
C14—C15	1.533 (6)	C27—C26	1.449 (7)
C16—H16A	0.9600	C27—H27A	0.9700
C16—H16B	0.9600	C27—H27B	0.9700
C16—H16C	0.9600	C26—H26A	0.9700
C15—H15A	0.9600	C26—H26B	0.9700
C15—H15B	0.9600	C33—C34	1.513 (7)
C15—H15C	0.9600	C33—H33A	0.9700
C17—H17A	0.9600	C33—H33B	0.9700
C17—H17B	0.9600	C34—H34A	0.9700
C17—H17C	0.9600	C34—H34B	0.9700
C18—C23	1.513 (6)		
O2—Sn1—C18	109.65 (13)	C18—C23—H23B	109.2
O2—Sn1—C24	108.65 (15)	C22—C23—H23B	109.2
C18—Sn1—C24	115.72 (18)	H23A—C23—H23B	107.9
O2—Sn1—C30	95.82 (14)	C21—C22—C23	111.7 (4)
C18—Sn1—C30	108.43 (16)	C21—C22—H22A	109.3
C24—Sn1—C30	116.65 (18)	C23—C22—H22A	109.3
C2—S1—C3	100.3 (2)	C21—C22—H22B	109.3
C7—O1—H1	109.5	C23—C22—H22B	109.3
C1—O2—Sn1	112.7 (3)	H22A—C22—H22B	107.9
O3—C1—O2	122.7 (4)	C20—C21—C22	111.5 (4)
O3—C1—C2	122.8 (4)	C20—C21—H21A	109.3
O2—C1—C2	114.4 (4)	C22—C21—H21A	109.3

C1—C2—S1	113.8 (3)	C20—C21—H21B	109.3
C1—C2—H2A	108.8	C22—C21—H21B	109.3
S1—C2—H2A	108.8	H21A—C21—H21B	108.0
C1—C2—H2B	108.8	C21—C20—C19	110.8 (4)
S1—C2—H2B	108.8	C21—C20—H20A	109.5
H2A—C2—H2B	107.7	C19—C20—H20A	109.5
C4—C3—S1	114.4 (3)	C21—C20—H20B	109.5
C4—C3—H3A	108.7	C19—C20—H20B	109.5
S1—C3—H3A	108.7	H20A—C20—H20B	108.1
C4—C3—H3B	108.7	C18—C19—C20	111.9 (4)
S1—C3—H3B	108.7	C18—C19—H19A	109.2
H3A—C3—H3B	107.6	C20—C19—H19A	109.2
C5—C4—C9	119.0 (4)	C18—C19—H19B	109.2
C5—C4—C3	121.0 (4)	C20—C19—H19B	109.2
C9—C4—C3	120.1 (4)	H19A—C19—H19B	107.9
C4—C9—C8	122.6 (4)	C35—C30—C31	111.3 (4)
C4—C9—H9	118.7	C35—C30—Sn1	113.9 (3)
C8—C9—H9	118.7	C31—C30—Sn1	110.9 (3)
C9—C8—C7	116.6 (3)	C35—C30—H30	106.7
C9—C8—C14	120.5 (3)	C31—C30—H30	106.7
C7—C8—C14	122.9 (3)	Sn1—C30—H30	106.7
O1—C7—C8	121.4 (3)	C30—C35—C34	112.5 (4)
O1—C7—C6	115.6 (3)	C30—C35—H35A	109.1
C8—C7—C6	123.0 (3)	C34—C35—H35A	109.1
C5—C6—C7	116.4 (3)	C30—C35—H35B	109.1
C5—C6—C10	120.9 (4)	C34—C35—H35B	109.1
C7—C6—C10	122.6 (3)	H35A—C35—H35B	107.8
C4—C5—C6	122.4 (4)	C30—C31—C32	111.2 (4)
C4—C5—H5	118.8	C30—C31—H31A	109.4
C6—C5—H5	118.8	C32—C31—H31A	109.4
C13—C10—C6	111.8 (4)	C30—C31—H31B	109.4
C13—C10—C12	108.2 (4)	C32—C31—H31B	109.4
C6—C10—C12	110.0 (4)	H31A—C31—H31B	108.0
C13—C10—C11	107.4 (4)	C29—C24—C25	112.7 (4)
C6—C10—C11	110.6 (3)	C29—C24—Sn1	116.1 (4)
C12—C10—C11	108.7 (4)	C25—C24—Sn1	110.8 (3)
C10—C11—H11A	109.5	C29—C24—H24	105.4
C10—C11—H11B	109.5	C25—C24—H24	105.4
H11A—C11—H11B	109.5	Sn1—C24—H24	105.4
C10—C11—H11C	109.5	C24—C25—C26	113.5 (5)
H11A—C11—H11C	109.5	C24—C25—H25A	108.9
H11B—C11—H11C	109.5	C26—C25—H25A	108.9
C10—C13—H13A	109.5	C24—C25—H25B	108.9
C10—C13—H13B	109.5	C26—C25—H25B	108.9
H13A—C13—H13B	109.5	H25A—C25—H25B	107.7
C10—C13—H13C	109.5	C33—C32—C31	112.1 (5)
H13A—C13—H13C	109.5	C33—C32—H32A	109.2
H13B—C13—H13C	109.5	C31—C32—H32A	109.2
C10—C12—H12A	109.5	C33—C32—H32B	109.2

C10—C12—H12B	109.5	C31—C32—H32B	109.2
H12A—C12—H12B	109.5	H32A—C32—H32B	107.9
C10—C12—H12C	109.5	C24—C29—C28	112.1 (5)
H12A—C12—H12C	109.5	C24—C29—H29A	109.2
H12B—C12—H12C	109.5	C28—C29—H29A	109.2
C16—C14—C17	107.5 (4)	C24—C29—H29B	109.2
C16—C14—C15	109.7 (4)	C28—C29—H29B	109.2
C17—C14—C15	105.5 (4)	H29A—C29—H29B	107.9
C16—C14—C8	110.2 (4)	C27—C28—C29	113.4 (5)
C17—C14—C8	111.9 (3)	C27—C28—H28A	108.9
C15—C14—C8	111.9 (3)	C29—C28—H28A	108.9
C14—C16—H16A	109.5	C27—C28—H28B	108.9
C14—C16—H16B	109.5	C29—C28—H28B	108.9
H16A—C16—H16B	109.5	H28A—C28—H28B	107.7
C14—C16—H16C	109.5	C26—C27—C28	113.0 (5)
H16A—C16—H16C	109.5	C26—C27—H27A	109.0
H16B—C16—H16C	109.5	C28—C27—H27A	109.0
C14—C15—H15A	109.5	C26—C27—H27B	109.0
C14—C15—H15B	109.5	C28—C27—H27B	109.0
H15A—C15—H15B	109.5	H27A—C27—H27B	107.8
C14—C15—H15C	109.5	C27—C26—C25	112.8 (5)
H15A—C15—H15C	109.5	C27—C26—H26A	109.0
H15B—C15—H15C	109.5	C25—C26—H26A	109.0
C14—C17—H17A	109.5	C27—C26—H26B	109.0
C14—C17—H17B	109.5	C25—C26—H26B	109.0
H17A—C17—H17B	109.5	H26A—C26—H26B	107.8
C14—C17—H17C	109.5	C32—C33—C34	110.9 (5)
H17A—C17—H17C	109.5	C32—C33—H33A	109.5
H17B—C17—H17C	109.5	C34—C33—H33A	109.5
C23—C18—C19	111.4 (3)	C32—C33—H33B	109.5
C23—C18—Sn1	114.5 (3)	C34—C33—H33B	109.5
C19—C18—Sn1	111.3 (3)	H33A—C33—H33B	108.1
C23—C18—H18	106.4	C33—C34—C35	111.5 (4)
C19—C18—H18	106.4	C33—C34—H34A	109.3
Sn1—C18—H18	106.4	C35—C34—H34A	109.3
C18—C23—C22	112.2 (4)	C33—C34—H34B	109.3
C18—C23—H23A	109.2	C35—C34—H34B	109.3
C22—C23—H23A	109.2	H34A—C34—H34B	108.0
C18—Sn1—O2—C1	60.5 (3)	C30—Sn1—C18—C23	162.2 (3)
C24—Sn1—O2—C1	−66.9 (3)	O2—Sn1—C18—C19	33.1 (3)
C30—Sn1—O2—C1	172.5 (3)	C24—Sn1—C18—C19	156.4 (3)
Sn1—O2—C1—O3	2.4 (5)	C30—Sn1—C18—C19	−70.4 (3)
Sn1—O2—C1—C2	−176.0 (3)	C19—C18—C23—C22	52.1 (5)
O3—C1—C2—S1	41.6 (6)	Sn1—C18—C23—C22	179.5 (3)
O2—C1—C2—S1	−140.0 (3)	C18—C23—C22—C21	−53.4 (6)
C3—S1—C2—C1	72.6 (3)	C23—C22—C21—C20	55.6 (6)
C2—S1—C3—C4	74.6 (3)	C22—C21—C20—C19	−56.4 (6)
S1—C3—C4—C5	−101.0 (4)	C23—C18—C19—C20	−53.3 (5)
S1—C3—C4—C9	79.7 (4)	Sn1—C18—C19—C20	177.6 (3)

C5—C4—C9—C8	−0.9 (6)	C21—C20—C19—C18	55.5 (5)
C3—C4—C9—C8	178.4 (4)	O2—Sn1—C30—C35	56.5 (4)
C4—C9—C8—C7	0.2 (6)	C18—Sn1—C30—C35	169.5 (3)
C4—C9—C8—C14	−177.6 (4)	C24—Sn1—C30—C35	−57.8 (4)
C9—C8—C7—O1	−178.1 (4)	O2—Sn1—C30—C31	−176.9 (3)
C14—C8—C7—O1	−0.3 (6)	C18—Sn1—C30—C31	−64.0 (3)
C9—C8—C7—C6	1.3 (6)	C24—Sn1—C30—C31	68.8 (4)
C14—C8—C7—C6	179.0 (4)	C31—C30—C35—C34	52.7 (6)
O1—C7—C6—C5	177.5 (4)	Sn1—C30—C35—C34	179.1 (4)
C8—C7—C6—C5	−1.9 (6)	C35—C30—C31—C32	−53.2 (6)
O1—C7—C6—C10	−2.6 (6)	Sn1—C30—C31—C32	178.9 (4)
C8—C7—C6—C10	178.0 (4)	O2—Sn1—C24—C29	−22.1 (5)
C9—C4—C5—C6	0.2 (6)	C18—Sn1—C24—C29	−145.9 (4)
C3—C4—C5—C6	−179.2 (4)	C30—Sn1—C24—C29	84.7 (4)
C7—C6—C5—C4	1.2 (6)	O2—Sn1—C24—C25	−152.3 (4)
C10—C6—C5—C4	−178.7 (4)	C18—Sn1—C24—C25	83.9 (4)
C5—C6—C10—C13	1.4 (6)	C30—Sn1—C24—C25	−45.5 (4)
C7—C6—C10—C13	−178.6 (4)	C29—C24—C25—C26	49.7 (7)
C5—C6—C10—C12	121.6 (4)	Sn1—C24—C25—C26	−178.3 (4)
C7—C6—C10—C12	−58.3 (5)	C30—C31—C32—C33	55.7 (7)
C5—C6—C10—C11	−118.3 (4)	C25—C24—C29—C28	−49.2 (7)
C7—C6—C10—C11	61.7 (5)	Sn1—C24—C29—C28	−178.5 (4)
C9—C8—C14—C16	112.1 (4)	C24—C29—C28—C27	50.5 (8)
C7—C8—C14—C16	−65.6 (5)	C29—C28—C27—C26	−51.6 (9)
C9—C8—C14—C17	−7.5 (6)	C28—C27—C26—C25	51.1 (9)
C7—C8—C14—C17	174.8 (4)	C24—C25—C26—C27	−50.4 (8)
C9—C8—C14—C15	−125.6 (4)	C31—C32—C33—C34	−56.3 (7)
C7—C8—C14—C15	56.7 (5)	C32—C33—C34—C35	54.8 (7)
O2—Sn1—C18—C23	−94.4 (3)	C30—C35—C34—C33	−53.6 (6)
C24—Sn1—C18—C23	28.9 (4)		

Fig. 1


C27
C28
C26
C29
C25
C24
O3
C1
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S1
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C9
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C14
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C22
C23
Sn1
O2
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C32

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Hexaaquamanganese(II) 4,4′-(1,2-dihydroxyethane-1,2-diyl)dibenzoate monohydrate

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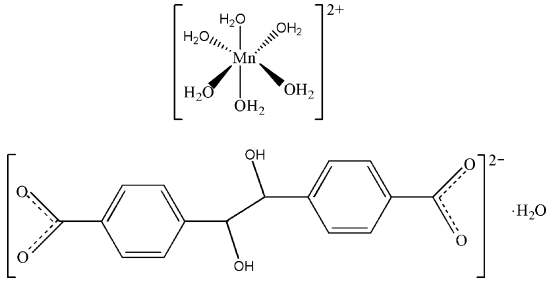
Key indicators: single-crystal X-ray study; T = 298 K; mean σ(C–C) = 0.006 Å; R factor = 0.057; wR factor = 0.140; data-to-parameter ratio = 13.4.

In the title compound, $[Mn(H_2O)_6](C_{16}H_{12}O_6)\cdot H_2O$, the $[Mn(H_2O)_6]^{2+}$ complex cation lies on a mirror plane, the 4,4′-(1,2-dihydroxyethane-1,2-diyl)dibenzoate anion is located on an inversion center and the solvent water molecule also lies on a mirror plane. Extensive O—H···O hydrogen-bonding interactions between the cations, anions and water molecules stabilize the three-dimensional network.

Related literature

For the intriguing architectures and potential applications of polymeric coordination networks, see: Carlucci *et al.* (2003); Rosi *et al.* (2003).



Experimental

Crystal data

$[Mn(H_2O)_6](C_{16}H_{12}O_6)\cdot H_2O$
M_r = 481.31
Monoclinic, $P2_1/m$
a = 6.0803 (6) Å
b = 20.643 (2) Å
c = 8.6610 (9) Å
β = 104.420 (1)°
V = 1052.84 (19) Å^3
Z = 2
Mo $K\alpha$ radiation
μ = 0.69 mm^{-1}
T = 298 K
0.42 × 0.21 × 0.18 mm

Data collection

Bruker SMART 1000 CCD diffractometer
Absorption correction: multi-scan (*SADABS*; Bruker, 2001)
T_{min} = 0.760, T_{max} = 0.886
5275 measured reflections
1899 independent reflections
1647 reflections with $I > 2\sigma(I)$
R_{int} = 0.024

Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.057
$wR(F^2)$ = 0.140
S = 1.23
1899 reflections
142 parameters
H-atom parameters constrained
$\Delta\rho_{max}$ = 0.84 e Å^{-3}
$\Delta\rho_{min}$ = −0.33 e Å^{-3}

Table 1
Hydrogen-bond geometry (Å, °).

D—H···A	D—H	H···A	D···A	D—H···A
O3—H3···O1^{i}	0.82	2.02	2.830 (5)	172
O4—H4*C*···O1^{ii}	0.85	1.86	2.712 (4)	177
O5—H5*C*···O4^{iii}	0.85	1.93	2.777 (6)	175
O5—H5*D*···O8^{iii}	0.85	1.88	2.728 (7)	175
O6—H6*C*···O3^{iv}	0.85	1.99	2.840 (5)	178
O6—H6*D*···O8	0.85	2.19	3.040 (6)	178
O7—H7*C*···O1^{v}	0.85	1.95	2.799 (5)	180
O7—H7*D*···O2^{ii}	0.85	1.82	2.673 (4)	180
O8—H8*C*···O2^{vi}	0.85	1.92	2.767 (5)	172

Symmetry codes: (i) $-x+2, -y+1, -z+2$; (ii) $x-1, y, z-1$; (iii) $x+1, y, z$; (iv) $-x+1, -y+1, -z+1$; (v) $x, y, z-1$; (vi) $x-1, y, z$.

Data collection: *SMART* (Bruker, 2007); cell refinement: *SAINT* (Bruker, 2007); data reduction: *SAINT*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *SHELXTL* (Sheldrick, 2008); software used to prepare material for publication: *SHELXTL*.

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Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: HY2318).

References

Bruker (2001). *SADABS*. Bruker AXS Inc., Madison, Wisconsin, USA.
Bruker (2007). *SMART* and *SAINT*. Bruker AXS Inc., Madison, Wisconsin, USA.
Carlucci, L., Ciani, G. & Proserpio, D. M. (2003). *Coord. Chem. Rev.* **246**, 247–289.
Rosi, N. L., Eckert, J., Eddaoudi, M., Vodak, D. T., Kim, J., O'Keeffe, M. & Yaghi, O. M. (2003). *Science*, **300**, 1127–1129.
Sheldrick, G. M. (2008). *Acta Cryst.* A**64**, 112–122.

supplementary materials

Acta Cryst. (2010). E**66**, m809 [**doi:10.1107/S1600536810022300**]

Hexaaquamanganese(II) 4,4'-(1,2-dihydroxyethane-1,2-diyl)dibenzoate monohydrate

C.-J. Hao and Y.-L. Cao

Comment

Current interest in polymeric coordination networks is rapidly expanding for their intriguing architectures (Carlucci *et al.*, 2003) and potential applications (Rosi *et al.*, 2003). We have reacted 1,2-bis(4-carboxyphenyl)-1,2-ethanediol with $MnCl_2$ under hydrothermal conditions to obtain the title compound and its structure is reported here.

As illustrated in Fig. 1, the title compound contains one $[Mn(H_2O)_6]^{2+}$ complex cation lying on a mirror plan, one 1,2-dihydroxyethane-1,2-bis(4-benzenecarboxylate) anion located on an inversion center and one solvent water molecule lying on a mirror plan. The carboxylate group lies in the plane of the benzene ring as indicated by the O1—C1—C2—C3 and O2—C1—C2—C7 torsion angles of -3.0 (6) and -1.2 (6)°. The benzene ring is nearly planar with maximum deviations from the mean plane being -0.003 (6) Å for C6. The cation, anion and solvent water molecule interact via O—H···O hydrogen bonds, consolidating the three-dimensional network (Fig. 2, Table 1).

Experimental

A mixture of $MnCl_2$ (0.1 mmol, 0.013 g), 1,2-bis(4-carboxyphenyl)-1,2-ethanediol (0.1 mmol, 0.03 g) and 10 ml of H_2O was sealed in a 20 ml Telflon-lined stainless steel vessel and heated at 303 K for 2 d. Colorless crystals were obtained when the solution was cooled to room temperature slowly.

Refinement

H atoms bound to C atoms were placed at calculated positions and were treated as riding on the parent atoms, with C—H = 0.93 (aromatic) and 0.98 (CH) Å and with U_{iso}(H) = 1.2U_{eq}(C). H atoms of hydroxyl group and water molecules were located in a difference Fourier map and refined as riding, with O—H = 0.85 Å and U_{iso}(H) = 1.2(1.5 for hydroxyl)U_{eq}(O).

Figures

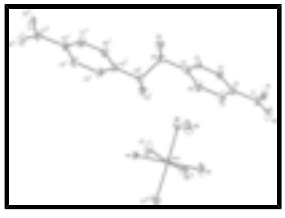


Fig. 1. Molecular structure of the title compound. Displacement ellipsoids are shown at the 30% probability level. H atoms and water molecule are omitted for clarity. [Symmetry codes: (i) 1-x, 1-y, 1-z; (ii) x, 3/2-y, z.]

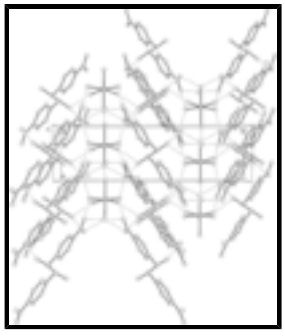


Fig. 2. View of the three-dimensional network constructed by O—H···O hydrogen bonds (dashed lines). H atoms are omitted for clarity.

Hexaaquamanganese(II) 4,4'-(1,2-dihydroxyethane-1,2-diyl)dibenzoate monohydrate

Crystal data

$[Mn(H_2O)_6](C_{16}H_{12}O_6)\cdot H_2O$	$F(000) = 502$
$M_r = 481.31$	$D_x = 1.518$ Mg m^{-3}
Monoclinic, $P2_1/m$	Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å
Hall symbol: -P 2yb	Cell parameters from 2215 reflections
$a = 6.0803$ (6) Å	$\theta = 2.5$–$24.0°$
$b = 20.643$ (2) Å	$\mu = 0.69$ mm^{-1}
$c = 8.6610$ (9) Å	$T = 298$ K
$\beta = 104.420$ (1)°	Block, colorless
$V = 1052.84$ (19) Å^3	0.42 × 0.21 × 0.18 mm
$Z = 2$	

Data collection

Bruker SMART 1000 CCD diffractometer	1899 independent reflections
Radiation source: fine-focus sealed tube	1647 reflections with $I > 2\sigma(I)$
graphite	$R_{int} = 0.024$
φ and ω scans	$\theta_{max} = 25.0°$, $\theta_{min} = 2.0°$
Absorption correction: multi-scan (*SADABS*; Bruker, 2001)	$h = -7\rightarrow6$
$T_{min} = 0.760$, $T_{max} = 0.886$	$k = -24\rightarrow22$
5275 measured reflections	$l = -10\rightarrow9$

Refinement

Refinement on F^2	Primary atom site location: structure-invariant direct methods
Least-squares matrix: full	Secondary atom site location: difference Fourier map
$R[F^2 > 2\sigma(F^2)] = 0.057$	Hydrogen site location: inferred from neighbouring sites
$wR(F^2) = 0.140$	H-atom parameters constrained
$S = 1.23$	$w = 1/[\sigma^2(F_o^2) + (0.0292P)^2 + 3.0592P]$ where $P = (F_o^2 + 2F_c^2)/3$

1899 reflections	$(\Delta/\sigma)_{max} < 0.001$
142 parameters	$\Delta\rho_{max} = 0.84$ e Å^{-3}
0 restraints	$\Delta\rho_{min} = -0.33$ e Å^{-3}

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å^2)

	x	*y*	*z*	U_{iso}*/U_{eq}
Mn1	0.65486 (15)	0.7500	0.46088 (10)	0.0289 (3)
O1	1.0818 (5)	0.64065 (16)	1.2067 (4)	0.0444 (8)
O2	1.3265 (5)	0.64967 (19)	1.0567 (4)	0.0567 (10)
O3	0.6710 (6)	0.42818 (15)	0.5229 (4)	0.0472 (9)
H3	0.7538	0.4103	0.6004	0.071*
O4	0.2836 (6)	0.7500	0.3483 (5)	0.0296 (9)
H4C	0.2168	0.7166	0.3015	0.036*
O5	1.0130 (7)	0.7500	0.5635 (5)	0.0533 (14)
H5C	1.0885	0.7500	0.4931	0.064*
H5D	1.1062	0.7500	0.6548	0.064*
O6	0.5811 (6)	0.67978 (16)	0.6304 (4)	0.0477 (8)
H6C	0.5029	0.6476	0.5861	0.057*
H6D	0.5095	0.6985	0.6904	0.057*
O7	0.6863 (5)	0.67266 (18)	0.2996 (4)	0.0548 (10)
H7C	0.8061	0.6629	0.2710	0.066*
H7D	0.5724	0.6653	0.2220	0.066*
O8	0.3346 (10)	0.7500	0.8464 (6)	0.090 (2)
H8C	0.3323	0.7167	0.9035	0.109*
C1	1.1422 (7)	0.6306 (2)	1.0792 (5)	0.0377 (11)
C2	0.9858 (7)	0.5932 (2)	0.9471 (5)	0.0321 (10)
C3	0.7845 (7)	0.5675 (2)	0.9661 (5)	0.0364 (10)
H3A	0.7415	0.5747	1.0605	0.044*
C4	0.6454 (7)	0.5311 (2)	0.8455 (5)	0.0371 (10)
H4	0.5098	0.5144	0.8597	0.045*
C5	0.7062 (7)	0.5195 (2)	0.7053 (5)	0.0335 (10)
C6	0.9078 (8)	0.5454 (2)	0.6850 (5)	0.0398 (11)
H6	0.9505	0.5381	0.5906	0.048*
C7	1.0457 (7)	0.5820 (2)	0.8053 (5)	0.0387 (11)
H7	1.1802	0.5993	0.7905	0.046*
C8	0.5518 (8)	0.4795 (2)	0.5750 (5)	0.0365 (10)
H8	0.4286	0.4613	0.6160	0.044*

Atomic displacement parameters (Å^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Mn1	0.0245 (5)	0.0337 (5)	0.0272 (5)	0.000	0.0039 (4)	0.000
O1	0.0364 (17)	0.051 (2)	0.0399 (18)	0.0007 (15)	−0.0016 (14)	−0.0157 (15)
O2	0.0333 (19)	0.078 (3)	0.052 (2)	−0.0144 (18)	−0.0013 (15)	−0.0261 (19)
O3	0.053 (2)	0.0349 (18)	0.0454 (19)	0.0047 (15)	−0.0045 (15)	−0.0064 (15)
O4	0.026 (2)	0.029 (2)	0.031 (2)	0.000	0.0003 (16)	0.000
O5	0.025 (2)	0.100 (4)	0.032 (2)	0.000	0.0016 (19)	0.000

O6	0.058 (2)	0.0403 (19)	0.0434 (19)	−0.0019 (16)	0.0097 (16)	0.0080 (15)
O7	0.0285 (17)	0.078 (3)	0.053 (2)	0.0039 (17)	0.0007 (15)	−0.0328 (19)
O8	0.065 (4)	0.169 (7)	0.037 (3)	0.000	0.012 (3)	0.000
C1	0.030 (2)	0.037 (3)	0.038 (3)	0.009 (2)	−0.0053 (19)	−0.011 (2)
C2	0.028 (2)	0.029 (2)	0.032 (2)	0.0044 (18)	−0.0058 (18)	−0.0058 (18)
C3	0.037 (2)	0.037 (2)	0.032 (2)	−0.001 (2)	0.0018 (18)	−0.0065 (19)
C4	0.033 (2)	0.036 (2)	0.038 (2)	−0.0057 (19)	−0.0007 (19)	−0.003 (2)
C5	0.030 (2)	0.028 (2)	0.035 (2)	0.0017 (18)	−0.0063 (18)	−0.0048 (18)
C6	0.038 (3)	0.044 (3)	0.034 (2)	0.002 (2)	0.0021 (19)	−0.012 (2)
C7	0.027 (2)	0.045 (3)	0.041 (3)	−0.001 (2)	0.0030 (19)	−0.012 (2)
C8	0.037 (2)	0.033 (2)	0.032 (2)	0.001 (2)	−0.0043 (19)	−0.0060 (19)

Geometric parameters (Å, °)

Mn1—O5	2.137 (4)	O7—H7D	0.8500
Mn1—O7	2.161 (3)	O8—H8C	0.8500
Mn1—O7^{i}	2.161 (3)	C1—C2	1.506 (6)
Mn1—O6^{i}	2.187 (3)	C2—C3	1.381 (6)
Mn1—O6	2.187 (3)	C2—C7	1.384 (6)
Mn1—O4	2.225 (4)	C3—C4	1.390 (6)
O1—C1	1.265 (5)	C3—H3A	0.9300
O2—C1	1.248 (6)	C4—C5	1.375 (6)
O3—C8	1.419 (5)	C4—H4	0.9300
O3—H3	0.8200	C5—C6	1.387 (6)
O4—H4C	0.8500	C5—C8	1.520 (6)
O5—H5C	0.8500	C6—C7	1.388 (6)
O5—H5D	0.8500	C6—H6	0.9300
O6—H6C	0.8500	C7—H7	0.9300
O6—H6D	0.8500	C8—C8^{ii}	1.548 (8)
O7—H7C	0.8500	C8—H8	0.9800
O5—Mn1—O7	91.37 (12)	O2—C1—C2	117.7 (4)
O5—Mn1—O7^{i}	91.37 (12)	O1—C1—C2	118.8 (4)
O7—Mn1—O7^{i}	95.3 (2)	C3—C2—C7	118.6 (4)
O5—Mn1—O6^{i}	94.52 (13)	C3—C2—C1	121.1 (4)
O7—Mn1—O6^{i}	171.61 (14)	C7—C2—C1	120.2 (4)
O7^{i}—Mn1—O6^{i}	90.57 (14)	C2—C3—C4	120.6 (4)
O5—Mn1—O6	94.52 (13)	C2—C3—H3A	119.7
O7—Mn1—O6	90.57 (14)	C4—C3—H3A	119.7
O7^{i}—Mn1—O6	171.61 (14)	C5—C4—C3	120.7 (4)
O6^{i}—Mn1—O6	83.01 (19)	C5—C4—H4	119.6
O5—Mn1—O4	178.63 (17)	C3—C4—H4	119.6
O7—Mn1—O4	87.71 (11)	C4—C5—C6	119.0 (4)
O7^{i}—Mn1—O4	87.71 (11)	C4—C5—C8	119.9 (4)
O6^{i}—Mn1—O4	86.50 (12)	C6—C5—C8	121.1 (4)
O6—Mn1—O4	86.50 (12)	C5—C6—C7	120.1 (4)
C8—O3—H3	109.5	C5—C6—H6	119.9

Mn1—O4—H4C	121.4	C7—C6—H6	119.9
Mn1—O5—H5C	112.2	C2—C7—C6	120.9 (4)
Mn1—O5—H5D	139.5	C2—C7—H7	119.5
H5C—O5—H5D	108.3	C6—C7—H7	119.5
Mn1—O6—H6C	113.5	O3—C8—C5	111.9 (3)
Mn1—O6—H6D	109.4	O3—C8—C8^{ii}	105.9 (4)
H6C—O6—H6D	108.4	C5—C8—C8^{ii}	111.9 (4)
Mn1—O7—H7C	125.7	O3—C8—H8	109.0
Mn1—O7—H7D	117.3	C5—C8—H8	109.0
H7C—O7—H7D	108.4	C8^{ii}—C8—H8	109.0
O2—C1—O1	123.5 (4)		
O2—C1—C2—C3	176.5 (4)	C4—C5—C6—C7	0.3 (7)
O1—C1—C2—C3	−3.0 (6)	C8—C5—C6—C7	179.7 (4)
O2—C1—C2—C7	−1.2 (6)	C3—C2—C7—C6	−0.5 (7)
O1—C1—C2—C7	179.3 (4)	C1—C2—C7—C6	177.3 (4)
C7—C2—C3—C4	0.1 (7)	C5—C6—C7—C2	0.3 (7)
C1—C2—C3—C4	−177.6 (4)	C4—C5—C8—O3	−128.0 (4)
C2—C3—C4—C5	0.5 (7)	C6—C5—C8—O3	52.5 (6)
C3—C4—C5—C6	−0.7 (7)	C4—C5—C8—C8^{ii}	113.3 (6)
C3—C4—C5—C8	179.9 (4)	C6—C5—C8—C8^{ii}	−66.1 (6)

Symmetry codes: (i) *x*, −*y*+3/2, *z*; (ii) −*x*+1, −*y*+1, −*z*+1.

Hydrogen-bond geometry (Å, °)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
O3—H3···O1^{iii}	0.82	2.02	2.830 (5)	172.
O4—H4C···O1^{iv}	0.85	1.86	2.712 (4)	177.
O5—H5C···O4^{v}	0.85	1.93	2.777 (6)	175.
O5—H5D···O8^{v}	0.85	1.88	2.728 (7)	175.
O6—H6C···O3^{ii}	0.85	1.99	2.840 (5)	178.
O6—H6D···O8	0.85	2.19	3.040 (6)	178.
O7—H7C···O1^{vi}	0.85	1.95	2.799 (5)	180.
O7—H7D···O2^{iv}	0.85	1.82	2.673 (4)	180.
O8—H8C···O2^{vii}	0.85	1.92	2.767 (5)	172.

Symmetry codes: (iii) −*x*+2, −*y*+1, −*z*+2; (iv) *x*−1, *y*, *z*−1; (v) *x*+1, *y*, *z*; (ii) −*x*+1, −*y*+1, −*z*+1; (vi) *x*, *y*, *z*−1; (vii) *x*−1, *y*, *z*.

Fig. 1

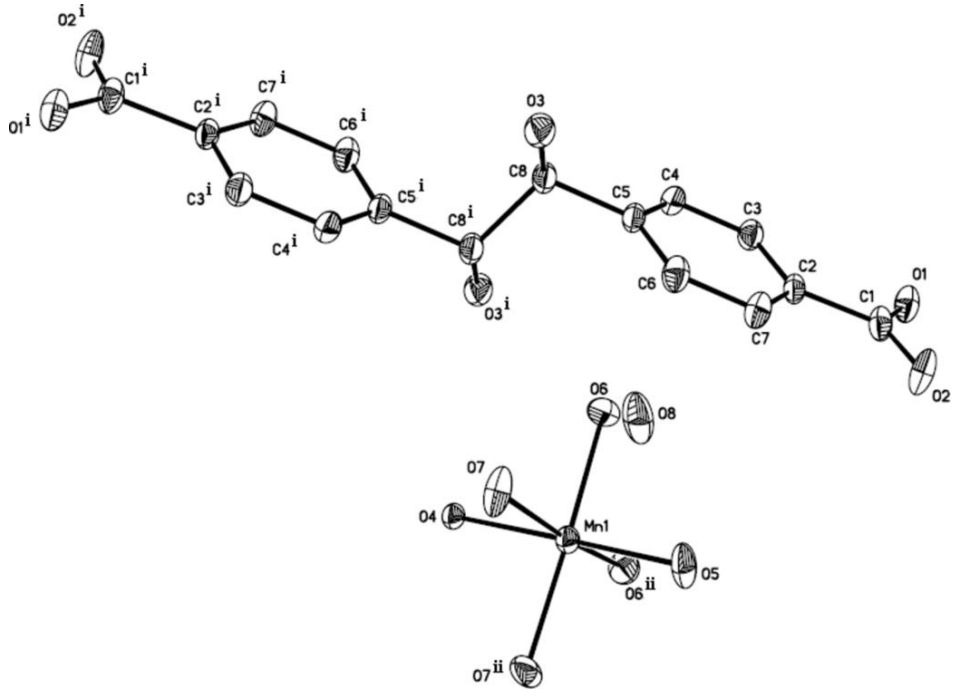
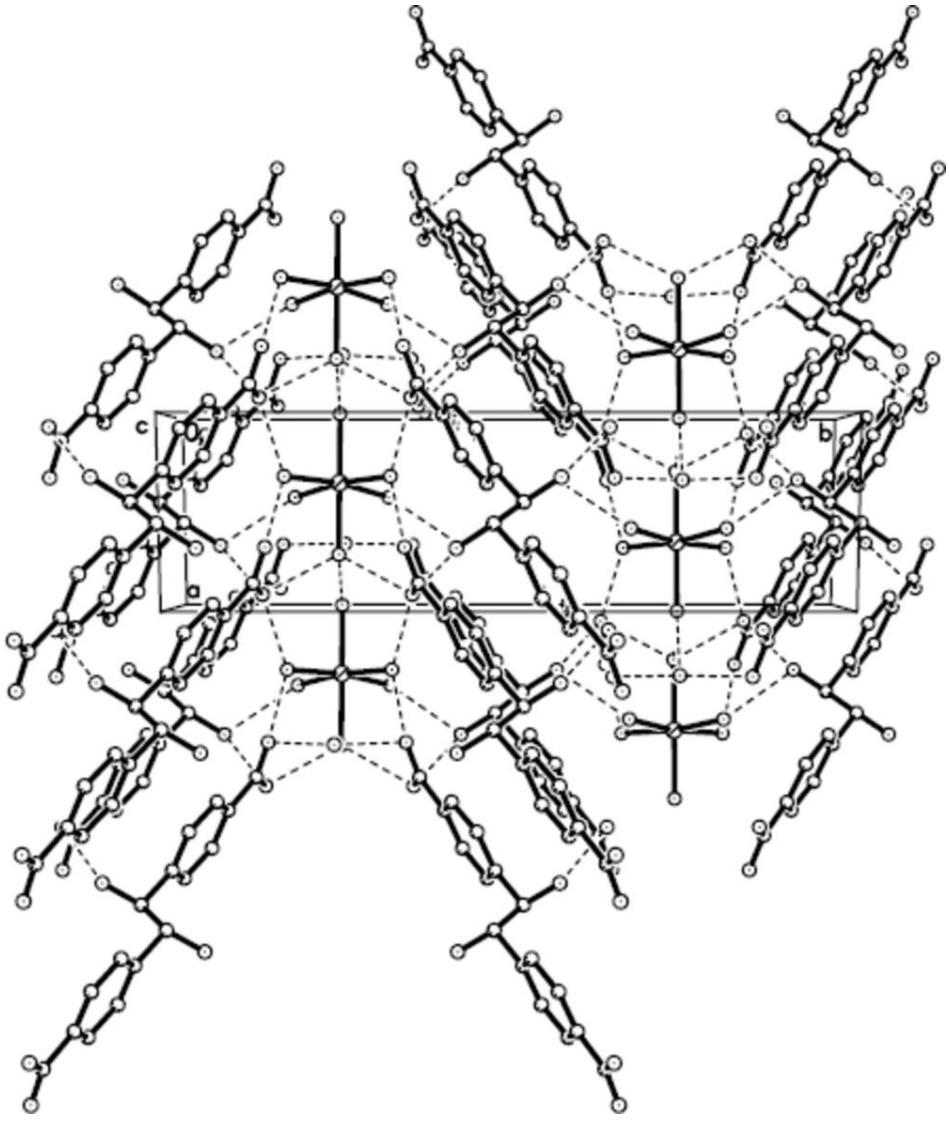

O2 i
C1 i
O1 i
C2 i
C7 i
C6 i
C3 i
C5 i
C4 i
C8 i
O3 i
O3
C8
C5
C4
C3
C2
C1
O1
O2
C6
C7
O6
O8
O7
O4
Mn1
O5
O6 ii
O7 ii

Fig. 2



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Hexakis(dimethyl sulfoxide-κO)-thallium(III) trinitrate

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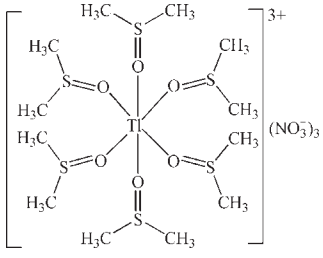
Key indicators: single-crystal X-ray study; T = 100 K; mean σ(S–C) = 0.004 Å; disorder in solvent or counterion; R factor = 0.022; wR factor = 0.058; data-to-parameter ratio = 25.1.

The title compound, $[Tl(C_2H_6OS)_6](NO_3)_3$, consists of six dimethyl sulfoxide (DMSO) molecules coordinated to a Tl^{III} atom, which lies on a $\overline{3}$ axis, and three nitrate anions (3. symmetry) to neutralize the charge. The coordination polyhedron around the Tl^{III} atom is octahedral, defined by six O atoms of the DMSO molecules. In the crystal structure, C—H···O hydrogen bonds are observed. One of the nitrate groups exhibits half-occupation.

Related literature

For general background to thallium(III) chemistry, see: Tóth & Gyõri (1994). For related structures, see: Aghabozorg, Ghadermazi *et al.* (2006); Aghabozorg, Ramezanipour *et al.* (2006); Ma *et al.* (2002); Notash *et al.* (2008).



Experimental

Crystal data

$[Tl(C_2H_6OS)_6](NO_3)_3$
M_r = 859.17
Trigonal, $R\overline{3}$
a = 11.7207 (9) Å
c = 19.209 (3) Å
V = 2285.3 (4) Å^3
Z = 3
Mo $K\alpha$ radiation
μ = 5.78 mm^{-1}
T = 100 K
0.23 × 0.12 × 0.04 mm

Data collection

Bruker APEXII CCD diffractometer
Absorption correction: multi-scan (*SADABS*; Sheldrick, 1996)
T_{min} = 0.442, T_{max} = 0.786
9649 measured reflections
1480 independent reflections
1480 reflections with $I > 2\sigma(I)$
R_{int} = 0.036

Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.022
$wR(F^2)$ = 0.058
S = 0.99
1480 reflections
59 parameters
H-atom parameters constrained
$\Delta\rho_{max}$ = 1.97 e Å^{-3}
$\Delta\rho_{min}$ = −0.76 e Å^{-3}

Table 1
Hydrogen-bond geometry (Å, °).

D—H···A	D—H	H···A	D···A	D—H···A
C1—H1B···O1	0.96	2.42	3.311 (4)	154
C1—H1C···O2^{i}	0.96	2.54	3.448 (11)	158
C2—H2A···O1^{ii}	0.96	2.55	3.380 (6)	145
C2—H2B···O2	0.96	1.99	2.915 (10)	161
C2—H2C···O1	0.96	2.55	3.423 (6)	152

Symmetry codes: (i) $y-\frac{1}{3}, -x+y+\frac{1}{3}, -z+\frac{1}{3}$; (ii) $x-y+\frac{2}{3}, x+\frac{1}{3}, -z+\frac{1}{3}$.

Data collection: *APEX2* (Bruker, 2007); cell refinement: *SAINT* (Bruker, 2007); data reduction: *SAINT*; program(s) used to solve structure: *SHELXTL* (Sheldrick, 2008); program(s) used to refine structure: *SHELXTL*; molecular graphics: *SHELXTL*; software used to prepare material for publication: *SHELXTL*.

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Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: HY2321).

References

Aghabozorg, H., Ghadermazi, M., Manteghi, F. & Nakhjavan, B. (2006). *Z. Anorg. Allg. Chem.* **632**, 2058–2064.
Aghabozorg, H., Ramezanipour, F., Kheirollahi, P. D., Saei, A. A., Shokrollahi, A., Shamsipur, M., Manteghi, F., Soleimannejad, J. & Sharif, M. A. (2006). *Z. Anorg. Allg. Chem.* **632**, 147–154.
Bruker (2007). *APEX2* and *SAINT*. Bruker AXS Inc., Madison, Wisconsin, USA.
Ma, G., Fischer, A. & Glaser, J. (2002). *Acta Cryst.* C**58**, m177–m178.
Notash, B., Safari, N., Khavasi, H. R., Amani, V. & Abedi, A. (2008). *J. Organomet. Chem.* **693**, 3553–3557.
Sheldrick, G. M. (1996). *SADABS*. University of Göttingen, Germany.
Sheldrick, G. M. (2008). *Acta Cryst.* A**64**, 112–122.
Tóth, I. & Gyõri, B. (1994). *Thallium: Inorganic Chemistry*, Vol. 8, *In Encyclopedia of Inorganic Chemistry*, p. 4134. New York: John Wiley and Sons.

supplementary materials

Acta Cryst. (2010). E**66**, m812 [**doi:10.1107/S1600536810022646**]

Hexakis(dimethyl sulfoxide-*κO*)thallium(III) trinitrate

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Comment

There are some reports on coordination of dimethyl sulfoxide (DMSO) as a neutral ligand to Tl(III), such as a triiodo complex [$TlI_3(DMSO)_2$] (Ma *et al.*, 2002) and [$Tl(dm4bt)_2(NO_3)(DMSO)$] (dm4bt = 2,2'-dimethyl-4,4'-bithiazole) (Notash *et al.*, 2008). Thallium(III) can be classified as a medium-soft metal ion in contrast to the other trivalent ions of group 13, aluminium(III), gallium(III) and indium(III), which are regarded as hard from their coordination properties (Tóth & Gyõri, 1994). The title compound has a coordination number of six around the metal (Figs. 1 and 2). However, the coordination numbers 4 to 9 are observed in different thallium(III) complexes (Aghabozorg, Ramezanipour *et al.*, 2006). Compared with [$Tl(dm4bt)_2(NO_3)(DMSO)$] and [$TlI_3(DMSO)_2$] mentioned above, in which the bond lengths of Tl(III) to O atoms of DMSO are 2.644 (7) and 2.468 (6) Å, the title compound has shorter Tl—O bonds [2.223 (2)–2.224 (2) Å]. This can be attributed to the less hindrance around the Tl centre. Also, compared with [$Tl_2(pydcH)_3(pydc)(H_2O)_2$] ($pydcH_2$ = pyridine-2,6-dicarboxylic acid) (Aghabozorg, Ramezanipour *et al.*, 2006) and ($pipzH_2$)[$Tl_2(pydc)_2Cl_4(H_2O)_2$].$4H_2O$ (pipz = piperazine) (Aghabozorg, Ghadermazi *et al.*, 2006), whose Tl—O bond lengths vary in the range of 2.680 (4)–3.122 (4) and 2.436 (5)–2.508 (5) Å, respectively, again the Tl—O bond lengths in the title compound are obviously shorter. As shown in Table 1, only C—H···O hydrogen bonds can be seen in the lattice. The shortest C—H···O bond is C2—H2B···O2 with the best angle.

Experimental

To a DMSO solution of $Tl(NO_3)_3.3H_2O$ (1 mmol, 443 mg) was added piperazinediium pyridine-2,6-dicarboxylate (3 mmol, 759 mg) prepared as literature (Aghabozorg, Ghadermazi *et al.*, 2006). The total volume of solution was 40 ml. The colourless crystals suitable for crystallography were obtained after six months.

Refinement

H atoms on C atoms were positioned geometrically and refined as riding atoms, with C—H = 0.96 Å and U_{iso}(H) = 1.5U_{eq}(C). There is a high positive residual density of 1.97 e $Å^{-3}$ near the Tl1 atom (distance 0.76 Å) due to considerable absorption effects which could not be completely corrected.

Figures

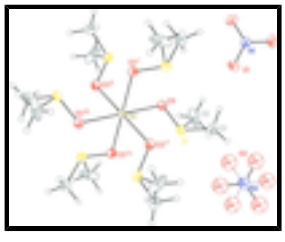


Fig. 1. Molecular structure of the title compound. Displacement ellipsoids are shown at the 50% probability level. [Symmetry codes: (i) 1/3+x-y, -1/3+x, 2/3-z; (ii) 1-y, x-y, z; (iii) 4/3-x, 2/3-y, 2/3-z; (iv) 1-x+y, 1-x, z; (v) 1/3+y, 2/3-x+y, 2/3-z.]

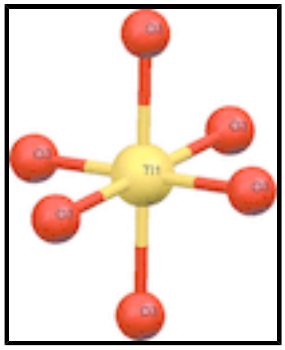


Fig. 2. Coordination polyhedron around the metal centre.

Hexakis(dimethyl sulfoxide-κ*O*)thallium(III) trinitrate

Crystal data

$[Tl(C_2H_6OS)_6](NO_3)_3$	$D_x = 1.873$ Mg m^{-3}
$M_r = 859.17$	Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å
Trigonal, $R\bar{3}$	Cell parameters from 1197 reflections
Hall symbol: -R 3	$\theta = 2.3$–$34.3°$
$a = 11.7207$ (9) Å	$\mu = 5.78$ mm^{-1}
$c = 19.209$ (3) Å	$T = 100$ K
$V = 2285.3$ (4) Å^3	Plate, colourless
$Z = 3$	0.23 × 0.12 × 0.04 mm
$F(000) = 1278$	

Data collection

Bruker APEXII CCD diffractometer	1480 independent reflections
Radiation source: fine-focus sealed tube	1480 reflections with $I > 2\sigma(I)$
graphite	$R_{int} = 0.036$
φ and ω scans	$\theta_{max} = 30.0°$, $\theta_{min} = 2.3°$
Absorption correction: multi-scan (*SADABS*; Sheldrick, 1996)	$h = -16\rightarrow16$
$T_{min} = 0.442$, $T_{max} = 0.786$	$k = -16\rightarrow16$
9649 measured reflections	$l = -27\rightarrow27$

Refinement

Refinement on F^2	Primary atom site location: structure-invariant direct methods
Least-squares matrix: full	Secondary atom site location: difference Fourier map
$R[F^2 > 2\sigma(F^2)] = 0.022$	Hydrogen site location: inferred from neighbouring sites
$wR(F^2) = 0.058$	H-atom parameters constrained
$S = 0.99$	$w = 1/[\sigma^2(F_o^2) + (0.040P)^2 + 9.P]$ where $P = (F_o^2 + 2F_c^2)/3$
1480 reflections	$(\Delta/\sigma)_{max} < 0.001$

59 parameters	$\Delta\rho_{max}$ = 1.97 e Å^{-3}
0 restraints	$\Delta\rho_{min}$ = −0.76 e Å^{-3}

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å^2)

	x	*y*	*z*	U_{iso}*/U_{eq}	Occ. (<1)
Tl1	0.6667	0.3333	0.3333	0.01735 (8)	
S1	0.47065 (6)	0.40706 (7)	0.24746 (4)	0.02613 (15)	
N1	0.0000	0.0000	0.2520 (2)	0.0268 (8)	
O3	0.48799 (19)	0.29141 (19)	0.27294 (11)	0.0235 (4)	
O1	0.1049 (2)	0.1084 (2)	0.25261 (16)	0.0383 (5)	
C1	0.3450 (3)	0.4021 (3)	0.30137 (19)	0.0333 (6)	
H1A	0.3792	0.4312	0.3474	0.050*	
H1B	0.2722	0.3136	0.3034	0.050*	
H1C	0.3158	0.4589	0.2824	0.050*	
C2	0.3806 (4)	0.3443 (5)	0.16924 (19)	0.0498 (11)	
H2A	0.4345	0.3328	0.1355	0.075*	
H2B	0.3554	0.4051	0.1515	0.075*	
H2C	0.3031	0.2610	0.1783	0.075*	
N2	0.3333	0.6667	0.1861 (4)	0.0280 (17)*	0.50
O2	0.3414 (8)	0.5668 (8)	0.1413 (4)	0.0609 (17)*	0.50

Atomic displacement parameters (Å^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Tl1	0.01458 (8)	0.01458 (8)	0.02288 (12)	0.00729 (4)	0.000	0.000
S1	0.0176 (3)	0.0250 (3)	0.0332 (4)	0.0087 (2)	−0.0008 (2)	0.0090 (2)
N1	0.0221 (11)	0.0221 (11)	0.036 (2)	0.0110 (6)	0.000	0.000
O3	0.0209 (9)	0.0206 (8)	0.0287 (9)	0.0103 (7)	−0.0054 (7)	−0.0025 (7)
O1	0.0234 (10)	0.0229 (10)	0.0617 (16)	0.0063 (8)	−0.0014 (10)	−0.0006 (10)
C1	0.0278 (14)	0.0317 (15)	0.0436 (17)	0.0173 (12)	−0.0005 (12)	−0.0059 (12)
C2	0.0282 (16)	0.094 (3)	0.0273 (15)	0.0302 (19)	−0.0020 (12)	0.0109 (18)

Geometric parameters (Å, °)

Tl1—O3^{i}	2.2234 (19)	N1—O1^{vii}	1.250 (2)
Tl1—O3^{ii}	2.2235 (19)	C1—H1A	0.9600
Tl1—O3^{iii}	2.2235 (19)	C1—H1B	0.9600
Tl1—O3^{iv}	2.2235 (19)	C1—H1C	0.9600
Tl1—O3	2.2235 (19)	C2—H2A	0.9600
Tl1—O3^{v}	2.2235 (19)	C2—H2B	0.9600
S1—O3	1.547 (2)	C2—H2C	0.9600
S1—C2	1.771 (4)	N2—O2^{viii}	1.226 (8)
S1—C1	1.777 (3)	N2—O2^{ix}	1.226 (8)
N1—O1	1.250 (2)	N2—O2^{x}	1.226 (8)
N1—O1^{vi}	1.250 (2)	O2—N2^{x}	1.226 (8)

O3^{i}—Tl1—O3^{ii}	95.26 (7)	O1—N1—O1^{vii}	119.993 (9)
O3^{i}—Tl1—O3^{iii}	180.0	O1^{vi}—N1—O1^{vii}	119.993 (9)
O3^{ii}—Tl1—O3^{iii}	84.74 (7)	S1—O3—Tl1	119.56 (11)
O3^{i}—Tl1—O3^{iv}	84.74 (7)	S1—C1—H1A	109.5
O3^{ii}—Tl1—O3^{iv}	180.0	S1—C1—H1B	109.5
O3^{iii}—Tl1—O3^{iv}	95.26 (7)	H1A—C1—H1B	109.5
O3^{i}—Tl1—O3	84.74 (7)	S1—C1—H1C	109.5
O3^{ii}—Tl1—O3	84.74 (7)	H1A—C1—H1C	109.5
O3^{iii}—Tl1—O3	95.26 (7)	H1B—C1—H1C	109.5
O3^{iv}—Tl1—O3	95.26 (7)	S1—C2—H2A	109.5
O3^{i}—Tl1—O3^{v}	95.26 (7)	S1—C2—H2B	109.5
O3^{ii}—Tl1—O3^{v}	95.26 (7)	H2A—C2—H2B	109.5
O3^{iii}—Tl1—O3^{v}	84.74 (7)	S1—C2—H2C	109.5
O3^{iv}—Tl1—O3^{v}	84.74 (7)	H2A—C2—H2C	109.5
O3—Tl1—O3^{v}	180.0	H2B—C2—H2C	109.5
O3—S1—C2	102.52 (19)	O2^{viii}—N2—O2^{ix}	119.14 (17)
O3—S1—C1	104.88 (14)	O2^{viii}—N2—O2^{x}	119.14 (17)
C2—S1—C1	99.72 (17)	O2^{ix}—N2—O2^{x}	119.13 (17)
O1—N1—O1^{vi}	119.993 (9)		
C2—S1—O3—Tl1	148.95 (15)	O2^{x}—N2—O2—O2^{viii}	112.8 (4)
C1—S1—O3—Tl1	−107.29 (16)	O2^{xi}—N2—O2—O2^{viii}	157.9 (4)
O3^{i}—Tl1—O3—S1	46.66 (9)	O2^{xii}—N2—O2—O2^{viii}	67.8 (6)
O3^{ii}—Tl1—O3—S1	142.45 (17)	N2^{x}—N2—O2—O2^{ix}	−112.8 (4)
O3^{iii}—Tl1—O3—S1	−133.34 (9)	O2^{viii}—N2—O2—O2^{ix}	134.3 (9)
O3^{iv}—Tl1—O3—S1	−37.55 (17)	O2^{x}—N2—O2—O2^{ix}	−112.8 (4)
N2^{x}—N2—O2—O2^{viii}	112.8 (4)	O2^{xi}—N2—O2—O2^{ix}	−67.8 (6)
O2^{ix}—N2—O2—O2^{viii}	−134.3 (9)	O2^{xii}—N2—O2—O2^{ix}	−157.9 (4)

Symmetry codes: (i) *y*+1/3, −*x*+*y*+2/3, −*z*+2/3; (ii) *x*−*y*+1/3, *x*−1/3, −*z*+2/3; (iii) −*y*+1, *x*−*y*, *z*; (iv) −*x*+*y*+1, −*x*+1, *z*; (v) −*x*+4/3, −*y*+2/3, −*z*+2/3; (vi) −*y*, *x*−*y*, *z*; (vii) −*x*+*y*, −*x*, *z*; (viii) *x*−*y*+2/3, *x*+1/3, −*z*+1/3; (ix) *y*−1/3, −*x*+*y*+1/3, −*z*+1/3; (x) −*x*+2/3, −*y*+4/3, −*z*+1/3; (xi) −*x*+*y*, −*x*+1, *z*; (xii) −*y*+1, *x*−*y*+1, *z*.

Hydrogen-bond geometry (Å, °)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
C1—H1B···O1	0.96	2.42	3.311 (4)	154
C1—H1C···O2^{ix}	0.96	2.54	3.448 (11)	158
C2—H2A···O1^{xiii}	0.96	2.55	3.380 (6)	145
C2—H2B···O2	0.96	1.99	2.915 (10)	161
C2—H2C···O1	0.96	2.55	3.423 (6)	152

Symmetry codes: (ix) *y*−1/3, −*x*+*y*+1/3, −*z*+1/3; (xiii) *x*−*y*+2/3, *x*+1/3, −*z*+1/3.

Fig. 1

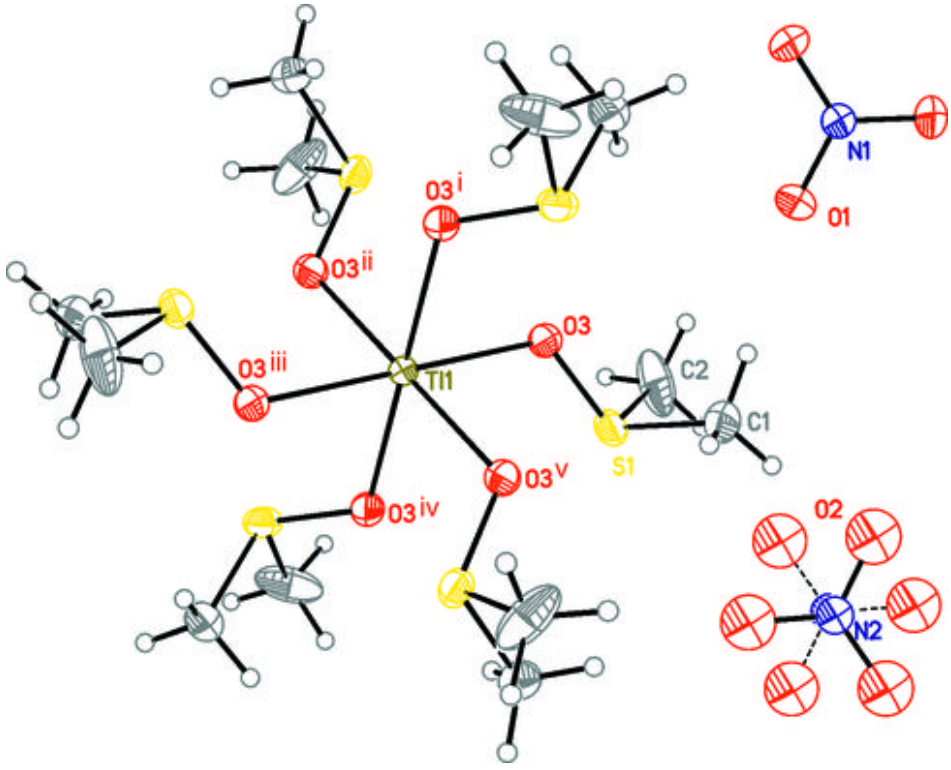
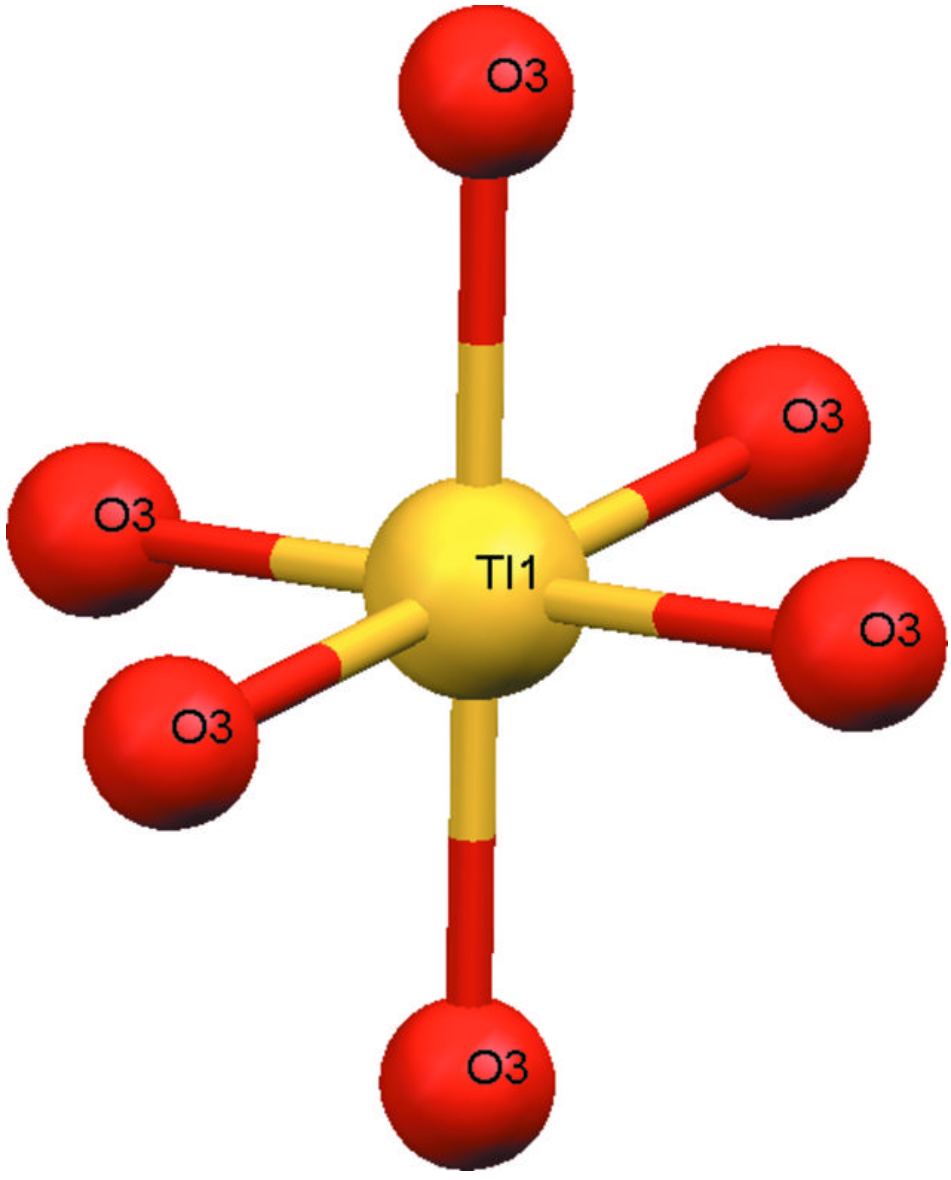


Fig. 2



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Bis{2-[(2-benzoylhydrazin-1-ylidene)-methyl]-6-methoxyphenolato}iron(III) chloride monohydrate

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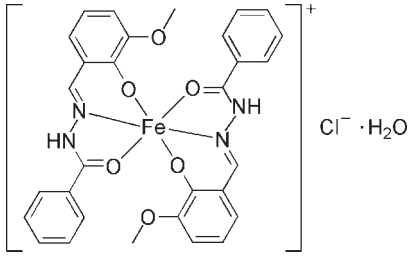
Key indicators: single-crystal X-ray study; T = 296 K; mean σ(C–C) = 0.006 Å; R factor = 0.051; wR factor = 0.153; data-to-parameter ratio = 13.1.

In the title mononuclear iron(III) complex, $[Fe(C_{15}H_{13}N_2O_3)_2]Cl\cdot H_2O$, the Fe^{III} atom has a distorted octahedral geometry and is six-coordinated by four O atoms and two N atoms from two ligands. In the crystal structure, the complex cations, Cl^- anions and water molecules are connected into a chain along [100] through N—H···O, O—H···Cl and N—H···Cl hydrogen bonds. Two adjacent chains are linked by O—H···O hydrogen bonds.

Related literature

For the applications of metal–Schiff base compounds, see: Dilworth (1976); Merchant & Clothia (1970); Pickart *et al.* (1983). For the ligand synthesis, see: Pouralimardan *et al.* (2007); Sacconi (1954). For related structures, see: Gao *et al.* (1998); Monfared *et al.* (2007); Yu *et al.* (2010).



Experimental

Crystal data

$[Fe(C_{15}H_{13}N_2O_3)_2]Cl\cdot H_2O$
M_r = 647.86
Monoclinic, $P2_1/c$
a = 12.7778 (10) Å
b = 22.7113 (18) Å
c = 10.0604 (7) Å
β = 94.542 (1)°
V = 2910.4 (4) Å^3
Z = 4
Mo $K\alpha$ radiation
μ = 0.67 mm^{-1}
T = 296 K
0.24 × 0.18 × 0.15 mm

Data collection

Bruker SMART APEX CCD diffractometer
Absorption correction: multi-scan (*SADABS*; Sheldrick, 1996)
T_{min} = 0.857, T_{max} = 0.907
14540 measured reflections
5098 independent reflections
3508 reflections with $I > 2\sigma(I)$
R_{int} = 0.052

Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.051
$wR(F^2)$ = 0.153
S = 0.98
5098 reflections
390 parameters
H-atom parameters constrained
$\Delta\rho_{max}$ = 0.95 e Å^{-3}
$\Delta\rho_{min}$ = −0.48 e Å^{-3}

Table 1
Selected bond lengths (Å).

Fe1—O1	2.070 (3)	Fe1—O5	1.901 (3)
Fe1—O2	1.904 (3)	Fe1—N2	2.106 (3)
Fe1—O4	2.062 (3)	Fe1—N4	2.124 (3)

Table 2
Hydrogen-bond geometry (Å, °).

D—H···A	D—H	H···A	D···A	D—H···A
N1—H1B···Cl1^{i}	0.86	2.25	3.087 (3)	163
N3—H3B···O1W	0.86	1.92	2.759 (4)	164
O1W—H1WA···O5^{ii}	0.85	2.39	3.045 (4)	134
O1W—H1WB···Cl1	0.85	2.37	3.198 (3)	163

Symmetry codes: (i) $x-1, y, z$; (ii) $-x+1, -y+1, -z+2$.

Data collection: *SMART* (Bruker, 2007); cell refinement: *SAINT-Plus* (Bruker, 2007); data reduction: *SAINT-Plus*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *DIAMOND* (Brandenburg, 1999); software used to prepare material for publication: *SHELXL97* and *publCIF* (Westrip, 2010).

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Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: HY2322).

References

Brandenburg, K. (1999). *DIAMOND*. Crystal Impact GbR, Bonn, Germany.
Bruker (2007). *SMART* and *SAINT-Plus*. Bruker AXS Inc., Madison, Wisconsin, USA.
Dilworth, J.-R. (1976). *Coord. Chem. Rev.* **21**, 29–62.
Gao, S., Weng, Z.-Q. & Liu, S.-X. (1998). *Polyhedron*, **17**, 3595–3606.
Merchant, J. R. & Clothia, D. S. (1970). *J. Med. Chem.* **13**, 335–336.
Monfared, H. H., Sadighian, S., Kamyabi, M. A. & Mayer, P. (2007). *J. Mol. Catal. A*, **304**, 139–146.
Pickart, L., Goodwin, W. H., Burgua, W., Murphy, T. B. & Johnson, D. K. (1983). *Biochem. Pharmacol.* **32**, 3868–3871.
Pouralimardan, O., Chamayou, A. C., Janiak, C. & Monfared, H. H. (2007). *Inorg. Chim. Acta*, **360**, 1599–1608.
Sacconi, L. (1954). *Z. Anorg. Allg. Chem.* **275**, 249–256.
Sheldrick, G. M. (1996). *SADABS*. University of Göttingen, Germany.
Sheldrick, G. M. (2008). *Acta Cryst.* A**64**, 112–122.
Westrip, S. P. (2010). *J. Appl. Cryst.* **43**. Submitted.
Yu, G.-M., Li, Y.-H., Zou, L.-F., Zhu, J.-W. & Liu, X.-Q. (2010). *Acta Cryst.* E**66**, m693–m694.

supplementary materials

Acta Cryst. (2010). E**66**, m828 [**doi:10.1107/S1600536810023226**]

Bis{2-[(2-benzoylhydrazin-1-ylidene)methyl]-6-methoxyphenolato}iron(III) chloride monohydrate

L.-F. Zou, Y.-Q. Ma, G.-M. Yu, F.-J. Gan and Y.-H. Li

Comment

Studies of acylhydrazone Schiff base and the dependence of their chelation mode with transition metal ions have been of significant interest. On one hand, their metal compounds have been reported to act as enzyme inhibitors (Dilworth, 1976) and are useful due to their pharmacological applications (Merchant & Clothia, 1970). On the other hand, it seems to be a good candidate for catalytic oxidation studies because of their stability to resist oxidation (Pickart *et al.*, 1983). These findings have triggered the exploration of new molecular clusters based on acylhydrazone Schiff base. During the last several years, the crystal structures of metal compounds with 3-methoxysalicylaldehyde benzoylhydrazide have been attracted tremendous interest (Gao *et al.*, 1998; Monfared *et al.*, 2007; Yu *et al.*, 2010). As a continuation of our effort in this system, the preparation and crystal structure of the title Schiff base iron(III) compound are reported here.

The molecular structure of the title compound is illustrated in Fig. 1, which consists of one mononuclear $[Fe(C_{15}H_{13}N_2O_3)_2]^+$ cation, one Cl^- anion and one water molecule. The Fe^{III} atom has a distorted octahedral geometry and is six-coordinated by four O atoms and two N atoms from two ligands (Table 1). In one ligand, the strained angle of O1—Fe1—N2 [74.54 (11)°] correlates with the bite angle for the five-membered chelate ring Fe1—O1—C7—N1—N2, and the loose angle of O2—Fe1—N2 [84.74 (11)°] correlates with the six-membered ring Fe1—N2—C8—C9—C10—O2. The axial angle N2—Fe1—N4 [159.46 (12)°] deviates significantly from the ideal 180°. Similar case occurrs for another ligand. In the crystal structure, the complex cations, Cl^- anions and water molecules are connected into a chain through N—H···O, O—H···Cl and N—H···Cl hydrogen bonds. Two adjacent chains are linked by O—H···O hydrogen bonds. (Fig. 2 and Table 2).

Experimental

The 3-methoxysalicylaldehyde benzoylhydrazide ligand (H_2L) was prepared in a similar manner according to the reported procedures (Pouralimardan *et al.*, 2007; Sacconi, 1954). The title compound was synthesized by adding $FeCl_3.6H_2O$ (27.0 mg, 0.1 mmol) to a solution of H_2L (27.3 mg, 0.10 mmol) in methanol (15 ml). The resulting mixture was stirred for 3 h at room temperature to afford a dark brown solution and then filtered. The filtrate was allowed to stand at room temperature for about three weeks and black crystals were produced at the bottom of the vessel on slow evaporation of methanol.

Refinement

All H atoms were placed in calculated positions and refined using a riding model, with C—H = 0.93 (aromatic), 0.96 (methyl) Å and N—H = 0.86 Å and with U_{iso}(H) = 1.2(1.5 for methyl)U_{eq}(C, N). Water H atoms were located in a difference Fourier map and refined as riding, with O—H = 0.85 Å and U_{iso}(H) = 1.2U_{eq}(O).

Figures

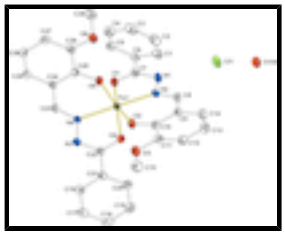


Fig. 1. Molecular structure of the title compound. H atoms are omitted for clarity. Displacement ellipsoids are drawn at the 30% probability level.

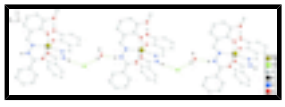


Fig. 2. One-dimensional chain structure in the title compound. Hydrogen bonds are shown as green dashed lines.

Bis{2-[(2-benzoylhydrazin-1-ylidene)methyl]-6-methoxyphenolato}iron(III) chloride monohydrate

Crystal data

$[Fe(C_{15}H_{13}N_2O_3)_2]Cl·H_2O$	$F(000) = 1340$
$M_r = 647.86$	$D_x = 1.479$ Mg m^{-3}
Monoclinic, $P2_1/c$	Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å
Hall symbol: -P 2ybc	Cell parameters from 4767 reflections
$a = 12.7778$ (10) Å	$\theta = 4.8–51.7°$
$b = 22.7113$ (18) Å	$\mu = 0.67$ mm^{-1}
$c = 10.0604$ (7) Å	$T = 296$ K
$\beta = 94.542$ (1)°	Block, black
$V = 2910.4$ (4) Å^3	0.24 × 0.18 × 0.15 mm
$Z = 4$	

Data collection

Bruker SMART APEX CCD diffractometer	5098 independent reflections
Radiation source: fine-focus sealed tube	3508 reflections with $I > 2\sigma(I)$
graphite	$R_{int} = 0.052$
φ and ω scans	$\theta_{max} = 25.0°$, $\theta_{min} = 1.8°$
Absorption correction: multi-scan (*SADABS*; Sheldrick, 1996)	$h = -15\rightarrow15$
$T_{min} = 0.857$, $T_{max} = 0.907$	$k = -27\rightarrow23$
14540 measured reflections	$l = -11\rightarrow10$

Refinement

Refinement on F^2	Primary atom site location: structure-invariant direct methods
Least-squares matrix: full	Secondary atom site location: difference Fourier map
$R[F^2 > 2\sigma(F^2)] = 0.051$	Hydrogen site location: inferred from neighbouring sites
$wR(F^2) = 0.153$	H-atom parameters constrained

$S = 0.98$	$w = 1/[\sigma^2(F_o^2) + (0.0933P)^2 + 0.1872P]$ where $P = (F_o^2 + 2F_c^2)/3$
5098 reflections	$(\Delta/\sigma)_{max} < 0.001$
390 parameters	$\Delta\rho_{max} = 0.95$ e Å^{-3}
0 restraints	$\Delta\rho_{min} = -0.47$ e Å^{-3}

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å^2)

	x	*y*	*z*	U_{iso}*/U_{eq}
Fe1	0.28270 (4)	0.56160 (2)	0.90592 (5)	0.02612 (19)
Cl1	0.87327 (8)	0.66511 (5)	0.74420 (12)	0.0455 (3)
C1	0.0861 (3)	0.69236 (18)	0.5203 (4)	0.0376 (10)
H1A	0.0396	0.7024	0.5832	0.045*
C2	0.0804 (4)	0.7195 (2)	0.3979 (5)	0.0449 (12)
H2A	0.0305	0.7487	0.3787	0.054*
C3	0.1472 (4)	0.7040 (2)	0.3036 (5)	0.0511 (13)
H3A	0.1416	0.7227	0.2211	0.061*
C4	0.2219 (4)	0.6615 (2)	0.3292 (4)	0.0433 (11)
H4A	0.2659	0.6508	0.2640	0.052*
C5	0.2313 (3)	0.63511 (19)	0.4515 (4)	0.0350 (10)
H5A	0.2837	0.6073	0.4703	0.042*
C6	0.1631 (3)	0.64933 (18)	0.5489 (4)	0.0307 (9)
C7	0.1786 (3)	0.61984 (17)	0.6799 (4)	0.0275 (9)
C8	0.0525 (3)	0.58652 (18)	0.9627 (4)	0.0310 (9)
H8A	−0.0129	0.6023	0.9359	0.037*
C9	0.0651 (3)	0.55879 (18)	1.0885 (4)	0.0294 (9)
C10	0.1608 (3)	0.53399 (17)	1.1403 (4)	0.0290 (9)
C11	0.1644 (3)	0.50693 (18)	1.2666 (4)	0.0319 (10)
C12	0.0756 (3)	0.5034 (2)	1.3356 (4)	0.0397 (11)
H12A	0.0786	0.4844	1.4177	0.048*
C13	−0.0175 (3)	0.5278 (2)	1.2842 (4)	0.0440 (12)
H13A	−0.0766	0.5256	1.3322	0.053*
C14	−0.0234 (3)	0.5551 (2)	1.1631 (4)	0.0405 (11)
H14A	−0.0867	0.5716	1.1294	0.049*
C15	0.2726 (4)	0.4590 (2)	1.4393 (4)	0.0500 (13)
H15A	0.3446	0.4478	1.4594	0.075*
H15B	0.2288	0.4246	1.4392	0.075*
H15C	0.2522	0.4862	1.5056	0.075*
C16	0.5865 (3)	0.71820 (18)	1.0512 (4)	0.0353 (10)
H16A	0.6324	0.6914	1.0169	0.042*
C17	0.6243 (4)	0.76907 (19)	1.1109 (4)	0.0400 (11)
H17A	0.6961	0.7766	1.1178	0.048*
C18	0.5563 (4)	0.8090 (2)	1.1605 (4)	0.0435 (12)
H18A	0.5822	0.8436	1.2003	0.052*
C19	0.4499 (4)	0.7979 (2)	1.1514 (4)	0.0444 (12)
H19A	0.4043	0.8250	1.1852	0.053*
C20	0.4108 (3)	0.74682 (18)	1.0923 (4)	0.0356 (10)
H20A	0.3389	0.7395	1.0863	0.043*

C21	0.4784 (3)	0.70675 (17)	1.0423 (4)	0.0294 (9)
C22	0.4344 (3)	0.65140 (17)	0.9850 (4)	0.0257 (9)
C23	0.5028 (3)	0.52154 (17)	0.8316 (4)	0.0257 (9)
H23A	0.5735	0.5297	0.8244	0.031*
C24	0.4618 (3)	0.46776 (17)	0.7770 (4)	0.0267 (9)
C25	0.3558 (3)	0.45109 (17)	0.7842 (4)	0.0269 (9)
C26	0.3226 (3)	0.39603 (18)	0.7277 (4)	0.0303 (9)
C27	0.3928 (3)	0.36044 (19)	0.6688 (4)	0.0351 (10)
H27A	0.3703	0.3246	0.6319	0.042*
C28	0.4968 (3)	0.37752 (19)	0.6638 (4)	0.0366 (10)
H28A	0.5434	0.3527	0.6246	0.044*
C29	0.5312 (3)	0.42949 (18)	0.7147 (4)	0.0327 (10)
H29A	0.6008	0.4404	0.7091	0.039*
C30	0.1794 (4)	0.3313 (2)	0.6782 (6)	0.0551 (14)
H30A	0.1063	0.3280	0.6928	0.083*
H30B	0.2167	0.2981	0.7175	0.083*
H30C	0.1874	0.3321	0.5842	0.083*
N1	0.1015 (3)	0.61943 (14)	0.7608 (3)	0.0307 (8)
H1B	0.0412	0.6352	0.7399	0.037*
N2	0.1262 (2)	0.59143 (14)	0.8822 (3)	0.0260 (7)
N3	0.4973 (2)	0.61077 (13)	0.9384 (3)	0.0277 (8)
H3B	0.5640	0.6158	0.9378	0.033*
N4	0.4475 (2)	0.55953 (13)	0.8906 (3)	0.0231 (7)
O1	0.2638 (2)	0.59602 (12)	0.7150 (3)	0.0307 (6)
O1W	0.7122 (2)	0.60423 (13)	0.9294 (3)	0.0421 (8)
H1WA	0.7368	0.5719	0.9611	0.050*
H1WB	0.7434	0.6240	0.8725	0.050*
O2	0.2468 (2)	0.53545 (13)	1.0763 (3)	0.0346 (7)
O3	0.2611 (2)	0.48627 (13)	1.3112 (3)	0.0396 (7)
O4	0.3375 (2)	0.64162 (12)	0.9791 (3)	0.0318 (7)
O5	0.2873 (2)	0.48311 (12)	0.8409 (3)	0.0323 (7)
O6	0.2204 (2)	0.38391 (13)	0.7375 (3)	0.0423 (8)

Atomic displacement parameters (Å^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Fe1	0.0196 (3)	0.0345 (3)	0.0245 (3)	0.0041 (2)	0.0039 (2)	0.0024 (3)
Cl1	0.0289 (6)	0.0524 (7)	0.0550 (8)	0.0074 (5)	0.0009 (5)	0.0078 (6)
C1	0.036 (3)	0.040 (3)	0.036 (3)	0.001 (2)	−0.0045 (19)	0.007 (2)
C2	0.045 (3)	0.045 (3)	0.043 (3)	0.001 (2)	−0.008 (2)	0.013 (2)
C3	0.055 (3)	0.062 (3)	0.034 (3)	−0.011 (3)	−0.010 (2)	0.024 (2)
C4	0.046 (3)	0.055 (3)	0.029 (3)	−0.001 (2)	0.001 (2)	0.008 (2)
C5	0.036 (2)	0.042 (3)	0.027 (2)	0.001 (2)	0.0000 (19)	0.002 (2)
C6	0.029 (2)	0.036 (2)	0.027 (2)	−0.0047 (18)	−0.0044 (18)	0.0020 (18)
C7	0.028 (2)	0.028 (2)	0.026 (2)	−0.0035 (17)	0.0018 (17)	−0.0018 (17)
C8	0.026 (2)	0.041 (2)	0.026 (2)	0.0031 (18)	0.0046 (18)	0.0017 (19)
C9	0.024 (2)	0.038 (2)	0.026 (2)	0.0022 (18)	0.0032 (17)	−0.0015 (19)
C10	0.028 (2)	0.032 (2)	0.028 (2)	0.0005 (17)	0.0064 (17)	−0.0040 (18)

C11	0.036 (2)	0.035 (2)	0.025 (2)	−0.0016 (19)	0.0011 (18)	−0.0016 (19)
C12	0.037 (3)	0.056 (3)	0.026 (2)	−0.003 (2)	0.0081 (19)	0.001 (2)
C13	0.034 (3)	0.068 (3)	0.032 (3)	−0.002 (2)	0.013 (2)	0.005 (2)
C14	0.030 (2)	0.058 (3)	0.034 (3)	0.006 (2)	0.0046 (19)	0.007 (2)
C15	0.056 (3)	0.068 (3)	0.026 (2)	0.006 (3)	0.003 (2)	0.017 (2)
C16	0.033 (2)	0.036 (2)	0.037 (3)	0.0015 (19)	0.0023 (19)	−0.001 (2)
C17	0.043 (3)	0.039 (3)	0.036 (3)	−0.005 (2)	−0.005 (2)	0.002 (2)
C18	0.062 (3)	0.039 (3)	0.028 (2)	−0.006 (2)	−0.003 (2)	−0.009 (2)
C19	0.052 (3)	0.041 (3)	0.040 (3)	0.010 (2)	0.003 (2)	−0.009 (2)
C20	0.040 (3)	0.038 (2)	0.029 (2)	0.006 (2)	0.0011 (19)	−0.0023 (19)
C21	0.032 (2)	0.033 (2)	0.022 (2)	−0.0003 (18)	−0.0045 (17)	0.0024 (18)
C22	0.023 (2)	0.033 (2)	0.021 (2)	0.0052 (17)	−0.0003 (16)	0.0050 (17)
C23	0.020 (2)	0.037 (2)	0.020 (2)	0.0047 (17)	0.0027 (16)	0.0028 (17)
C24	0.022 (2)	0.037 (2)	0.020 (2)	0.0021 (17)	−0.0017 (16)	0.0021 (18)
C25	0.028 (2)	0.033 (2)	0.019 (2)	0.0039 (17)	0.0007 (17)	0.0034 (17)
C26	0.027 (2)	0.037 (2)	0.027 (2)	−0.0001 (18)	−0.0022 (17)	0.0054 (18)
C27	0.043 (3)	0.035 (2)	0.027 (2)	0.002 (2)	−0.0001 (19)	−0.0036 (19)
C28	0.033 (2)	0.043 (3)	0.034 (2)	0.008 (2)	0.0037 (19)	−0.010 (2)
C29	0.025 (2)	0.041 (3)	0.032 (2)	0.0027 (18)	0.0034 (18)	−0.0056 (19)
C30	0.041 (3)	0.047 (3)	0.077 (4)	−0.013 (2)	−0.001 (3)	−0.012 (3)
N1	0.0245 (18)	0.040 (2)	0.0274 (19)	0.0083 (15)	0.0023 (14)	0.0098 (15)
N2	0.0231 (17)	0.0344 (19)	0.0201 (17)	0.0038 (14)	−0.0001 (14)	0.0063 (14)
N3	0.0231 (17)	0.0315 (18)	0.0281 (19)	−0.0025 (14)	0.0002 (14)	−0.0003 (15)
N4	0.0208 (16)	0.0286 (17)	0.0197 (16)	0.0011 (14)	−0.0008 (13)	−0.0002 (14)
O1	0.0250 (15)	0.0424 (17)	0.0251 (15)	0.0053 (13)	0.0053 (12)	0.0069 (13)
O1W	0.0332 (17)	0.0456 (19)	0.0476 (19)	0.0050 (14)	0.0044 (14)	0.0046 (15)
O2	0.0249 (15)	0.0553 (19)	0.0242 (15)	0.0088 (13)	0.0043 (12)	0.0116 (13)
O3	0.0346 (17)	0.059 (2)	0.0248 (16)	0.0076 (15)	0.0022 (13)	0.0145 (14)
O4	0.0279 (16)	0.0359 (16)	0.0318 (16)	0.0046 (12)	0.0033 (12)	−0.0048 (13)
O5	0.0235 (15)	0.0342 (16)	0.0399 (17)	0.0001 (12)	0.0073 (12)	−0.0046 (13)
O6	0.0303 (17)	0.0440 (18)	0.053 (2)	−0.0081 (14)	0.0050 (14)	−0.0108 (15)

Geometric parameters (Å, °)

Fe1—O1	2.070 (3)	C16—C17	1.372 (6)
Fe1—O2	1.904 (3)	C16—C21	1.402 (6)
Fe1—O4	2.062 (3)	C16—H16A	0.9300
Fe1—O5	1.901 (3)	C17—C18	1.377 (6)
Fe1—N2	2.106 (3)	C17—H17A	0.9300
Fe1—N4	2.124 (3)	C18—C19	1.379 (7)
C1—C2	1.373 (6)	C18—H18A	0.9300
C1—C6	1.401 (6)	C19—C20	1.379 (6)
C1—H1A	0.9300	C19—H19A	0.9300
C2—C3	1.372 (7)	C20—C21	1.377 (5)
C2—H2A	0.9300	C20—H20A	0.9300
C3—C4	1.367 (6)	C21—C22	1.476 (5)
C3—H3A	0.9300	C22—O4	1.254 (4)
C4—C5	1.365 (6)	C22—N3	1.334 (5)
C4—H4A	0.9300	C23—N4	1.289 (5)

C5—C6	1.399 (6)	C23—C24	1.422 (5)
C5—H5A	0.9300	C23—H23A	0.9300
C6—C7	1.478 (5)	C24—C25	1.413 (5)
C7—O1	1.241 (5)	C24—C29	1.422 (5)
C7—N1	1.328 (5)	C25—O5	1.303 (4)
C8—N2	1.294 (4)	C25—C26	1.425 (5)
C8—C9	1.411 (5)	C26—O6	1.346 (5)
C8—H8A	0.9300	C26—C27	1.375 (6)
C9—C10	1.408 (5)	C27—C28	1.389 (6)
C9—C14	1.409 (5)	C27—H27A	0.9300
C10—O2	1.317 (4)	C28—C29	1.347 (6)
C10—C11	1.409 (5)	C28—H28A	0.9300
C11—O3	1.364 (5)	C29—H29A	0.9300
C11—C12	1.379 (5)	C30—O6	1.417 (5)
C12—C13	1.375 (6)	C30—H30A	0.9600
C12—H12A	0.9300	C30—H30B	0.9600
C13—C14	1.364 (6)	C30—H30C	0.9600
C13—H13A	0.9300	N1—N2	1.391 (4)
C14—H14A	0.9300	N1—H1B	0.8600
C15—O3	1.428 (5)	N3—N4	1.394 (4)
C15—H15A	0.9600	N3—H3B	0.8600
C15—H15B	0.9600	O1W—H1WA	0.8500
C15—H15C	0.9600	O1W—H1WB	0.8502
O5—Fe1—O2	91.94 (12)	C21—C16—H16A	120.1
O5—Fe1—O4	158.43 (11)	C16—C17—C18	120.2 (4)
O2—Fe1—O4	93.00 (12)	C16—C17—H17A	119.9
O5—Fe1—O1	92.26 (11)	C18—C17—H17A	119.9
O2—Fe1—O1	159.12 (11)	C17—C18—C19	120.2 (4)
O4—Fe1—O1	90.57 (11)	C17—C18—H18A	119.9
O5—Fe1—N2	108.53 (12)	C19—C18—H18A	119.9
O2—Fe1—N2	84.74 (11)	C18—C19—C20	120.3 (4)
O4—Fe1—N2	92.83 (11)	C18—C19—H19A	119.9
O1—Fe1—N2	74.54 (11)	C20—C19—H19A	119.9
O5—Fe1—N4	84.04 (11)	C21—C20—C19	119.8 (4)
O2—Fe1—N4	111.65 (11)	C21—C20—H20A	120.1
O4—Fe1—N4	74.63 (11)	C19—C20—H20A	120.1
O1—Fe1—N4	89.13 (11)	C20—C21—C16	119.9 (4)
N2—Fe1—N4	159.46 (12)	C20—C21—C22	118.4 (4)
C2—C1—C6	118.9 (4)	C16—C21—C22	121.7 (4)
C2—C1—H1A	120.5	O4—C22—N3	118.8 (4)
C6—C1—H1A	120.5	O4—C22—C21	120.9 (3)
C3—C2—C1	120.9 (4)	N3—C22—C21	120.3 (3)
C3—C2—H2A	119.6	N4—C23—C24	123.6 (3)
C1—C2—H2A	119.6	N4—C23—H23A	118.2
C4—C3—C2	121.0 (4)	C24—C23—H23A	118.2
C4—C3—H3A	119.5	C25—C24—C29	119.5 (4)
C2—C3—H3A	119.5	C25—C24—C23	122.4 (3)
C5—C4—C3	119.3 (4)	C29—C24—C23	118.1 (3)
C5—C4—H4A	120.3	O5—C25—C24	123.5 (4)

C3—C4—H4A	120.3	O5—C25—C26	118.4 (3)
C4—C5—C6	120.9 (4)	C24—C25—C26	118.1 (3)
C4—C5—H5A	119.5	O6—C26—C27	125.5 (4)
C6—C5—H5A	119.5	O6—C26—C25	114.2 (3)
C5—C6—C1	118.9 (4)	C27—C26—C25	120.3 (4)
C5—C6—C7	118.2 (4)	C26—C27—C28	120.6 (4)
C1—C6—C7	122.8 (4)	C26—C27—H27A	119.7
O1—C7—N1	120.0 (4)	C28—C27—H27A	119.7
O1—C7—C6	120.3 (3)	C29—C28—C27	121.0 (4)
N1—C7—C6	119.8 (4)	C29—C28—H28A	119.5
N2—C8—C9	124.2 (4)	C27—C28—H28A	119.5
N2—C8—H8A	117.9	C28—C29—C24	120.5 (4)
C9—C8—H8A	117.9	C28—C29—H29A	119.8
C10—C9—C14	119.3 (4)	C24—C29—H29A	119.8
C10—C9—C8	123.0 (3)	O6—C30—H30A	109.5
C14—C9—C8	117.7 (4)	O6—C30—H30B	109.5
O2—C10—C9	122.9 (3)	H30A—C30—H30B	109.5
O2—C10—C11	118.8 (4)	O6—C30—H30C	109.5
C9—C10—C11	118.3 (3)	H30A—C30—H30C	109.5
O3—C11—C12	125.1 (4)	H30B—C30—H30C	109.5
O3—C11—C10	114.3 (3)	C7—N1—N2	114.4 (3)
C12—C11—C10	120.6 (4)	C7—N1—H1B	122.8
C13—C12—C11	120.6 (4)	N2—N1—H1B	122.8
C13—C12—H12A	119.7	C8—N2—N1	117.5 (3)
C11—C12—H12A	119.7	C8—N2—Fe1	129.2 (3)
C14—C13—C12	120.3 (4)	N1—N2—Fe1	113.2 (2)
C14—C13—H13A	119.8	C22—N3—N4	115.3 (3)
C12—C13—H13A	119.8	C22—N3—H3B	122.4
C13—C14—C9	120.8 (4)	N4—N3—H3B	122.4
C13—C14—H14A	119.6	C23—N4—N3	117.7 (3)
C9—C14—H14A	119.6	C23—N4—Fe1	129.1 (3)
O3—C15—H15A	109.5	N3—N4—Fe1	112.6 (2)
O3—C15—H15B	109.5	C7—O1—Fe1	117.7 (2)
H15A—C15—H15B	109.5	H1WA—O1W—H1WB	121.9
O3—C15—H15C	109.5	C10—O2—Fe1	135.8 (3)
H15A—C15—H15C	109.5	C11—O3—C15	118.2 (3)
H15B—C15—H15C	109.5	C22—O4—Fe1	118.6 (2)
C17—C16—C21	119.7 (4)	C25—O5—Fe1	135.6 (2)
C17—C16—H16A	120.1	C26—O6—C30	118.0 (3)

Hydrogen-bond geometry (Å, °)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
N1—H1B···Cl1^{i}	0.86	2.25	3.087 (3)	163
N3—H3B···O1W	0.86	1.92	2.759 (4)	164
O1W—H1WA···O5^{ii}	0.85	2.39	3.045 (4)	134
O1W—H1WB···Cl1	0.85	2.37	3.198 (3)	163

Symmetry codes: (i) *x*−1, *y*, *z*; (ii) −*x*+1, −*y*+1, −*z*+2.

Fig. 1

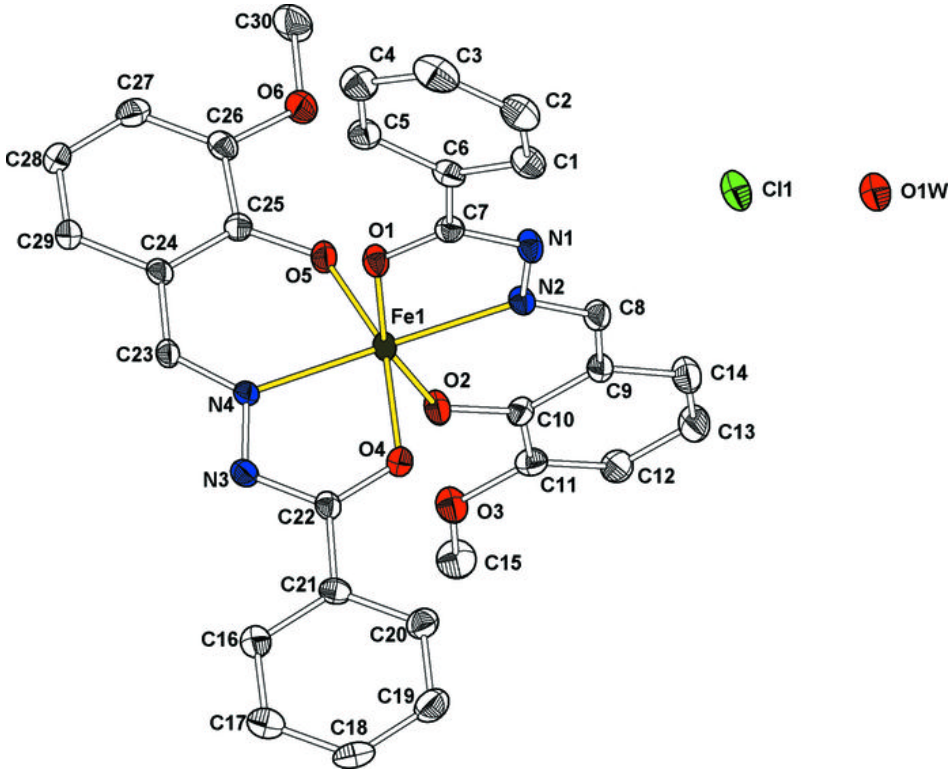
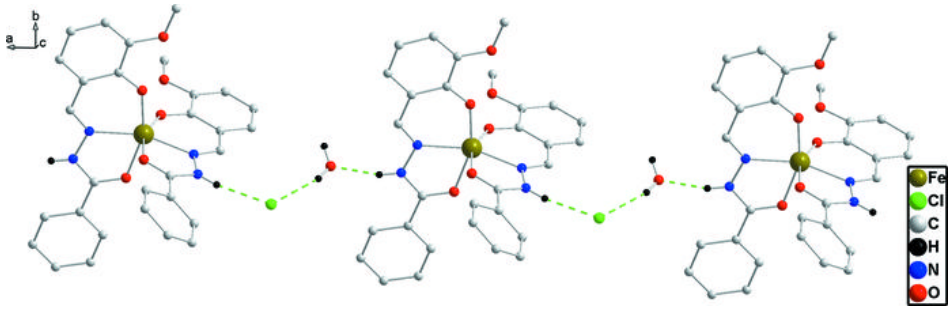

C30
C4
C3
C27
O6
C2
C26
C5
C28
C6
C1
Cl1
O1W
C25
C7
C29
C24
O1
N1
O5
N2
C8
Fe1
C23
C14
O2
C9
N4
C10
C13
O4
N3
C11
C12
C22
O3
C15
C21
C16
C20
C19
C17
C18

Fig. 2



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catena-Poly[[(4-methylbenzoato-κO)-manganese(II)]-μ-aqua-bis(μ-4-methylbenzoato-$\kappa^2 O:O'$)[(4-methylbenzoato-κO)manganese(II)]-bis(μ-*N*,*N*-diethylnicotinamide)-$\kappa^2 N^3:O;O:N^3$]

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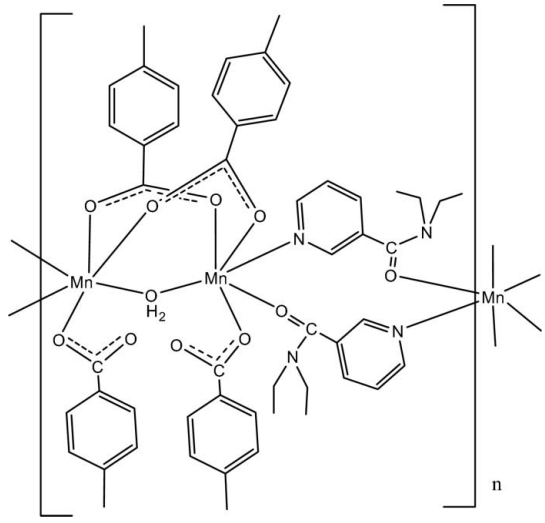
Key indicators: single-crystal X-ray study; T = 100 K; mean σ(C–C) = 0.003 Å; R factor = 0.042; wR factor = 0.102; data-to-parameter ratio = 19.3.

The asymmetric unit of the title complex, $[Mn_2(C_8H_7O_2)_4(C_{10}H_{14}N_2O)_2(H_2O)]_n$, contains two crystallographically independent units. In each one, the Mn^{II} ions are bridged by two 4-methylbenzoate (PMB) ligands and one water molecule. In the crystal structure, each Mn^{II} ion is coordinated by three PMB ligands, one water molecule and two symmetry-related *N*,*N*-diethylnicotinamide (DENA) ligands. Symmetry-related Mn^{II} ions are bridged by the N and O atoms of symmetry-related DENA ligands, forming polymeric chains parallel to [100]. The coordination environmnts for the Mn^{II} ions are slightly distorted octahedral. Intramolecular O—H···O hydrogen bonds link bridging water molecules to the carboxylate O atoms of a neighboring polymeric chain. In the crystal structure, π–π contacts between benzene rings [centroid–centroid distance = 3.562 (1) Å] and weak C—H···π interactions are also observed.

Related literature

For applications of transition-metal complexes with biochemically relevant ligands in biological systems, see: Antolini *et al.* (1982); Krishnamachari (1974). For the use of 4-aminobenzoic acids in coordination chemistry, see: Amiraslanov *et al.* (1979); Chen & Chen (2002); Hauptmann *et al.* (2000). *N*,*N*-Diethylnicotinamide (DENA) is an important respiratory stimulant, see: Bigoli *et al.* (1972). For structure–function–coordination relationships of the arylcarboxylate ion in Mn^{II} complexes of benzoic acid derivatives, see: Adiwidjaja *et al.* (1978); Antsyshkina *et al.* (1980); Catterick *et al.* (1974); Shnulin *et al.* (1981). For related structures, see: Hökelek *et al.* (2009*a*,*b*).



Experimental

Crystal data

$[Mn_2(C_8H_7O_2)_4(C_{10}H_{14}N_2O)_2(H_2O)]$
M_r = 1024.90
Triclinic, $P\overline{1}$
a = 10.5228 (2) Å
b = 19.1361 (3) Å
c = 26.6008 (4) Å
α = 70.537 (2)°
β = 78.836 (3)°
γ = 88.485 (3)°
V = 4950.63 (17) Å^3
Z = 4
Mo $K\alpha$ radiation
μ = 0.57 mm^{-1}
T = 100 K
0.35 × 0.24 × 0.15 mm

Data collection

Bruker Kappa APEXII CCD area-detector diffractometer
Absorption correction: multi-scan (*SADABS*; Bruker, 2005)
T_{min} = 0.848, T_{max} = 0.917
87669 measured reflections
24563 independent reflections
17121 reflections with $I > 2\sigma(I)$
R_{int} = 0.049

Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.042
$wR(F^2)$ = 0.102
S = 1.02
24563 reflections
1275 parameters
1 restraint
H atoms treated by a mixture of independent and constrained refinement
$\Delta\rho_{max}$ = 0.40 e Å^{-3}
$\Delta\rho_{min}$ = −0.51 e Å^{-3}

Table 1
Hydrogen-bond geometry (Å, °).

*Cg*1, *Cg*5, *Cg*10 and *Cg*12 are the centroids of the C2–C7, N1/C33–C37, C78–C83 and N6/C90–C94 rings, respectively.

D—H···A	D—H	H···A	D···A	D—H···A
O9—H9*A*···O7	0.94 (3)	1.62 (3)	2.552 (2)	170 (3)
O9—H9*B*···O5	0.94 (2)	1.59 (2)	2.520 (2)	173 (3)
O22—H22*A*···O16	0.92 (3)	1.64 (3)	2.544 (2)	166 (2)
O22—H22*B*···O18	0.97 (4)	1.60 (4)	2.558 (2)	169 (3)
C52—H52*A*···*Cg*12^{i}	0.96	2.87	3.782 (3)	160
C60—H60*C*···*Cg*1^{ii}	0.96	2.99	3.841 (3)	149
C84—H84*B*···*Cg*10^{iii}	0.96	2.88	3.609 (3)	134
C104—H10*E*···*Cg*5^{iv}	0.96	2.82	3.709 (3)	155

Symmetry codes: (i) $x+1, y, z$; (ii) $-x, -y, -z+1$; (iii) $-x+1, -y, -z+1$; (iv) $x-1, y, z$.

Data collection: *APEX2* (Bruker, 2007); cell refinement: *SAINT* (Bruker, 2007); data reduction: *SAINT*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *Mercury* (Macrae *et al.*, 2006); software used to prepare material for publication: *WinGX* (Farrugia, 1999) and *PLATON* (Spek, 2009).

The authors are indebted to Anadolu University and the Medicinal Plants and Medicine Research Centre of Anadolu University for the use of the diffractometer. This work was supported financially by Kafkas University Research Fund (grant No. 2009-FEF-03).

Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: IM2201).

References

Adiwidjaja, G., Rossmanith, E. & Küppers, H. (1978). *Acta Cryst.* B**34**, 3079–3083.
Amiraslanov, I. R., Mamedov, Kh. S., Movsumov, E. M., Musaev, F. N. & Nadzhafov, G. N. (1979). *Zh. Strukt. Khim.* **20**, 1075–1080.
Antolini, L., Battaglia, L. P., Corradi, A. B., Marcotrigiano, G., Menabue, L., Pellacani, G. C. & Saladini, M. (1982). *Inorg. Chem.* **21**, 1391–1395.
Antsyshkina, A. S., Chiragov, F. M. & Poray-Koshits, M. A. (1980). *Koord. Khim.* **15**, 1098–1103.
Bigoli, F., Braibanti, A., Pellinghelli, M. A. & Tiripicchio, A. (1972). *Acta Cryst.* B**28**, 962–966.
Bruker (2005). *SADABS*. Bruker AXS Inc., Madison, Wisconsin, USA.
Bruker (2007). *APEX2* and *SAINT*. Bruker AXS Inc., Madison, Wisconsin, USA.
Catterick, J., Hursthouse, M. B., New, D. B. & Thorhton, P. (1974). *J. Chem. Soc. Chem. Commun.* pp. 843–844.
Chen, H. J. & Chen, X. M. (2002). *Inorg. Chim. Acta*, **329**, 13–21.
Farrugia, L. J. (1999). *J. Appl. Cryst.* **32**, 837–838.
Hauptmann, R., Kondo, M. & Kitagawa, S. (2000). *Z. Kristallogr. New Cryst. Struct.* **215**, 169–172.
Hökelek, T., Dal, H., Tercan, B., Aybirdi, Ö. & Necefoğlu, H. (2009*a*). *Acta Cryst.* E**65**, m747–m748.
Hökelek, T., Yılmaz, F., Tercan, B., Sertçelik, M. & Necefoğlu, H. (2009*b*). *Acta Cryst.* E**65**, m1399–m1400.
Krishnamachari, K. A. V. R. (1974). *Am. J. Clin. Nutr.* **27**, 108–111.
Macrae, C. F., Edgington, P. R., McCabe, P., Pidcock, E., Shields, G. P., Taylor, R., Towler, M. & van de Streek, J. (2006). *J. Appl. Cryst.* **39**, 453–457.
Sheldrick, G. M. (2008). *Acta Cryst.* A**64**, 112–122.
Shnulin, A. N., Nadzhafov, G. N., Amiraslanov, I. R., Usubaliev, B. T. & Mamedov, Kh. S. (1981). *Koord. Khim.* **7**, 1409–1416.
Spek, A. L. (2009). *Acta Cryst.* D**65**, 148–155.

supplementary materials

Acta Cryst. (2010). E**66**, m734-m735 [**doi:10.1107/S1600536810020076**]

catena-Poly[[(4-methylbenzoato-κO)manganese(II)]-μ-aqua-bis(μ-4-methylbenzoato-$\kappa^2 O$:O')[(4-methylbenzoato-κO)manganese(II)]-bis(μ-*N*,*N*-diethylnicotinamide)-$\kappa^2 N^3$:O;O:N^3]

T. Hökelek, H. Dal, B. Tercan, E. Çimen and H. Necefoglu

Comment

Transition metal complexes with biochemicaly relevant ligands show interesting physical and/or chemical properties, through which they may find applications in biological systems (Antolini *et al.*, 1982). Some benzoic acid derivatives, such as 4-aminobenzoic acid, have been extensively reported in coordination chemistry as bifunctional organic ligands due to the varieties of their coordination modes (Chen & Chen, 2002; Amiraslanov *et al.*, 1979; Hauptmann *et al.*, 2000). Nicotinamide (NA) is one form of niacin. A deficiency of this vitamin leads to loss of copper from the body, known as pellagra disease. Victims of pellagra show unusually high serum and urinary copper levels (Krishnamachari, 1974). The nicotinic acid derivative *N*,*N*-Diethylnicotinamide (DENA) is an important respiratory stimulant (Bigoli *et al.*, 1972).

The structure-function-coordination relationships of arylcarboxylate ions in Mn^{II} complexes of benzoic acid derivatives may also change depending on the nature and position of the substituted groups on the benzene ring, the nature of the additional ligand molecule or solvent, and the pH and temperature of synthesis (Shnulin *et al.*, 1981; Antsyshkina *et al.*, 1980; Adiwidjaja *et al.*, 1978). When pyridine and its derivatives are used instead of water molecules, the structure is completely different (Catterick *et al.*, 1974). The title complex, (I), was synthesized and its crystal structure is reported herein.

The asymmetric unit of the title complex, (I), contains two crystallographically independent moieties. In each moiety, Mn^{II} ions are bridged by two 4-methylbenzoate (PMB) ligands and one water molecule. In the crystal structure of the title complex, each Mn^{II} ion is coordinated by three PMB ligands, one water molecule and two symmetry related DENA ligands. Symmetry related Mn^{II} ions are bridged by the N and O atoms of symmetry related DENA ligands forming polymeric chains (Fig. 1).

Coordination spheres around Mn1 and Mn2 (corresponding to Mn3 and Mn4 in the second moiety) are different. In the octahedron around Mn1 the nitrogen atom of a DENA ligand is in *trans*-position with respect to the bridging water ligand. The monodentate 4-methylbenzoate oxygen and another oxygen from the DENA ligand are *trans* to the bridging 4-methylbenzoate ligands. Around Mn2 bridging 4-methylbenzoate ligands are *trans* with respect to a DENA nitrogen atom and an oxygen from a another monodentate 4-methylbenzoate ligand.

Atoms (O2, O3, O8, O10), (O1, O4, O6, N1''), (O13, O15, O17, O21) and (O12, O14, O19, N6') in the equatorial planes around Mn1, Mn2, Mn3 and Mn4, respectively, form slightly distorted square-planar arrangements, while the slightly distorted octahedral coordinations are completed by the atoms (O9, N2), (O9, O11''), (O22, N5'') and (O20, O22) in the axial positions (Table 1 and Fig. 1) [symmetry codes:(') 1 + x, y, z, ('') x - 1, y, z]. The structures of similar Mn^{II} and Zn(II) polymeric complexes $\{[Mn(C_{11}H_{14}NO_2)_2(H_2O)_3].2H_2O\}_n$ (Hökelek *et al.*, 2009a) and $[Zn(C_8H_5O_3)_2(C_6H_6N_2O)]_n$ (Hökelek *et al.*, 2009b) have also been determined.

The average Mn—O bond length (Table 1) is 2.1699 (14) Å and Mn atoms are displaced out of the least-squares planes of the carboxylate groups: Mn1 atom for (O1/C1/O2), (O3/C9/O4) and (O7/C25/O8) by 0.3349 (3), 0.2642 (4) and -0.5844 (4) Å, respectively, Mn2 atom for (O1/C1/O2), (O3/C9/O4) and (O5/C17/O6) by -0.0412 (3), 0.4940 (4) and 0.1143 (3) Å, respectively, Mn3 atom for (O12/C53/O13), (O14/C61/O15) and (O16/C69/O17) by 0.3463 (4), -0.2062 (3) and 0.2611 (4) Å, respectively, and Mn4 atom for (O12/C53/O13), (O14/C61/O15) and (O18/C77/O19) by 0.6423 (4), 0.0305 (3) and 0.3320 (3) Å, respectively. The dihedral angles between the planar carboxylate groups and the adjacent benzene rings A (C2—C7), B (C10—C15), C (C18—C23), D (C26—C31), G (C54—C59), H (C62—C67), I (C70—C75) and J (C78—C83) are 13.35 (16), 10.82 (12), 7.48 (15), 7.33 (9), 11.86 (10), 11.42 (10), 6.68 (18) and 1.79 (11) °, respectively, while those between rings A, B, C, D, E (N1/C33—C37), F (N2/C38—C42) and G, H, I, J, K (N5/C86—C89), L (N6/C90—C94) are A/B = 64.86 (7), A/C = 35.09 (7), A/D = 63.93 (9), B/C = 83.44 (7), B/D = 22.10 (8), C/D = 87.56 (8), E/F = 33.93 (6) ° and G/H = 60.41 (6), G/I = 14.54 (8), G/J = 62.80 (7), H/I = 68.14 (7), H/J = 23.40 (7), I/J = 75.02 (8), K/L = 43.80 (8) °.

Intramolecular O—H···O hydrogen bonds (Table 1) link bridging water molecules to carboxylate O atoms of neighboring polymeric chains. In the crystal structure, π–π contacts between the benzene rings, Cg3—$Cg3^{i}$ with a centroid-centroid distance of 3.562 (1) Å [symmetry code: (i) -x, 1 - y, -z, where Cg3 is the centroid of the ring C (C18—C23)] and four weak C—H···π interactions are also observed (Table 1).

Experimental

The title compound was prepared by the reaction of $MnSO_4.H_2O$ (0.84 g, 5 mmol) in H_2O (10 ml) and DENA (1.78 g, 10 mmol) in H_2O (10 ml) with sodium 4-methylbenzoate (1.58 g, 10 mmol) in H_2O (150 ml). The mixture was filtered and set aside to crystallize at ambient temperature for one week, giving colorless single crystals (yield 2.05 g, 40.02 %).

Refinement

Atoms H9A, H9B, H22A and H22B (for water molecules) were located in difference Fourier maps and refined isotropically, with restrain of O9—H9B = 0.937 (18) Å. [U_{iso}(H) = 0.046 (8), 0.069 (11), 0.035 (7) and 0.081 (12) $Å^2$ for H9A, H9B, H22A and H22B, respectively]. The remaining H atoms were positioned geometrically with C—H = 0.93, 0.97 and 0.96 Å for aromatic, methylene and methyl H atoms, respectively, and constrained to ride on their parent atoms, with U_{iso}(H) = xU_{eq}(C), where x = 1.5 for methyl H and x = 1.2 for all other H atoms.

Figures

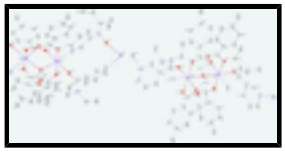


Fig. 1. The molecular structure of the title molecule with the atom-numbering scheme. Displacement ellipsoids are drawn at the 35% probability level. Hydrogen bonds are shown as dashed lines. Hydrogen atoms not involved in hydrogen bonding are omitted for clarity. Primed atoms are generated by the symmetry operators:(') 1 + x, y, z, (") x - 1, y, z.

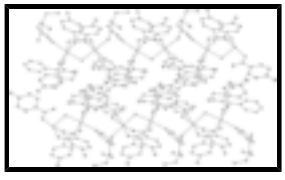


Fig. 2. Part of the polymeric chains of the title compound.

catena-Poly[[(4-methylbenzoato-κ_O_)manganese(II)]-μ-aqua- bis(μ-4-methylbenzoato-κ^2_O_:_O_^{1})[(4-methylbenzoato- κ_O_)manganese(II)]-bis(μ-_N_,_N_-diethylnicotinamide)- κ^2_N_^{3}:_O_;_O_:_N_^{3}]

Crystal data

$[Mn_2(C_8H_7O_2)_4(C_{10}H_{14}N_2O)_2(H_2O)]$	$Z = 4$
$M_r = 1024.90$	$F(000) = 2144$
Triclinic, $P\overline{1}$	$D_x = 1.375$ Mg m^{-3}
Hall symbol: -P 1	Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å
$a = 10.5228$ (2) Å	Cell parameters from 9867 reflections
$b = 19.1361$ (3) Å	$\theta = 2.3$–$28.0°$
$c = 26.6008$ (4) Å	$\mu = 0.57$ mm^{-1}
$\alpha = 70.537$ (2)°	$T = 100$ K
$\beta = 78.836$ (3)°	Block, colorless
$\gamma = 88.485$ (3)°	0.35 × 0.24 × 0.15 mm
$V = 4950.63$ (17) Å^3	

Data collection

Bruker Kappa APEXII CCD area-detector diffractometer	24563 independent reflections
Radiation source: fine-focus sealed tube	17121 reflections with $I > 2\sigma(I)$
graphite	$R_{int} = 0.049$
φ and ω scans	$\theta_{max} = 28.4°$, $\theta_{min} = 1.7°$
Absorption correction: multi-scan (*SADABS*; Bruker, 2005)	$h = -14 \rightarrow 14$
$T_{min} = 0.848$, $T_{max} = 0.917$	$k = -25 \rightarrow 25$
87669 measured reflections	$l = -35 \rightarrow 35$

Refinement

Refinement on F^2	Primary atom site location: structure-invariant direct methods
Least-squares matrix: full	Secondary atom site location: difference Fourier map
$R[F^2 > 2\sigma(F^2)] = 0.042$	Hydrogen site location: inferred from neighbouring sites
$wR(F^2) = 0.102$	H atoms treated by a mixture of independent and constrained refinement
$S = 1.02$	$w = 1/[\sigma^2(F_o^2) + (0.0376P)^2 + 2.5004P]$ where $P = (F_o^2 + 2F_c^2)/3$
24563 reflections	$(\Delta/\sigma)_{max} = 0.001$
1275 parameters	$\Delta\rho_{max} = 0.40$ e Å^{-3}
1 restraint	$\Delta\rho_{min} = -0.51$ e Å^{-3}

Special details

Geometry. All esds (except the esd in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell esds are taken into account individually in the estimation of esds in distances, angles and torsion angles; correlations between esds in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell esds is used for estimating esds involving l.s. planes.

Refinement. Refinement of F^2 against ALL reflections. The weighted *R*-factor wR and goodness of fit *S* are based on F^2, conventional *R*-factors *R* are based on *F*, with *F* set to zero for negative F^2. The threshold expression of $F^2 > \sigma(F^2)$ is used only for calculating *R*-factors(gt) etc. and is not relevant to the choice of reflections for refinement. *R*-factors based on F^2 are statistically about twice as large as those based on *F*, and *R*- factors based on ALL data will be even larger.

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å^2)

	x	*y*	*z*	U_{iso}*/U_{eq}
Mn1	0.29102 (3)	0.092307 (17)	0.156751 (12)	0.01457 (7)
Mn2	−0.02201 (3)	0.133661 (17)	0.112030 (12)	0.01425 (7)
Mn3	0.20220 (3)	0.461244 (17)	0.326281 (12)	0.01420 (7)
Mn4	0.51449 (3)	0.407633 (17)	0.366892 (12)	0.01429 (7)
O1	−0.00798 (14)	0.01586 (8)	0.14766 (6)	0.0216 (3)
O2	0.19077 (14)	−0.00928 (8)	0.16623 (6)	0.0215 (3)
O3	0.32961 (14)	0.13578 (8)	0.06967 (6)	0.0203 (3)
O4	0.13544 (14)	0.15161 (8)	0.04538 (6)	0.0210 (3)
O5	0.10170 (14)	0.28937 (8)	0.11920 (6)	0.0223 (3)
O6	−0.05798 (14)	0.25125 (8)	0.08837 (6)	0.0191 (3)
O7	0.05950 (15)	0.08986 (9)	0.26520 (6)	0.0245 (3)
O8	0.26278 (14)	0.05493 (9)	0.24495 (6)	0.0220 (3)
O9	0.11046 (14)	0.15084 (8)	0.16200 (6)	0.0164 (3)
H9A	0.085 (3)	0.1322 (15)	0.1999 (12)	0.046 (8)*
H9B	0.112 (3)	0.2027 (10)	0.1476 (13)	0.069 (11)*
O10	0.40261 (14)	0.18976 (8)	0.15298 (6)	0.0210 (3)
O11	−0.15129 (14)	0.11306 (8)	0.06165 (6)	0.0183 (3)
O12	0.35950 (14)	0.37541 (9)	0.43431 (6)	0.0217 (3)
O13	0.16363 (14)	0.39528 (8)	0.41208 (6)	0.0193 (3)
O14	0.49611 (14)	0.52498 (8)	0.34726 (6)	0.0222 (3)
O15	0.30051 (14)	0.55792 (8)	0.32796 (6)	0.0205 (3)
O16	0.42449 (14)	0.47310 (9)	0.21309 (6)	0.0236 (3)
O17	0.22779 (14)	0.51251 (8)	0.23789 (6)	0.0217 (3)
O18	0.38854 (15)	0.25966 (8)	0.35204 (6)	0.0243 (4)
O19	0.55809 (14)	0.29317 (8)	0.37939 (6)	0.0207 (3)
O20	0.65101 (13)	0.41069 (8)	0.41920 (6)	0.0187 (3)
O21	0.08786 (14)	0.37412 (8)	0.31793 (6)	0.0217 (3)
O22	0.37934 (14)	0.40100 (9)	0.31456 (6)	0.0160 (3)
H22A	0.406 (2)	0.4217 (14)	0.2775 (11)	0.035 (7)*
H22B	0.374 (3)	0.347 (2)	0.3269 (14)	0.081 (12)*
N1	−0.20574 (17)	0.12154 (10)	0.17872 (7)	0.0171 (4)
N2	0.47393 (17)	0.02732 (10)	0.14640 (7)	0.0172 (4)
N3	0.83418 (17)	0.05090 (10)	0.00421 (7)	0.0181 (4)

N4	0.45429 (17)	0.27187 (10)	0.19043 (7)	0.0195 (4)
N5	0.01818 (16)	0.51791 (10)	0.35032 (7)	0.0166 (4)
N6	0.68991 (16)	0.43439 (9)	0.29721 (7)	0.0168 (4)
N7	0.65443 (17)	0.44424 (10)	0.49232 (7)	0.0193 (4)
N8	0.03462 (17)	0.29462 (10)	0.27868 (7)	0.0179 (4)
C1	0.0784 (2)	−0.02758 (12)	0.16489 (8)	0.0169 (4)
C2	0.0427 (2)	−0.10932 (11)	0.18415 (8)	0.0169 (4)
C3	−0.0853 (2)	−0.13269 (12)	0.19115 (8)	0.0186 (4)
H3	−0.1495	−0.0980	0.1870	0.022*
C4	−0.1182 (2)	−0.20697 (12)	0.20415 (9)	0.0208 (5)
H4	−0.2045	−0.2217	0.2088	0.025*
C5	−0.0241 (2)	−0.25999 (12)	0.21033 (9)	0.0208 (5)
C6	0.1028 (2)	−0.23687 (12)	0.20604 (9)	0.0216 (5)
H6	0.1662	−0.2718	0.2120	0.026*
C7	0.1363 (2)	−0.16242 (12)	0.19306 (9)	0.0201 (5)
H7	0.2218	−0.1479	0.1903	0.024*
C8	−0.0587 (2)	−0.33925 (12)	0.21777 (10)	0.0281 (5)
H8A	0.0082	−0.3707	0.2316	0.042*
H8B	−0.0667	−0.3431	0.1834	0.042*
H8C	−0.1395	−0.3545	0.2431	0.042*
C9	0.2572 (2)	0.15832 (11)	0.03538 (8)	0.0165 (4)
C10	0.3218 (2)	0.19464 (11)	−0.02273 (8)	0.0171 (4)
C11	0.2489 (2)	0.23152 (12)	−0.06148 (9)	0.0210 (5)
H11	0.1593	0.2321	−0.0513	0.025*
C12	0.3087 (2)	0.26728 (13)	−0.11504 (9)	0.0248 (5)
H12	0.2587	0.2920	−0.1403	0.030*
C13	0.4422 (2)	0.26688 (12)	−0.13162 (9)	0.0233 (5)
C14	0.5145 (2)	0.22896 (13)	−0.09326 (9)	0.0238 (5)
H14	0.6037	0.2270	−0.1037	0.029*
C15	0.4551 (2)	0.19386 (12)	−0.03941 (9)	0.0201 (5)
H15	0.5054	0.1695	−0.0142	0.024*
C16	0.5066 (3)	0.30636 (14)	−0.18978 (9)	0.0347 (6)
H16A	0.4432	0.3328	−0.2097	0.052*
H16B	0.5447	0.2708	−0.2059	0.052*
H16C	0.5728	0.3407	−0.1909	0.052*
C17	0.0039 (2)	0.30073 (11)	0.09722 (8)	0.0171 (4)
C18	−0.0438 (2)	0.37802 (12)	0.08131 (8)	0.0178 (4)
C19	−0.1414 (2)	0.39756 (13)	0.05159 (10)	0.0274 (5)
H19	−0.1782	0.3622	0.0412	0.033*
C20	−0.1848 (2)	0.46928 (13)	0.03717 (10)	0.0298 (5)
H20	−0.2504	0.4813	0.0172	0.036*
C21	−0.1322 (2)	0.52330 (13)	0.05200 (9)	0.0260 (5)
C22	−0.0330 (2)	0.50357 (13)	0.08122 (10)	0.0281 (5)
H22	0.0050	0.5391	0.0911	0.034*
C23	0.0104 (2)	0.43205 (12)	0.09590 (9)	0.0231 (5)
H23	0.0764	0.4200	0.1157	0.028*
C24	−0.1783 (2)	0.60127 (13)	0.03638 (11)	0.0342 (6)
H24A	−0.1075	0.6352	0.0311	0.051*
H24B	−0.2463	0.6057	0.0648	0.051*

H24C	−0.2105	0.6127	0.0033	0.051*
C25	0.1568 (2)	0.05343 (12)	0.27750 (9)	0.0187 (4)
C26	0.1452 (2)	0.00386 (12)	0.33574 (9)	0.0204 (5)
C27	0.0350 (2)	0.00399 (14)	0.37437 (9)	0.0300 (5)
H27	−0.0304	0.0362	0.3645	0.036*
C28	0.0225 (3)	−0.04345 (15)	0.42726 (10)	0.0391 (7)
H28	−0.0509	−0.0419	0.4527	0.047*
C29	0.1168 (3)	−0.09347 (14)	0.44339 (10)	0.0361 (7)
C30	0.2254 (3)	−0.09338 (14)	0.40479 (11)	0.0367 (7)
H30	0.2900	−0.1264	0.4146	0.044*
C31	0.2404 (2)	−0.04492 (13)	0.35141 (10)	0.0281 (5)
H31	0.3150	−0.0455	0.3263	0.034*
C32	0.0996 (3)	−0.14617 (17)	0.50102 (11)	0.0553 (9)
H32A	0.0816	−0.1187	0.5257	0.083*
H32B	0.1775	−0.1726	0.5060	0.083*
H32C	0.0286	−0.1808	0.5080	0.083*
C33	−0.2241 (2)	0.07042 (11)	0.22842 (9)	0.0183 (4)
H33	−0.1566	0.0398	0.2383	0.022*
C34	−0.3392 (2)	0.06135 (12)	0.26569 (9)	0.0214 (5)
H34	−0.3481	0.0256	0.3000	0.026*
C35	−0.4409 (2)	0.10575 (12)	0.25143 (9)	0.0199 (5)
H35	−0.5198	0.0997	0.2756	0.024*
C36	−0.42287 (19)	0.15955 (11)	0.20030 (8)	0.0155 (4)
C37	−0.30381 (19)	0.16563 (11)	0.16559 (8)	0.0161 (4)
H37	−0.2914	0.2021	0.1315	0.019*
C38	0.4733 (2)	−0.04641 (12)	0.17108 (9)	0.0190 (4)
H38	0.4031	−0.0693	0.1985	0.023*
C39	0.5722 (2)	−0.08989 (12)	0.15759 (9)	0.0213 (5)
H39	0.5682	−0.1408	0.1756	0.026*
C40	0.6768 (2)	−0.05651 (12)	0.11698 (9)	0.0211 (5)
H40	0.7433	−0.0848	0.1066	0.025*
C41	0.6813 (2)	0.02013 (11)	0.09173 (8)	0.0164 (4)
C42	0.5773 (2)	0.05918 (11)	0.10813 (8)	0.0160 (4)
H42	0.5799	0.1104	0.0915	0.019*
C43	0.79495 (19)	0.06378 (11)	0.05116 (8)	0.0159 (4)
C44	0.7643 (2)	0.00135 (13)	−0.01427 (9)	0.0240 (5)
H44A	0.7213	−0.0388	0.0173	0.029*
H44B	0.8267	−0.0203	−0.0362	0.029*
C45	0.6646 (2)	0.03952 (14)	−0.04705 (10)	0.0317 (6)
H45A	0.6249	0.0046	−0.0587	0.047*
H45B	0.7061	0.0796	−0.0783	0.047*
H45C	0.5995	0.0586	−0.0250	0.047*
C46	0.9449 (2)	0.09632 (12)	−0.03440 (9)	0.0228 (5)
H46A	0.9768	0.0736	−0.0618	0.027*
H46B	1.0140	0.0968	−0.0151	0.027*
C47	0.9114 (2)	0.17535 (13)	−0.06227 (10)	0.0287 (5)
H47A	0.9843	0.2008	−0.0896	0.043*
H47B	0.8905	0.2002	−0.0359	0.043*
H47C	0.8383	0.1753	−0.0789	0.043*

C48	0.47036 (19)	0.20863 (12)	0.18015 (8)	0.0162 (4)
C49	0.3529 (2)	0.32107 (13)	0.16928 (10)	0.0244 (5)
H49A	0.3339	0.3552	0.1895	0.029*
H49B	0.2745	0.2913	0.1756	0.029*
C50	0.3893 (2)	0.36527 (14)	0.10934 (10)	0.0342 (6)
H50A	0.3243	0.4005	0.0993	0.051*
H50B	0.3954	0.3323	0.0886	0.051*
H50C	0.4714	0.3911	0.1020	0.051*
C51	0.5357 (2)	0.29619 (13)	0.22146 (9)	0.0248 (5)
H51A	0.5711	0.2529	0.2448	0.030*
H51B	0.4816	0.3197	0.2446	0.030*
C52	0.6457 (2)	0.34963 (14)	0.18583 (11)	0.0342 (6)
H52A	0.6961	0.3623	0.2082	0.051*
H52B	0.6113	0.3937	0.1639	0.051*
H52C	0.6997	0.3268	0.1627	0.051*
C53	0.2385 (2)	0.36444 (11)	0.44399 (8)	0.0167 (4)
C54	0.1792 (2)	0.31129 (11)	0.49916 (8)	0.0170 (4)
C55	0.0468 (2)	0.30495 (12)	0.51870 (9)	0.0204 (5)
H55	−0.0082	0.3327	0.4968	0.024*
C56	−0.0045 (2)	0.25787 (13)	0.57045 (9)	0.0240 (5)
H56	−0.0938	0.2550	0.5829	0.029*
C57	0.0741 (2)	0.21472 (12)	0.60428 (9)	0.0238 (5)
C58	0.2070 (2)	0.21989 (12)	0.58382 (9)	0.0232 (5)
H58	0.2618	0.1908	0.6052	0.028*
C59	0.2591 (2)	0.26750 (12)	0.53229 (9)	0.0219 (5)
H59	0.3483	0.2703	0.5196	0.026*
C60	0.0182 (3)	0.16500 (14)	0.66114 (10)	0.0340 (6)
H60A	0.0653	0.1203	0.6696	0.051*
H60B	−0.0713	0.1529	0.6637	0.051*
H60C	0.0250	0.1901	0.6864	0.051*
C61	0.4106 (2)	0.57161 (12)	0.33415 (8)	0.0165 (4)
C62	0.4477 (2)	0.65083 (11)	0.32589 (8)	0.0158 (4)
C63	0.3573 (2)	0.70589 (12)	0.32052 (9)	0.0202 (5)
H63	0.2711	0.6941	0.3220	0.024*
C64	0.3946 (2)	0.77828 (12)	0.31296 (9)	0.0220 (5)
H64	0.3330	0.8145	0.3095	0.026*
C65	0.5228 (2)	0.79759 (12)	0.31052 (9)	0.0200 (5)
C66	0.6129 (2)	0.74237 (12)	0.31522 (9)	0.0202 (5)
H66	0.6992	0.7541	0.3134	0.024*
C67	0.5759 (2)	0.67020 (12)	0.32261 (8)	0.0183 (4)
H67	0.6378	0.6342	0.3254	0.022*
C68	0.5636 (2)	0.87545 (12)	0.30437 (10)	0.0278 (5)
H68A	0.5172	0.9104	0.2800	0.042*
H68B	0.6550	0.8835	0.2900	0.042*
H68C	0.5446	0.8821	0.3392	0.042*
C69	0.3274 (2)	0.51141 (12)	0.20306 (9)	0.0179 (4)
C70	0.3331 (2)	0.56018 (12)	0.14482 (8)	0.0190 (4)
C71	0.2283 (2)	0.60070 (12)	0.12891 (9)	0.0229 (5)
H71	0.1515	0.5965	0.1540	0.027*

C72	0.2373 (2)	0.64770 (13)	0.07557 (10)	0.0272 (5)
H72	0.1654	0.6738	0.0654	0.033*
C73	0.3505 (2)	0.65661 (13)	0.03725 (9)	0.0272 (5)
C74	0.4538 (2)	0.61449 (14)	0.05329 (9)	0.0304 (6)
H74	0.5302	0.6182	0.0280	0.036*
C75	0.4457 (2)	0.56714 (13)	0.10592 (9)	0.0255 (5)
H75	0.5166	0.5395	0.1155	0.031*
C76	0.3644 (3)	0.71158 (14)	−0.01987 (10)	0.0355 (6)
H76A	0.4412	0.7426	−0.0283	0.053*
H76B	0.2900	0.7418	−0.0223	0.053*
H76C	0.3709	0.6852	−0.0452	0.053*
C77	0.4867 (2)	0.24556 (12)	0.37353 (8)	0.0185 (4)
C78	0.5223 (2)	0.16569 (12)	0.39390 (9)	0.0198 (5)
C79	0.4467 (2)	0.11043 (12)	0.38984 (9)	0.0245 (5)
H79	0.3736	0.1228	0.3744	0.029*
C80	0.4790 (2)	0.03679 (13)	0.40862 (10)	0.0287 (5)
H80	0.4263	0.0004	0.4060	0.034*
C81	0.5883 (2)	0.01624 (13)	0.43122 (10)	0.0277 (5)
C82	0.6634 (3)	0.07218 (14)	0.43503 (11)	0.0346 (6)
H82	0.7368	0.0600	0.4503	0.042*
C83	0.6311 (2)	0.14594 (13)	0.41647 (10)	0.0289 (5)
H83	0.6833	0.1824	0.4193	0.035*
C84	0.6237 (3)	−0.06375 (13)	0.45167 (11)	0.0393 (7)
H84A	0.5581	−0.0947	0.4481	0.059*
H84B	0.6300	−0.0773	0.4892	0.059*
H84C	0.7055	−0.0702	0.4307	0.059*
C85	−0.08494 (19)	0.47597 (12)	0.38283 (8)	0.0156 (4)
H85	−0.0835	0.4250	0.3899	0.019*
C86	−0.19401 (19)	0.50452 (12)	0.40655 (8)	0.0159 (4)
C87	−0.1961 (2)	0.58115 (12)	0.39485 (9)	0.0196 (5)
H87	−0.2671	0.6026	0.4099	0.023*
C88	−0.0908 (2)	0.62472 (12)	0.36043 (9)	0.0211 (5)
H88	−0.0906	0.6760	0.3515	0.025*
C89	0.0139 (2)	0.59133 (12)	0.33947 (9)	0.0186 (4)
H89	0.0848	0.6211	0.3167	0.022*
C90	0.7032 (2)	0.48943 (11)	0.24927 (8)	0.0180 (4)
H90	0.6323	0.5181	0.2412	0.022*
C91	0.8177 (2)	0.50526 (12)	0.21137 (9)	0.0211 (5)
H91	0.8227	0.5434	0.1783	0.025*
C92	0.9247 (2)	0.46414 (12)	0.22288 (9)	0.0195 (4)
H92	1.0036	0.4752	0.1985	0.023*
C93	0.9114 (2)	0.40577 (11)	0.27179 (8)	0.0159 (4)
C94	0.79259 (19)	0.39322 (11)	0.30731 (8)	0.0160 (4)
H94	0.7838	0.3540	0.3400	0.019*
C95	0.69637 (19)	0.45079 (12)	0.44036 (8)	0.0160 (4)
C96	0.7140 (2)	0.48486 (13)	0.52104 (9)	0.0246 (5)
H96A	0.6495	0.4891	0.5512	0.030*
H96B	0.7400	0.5346	0.4963	0.030*
C97	0.8309 (2)	0.44791 (14)	0.54251 (10)	0.0290 (5)

H97A	0.8634	0.4759	0.5617	0.044*
H97B	0.8972	0.4460	0.5127	0.044*
H97C	0.8062	0.3984	0.5668	0.044*
C98	0.5546 (2)	0.38594 (13)	0.52469 (9)	0.0257 (5)
H98A	0.4857	0.3888	0.5046	0.031*
H98B	0.5175	0.3950	0.5582	0.031*
C99	0.6063 (2)	0.30848 (14)	0.53846 (10)	0.0317 (6)
H99A	0.5389	0.2732	0.5620	0.048*
H99B	0.6779	0.3061	0.5564	0.048*
H99C	0.6348	0.2971	0.5056	0.048*
C100	0.01980 (19)	0.35729 (12)	0.29004 (8)	0.0156 (4)
C101	0.1292 (2)	0.24234 (12)	0.30289 (9)	0.0228 (5)
H10A	0.2107	0.2691	0.2970	0.027*
H10B	0.1446	0.2056	0.2848	0.027*
C102	0.0828 (2)	0.20352 (14)	0.36308 (10)	0.0324 (6)
H10H	0.1444	0.1678	0.3768	0.049*
H10I	0.0003	0.1787	0.3692	0.049*
H10J	0.0742	0.2393	0.3815	0.049*
C103	−0.0447 (2)	0.27293 (13)	0.24597 (9)	0.0232 (5)
H10C	0.0103	0.2505	0.2223	0.028*
H10D	−0.0790	0.3171	0.2231	0.028*
C104	−0.1561 (2)	0.21903 (13)	0.27990 (10)	0.0298 (6)
H10E	−0.2054	0.2081	0.2564	0.045*
H10F	−0.2109	0.2407	0.3036	0.045*
H10G	−0.1227	0.1741	0.3012	0.045*

Atomic displacement parameters (Å^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Mn1	0.01369 (16)	0.01606 (16)	0.01613 (16)	0.00008 (12)	−0.00361 (12)	−0.00779 (13)
Mn2	0.01361 (16)	0.01591 (16)	0.01577 (16)	0.00055 (12)	−0.00323 (12)	−0.00843 (13)
Mn3	0.01195 (15)	0.01724 (16)	0.01632 (16)	0.00047 (12)	−0.00281 (12)	−0.00939 (13)
Mn4	0.01224 (16)	0.01742 (16)	0.01566 (16)	0.00045 (12)	−0.00275 (12)	−0.00872 (13)
O1	0.0193 (8)	0.0177 (8)	0.0293 (9)	0.0016 (6)	−0.0071 (7)	−0.0088 (7)
O2	0.0157 (8)	0.0183 (8)	0.0322 (9)	−0.0017 (6)	−0.0047 (7)	−0.0106 (7)
O3	0.0197 (8)	0.0242 (8)	0.0175 (8)	0.0028 (6)	−0.0042 (6)	−0.0075 (7)
O4	0.0171 (8)	0.0281 (9)	0.0206 (8)	−0.0017 (7)	−0.0013 (6)	−0.0129 (7)
O5	0.0234 (8)	0.0175 (8)	0.0283 (9)	0.0012 (6)	−0.0121 (7)	−0.0069 (7)
O6	0.0197 (8)	0.0154 (7)	0.0243 (8)	−0.0007 (6)	−0.0073 (6)	−0.0078 (6)
O7	0.0248 (9)	0.0285 (9)	0.0197 (8)	0.0076 (7)	−0.0033 (7)	−0.0087 (7)
O8	0.0181 (8)	0.0301 (9)	0.0177 (8)	0.0011 (7)	−0.0040 (6)	−0.0078 (7)
O9	0.0179 (8)	0.0170 (8)	0.0169 (8)	0.0024 (6)	−0.0051 (6)	−0.0084 (7)
O10	0.0223 (8)	0.0192 (8)	0.0252 (8)	−0.0021 (6)	−0.0095 (7)	−0.0093 (7)
O11	0.0180 (8)	0.0212 (8)	0.0196 (8)	−0.0012 (6)	−0.0056 (6)	−0.0108 (6)
O12	0.0158 (8)	0.0331 (9)	0.0180 (8)	−0.0028 (7)	−0.0012 (6)	−0.0117 (7)
O13	0.0181 (8)	0.0220 (8)	0.0177 (8)	0.0013 (6)	−0.0028 (6)	−0.0072 (6)
O14	0.0190 (8)	0.0193 (8)	0.0323 (9)	0.0023 (6)	−0.0055 (7)	−0.0139 (7)
O15	0.0156 (8)	0.0210 (8)	0.0284 (9)	−0.0019 (6)	−0.0032 (6)	−0.0133 (7)

O16	0.0215 (8)	0.0279 (9)	0.0193 (8)	0.0078 (7)	−0.0035 (6)	−0.0061 (7)
O17	0.0189 (8)	0.0281 (9)	0.0181 (8)	0.0040 (7)	−0.0021 (6)	−0.0089 (7)
O18	0.0247 (9)	0.0191 (8)	0.0307 (9)	−0.0009 (7)	−0.0136 (7)	−0.0056 (7)
O19	0.0186 (8)	0.0177 (8)	0.0279 (9)	0.0000 (6)	−0.0067 (6)	−0.0093 (7)
O20	0.0155 (7)	0.0256 (8)	0.0188 (8)	−0.0005 (6)	−0.0053 (6)	−0.0111 (7)
O21	0.0201 (8)	0.0226 (8)	0.0294 (9)	−0.0015 (6)	−0.0091 (7)	−0.0153 (7)
O22	0.0171 (8)	0.0180 (8)	0.0151 (8)	0.0023 (6)	−0.0037 (6)	−0.0081 (6)
N1	0.0189 (9)	0.0196 (9)	0.0170 (9)	0.0013 (7)	−0.0048 (7)	−0.0107 (8)
N2	0.0170 (9)	0.0184 (9)	0.0182 (9)	−0.0009 (7)	−0.0062 (7)	−0.0071 (8)
N3	0.0197 (9)	0.0193 (9)	0.0183 (9)	0.0004 (7)	−0.0038 (7)	−0.0103 (8)
N4	0.0161 (9)	0.0232 (10)	0.0257 (10)	0.0042 (7)	−0.0068 (8)	−0.0155 (8)
N5	0.0156 (9)	0.0197 (9)	0.0169 (9)	0.0011 (7)	−0.0047 (7)	−0.0086 (7)
N6	0.0168 (9)	0.0179 (9)	0.0179 (9)	0.0002 (7)	−0.0033 (7)	−0.0091 (7)
N7	0.0160 (9)	0.0274 (10)	0.0171 (9)	0.0022 (8)	−0.0024 (7)	−0.0115 (8)
N8	0.0173 (9)	0.0200 (9)	0.0223 (10)	0.0030 (7)	−0.0063 (7)	−0.0135 (8)
C1	0.0172 (11)	0.0189 (11)	0.0167 (10)	0.0009 (8)	−0.0019 (8)	−0.0093 (9)
C2	0.0195 (11)	0.0170 (10)	0.0148 (10)	0.0006 (8)	−0.0033 (8)	−0.0062 (9)
C3	0.0170 (11)	0.0205 (11)	0.0185 (11)	0.0001 (9)	−0.0018 (8)	−0.0075 (9)
C4	0.0183 (11)	0.0219 (11)	0.0220 (11)	−0.0048 (9)	−0.0015 (9)	−0.0082 (9)
C5	0.0283 (12)	0.0163 (11)	0.0179 (11)	−0.0035 (9)	−0.0045 (9)	−0.0058 (9)
C6	0.0230 (12)	0.0196 (11)	0.0221 (12)	0.0040 (9)	−0.0056 (9)	−0.0062 (9)
C7	0.0185 (11)	0.0197 (11)	0.0229 (11)	−0.0016 (9)	−0.0048 (9)	−0.0077 (9)
C8	0.0353 (14)	0.0197 (12)	0.0301 (13)	−0.0025 (10)	−0.0080 (11)	−0.0084 (10)
C9	0.0199 (11)	0.0148 (10)	0.0185 (11)	−0.0004 (8)	−0.0028 (9)	−0.0109 (9)
C10	0.0220 (11)	0.0146 (10)	0.0170 (10)	−0.0008 (8)	−0.0035 (9)	−0.0084 (9)
C11	0.0197 (11)	0.0248 (12)	0.0212 (11)	0.0034 (9)	−0.0059 (9)	−0.0105 (10)
C12	0.0327 (13)	0.0243 (12)	0.0225 (12)	0.0068 (10)	−0.0126 (10)	−0.0108 (10)
C13	0.0340 (13)	0.0201 (11)	0.0171 (11)	−0.0031 (10)	−0.0027 (10)	−0.0090 (9)
C14	0.0184 (11)	0.0319 (13)	0.0216 (12)	−0.0036 (10)	−0.0006 (9)	−0.0110 (10)
C15	0.0195 (11)	0.0246 (12)	0.0177 (11)	−0.0003 (9)	−0.0037 (9)	−0.0090 (9)
C16	0.0463 (16)	0.0360 (15)	0.0188 (12)	−0.0075 (12)	−0.0016 (11)	−0.0073 (11)
C17	0.0186 (11)	0.0161 (10)	0.0151 (10)	−0.0006 (8)	−0.0008 (8)	−0.0047 (8)
C18	0.0174 (11)	0.0185 (11)	0.0164 (10)	0.0002 (9)	0.0000 (8)	−0.0061 (9)
C19	0.0270 (13)	0.0223 (12)	0.0368 (14)	0.0034 (10)	−0.0125 (11)	−0.0116 (11)
C20	0.0261 (13)	0.0277 (13)	0.0364 (14)	0.0074 (10)	−0.0114 (11)	−0.0093 (11)
C21	0.0273 (13)	0.0214 (12)	0.0230 (12)	0.0048 (10)	0.0050 (10)	−0.0049 (10)
C22	0.0346 (14)	0.0213 (12)	0.0307 (13)	0.0005 (10)	−0.0039 (11)	−0.0131 (11)
C23	0.0248 (12)	0.0210 (11)	0.0254 (12)	0.0010 (9)	−0.0069 (10)	−0.0092 (10)
C24	0.0328 (14)	0.0240 (13)	0.0397 (15)	0.0092 (11)	0.0024 (12)	−0.0088 (12)
C25	0.0224 (12)	0.0182 (11)	0.0190 (11)	−0.0020 (9)	−0.0046 (9)	−0.0102 (9)
C26	0.0238 (12)	0.0188 (11)	0.0194 (11)	−0.0049 (9)	−0.0063 (9)	−0.0058 (9)
C27	0.0369 (15)	0.0299 (13)	0.0223 (12)	0.0016 (11)	−0.0015 (11)	−0.0100 (11)
C28	0.0489 (18)	0.0406 (16)	0.0227 (13)	−0.0093 (13)	0.0027 (12)	−0.0087 (12)
C29	0.0511 (18)	0.0326 (14)	0.0220 (13)	−0.0196 (13)	−0.0120 (12)	−0.0015 (11)
C30	0.0416 (16)	0.0293 (14)	0.0371 (15)	−0.0065 (12)	−0.0240 (13)	0.0015 (12)
C31	0.0267 (13)	0.0288 (13)	0.0284 (13)	−0.0056 (10)	−0.0084 (10)	−0.0068 (11)
C32	0.088 (3)	0.0488 (19)	0.0237 (15)	−0.0261 (18)	−0.0187 (15)	0.0022 (13)
C33	0.0187 (11)	0.0153 (10)	0.0232 (11)	0.0000 (8)	−0.0066 (9)	−0.0080 (9)
C34	0.0259 (12)	0.0164 (11)	0.0196 (11)	−0.0045 (9)	−0.0017 (9)	−0.0042 (9)

C35	0.0179 (11)	0.0219 (11)	0.0203 (11)	−0.0041 (9)	0.0011 (9)	−0.0101 (9)
C36	0.0149 (10)	0.0180 (10)	0.0183 (11)	−0.0024 (8)	−0.0037 (8)	−0.0117 (9)
C37	0.0179 (11)	0.0173 (10)	0.0155 (10)	−0.0008 (8)	−0.0047 (8)	−0.0077 (9)
C38	0.0173 (11)	0.0193 (11)	0.0201 (11)	−0.0013 (9)	−0.0060 (9)	−0.0047 (9)
C39	0.0238 (12)	0.0149 (10)	0.0243 (12)	0.0008 (9)	−0.0080 (9)	−0.0036 (9)
C40	0.0226 (12)	0.0207 (11)	0.0245 (12)	0.0063 (9)	−0.0087 (9)	−0.0118 (10)
C41	0.0176 (11)	0.0193 (11)	0.0168 (10)	0.0005 (8)	−0.0066 (8)	−0.0101 (9)
C42	0.0192 (11)	0.0156 (10)	0.0160 (10)	0.0006 (8)	−0.0070 (8)	−0.0068 (8)
C43	0.0140 (10)	0.0204 (11)	0.0163 (10)	0.0041 (8)	−0.0058 (8)	−0.0087 (9)
C44	0.0320 (13)	0.0257 (12)	0.0222 (12)	0.0028 (10)	−0.0078 (10)	−0.0169 (10)
C45	0.0306 (14)	0.0350 (14)	0.0400 (15)	0.0027 (11)	−0.0156 (12)	−0.0218 (12)
C46	0.0230 (12)	0.0285 (12)	0.0178 (11)	0.0020 (10)	0.0003 (9)	−0.0114 (10)
C47	0.0297 (13)	0.0298 (13)	0.0243 (12)	−0.0040 (11)	−0.0060 (10)	−0.0053 (11)
C48	0.0135 (10)	0.0199 (11)	0.0149 (10)	−0.0014 (8)	0.0004 (8)	−0.0072 (9)
C49	0.0200 (12)	0.0258 (12)	0.0352 (13)	0.0069 (10)	−0.0102 (10)	−0.0183 (11)
C50	0.0302 (14)	0.0300 (14)	0.0400 (15)	−0.0003 (11)	−0.0114 (12)	−0.0057 (12)
C51	0.0236 (12)	0.0309 (13)	0.0333 (13)	0.0088 (10)	−0.0118 (10)	−0.0257 (11)
C52	0.0260 (13)	0.0370 (15)	0.0519 (17)	0.0011 (11)	−0.0151 (12)	−0.0267 (13)
C53	0.0190 (11)	0.0179 (11)	0.0168 (10)	0.0003 (9)	−0.0021 (8)	−0.0111 (9)
C54	0.0194 (11)	0.0163 (10)	0.0187 (11)	−0.0006 (8)	−0.0044 (8)	−0.0102 (9)
C55	0.0193 (11)	0.0214 (11)	0.0213 (11)	0.0008 (9)	−0.0043 (9)	−0.0080 (9)
C56	0.0195 (12)	0.0270 (12)	0.0254 (12)	−0.0048 (10)	−0.0004 (9)	−0.0103 (10)
C57	0.0339 (14)	0.0190 (11)	0.0200 (11)	−0.0076 (10)	−0.0040 (10)	−0.0086 (9)
C58	0.0296 (13)	0.0197 (11)	0.0235 (12)	0.0037 (10)	−0.0106 (10)	−0.0085 (10)
C59	0.0201 (11)	0.0239 (12)	0.0244 (12)	0.0015 (9)	−0.0052 (9)	−0.0112 (10)
C60	0.0466 (16)	0.0286 (13)	0.0246 (13)	−0.0117 (12)	−0.0068 (11)	−0.0051 (11)
C61	0.0168 (11)	0.0197 (11)	0.0154 (10)	0.0009 (8)	0.0000 (8)	−0.0109 (9)
C62	0.0180 (11)	0.0172 (10)	0.0134 (10)	−0.0001 (8)	−0.0020 (8)	−0.0073 (8)
C63	0.0150 (11)	0.0239 (11)	0.0236 (12)	−0.0016 (9)	−0.0037 (9)	−0.0103 (10)
C64	0.0215 (12)	0.0193 (11)	0.0268 (12)	0.0046 (9)	−0.0061 (9)	−0.0092 (10)
C65	0.0228 (12)	0.0199 (11)	0.0175 (11)	−0.0035 (9)	−0.0030 (9)	−0.0067 (9)
C66	0.0180 (11)	0.0219 (11)	0.0211 (11)	−0.0060 (9)	−0.0038 (9)	−0.0073 (9)
C67	0.0182 (11)	0.0205 (11)	0.0171 (11)	0.0020 (9)	−0.0040 (8)	−0.0072 (9)
C68	0.0296 (13)	0.0200 (12)	0.0337 (14)	−0.0031 (10)	−0.0081 (11)	−0.0075 (10)
C69	0.0189 (11)	0.0180 (11)	0.0189 (11)	−0.0012 (9)	−0.0038 (9)	−0.0087 (9)
C70	0.0237 (12)	0.0177 (11)	0.0168 (11)	−0.0010 (9)	−0.0052 (9)	−0.0067 (9)
C71	0.0212 (12)	0.0216 (11)	0.0263 (12)	0.0016 (9)	−0.0062 (9)	−0.0078 (10)
C72	0.0311 (13)	0.0212 (12)	0.0306 (13)	0.0039 (10)	−0.0163 (11)	−0.0049 (10)
C73	0.0383 (15)	0.0231 (12)	0.0214 (12)	−0.0035 (11)	−0.0109 (11)	−0.0057 (10)
C74	0.0307 (14)	0.0387 (15)	0.0187 (12)	−0.0002 (11)	−0.0013 (10)	−0.0074 (11)
C75	0.0269 (13)	0.0274 (13)	0.0213 (12)	0.0055 (10)	−0.0062 (10)	−0.0064 (10)
C76	0.0464 (17)	0.0319 (14)	0.0253 (13)	−0.0074 (12)	−0.0144 (12)	−0.0009 (11)
C77	0.0182 (11)	0.0186 (11)	0.0171 (11)	−0.0011 (9)	−0.0011 (8)	−0.0053 (9)
C78	0.0223 (12)	0.0179 (11)	0.0196 (11)	0.0002 (9)	−0.0029 (9)	−0.0076 (9)
C79	0.0273 (13)	0.0228 (12)	0.0249 (12)	−0.0016 (10)	−0.0067 (10)	−0.0089 (10)
C80	0.0380 (15)	0.0194 (12)	0.0311 (13)	−0.0035 (10)	−0.0069 (11)	−0.0111 (10)
C81	0.0354 (14)	0.0200 (12)	0.0262 (13)	0.0021 (10)	−0.0011 (11)	−0.0085 (10)
C82	0.0329 (15)	0.0267 (13)	0.0471 (16)	0.0079 (11)	−0.0181 (12)	−0.0107 (12)
C83	0.0296 (13)	0.0205 (12)	0.0397 (15)	0.0007 (10)	−0.0135 (11)	−0.0103 (11)

C84	0.0519 (18)	0.0225 (13)	0.0447 (17)	0.0081 (12)	−0.0090 (14)	−0.0136 (12)
C85	0.0170 (11)	0.0172 (10)	0.0163 (10)	0.0006 (8)	−0.0051 (8)	−0.0093 (9)
C86	0.0136 (10)	0.0228 (11)	0.0160 (10)	0.0022 (8)	−0.0057 (8)	−0.0113 (9)
C87	0.0174 (11)	0.0244 (12)	0.0233 (11)	0.0071 (9)	−0.0074 (9)	−0.0149 (10)
C88	0.0216 (12)	0.0155 (11)	0.0303 (12)	0.0032 (9)	−0.0105 (10)	−0.0101 (10)
C89	0.0174 (11)	0.0186 (11)	0.0215 (11)	−0.0015 (9)	−0.0068 (9)	−0.0070 (9)
C90	0.0186 (11)	0.0170 (11)	0.0217 (11)	0.0016 (9)	−0.0056 (9)	−0.0102 (9)
C91	0.0239 (12)	0.0181 (11)	0.0193 (11)	−0.0030 (9)	−0.0025 (9)	−0.0042 (9)
C92	0.0151 (11)	0.0205 (11)	0.0222 (11)	−0.0043 (9)	0.0014 (9)	−0.0085 (9)
C93	0.0167 (10)	0.0170 (10)	0.0196 (11)	0.0004 (8)	−0.0040 (8)	−0.0133 (9)
C94	0.0170 (11)	0.0170 (10)	0.0159 (10)	−0.0002 (8)	−0.0027 (8)	−0.0081 (9)
C95	0.0119 (10)	0.0218 (11)	0.0176 (10)	0.0045 (8)	−0.0046 (8)	−0.0102 (9)
C96	0.0280 (13)	0.0331 (13)	0.0196 (11)	0.0038 (10)	−0.0052 (9)	−0.0176 (10)
C97	0.0289 (13)	0.0365 (14)	0.0314 (13)	0.0054 (11)	−0.0134 (11)	−0.0203 (12)
C98	0.0191 (12)	0.0404 (14)	0.0173 (11)	−0.0013 (10)	−0.0013 (9)	−0.0101 (10)
C99	0.0274 (13)	0.0345 (14)	0.0287 (13)	−0.0051 (11)	−0.0086 (11)	−0.0024 (11)
C100	0.0110 (10)	0.0210 (11)	0.0152 (10)	−0.0016 (8)	0.0013 (8)	−0.0087 (9)
C101	0.0208 (12)	0.0235 (12)	0.0315 (13)	0.0064 (9)	−0.0113 (10)	−0.0157 (10)
C102	0.0308 (14)	0.0304 (14)	0.0337 (14)	−0.0001 (11)	−0.0121 (11)	−0.0045 (11)
C103	0.0268 (12)	0.0272 (12)	0.0282 (12)	0.0072 (10)	−0.0134 (10)	−0.0217 (10)
C104	0.0266 (13)	0.0288 (13)	0.0458 (15)	0.0027 (10)	−0.0162 (11)	−0.0228 (12)

Geometric parameters (Å, °)

Mn1—O2	2.1528 (14)	C41—C40	1.393 (3)
Mn1—O3	2.1429 (15)	C41—C42	1.391 (3)
Mn1—O8	2.1743 (15)	C41—C43	1.498 (3)
Mn1—O9	2.1848 (15)	C42—N2	1.336 (3)
Mn1—O10	2.1936 (14)	C42—H42	0.9300
Mn1—N2	2.2854 (18)	C43—O11^{ii}	1.246 (2)
Mn2—O1	2.1482 (15)	C44—C45	1.511 (3)
Mn2—O4	2.1197 (15)	C44—H44A	0.9700
Mn2—O6	2.1694 (14)	C44—H44B	0.9700
Mn2—O9	2.2026 (14)	C45—H45A	0.9600
Mn2—O11	2.2109 (13)	C45—H45B	0.9600
Mn2—N1	2.3152 (18)	C45—H45C	0.9600
Mn3—O13	2.1716 (14)	C46—C47	1.512 (3)
Mn3—O15	2.1608 (14)	C46—H46A	0.9700
Mn3—O17	2.1898 (15)	C46—H46B	0.9700
Mn3—O21	2.1755 (14)	C47—H47A	0.9600
Mn3—O22	2.1913 (15)	C47—H47B	0.9600
Mn3—N5	2.2817 (17)	C47—H47C	0.9600
Mn4—O12	2.1071 (15)	C48—O10	1.244 (2)
Mn4—O14	2.1419 (15)	C48—C36^{ii}	1.508 (3)
Mn4—O19	2.1540 (15)	C49—C50	1.512 (3)
Mn4—O20	2.1990 (13)	C49—H49A	0.9700
Mn4—O22	2.2069 (14)	C49—H49B	0.9700
Mn4—N6	2.2799 (18)	C50—H50A	0.9600
O1—C1	1.263 (2)	C50—H50B	0.9600

O2—C1	1.252 (2)	C50—H50C	0.9600
O3—C9	1.260 (2)	C51—C52	1.509 (3)
O4—C9	1.258 (2)	C51—H51A	0.9700
O5—C17	1.259 (2)	C51—H51B	0.9700
O6—C17	1.271 (2)	C52—H52A	0.9600
O7—C25	1.257 (3)	C52—H52B	0.9600
O9—H9A	0.94 (3)	C52—H52C	0.9600
O9—H9B	0.937 (18)	C53—C54	1.504 (3)
O11—C43^{i}	1.246 (2)	C54—C55	1.383 (3)
O12—C53	1.258 (2)	C54—C59	1.394 (3)
O13—C53	1.261 (2)	C55—H55	0.9300
O14—C61	1.264 (2)	C56—C55	1.382 (3)
O15—C61	1.248 (2)	C56—C57	1.391 (3)
O16—C69	1.260 (2)	C56—H56	0.9300
O17—C69	1.262 (3)	C57—C60	1.505 (3)
O18—C77	1.256 (2)	C58—C59	1.383 (3)
O19—C77	1.263 (2)	C58—C57	1.392 (3)
O22—H22A	0.92 (3)	C58—H58	0.9300
O22—H22B	0.98 (4)	C59—H59	0.9300
N1—C33	1.338 (3)	C60—H60A	0.9600
N1—C37	1.340 (3)	C60—H60B	0.9600
N2—C38	1.343 (3)	C60—H60C	0.9600
N3—C43	1.338 (3)	C62—C61	1.508 (3)
N3—C44	1.473 (3)	C62—C67	1.387 (3)
N3—C46	1.470 (3)	C63—C62	1.392 (3)
N4—C48	1.327 (3)	C63—C64	1.388 (3)
N4—C49	1.472 (3)	C63—H63	0.9300
N4—C51	1.477 (3)	C64—H64	0.9300
N5—C85	1.338 (3)	C65—C66	1.391 (3)
N5—C89	1.338 (3)	C65—C64	1.392 (3)
N6—C90	1.341 (3)	C65—C68	1.509 (3)
N6—C94	1.337 (3)	C66—H66	0.9300
N7—C95	1.331 (3)	C67—C66	1.384 (3)
N7—C96	1.479 (3)	C67—H67	0.9300
N7—C98	1.470 (3)	C68—H68A	0.9600
N8—C100	1.329 (3)	C68—H68B	0.9600
N8—C101	1.474 (3)	C68—H68C	0.9600
N8—C103	1.472 (2)	C70—C69	1.509 (3)
C1—C2	1.508 (3)	C70—C71	1.383 (3)
C3—C2	1.389 (3)	C70—C75	1.391 (3)
C3—H3	0.9300	C71—C72	1.390 (3)
C4—C3	1.383 (3)	C71—H71	0.9300
C4—H4	0.9300	C72—C73	1.382 (3)
C5—C6	1.390 (3)	C72—H72	0.9300
C5—C4	1.391 (3)	C73—C74	1.385 (3)
C5—C8	1.507 (3)	C74—H74	0.9300
C6—C7	1.387 (3)	C75—C74	1.379 (3)
C6—H6	0.9300	C75—H75	0.9300
C7—C2	1.391 (3)	C76—C73	1.514 (3)

C7—H7	0.9300	C76—H76A	0.9600
C8—H8A	0.9600	C76—H76B	0.9600
C8—H8B	0.9600	C76—H76C	0.9600
C8—H8C	0.9600	C77—C78	1.506 (3)
C9—C10	1.496 (3)	C78—C83	1.381 (3)
C10—C15	1.388 (3)	C79—C78	1.384 (3)
C11—C12	1.386 (3)	C79—C80	1.386 (3)
C11—C10	1.394 (3)	C79—H79	0.9300
C11—H11	0.9300	C80—H80	0.9300
C12—C13	1.388 (3)	C81—C80	1.388 (3)
C12—H12	0.9300	C81—C84	1.507 (3)
C14—C13	1.387 (3)	C82—C81	1.389 (3)
C14—C15	1.388 (3)	C82—C83	1.388 (3)
C14—H14	0.9300	C82—H82	0.9300
C15—H15	0.9300	C83—H83	0.9300
C16—C13	1.505 (3)	C84—H84A	0.9600
C16—H16A	0.9600	C84—H84B	0.9600
C16—H16B	0.9600	C84—H84C	0.9600
C16—H16C	0.9600	C85—H85	0.9300
C18—C17	1.498 (3)	C86—C85	1.389 (3)
C18—C19	1.384 (3)	C86—C95^{i}	1.497 (3)
C18—C23	1.389 (3)	C87—C88	1.382 (3)
C19—H19	0.9300	C87—C86	1.395 (3)
C20—C21	1.385 (3)	C87—H87	0.9300
C20—C19	1.387 (3)	C88—H88	0.9300
C20—H20	0.9300	C89—C88	1.376 (3)
C21—C22	1.391 (3)	C89—H89	0.9300
C21—C24	1.504 (3)	C90—H90	0.9300
C22—C23	1.383 (3)	C91—C90	1.380 (3)
C22—H22	0.9300	C91—C92	1.381 (3)
C23—H23	0.9300	C91—H91	0.9300
C24—H24A	0.9600	C92—H92	0.9300
C24—H24B	0.9600	C93—C92	1.389 (3)
C24—H24C	0.9600	C93—C94	1.386 (3)
C25—O8	1.267 (3)	C93—C100^{ii}	1.502 (3)
C25—C26	1.506 (3)	C94—H94	0.9300
C26—C27	1.393 (3)	C95—O20	1.243 (2)
C26—C31	1.379 (3)	C95—C86^{ii}	1.497 (3)
C27—H27	0.9300	C96—C97	1.516 (3)
C28—C27	1.380 (3)	C96—H96A	0.9700
C28—H28	0.9300	C96—H96B	0.9700
C29—C28	1.388 (4)	C97—H97A	0.9600
C29—C30	1.380 (4)	C97—H97B	0.9600
C30—H30	0.9300	C97—H97C	0.9600
C31—C30	1.394 (3)	C98—C99	1.517 (3)
C31—H31	0.9300	C98—H98A	0.9700
C32—C29	1.507 (3)	C98—H98B	0.9700
C32—H32A	0.9600	C99—H99A	0.9600

C32—H32B	0.9600	C99—H99B	0.9600
C32—H32C	0.9600	C99—H99C	0.9600
C33—C34	1.383 (3)	C100—O21	1.243 (2)
C33—H33	0.9300	C100—C93^{i}	1.502 (3)
C34—H34	0.9300	C101—C102	1.509 (3)
C35—C34	1.380 (3)	C101—H10A	0.9700
C35—C36	1.387 (3)	C101—H10B	0.9700
C35—H35	0.9300	C102—H10H	0.9600
C36—C48^{i}	1.508 (3)	C102—H10I	0.9600
C37—C36	1.387 (3)	C102—H10J	0.9600
C37—H37	0.9300	C103—C104	1.512 (3)
C38—H38	0.9300	C103—H10C	0.9700
C39—C38	1.383 (3)	C103—H10D	0.9700
C39—C40	1.380 (3)	C104—H10E	0.9600
C39—H39	0.9300	C104—H10F	0.9600
C40—H40	0.9300	C104—H10G	0.9600
O2—Mn1—O8	86.85 (6)	N2—C42—H42	118.1
O2—Mn1—O9	92.31 (6)	C41—C42—H42	118.1
O2—Mn1—O10	174.70 (6)	O11^{ii}—C43—N3	121.49 (19)
O2—Mn1—N2	84.43 (6)	O11^{ii}—C43—C41	118.48 (18)
O3—Mn1—O2	97.60 (6)	N3—C43—C41	120.00 (18)
O3—Mn1—O8	175.43 (6)	N3—C44—C45	113.85 (19)
O3—Mn1—O9	91.91 (6)	N3—C44—H44A	108.8
O3—Mn1—O10	86.29 (6)	N3—C44—H44B	108.8
O3—Mn1—N2	85.17 (6)	C45—C44—H44A	108.8
O8—Mn1—O9	88.92 (6)	C45—C44—H44B	108.8
O8—Mn1—O10	89.21 (6)	H44A—C44—H44B	107.7
O8—Mn1—N2	94.29 (6)	C44—C45—H45A	109.5
O9—Mn1—O10	91.16 (6)	C44—C45—H45B	109.5
O9—Mn1—N2	175.29 (6)	C44—C45—H45C	109.5
O10—Mn1—N2	92.34 (6)	H45A—C45—H45B	109.5
O1—Mn2—O6	170.61 (6)	H45A—C45—H45C	109.5
O1—Mn2—O9	89.49 (6)	H45B—C45—H45C	109.5
O1—Mn2—O11	88.90 (5)	N3—C46—C47	113.19 (18)
O1—Mn2—N1	86.27 (6)	N3—C46—H46A	108.9
O4—Mn2—O1	97.75 (6)	N3—C46—H46B	108.9
O4—Mn2—O6	91.45 (6)	C47—C46—H46A	108.9
O4—Mn2—O9	90.02 (6)	C47—C46—H46B	108.9
O4—Mn2—O11	89.10 (5)	H46A—C46—H46B	107.8
O4—Mn2—N1	174.27 (6)	C46—C47—H47A	109.5
O6—Mn2—O9	88.61 (5)	C46—C47—H47B	109.5
O6—Mn2—O11	93.15 (5)	C46—C47—H47C	109.5
O6—Mn2—N1	84.69 (6)	H47A—C47—H47B	109.5
O9—Mn2—O11	178.04 (6)	H47A—C47—H47C	109.5
O9—Mn2—N1	94.11 (6)	H47B—C47—H47C	109.5
O11—Mn2—N1	86.89 (6)	O10—C48—N4	121.96 (19)
O13—Mn3—O17	170.86 (6)	O10—C48—C36^{ii}	119.09 (18)

O13—Mn3—O21	84.47 (6)	N4—C48—C36^{ii}	118.91 (17)
O13—Mn3—O22	89.52 (6)	N4—C49—C50	113.82 (19)
O13—Mn3—N5	83.28 (6)	N4—C49—H49A	108.8
O15—Mn3—O13	100.63 (6)	N4—C49—H49B	108.8
O15—Mn3—O17	88.49 (6)	C50—C49—H49A	108.8
O15—Mn3—O21	172.45 (6)	C50—C49—H49B	108.8
O15—Mn3—O22	95.02 (6)	H49A—C49—H49B	107.7
O15—Mn3—N5	84.32 (6)	C49—C50—H50A	109.5
O17—Mn3—O22	89.03 (6)	C49—C50—H50B	109.5
O17—Mn3—N5	98.40 (6)	C49—C50—H50C	109.5
O21—Mn3—O17	86.52 (6)	H50A—C50—H50B	109.5
O21—Mn3—O22	90.55 (6)	H50A—C50—H50C	109.5
O21—Mn3—N5	90.82 (6)	H50B—C50—H50C	109.5
O22—Mn3—N5	172.51 (6)	N4—C51—C52	113.39 (19)
O12—Mn4—O14	97.04 (6)	N4—C51—H51A	108.9
O12—Mn4—O19	90.47 (6)	N4—C51—H51B	108.9
O12—Mn4—O20	91.25 (5)	C52—C51—H51A	108.9
O12—Mn4—O22	88.94 (6)	C52—C51—H51B	108.9
O12—Mn4—N6	175.55 (6)	H51A—C51—H51B	107.7
O14—Mn4—O19	172.28 (6)	C51—C52—H52A	109.5
O14—Mn4—O20	89.45 (6)	C51—C52—H52B	109.5
O14—Mn4—O22	92.31 (6)	C51—C52—H52C	109.5
O14—Mn4—N6	86.78 (6)	H52A—C52—H52B	109.5
O19—Mn4—O20	88.57 (5)	H52A—C52—H52C	109.5
O19—Mn4—O22	89.64 (6)	H52B—C52—H52C	109.5
O19—Mn4—N6	85.65 (6)	O12—C53—O13	125.68 (19)
O20—Mn4—O22	178.20 (6)	O12—C53—C54	116.39 (18)
O20—Mn4—N6	86.48 (6)	O13—C53—C54	117.92 (18)
O22—Mn4—N6	93.20 (6)	C55—C54—C53	121.96 (19)
C1—O1—Mn2	136.20 (13)	C55—C54—C59	118.4 (2)
C1—O2—Mn1	135.80 (14)	C59—C54—C53	119.61 (19)
C9—O3—Mn1	132.79 (14)	C54—C55—H55	119.7
C9—O4—Mn2	139.38 (13)	C56—C55—C54	120.7 (2)
C17—O6—Mn2	126.66 (13)	C56—C55—H55	119.7
C25—O8—Mn1	126.00 (13)	C55—C56—C57	121.5 (2)
Mn1—O9—Mn2	114.68 (6)	C55—C56—H56	119.2
Mn1—O9—H9A	96.9 (17)	C57—C56—H56	119.2
Mn1—O9—H9B	120 (2)	C56—C57—C58	117.5 (2)
Mn2—O9—H9A	118.6 (17)	C56—C57—C60	121.4 (2)
Mn2—O9—H9B	95 (2)	C58—C57—C60	121.1 (2)
H9A—O9—H9B	113 (3)	C57—C58—H58	119.4
C48—O10—Mn1	139.39 (14)	C59—C58—C57	121.2 (2)
C43^{i}—O11—Mn2	144.18 (14)	C59—C58—H58	119.4
C53—O12—Mn4	138.85 (13)	C54—C59—H59	119.7
C53—O13—Mn3	131.60 (14)	C58—C59—C54	120.6 (2)
C61—O14—Mn4	137.28 (13)	C58—C59—H59	119.7
C61—O15—Mn3	134.89 (14)	C57—C60—H60A	109.5
C69—O17—Mn3	126.80 (13)	C57—C60—H60B	109.5

C77—O19—Mn4	125.56 (13)	C57—C60—H60C	109.5
C95—O20—Mn4	143.45 (14)	H60A—C60—H60B	109.5
C100—O21—Mn3	146.13 (14)	H60A—C60—H60C	109.5
Mn3—O22—Mn4	113.16 (6)	H60B—C60—H60C	109.5
Mn3—O22—H22A	99.9 (16)	O14—C61—C62	115.51 (18)
Mn3—O22—H22B	119 (2)	O15—C61—O14	126.27 (19)
Mn4—O22—H22A	118.4 (16)	O15—C61—C62	118.21 (18)
Mn4—O22—H22B	95 (2)	C63—C62—C61	121.92 (18)
H22A—O22—H22B	113 (3)	C67—C62—C61	119.52 (18)
C33—N1—Mn2	124.49 (14)	C67—C62—C63	118.56 (19)
C33—N1—C37	117.62 (18)	C62—C63—H63	119.8
C37—N1—Mn2	117.75 (14)	C64—C63—C62	120.5 (2)
C38—N2—Mn1	121.24 (14)	C64—C63—H63	119.8
C42—N2—Mn1	120.29 (13)	C63—C64—C65	121.0 (2)
C42—N2—C38	117.38 (18)	C63—C64—H64	119.5
C43—N3—C44	124.34 (18)	C65—C64—H64	119.5
C43—N3—C46	117.55 (17)	C64—C65—C68	121.5 (2)
C46—N3—C44	117.64 (17)	C66—C65—C64	118.06 (19)
C48—N4—C49	119.05 (17)	C66—C65—C68	120.40 (19)
C48—N4—C51	122.86 (18)	C65—C66—H66	119.5
C49—N4—C51	118.08 (17)	C67—C66—C65	121.0 (2)
C85—N5—Mn3	118.94 (13)	C67—C66—H66	119.5
C85—N5—C89	117.71 (18)	C62—C67—H67	119.6
C89—N5—Mn3	122.73 (14)	C66—C67—C62	120.9 (2)
C90—N6—Mn4	126.99 (14)	C66—C67—H67	119.6
C94—N6—Mn4	115.46 (14)	C65—C68—H68A	109.5
C94—N6—C90	117.40 (18)	C65—C68—H68B	109.5
C95—N7—C96	123.95 (18)	C65—C68—H68C	109.5
C95—N7—C98	117.56 (18)	H68A—C68—H68B	109.5
C98—N7—C96	117.96 (17)	H68A—C68—H68C	109.5
C100—N8—C101	118.32 (17)	H68B—C68—H68C	109.5
C100—N8—C103	123.07 (17)	O16—C69—O17	125.0 (2)
C103—N8—C101	118.50 (17)	O16—C69—C70	116.66 (19)
O1—C1—C2	116.18 (18)	O17—C69—C70	118.28 (19)
O2—C1—O1	126.35 (19)	C71—C70—C69	121.2 (2)
O2—C1—C2	117.45 (18)	C71—C70—C75	118.2 (2)
C3—C2—C1	119.81 (19)	C75—C70—C69	120.65 (19)
C3—C2—C7	118.72 (19)	C70—C71—C72	120.3 (2)
C7—C2—C1	121.42 (18)	C70—C71—H71	119.8
C2—C3—H3	119.7	C72—C71—H71	119.8
C4—C3—C2	120.7 (2)	C71—C72—H72	119.2
C4—C3—H3	119.7	C73—C72—C71	121.7 (2)
C3—C4—C5	120.9 (2)	C73—C72—H72	119.2
C3—C4—H4	119.5	C72—C73—C74	117.5 (2)
C5—C4—H4	119.5	C72—C73—C76	122.1 (2)
C4—C5—C8	120.3 (2)	C74—C73—C76	120.3 (2)
C6—C5—C4	118.21 (19)	C73—C74—H74	119.3
C6—C5—C8	121.4 (2)	C75—C74—C73	121.4 (2)
C5—C6—H6	119.5	C75—C74—H74	119.3

C7—C6—C5	121.0 (2)	C70—C75—H75	119.5
C7—C6—H6	119.5	C74—C75—C70	120.9 (2)
C2—C7—H7	119.8	C74—C75—H75	119.5
C6—C7—C2	120.3 (2)	C73—C76—H76A	109.5
C6—C7—H7	119.8	C73—C76—H76B	109.5
C5—C8—H8A	109.5	C73—C76—H76C	109.5
C5—C8—H8B	109.5	H76A—C76—H76B	109.5
C5—C8—H8C	109.5	H76A—C76—H76C	109.5
H8A—C8—H8B	109.5	H76B—C76—H76C	109.5
H8A—C8—H8C	109.5	O18—C77—O19	125.1 (2)
H8B—C8—H8C	109.5	O18—C77—C78	117.55 (19)
O3—C9—C10	117.14 (18)	O19—C77—C78	117.31 (18)
O4—C9—O3	125.93 (19)	C83—C78—C79	118.6 (2)
O4—C9—C10	116.90 (18)	C83—C78—C77	121.03 (19)
C11—C10—C9	120.30 (19)	C79—C78—C77	120.38 (19)
C15—C10—C9	121.41 (19)	C78—C79—C80	120.6 (2)
C15—C10—C11	118.3 (2)	C78—C79—H79	119.7
C10—C11—H11	119.7	C80—C79—H79	119.7
C12—C11—C10	120.5 (2)	C79—C80—C81	121.4 (2)
C12—C11—H11	119.7	C79—C80—H80	119.3
C11—C12—C13	121.1 (2)	C81—C80—H80	119.3
C11—C12—H12	119.4	C80—C81—C82	117.5 (2)
C13—C12—H12	119.4	C80—C81—C84	121.5 (2)
C12—C13—C16	120.8 (2)	C82—C81—C84	121.0 (2)
C14—C13—C12	118.3 (2)	C81—C82—H82	119.3
C14—C13—C16	120.9 (2)	C83—C82—C81	121.3 (2)
C13—C14—C15	120.7 (2)	C83—C82—H82	119.3
C13—C14—H14	119.6	C78—C83—C82	120.6 (2)
C15—C14—H14	119.6	C78—C83—H83	119.7
C10—C15—C14	121.0 (2)	C82—C83—H83	119.7
C10—C15—H15	119.5	C81—C84—H84A	109.5
C14—C15—H15	119.5	C81—C84—H84B	109.5
C13—C16—H16A	109.5	C81—C84—H84C	109.5
C13—C16—H16B	109.5	H84A—C84—H84B	109.5
C13—C16—H16C	109.5	H84A—C84—H84C	109.5
H16A—C16—H16B	109.5	H84B—C84—H84C	109.5
H16A—C16—H16C	109.5	N5—C85—C86	123.48 (19)
H16B—C16—H16C	109.5	N5—C85—H85	118.3
O5—C17—O6	124.73 (19)	C86—C85—H85	118.3
O5—C17—C18	117.28 (18)	C85—C86—C87	117.8 (2)
O6—C17—C18	117.99 (18)	C85—C86—C95^{i}	117.21 (18)
C19—C18—C17	121.26 (19)	C87—C86—C95^{i}	124.91 (19)
C19—C18—C23	118.5 (2)	C88—C87—C86	118.8 (2)
C23—C18—C17	120.26 (19)	C88—C87—H87	120.6
C18—C19—C20	120.7 (2)	C86—C87—H87	120.6
C18—C19—H19	119.6	C87—C88—H88	120.4
C20—C19—H19	119.6	C89—C88—C87	119.3 (2)
C19—C20—H20	119.4	C89—C88—H88	120.4

C21—C20—C19	121.2 (2)	N5—C89—C88	122.9 (2)
C21—C20—H20	119.4	N5—C89—H89	118.5
C20—C21—C22	117.8 (2)	C88—C89—H89	118.5
C20—C21—C24	121.6 (2)	N6—C90—C91	122.7 (2)
C22—C21—C24	120.6 (2)	N6—C90—H90	118.7
C21—C22—H22	119.4	C91—C90—H90	118.7
C23—C22—C21	121.3 (2)	C90—C91—C92	119.6 (2)
C23—C22—H22	119.4	C90—C91—H91	120.2
C18—C23—H23	119.7	C92—C91—H91	120.2
C22—C23—C18	120.5 (2)	C91—C92—C93	118.3 (2)
C22—C23—H23	119.7	C91—C92—H92	120.8
C21—C24—H24A	109.5	C93—C92—H92	120.8
C21—C24—H24B	109.5	C92—C93—C100^{ii}	124.11 (19)
C21—C24—H24C	109.5	C94—C93—C92	118.32 (19)
H24A—C24—H24B	109.5	C94—C93—C100^{ii}	117.50 (18)
H24A—C24—H24C	109.5	N6—C94—C93	123.62 (19)
H24B—C24—H24C	109.5	N6—C94—H94	118.2
O7—C25—O8	125.4 (2)	C93—C94—H94	118.2
O7—C25—C26	116.86 (19)	O20—C95—N7	121.7 (2)
O8—C25—C26	117.77 (19)	O20—C95—C86^{ii}	118.05 (18)
C31—C26—C27	118.6 (2)	N7—C95—C86^{ii}	120.13 (18)
C31—C26—C25	120.8 (2)	N7—C96—C97	113.40 (19)
C27—C26—C25	120.5 (2)	N7—C96—H96A	108.9
C26—C27—H27	119.8	N7—C96—H96B	108.9
C28—C27—C26	120.4 (2)	C97—C96—H96A	108.9
C28—C27—H27	119.8	C97—C96—H96B	108.9
C27—C28—C29	121.5 (3)	H96A—C96—H96B	107.7
C27—C28—H28	119.2	C96—C97—H97A	109.5
C29—C28—H28	119.2	C96—C97—H97B	109.5
C28—C29—C32	120.7 (3)	C96—C97—H97C	109.5
C30—C29—C28	117.6 (2)	H97A—C97—H97B	109.5
C30—C29—C32	121.7 (3)	H97A—C97—H97C	109.5
C29—C30—C31	121.5 (3)	H97B—C97—H97C	109.5
C29—C30—H30	119.3	N7—C98—C99	113.18 (19)
C31—C30—H30	119.3	N7—C98—H98A	108.9
C26—C31—C30	120.3 (2)	N7—C98—H98B	108.9
C26—C31—H31	119.8	C99—C98—H98A	108.9
C30—C31—H31	119.8	C99—C98—H98B	108.9
C29—C32—H32A	109.5	H98A—C98—H98B	107.8
C29—C32—H32B	109.5	C98—C99—H99A	109.5
C29—C32—H32C	109.5	C98—C99—H99B	109.5
H32A—C32—H32B	109.5	C98—C99—H99C	109.5
H32A—C32—H32C	109.5	H99A—C99—H99B	109.5
H32B—C32—H32C	109.5	H99A—C99—H99C	109.5
N1—C33—C34	122.7 (2)	H99B—C99—H99C	109.5
N1—C33—H33	118.7	O21—C100—N8	121.72 (19)
C34—C33—H33	118.7	O21—C100—C93^{i}	119.68 (18)
C33—C34—H34	120.3	N8—C100—C93^{i}	118.45 (17)

C35—C34—C33	119.4 (2)	N8—C101—C102	112.10 (19)
C35—C34—H34	120.3	N8—C101—H10A	109.2
C34—C35—C36	118.6 (2)	N8—C101—H10B	109.2
C34—C35—H35	120.7	C102—C101—H10A	109.2
C36—C35—H35	120.7	C102—C101—H10B	109.2
C35—C36—C37	118.39 (19)	H10A—C101—H10B	107.9
C35—C36—C48^{i}	122.52 (19)	C101—C102—H10H	109.5
C37—C36—C48^{i}	119.01 (18)	C101—C102—H10I	109.5
N1—C37—C36	123.30 (19)	C101—C102—H10J	109.5
N1—C37—H37	118.3	H10H—C102—H10I	109.5
C36—C37—H37	118.3	H10H—C102—H10J	109.5
N2—C38—C39	123.0 (2)	H10I—C102—H10J	109.5
N2—C38—H38	118.5	N8—C103—C104	113.38 (18)
C39—C38—H38	118.5	N8—C103—H10C	108.9
C38—C39—H39	120.5	N8—C103—H10D	108.9
C40—C39—C38	119.0 (2)	C104—C103—H10C	108.9
C40—C39—H39	120.5	C104—C103—H10D	108.9
C39—C40—C41	119.1 (2)	H10C—C103—H10D	107.7
C39—C40—H40	120.5	C103—C104—H10E	109.5
C41—C40—H40	120.5	C103—C104—H10F	109.5
C40—C41—C43	124.26 (19)	C103—C104—H10G	109.5
C42—C41—C40	117.7 (2)	H10E—C104—H10F	109.5
C42—C41—C43	117.84 (18)	H10E—C104—H10G	109.5
N2—C42—C41	123.75 (19)	H10F—C104—H10G	109.5
O3—Mn1—O2—C1	−79.9 (2)	C96—N7—C95—C86^{ii}	−3.1 (3)
O8—Mn1—O2—C1	101.1 (2)	C98—N7—C95—O20	1.9 (3)
O9—Mn1—O2—C1	12.3 (2)	C98—N7—C95—C86^{ii}	−174.63 (18)
N2—Mn1—O2—C1	−164.3 (2)	C95—N7—C96—C97	−83.4 (3)
O2—Mn1—O3—C9	66.64 (18)	C98—N7—C96—C97	88.1 (2)
O9—Mn1—O3—C9	−25.94 (18)	C95—N7—C98—C99	72.9 (2)
O10—Mn1—O3—C9	−116.98 (18)	C96—N7—C98—C99	−99.1 (2)
N2—Mn1—O3—C9	150.36 (18)	C101—N8—C100—O21	3.8 (3)
O2—Mn1—O8—C25	−73.48 (17)	C101—N8—C100—C93^{i}	−171.83 (18)
O9—Mn1—O8—C25	18.89 (17)	C103—N8—C100—O21	179.7 (2)
O10—Mn1—O8—C25	110.06 (17)	C103—N8—C100—C93^{i}	4.2 (3)
N2—Mn1—O8—C25	−157.65 (17)	C100—N8—C101—C102	72.1 (2)
O3—Mn1—O9—Mn2	51.35 (8)	C103—N8—C101—C102	−104.1 (2)
O2—Mn1—O9—Mn2	−46.34 (8)	C100—N8—C103—C104	−98.1 (2)
O8—Mn1—O9—Mn2	−133.14 (8)	C101—N8—C103—C104	77.9 (2)
O10—Mn1—O9—Mn2	137.67 (7)	O1—C1—C2—C3	−11.1 (3)
O3—Mn1—O10—C48	−152.6 (2)	O1—C1—C2—C7	166.19 (19)
O8—Mn1—O10—C48	26.7 (2)	O2—C1—C2—C3	170.53 (19)
O9—Mn1—O10—C48	115.6 (2)	O2—C1—C2—C7	−12.2 (3)
N2—Mn1—O10—C48	−67.6 (2)	C4—C3—C2—C1	174.29 (19)
O2—Mn1—N2—C38	−29.95 (15)	C4—C3—C2—C7	−3.1 (3)
O2—Mn1—N2—C42	137.82 (15)	C5—C4—C3—C2	−0.2 (3)
O3—Mn1—N2—C38	−128.09 (15)	C6—C5—C4—C3	3.5 (3)

O3—Mn1—N2—C42	39.68 (14)	C8—C5—C4—C3	−172.6 (2)
O8—Mn1—N2—C38	56.46 (15)	C4—C5—C6—C7	−3.4 (3)
O8—Mn1—N2—C42	−135.77 (14)	C8—C5—C6—C7	172.6 (2)
O10—Mn1—N2—C38	145.84 (15)	C5—C6—C7—C2	0.1 (3)
O10—Mn1—N2—C42	−46.39 (15)	C6—C7—C2—C1	−174.18 (19)
O4—Mn2—O1—C1	56.3 (2)	C6—C7—C2—C3	3.1 (3)
O9—Mn2—O1—C1	−33.7 (2)	O4—C9—C10—C15	−169.21 (19)
O11—Mn2—O1—C1	145.2 (2)	O3—C9—C10—C15	9.3 (3)
N1—Mn2—O1—C1	−127.8 (2)	O4—C9—C10—C11	11.9 (3)
O1—Mn2—O4—C9	−79.6 (2)	O3—C9—C10—C11	−169.58 (19)
O6—Mn2—O4—C9	98.5 (2)	C11—C10—C15—C14	0.1 (3)
O9—Mn2—O4—C9	9.9 (2)	C9—C10—C15—C14	−178.75 (19)
O11—Mn2—O4—C9	−168.3 (2)	C12—C11—C10—C15	−0.9 (3)
O4—Mn2—O6—C17	−79.50 (17)	C12—C11—C10—C9	177.93 (19)
O9—Mn2—O6—C17	10.48 (17)	C10—C11—C12—C13	0.5 (3)
O11—Mn2—O6—C17	−168.68 (17)	C15—C14—C13—C12	−1.5 (3)
N1—Mn2—O6—C17	104.74 (17)	C15—C14—C13—C16	178.7 (2)
O1—Mn2—O9—Mn1	51.85 (8)	C11—C12—C13—C14	0.7 (3)
O4—Mn2—O9—Mn1	−45.90 (8)	C11—C12—C13—C16	−179.5 (2)
O6—Mn2—O9—Mn1	−137.35 (8)	C13—C14—C15—C10	1.1 (3)
N1—Mn2—O9—Mn1	138.08 (8)	C19—C18—C17—O5	172.8 (2)
O1—Mn2—N1—C33	30.76 (16)	C19—C18—C17—O6	−8.2 (3)
O1—Mn2—N1—C37	−144.83 (14)	C23—C18—C17—O5	−6.7 (3)
O6—Mn2—N1—C33	−146.69 (16)	C23—C18—C17—O6	172.3 (2)
O6—Mn2—N1—C37	37.72 (14)	C17—C18—C19—C20	179.9 (2)
O9—Mn2—N1—C33	−58.46 (16)	C23—C18—C19—C20	−0.6 (4)
O9—Mn2—N1—C37	125.94 (14)	C17—C18—C23—C22	179.8 (2)
O11—Mn2—N1—C33	119.86 (16)	C19—C18—C23—C22	0.3 (3)
O11—Mn2—N1—C37	−55.74 (14)	C21—C20—C19—C18	0.0 (4)
O15—Mn3—O13—C53	−66.18 (18)	C19—C20—C21—C22	0.9 (4)
O21—Mn3—O13—C53	119.44 (18)	C19—C20—C21—C24	179.8 (2)
O22—Mn3—O13—C53	28.84 (18)	C20—C21—C22—C23	−1.1 (4)
N5—Mn3—O13—C53	−149.08 (18)	C24—C21—C22—C23	180.0 (2)
O13—Mn3—O15—C61	74.1 (2)	C21—C22—C23—C18	0.5 (4)
O17—Mn3—O15—C61	−105.2 (2)	O7—C25—O8—Mn1	−19.4 (3)
O22—Mn3—O15—C61	−16.3 (2)	C26—C25—O8—Mn1	160.32 (13)
N5—Mn3—O15—C61	156.2 (2)	O7—C25—C26—C27	−5.1 (3)
O15—Mn3—O17—C69	83.06 (17)	O7—C25—C26—C31	171.9 (2)
O21—Mn3—O17—C69	−102.60 (17)	O8—C25—C26—C27	175.1 (2)
O22—Mn3—O17—C69	−11.99 (17)	O8—C25—C26—C31	−7.9 (3)
N5—Mn3—O17—C69	167.09 (17)	C31—C26—C27—C28	0.5 (3)
O13—Mn3—O21—C100	156.8 (3)	C25—C26—C27—C28	177.6 (2)
O17—Mn3—O21—C100	−24.7 (3)	C25—C26—C31—C30	−176.5 (2)
O22—Mn3—O21—C100	−113.7 (3)	C27—C26—C31—C30	0.6 (3)
N5—Mn3—O21—C100	73.6 (3)	C29—C28—C27—C26	−1.3 (4)
O13—Mn3—O22—Mn4	−56.91 (8)	C30—C29—C28—C27	1.1 (4)
O15—Mn3—O22—Mn4	43.72 (8)	C32—C29—C28—C27	−178.4 (2)
O17—Mn3—O22—Mn4	132.11 (8)	C28—C29—C30—C31	0.0 (4)
O21—Mn3—O22—Mn4	−141.38 (8)	C32—C29—C30—C31	179.5 (2)

O13—Mn3—N5—C85	−44.99 (14)	C26—C31—C30—C29	−0.8 (4)
O13—Mn3—N5—C89	125.77 (16)	N1—C33—C34—C35	0.8 (3)
O15—Mn3—N5—C85	−146.43 (14)	C36—C35—C34—C33	−1.5 (3)
O15—Mn3—N5—C89	24.33 (15)	C34—C35—C36—C37	0.8 (3)
O17—Mn3—N5—C85	125.95 (14)	C34—C35—C36—C48^{i}	177.45 (18)
O17—Mn3—N5—C89	−63.30 (16)	N1—C37—C36—C35	0.8 (3)
O21—Mn3—N5—C85	39.35 (14)	N1—C37—C36—C48^{i}	−175.99 (18)
O21—Mn3—N5—C89	−149.90 (15)	C40—C39—C38—N2	0.0 (3)
O14—Mn4—O12—C53	84.7 (2)	C38—C39—C40—C41	1.6 (3)
O19—Mn4—O12—C53	−97.1 (2)	C42—C41—C40—C39	−1.5 (3)
O20—Mn4—O12—C53	174.3 (2)	C43—C41—C40—C39	173.70 (18)
O22—Mn4—O12—C53	−7.5 (2)	C40—C41—C42—N2	−0.2 (3)
O12—Mn4—O14—C61	−59.5 (2)	C43—C41—C42—N2	−175.73 (17)
O20—Mn4—O14—C61	−150.7 (2)	C40—C41—C43—O11^{ii}	−120.2 (2)
O22—Mn4—O14—C61	29.7 (2)	C40—C41—C43—N3	61.7 (3)
N6—Mn4—O14—C61	122.8 (2)	C42—C41—C43—O11^{ii}	55.0 (3)
O12—Mn4—O19—C77	66.94 (17)	C42—C41—C43—N3	−123.1 (2)
O20—Mn4—O19—C77	158.19 (17)	C41—C42—N2—Mn1	−166.44 (15)
O22—Mn4—O19—C77	−22.00 (17)	C41—C42—N2—C38	1.8 (3)
N6—Mn4—O19—C77	−115.24 (17)	N4—C48—O10—Mn1	−132.5 (2)
O12—Mn4—O20—C95	−86.5 (2)	C36^{ii}—C48—O10—Mn1	49.8 (3)
O14—Mn4—O20—C95	10.5 (2)	O12—C53—C54—C55	167.60 (19)
O19—Mn4—O20—C95	−177.0 (2)	O12—C53—C54—C59	−11.5 (3)
N6—Mn4—O20—C95	97.3 (2)	O13—C53—C54—C55	−10.8 (3)
O12—Mn4—O22—Mn3	50.24 (8)	O13—C53—C54—C59	170.05 (19)
O14—Mn4—O22—Mn3	−46.76 (8)	C53—C54—C55—C56	−177.29 (19)
O19—Mn4—O22—Mn3	140.72 (8)	C59—C54—C55—C56	1.8 (3)
N6—Mn4—O22—Mn3	−133.66 (8)	C55—C54—C59—C58	−1.1 (3)
O14—Mn4—N6—C90	−37.95 (16)	C53—C54—C59—C58	178.02 (19)
O14—Mn4—N6—C94	137.43 (14)	C57—C56—C55—C54	−0.9 (3)
O19—Mn4—N6—C90	143.58 (17)	C55—C56—C57—C58	−0.8 (3)
O19—Mn4—N6—C94	−41.05 (14)	C55—C56—C57—C60	178.4 (2)
O20—Mn4—N6—C90	−127.59 (17)	C59—C58—C57—C56	1.6 (3)
O20—Mn4—N6—C94	47.78 (14)	C59—C58—C57—C60	−177.7 (2)
O22—Mn4—N6—C90	54.18 (17)	C57—C58—C59—C54	−0.6 (3)
O22—Mn4—N6—C94	−130.44 (14)	C67—C62—C61—O14	12.2 (3)
Mn2—O1—C1—O2	1.6 (4)	C67—C62—C61—O15	−168.26 (19)
Mn2—O1—C1—C2	−176.61 (13)	C63—C62—C61—O14	−168.89 (19)
Mn1—O2—C1—O1	12.9 (3)	C63—C62—C61—O15	10.7 (3)
Mn1—O2—C1—C2	−168.92 (14)	C61—C62—C67—C66	−179.78 (19)
Mn1—O3—C9—O4	−9.7 (3)	C63—C62—C67—C66	1.3 (3)
Mn1—O3—C9—C10	172.00 (13)	C64—C63—C62—C61	−179.99 (19)
Mn2—O4—C9—O3	21.0 (3)	C64—C63—C62—C67	−1.1 (3)
Mn2—O4—C9—C10	−160.69 (15)	C62—C63—C64—C65	0.0 (3)
Mn2—O6—C17—O5	3.8 (3)	C66—C65—C64—C63	0.8 (3)
Mn2—O6—C17—C18	−175.16 (13)	C68—C65—C64—C63	−177.7 (2)
C43^{i}—O11—Mn2—O1	0.3 (2)	C64—C65—C66—C67	−0.6 (3)

C43^{i}—O11—Mn2—O4	98.0 (2)	C68—C65—C66—C67	177.9 (2)
C43^{i}—O11—Mn2—O6	−170.5 (2)	C62—C67—C66—C65	−0.4 (3)
C43^{i}—O11—Mn2—N1	−86.0 (2)	C71—C70—C69—O16	175.77 (19)
Mn4—O12—C53—O13	−27.6 (3)	C71—C70—C69—O17	−5.0 (3)
Mn4—O12—C53—C54	154.13 (16)	C75—C70—C69—O16	−6.0 (3)
Mn3—O13—C53—O12	12.3 (3)	C75—C70—C69—O17	173.2 (2)
Mn3—O13—C53—C54	−169.43 (13)	C69—C70—C71—C72	177.3 (2)
Mn4—O14—C61—O15	−1.2 (4)	C75—C70—C71—C72	−0.9 (3)
Mn4—O14—C61—C62	178.30 (14)	C69—C70—C75—C74	−176.7 (2)
Mn3—O15—C61—O14	−7.7 (3)	C71—C70—C75—C74	1.6 (3)
Mn3—O15—C61—C62	172.76 (13)	C70—C71—C72—C73	−1.2 (3)
Mn3—O17—C69—O16	8.6 (3)	C71—C72—C73—C74	2.7 (3)
Mn3—O17—C69—C70	−170.54 (13)	C71—C72—C73—C76	−175.6 (2)
Mn4—O19—C77—O18	10.9 (3)	C72—C73—C74—C75	−2.0 (4)
Mn4—O19—C77—C78	−169.13 (14)	C76—C73—C74—C75	176.3 (2)
Mn2—N1—C33—C34	−174.91 (15)	C70—C75—C74—C73	−0.1 (4)
C37—N1—C33—C34	0.7 (3)	O18—C77—C78—C79	−1.4 (3)
Mn2—N1—C37—C36	174.37 (15)	O18—C77—C78—C83	178.0 (2)
C33—N1—C37—C36	−1.5 (3)	O19—C77—C78—C79	178.6 (2)
Mn1—N2—C38—C39	166.40 (15)	O19—C77—C78—C83	−2.0 (3)
C42—N2—C38—C39	−1.7 (3)	C77—C78—C83—C82	−179.8 (2)
C44—N3—C43—O11^{ii}	−170.87 (19)	C79—C78—C83—C82	−0.4 (4)
C44—N3—C43—C41	7.1 (3)	C80—C79—C78—C77	−179.9 (2)
C46—N3—C43—O11^{ii}	1.0 (3)	C80—C79—C78—C83	0.7 (3)
C46—N3—C43—C41	178.99 (18)	C78—C79—C80—C81	−0.9 (4)
C43—N3—C44—C45	89.3 (3)	C82—C81—C80—C79	0.9 (4)
C46—N3—C44—C45	−82.6 (2)	C84—C81—C80—C79	−180.0 (2)
C43—N3—C46—C47	−72.9 (2)	C83—C82—C81—C80	−0.6 (4)
C44—N3—C46—C47	99.5 (2)	C83—C82—C81—C84	−179.8 (2)
C49—N4—C48—O10	0.3 (3)	C81—C82—C83—C78	0.4 (4)
C49—N4—C48—C36^{ii}	178.03 (18)	C87—C86—C85—N5	1.1 (3)
C51—N4—C48—O10	−178.5 (2)	C95^{i}—C86—C85—N5	177.86 (17)
C51—N4—C48—C36^{ii}	−0.8 (3)	C88—C87—C86—C85	0.2 (3)
C48—N4—C49—C50	−77.2 (3)	C88—C87—C86—C95^{i}	−176.26 (18)
C51—N4—C49—C50	101.6 (2)	N5—C89—C88—C87	0.9 (3)
C48—N4—C51—C52	97.0 (3)	C86—C87—C88—C89	−1.1 (3)
C49—N4—C51—C52	−81.8 (2)	C92—C91—C90—N6	−1.1 (3)
Mn3—N5—C85—C86	169.80 (15)	C90—C91—C92—C93	2.6 (3)
Mn3—N5—C89—C88	−170.47 (15)	C94—C93—C92—C91	−2.0 (3)
C85—N5—C89—C88	0.4 (3)	C100^{ii}—C93—C92—C91	−178.93 (19)
C89—N5—C85—C86	−1.4 (3)	C92—C93—C94—N6	−0.3 (3)
Mn4—N6—C90—C91	174.16 (15)	C100^{ii}—C93—C94—N6	176.89 (18)
Mn4—N6—C94—C93	−174.02 (15)	N7—C95—O20—Mn4	100.6 (3)
C94—N6—C90—C91	−1.1 (3)	C86^{ii}—C95—O20—Mn4	−82.8 (3)
C90—N6—C94—C93	1.8 (3)	N8—C100—O21—Mn3	134.9 (2)
C96—N7—C95—O20	173.37 (19)	C93^{i}—C100—O21—Mn3	−49.5 (3)

Symmetry codes: (i) *x*−1, *y*, *z*; (ii) *x*+1, *y*, *z*.

Hydrogen-bond geometry (Å, °)

Cg1, Cg5, Cg10 and Cg12 are the centroids of the C2–C7, N1/C33–C37, C78–C83 and N6/C90–C94 rings, respectively.

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
O9—H9A···O7	0.94 (3)	1.62 (3)	2.552 (2)	170 (3)
O9—H9B···O5	0.94 (2)	1.59 (2)	2.520 (2)	173 (3)
O22—H22A···O16	0.92 (3)	1.64 (3)	2.544 (2)	166 (2)
O22—H22B···O18	0.97 (4)	1.60 (4)	2.558 (2)	169 (3)
C52—H52A···Cg12^{ii}	0.96	2.87	3.782 (3)	160
C60—H60C···Cg1^{iii}	0.96	2.99	3.841 (3)	149
C84—H84B···Cg10^{iv}	0.96	2.88	3.609 (3)	134
C104—H10E···Cg5^{i}	0.96	2.82	3.709 (3)	155

Symmetry codes: (ii) *x*+1, *y*, *z*; (iii) −*x*, −*y*, −*z*+1; (iv) −*x*+1, −*y*, −*z*+1; (i) *x*−1, *y*, *z*.

Fig. 1

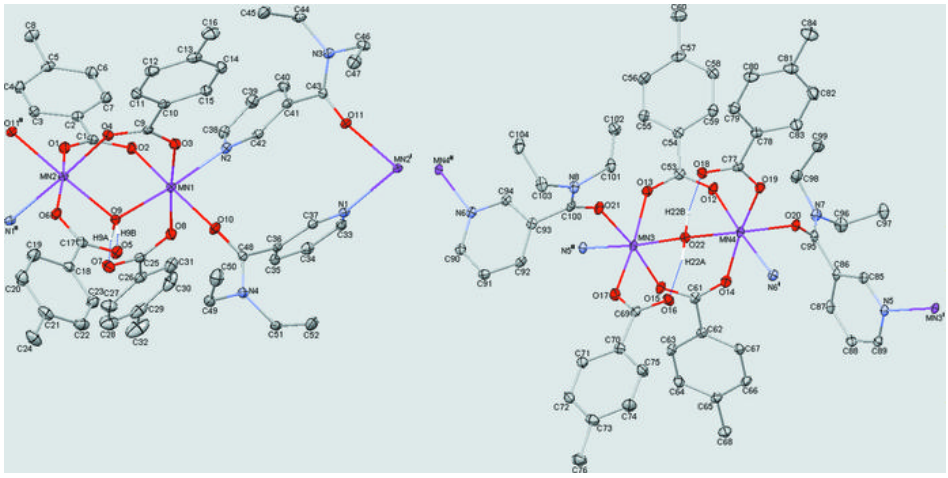
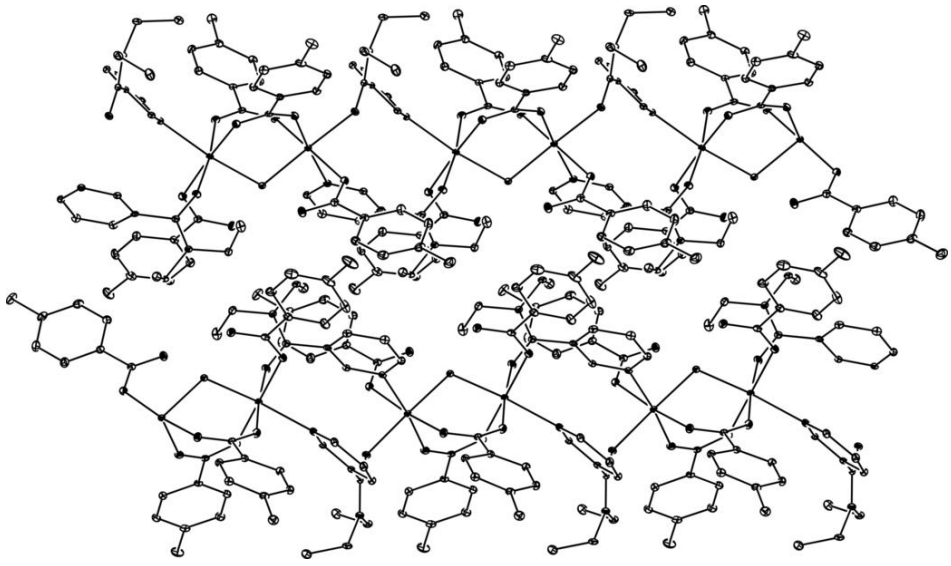


Fig. 2



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3-Fluoro-4-(4-hydroxyphenoxy)-benzonitrile

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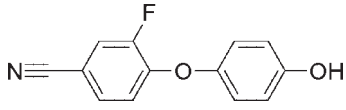
Key indicators: single-crystal X-ray study; T = 295 K; mean σ(C–C) = 0.005 Å; R factor = 0.037; wR factor = 0.117; data-to-parameter ratio = 9.6.

The title compound, $C_{13}H_8FNO_2$, was synthesized from 3,4-difluorobenzonitrile and hydroquinone. The dihedral angle between the two aromatic rings is 70.9 (2)°. In the crystal structure, molecules are linked by O—H···N hydrogen bonds, forming zigzag chains.

Related literature

For the herbicidal actvity of hydroquinone derivatives, see: Bao *et al.* (2007); Liu (2002). For related structures, see: Sørensen *et al.* (2009); Luo *et al.* (2009); Zhang *et al.* (2009).



Experimental

Crystal data

$C_{13}H_8FNO_2$
M_r = 229.20
Orthorhombic, $P2_12_12_1$
a = 6.1932 (4) Å
b = 8.8109 (5) Å
c = 20.5269 (12) Å
V = 1120.11 (12) Å^3
Z = 4
Mo $K\alpha$ radiation
μ = 0.10 mm^{-1}
T = 295 K
0.39 × 0.31 × 0.22 mm

Data collection

Rigaku R-AXIS RAPID diffractometer
Absorption correction: multi-scan (*ABSCOR*; Higashi, 1995)
T_{min} = 0.959, T_{max} = 0.976
10999 measured reflections
1498 independent reflections
928 reflections with $I > 2\sigma(I)$
R_{int} = 0.032

Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.037
$wR(F^2)$ = 0.117
S = 1.01
1498 reflections
156 parameters
H-atom parameters constrained
$\Delta\rho_{max}$ = 0.17 e Å^{-3}
$\Delta\rho_{min}$ = −0.15 e Å^{-3}

Table 1
Hydrogen-bond geometry (Å, °).

D—H···A	D—H	H···A	D···A	D—H···A
O2—H201···N1^{i}	0.82	2.03	2.839 (4)	168

Symmetry code: (i) $-x+\frac{1}{2}, -y+2, z+\frac{1}{2}$.

Data collection: *PROCESS-AUTO* (Rigaku, 2006); cell refinement: *PROCESS-AUTO*; data reduction: *CrystalStructure* (Rigaku/MSC, 2007); program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *ORTEP-3 for Windows* (Farrugia,1997); software used to prepare material for publication: *WinGX* (Farrugia, 1999).

The authors are grateful to Mr Jianming Gu for the crystal structure analysis.

Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: IM2202).

References

Bao, W. J., Wu, Y. G., Mao, C. H., Chen, M. & Huang, M. Z. (2007). *Fine Chem. Intermed.* **37**, 9–13.
Farrugia, L. J. (1997). *J. Appl. Cryst.* **30**, 565.
Farrugia, L. J. (1999). *J. Appl. Cryst.* **32**, 837–838.
Higashi, T. (1995). *ABSCOR*. Rigaku Corporation, Tokyo, Japan.
Liu (2002). Please supply full reference.
Luo, S., Zhang, J., Wang, J. & Li, B. (2009). *Acta Cryst.* E**65**, o2011.
Rigaku (2006). *PROCESS-AUTO*. Rigaku Corporation, Tokyo, Japan
Rigaku/MSC (2007). *CrystalStructure*. Rigaku/MSC, The Woodlands, Texas, USA.
Sheldrick, G. M. (2008). *Acta Cryst.* A**64**, 112–122.
Sørensen, H. O. & Stuhr-Hansen, N. (2009). *Acta Cryst.* E**65**, o13.
Zhang, J., Wu, J., Wang, J., Li, Y. & Luo, S. (2009). *Acta Cryst.* E**65**, o2340.

supplementary materials

Acta Cryst. (2010). E**66**, o1856 [**doi:10.1107/S1600536810024360**]

3-Fluoro-4-(4-hydroxyphenoxy)benzonitrile

M. Zheng, J. Wang, J. Zhang and S. Luo

Comment

Hydroquinone derivatives are important intermediates of herbicide synthesis and have therefore received growing attention recently (Liu, 2002; Bao *et al.*, 2007). Several hydroquinone derivatives were synthesized and investigated by X-ray diffraction in our laboratory. 4-(4-Cyano-2-fluoro-phenoxy)-phenol was obtained reacting hydroquinone and 3,4-difluorobenzonitrile and it's molecular structure is shown in Fig.1.

As it is expected substituents at both aromatic rings are coplanar with repect to the aromatic planes. The dihedral angle between the two planes is 70.66°. The molecule is bent with a C6—O1—C7 angle of 118.0 (2)°. The crystal structure is determined by intermolecular O—H···N interactions. The resulting supramolecular chains of the title compound showing H-bridge interactions is shown in Fig.2.

Experimental

A DMSO (10 ml) solution of hydroquinone (0.0012 mol) and NaOH (0.0024 mol) was stirred at room temperature for 5 h. Then the mixture was heated to 80°C and 3,4-difluorobenzonitrile (0.001 mol) was added dropwise and stirred for 10 h. Then the mixture was washed with water (30 ml) and extracted with ethyl acetate (three times). The organic solvent was removed under reduced pressure and the resulting crude product was purified by silica gel chromatography (pentane: ethyl acetate mixtures, yield 86%). Single crystals were obtained by slow evaporation of ethyl acetate at room temperature.

Refinement

In the absence of significant anomalous dispersion effects, Friedel pairs were averaged. H atoms were placed in calculated positions with C—H = 0.98 Å (sp), C—H = 0.97 Å (sp^2), C—H = 0.93 Å (aromatic). All H atoms were included in the final cycles of refinement using a riding model, with $U_{iso}(H)=1.2U_{eq}$ of the respective carrier atoms.

Figures

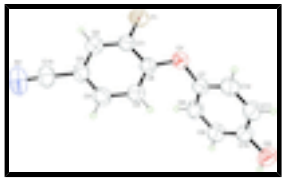


Fig. 1. Molecular structure of title compound, with the atomic labeling scheme. Displacement ellipsoids are drawn at the 50% probability level.

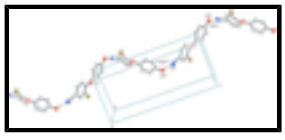


Fig. 2. A partial packing diagram of title compound. Hydrogen bonds are shown as dashed lines. [Symmetry code: (i) -x+1/2, -y+2, z+1/2].

3-Fluoro-4-(4-hydroxyphenoxy)benzonitrile

Crystal data

$C_{13}H_8FNO_2$	$F(000) = 472$
$M_r = 229.20$	$D_x = 1.359$ Mg m^{-3}
Orthorhombic, $P2_12_12_1$	Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å
Hall symbol: P 2ac 2ab	Cell parameters from 6842 reflections
$a = 6.1932$ (4) Å	$\theta = 3.0$–$27.4°$
$b = 8.8109$ (5) Å	$\mu = 0.10$ mm^{-1}
$c = 20.5269$ (12) Å	$T = 295$ K
$V = 1120.11$ (12) Å^3	Chunk, colorless
$Z = 4$	0.39 × 0.31 × 0.22 mm

Data collection

Rigaku R-AXIS RAPID diffractometer	1498 independent reflections
Radiation source: rolling anode	928 reflections with $I > 2\sigma(I)$
graphite	$R_{int} = 0.032$
Detector resolution: 10.00 pixels mm^{-1}	$\theta_{max} = 27.4°$, $\theta_{min} = 3.1°$
ω scans	$h = -8\rightarrow8$
Absorption correction: multi-scan (*ABSCOR*; Higashi, 1995)	$k = -11\rightarrow11$
$T_{min} = 0.959$, $T_{max} = 0.976$	$l = -26\rightarrow26$
10999 measured reflections	

Refinement

Refinement on F^2	Secondary atom site location: difference Fourier map
Least-squares matrix: full	Hydrogen site location: inferred from neighbouring sites
$R[F^2 > 2\sigma(F^2)] = 0.037$	H-atom parameters constrained
$wR(F^2) = 0.117$	$w = 1/[\sigma^2(F_o^2) + (0.0487P)^2 + 0.2503P]$ where $P = (F_o^2 + 2F_c^2)/3$
$S = 1.01$	$(\Delta/\sigma)_{max} < 0.001$
1498 reflections	$\Delta\rho_{max} = 0.17$ e Å^{-3}
156 parameters	$\Delta\rho_{min} = -0.15$ e Å^{-3}
0 restraints	Extinction correction: *SHELXL97* (Sheldrick, 2008), $Fc^* = kFc[1+0.001xFc^2\lambda^3/\sin(2\theta)]^{-1/4}$
Primary atom site location: structure-invariant direct methods	Extinction coefficient: 0.031 (5)

Special details

Geometry. All esds (except the esd in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell esds are taken into account individually in the estimation of esds in distances, angles and torsion angles; correlations between esds in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell esds is used for estimating esds involving l.s. planes.

Refinement. Refinement of F^2 against ALL reflections. The weighted *R*-factor wR and goodness of fit *S* are based on F^2, conventional *R*-factors *R* are based on *F*, with *F* set to zero for negative F^2. The threshold expression of $F^2 > \sigma(F^2)$ is used only for calculating *R*-factors(gt) etc. and is not relevant to the choice of reflections for refinement. *R*-factors based on F^2 are statistically about twice as large as those based on *F*, and *R*- factors based on ALL data will be even larger.

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å^2)

	x	*y*	*z*	U_{iso}*/U_{eq}
O1	0.8260 (4)	0.8262 (3)	0.91021 (10)	0.0842 (7)
F1	0.7477 (4)	0.5751 (2)	0.84401 (10)	0.0994 (7)
C3	0.2965 (5)	0.7967 (4)	0.78841 (13)	0.0647 (8)
C13	0.1155 (6)	0.7849 (4)	0.74589 (16)	0.0797 (10)
C7	0.8277 (5)	0.9255 (4)	0.96363 (13)	0.0662 (8)
O2	0.8846 (4)	1.2010 (3)	1.12504 (11)	0.0890 (8)
H201	0.7775	1.1944	1.1484	0.134*
C4	0.3341 (5)	0.9302 (4)	0.82157 (14)	0.0706 (8)
H4	0.2411	1.0120	0.8158	0.085*
C10	0.8605 (5)	1.1076 (3)	1.07184 (13)	0.0647 (8)
C1	0.6082 (5)	0.6918 (4)	0.83712 (14)	0.0689 (8)
C8	0.6707 (5)	0.9204 (4)	1.01045 (14)	0.0720 (8)
H8	0.5543	0.8546	1.0059	0.086*
C6	0.6460 (5)	0.8233 (4)	0.87182 (13)	0.0648 (8)
C2	0.4369 (5)	0.6748 (4)	0.79642 (14)	0.0712 (8)
H2	0.4141	0.5839	0.7744	0.085*
C9	0.6853 (5)	1.0130 (4)	1.06440 (14)	0.0718 (9)
H9	0.5769	1.0115	1.0958	0.086*
C11	1.0188 (6)	1.1111 (4)	1.02514 (15)	0.0789 (10)
H11	1.1376	1.1745	1.0301	0.095*
C12	1.0011 (6)	1.0202 (4)	0.97087 (15)	0.0805 (10)
H12	1.1076	1.0231	0.9390	0.097*
C5	0.5080 (6)	0.9438 (4)	0.86314 (14)	0.0710 (9)
H5	0.5319	1.0344	0.8853	0.085*
N1	−0.0310 (6)	0.7800 (4)	0.71268 (15)	0.1078 (12)

Atomic displacement parameters (Å^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
O1	0.0678 (14)	0.1042 (16)	0.0805 (13)	0.0258 (14)	−0.0173 (12)	−0.0286 (13)
F1	0.0986 (16)	0.0867 (12)	0.1129 (14)	0.0398 (13)	−0.0214 (12)	−0.0218 (12)
C3	0.0581 (18)	0.083 (2)	0.0534 (14)	−0.0009 (17)	−0.0006 (13)	0.0069 (16)

C13	0.076 (2)	0.092 (2)	0.0710 (19)	−0.009 (2)	−0.0057 (19)	0.0122 (18)
C7	0.0610 (18)	0.0736 (17)	0.0642 (15)	0.0089 (17)	−0.0031 (16)	−0.0066 (15)
O2	0.0893 (19)	0.0916 (15)	0.0861 (15)	−0.0181 (15)	0.0185 (13)	−0.0244 (14)
C4	0.069 (2)	0.0754 (19)	0.0671 (16)	0.0133 (18)	−0.0032 (17)	0.0033 (16)
C10	0.066 (2)	0.0648 (17)	0.0632 (15)	−0.0042 (16)	0.0052 (16)	−0.0025 (14)
C1	0.068 (2)	0.0692 (18)	0.0697 (17)	0.0159 (17)	0.0009 (16)	−0.0051 (17)
C8	0.065 (2)	0.0776 (18)	0.0733 (17)	−0.0135 (18)	0.0016 (17)	−0.0006 (17)
C6	0.0592 (19)	0.0778 (18)	0.0572 (15)	0.0090 (17)	0.0002 (14)	−0.0069 (15)
C2	0.072 (2)	0.0751 (19)	0.0665 (17)	0.0011 (18)	−0.0016 (16)	−0.0044 (17)
C9	0.068 (2)	0.084 (2)	0.0632 (16)	−0.0165 (19)	0.0125 (16)	−0.0001 (16)
C11	0.063 (2)	0.094 (2)	0.0801 (19)	−0.0177 (19)	0.0167 (18)	−0.0068 (19)
C12	0.066 (2)	0.107 (2)	0.0689 (17)	−0.004 (2)	0.0148 (18)	−0.0094 (19)
C5	0.072 (2)	0.0706 (18)	0.0706 (17)	0.0124 (17)	−0.0058 (17)	−0.0094 (17)
N1	0.094 (2)	0.128 (3)	0.101 (2)	−0.030 (2)	−0.031 (2)	0.034 (2)

Geometric parameters (Å, °)

O1—C6	1.365 (4)	C10—C11	1.371 (4)
O1—C7	1.403 (4)	C10—C9	1.377 (4)
F1—C1	1.350 (3)	C1—C2	1.359 (4)
C3—C4	1.379 (5)	C1—C6	1.380 (4)
C3—C2	1.391 (4)	C8—C9	1.378 (4)
C3—C13	1.425 (4)	C8—H8	0.9300
C13—N1	1.135 (4)	C6—C5	1.375 (4)
C7—C12	1.368 (5)	C2—H2	0.9300
C7—C8	1.368 (4)	C9—H9	0.9300
O2—C10	1.375 (3)	C11—C12	1.376 (4)
O2—H201	0.8200	C11—H11	0.9300
C4—C5	1.379 (4)	C12—H12	0.9300
C4—H4	0.9300	C5—H5	0.9300
C6—O1—C7	118.0 (2)	C9—C8—H8	120.0
C4—C3—C2	119.7 (3)	O1—C6—C5	124.6 (3)
C4—C3—C13	119.8 (3)	O1—C6—C1	116.9 (3)
C2—C3—C13	120.5 (3)	C5—C6—C1	118.4 (3)
N1—C13—C3	177.8 (5)	C1—C2—C3	118.4 (3)
C12—C7—C8	120.1 (3)	C1—C2—H2	120.8
C12—C7—O1	118.1 (3)	C3—C2—H2	120.8
C8—C7—O1	121.6 (3)	C10—C9—C8	119.9 (3)
C10—O2—H201	109.5	C10—C9—H9	120.0
C5—C4—C3	120.7 (3)	C8—C9—H9	120.0
C5—C4—H4	119.6	C10—C11—C12	119.7 (3)
C3—C4—H4	119.6	C10—C11—H11	120.1
C11—C10—O2	117.7 (3)	C12—C11—H11	120.1
C11—C10—C9	119.9 (3)	C7—C12—C11	120.3 (3)
O2—C10—C9	122.4 (3)	C7—C12—H12	119.8
F1—C1—C2	118.7 (3)	C11—C12—H12	119.8
F1—C1—C6	118.5 (3)	C6—C5—C4	119.9 (3)
C2—C1—C6	122.8 (3)	C6—C5—H5	120.0
C7—C8—C9	119.9 (3)	C4—C5—H5	120.0

C7—C8—H8	120.0		
C6—O1—C7—C12	−129.3 (3)	C4—C3—C2—C1	0.0 (5)
C6—O1—C7—C8	56.0 (4)	C13—C3—C2—C1	179.5 (3)
C2—C3—C4—C5	−0.7 (5)	C11—C10—C9—C8	0.8 (5)
C13—C3—C4—C5	179.8 (3)	O2—C10—C9—C8	−179.2 (3)
C12—C7—C8—C9	1.2 (5)	C7—C8—C9—C10	−1.6 (5)
O1—C7—C8—C9	175.8 (3)	O2—C10—C11—C12	−179.7 (3)
C7—O1—C6—C5	27.9 (4)	C9—C10—C11—C12	0.3 (5)
C7—O1—C6—C1	−155.4 (3)	C8—C7—C12—C11	−0.1 (5)
F1—C1—C6—O1	1.0 (4)	O1—C7—C12—C11	−174.8 (3)
C2—C1—C6—O1	−179.0 (3)	C10—C11—C12—C7	−0.7 (5)
F1—C1—C6—C5	177.9 (3)	O1—C6—C5—C4	178.0 (3)
C2—C1—C6—C5	−2.1 (5)	C1—C6—C5—C4	1.4 (5)
F1—C1—C2—C3	−178.6 (3)	C3—C4—C5—C6	0.0 (5)
C6—C1—C2—C3	1.4 (5)		

Hydrogen-bond geometry (Å, °)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
O2—H201···N1^{i}	0.82	2.03	2.839 (4)	168

Symmetry codes: (i) −*x*+1/2, −*y*+2, *z*+1/2.

Fig. 1

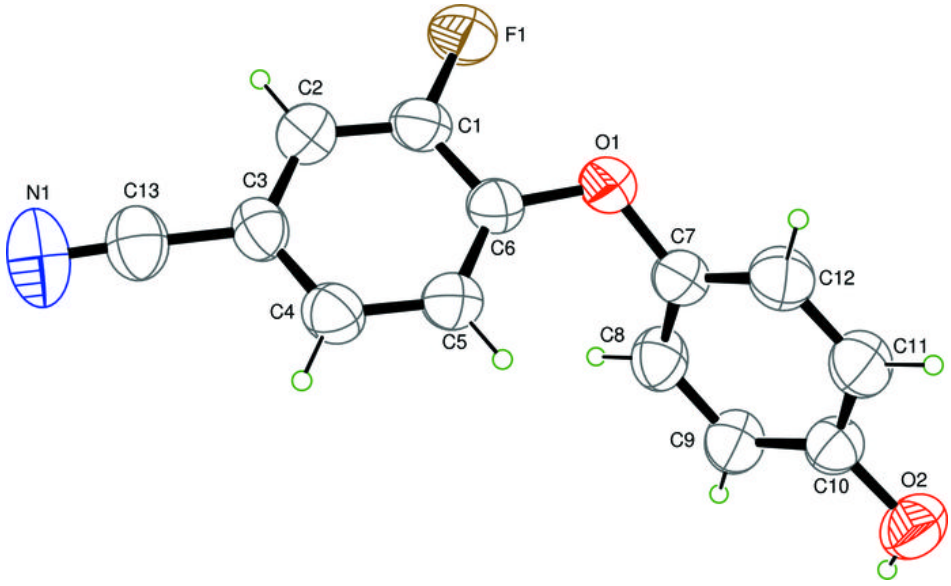
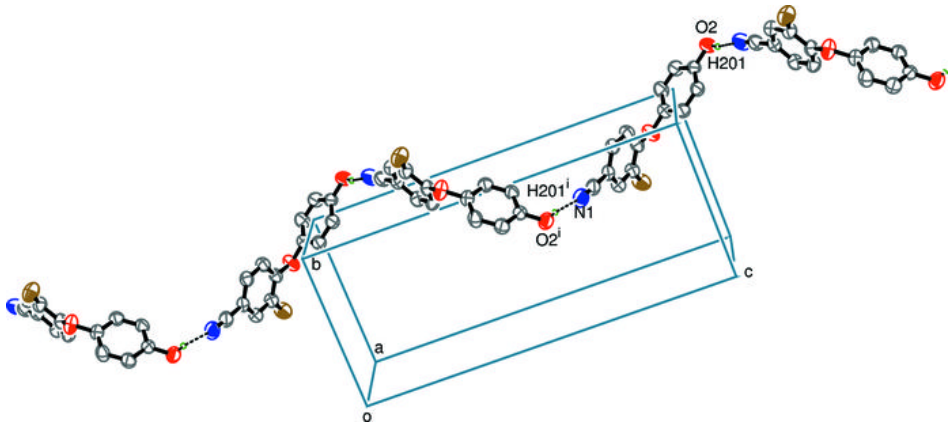


Fig. 2



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4-Fluoroanilinium tetrachloridoferrate(III) 18-crown-6 clathrate

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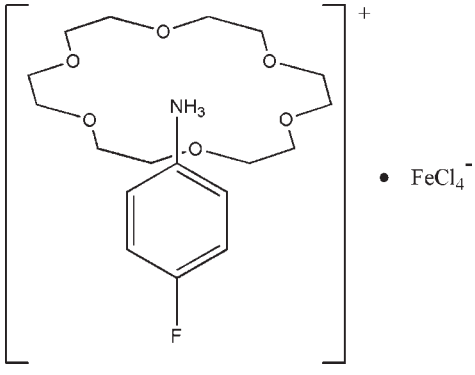
Received 15 May 2010; accepted 27 May 2010

Key indicators: single-crystal X-ray study; T = 293 K; mean σ(C–C) = 0.010 Å; R factor = 0.078; wR factor = 0.271; data-to-parameter ratio = 21.5.

The reaction of 4-fluoroaniline hydrochloride, 18-crown-6 and ferric chloride in methanolic solution yields the title compound, $(C_6H_7FN)[FeCl_4]\cdot C_{12}H_{24}O_6$, which has an unusual supramolecular structure. N—H···O hydrogen-bonding interactions between the NH_3^+ substituents of the 4-fluoroanilinium cations and the O atoms of the crown ether molecules result in a rotator–stator-like structure.

Related literature

For a related 18-crown-6 clathrate, see: Fender *et al.* (2002). For the ferroelectric properties of selected transition metal complexes, see: Fu *et al.* (2007); Ye *et al.* (2009); Zhang *et al.* (2009).



Experimental

Crystal data

$(C_6H_7FN)[FeCl_4]\cdot C_{12}H_{24}O_6$ M_r = 574.09
Monoclinic, $P2_1/c$
a = 11.45 (1) Å
b = 24.14 (2) Å
c = 9.719 (9) Å
β = 96.82 (2)°
V = 2667 (4) Å^3
Z = 4
Mo $K\alpha$ radiation
μ = 1.00 mm^{-1}
T = 293 K
0.20 × 0.20 × 0.20 mm

Data collection

Rigaku SCXmini diffractometer
Absorption correction: multi-scan (*CrystalClear*; Rigaku, 2005)
T_{min} = 0.818, T_{max} = 0.818
26978 measured reflections
6039 independent reflections
3173 reflections with $I > 2\sigma(I)$
R_{int} = 0.068

Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.078
$wR(F^2)$ = 0.271
S = 1.07
6039 reflections
281 parameters
H-atom parameters constrained
$\Delta\rho_{max}$ = 0.49 e Å^{-3}
$\Delta\rho_{min}$ = −0.35 e Å^{-3}

Table 1
Hydrogen-bond geometry (Å, °).

D—H···A	D—H	H···A	D···A	D—H···A
N1—H1C···O4^{i}	0.89	1.98	2.868 (6)	176
N1—H1D···O6^{i}	0.89	2.04	2.924 (6)	173
N1—H1E···O2^{i}	0.89	1.98	2.840 (6)	162

Symmetry code: (i) $x, y, z-1$.

Data collection: *CrystalClear* (Rigaku, 2005); cell refinement: *CrystalClear*; data reduction: *CrystalClear*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *SHELXTL* (Sheldrick, 2008); software used to prepare material for publication: *PRPKAPPA* (Ferguson, 1999).

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Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: IM2203).

References

Fender, N. S., Kahwa, I. A. & Fronczek, F. R. (2002). *J. Solid State Chem.* **163**, 286–293.
Ferguson, G. (1999). *PRPKAPPA*. University of Guelph, Canada.
Fu, D. W., Song, Y. M., Wang, G. X., Ye, Q., Xiong, R. G., Akutagawa, T., Nakamura, T., Chan, P. W. H. & Huang, S. P. (2007). *J. Am. Chem. Soc.* **129**, 5346–5347.
Rigaku (2005). *CrystalClear*. Rigaku Corporation, Tokyo, Japan.
Sheldrick, G. M. (2008). *Acta Cryst.* A**64**, 112–122.
Ye, H. Y., Fu, D. W., Zhang, Y., Zhang, W., Xiong, R. G. & Huang, S. P. (2009). *J. Am. Chem. Soc.* **131**, 42–43.
Zhang, W., Cheng, L. Z., Xiong, R. G., Nakamura, T. & Huang, S. P. (2009). *J. Am. Chem. Soc.* **131**, 12544–12545.

supplementary materials

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4-Fluoroanilinium tetrachloridoferrate(III) 18-crown-6 clathrate

J.-Z. Ge and M.-M. Zhao

Comment

Crown ethers have attracted much attention because of their ability to form non-covalent, H-bonding complexes with ammonium cations both in solid and in solution (Fender *et al.* 2002). Both the size of the crown ether and the nature of the ammonium cation (-NH_4^+, RNH_3^+, *etc*) can influence the stoichiometry and stability of these host-guest complexes. The host molecules combine with the guest species by intermolecular interactions, and if the host molecule possess some specific sites (by chelate effect), it is easy to realise high selectivity in ion or molecular recognitions.18-crown-6 have the highest affinity for ammonium cation RNH_3^+ and most studies of 18-crown-6 and its derivatives invariably showed a 1:1 stoichiometry with RNH_3^+ cations.

In continuation of our investigations on ferroelectric phase transitions materials the dielectric permittivity of the title compound was tested (Fu *et al.* 2007; Ye *et al.* 2009; Zhang *et al.* 2009). The title compound shows no dielectric anomalies with values of 6-8 and 7-10 in the temperature ranges from 80 to 300 K and 300 K to 400 K (below the compound melting point 433 K), respectively. These findings suggest that the compound should exhibit no distinct phase transition within the measured temperature range.

The title compound crystallizes in the $P2_1/c$ space group. The asymmetric unit of the title compound is composed of a cationic $[(C_6H_4FN_3)\ (18\text{-Crown-6})]^+$ moiety and one isolated anionic $[FeCl_4]^-$ (Fig 1). The protonated *p*-fluoroanilinium $[C_6H_4FNH_3]^+$ and 18-crown-6 form a superamolecular rotator-stator-like structure by forming N—H···O hydrogen bonds between the -NH_3^+ substitutents of the cations and oxygen atoms of crown ethers. Intramolecular N—H···O hydrogen distances within the usual range: 2.950 (6) and 2.840 (6) Å. The crown ring is slight distorted. The six oxygen atoms of the crown ether lie approximately in a plane. The C—N bonds of $[C_6H_4FNH_3]^+$ are almost perpendicular to the mean oxygen plane.

The typical Fe—Cl bond lengths in the tetrahedral coordinate anion $[FeCl_4]^-$ are within 2.170 (3)-2.184 (2) Å. The Cl—Fe—Cl bond angles indicate little distortion from a regular tetrahedron [spread of values 108.3 (1)-110.7 (1)°].

Fig. 2 shows a view down the *a* axis. An alternate arrangement of cation and anion layers is observed along the *c* axis, a couple of head-to-head rotator-stator cations and an anion $[FeCl_4]^-$ along the *b* axis. No significantly short intermolecular hydrogen bond was observed.

Experimental

p-F-C_6H_4-NH_2 × HCl (2 mmol, 0.295 g) and 18-crown-6 (2 mmol, 0.528 g) were dissolved in methanol. After addition of ferric chloride (2 mmol, 0.54 g) in concentrated hydrochloric acid, a precipitate (yield is about 95%) was formed, filtered

and washed with a small amount of methanol. Single crystals suitable for X-ray diffraction analysis were obtained from slow evaporation of methanol and DMF (*v*/*v* 3/1) from the solution at room temperature after two days.

Refinement

All hydrogens were were calculated geometrically. The positions of the H atoms of the nitrogen atoms were refined using a riding model with N—H = 0.89 Å and U_{iso}(H) = 1.5U_{eq}(N). C—H groups were also refined using a riding model for hydrogen atoms with C—H distances ranging from 0.93 to 0.97 Å and U_{iso}(H) = 1.2Ueq(C).

Figures

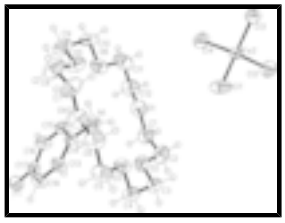


Fig. 1. The molecular structure of the title compound, with the atomic numbering scheme. Displacement ellipsoids are drawn at the 30% probability level.

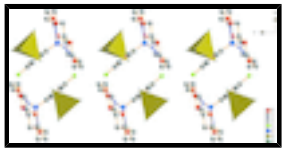


Fig. 2. A view of the packing of the title compound, stacking along the *a* axis. Dashed lines indicate hydrogen bonds.

4-Fluoroanilinium tetrachloridoferrate(III)–1,4,7,10,13,16-hexaoxacyclooctadecane (1/1)

Crystal data

$(C_6H_7FN)[FeCl_4]\cdot C_{12}H_{24}O_6$	$F(000)$ = 1188
M_r = 574.09	D_x = 1.430 Mg m^{-3}
Monoclinic, $P2_1/c$	Mo $K\alpha$ radiation, λ = 0.71073 Å
Hall symbol: -P 2ybc	Cell parameters from 5625 reflections
a = 11.45 (1) Å	θ = 2.3–27.5°
b = 24.14 (2) Å	μ = 1.00 mm^{-1}
c = 9.719 (9) Å	*T* = 293 K
β = 96.82 (2)°	Block, pale yellow
V = 2667 (4) Å^3	0.20 × 0.20 × 0.20 mm
Z = 4	

Data collection

Rigaku SCXmini diffractometer	6039 independent reflections
Radiation source: fine-focus sealed tube	3173 reflections with $I > 2\sigma(I)$
graphite	R_{int} = 0.068
Detector resolution: 13.6612 pixels mm^{-1}	θ_{max} = 27.5°, θ_{min} = 2.3°
ω scans	*h* = −14→14
Absorption correction: multi-scan	*k* = −31→31

(*CrystalClear*; Rigaku, 2005)
T_{min} = 0.818, T_{max} = 0.818
26978 measured reflections

l = −12→12

Refinement

Refinement on F^2	Primary atom site location: structure-invariant direct methods
Least-squares matrix: full	Secondary atom site location: difference Fourier map
$R[F^2 > 2\sigma(F^2)]$ = 0.078	Hydrogen site location: inferred from neighbouring sites
$wR(F^2)$ = 0.271	H-atom parameters constrained
S = 1.07	$w = 1/[\sigma^2(F_o^2) + (0.1312P)^2 + 0.8151P]$ where $P = (F_o^2 + 2F_c^2)/3$
6039 reflections	$(\Delta/\sigma)_{max}$ = 0.005
281 parameters	$\Delta\rho_{max}$ = 0.49 e Å^{-3}
0 restraints	$\Delta\rho_{min}$ = −0.35 e Å^{-3}

Special details

Geometry. All esds (except the esd in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell esds are taken into account individually in the estimation of esds in distances, angles and torsion angles; correlations between esds in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell esds is used for estimating esds involving l.s. planes.

Refinement. Refinement of F^2 against ALL reflections. The weighted *R*-factor wR and goodness of fit *S* are based on F^2, conventional *R*-factors *R* are based on *F*, with *F* set to zero for negative F^2. The threshold expression of $F^2 > \sigma(F^2)$ is used only for calculating *R*-factors(gt) etc. and is not relevant to the choice of reflections for refinement. *R*-factors based on F^2 are statistically about twice as large as those based on *F*, and *R*- factors based on ALL data will be even larger.

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å^2)

	x	*y*	*z*	U_{iso}*/U_{eq}
O1	0.5434 (4)	0.09467 (19)	0.7021 (5)	0.0842 (13)
O2	0.7834 (4)	0.06611 (18)	0.6808 (4)	0.0816 (12)
O3	0.9463 (3)	0.14900 (18)	0.7297 (5)	0.0741 (11)
O4	0.8972 (4)	0.23864 (18)	0.8904 (5)	0.0849 (13)
O5	0.6635 (4)	0.25943 (19)	0.9254 (5)	0.0903 (14)
O6	0.4892 (4)	0.1787 (2)	0.8722 (5)	0.0895 (14)
C1	0.5820 (8)	0.0397 (3)	0.6788 (9)	0.102 (2)
H1A	0.5188	0.0190	0.6268	0.122*
H1B	0.6025	0.0212	0.7670	0.122*
C2	0.6847 (7)	0.0408 (3)	0.6013 (8)	0.093 (2)
H2A	0.7049	0.0033	0.5776	0.112*
H2B	0.6653	0.0613	0.5158	0.112*
C3	0.8831 (6)	0.0647 (3)	0.6178 (7)	0.0800 (18)
H3A	0.8688	0.0824	0.5278	0.096*
H3B	0.9053	0.0265	0.6039	0.096*

C4	0.9802 (6)	0.0937 (3)	0.7041 (7)	0.0798 (18)
H4A	0.9987	0.0743	0.7913	0.096*
H4B	1.0500	0.0939	0.6565	0.096*
C5	1.0380 (5)	0.1806 (3)	0.7950 (8)	0.086 (2)
H5A	1.1034	0.1806	0.7400	0.104*
H5B	1.0650	0.1648	0.8850	0.104*
C6	0.9964 (6)	0.2383 (3)	0.8120 (9)	0.091 (2)
H6A	1.0596	0.2603	0.8595	0.109*
H6B	0.9739	0.2546	0.7216	0.109*
C7	0.8554 (8)	0.2921 (3)	0.9050 (10)	0.104 (3)
H7A	0.8286	0.3074	0.8145	0.124*
H7B	0.9180	0.3154	0.9488	0.124*
C8	0.7560 (8)	0.2905 (3)	0.9917 (11)	0.113 (3)
H8A	0.7825	0.2743	1.0812	0.136*
H8B	0.7293	0.3280	1.0067	0.136*
C9	0.5658 (7)	0.2584 (4)	0.9976 (9)	0.100 (2)
H9A	0.5470	0.2955	1.0261	0.120*
H9B	0.5813	0.2355	1.0798	0.120*
C10	0.4667 (6)	0.2353 (3)	0.9035 (9)	0.091 (2)
H10A	0.3948	0.2377	0.9469	0.109*
H10B	0.4561	0.2567	0.8184	0.109*
C11	0.4035 (6)	0.1551 (4)	0.7758 (10)	0.101 (2)
H11A	0.3981	0.1759	0.6899	0.122*
H11B	0.3276	0.1569	0.8108	0.122*
C12	0.4324 (6)	0.0968 (3)	0.7491 (10)	0.100 (2)
H12A	0.4329	0.0753	0.8334	0.119*
H12B	0.3736	0.0813	0.6797	0.119*
F1	0.8204 (4)	0.00256 (15)	0.3199 (4)	0.0906 (12)
N1	0.7364 (3)	0.14716 (16)	−0.1213 (4)	0.0498 (9)
H1C	0.7853	0.1760	−0.1140	0.075*
H1D	0.6625	0.1592	−0.1276	0.075*
H1E	0.7467	0.1277	−0.1967	0.075*
C13	0.8711 (5)	0.0971 (3)	0.0489 (7)	0.0748 (17)
H13A	0.9340	0.1117	0.0085	0.090*
C14	0.7606 (4)	0.11179 (19)	0.0016 (5)	0.0493 (11)
C15	0.6684 (5)	0.0924 (3)	0.0657 (7)	0.0699 (16)
H15A	0.5920	0.1037	0.0355	0.084*
C16	0.6894 (6)	0.0558 (3)	0.1752 (7)	0.0758 (17)
H16A	0.6279	0.0427	0.2206	0.091*
C17	0.8011 (6)	0.0396 (2)	0.2148 (6)	0.0658 (15)
C18	0.8913 (6)	0.0598 (3)	0.1588 (7)	0.0804 (18)
H18A	0.9676	0.0493	0.1922	0.096*
Fe2	0.25883 (7)	0.12580 (3)	0.22601 (9)	0.0635 (3)
Cl1	0.44359 (16)	0.11643 (9)	0.3030 (3)	0.1179 (8)
Cl2	0.2109 (2)	0.06493 (9)	0.0642 (2)	0.1121 (7)
Cl3	0.22522 (16)	0.20828 (7)	0.13775 (19)	0.0840 (5)
Cl4	0.1561 (2)	0.11388 (10)	0.3981 (2)	0.1144 (8)

Atomic displacement parameters (Å^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
O1	0.079 (3)	0.078 (3)	0.094 (3)	−0.018 (2)	0.006 (2)	−0.002 (2)
O2	0.104 (4)	0.073 (3)	0.070 (3)	0.002 (2)	0.015 (2)	−0.007 (2)
O3	0.058 (2)	0.079 (3)	0.086 (3)	0.010 (2)	0.012 (2)	0.006 (2)
O4	0.081 (3)	0.076 (3)	0.100 (3)	−0.021 (2)	0.021 (2)	−0.006 (2)
O5	0.086 (3)	0.078 (3)	0.109 (4)	0.010 (2)	0.022 (3)	−0.015 (3)
O6	0.062 (3)	0.098 (3)	0.109 (4)	0.013 (2)	0.013 (2)	0.017 (3)
C1	0.122 (7)	0.089 (5)	0.091 (5)	−0.017 (5)	0.003 (5)	−0.016 (4)
C2	0.115 (6)	0.074 (4)	0.090 (5)	−0.018 (4)	0.011 (4)	−0.024 (4)
C3	0.093 (5)	0.077 (4)	0.073 (4)	0.029 (4)	0.017 (3)	−0.005 (3)
C4	0.080 (4)	0.072 (4)	0.089 (5)	0.020 (3)	0.017 (4)	0.000 (3)
C5	0.045 (3)	0.101 (5)	0.114 (5)	−0.010 (3)	0.010 (3)	0.013 (4)
C6	0.068 (4)	0.097 (5)	0.110 (6)	−0.021 (4)	0.020 (4)	0.006 (4)
C7	0.127 (7)	0.066 (4)	0.120 (6)	−0.022 (4)	0.025 (5)	−0.029 (4)
C8	0.112 (6)	0.092 (5)	0.136 (7)	−0.022 (5)	0.017 (5)	−0.046 (5)
C9	0.091 (5)	0.109 (6)	0.108 (6)	0.024 (4)	0.044 (5)	0.002 (5)
C10	0.071 (4)	0.085 (5)	0.121 (6)	0.029 (4)	0.036 (4)	0.012 (4)
C11	0.057 (4)	0.117 (6)	0.129 (6)	−0.003 (4)	0.011 (4)	0.036 (5)
C12	0.059 (4)	0.102 (6)	0.135 (7)	−0.028 (4)	0.002 (4)	0.013 (5)
F1	0.122 (3)	0.087 (2)	0.065 (2)	0.032 (2)	0.019 (2)	0.0282 (19)
N1	0.048 (2)	0.049 (2)	0.053 (2)	0.0015 (17)	0.0086 (18)	0.0046 (18)
C13	0.053 (3)	0.096 (4)	0.075 (4)	−0.004 (3)	0.006 (3)	0.019 (3)
C14	0.054 (3)	0.048 (3)	0.047 (3)	0.002 (2)	0.011 (2)	−0.003 (2)
C15	0.053 (3)	0.078 (4)	0.081 (4)	0.012 (3)	0.018 (3)	0.022 (3)
C16	0.072 (4)	0.075 (4)	0.086 (4)	0.011 (3)	0.032 (3)	0.024 (3)
C17	0.090 (4)	0.055 (3)	0.053 (3)	0.007 (3)	0.010 (3)	0.005 (2)
C18	0.061 (4)	0.105 (5)	0.074 (4)	0.015 (3)	0.003 (3)	0.026 (4)
Fe2	0.0551 (5)	0.0653 (5)	0.0706 (5)	0.0049 (4)	0.0089 (4)	−0.0102 (4)
Cl1	0.0592 (10)	0.1006 (14)	0.187 (2)	0.0182 (9)	−0.0152 (12)	−0.0312 (14)
Cl2	0.1251 (17)	0.0938 (13)	0.1119 (15)	0.0013 (11)	−0.0090 (12)	−0.0418 (12)
Cl3	0.0859 (11)	0.0766 (10)	0.0914 (11)	0.0080 (8)	0.0180 (9)	0.0043 (9)
Cl4	0.1298 (18)	0.1178 (16)	0.1061 (15)	0.0209 (13)	0.0577 (13)	0.0211 (12)

Geometric parameters (Å, °)

O1—C12	1.401 (8)	C8—H8B	0.9700
O1—C1	1.425 (9)	C9—C10	1.480 (12)
O2—C3	1.357 (8)	C9—H9A	0.9700
O2—C2	1.428 (8)	C9—H9B	0.9700
O3—C5	1.388 (7)	C10—H10A	0.9700
O3—C4	1.420 (7)	C10—H10B	0.9700
O4—C7	1.388 (8)	C11—C12	1.476 (11)
O4—C6	1.441 (8)	C11—H11A	0.9700
O5—C9	1.390 (8)	C11—H11B	0.9700
O5—C8	1.391 (9)	C12—H12A	0.9700
O6—C11	1.396 (9)	C12—H12B	0.9700

O6—C10	1.428 (8)	F1—C17	1.356 (6)
C1—C2	1.471 (11)	N1—C14	1.467 (6)
C1—H1A	0.9700	N1—H1C	0.8900
C1—H1B	0.9700	N1—H1D	0.8900
C2—H2A	0.9700	N1—H1E	0.8900
C2—H2B	0.9700	C13—C14	1.341 (8)
C3—C4	1.486 (10)	C13—C18	1.396 (8)
C3—H3A	0.9700	C13—H13A	0.9300
C3—H3B	0.9700	C14—C15	1.371 (7)
C4—H4A	0.9700	C15—C16	1.381 (8)
C4—H4B	0.9700	C15—H15A	0.9300
C5—C6	1.487 (10)	C16—C17	1.349 (9)
C5—H5A	0.9700	C16—H16A	0.9300
C5—H5B	0.9700	C17—C18	1.317 (8)
C6—H6A	0.9700	C18—H18A	0.9300
C6—H6B	0.9700	Fe2—Cl1	2.170 (3)
C7—C8	1.495 (12)	Fe2—Cl2	2.175 (2)
C7—H7A	0.9700	Fe2—Cl4	2.175 (3)
C7—H7B	0.9700	Fe2—Cl3	2.184 (2)
C8—H8A	0.9700		
C12—O1—C1	113.4 (6)	O5—C9—C10	107.4 (7)
C3—O2—C2	113.5 (5)	O5—C9—H9A	110.2
C5—O3—C4	112.9 (5)	C10—C9—H9A	110.2
C7—O4—C6	111.2 (5)	O5—C9—H9B	110.2
C9—O5—C8	113.0 (7)	C10—C9—H9B	110.2
C11—O6—C10	113.7 (6)	H9A—C9—H9B	108.5
O1—C1—C2	110.2 (6)	O6—C10—C9	110.3 (6)
O1—C1—H1A	109.6	O6—C10—H10A	109.6
C2—C1—H1A	109.6	C9—C10—H10A	109.6
O1—C1—H1B	109.6	O6—C10—H10B	109.6
C2—C1—H1B	109.6	C9—C10—H10B	109.6
H1A—C1—H1B	108.1	H10A—C10—H10B	108.1
O2—C2—C1	111.2 (6)	O6—C11—C12	110.7 (6)
O2—C2—H2A	109.4	O6—C11—H11A	109.5
C1—C2—H2A	109.4	C12—C11—H11A	109.5
O2—C2—H2B	109.4	O6—C11—H11B	109.5
C1—C2—H2B	109.4	C12—C11—H11B	109.5
H2A—C2—H2B	108.0	H11A—C11—H11B	108.1
O2—C3—C4	110.3 (6)	O1—C12—C11	108.9 (6)
O2—C3—H3A	109.6	O1—C12—H12A	109.9
C4—C3—H3A	109.6	C11—C12—H12A	109.9
O2—C3—H3B	109.6	O1—C12—H12B	109.9
C4—C3—H3B	109.6	C11—C12—H12B	109.9
H3A—C3—H3B	108.1	H12A—C12—H12B	108.3
O3—C4—C3	109.9 (5)	C14—N1—H1C	109.5
O3—C4—H4A	109.7	C14—N1—H1D	109.5
C3—C4—H4A	109.7	H1C—N1—H1D	109.5
O3—C4—H4B	109.7	C14—N1—H1E	109.5
C3—C4—H4B	109.7	H1C—N1—H1E	109.5

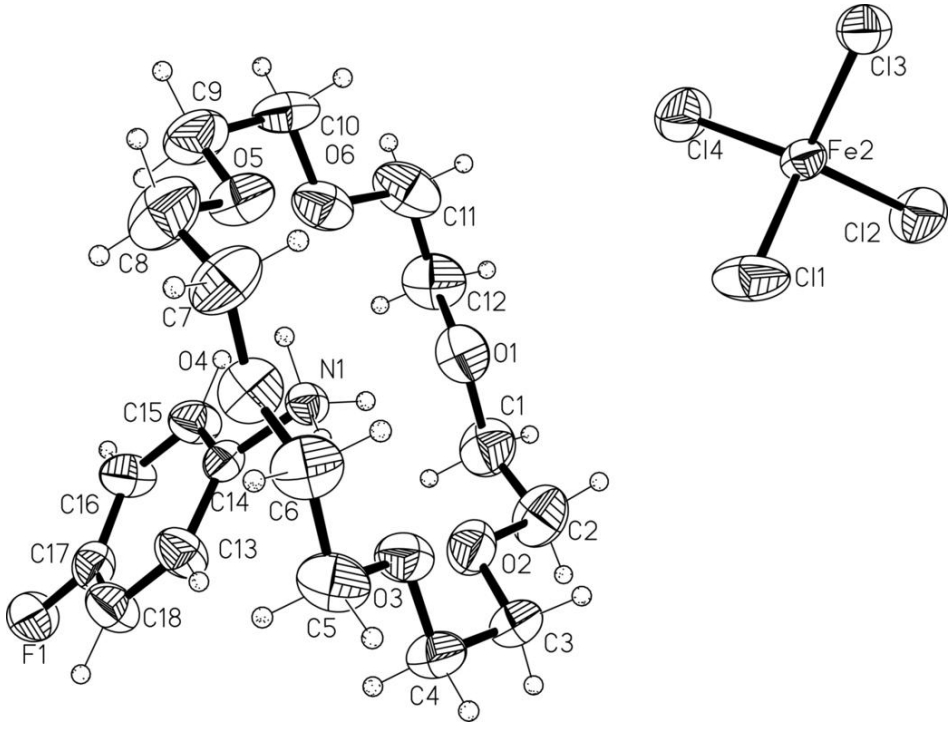
H4A—C4—H4B	108.2	H1D—N1—H1E	109.5
O3—C5—C6	109.3 (5)	C14—C13—C18	119.8 (5)
O3—C5—H5A	109.8	C14—C13—H13A	120.1
C6—C5—H5A	109.8	C18—C13—H13A	120.1
O3—C5—H5B	109.8	C13—C14—C15	120.0 (5)
C6—C5—H5B	109.8	C13—C14—N1	120.8 (5)
H5A—C5—H5B	108.3	C15—C14—N1	119.2 (5)
O4—C6—C5	110.3 (5)	C14—C15—C16	119.7 (5)
O4—C6—H6A	109.6	C14—C15—H15A	120.1
C5—C6—H6A	109.6	C16—C15—H15A	120.1
O4—C6—H6B	109.6	C17—C16—C15	118.5 (5)
C5—C6—H6B	109.6	C17—C16—H16A	120.7
H6A—C6—H6B	108.1	C15—C16—H16A	120.7
O4—C7—C8	109.2 (7)	C18—C17—C16	122.6 (6)
O4—C7—H7A	109.8	C18—C17—F1	119.3 (6)
C8—C7—H7A	109.8	C16—C17—F1	118.1 (6)
O4—C7—H7B	109.8	C17—C18—C13	119.2 (6)
C8—C7—H7B	109.8	C17—C18—H18A	120.4
H7A—C7—H7B	108.3	C13—C18—H18A	120.4
O5—C8—C7	109.9 (7)	Cl1—Fe2—Cl2	109.35 (9)
O5—C8—H8A	109.7	Cl1—Fe2—Cl4	108.36 (13)
C7—C8—H8A	109.7	Cl2—Fe2—Cl4	110.70 (12)
O5—C8—H8B	109.7	Cl1—Fe2—Cl3	110.46 (9)
C7—C8—H8B	109.7	Cl2—Fe2—Cl3	108.32 (11)
H8A—C8—H8B	108.2	Cl4—Fe2—Cl3	109.66 (8)

Hydrogen-bond geometry (Å, °)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
N1—H1C···O4^{i}	0.89	1.98	2.868 (6)	176.
N1—H1D···O6^{i}	0.89	2.04	2.924 (6)	173.
N1—H1E···O2^{i}	0.89	1.98	2.840 (6)	162.

Symmetry codes: (i) *x*, *y*, *z*−1.

Fig. 1


C9
C10
O5
O6
C11
C8
C12
C7
O4
N1
O1
C15
C1
C16
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C6
C2
C17
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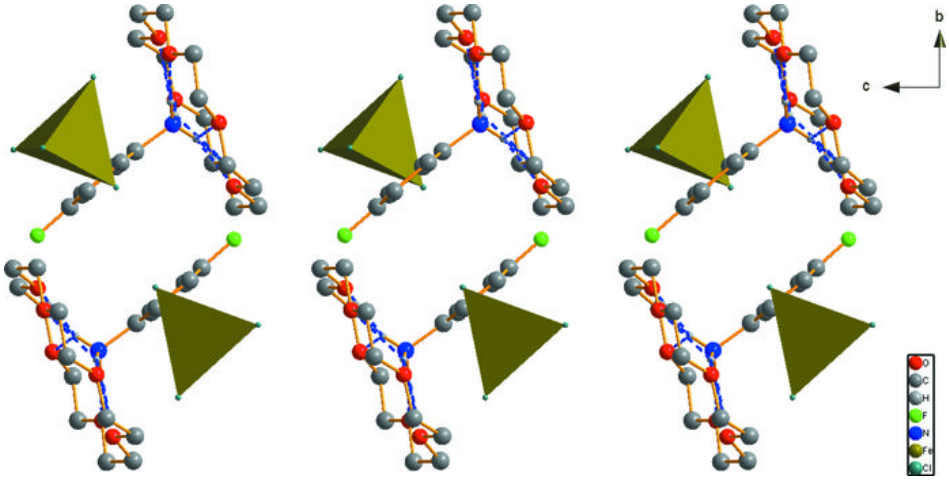
C4
Cl3
Cl4
Fe2
Cl2
Cl1

Fig. 2



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1,4-Dibromo-2,5-dimethoxybenzene

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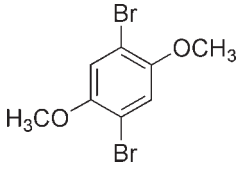
Received 17 May 2010; accepted 17 June 2010

Key indicators: single-crystal X-ray study; T = 298 K; mean σ(C–C) = 0.008 Å; R factor = 0.044; wR factor = 0.102; data-to-parameter ratio = 16.1.

The asymmetric unit of the title compound, $C_8H_8Br_2O_2$, contains one half-molecule, the complete molecule being generated by inversion symmetry.

Related literature

For standard bond lengths, see: Allen *et al.* (1987). For the synthetic procedure, see: Lopez-Alvarado *et al.* (2002). For potential uses of compounds derived from the title compound, see: Chen *et al.* (2006).



Experimental

Crystal data

$C_8H_8Br_2O_2$
M_r = 295.94
Monoclinic, $P2_1/n$
a = 6.573 (1) Å
b = 8.438 (2) Å
c = 8.756 (2) Å
β = 90.14 (3)°
V = 485.6 (2) Å^3
Z = 2
Mo $K\alpha$ radiation
μ = 8.30 mm^{-1}
T = 298 K
0.20 × 0.10 × 0.10 mm

Data collection

Enraf–Nonius CAD-4 diffractometer
Absorption correction: ψ scan (North *et al.*, 1968)
T_{min} = 0.288, T_{max} = 0.491
1761 measured reflections
884 independent reflections
622 reflections with $I > 2\sigma(I)$
R_{int} = 0.112
3 standard reflections every 200 reflections
intensity decay: 1%

Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.044
$wR(F^2)$ = 0.102
S = 1.01
884 reflections
55 parameters
H-atom parameters constrained
$\Delta\rho_{max}$ = 0.58 e Å^{-3}
$\Delta\rho_{min}$ = −0.41 e Å^{-3}

Data collection: *CAD-4 Software* (Enraf–Nonius, 1985); cell refinement: *CAD-4 Software*; data reduction: *XCAD4* (Harms & Wocadlo, 1995); program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *SHELXTL* (Sheldrick, 2008); software used to prepare material for publication: *SHELXTL*.

The authors thank the Center of Testing and Analysis, Nanjing University, for support.

Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: IM2205).

References

Allen, F. H., Kennard, O., Watson, D. G., Brammer, L., Orpen, A. G. & Taylor, R. (1987). *J. Chem. Soc. Perkin Trans. 2*, pp. S1–19.
Chen, Z. K., Huang, C., Yang, J. S., O'Shea, S. & Loh, K. P. (2006). National University of Singapore, Singapore. WO patent number. 2006093467.
Enraf–Nonius (1985). *CAD-4 Software*. Enraf–Nonius, Delft, The Netherlands.
Harms, K. & Wocadlo, S. (1995). *XCAD4*. University of Marburg, Germany.
Lopez-Alvarado, P., Avendano, C. & Menendez, J. C. (2002). *Synthetic. Commun.* **32**, 3233–3239.
North, A. C. T., Phillips, D. C. & Mathews, F. S. (1968). *Acta Cryst.* A**24**, 351–359.
Sheldrick, G. M. (2008). *Acta Cryst.* A**64**, 112–122.

supplementary materials

Acta Cryst. (2010). E**66**, o1806 [**doi:10.1107/S1600536810023548**]

1,4-Dibromo-2,5-dimethoxybenzene

Z.-H. Luo, J. Chang, M.-L. Feng, Q. Zhang and H.-J. Zhu

Comment

The title compound, 1,4-dibromo-2,5-dimethoxybenzene is an important intermediate in the synthesis of 4-(2',5'-dimethoxy-4'-acetylthiophenyl)phenyl-nonafluorobiphenyl, which can be used as molecular switch, transistor and in the manufacture of memory devices (Chen *et al.*, 2006). We report here the crystal structure of the title compound, (I).

The molecular structure of (I) is shown in Fig. 1. Bond lengths and angles are within normal ranges (Allen *et al.*, 1987).

The benzene ring is planar and it's center respresents a crystallographic center of inversion. So only half of the molecule was observed in the asymmetric unit. No hydrogen bond interactions were observed in the crystal structure.

Experimental

The title compound, (I) was synthesized according to a literature method reported before (Lopez-Alvarado *et al.*, 2002). Single crystals were obtained by slow evaporation of a methanolic (25 ml) solution of the compound (0.30 g, 1.0 mmol) at room temperature for about 15 d.

Refinement

H atoms were positioned geometrically, with C—H = 0.93 Å for aromatic H and 0.96 Å for methyl H, and constrained to ride on their parent atoms, with U_{iso}(H) = xU_{eq}(C/O), where x = 1.2 for aromatic H and x = 1.5 for other H.

Figures

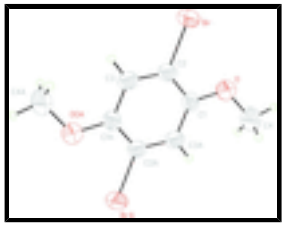


Fig. 1. Molecular structure of the title compound showing the atom-numbering scheme. Displacement ellipsoids are drawn at the 40% probability level.

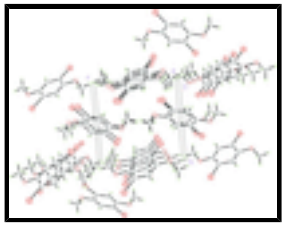


Fig. 2. Molecular packing of the title compound.

1,4-Dibromo-2,5-dimethoxybenzene

Crystal data

$C_8H_8Br_2O_2$	$F(000) = 284$
$M_r = 295.94$	$D_x = 2.024$ Mg m^{-3}
Monoclinic, $P2_1/n$	Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å
Hall symbol: -P 2yn	Cell parameters from 25 reflections
$a = 6.573$ (1) Å	$\theta = 9$–$13°$
$b = 8.438$ (2) Å	$\mu = 8.30$ mm^{-1}
$c = 8.756$ (2) Å	$T = 298$ K
$\beta = 90.14$ (3)°	Block, colourless
$V = 485.6$ (2) Å^3	0.20 × 0.10 × 0.10 mm
$Z = 2$	

Data collection

Enraf–Nonius CAD-4 diffractometer	622 reflections with $I > 2\sigma(I)$
Radiation source: fine-focus sealed tube	$R_{int} = 0.112$
graphite	$\theta_{max} = 25.3°$, $\theta_{min} = 3.4°$
ω/2θ scans	$h = -7 \rightarrow 7$
Absorption correction: ψ scan (North *et al.*, 1968)	$k = -10 \rightarrow 0$
$T_{min} = 0.288$, $T_{max} = 0.491$	$l = -10 \rightarrow 10$
1761 measured reflections	3 standard reflections every 200 reflections
884 independent reflections	intensity decay: 1%

Refinement

Refinement on F^2	Primary atom site location: structure-invariant direct methods
Least-squares matrix: full	Secondary atom site location: difference Fourier map
$R[F^2 > 2\sigma(F^2)] = 0.044$	Hydrogen site location: inferred from neighbouring sites
$wR(F^2) = 0.102$	H-atom parameters constrained
$S = 1.01$	$w = 1/[\sigma^2(F_o^2) + (0.03P)^2 + 0.0P]$ where $P = (F_o^2 + 2F_c^2)/3$
884 reflections	$(\Delta/\sigma)_{max} < 0.001$
55 parameters	$\Delta\rho_{max} = 0.58$ e Å^{-3}
0 restraints	$\Delta\rho_{min} = -0.41$ e Å^{-3}

Special details

Geometry. All e.s.d.'s (except the e.s.d. in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell e.s.d.'s are taken into account individually in the estimation of e.s.d.'s in distances, angles and torsion angles; correlations

between e.s.d.'s in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell e.s.d.'s is used for estimating e.s.d.'s involving l.s. planes.

Refinement. Refinement of F^2 against ALL reflections. The weighted *R*-factor *wR* and goodness of fit *S* are based on F^2, conventional *R*-factors *R* are based on *F*, with *F* set to zero for negative F^2. The threshold expression of $F^2 > \sigma(F^2)$ is used only for calculating *R*-factors(gt) *etc*. and is not relevant to the choice of reflections for refinement. *R*-factors based on F^2 are statistically about twice as large as those based on *F*, and *R*- factors based on ALL data will be even larger.

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å^2)

	x	*y*	*z*	U_{iso}*/U_{eq}
Br	0.26386 (11)	0.73471 (7)	0.78061 (8)	0.0598 (3)
O	−0.1091 (7)	0.5578 (5)	0.7000 (5)	0.0551 (11)
C1	−0.0605 (9)	0.5256 (6)	0.8479 (6)	0.0394 (13)
C2	0.1090 (9)	0.5986 (5)	0.9077 (7)	0.0400 (13)
C3	0.1721 (9)	0.5752 (5)	1.0558 (7)	0.0433 (14)
H3A	0.2881	0.6260	1.0922	0.052*
C4	−0.2593 (11)	0.4649 (8)	0.6294 (8)	0.0649 (19)
H4A	−0.2775	0.4993	0.5257	0.097*
H4B	−0.3852	0.4761	0.6837	0.097*
H4C	−0.2181	0.3558	0.6304	0.097*

Atomic displacement parameters (Å^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Br	0.0762 (5)	0.0516 (4)	0.0517 (5)	−0.0207 (3)	0.0162 (3)	0.0026 (3)
O	0.065 (3)	0.055 (2)	0.045 (3)	−0.011 (2)	−0.004 (2)	0.0031 (19)
C1	0.049 (3)	0.036 (3)	0.033 (3)	0.002 (3)	0.007 (3)	−0.003 (2)
C2	0.047 (3)	0.031 (3)	0.042 (4)	−0.004 (3)	0.009 (3)	−0.002 (2)
C3	0.049 (3)	0.034 (3)	0.046 (4)	−0.006 (3)	0.007 (3)	−0.003 (2)
C4	0.070 (5)	0.078 (4)	0.047 (5)	−0.004 (4)	−0.014 (4)	0.009 (4)

Geometric parameters (Å, °)

Br—C2	1.897 (5)	C3—C1^{i}	1.405 (7)
O—C1	1.361 (7)	C3—H3A	0.9300
O—C4	1.403 (8)	C4—H4A	0.9600
C1—C2	1.375 (8)	C4—H4B	0.9600
C1—C3^{i}	1.405 (7)	C4—H4C	0.9600
C2—C3	1.375 (8)		
C1—O—C4	118.1 (5)	C2—C3—H3A	120.1
O—C1—C2	117.4 (5)	C1^{i}—C3—H3A	120.1
O—C1—C3^{i}	124.8 (5)	O—C4—H4A	109.5
C2—C1—C3^{i}	117.8 (5)	O—C4—H4B	109.5
C1—C2—C3	122.5 (5)	H4A—C4—H4B	109.5
C1—C2—Br	118.9 (4)	O—C4—H4C	109.5
C3—C2—Br	118.6 (4)	H4A—C4—H4C	109.5

C2—C3—C1^{i}	119.7 (5)	H4B—C4—H4C	109.5
C4—O—C1—C2	169.3 (5)	O—C1—C2—Br	−1.0 (6)
C4—O—C1—C3^{i}	−11.4 (8)	C3^{i}—C1—C2—Br	179.7 (4)
O—C1—C2—C3	179.8 (5)	C1—C2—C3—C1^{i}	−0.5 (8)
C3^{i}—C1—C2—C3	0.5 (8)	Br—C2—C3—C1^{i}	−179.7 (4)

Symmetry codes: (i) −*x*, −*y*+1, −*z*+2.

Fig. 1

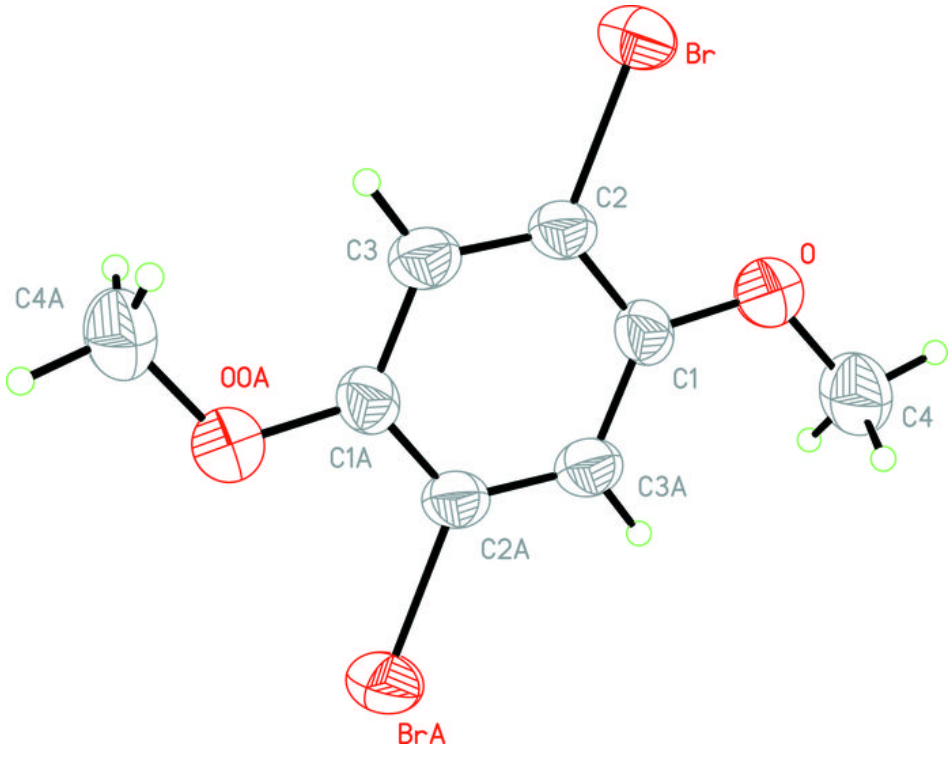
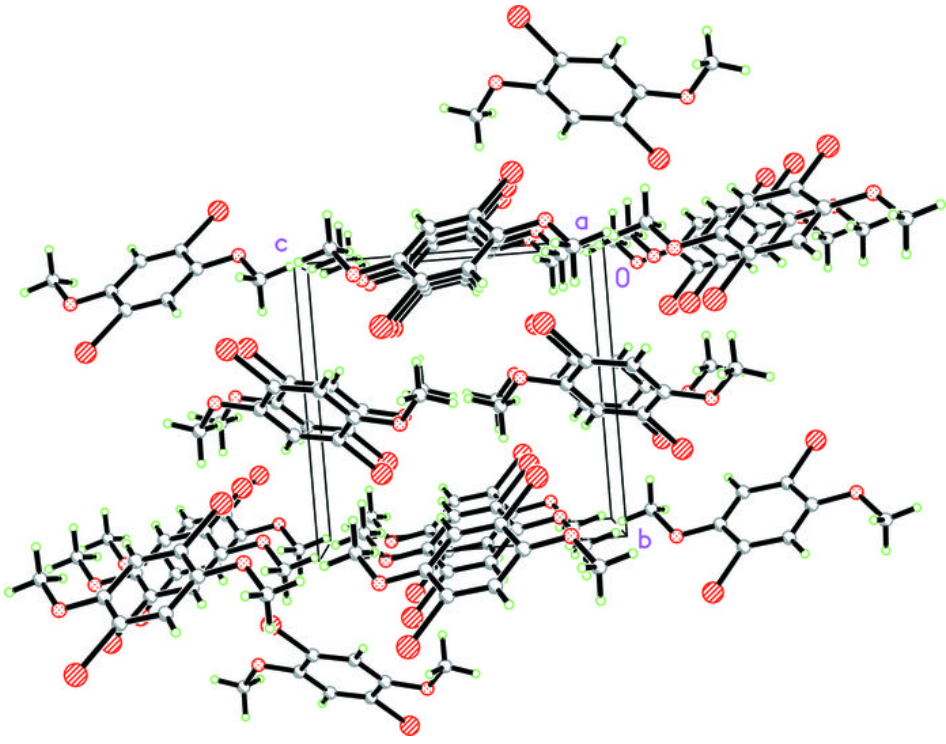


Fig. 2



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Structure Reports Online
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4-Methoxyanilinium hexafluorophosphate monohydrate

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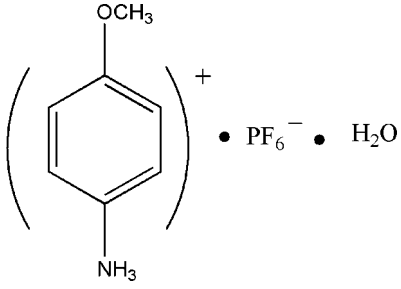
Received 25 May 2010; accepted 10 June 2010

Key indicators: single-crystal X-ray study; T = 298 K; mean σ(C–C) = 0.004 Å; disorder in main residue; R factor = 0.053; wR factor = 0.145; data-to-parameter ratio = 13.1.

In the structure of the title compound, $C_7H_{10}NO^+\cdot PF_6^-\cdot H_2O$, the protonated 4-methoxyanilinium cations and hexafluorophosphate anions are bridged by the water molecule *via* N—H···O and O—H···F hydrogen bonds. The resulting zigzag chains extend along the *c* axis. In addition, C—H···π interactions are observed in the crystal packing.

Related literature

The title compound was studied as part of our search for ferroelectric compounds, which usually have a phase transition. For background to phase-transition materials, see: Li *et al.* (2008); Zhang *et al.* (2009); Fu (2009).



Experimental

Crystal data

$C_7H_{10}NO^+\cdot PF_6^-\cdot H_2O$
M_r = 287.15
Monoclinic, $P2_1/c$
a = 15.152 (3) Å
b = 5.079 (1) Å
c = 14.758 (3) Å
β = 94.26 (3)°
V = 1132.6 (4) Å^3
Z = 4
Mo $K\alpha$ radiation
μ = 0.32 mm^{-1}
T = 298 K
0.20 × 0.20 × 0.20 mm

Data collection

Rigaku SCXmini diffractometer
Absorption correction: multi-scan (*CrystalClear*; Rigaku, 2005)
T_{min} = 0.939, T_{max} = 0.939
11166 measured reflections
2602 independent reflections
2083 reflections with $I > 2\sigma(I)$
R_{int} = 0.052

Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.053
$wR(F^2)$ = 0.145
S = 1.06
2602 reflections
199 parameters
3 restraints
H atoms treated by a mixture of independent and constrained refinement
$\Delta\rho_{max}$ = 0.45 e Å^{-3}
$\Delta\rho_{min}$ = −0.43 e Å^{-3}

Table 1
Hydrogen-bond geometry (Å, °).

D—H···A	D—H	H···A	D···A	D—H···A
N1—H1*C*···O1*W*	0.84 (3)	2.06 (3)	2.896 (3)	172 (3)
N1—H1*A*···O1*W*^{i}	0.92 (3)	2.00 (3)	2.917 (3)	172 (3)
N1—H1*B*···F3^{ii}	0.87 (3)	2.32 (3)	3.056 (5)	142 (2)
N1—H1*B*···F1^{iii}	0.87 (3)	2.49 (3)	3.049 (5)	123 (2)
O1*W*—H1*WB*···F6^{iv}	0.85 (2)	2.21 (4)	2.91 (2)	139 (3)
O1*W*—H1*WB*···F4^{v}	0.85 (2)	2.57 (4)	3.04 (3)	116 (3)
C7—H7*B*···*Cg*1^{vi}	0.96	3.18	4.013 (5)	146

Symmetry codes: (i) $x, y+1, z$; (ii) $x, -y+\frac{1}{2}, z-\frac{1}{2}$; (iii) $x, -y+\frac{3}{2}, z-\frac{1}{2}$; (iv) $-x+2, -y, -z+1$; (v) $-x+2, -y+1, -z+1$; (vi) $-x+1, y+\frac{1}{2}, -z+\frac{1}{2}$.

Data collection: *CrystalClear* (Rigaku, 2005); cell refinement: *CrystalClear*; data reduction: *CrystalClear*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *SHELXTL* (Sheldrick, 2008); software used to prepare material for publication: *PRPKAPPA* (Ferguson, 1999).

The authors are grateful to the Starter Fund of Southeast University for financial support in purchasing the X-ray diffractometer.

Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: IM2206).

References

Ferguson, G. (1999). *PRPKAPPA*. University of Guelph, Canada.
Fu, X. (2009). *Acta Cryst.* E**65**, o2344.
Li, X. Z., Qu, Z. R. & Xiong, R. G. (2008). *Chin. J. Chem.* **11**, 1959–1962.
Rigaku (2005). *CrystalClear*. Rigaku Corporation, Tokyo, Japan.
Sheldrick, G. M. (2008). *Acta Cryst.* A**64**, 112–122.
Zhang, W., Chen, L. Z., Xiong, R. G., Nakamura, T. & Huang, S. D. (2009). *J. Am. Chem. Soc.* **131**, 12544–12545.

supplementary materials

Acta Cryst. (2010). E**66**, o1726 [**doi:10.1107/S1600536810022348**]

4-Methoxyanilinium hexafluorophosphate monohydrate

Y. Yang and X. Fu

Comment

As a continuation of our study of dielectric-ferroelectric materials, including organic ligands (Li *et al.*, 2008), metal-organic coordination compounds (Zhang *et al.*, 2009) and organic-inorganic hybrid materials, we studied the dielectric properties of the title compound. Unfortunately, there was no distinct anomaly observed from 93 K to 350 K, suggesting that this compound should be not a real ferroelectric material or there may be no distinct phase transition occurred within the measured temperature range. The crystal structure of 4-methoxyanilinium bromide is known (Fu, 2009). In this article, the crystal structure of the title compound is presented.

The asymmetric unit of the title compound consists of an almost planar 4-methoxyanilinium cation with a mean deviation from the plan of 0.0512 Å, a disordered hexafluorophosphate anion and a water molecule (Fig.1). N—H···F, N—H···O and O—H···F hydrogen bonds link the cations, anions and water molecules to chains along *c* axis (Fig.2). The C—H···π interactions with a C7···*Cg*1 distance of 4.013 (5) Å are also observed in the crystal packing.

Experimental

1.23 g (10 mmol) 4-Methoxyaniline was dissolved in 10 ml e thanol, to which hexafluorophosphoric acid in aqueous solution (70% *w*/*w*) was then added under stirring until the pH of the solution was *ca* 6. Ethanol was added until all suspended substrates disappeared. Single crystals of the title compound were prepared by slow evaporation of the acidic solution at room temperature of the acidic solution after 3 days giving a yield of 85%.

Refinement

Positional parameters of all the H atoms bonded to C atoms were calculated geometrically and were allowed to ride on the C atoms to which they are bonded, with U_{iso}(H) = 1.2U_{eq}(C) and U_{iso}(H) = 1.5U_{eq}(C) for the methyl group. H atoms bonded to N and O atoms were found in the difference Fourier maps and were refined using restraints for O—H and N—H bond distances (0.85–0.86 Å) and angles at the corresponding O and N atoms. Thermal parameters of these hydrogen atoms were refined freely.

Figures

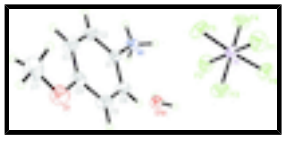


Fig. 1. Molecular structure of the title compound, with the atomic numbering scheme. Displacement ellipsoids are drawn at the 30% probability level.

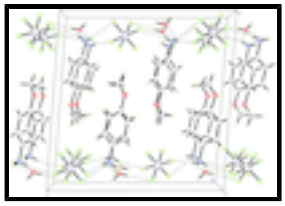


Fig. 2. View of the packing of the title compound, stacking along the *b* axis. Dashed lines indicate hydrogen bonds.

4-Methoxyanilinium hexafluorophosphate monohydrate

Crystal data

$C_7H_{10}NO^+ \cdot PF_6^- \cdot H_2O$	$F(000) = 584$
$M_r = 287.15$	$D_x = 1.684$ Mg m^{-3}
Monoclinic, $P2_1/c$	Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å
Hall symbol: -P 2ybc	Cell parameters from 5000 reflections
$a = 15.152$ (3) Å	$\theta = 3.1$–$27.6°$
$b = 5.079$ (1) Å	$\mu = 0.32$ mm^{-1}
$c = 14.758$ (3) Å	$T = 298$ K
$\beta = 94.26$ (3)°	Prism, colourless
$V = 1132.6$ (4) Å^3	0.20 × 0.20 × 0.20 mm
$Z = 4$	

Data collection

Rigaku SCXmini diffractometer	2602 independent reflections
Radiation source: fine-focus sealed tube	2083 reflections with $I > 2\sigma(I)$
graphite	$R_{int} = 0.052$
Detector resolution: 13.6612 pixels mm^{-1}	$\theta_{max} = 27.5°$, $\theta_{min} = 3.2°$
ω scans	$h = -19 \rightarrow 19$
Absorption correction: multi-scan (*CrystalClear*; Rigaku, 2005)	$k = -6 \rightarrow 6$
$T_{min} = 0.939$, $T_{max} = 0.939$	$l = -19 \rightarrow 18$
11166 measured reflections	

Refinement

Refinement on F^2	Primary atom site location: structure-invariant direct methods
Least-squares matrix: full	Secondary atom site location: difference Fourier map
$R[F^2 > 2\sigma(F^2)] = 0.053$	Hydrogen site location: inferred from neighbouring sites
$wR(F^2) = 0.145$	H atoms treated by a mixture of independent and constrained refinement
$S = 1.06$	$w = 1/[\sigma^2(F_o^2) + (0.0694P)^2 + 0.5932P]$ where $P = (F_o^2 + 2F_c^2)/3$
2602 reflections	$(\Delta/\sigma)_{max} < 0.001$
199 parameters	$\Delta\rho_{max} = 0.45$ e Å^{-3}

3 restraints $\Delta\rho_{min} = -0.43$ e Å^{-3}

Special details

Geometry. All e.s.d.'s (except the e.s.d. in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell e.s.d.'s are taken into account individually in the estimation of e.s.d.'s in distances, angles and torsion angles; correlations between e.s.d.'s in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell e.s.d.'s is used for estimating e.s.d.'s involving l.s. planes.

Refinement. Refinement of F^2 against ALL reflections. The weighted *R*-factor *wR* and goodness of fit *S* are based on F^2, conventional *R*-factors *R* are based on *F*, with *F* set to zero for negative F^2. The threshold expression of $F^2 > \sigma(F^2)$ is used only for calculating *R*-factors(gt) *etc*. and is not relevant to the choice of reflections for refinement. *R*-factors based on F^2 are statistically about twice as large as those based on *F*, and *R*- factors based on ALL data will be even larger.

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å^2)

	x	*y*	*z*	U_{iso}*/U_{eq}	Occ. (<1)
N1	0.83257 (13)	0.3532 (5)	0.34412 (16)	0.0380 (5)	
H1B	0.8411 (18)	0.369 (5)	0.287 (2)	0.044 (7)*	
H1A	0.8573 (19)	0.507 (6)	0.368 (2)	0.054 (8)*	
H1C	0.858 (2)	0.217 (7)	0.365 (2)	0.059 (9)*	
C1	0.73739 (14)	0.3340 (4)	0.35733 (15)	0.0341 (5)	
C6	0.70834 (17)	0.1498 (5)	0.41677 (18)	0.0464 (6)	
H6A	0.7482	0.0365	0.4479	0.056*	
C4	0.56043 (16)	0.3061 (5)	0.38507 (18)	0.0456 (6)	
C2	0.67959 (18)	0.5003 (5)	0.3115 (2)	0.0523 (7)	
H2A	0.7001	0.6220	0.2709	0.063*	
O1	0.47356 (12)	0.2800 (5)	0.40334 (16)	0.0671 (6)	
C5	0.61892 (17)	0.1359 (6)	0.42951 (19)	0.0520 (7)	
H5A	0.5984	0.0100	0.4686	0.062*	
C3	0.58996 (18)	0.4883 (6)	0.3253 (2)	0.0568 (8)	
H3A	0.5503	0.6025	0.2945	0.068*	
C7	0.4131 (2)	0.4775 (8)	0.3713 (3)	0.0747 (10)	
H7A	0.3550	0.4345	0.3887	0.112*	
H7B	0.4122	0.4878	0.3063	0.112*	
H7C	0.4312	0.6440	0.3973	0.112*	
O1W	0.91135 (11)	−0.1445 (4)	0.40178 (13)	0.0430 (4)	
H1WA	0.925 (2)	−0.165 (7)	0.4589 (12)	0.069 (10)*	
H1WB	0.9587 (16)	−0.128 (8)	0.3745 (18)	0.082 (12)*	
P1	0.87333 (4)	0.53074 (12)	0.62599 (4)	0.0359 (2)	
F5	0.8065 (12)	0.680 (4)	0.5640 (14)	0.067 (5)	0.582 (6)
F3	0.7987 (3)	0.3110 (9)	0.6454 (3)	0.0524 (4)	0.582 (6)
F1	0.8401 (3)	0.7005 (8)	0.7068 (3)	0.0524 (4)	0.582 (6)
F4	0.9546 (19)	0.699 (6)	0.5972 (19)	0.069 (5)	0.582 (6)
F6	0.9439 (11)	0.379 (3)	0.6897 (13)	0.067 (4)	0.582 (6)
F2	0.9045 (3)	0.3475 (11)	0.5434 (3)	0.0524 (4)	0.582 (6)
F3'	0.7951 (4)	0.3803 (12)	0.6680 (4)	0.0524 (4)	0.418 (6)
F5'	0.8045 (13)	0.667 (4)	0.5461 (19)	0.046 (2)	0.418 (6)

F1'	0.8666 (4)	0.7675 (12)	0.6988 (4)	0.0524 (4)	0.418 (6)
F6'	0.9394 (13)	0.388 (4)	0.7046 (18)	0.047 (2)	0.418 (6)
F4'	0.945 (2)	0.740 (8)	0.598 (2)	0.065 (6)	0.418 (6)
F2'	0.8876 (4)	0.3068 (15)	0.5555 (5)	0.0524 (4)	0.418 (6)

Atomic displacement parameters (Å^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
N1	0.0359 (11)	0.0378 (11)	0.0412 (12)	−0.0003 (9)	0.0080 (9)	0.0002 (9)
C1	0.0338 (11)	0.0351 (11)	0.0340 (11)	−0.0031 (9)	0.0065 (9)	−0.0053 (9)
C6	0.0441 (13)	0.0461 (14)	0.0498 (14)	0.0043 (11)	0.0088 (11)	0.0103 (11)
C4	0.0356 (12)	0.0542 (15)	0.0479 (14)	−0.0046 (11)	0.0088 (10)	−0.0055 (12)
C2	0.0456 (14)	0.0516 (15)	0.0606 (17)	0.0013 (12)	0.0091 (12)	0.0214 (13)
O1	0.0357 (10)	0.0845 (15)	0.0826 (15)	−0.0045 (10)	0.0152 (9)	0.0085 (12)
C5	0.0486 (15)	0.0540 (16)	0.0552 (16)	−0.0036 (12)	0.0156 (12)	0.0134 (13)
C3	0.0411 (14)	0.0623 (18)	0.0668 (18)	0.0074 (13)	0.0021 (13)	0.0176 (14)
C7	0.0395 (15)	0.100 (3)	0.086 (2)	0.0104 (17)	0.0084 (15)	−0.015 (2)
O1W	0.0348 (9)	0.0483 (10)	0.0466 (10)	−0.0002 (8)	0.0074 (8)	0.0041 (8)
P1	0.0356 (3)	0.0405 (3)	0.0323 (3)	0.0051 (2)	0.0072 (2)	0.0037 (2)
F5	0.067 (4)	0.088 (5)	0.045 (8)	0.016 (3)	−0.004 (3)	0.024 (4)
F3	0.0545 (9)	0.0554 (14)	0.0500 (10)	−0.0045 (8)	0.0216 (9)	−0.0070 (6)
F1	0.0545 (9)	0.0554 (14)	0.0500 (10)	−0.0045 (8)	0.0216 (9)	−0.0070 (6)
F4	0.053 (3)	0.074 (11)	0.079 (5)	−0.014 (4)	0.008 (3)	0.016 (5)
F6	0.059 (4)	0.102 (5)	0.039 (6)	0.035 (4)	0.005 (3)	0.008 (3)
F2	0.0545 (9)	0.0554 (14)	0.0500 (10)	−0.0045 (8)	0.0216 (9)	−0.0070 (6)
F3'	0.0545 (9)	0.0554 (14)	0.0500 (10)	−0.0045 (8)	0.0216 (9)	−0.0070 (6)
F5'	0.043 (4)	0.060 (4)	0.034 (7)	0.016 (3)	−0.003 (3)	0.020 (4)
F1'	0.0545 (9)	0.0554 (14)	0.0500 (10)	−0.0045 (8)	0.0216 (9)	−0.0070 (6)
F6'	0.038 (4)	0.068 (5)	0.037 (7)	0.008 (4)	0.006 (3)	0.017 (4)
F4'	0.070 (13)	0.058 (8)	0.065 (6)	−0.033 (10)	−0.001 (7)	0.003 (5)
F2'	0.0545 (9)	0.0554 (14)	0.0500 (10)	−0.0045 (8)	0.0216 (9)	−0.0070 (6)

Geometric parameters (Å, °)

N1—C1	1.473 (3)	C7—H7B	0.9600
N1—H1B	0.87 (3)	C7—H7C	0.9600
N1—H1A	0.92 (3)	O1W—H1WA	0.860 (17)
N1—H1C	0.84 (3)	O1W—H1WB	0.853 (17)
C1—C2	1.360 (3)	P1—F5	1.516 (17)
C1—C6	1.377 (3)	P1—F2'	1.567 (8)
C6—C5	1.383 (3)	P1—F6	1.571 (17)
C6—H6A	0.9300	P1—F3'	1.576 (7)
C4—O1	1.370 (3)	P1—F4	1.58 (3)
C4—C5	1.370 (4)	P1—F1	1.584 (4)
C4—C3	1.376 (4)	P1—F4'	1.60 (4)
C2—C3	1.390 (4)	P1—F1'	1.621 (6)
C2—H2A	0.9300	P1—F3	1.629 (5)
O1—C7	1.415 (4)	P1—F2	1.631 (6)
C5—H5A	0.9300	P1—F6'	1.64 (2)

C3—H3A	0.9300	P1—F5'	1.67 (2)
C7—H7A	0.9600		
C1—N1—H1B	110.7 (18)	F4—P1—F1	101.9 (11)
C1—N1—H1A	112.3 (18)	F5—P1—F4'	87.0 (17)
H1B—N1—H1A	102 (3)	F2'—P1—F4'	100.4 (14)
C1—N1—H1C	108 (2)	F6—P1—F4'	92.0 (16)
H1B—N1—H1C	110 (3)	F3'—P1—F4'	166.3 (15)
H1A—N1—H1C	113 (3)	F1—P1—F4'	95.4 (14)
C2—C1—C6	121.0 (2)	F5—P1—F1'	87.6 (8)
C2—C1—N1	119.6 (2)	F2'—P1—F1'	175.6 (2)
C6—C1—N1	119.5 (2)	F6—P1—F1'	92.3 (8)
C1—C6—C5	118.9 (2)	F3'—P1—F1'	90.73 (19)
C1—C6—H6A	120.5	F4—P1—F1'	82.4 (11)
C5—C6—H6A	120.5	F4'—P1—F1'	75.9 (14)
O1—C4—C5	116.2 (2)	F5—P1—F3	90.4 (8)
O1—C4—C3	123.7 (3)	F2'—P1—F3	75.58 (18)
C5—C4—C3	120.1 (2)	F6—P1—F3	90.6 (5)
C1—C2—C3	120.0 (2)	F4—P1—F3	168.8 (12)
C1—C2—H2A	120.0	F1—P1—F3	88.68 (14)
C3—C2—H2A	120.0	F4'—P1—F3	175.0 (12)
C4—O1—C7	118.2 (2)	F1'—P1—F3	108.24 (18)
C4—C5—C6	120.5 (2)	F5—P1—F2	93.0 (8)
C4—C5—H5A	119.7	F6—P1—F2	86.9 (8)
C6—C5—H5A	119.7	F3'—P1—F2	106.6 (2)
C4—C3—C2	119.4 (3)	F4—P1—F2	80.3 (11)
C4—C3—H3A	120.3	F1—P1—F2	177.73 (15)
C2—C3—H3A	120.3	F4'—P1—F2	86.8 (14)
O1—C7—H7A	109.5	F1'—P1—F2	162.7 (2)
O1—C7—H7B	109.5	F3—P1—F2	89.06 (16)
H7A—C7—H7B	109.5	F5—P1—F6'	172.2 (12)
O1—C7—H7C	109.5	F2'—P1—F6'	92.5 (9)
H7A—C7—H7C	109.5	F3'—P1—F6'	86.9 (6)
H7B—C7—H7C	109.5	F4—P1—F6'	88.9 (13)
H1WA—O1W—H1WB	109 (2)	F1—P1—F6'	85.4 (10)
F5—P1—F2'	94.6 (9)	F4'—P1—F6'	94.9 (16)
F5—P1—F6	179.0 (9)	F1'—P1—F6'	85.6 (9)
F2'—P1—F6	85.5 (8)	F3—P1—F6'	88.3 (5)
F5—P1—F3'	89.5 (8)	F2—P1—F6'	94.7 (10)
F2'—P1—F3'	93.1 (2)	F2'—P1—F5'	86.7 (9)
F6—P1—F3'	91.5 (6)	F6—P1—F5'	171.6 (12)
F5—P1—F4	93.9 (14)	F3'—P1—F5'	91.7 (8)
F2'—P1—F4	93.7 (11)	F4—P1—F5'	92.6 (14)
F6—P1—F4	85.1 (13)	F1—P1—F5'	95.1 (9)
F3'—P1—F4	172.2 (10)	F4'—P1—F5'	86.6 (16)
F5—P1—F1	86.9 (8)	F1'—P1—F5'	95.4 (9)
F2'—P1—F1	164.18 (19)	F3—P1—F5'	90.2 (8)
F6—P1—F1	93.3 (8)	F2—P1—F5'	84.8 (9)
F3'—P1—F1	71.17 (18)	F6'—P1—F5'	178.4 (10)

C2—C1—C6—C5	−0.1 (4)	O1—C4—C5—C6	−178.9 (3)
N1—C1—C6—C5	179.2 (2)	C3—C4—C5—C6	1.7 (4)
C6—C1—C2—C3	0.9 (4)	C1—C6—C5—C4	−1.3 (4)
N1—C1—C2—C3	−178.3 (3)	O1—C4—C3—C2	179.8 (3)
C5—C4—O1—C7	169.6 (3)	C5—C4—C3—C2	−0.8 (4)
C3—C4—O1—C7	−11.0 (4)	C1—C2—C3—C4	−0.5 (5)

Hydrogen-bond geometry (Å, °)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
N1—H1C···O1W	0.84 (3)	2.06 (3)	2.896 (3)	172 (3)
N1—H1A···O1W^{i}	0.92 (3)	2.00 (3)	2.917 (3)	172 (3)
N1—H1B···F3^{ii}	0.87 (3)	2.32 (3)	3.056 (5)	142 (2)
N1—H1B···F1^{iii}	0.87 (3)	2.49 (3)	3.049 (5)	123 (2)
O1W—H1WB···F6^{iv}	0.85 (2)	2.21 (4)	2.91 (2)	139 (3)
O1W—H1WB···F4^{v}	0.85 (2)	2.57 (4)	3.04 (3)	116 (3)
C7—H7B···Cg1^{vi}	0.96	3.18	4.013 (5)	146

Symmetry codes: (i) *x*, *y*+1, *z*; (ii) *x*, −*y*+1/2, *z*−1/2; (iii) *x*, −*y*+3/2, *z*−1/2; (iv) −*x*+2, −*y*, −*z*+1; (v) −*x*+2, −*y*+1, −*z*+1; (vi) −*x*+1, *y*+1/2, −*z*+1/2.

Fig. 1

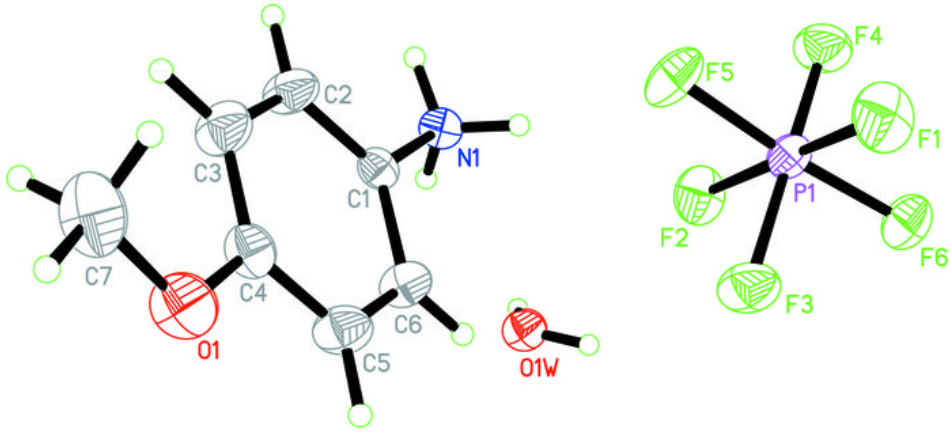
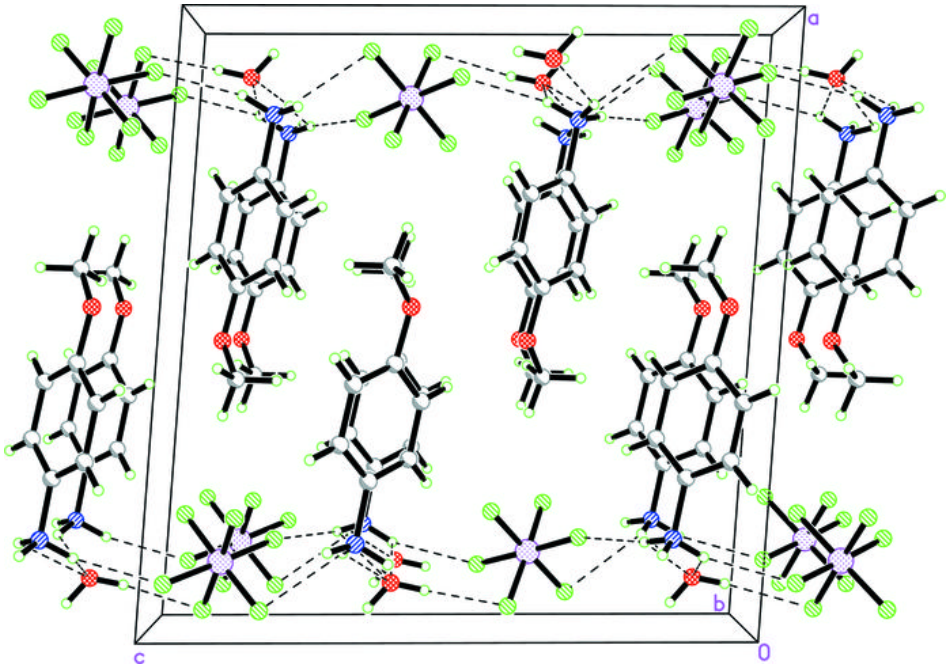


Fig. 2



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Benzylammonium tetrafluoroborate 18-crown-6 clathrate

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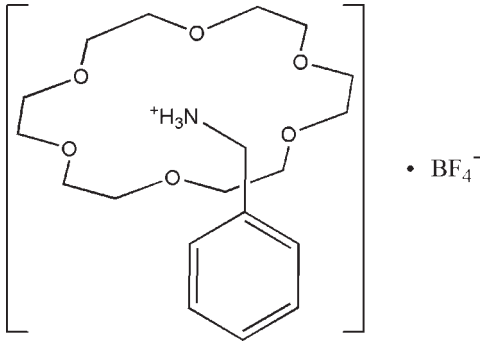
Key indicators: single-crystal X-ray study; T = 293 K; mean σ(C–C) = 0.002 Å; R factor = 0.045; wR factor = 0.103; data-to-parameter ratio = 18.1.

The reaction of benzylammonium tetrafluoroborate and 18-crown-6 in a methanolic solution yields the title compound, $C_7H_{10}N^+\cdot BF_4^-\cdot C_{12}H_{24}O_6$O6, which displays a supramolecular structure. The $-NH_3^+$ substituent of the benzylammonium cation forms a 1:1 supramolecular rotator–stator structure by N—H···O hydrogen-bonding interactions.

Related literature

For similar crown ether clathrates, see: Akutagawa *et al.* (2002); Kryatova *et al.* (2004). For their ferroelectric properties, see: Zhang *et al.* (2009); Ye *et al.* (2009).



Experimental

Crystal data

$C_7H_{10}N^+\cdot BF_4^-\cdot C_{12}H_{24}O_6$ M_r = 459.28
Triclinic, $P\overline{1}$
a = 9.281 (6) Å
b = 10.673 (6) Å
c = 11.863 (7) Å
α = 76.418 (16)°
β = 86.244 (17)°
γ = 78.274 (15)°
V = 1118.2 (12) Å^3
Z = 2
Mo $K\alpha$ radiation
μ = 0.12 mm^{-1}
T = 293 K
0.40 × 0.30 × 0.20 mm

Data collection

Rigaku SCXmini diffractometer
Absorption correction: multi-scan (*CrystalClear*; Rigaku, 2005)
T_{min} = 0.958, T_{max} = 0.976
12286 measured reflections
5057 independent reflections
4153 reflections with $I > 2\sigma(I)$
R_{int} = 0.031

Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.045
$wR(F^2)$ = 0.103
S = 1.03
5057 reflections
280 parameters
H-atom parameters constrained
$\Delta\rho_{max}$ = 0.25 e Å^{-3}
$\Delta\rho_{min}$ = −0.24 e Å^{-3}

Table 1
Hydrogen-bond geometry (Å, °).

D—H···A	D—H	H···A	D···A	D—H···A
N2—H2A···O6	0.89	1.99	2.866 (2)	167
N2—H2B···O3	0.89	2.15	2.986 (2)	157
N2—H2C···O1	0.89	2.05	2.936 (2)	173

Data collection: *CrystalClear* (Rigaku, 2005); cell refinement: *CrystalClear*; data reduction: *CrystalClear*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *SHELXTL* (Sheldrick, 2008); software used to prepare material for publication: *PRPKAPPA* (Ferguson, 1999).

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Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: IM2207).

References

Akutagawa, T., Hashimoto, A., Nishihara, S., Hasegawa, T. & Nakamura, T. (2002). *J. Supramol. Chem.* **2**, 175–186.
Ferguson, G. (1999). *PRPKAPPA*. University of Guelph, Canada.
Kryatova, O. P., Korendovych, I. V. & Rybak-Akimova, E. V. (2004). *Tetrahedron*, **60**, 4579–4588.
Rigaku (2005). *CrystalClear*. Rigaku Corporation, Tokyo, Japan.
Sheldrick, G. M. (2008). *Acta Cryst.* A**64**, 112–122.
Ye, H. Y., Fu, D. W., Zhang, Y., Zhang, W., Xiong, R. G. & Huang, S. P. (2009). *J. Am. Chem. Soc.* **131**, 42–43.
Zhang, W., Cheng, L. Z., Xiong, R. G., Nakamura, T. & Huang, S. P. (2009). *J. Am. Chem. Soc.* **131**, 12544–12545.

supplementary materials

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Benzylammonium tetrafluoroborate 18-crown-6 clathrate

M. M. Zhao

Comment

There is currently a great deal of interest in crown ethers because of their ability to form non-covalent, H-bonding complexes with ammonium cations both in solid and in solution (Akutagawa *et al.*, 2002; Kryatova *et al.* 2004). Not only the size of the crown ether, but also the nature of the ammonium cation ($–NH_4^+$, RNH_3^+, $R_2NH_2^+$, *etc*) can influence both stoichiometry and stability of these host–guest complexes. The host molecules combine with the guest species by intermolecular interactions, and if the host molecule possesses some specific sites, it is easy to realise high selectivity in ion or molecular recognitions. 18-Crown-6 exhibits the highest affinity for ammonium cations RNH_3^+, mostly resulting in a 1:1 stoichiometry.

Dielectric permittivity of the title compound was tested to systematically investigate the ferroelectric phase transitions of new materials (Ye *et al.*, 2009; Zhang *et al.*, 2009). The title compound has no dielectric anomaly with the value of 5 and 8 under 1*M* Hz in the temperature range from 80 to 433 K (m.p.> 453 K), suggesting that the compound should show no distinct phase transition occurring within the measured temperature range.

The title compound is composed of cationic $[C_7H_{10}N(18\text{-Crown-6})]^+$ and anionic $[BF_4]^-$ ions in a 1:1 stoichiometry (Fig. 1). Supramolecular rotator-like structures are assembled between benzylammonium cations and 18-crown-6 molecules by N—H···O hydrogen-bonding. Intramolecular N—H···O hydrogen bonding lengths are within the usual range around 2.9 Å. No intermolecular hydrogen bond was observed.

The crown ether adopts a conformation in which the rings show some distortion from planarity, with torsion angles: O5—C8—C9—O3 = 64.5 (2) °; O2—C10—C13—O1 = 68.1 (2) °; C16—C17—O2—C10 = 176.0 (1) °; C10—C13—O1—C14 = 179.5 (1) ° and C8—C9—O3—C11 = 167.9 (1) °. C—N bonds of $[C_7H_{10}N]^+$ are almost perpendicular to the mean plane formed by oxygen atoms of the crown ether. Boron shows a slightly distorted tetrahedral coordination by four F^- ions [range of *cis*-bond angles = 108.9 (1) – 110.2 (1) °; average distance (B—F) = 1.383 (2)–1.397 (2) Å].

Experimental

$C_7H_{10}N^+BF_4^-$ (2 mmol, 0.388 g) and 18-crown-6 (2 mmol, 0.528 g) were dissolved in 15 ml methanol. The resulting precipitate was filtered. Two days later, single crystals suitable for X-ray diffraction analysis were obtained from slow evaporation of the remaining methanolic solution at 0°C (yield: 95%).

Refinement

All hydrogen atoms were calculated geometrically with C—H distances ranging from 0.93 to 0.97 Å and N—H = 0.90 Å. refinement of hydrogen atoms was performed using a riding model with $U_{iso}(H) = 1.2U_{eq}(C,N)$.

Figures

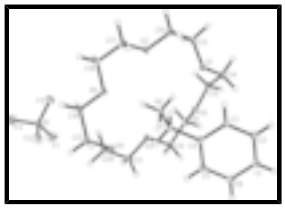


Fig. 1. Molecular structure of the title compound showingh the atom numbering scheme. Displacement ellipsoids are drawn at the 30% probability level.

Benzylammonium tetrafluoroborate 1,4,7,10,13,16-hexaoxacyclooctadecane solvate

Crystal data

$C_7H_{10}N^+·BF_4^-·C_{12}H_{24}O_6$	$Z = 2$
$M_r = 459.28$	$F(000) = 488$
Triclinic, $P\overline{1}$	$D_x = 1.364$ Mg m^{-3}
Hall symbol: -P 1	Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å
$a = 9.281$ (6) Å	Cell parameters from 2953 reflections
$b = 10.673$ (6) Å	$\theta = 2.9$–$27.5°$
$c = 11.863$ (7) Å	$\mu = 0.12$ mm^{-1}
$\alpha = 76.418$ (16)°	$T = 293$ K
$\beta = 86.244$ (17)°	Prism, colorless
$\gamma = 78.274$ (15)°	0.40 × 0.30 × 0.20 mm
$V = 1118.2$ (12) Å^3	

Data collection

Rigaku SCXmini diffractometer	5057 independent reflections
Radiation source: fine-focus sealed tube	4153 reflections with $I > 2\sigma(I)$
graphite	$R_{int} = 0.031$
Detector resolution: 28.5714 pixels mm^{-1}	$\theta_{max} = 27.5°$, $\theta_{min} = 2.7°$
ω scans	$h = -12 \rightarrow 12$
Absorption correction: multi-scan (*CrystalClear*; Rigaku, 2005)	$k = -13 \rightarrow 13$
$T_{min} = 0.958$, $T_{max} = 0.976$	$l = -15 \rightarrow 15$
12286 measured reflections	

Refinement

Refinement on F^2	Primary atom site location: structure-invariant direct methods
Least-squares matrix: full	Secondary atom site location: difference Fourier map
$R[F^2 > 2\sigma(F^2)] = 0.045$	Hydrogen site location: inferred from neighbouring sites
$wR(F^2) = 0.103$	H-atom parameters constrained
$S = 1.03$	$w = 1/[\sigma^2(F_o^2) + (0.0454P)^2 + 0.2316P]$

	where $P = (F_o^2 + 2F_c^2)/3$
5057 reflections	$(\Delta/\sigma)_{max} < 0.001$
280 parameters	$\Delta\rho_{max} = 0.25$ e Å^{-3}
0 restraints	$\Delta\rho_{min} = -0.24$ e Å^{-3}

Special details

Geometry. All e.s.d.'s (except the e.s.d. in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell e.s.d.'s are taken into account individually in the estimation of e.s.d.'s in distances, angles and torsion angles; correlations between e.s.d.'s in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell e.s.d.'s is used for estimating e.s.d.'s involving l.s. planes.

Refinement. Refinement of F^2 against ALL reflections. The weighted *R*-factor *wR* and goodness of fit *S* are based on F^2, conventional *R*-factors *R* are based on *F*, with *F* set to zero for negative F^2. The threshold expression of $F^2 > \sigma(F^2)$ is used only for calculating *R*-factors(gt) *etc*. and is not relevant to the choice of reflections for refinement. *R*-factors based on F^2 are statistically about twice as large as those based on *F*, and *R*- factors based on ALL data will be even larger.

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å^2)

	x	*y*	*z*	U_{iso}*/U_{eq}
C8	−0.24636 (17)	0.50111 (14)	0.10270 (14)	0.0196 (3)
H8A	−0.3497	0.5175	0.0841	0.024*
H8B	−0.1973	0.5562	0.0418	0.024*
C9	−0.23023 (16)	0.53375 (15)	0.21673 (14)	0.0194 (3)
H9A	−0.2804	0.6232	0.2153	0.023*
H9B	−0.2738	0.4751	0.2785	0.023*
C10	0.27734 (17)	0.10959 (14)	0.00480 (13)	0.0189 (3)
H10A	0.2860	0.0238	0.0573	0.023*
H10B	0.3479	0.1025	−0.0585	0.023*
C11	−0.05246 (17)	0.57472 (15)	0.33132 (13)	0.0203 (3)
H11A	−0.1023	0.5345	0.4007	0.024*
H11B	−0.0922	0.6684	0.3133	0.024*
C12	0.31163 (16)	0.37847 (15)	0.42392 (13)	0.0188 (3)
H12A	0.3308	0.2915	0.4748	0.023*
H12B	0.3345	0.4397	0.4657	0.023*
C13	0.12451 (16)	0.15430 (14)	−0.04151 (12)	0.0176 (3)
H13A	0.1122	0.2444	−0.0861	0.021*
H13B	0.1080	0.0996	−0.0923	0.021*
C14	−0.12985 (16)	0.18795 (15)	0.01623 (13)	0.0186 (3)
H14A	−0.1928	0.1430	0.0735	0.022*
H14B	−0.1384	0.1631	−0.0563	0.022*
C15	−0.18267 (17)	0.33378 (15)	−0.00050 (13)	0.0194 (3)
H15A	−0.1180	0.3802	−0.0547	0.023*
H15B	−0.2811	0.3590	−0.0315	0.023*
C16	0.48137 (16)	0.27382 (15)	0.16325 (13)	0.0180 (3)
H16A	0.5828	0.2546	0.1875	0.022*
H16B	0.4647	0.3574	0.1072	0.022*
C17	0.45350 (16)	0.16760 (15)	0.10879 (13)	0.0189 (3)

H17A	0.5241	0.1570	0.0461	0.023*
H17B	0.4648	0.0849	0.1660	0.023*
C18	0.41154 (16)	0.37904 (14)	0.31845 (13)	0.0184 (3)
H18A	0.3924	0.4650	0.2660	0.022*
H18B	0.5136	0.3596	0.3414	0.022*
C29	0.10945 (17)	0.55084 (14)	0.35178 (13)	0.0195 (3)
H29A	0.1614	0.5798	0.2798	0.023*
H29B	0.1286	0.5993	0.4070	0.023*
O1	0.02026 (11)	0.14543 (10)	0.05354 (8)	0.0168 (2)
O2	0.30731 (11)	0.20280 (9)	0.06498 (9)	0.0164 (2)
O3	−0.07640 (11)	0.51969 (10)	0.23695 (8)	0.0160 (2)
O4	0.15806 (11)	0.41358 (9)	0.39606 (9)	0.0170 (2)
O5	−0.18295 (11)	0.36644 (9)	0.10949 (9)	0.0171 (2)
O6	0.38446 (11)	0.28133 (10)	0.26150 (9)	0.0165 (2)
B1	0.40157 (19)	0.76448 (17)	0.26818 (15)	0.0188 (3)
F1	0.26267 (12)	0.84348 (11)	0.26112 (10)	0.0428 (3)
F2	0.42418 (11)	0.70503 (10)	0.17371 (8)	0.0311 (2)
F3	0.41256 (12)	0.66888 (9)	0.37036 (8)	0.0327 (2)
F4	0.50826 (12)	0.83934 (11)	0.26526 (10)	0.0401 (3)
N2	0.08837 (13)	0.24571 (11)	0.25008 (10)	0.0149 (3)
H2A	0.1771	0.2666	0.2431	0.022*
H2B	0.0208	0.3151	0.2588	0.022*
H2C	0.0698	0.2211	0.1867	0.022*
C1	−0.34030 (17)	0.02500 (15)	0.39415 (13)	0.0193 (3)
H1A	−0.4325	0.0021	0.4017	0.023*
C2	−0.23098 (17)	−0.03380 (14)	0.32762 (13)	0.0186 (3)
H2D	−0.2498	−0.0965	0.2907	0.022*
C3	−0.09306 (16)	0.00054 (14)	0.31579 (12)	0.0171 (3)
H3A	−0.0195	−0.0406	0.2722	0.020*
C4	−0.06450 (16)	0.09625 (14)	0.36893 (12)	0.0158 (3)
C5	−0.17497 (17)	0.15401 (14)	0.43633 (13)	0.0189 (3)
H5A	−0.1568	0.2172	0.4729	0.023*
C6	−0.31203 (17)	0.11841 (15)	0.44960 (13)	0.0202 (3)
H6A	−0.3847	0.1570	0.4955	0.024*
C7	0.08405 (16)	0.13519 (14)	0.35362 (13)	0.0186 (3)
H7A	0.1060	0.1616	0.4225	0.022*
H7B	0.1589	0.0601	0.3446	0.022*

Atomic displacement parameters (Å^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
C8	0.0179 (8)	0.0141 (7)	0.0260 (8)	−0.0017 (6)	−0.0072 (6)	−0.0024 (6)
C9	0.0139 (7)	0.0176 (7)	0.0268 (8)	−0.0023 (6)	−0.0005 (6)	−0.0053 (6)
C10	0.0220 (8)	0.0162 (7)	0.0199 (8)	−0.0036 (6)	0.0026 (6)	−0.0077 (6)
C11	0.0247 (8)	0.0196 (7)	0.0169 (7)	0.0011 (6)	−0.0016 (6)	−0.0092 (6)
C12	0.0185 (8)	0.0198 (7)	0.0192 (7)	−0.0042 (6)	−0.0039 (6)	−0.0047 (6)
C13	0.0231 (8)	0.0161 (7)	0.0149 (7)	−0.0055 (6)	0.0027 (6)	−0.0055 (6)
C14	0.0175 (7)	0.0207 (7)	0.0200 (8)	−0.0065 (6)	−0.0030 (6)	−0.0062 (6)

C15	0.0208 (8)	0.0211 (7)	0.0169 (7)	−0.0050 (6)	−0.0054 (6)	−0.0030 (6)
C16	0.0131 (7)	0.0207 (7)	0.0196 (7)	−0.0041 (6)	0.0031 (6)	−0.0037 (6)
C17	0.0140 (7)	0.0201 (7)	0.0208 (8)	0.0006 (6)	0.0009 (6)	−0.0045 (6)
C18	0.0172 (7)	0.0174 (7)	0.0230 (8)	−0.0060 (6)	−0.0012 (6)	−0.0072 (6)
C29	0.0256 (8)	0.0151 (7)	0.0191 (8)	−0.0035 (6)	−0.0047 (6)	−0.0058 (6)
O1	0.0165 (5)	0.0191 (5)	0.0152 (5)	−0.0044 (4)	0.0002 (4)	−0.0040 (4)
O2	0.0147 (5)	0.0149 (5)	0.0206 (5)	−0.0014 (4)	−0.0010 (4)	−0.0073 (4)
O3	0.0139 (5)	0.0184 (5)	0.0169 (5)	−0.0021 (4)	−0.0010 (4)	−0.0070 (4)
O4	0.0175 (5)	0.0151 (5)	0.0189 (5)	−0.0033 (4)	−0.0019 (4)	−0.0044 (4)
O5	0.0207 (5)	0.0131 (5)	0.0174 (5)	−0.0020 (4)	−0.0043 (4)	−0.0030 (4)
O6	0.0157 (5)	0.0172 (5)	0.0196 (5)	−0.0063 (4)	0.0032 (4)	−0.0080 (4)
B1	0.0194 (9)	0.0190 (8)	0.0189 (8)	−0.0056 (7)	−0.0011 (7)	−0.0040 (7)
F1	0.0308 (6)	0.0468 (7)	0.0417 (7)	0.0136 (5)	−0.0010 (5)	−0.0099 (5)
F2	0.0356 (6)	0.0352 (6)	0.0263 (5)	−0.0055 (4)	−0.0027 (4)	−0.0151 (4)
F3	0.0475 (6)	0.0251 (5)	0.0250 (5)	−0.0125 (5)	−0.0064 (5)	0.0013 (4)
F4	0.0464 (7)	0.0388 (6)	0.0443 (7)	−0.0292 (5)	−0.0010 (5)	−0.0094 (5)
N2	0.0148 (6)	0.0156 (6)	0.0149 (6)	−0.0038 (5)	0.0005 (5)	−0.0040 (5)
C1	0.0156 (7)	0.0234 (8)	0.0170 (7)	−0.0051 (6)	−0.0007 (6)	0.0005 (6)
C2	0.0220 (8)	0.0183 (7)	0.0170 (7)	−0.0072 (6)	−0.0020 (6)	−0.0037 (6)
C3	0.0182 (7)	0.0181 (7)	0.0141 (7)	−0.0026 (6)	0.0020 (6)	−0.0032 (6)
C4	0.0179 (7)	0.0152 (7)	0.0127 (7)	−0.0053 (6)	−0.0033 (6)	0.0026 (5)
C5	0.0249 (8)	0.0156 (7)	0.0160 (7)	−0.0037 (6)	−0.0026 (6)	−0.0026 (6)
C6	0.0194 (8)	0.0206 (8)	0.0176 (7)	0.0001 (6)	0.0021 (6)	−0.0028 (6)
C7	0.0180 (8)	0.0174 (7)	0.0185 (7)	−0.0054 (6)	−0.0042 (6)	0.0024 (6)

Geometric parameters (Å, °)

C8—O5	1.4236 (19)	C16—H16B	0.9700
C8—C9	1.497 (2)	C17—O2	1.4303 (19)
C8—H8A	0.9700	C17—H17A	0.9700
C8—H8B	0.9700	C17—H17B	0.9700
C9—O3	1.4351 (19)	C18—O6	1.4376 (18)
C9—H9A	0.9700	C18—H18A	0.9700
C9—H9B	0.9700	C18—H18B	0.9700
C10—O2	1.4313 (18)	C29—O4	1.4235 (19)
C10—C13	1.498 (2)	C29—H29A	0.9700
C10—H10A	0.9700	C29—H29B	0.9700
C10—H10B	0.9700	B1—F3	1.383 (2)
C11—O3	1.4290 (18)	B1—F1	1.385 (2)
C11—C29	1.498 (2)	B1—F4	1.387 (2)
C11—H11A	0.9700	B1—F2	1.397 (2)
C11—H11B	0.9700	N2—C7	1.4946 (19)
C12—O4	1.4380 (19)	N2—H2A	0.8900
C12—C18	1.507 (2)	N2—H2B	0.8900
C12—H12A	0.9700	N2—H2C	0.8900
C12—H12B	0.9700	C1—C2	1.384 (2)
C13—O1	1.4355 (18)	C1—C6	1.390 (2)
C13—H13A	0.9700	C1—H1A	0.9300
C13—H13B	0.9700	C2—C3	1.391 (2)

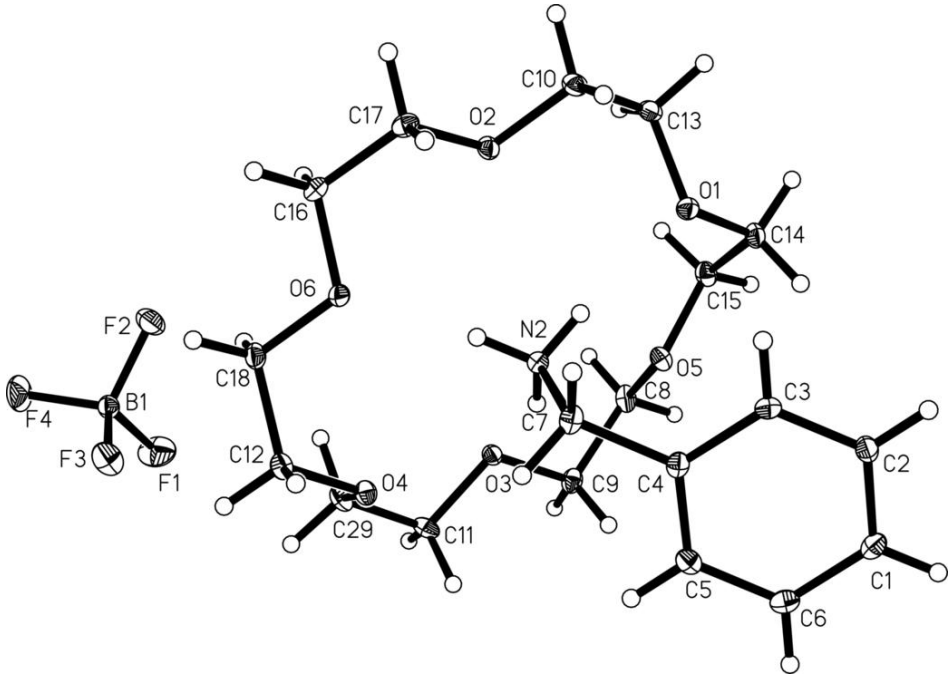
C14—O1	1.4395 (19)	C2—H2D	0.9300
C14—C15	1.503 (2)	C3—C4	1.395 (2)
C14—H14A	0.9700	C3—H3A	0.9300
C14—H14B	0.9700	C4—C5	1.392 (2)
C15—O5	1.4272 (19)	C4—C7	1.507 (2)
C15—H15A	0.9700	C5—C6	1.389 (2)
C15—H15B	0.9700	C5—H5A	0.9300
C16—O6	1.4322 (18)	C6—H6A	0.9300
C16—C17	1.501 (2)	C7—H7A	0.9700
C16—H16A	0.9700	C7—H7B	0.9700
O5—C8—C9	109.25 (12)	O2—C17—H17B	109.9
O5—C8—H8A	109.8	C16—C17—H17B	109.9
C9—C8—H8A	109.8	H17A—C17—H17B	108.3
O5—C8—H8B	109.8	O6—C18—C12	108.68 (12)
C9—C8—H8B	109.8	O6—C18—H18A	110.0
H8A—C8—H8B	108.3	C12—C18—H18A	110.0
O3—C9—C8	108.54 (12)	O6—C18—H18B	110.0
O3—C9—H9A	110.0	C12—C18—H18B	110.0
C8—C9—H9A	110.0	H18A—C18—H18B	108.3
O3—C9—H9B	110.0	O4—C29—C11	107.80 (12)
C8—C9—H9B	110.0	O4—C29—H29A	110.1
H9A—C9—H9B	108.4	C11—C29—H29A	110.1
O2—C10—C13	108.95 (12)	O4—C29—H29B	110.1
O2—C10—H10A	109.9	C11—C29—H29B	110.1
C13—C10—H10A	109.9	H29A—C29—H29B	108.5
O2—C10—H10B	109.9	C13—O1—C14	112.74 (12)
C13—C10—H10B	109.9	C17—O2—C10	111.77 (11)
H10A—C10—H10B	108.3	C11—O3—C9	111.85 (11)
O3—C11—C29	109.20 (12)	C29—O4—C12	113.18 (11)
O3—C11—H11A	109.8	C8—O5—C15	111.32 (11)
C29—C11—H11A	109.8	C16—O6—C18	110.94 (11)
O3—C11—H11B	109.8	F3—B1—F1	109.87 (14)
C29—C11—H11B	109.8	F3—B1—F4	109.19 (13)
H11A—C11—H11B	108.3	F1—B1—F4	110.24 (14)
O4—C12—C18	113.11 (12)	F3—B1—F2	109.64 (14)
O4—C12—H12A	109.0	F1—B1—F2	108.85 (13)
C18—C12—H12A	109.0	F4—B1—F2	109.04 (14)
O4—C12—H12B	109.0	C7—N2—H2A	109.5
C18—C12—H12B	109.0	C7—N2—H2B	109.5
H12A—C12—H12B	107.8	H2A—N2—H2B	109.5
O1—C13—C10	109.27 (13)	C7—N2—H2C	109.5
O1—C13—H13A	109.8	H2A—N2—H2C	109.5
C10—C13—H13A	109.8	H2B—N2—H2C	109.5
O1—C13—H13B	109.8	C2—C1—C6	119.87 (14)
C10—C13—H13B	109.8	C2—C1—H1A	120.1
H13A—C13—H13B	108.3	C6—C1—H1A	120.1
O1—C14—C15	112.86 (12)	C1—C2—C3	120.23 (14)
O1—C14—H14A	109.0	C1—C2—H2D	119.9
C15—C14—H14A	109.0	C3—C2—H2D	119.9

O1—C14—H14B	109.0	C2—C3—C4	120.39 (14)
C15—C14—H14B	109.0	C2—C3—H3A	119.8
H14A—C14—H14B	107.8	C4—C3—H3A	119.8
O5—C15—C14	108.15 (12)	C5—C4—C3	118.85 (14)
O5—C15—H15A	110.1	C5—C4—C7	120.99 (14)
C14—C15—H15A	110.1	C3—C4—C7	120.15 (13)
O5—C15—H15B	110.1	C6—C5—C4	120.80 (14)
C14—C15—H15B	110.1	C6—C5—H5A	119.6
H15A—C15—H15B	108.4	C4—C5—H5A	119.6
O6—C16—C17	109.34 (12)	C5—C6—C1	119.85 (14)
O6—C16—H16A	109.8	C5—C6—H6A	120.1
C17—C16—H16A	109.8	C1—C6—H6A	120.1
O6—C16—H16B	109.8	N2—C7—C4	111.37 (12)
C17—C16—H16B	109.8	N2—C7—H7A	109.4
H16A—C16—H16B	108.3	C4—C7—H7A	109.4
O2—C17—C16	109.06 (12)	N2—C7—H7B	109.4
O2—C17—H17A	109.9	C4—C7—H7B	109.4
C16—C17—H17A	109.9	H7A—C7—H7B	108.0
O5—C8—C9—O3	64.50 (15)	C9—C8—O5—C15	−174.28 (12)
O2—C10—C13—O1	−68.12 (15)	C14—C15—O5—C8	−173.89 (12)
O1—C14—C15—O5	−64.33 (16)	C17—C16—O6—C18	177.97 (12)
O6—C16—C17—O2	64.18 (15)	C12—C18—O6—C16	−177.47 (12)
O4—C12—C18—O6	−62.79 (15)	C6—C1—C2—C3	−0.2 (2)
O3—C11—C29—O4	−68.82 (15)	C1—C2—C3—C4	−1.2 (2)
C10—C13—O1—C14	179.48 (11)	C2—C3—C4—C5	1.7 (2)
C15—C14—O1—C13	−86.11 (15)	C2—C3—C4—C7	−178.64 (13)
C16—C17—O2—C10	176.00 (12)	C3—C4—C5—C6	−0.7 (2)
C13—C10—O2—C17	−178.41 (12)	C7—C4—C5—C6	179.59 (13)
C29—C11—O3—C9	177.14 (12)	C4—C5—C6—C1	−0.7 (2)
C8—C9—O3—C11	167.91 (12)	C2—C1—C6—C5	1.1 (2)
C11—C29—O4—C12	−177.59 (11)	C5—C4—C7—N2	−90.62 (17)
C18—C12—O4—C29	−76.33 (15)	C3—C4—C7—N2	89.72 (17)

Hydrogen-bond geometry (Å, °)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
N2—H2A···O6	0.89	1.99	2.866 (2)	167
N2—H2B···O3	0.89	2.15	2.986 (2)	157
N2—H2C···O1	0.89	2.05	2.936 (2)	173

Fig. 1


C10
C17
O2
C13
O1
C16
C14
O6
C15
F2
N2
C18
O5
C8
C3
B1
F4
C7
F3
C12
O4
O3
C9
C4
C2
F1
C29
C11
C5
C1
C6

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N-Methyl-*N*-(2-methylphenyl)acetamide

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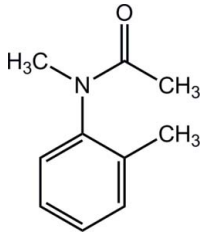
Key indicators: single-crystal X-ray study; T = 293 K; mean σ(C–C) = 0.005 Å; R factor = 0.070; wR factor = 0.180; data-to-parameter ratio = 15.4.

In the title compound, $C_{10}H_{13}NO$, the N atom and the methyl group are almost coplanar with the benzene ring to which they are bonded [deviations of 0.131 (1) and 0.038 (1) Å, respectively, from the ring plane]. In the crystal structure, intermolecular C—H···O hydrogen bonds form a three-dimensional network. Molecules are stacked parallel to the *b*-axis direction.

Related literature

For the use of related compounds as intermediates in syntheses of ligands for human β-amyloid plaques and for the preparation of the title compound, see Cai *et al.* (2007). For the use of related compounds in *N*-substituted glycine peptoid oligomers, see Shah *et al.* (2008). For a related structure, see: Li *et al.* (2008). For bond-length data, see: Allen *et al.* (1987)



Experimental

Crystal data

$C_{10}H_{13}NO$
M_r = 163.21
Monoclinic, $P2_1/n$
a = 11.288 (2) Å
b = 6.900 (1) Å
c = 12.234 (2) Å
β = 94.88 (3)°
V = 949.5 (3) Å^3
Z = 4
Mo $K\alpha$ radiation
μ = 0.07 mm^{-1}
T = 293 K
0.30 × 0.20 × 0.10 mm

Data collection

Enraf–Nonius CAD-4 diffractometer
Absorption correction: ψ scan (North *et al.*, 1968)
T_{min} = 0.978, T_{max} = 0.993
3465 measured reflections
1726 independent reflections
1044 reflections with $I > 2\sigma(I)$
R_{int} = 0.055
3 standard reflections every 200 reflections
intensity decay: 1%

Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.070
$wR(F^2)$ = 0.180
S = 1.00
1726 reflections
112 parameters
4 restraints
H-atom parameters constrained
$\Delta\rho_{max}$ = 0.32 e Å^{-3}
$\Delta\rho_{min}$ = −0.16 e Å^{-3}

Table 1
Hydrogen-bond geometry (Å, °).

D—H···A	D—H	H···A	D···A	D—H···A
C7—H7C···O^{i}	0.96	2.51	3.442 (4)	165
C1—H1A···O^{ii}	0.93	2.60	3.414 (4)	145

Symmetry codes: (i) $-x+\frac{3}{2}, y-\frac{1}{2}, -z-\frac{1}{2}$; (ii) $-x+2, -y+1, -z$.

Data collection: *CAD-4 Software* (Enraf–Nonius, 1985); cell refinement: *CAD-4 Software*; data reduction: *XCAD4* (Harms & Wocadlo,1995); program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *SHELXTL* (Sheldrick, 2008); software used to prepare material for publication: *SHELXTL*.

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Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: IM2208).

References

Allen, F. H., Kennard, O., Watson, D. G., Brammer, L., Orpen, A. G. & Taylor, R. (1987). *J. Chem. Soc. Perkin Trans. 2*, pp. S1–19.
Cai, L. S., Cuevas, J., Temme, S., Herman, M. M., Dagostin, C., Widdowson, D. A., Innis, R. B. & Pike, V. W. (2007). *J. Med. Chem.* **50**, 4746–4758.
Enraf–Nonius (1985). *CAD-4 Software*. Enraf–Nonius, Delft, The Netherlands.
Harms, K. & Wocadlo, S. (1995). *XCAD4*. University of Marburg, Germany.
Li, Y.-H., Liu, R., Zhang, X.-N. & Zhu, H.-J. (2008). *Acta Cryst.* E**64**, o533.
North, A. C. T., Phillips, D. C. & Mathews, F. S. (1968). *Acta Cryst.* A**24**, 351–359.
Shah, N. H., Butterfoss, G. L., Nguyen, K., Yoo, B., Bonneau, R., Rabenstein, D. L. & Kirshenbaum, K. (2008). *J. Am. Chem Soc.* **130**, 16622–16632.
Sheldrick, G. M. (2008). *Acta Cryst.* A**64**, 112–122.

supplementary materials

Acta Cryst. (2010). E**66**, o1679 [**doi:10.1107/S1600536810022361**]

N-Methyl-*N*-(2-methylphenyl)acetamide

Z.-W. Yan, Y.-H. Li, Q. Xiao, L. Zhao and H.-J. Zhu

Comment

The title compound, (I), contains acetyl group, which can react with different groups to prepare various function organic compounds. It is a kind of aromatic organic intermediate which can be used for many fields such as medicine. (Cai *et al.*, 2007). Herein we report its crystal structure.

In the molecule of (I), (Fig.1), the bond lengths (Allen *et al.*, 1987) and angles are within normal ranges. The N and C7 atoms are situated in the same plane as the benzene ring they are bonded to. The C—H···O intermolecular hydrogen bonds form a three dimensional network, which seems to be very effective in the stabilization of the crystal structure.

As can be seen from the packing diagram, (Fig. 2), the molecules are stacked along the *b* axis. There are also weak π-π interactions of benzene rings with a face-to-face stacking distance of 5.991 (4) Å.

Experimental

The title compound, (I) was prepared by the literature method (Cai *et al.*, 2007). Crystals suitable for X-ray analysis were obtained by dissolving (I) (0.5 g) in ethyl acetate (20 ml) and evaporating the solvent slowly at room temperature for about 7 d.

Refinement

All H atoms were positioned geometrically and constrained to ride on their parent atoms, with C—H = 0.93 Å and 0.96 Å for aromatic H and methyl group H, respectively. The U_{iso}(H) = xU_{eq}(C), where x = 1.2 for aromatic H, and x = 1.5 for other H.

Figures

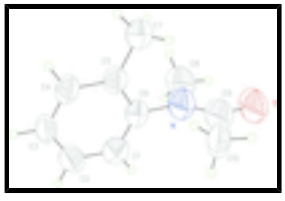


Fig. 1. Molecular structure of (I) with the atom-numbering scheme. Displacement ellipsoids are drawn at the 50% probability level.

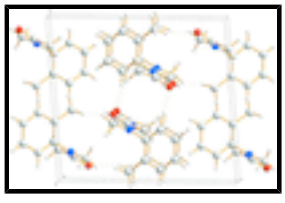


Fig. 2. Packing diagram of (I). Hydrogen bonds are shown as dashed lines.

N-Methyl-*N*-(2-methylphenyl)acetamide

Crystal data

$C_{10}H_{13}NO$	$F(000) = 352$
$M_r = 163.21$	$D_x = 1.142$ Mg m^{-3}
Monoclinic, $P2_1/n$	Melting point: 328 K
Hall symbol: -P 2yn	Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å
$a = 11.288$ (2) Å	Cell parameters from 25 reflections
$b = 6.900$ (1) Å	$\theta = 9–13°$
$c = 12.234$ (2) Å	$\mu = 0.07$ mm^{-1}
$\beta = 94.88$ (3)°	$T = 293$ K
$V = 949.5$ (3) Å^3	Block, colourless
$Z = 4$	0.30 × 0.20 × 0.10 mm

Data collection

Enraf–Nonius CAD-4 diffractometer	1044 reflections with $I > 2\sigma(I)$
Radiation source: fine-focus sealed tube	$R_{int} = 0.055$
graphite	$\theta_{max} = 25.3°$, $\theta_{min} = 2.4°$
$\omega/2\theta$ scans	$h = 0\rightarrow13$
Absorption correction: ψ scan (North *et al.*, 1968)	$k = -8\rightarrow8$
$T_{min} = 0.978$, $T_{max} = 0.993$	$l = -14\rightarrow14$
3465 measured reflections	3 standard reflections every 200 reflections
1726 independent reflections	intensity decay: 1%

Refinement

Refinement on F^2	Primary atom site location: structure-invariant direct methods
Least-squares matrix: full	Secondary atom site location: difference Fourier map
$R[F^2 > 2\sigma(F^2)] = 0.070$	Hydrogen site location: inferred from neighbouring sites
$wR(F^2) = 0.180$	H-atom parameters constrained
$S = 1.00$	$w = 1/[\sigma^2(F_o^2) + (0.060P)^2 + 0.550P]$ where $P = (F_o^2 + 2F_c^2)/3$
1726 reflections	$(\Delta/\sigma)_{max} < 0.001$
112 parameters	$\Delta\rho_{max} = 0.32$ e Å^{-3}
4 restraints	$\Delta\rho_{min} = -0.16$ e Å^{-3}

Special details

Geometry. All e.s.d.'s (except the e.s.d. in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell e.s.d.'s are taken into account individually in the estimation of e.s.d.'s in distances, angles and torsion angles; correlations

between e.s.d.'s in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell e.s.d.'s is used for estimating e.s.d.'s involving l.s. planes.

Refinement. Refinement of F^2 against ALL reflections. The weighted *R*-factor *wR* and goodness of fit *S* are based on F^2, conventional *R*-factors *R* are based on *F*, with *F* set to zero for negative F^2. The threshold expression of $F^2 > \sigma(F^2)$ is used only for calculating *R*-factors(gt) *etc*. and is not relevant to the choice of reflections for refinement. *R*-factors based on F^2 are statistically about twice as large as those based on *F*, and *R*- factors based on ALL data will be even larger.

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å^2)

	x	*y*	*z*	U_{iso}*/U_{eq}
N	0.8267 (3)	0.3421 (5)	−0.0762 (2)	0.0917 (9)
O	0.9121 (2)	0.5682 (4)	−0.1656 (2)	0.1110 (10)
C1	0.8287 (3)	0.1854 (5)	0.1029 (3)	0.0744 (9)
H1A	0.9111	0.1976	0.1095	0.089*
C2	0.7737 (3)	0.0925 (4)	0.1832 (2)	0.0696 (8)
H2A	0.8181	0.0387	0.2432	0.083*
C3	0.6508 (3)	0.0794 (4)	0.1741 (2)	0.0660 (8)
H3A	0.6121	0.0177	0.2285	0.079*
C4	0.5867 (3)	0.1571 (4)	0.0853 (2)	0.0629 (8)
H4A	0.5043	0.1465	0.0801	0.075*
C5	0.6408 (2)	0.2526 (4)	0.0015 (2)	0.0554 (7)
C6	0.7649 (3)	0.2603 (5)	0.0137 (2)	0.0682 (8)
C7	0.5689 (3)	0.3319 (5)	−0.0977 (2)	0.0733 (9)
H7A	0.5852	0.4676	−0.1048	0.110*
H7B	0.4858	0.3138	−0.0895	0.110*
H7C	0.5897	0.2648	−0.1621	0.110*
C8	0.8631 (3)	0.1932 (7)	−0.1620 (3)	0.1025 (12)
H8A	0.9102	0.2565	−0.2132	0.154*
H8B	0.7930	0.1397	−0.2006	0.154*
H8C	0.9087	0.0911	−0.1255	0.154*
C9	0.8569 (3)	0.5129 (7)	−0.0876 (3)	0.0931 (10)
C10	0.8173 (3)	0.6500 (5)	0.0004 (3)	0.0896 (10)
H10A	0.8712	0.6398	0.0652	0.134*
H10B	0.7386	0.6155	0.0177	0.134*
H10C	0.8171	0.7808	−0.0264	0.134*

Atomic displacement parameters (Å^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
N	0.0813 (19)	0.107 (2)	0.089 (2)	−0.0143 (17)	0.0181 (15)	0.0186 (16)
O	0.0849 (16)	0.150 (2)	0.1002 (17)	−0.0239 (16)	0.0217 (13)	0.0430 (16)
C1	0.0646 (18)	0.081 (2)	0.077 (2)	−0.0093 (16)	0.0022 (16)	0.0066 (18)
C2	0.090 (2)	0.0613 (17)	0.0576 (17)	−0.0028 (17)	0.0063 (15)	0.0046 (14)
C3	0.086 (2)	0.0624 (17)	0.0519 (15)	−0.0241 (16)	0.0178 (15)	0.0047 (14)
C4	0.0630 (17)	0.0684 (17)	0.0600 (17)	−0.0176 (14)	0.0214 (14)	−0.0081 (15)
C5	0.0601 (16)	0.0554 (15)	0.0517 (14)	−0.0082 (13)	0.0109 (12)	−0.0029 (12)
C6	0.0639 (18)	0.077 (2)	0.0650 (18)	−0.0171 (16)	0.0108 (14)	0.0132 (16)

C7	0.0699 (18)	0.083 (2)	0.0683 (18)	−0.0097 (17)	0.0101 (15)	0.0085 (17)
C8	0.083 (2)	0.159 (4)	0.070 (2)	−0.011 (2)	0.0350 (17)	0.007 (2)
C9	0.073 (2)	0.122 (3)	0.085 (2)	−0.017 (2)	0.0104 (16)	0.0221 (18)
C10	0.097 (2)	0.0670 (19)	0.106 (2)	−0.0223 (18)	0.0166 (19)	0.0247 (16)

Geometric parameters (Å, °)

N—C9	1.238 (5)	C5—C6	1.396 (4)
N—C6	1.465 (4)	C5—C7	1.505 (4)
N—C8	1.549 (5)	C7—H7A	0.9600
O—C9	1.243 (4)	C7—H7B	0.9600
C1—C6	1.358 (4)	C7—H7C	0.9600
C1—C2	1.366 (4)	C8—H8A	0.9600
C1—H1A	0.9300	C8—H8B	0.9600
C2—C3	1.384 (4)	C8—H8C	0.9600
C2—H2A	0.9300	C9—C10	1.528 (5)
C3—C4	1.363 (4)	C10—H10A	0.9600
C3—H3A	0.9300	C10—H10B	0.9600
C4—C5	1.401 (3)	C10—H10C	0.9600
C4—H4A	0.9300		
C9—N—C6	127.2 (3)	C5—C7—H7A	109.5
C9—N—C8	117.6 (3)	C5—C7—H7B	109.5
C6—N—C8	115.1 (3)	H7A—C7—H7B	109.5
C6—C1—C2	120.9 (3)	C5—C7—H7C	109.5
C6—C1—H1A	119.5	H7A—C7—H7C	109.5
C2—C1—H1A	119.5	H7B—C7—H7C	109.5
C1—C2—C3	119.1 (3)	N—C8—H8A	109.5
C1—C2—H2A	120.4	N—C8—H8B	109.5
C3—C2—H2A	120.4	H8A—C8—H8B	109.5
C4—C3—C2	119.9 (3)	N—C8—H8C	109.5
C4—C3—H3A	120.0	H8A—C8—H8C	109.5
C2—C3—H3A	120.0	H8B—C8—H8C	109.5
C3—C4—C5	122.2 (3)	N—C9—O	122.6 (4)
C3—C4—H4A	118.9	N—C9—C10	114.2 (3)
C5—C4—H4A	118.9	O—C9—C10	123.1 (4)
C6—C5—C4	115.8 (3)	C9—C10—H10A	109.5
C6—C5—C7	122.6 (2)	C9—C10—H10B	109.5
C4—C5—C7	121.5 (2)	H10A—C10—H10B	109.5
C1—C6—C5	122.0 (3)	C9—C10—H10C	109.5
C1—C6—N	119.8 (3)	H10A—C10—H10C	109.5
C5—C6—N	118.1 (3)	H10B—C10—H10C	109.5
C6—C1—C2—C3	−1.7 (5)	C7—C5—C6—N	−2.5 (4)
C1—C2—C3—C4	0.6 (5)	C9—N—C6—C1	−91.7 (5)
C2—C3—C4—C5	−0.4 (4)	C8—N—C6—C1	84.8 (4)
C3—C4—C5—C6	1.1 (4)	C9—N—C6—C5	91.8 (4)
C3—C4—C5—C7	178.0 (3)	C8—N—C6—C5	−91.7 (4)
C2—C1—C6—C5	2.4 (5)	C6—N—C9—O	178.1 (3)
C2—C1—C6—N	−174.0 (3)	C8—N—C9—O	1.6 (6)
C4—C5—C6—C1	−2.1 (4)	C6—N—C9—C10	−3.6 (5)

C7—C5—C6—C1	−179.0 (3)	C8—N—C9—C10	179.9 (3)
C4—C5—C6—N	174.4 (3)		

Hydrogen-bond geometry (Å, °)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
C7—H7C···O^{i}	0.96	2.51	3.442 (4)	165
C1—H1A···O^{ii}	0.93	2.60	3.414 (4)	145

Symmetry codes: (i) −*x*+3/2, *y*−1/2, −*z*−1/2; (ii) −*x*+2, −*y*+1, −*z*.

Fig. 1

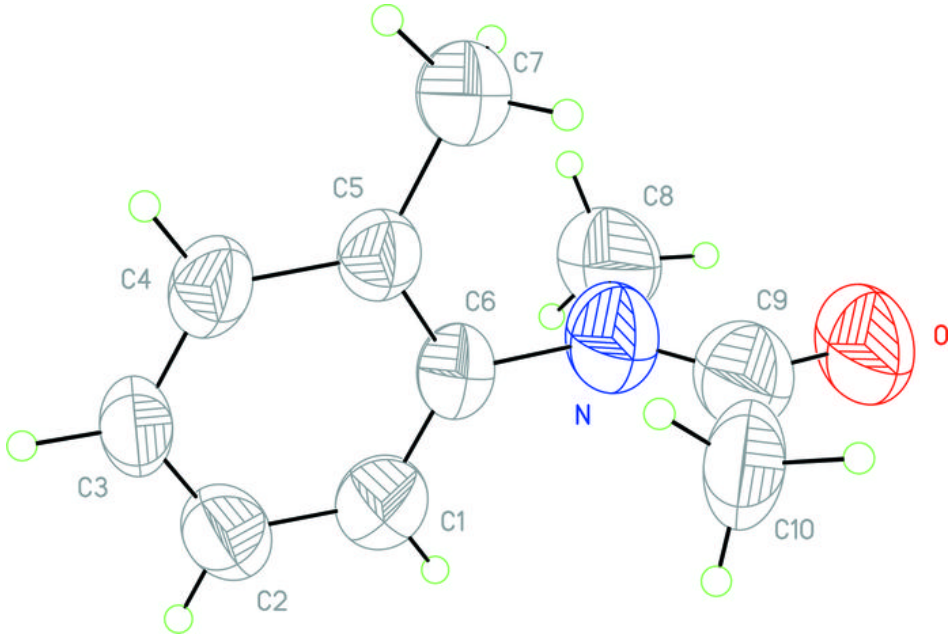
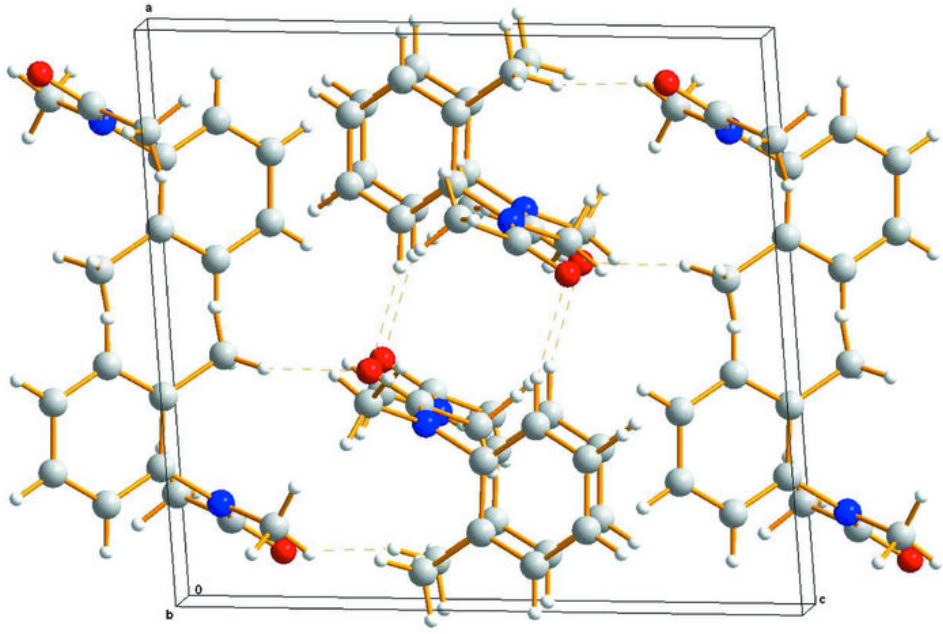


Fig. 2



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Polymorphic form II of 4,4′-methylenebis(benzenesulfonamide)

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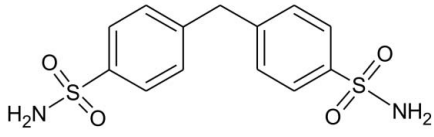
Key indicators: single-crystal X-ray study; T = 120 K; mean σ(C–C) = 0.004 Å; R factor = 0.038; wR factor = 0.087; data-to-parameter ratio = 11.3.

In the title compound, $C_{13}H_{14}N_2O_4S_2$ (alternative names: diphenylmethane-4,4′-disulfonamide, nirexon, CRN: 535–66-0), the two benzene rings form a dihedral angle of 70.8 (1)°. There are two sets of shorter (H···O < 2.1 Å) and longer (H···O > 2.4 Å) N—H···O hydrogen bonds per sulfonamide NH_2 group, which together result in hydrogen-bonded sheets parallel (102). Adjacent sheets are connected to one another by an additional N—H···N interaction so that a three-dimensional network of hydrogen-bonded molecules is formed. The investigated polymorph is identical with the form II previously described by Kuhnert-Brandstätter & Moser [(1981). *Mikrochim. Acta*, **75**, 421–440].

Related literature

For the polymorphism of diphenylmethane-4,4′-disulfonamide, see Kuhnert-Brandstätter & Moser (1981); Kuhnert-Brandstätter & Wunsch (1969).



Experimental

Crystal data

$C_{13}H_{14}N_2O_4S_2$
M_r = 326.38
Monoclinic, $P2_1$
a = 10.8251 (5) Å
b = 5.0791 (3) Å
c = 12.6912 (5) Å
β = 90.931 (3)°
V = 697.69 (6) Å^3
Z = 2
Mo $K\alpha$ radiation
μ = 0.40 mm^{-1}
T = 120 K
0.25 × 0.1 × 0.05 mm

Data collection

Bruker–Nonius Roper CCD camera on κ-goniostat diffractometer
Absorption correction: multi-scan (*SADABS*; Sheldrick, 2007)
T_{min} = 0.907, T_{max} = 0.980
7877 measured reflections
2438 independent reflections
2152 reflections with $I > 2\sigma(I)$
R_{int} = 0.054

Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.038
$wR(F^2)$ = 0.087
S = 1.06
2438 reflections
216 parameters
5 restraints
H atoms treated by a mixture of independent and constrained refinement
$\Delta\rho_{max}$ = 0.26 e Å^{-3}
$\Delta\rho_{min}$ = −0.46 e Å^{-3}
Absolute structure: Flack (1983), 904 Friedel pairs
Flack parameter: −0.18 (9)

Table 1
Hydrogen-bond geometry (Å, °).

D—H···A	D—H	H···A	D···A	D—H···A
N1—H1···O1^{i}	0.88 (2)	2.09 (2)	2.960 (4)	168 (4)
N1—H2···O1^{ii}	0.89 (2)	2.42 (3)	3.166 (4)	142 (3)
N1—H2···O4^{iii}	0.89 (2)	2.53 (3)	3.116 (4)	124 (3)
N2—H3···O3^{iv}	0.88 (2)	2.06 (2)	2.898 (3)	159 (3)
N2—H4···N1^{v}	0.88 (2)	2.50 (3)	3.182 (3)	135 (3)
N2—H4···O4^{vi}	0.88 (2)	2.50 (3)	3.149 (4)	131 (3)

Symmetry codes: (i) $-x, y+\frac{1}{2}, -z+1$; (ii) $x, y+1, z$; (iii) $-x+1, y-\frac{1}{2}, -z+1$; (iv) $-x+2, y-\frac{1}{2}, -z$; (v) $-x+1, y+\frac{1}{2}, -z+1$; (vi) $x, y-1, z$.

Data collection: *COLLECT* (Hooft, 1998); cell refinement: *SCALEPACK* (Otwinowski & Minor, 1997); data reduction: *DENZO* (Otwinowski & Minor, 1997) and *SCALEPACK*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *XP* in *SHELXTL* (Sheldrick, 2008) and *Mercury* (Macrae *et al.*, 2006); software used to prepare material for publication: *publCIF* (Westrip, 2010).

Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: IM2209).

References

Flack, H. D. (1983). *Acta Cryst.* A**39**, 876–881.
Hooft, R. W. W. (1998). *COLLECT*. Nonius BV, Delft, The Netherlands.
Kuhnert-Brandstätter, M. & Moser, I. (1981). *Mikrochim. Acta*, **75**, 421–440.
Kuhnert-Brandstätter, M. & Wunsch, S. (1969). *Mikrochim. Acta*, **57**, 1297–1370.
Macrae, C. F., Edgington, P. R., McCabe, P., Pidcock, E., Shields, G. P., Taylor, R., Towler, M. & van de Streek, J. (2006). *J. Appl. Cryst.* **39**, 453–457.
Otwinowski, Z. & Minor, W. (1997). *Methods in Enzymology*, Vol. 276, *Macromolecular Crystallography*, Part A, edited by C. W. Carter Jr & R. M. Sweet, pp. 307–326. New York: Academic Press.
Sheldrick, G. M. (2007). *SADABS*. University of Göttingen, Germany.
Sheldrick, G. M. (2008). *Acta Cryst.* A**64**, 112–122.
Westrip, S. P. (2010). *J. Appl. Cryst.* **43**. Submitted.

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supplementary materials

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Polymorphic form II of 4,4'-methylenebis(benzenesulfonamide)

T. Gelbrich, M. F. Haddow and U. J. Griesser

Comment

The polymorphic behaviour of the title compound, a carbonic anhydrase inhibitor with diuretic effects, was described by Kuhnert-Brandstätter & Moser (1981) and Kuhnert-Brandstätter & Wunsch (1969), who identified five distinct polymorphic modifications. The commercial product contained form II (mp. 172–174 °C), which was also found to be the stable polymorph at room temperature. The identity of the crystals investigated in the present study with form II reported by Kuhnert-Brandstätter & Moser (1981) was established by thermomicroscopy and IR spectroscopy. The asymmetric unit contains a single molecule (Fig. 1). Its central plane, defined by S1, S2, C1, C11, C14, C21 and C24, forms angles of 21.8 (1)° and 78.7 (1)° with the mean planes of the two phenyl rings C11 > C16 and C21 > C26, respectively. The two sulfonamide groups are differently oriented with respect to the adjacent phenyl ring, so that the corresponding torsion angles N1—S1—C1—C24 and N2—S2—C1—C14 are 115.6 (2)° and 53.3 (2)°, respectively. Each molecule is connected to four other molecules by four short N—H···O bonds (H···O < 2.1 Å, see Table 2) so that an H-bonded sheet parallel to (102) is formed. The symmetry operation between molecules linked by these primary interactions involving one H-bond donor and one acceptor site of each sulfonamide group is a twofold screw axis. There are two additional N—H···O contacts (H···O > 2.4 Å, see Table 2) within the same plane so that all four NH hydrogen bond donor sites are employed once. These secondary N—H···O bonds link molecules related by a translation along [010]. The O3 and O4 sites of one sulfonyl group accept one H-bond each, while in the group O1 accepts two H-bonds. Thus, the sulfonamide groups of molecules in the hydrogen bonded sheet form two distinct chains of fused rings both propagating parallel to [010]. One chain consists of ten-membered rings with two H-bond donor and two acceptor sites (labeled 'A' in Fig. 2), and the other is generated from 9-membered rings with two three H-bond donor and two acceptor sites ('B'). Each of the N—H···O sheets is linked to two neighbouring sheets by a N2—H···N1(-*x* + 1, *y* + 1/2, -*z* + 1) interaction (represented by arrows in Fig. 2). Thus, this crystal structure contains a three-dimensional network of N—H···O and N—H···N bonded molecules of diphenylmethane-4,4'-disulfonamide.

Experimental

The crystals for this study were obtained from a commercial sample of diphenylmethane-4,4'-disulfonamide (Farbenfabriken Bayer AG, Leverkusen).

Refinement

All H atoms were identified in a difference map. H atoms bonded to secondary CH_2 (C—H = 0.99 Å) and aromatic carbon atoms (C—H = 0.95 Å) were positioned geometrically. Hydrogen atoms attached to N were refined with restrained distances [N—H = 0.88 (12) Å].The U_{iso} parameters of all H atoms were refined freely.

Figures

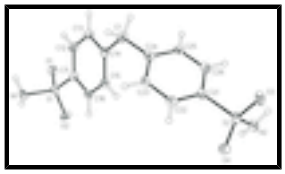


Fig. 1. The molecular structure with displacement ellipsoids drawn at the 50% probability level and hydrogen atoms shown as spheres of arbitrary size.

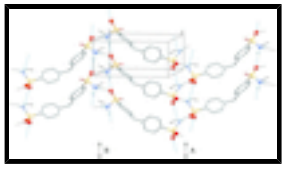


Fig. 2. Portion of a single hydrogen bonded sheet parallel to (102) and generated by shorter N—H···O bonds (dotted lines) and longer N—H···O bonds (dashed lines). N—H···N bonds (arrows) connect to neighbouring sheets. O, H and N atoms directly involved in hydrogen bonds are drawn as balls.

4,4'-methylenebis(benzenesulfonamide)

Crystal data

$C_{13}H_{14}N_2O_4S_2$	$F(000) = 340$
$M_r = 326.38$	$D_x = 1.554$ Mg m^{-3}
Monoclinic, $P2_1$	Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å
Hall symbol: P 2yb	Cell parameters from 6304 reflections
$a = 10.8251$ (5) Å	$\theta = 2.9$–$26.0°$
$b = 5.0791$ (3) Å	$\mu = 0.40$ mm^{-1}
$c = 12.6912$ (5) Å	$T = 120$ K
$\beta = 90.931$ (3)°	Needle, colourless
$V = 697.69$ (6) Å^3	0.25 × 0.1 × 0.05 mm
$Z = 2$	

Data collection

Bruker–Nonius Roper CCD camera on κ-goniostat diffractometer	2438 independent reflections
Radiation source: Bruker–Nonius FR591 rotating anode	2152 reflections with $I > 2\sigma(I)$
graphite	$R_{int} = 0.054$
Detector resolution: 9.091 pixels mm^{-1}	$\theta_{max} = 26.0°$, $\theta_{min} = 3.7°$
φ & ω scans	$h = -13 \rightarrow 12$
Absorption correction: multi-scan (*SADABS*; Sheldrick, 2007)	$k = -5 \rightarrow 6$
$T_{min} = 0.907$, $T_{max} = 0.980$	$l = -15 \rightarrow 15$
7877 measured reflections	

Refinement

Refinement on F^2	Secondary atom site location: difference Fourier map
Least-squares matrix: full	Hydrogen site location: inferred from neighbouring sites

$R[F^2 > 2\sigma(F^2)] = 0.038$	H atoms treated by a mixture of independent and constrained refinement
$wR(F^2) = 0.087$	$w = 1/[\sigma^2(F_o^2) + (0.0361P)^2 + 0.182P]$ where $P = (F_o^2 + 2F_c^2)/3$
$S = 1.06$	$(\Delta/\sigma)_{max} = 0.001$
2438 reflections	$\Delta\rho_{max} = 0.26$ e Å^{-3}
216 parameters	$\Delta\rho_{min} = -0.46$ e Å^{-3}
5 restraints	Absolute structure: Flack (1983), 904 Friedel pairs
Primary atom site location: structure-invariant direct methods	Flack parameter: −0.18 (9)

Special details

Geometry. All e.s.d.'s (except the e.s.d. in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell e.s.d.'s are taken into account individually in the estimation of e.s.d.'s in distances, angles and torsion angles; correlations between e.s.d.'s in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell e.s.d.'s is used for estimating e.s.d.'s involving l.s. planes.

Refinement. Refinement of F^2 against ALL reflections. The weighted *R*-factor *wR* and goodness of fit *S* are based on F^2, conventional *R*-factors *R* are based on *F*, with *F* set to zero for negative F^2. The threshold expression of $F^2 > \sigma(F^2)$ is used only for calculating *R*-factors(gt) *etc*. and is not relevant to the choice of reflections for refinement. *R*-factors based on F^2 are statistically about twice as large as those based on *F*, and *R*- factors based on ALL data will be even larger.

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å^2)

	x	*y*	*z*	U_{iso}*/U_{eq}
S1	0.20189 (6)	−0.23188 (15)	0.54432 (5)	0.01593 (18)
S2	0.88754 (6)	0.73072 (17)	0.14221 (5)	0.01695 (19)
O1	0.1335 (2)	−0.4632 (4)	0.51332 (16)	0.0205 (5)
O2	0.30683 (18)	−0.2579 (6)	0.61295 (14)	0.0238 (5)
O3	0.90887 (19)	0.8314 (5)	0.03829 (15)	0.0249 (6)
O4	0.90645 (19)	0.9060 (4)	0.23016 (16)	0.0208 (5)
N1	0.1033 (3)	−0.0417 (6)	0.6023 (2)	0.0189 (6)
H1	0.035 (3)	−0.039 (10)	0.563 (3)	0.053 (13)*
H2	0.129 (3)	0.124 (4)	0.608 (3)	0.035 (11)*
N2	0.9759 (2)	0.4794 (6)	0.1575 (2)	0.0197 (6)
H3	0.994 (3)	0.410 (7)	0.0960 (18)	0.030 (10)*
H4	0.965 (3)	0.381 (7)	0.213 (2)	0.042 (12)*
C1	0.3517 (3)	0.3849 (7)	0.1577 (2)	0.0208 (7)
H1A	0.3319	0.2784	0.0943	0.024 (8)*
H1B	0.2990	0.5441	0.1550	0.028 (10)*
C11	0.2504 (3)	−0.0654 (6)	0.4304 (2)	0.0169 (7)
C12	0.1806 (3)	−0.0834 (7)	0.3372 (2)	0.0212 (7)
H12	0.1097	−0.1934	0.3335	0.021 (8)*
C13	0.2160 (3)	0.0610 (7)	0.2502 (2)	0.0200 (7)
H13	0.1696	0.0470	0.1863	0.032 (10)*
C14	0.3184 (2)	0.2261 (7)	0.2547 (2)	0.0164 (6)
C15	0.3882 (2)	0.2386 (8)	0.3479 (2)	0.0189 (6)

H15	0.4599	0.3463	0.3514	0.045 (12)*
C16	0.3538 (3)	0.0945 (7)	0.4360 (2)	0.0188 (7)
H16	0.4011	0.1058	0.4995	0.026 (9)*
C21	0.7330 (3)	0.6228 (6)	0.1479 (2)	0.0151 (6)
C22	0.6511 (2)	0.7639 (7)	0.2093 (2)	0.0174 (6)
H22	0.6786	0.9108	0.2497	0.037 (11)*
C23	0.5271 (3)	0.6854 (6)	0.2106 (2)	0.0179 (7)
H23	0.4702	0.7814	0.2520	0.021 (8)*
C24	0.4857 (3)	0.4701 (6)	0.1528 (2)	0.0170 (7)
C25	0.5703 (3)	0.3302 (7)	0.0928 (2)	0.0183 (7)
H25	0.5432	0.1810	0.0536	0.030 (10)*
C26	0.6932 (3)	0.4053 (7)	0.0892 (2)	0.0187 (7)
H26	0.7498	0.3100	0.0473	0.043 (11)*

Atomic displacement parameters (Å^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
S1	0.0169 (3)	0.0134 (4)	0.0174 (3)	−0.0005 (4)	0.0005 (2)	0.0018 (4)
S2	0.0179 (4)	0.0157 (4)	0.0174 (3)	−0.0004 (4)	0.0033 (3)	0.0020 (4)
O1	0.0255 (12)	0.0093 (11)	0.0268 (12)	−0.0053 (10)	0.0004 (9)	−0.0009 (10)
O2	0.0203 (10)	0.0268 (13)	0.0241 (10)	−0.0016 (12)	−0.0057 (8)	0.0087 (13)
O3	0.0256 (12)	0.0306 (15)	0.0187 (10)	0.0016 (10)	0.0085 (8)	0.0113 (10)
O4	0.0222 (11)	0.0154 (12)	0.0249 (11)	−0.0026 (10)	0.0013 (9)	−0.0060 (10)
N1	0.0232 (15)	0.0143 (15)	0.0193 (14)	0.0003 (13)	0.0061 (11)	−0.0001 (12)
N2	0.0231 (14)	0.0191 (16)	0.0170 (14)	0.0058 (13)	0.0049 (11)	0.0032 (12)
C1	0.0209 (16)	0.0217 (18)	0.0196 (16)	−0.0019 (15)	−0.0019 (12)	0.0066 (14)
C11	0.0178 (15)	0.0145 (16)	0.0183 (14)	0.0002 (14)	0.0012 (12)	0.0014 (13)
C12	0.0173 (16)	0.0217 (19)	0.0246 (16)	−0.0055 (15)	−0.0045 (12)	0.0016 (15)
C13	0.0184 (16)	0.0229 (18)	0.0186 (15)	−0.0020 (15)	−0.0032 (12)	0.0005 (14)
C14	0.0155 (14)	0.0149 (16)	0.0189 (13)	0.0007 (15)	0.0011 (10)	0.0006 (15)
C15	0.0176 (14)	0.0204 (16)	0.0188 (13)	−0.0024 (17)	0.0009 (11)	0.0022 (17)
C16	0.0178 (16)	0.0191 (17)	0.0194 (15)	−0.0032 (14)	−0.0010 (12)	−0.0008 (13)
C21	0.0169 (15)	0.0134 (16)	0.0153 (13)	0.0005 (13)	0.0031 (11)	0.0024 (13)
C22	0.0228 (15)	0.0124 (15)	0.0169 (13)	−0.0014 (15)	−0.0009 (11)	0.0002 (16)
C23	0.0184 (15)	0.0181 (18)	0.0174 (14)	0.0015 (13)	0.0054 (12)	−0.0014 (13)
C24	0.0222 (16)	0.0168 (17)	0.0118 (14)	0.0009 (14)	−0.0020 (12)	0.0076 (13)
C25	0.0244 (16)	0.0183 (18)	0.0123 (13)	−0.0037 (13)	−0.0008 (12)	−0.0027 (12)
C26	0.0245 (16)	0.0153 (17)	0.0163 (14)	0.0028 (15)	0.0019 (12)	0.0002 (14)

Geometric parameters (Å, °)

S1—O2	1.4263 (19)	C12—C13	1.385 (4)
S1—O1	1.440 (2)	C12—H12	0.9500
S1—N1	1.624 (3)	C13—C14	1.390 (4)
S1—C11	1.762 (3)	C13—H13	0.9500
S2—O3	1.437 (2)	C14—C15	1.395 (4)
S2—O4	1.440 (2)	C15—C16	1.391 (4)
S2—N2	1.605 (3)	C15—H15	0.9500
S2—C21	1.763 (3)	C16—H16	0.9500

N1—H1	0.881 (19)	C21—C22	1.389 (4)
N1—H2	0.887 (19)	C21—C26	1.397 (4)
N2—H3	0.883 (18)	C22—C23	1.401 (4)
N2—H4	0.875 (19)	C22—H22	0.9500
C1—C24	1.516 (4)	C23—C24	1.387 (4)
C1—C14	1.520 (4)	C23—H23	0.9500
C1—H1A	0.9900	C24—C25	1.395 (4)
C1—H1B	0.9900	C25—C26	1.386 (4)
C11—C16	1.384 (4)	C25—H25	0.9500
C11—C12	1.396 (4)	C26—H26	0.9500
O2—S1—O1	119.49 (15)	C12—C13—C14	121.1 (3)
O2—S1—N1	107.52 (14)	C12—C13—H13	119.4
O1—S1—N1	105.68 (14)	C14—C13—H13	119.4
O2—S1—C11	107.49 (13)	C13—C14—C15	118.9 (3)
O1—S1—C11	109.03 (14)	C13—C14—C1	119.1 (3)
N1—S1—C11	107.02 (15)	C15—C14—C1	122.0 (3)
O3—S2—O4	117.93 (14)	C16—C15—C14	120.6 (3)
O3—S2—N2	106.86 (13)	C16—C15—H15	119.7
O4—S2—N2	108.72 (13)	C14—C15—H15	119.7
O3—S2—C21	108.36 (13)	C11—C16—C15	119.7 (3)
O4—S2—C21	106.48 (13)	C11—C16—H16	120.2
N2—S2—C21	108.18 (15)	C15—C16—H16	120.2
S1—N1—H1	108 (3)	C22—C21—C26	120.9 (3)
S1—N1—H2	114 (2)	C22—C21—S2	118.5 (2)
H1—N1—H2	107 (4)	C26—C21—S2	120.6 (2)
S2—N2—H3	111 (2)	C21—C22—C23	118.7 (3)
S2—N2—H4	118 (3)	C21—C22—H22	120.6
H3—N2—H4	121 (4)	C23—C22—H22	120.6
C24—C1—C14	115.1 (2)	C24—C23—C22	121.3 (3)
C24—C1—H1A	108.5	C24—C23—H23	119.4
C14—C1—H1A	108.5	C22—C23—H23	119.4
C24—C1—H1B	108.5	C23—C24—C25	118.8 (3)
C14—C1—H1B	108.5	C23—C24—C1	120.2 (3)
H1A—C1—H1B	107.5	C25—C24—C1	120.9 (3)
C16—C11—C12	120.5 (3)	C26—C25—C24	121.1 (3)
C16—C11—S1	119.5 (2)	C26—C25—H25	119.4
C12—C11—S1	120.0 (2)	C24—C25—H25	119.4
C13—C12—C11	119.2 (3)	C25—C26—C21	119.2 (3)
C13—C12—H12	120.4	C25—C26—H26	120.4
C11—C12—H12	120.4	C21—C26—H26	120.4

Hydrogen-bond geometry (Å, °)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
N1—H1···O1^{i}	0.88 (2)	2.09 (2)	2.960 (4)	168 (4)
N1—H2···O1^{ii}	0.89 (2)	2.42 (3)	3.166 (4)	142 (3)
N1—H2···O4^{iii}	0.89 (2)	2.53 (3)	3.116 (4)	124 (3)
N2—H3···O3^{iv}	0.88 (2)	2.06 (2)	2.898 (3)	159 (3)

N2—H4···N1^{v}	0.88 (2)	2.50 (3)	3.182 (3)	135 (3)
N2—H4···O4^{vi}	0.88 (2)	2.50 (3)	3.149 (4)	131 (3)

Symmetry codes: (i) −*x*, *y*+1/2, −*z*+1; (ii) *x*, *y*+1, *z*; (iii) −*x*+1, *y*−1/2, −*z*+1; (iv) −*x*+2, *y*−1/2, −*z*; (v) −*x*+1, *y*+1/2, −*z*+1; (vi) *x*, *y*−1, *z*.

Fig. 1

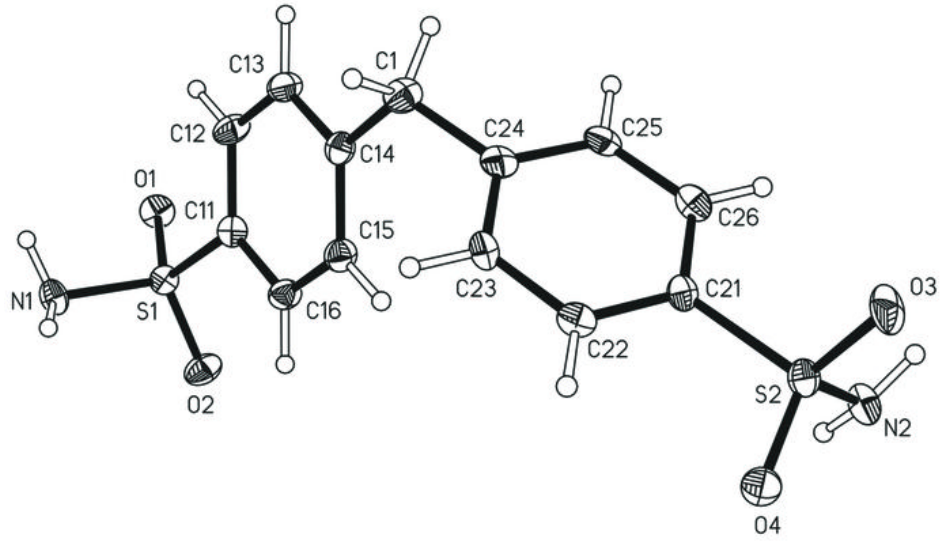
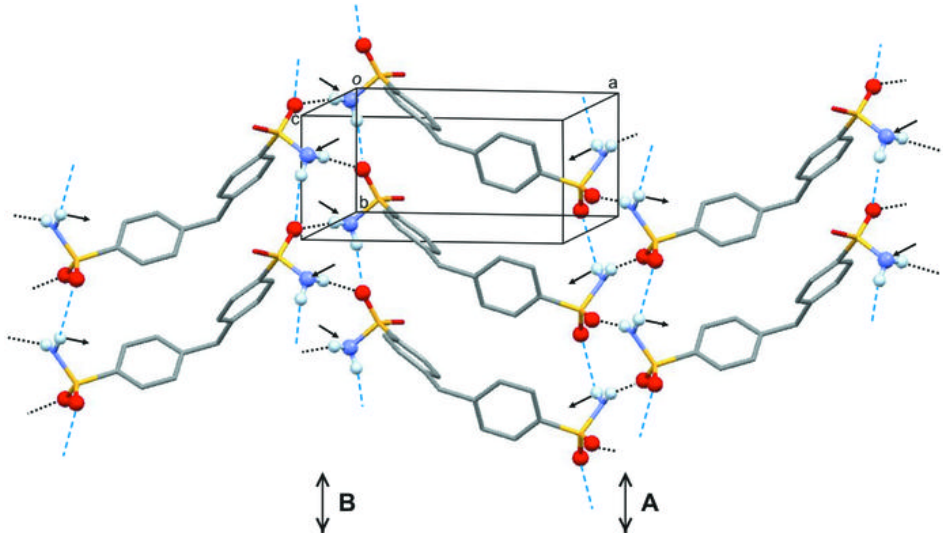

C13
C1
C12
C14
C24
C25
O1
C11
C15
C26
N1
S1
C16
C23
C21
O3
C22
S2
N2
O2
O4

Fig. 2



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2-(Bicyclo[2.2.1]hept-5-en-2-yl)-1*H*-pyrrolo[2,3-*b*]pyridine

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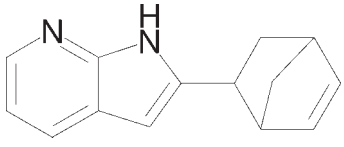
Received 7 June 2010; accepted 9 June 2010

Key indicators: single-crystal X-ray study; T = 193 K; mean σ(C–C) = 0.004 Å; R factor = 0.082; wR factor = 0.227; data-to-parameter ratio = 14.6.

The crystal structure of the title compound, $C_{14}H_{14}N_2$, displays intermolecular N—H···N hydrogen bonds, forming dimers of enantiomeric molecules *via* a crystallographic centre of inversion.

Related literature

For the general synthetic procedure for 2-substituted 7-aza-indoles, see Davis *et al.* (1992).



Experimental

Crystal data

$C_{14}H_{14}N_2$
M_r = 210.27
Monoclinic, $P2_1/n$
a = 7.7837 (12) Å
b = 8.9867 (14) Å
c = 15.973 (3) Å
β = 96.408 (8)°
V = 1110.3 (3) Å^3
Z = 4
Cu $K\alpha$ radiation
μ = 0.58 mm^{-1}
T = 193 K
0.40 × 0.30 × 0.20 mm

Data collection

Enraf–Nonius CAD-4 diffractometer
2274 measured reflections
2113 independent reflections
1940 reflections with $I > 2\sigma(I)$
R_{int} = 0.050
3 standard reflections every 60 min
intensity decay: 2%

Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.082
$wR(F^2)$ = 0.227
S = 1.09
2113 reflections
145 parameters
H-atom parameters constrained
$\Delta\rho_{max}$ = 0.47 e Å^{-3}
$\Delta\rho_{min}$ = −0.36 e Å^{-3}

Table 1
Hydrogen-bond geometry (Å, °).

D—H···A	D—H	H···A	D···A	D—H···A
N1—H1···N7^{i}	0.90	2.05	2.932 (3)	166

Symmetry code: (i) $-x+2, -y+1, -z+1$.

Data collection: *CAD-4 Software* (Enraf–Nonius, 1989); cell refinement: *CAD-4 Software*; data reduction: *CORINC* (Dräger & Gattow, 1971); program(s) used to solve structure: *SIR97* (Altomare *et al.*, 1999); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *PLATON* (Spek, 2009); software used to prepare material for publication: *PLATON*.

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Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: IM2211).

References

Altomare, A., Burla, M. C., Camalli, M., Cascarano, G. L., Giacovazzo, C., Guagliardi, A., Moliterni, A. G. G., Polidori, G. & Spagna, R. (1999). *J. Appl. Cryst.* **32**, 115–119.
Davis, M. L., Wakewfield, B. J. & Wardellt, J. A. (1992). *Tetrahedron*, **48**, 939–952.
Dräger, M. & Gattow, G. (1971). *Acta Chem. Scand.* **25**, 761–762.
Enraf–Nonius (1989). *CAD-4 Software*. Enraf–Nonius, Delft, The Netherlands.
Sheldrick, G. M. (2008). *Acta Cryst.* A**64**, 112–122.
Spek, A. L. (2009). *Acta Cryst.* D**65**, 148–155.

supplementary materials

Acta Cryst. (2010). E**66**, o1800 [**doi:10.1107/S1600536810022087**]

2-(Bicyclo[2.2.1]hept-5-en-2-yl)-1*H*-pyrrolo[2,3-*b*]pyridine

R. Selig, D. Schollmeyer, W. Albrecht and S. Laufer

Comment

The interest in 7- azaindoles as bioisoster of indole or purine has arisen in conjunction with recent pharmacological programs. Numerous publications on its derivatization reflect the increasing attention paid to this heterocyclic system. The crystal structure of 2-bicyclo[2.2.1]hept-5-en-2-yl-1*H*-pyrrolo[2,3-*b*]pyridine, $C_{14}H_{14}N_2$, is characterized by an intermolecular hydrogen bond N1—H1··· N7 (2.05 Å) forming dimers of enantiomeric molecules, which are related by a crystallographic centre of symmetry.

Experimental

3-methylpyridine (4 g, 43 mmol) was added dropwise to a freshly prepared solution of LDA in THF (0.9*M*) (59 ml, 53 mmol) at 273 K. The resulting suspension was stirred at 273 K for 30 min. Racemic 5-norbornene-2-carbonitrile (5.12 g, 43 mmol) was added dropwise at such a rate that the temperature did not rise above 283 K. Stirring was continued for 60 min. at 273 K. Another portion of LDA solution (59 ml, 53 mmol) was added and stirring was continued overnight at 333 K. The final reaction mixture was allowed to cool and ice-water was added. The mixture was extracted with ethylacetate and the combined extracts were dried (Na_2SO_4) and the solvent was evaporated under reduced pressure. The residue was subjected to flash chromatography. The title compound was obtained in a yield of 31% (2.834 g, 13.48 mmol). Crystals suitable for X-ray analysis were obtained by slow evaporation of the solvent from a methanolic solution.

Refinement

Hydrogen atoms attached to carbons were placed at calculated positions with C—H = 0.95 Å (aromatic) or 0.98–0.99 Å (sp^3 C-atom). All H atoms were refined in the riding-model approximation with isotropic displacement parameters (set at 1.2–1.5 times of the U_{eq} of the parent atom). The hydrogen atom attached to N1 was located in diff. Fourier maps and refined using a fixed isotropic displacement parameter and applying a riding motion model.

Figures

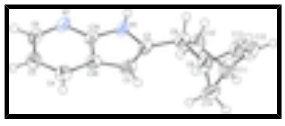


Fig. 1. Molecular structure of compound **I**. Displacement ellipsoids are drawn at the 50% probability level. H atoms are depicted as circles of arbitrary size.

2-(Bicyclo[2.2.1]hept-5-en-2-yl)-1*H*-pyrrolo[2,3-*b*]pyridine

Crystal data

$C_{14}H_{14}N_2$ $F(000) = 448$

M_r = 210.27	D_x = 1.258 Mg m^{-3}
Monoclinic, $P2_1/n$	Cu $K\alpha$ radiation, λ = 1.54178 Å
Hall symbol: -P 2yn	Cell parameters from 25 reflections
a = 7.7837 (12) Å	θ = 65–69°
b = 8.9867 (14) Å	μ = 0.58 mm^{-1}
c = 15.973 (3) Å	T = 193 K
β = 96.408 (8)°	Block, colourless
V = 1110.3 (3) Å^3	0.40 × 0.30 × 0.20 mm
Z = 4	

Data collection

Enraf–Nonius CAD-4 diffractometer	R_{int} = 0.050
Radiation source: rotating anode	θ_{max} = 70.0°, θ_{min} = 5.6°
graphite	h = −9→0
ω/2θ scans	k = −10→0
2274 measured reflections	l = −19→19
2113 independent reflections	3 standard reflections every 60 min
1940 reflections with $I > 2\sigma(I)$	intensity decay: 2%

Refinement

Refinement on F^2	Primary atom site location: structure-invariant direct methods
Least-squares matrix: full	Secondary atom site location: difference Fourier map
$R[F^2 > 2\sigma(F^2)]$ = 0.082	Hydrogen site location: inferred from neighbouring sites
$wR(F^2)$ = 0.227	H-atom parameters constrained
S = 1.09	$w = 1/[\sigma^2(F_o^2) + (0.1178P)^2 + 1.2641P]$ where $P = (F_o^2 + 2F_c^2)/3$
2113 reflections	$(\Delta/\sigma)_{max} < 0.001$
145 parameters	$\Delta\rho_{max}$ = 0.47 e Å^{-3}
0 restraints	$\Delta\rho_{min}$ = −0.36 e Å^{-3}

Special details

Geometry. All e.s.d.'s (except the e.s.d. in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell e.s.d.'s are taken into account individually in the estimation of e.s.d.'s in distances, angles and torsion angles; correlations between e.s.d.'s in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell e.s.d.'s is used for estimating e.s.d.'s involving l.s. planes.

Refinement. Refinement of F^2 against ALL reflections. The weighted R-factor wR and goodness of fit S are based on F^2, conventional R-factors R are based on F, with F set to zero for negative F^2. The threshold expression of $F^2 > \sigma(F^2)$ is used only for calculating R-factors(gt) *etc*. and is not relevant to the choice of reflections for refinement. R-factors based on F^2 are statistically about twice as large as those based on F, and R- factors based on ALL data will be even larger.

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å^2)

	x	*y*	*z*	U_{iso}*/U_{eq}
N1	0.8046 (3)	0.5132 (3)	0.41997 (15)	0.0360 (6)
H1	0.8691	0.5799	0.4519	0.043*
C2	0.6512 (3)	0.5373 (3)	0.36871 (17)	0.0362 (6)
C3	0.5981 (3)	0.4080 (3)	0.32996 (18)	0.0399 (7)
H3	0.4964	0.3943	0.2920	0.048*
C3A	0.7228 (3)	0.2965 (3)	0.35653 (16)	0.0345 (6)
C4	0.7490 (4)	0.1469 (3)	0.33978 (17)	0.0391 (7)
H4	0.6692	0.0929	0.3020	0.047*
C5	0.8949 (4)	0.0794 (3)	0.37998 (18)	0.0411 (7)
H5	0.9164	−0.0228	0.3700	0.049*
C6	1.0105 (3)	0.1604 (3)	0.43497 (18)	0.0387 (7)
H6	1.1092	0.1100	0.4615	0.046*
N7	0.9921 (3)	0.3044 (3)	0.45291 (14)	0.0355 (6)
C7A	0.8499 (3)	0.3677 (3)	0.41290 (16)	0.0317 (6)
C8	0.3998 (4)	0.7013 (4)	0.3032 (2)	0.0472 (8)
H8	0.3817	0.6311	0.2544	0.057*
C9	0.5793 (3)	0.6919 (3)	0.35899 (18)	0.0383 (7)
H9	0.6638	0.7548	0.3321	0.046*
C10	0.5422 (5)	0.7683 (4)	0.4420 (2)	0.0528 (9)
H10A	0.6201	0.8542	0.4552	0.063*
H10B	0.5561	0.6974	0.4897	0.063*
C11	0.3507 (4)	0.8199 (4)	0.4233 (2)	0.0545 (9)
H11	0.2909	0.8473	0.4734	0.065*
C12	0.3445 (4)	0.9316 (4)	0.3555 (2)	0.0485 (8)
H12	0.3232	1.0350	0.3612	0.058*
C13	0.3743 (4)	0.8614 (4)	0.2839 (2)	0.0532 (9)
H13	0.3782	0.9068	0.2304	0.064*
C14	0.2793 (4)	0.6819 (4)	0.3730 (2)	0.0573 (9)
H14A	0.3002	0.5879	0.4049	0.069*
H14B	0.1554	0.6913	0.3518	0.069*

Atomic displacement parameters (Å^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
N1	0.0236 (10)	0.0376 (12)	0.0445 (12)	0.0054 (9)	−0.0063 (9)	−0.0044 (10)
C2	0.0249 (12)	0.0446 (15)	0.0376 (13)	0.0056 (11)	−0.0034 (10)	0.0010 (11)
C3	0.0298 (13)	0.0458 (16)	0.0417 (14)	0.0002 (11)	−0.0058 (11)	−0.0010 (12)
C3A	0.0302 (13)	0.0406 (14)	0.0325 (12)	−0.0005 (11)	0.0024 (10)	−0.0005 (11)
C4	0.0386 (14)	0.0425 (15)	0.0365 (14)	−0.0024 (12)	0.0052 (11)	−0.0048 (12)
C5	0.0428 (15)	0.0378 (15)	0.0440 (15)	0.0057 (12)	0.0109 (12)	−0.0055 (12)
C6	0.0319 (13)	0.0412 (15)	0.0436 (15)	0.0109 (11)	0.0070 (11)	−0.0003 (12)
N7	0.0236 (10)	0.0402 (12)	0.0422 (12)	0.0070 (9)	0.0013 (9)	−0.0024 (10)
C7A	0.0246 (12)	0.0362 (13)	0.0342 (13)	0.0042 (10)	0.0028 (10)	0.0004 (10)
C8	0.0381 (15)	0.0533 (18)	0.0484 (17)	0.0099 (13)	−0.0028 (13)	−0.0038 (14)

C9	0.0264 (13)	0.0452 (16)	0.0424 (14)	0.0059 (11)	0.0006 (11)	0.0011 (12)
C10	0.0521 (19)	0.059 (2)	0.0451 (16)	0.0176 (15)	−0.0032 (14)	−0.0003 (15)
C11	0.0504 (19)	0.064 (2)	0.0525 (18)	0.0156 (16)	0.0187 (15)	0.0002 (16)
C12	0.0328 (14)	0.0534 (18)	0.0593 (19)	0.0152 (13)	0.0044 (13)	−0.0024 (14)
C13	0.0432 (17)	0.065 (2)	0.0508 (17)	0.0135 (15)	0.0010 (14)	0.0083 (16)
C14	0.0337 (16)	0.068 (2)	0.072 (2)	−0.0002 (15)	0.0140 (15)	−0.0068 (18)

Geometric parameters (Å, °)

N1—C7A	1.362 (3)	C8—C14	1.546 (5)
N1—C2	1.388 (3)	C8—C9	1.573 (4)
N1—H1	0.9027	C8—H8	1.0000
C2—C3	1.359 (4)	C9—C10	1.548 (4)
C2—C9	1.500 (4)	C9—H9	1.0000
C3—C3A	1.426 (4)	C10—C11	1.558 (5)
C3—H3	0.9500	C10—H10A	0.9900
C3A—C4	1.391 (4)	C10—H10B	0.9900
C3A—C7A	1.414 (4)	C11—C12	1.473 (5)
C4—C5	1.381 (4)	C11—C14	1.547 (5)
C4—H4	0.9500	C11—H11	1.0000
C5—C6	1.391 (4)	C12—C13	1.349 (5)
C5—H5	0.9500	C12—H12	0.9500
C6—N7	1.336 (4)	C13—H13	0.9500
C6—H6	0.9500	C14—H14A	0.9900
N7—C7A	1.342 (3)	C14—H14B	0.9900
C8—C13	1.480 (5)		
C7A—N1—C2	108.4 (2)	C2—C9—C10	115.2 (2)
C7A—N1—H1	123.5	C2—C9—C8	114.0 (2)
C2—N1—H1	128.1	C10—C9—C8	102.9 (2)
C3—C2—N1	109.4 (2)	C2—C9—H9	108.2
C3—C2—C9	130.9 (2)	C10—C9—H9	108.2
N1—C2—C9	119.5 (2)	C8—C9—H9	108.2
C2—C3—C3A	107.6 (2)	C9—C10—C11	103.5 (2)
C2—C3—H3	126.2	C9—C10—H10A	111.1
C3A—C3—H3	126.2	C11—C10—H10A	111.1
C4—C3A—C7A	116.9 (2)	C9—C10—H10B	111.1
C4—C3A—C3	137.0 (3)	C11—C10—H10B	111.1
C7A—C3A—C3	106.0 (2)	H10A—C10—H10B	109.0
C5—C4—C3A	117.8 (3)	C12—C11—C14	100.6 (3)
C5—C4—H4	121.1	C12—C11—C10	107.2 (3)
C3A—C4—H4	121.1	C14—C11—C10	98.1 (3)
C4—C5—C6	120.3 (3)	C12—C11—H11	116.1
C4—C5—H5	119.9	C14—C11—H11	116.1
C6—C5—H5	119.9	C10—C11—H11	116.1
N7—C6—C5	124.4 (3)	C13—C12—C11	108.0 (3)
N7—C6—H6	117.8	C13—C12—H12	126.0
C5—C6—H6	117.8	C11—C12—H12	126.0
C6—N7—C7A	114.3 (2)	C12—C13—C8	108.1 (3)
N7—C7A—N1	125.1 (2)	C12—C13—H13	126.0

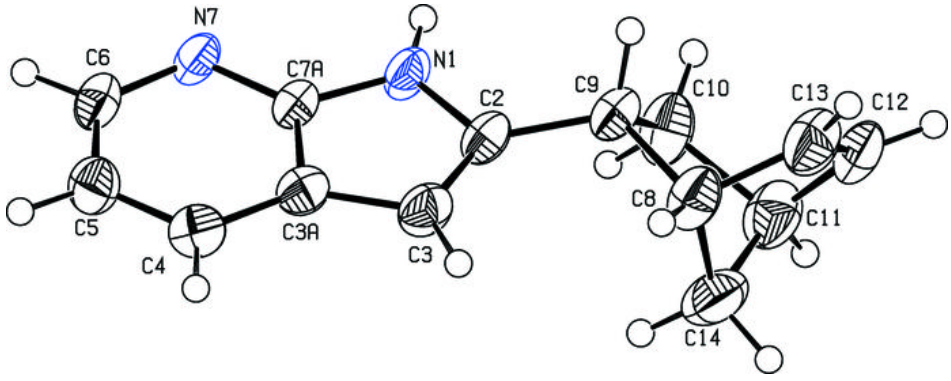
N7—C7A—C3A	126.3 (2)	C8—C13—H13	126.0
N1—C7A—C3A	108.6 (2)	C8—C14—C11	94.1 (3)
C13—C8—C14	100.5 (3)	C8—C14—H14A	112.9
C13—C8—C9	105.1 (3)	C11—C14—H14A	112.9
C14—C8—C9	99.0 (2)	C8—C14—H14B	112.9
C13—C8—H8	116.5	C11—C14—H14B	112.9
C14—C8—H8	116.5	H14A—C14—H14B	110.3
C9—C8—H8	116.5		
C7A—N1—C2—C3	0.6 (3)	N1—C2—C9—C10	−58.2 (4)
C7A—N1—C2—C9	−175.0 (2)	C3—C2—C9—C8	8.7 (4)
N1—C2—C3—C3A	−0.6 (3)	N1—C2—C9—C8	−176.8 (2)
C9—C2—C3—C3A	174.4 (3)	C13—C8—C9—C2	−166.1 (3)
C2—C3—C3A—C4	−177.8 (3)	C14—C8—C9—C2	90.4 (3)
C2—C3—C3A—C7A	0.3 (3)	C13—C8—C9—C10	68.6 (3)
C7A—C3A—C4—C5	0.8 (4)	C14—C8—C9—C10	−35.0 (3)
C3—C3A—C4—C5	178.8 (3)	C2—C9—C10—C11	−127.4 (3)
C3A—C4—C5—C6	−0.2 (4)	C8—C9—C10—C11	−2.8 (3)
C4—C5—C6—N7	−0.2 (4)	C9—C10—C11—C12	−64.3 (3)
C5—C6—N7—C7A	−0.1 (4)	C9—C10—C11—C14	39.5 (3)
C6—N7—C7A—N1	−179.0 (2)	C14—C11—C12—C13	−32.7 (3)
C6—N7—C7A—C3A	0.8 (4)	C10—C11—C12—C13	69.4 (4)
C2—N1—C7A—N7	179.4 (2)	C11—C12—C13—C8	0.3 (4)
C2—N1—C7A—C3A	−0.4 (3)	C14—C8—C13—C12	32.2 (3)
C4—C3A—C7A—N7	−1.1 (4)	C9—C8—C13—C12	−70.2 (3)
C3—C3A—C7A—N7	−179.7 (3)	C13—C8—C14—C11	−48.3 (3)
C4—C3A—C7A—N1	178.6 (2)	C9—C8—C14—C11	59.0 (3)
C3—C3A—C7A—N1	0.1 (3)	C12—C11—C14—C8	48.6 (3)
C3—C2—C9—C10	127.3 (3)	C10—C11—C14—C8	−60.7 (3)

Hydrogen-bond geometry (Å, °)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
N1—H1···N7^{i}	0.90	2.05	2.932 (3)	166

Symmetry codes: (i) −*x*+2, −*y*+1, −*z*+1.

Fig. 1



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(1*R*,3*S*,4*R*,4a*S*,7*R*,7a*S*,10*R*,12a*R*)-3-Azido-4,7,10-trimethyl-1,10-epidioxyperhydropyrano[4,3-*j*][1,2]benzodioxepine

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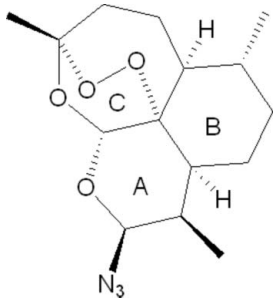
Key indicators: single-crystal X-ray study; T = 298 K; mean σ(C–C) = 0.006 Å; R factor = 0.040; wR factor = 0.103; data-to-parameter ratio = 8.2.

In the title compound, $C_{15}H_{23}N_3O_4$, the six-membered pyran, cyclohexane and trioxane rings adopt chair, chair and boat conformations, respectively, while the seven-membered rings adopt distorted boat and very distorted chair conformations. In the crystal, adjacent molecules are connected by weak C—H···N and C—H···O interactions.

Related literature

For general background to artemisinin, a sesquiterpene endoperoxide widely used to treat drug-resistant malaria, see: Liu *et al.* (1979). For the anticancer properties of the title compound, see: Efferth *et al.* (1996); Chadwick *et al.* (2009); Galal *et al.* (2009). For structural analyses of highly related compounds, see: Gul *et al.* (2009); Jasinski*et al.* (2008).



Experimental

Crystal data

$C_{15}H_{23}N_3O_4$
M_r = 309.36
Orthorhombic, $P2_12_12_1$
a = 7.9938 (9) Å
b = 11.207 (1) Å
c = 17.984 (2) Å
V = 1611.1 (3) Å^3
Z = 4
Mo $K\alpha$ radiation
μ = 0.09 mm^{-1}
T = 298 K
0.50 × 0.40 × 0.38 mm

Data collection

Bruker SMART CCD area-detector diffractometer
Absorption correction: multi-scan (*SADABS*; Sheldrick, 1996)
T_{min} = 0.955, T_{max} = 0.965
7585 measured reflections
1657 independent reflections
1130 reflections with $I > 2\sigma(I)$
R_{int} = 0.043

Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.040
$wR(F^2)$ = 0.103
S = 1.09
1657 reflections
202 parameters
H-atom parameters constrained
$\Delta\rho_{max}$ = 0.12 e Å^{-3}
$\Delta\rho_{min}$ = −0.16 e Å^{-3}

Table 1
Hydrogen-bond geometry (Å, °).

D—H···A	D—H	H···A	D···A	D—H···A
C7—H7*B*···N3^{i}	0.97	2.68	3.628 (6)	167
C10—H10···O3^{ii}	0.98	2.67	3.535 (5)	148
C12—H12*A*···O3^{ii}	0.97	2.65	3.508 (5)	147

Symmetry codes: (i) $-x+\frac{1}{2}, -y+1, z-\frac{1}{2}$; (ii) $-x+1, y+\frac{1}{2}, -z+\frac{1}{2}$.

Data collection: *SMART* (Bruker, 2003); cell refinement: *SAINT* (Bruker, 2003); data reduction: *SAINT*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *SHELXTL* (Sheldrick, 2008); software used to prepare material for publication: *SHELXTL*.

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Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: IM2212).

References

Bruker (2003). *SMART* and *SAINT*. Bruker AXS Inc., Madison, Wisconsin, USA.
Chadwick, J., Mercer, A. E. & Park, B. K. (2009). *Bioorg. Med. Chem.* **17**, 1325–1338.
Efferth, T., Rucker, G. & Falkenberg, M. (1996). *Arzneimittelforschung*, **46**, 196–200.
Galal, A. M., Gul, W. & Slade, D. (2009). *Bioorg. Med. Chem.* **17**, 741–745.
Gul, W., Carvalho, P., Galal, A., Avery, M. A. & El Sohly, M. A. (2009). *Acta Cryst.* E**65**, o358–o359.
Jasinski, J. P., Butcher, R. J., Yathirajan, H. S., Narayana, B. & Sreevidya, T. V. (2008). *Acta Cryst.* E**64**, o585–o586.
Liu, J. M., Ni, M. Y. & Fan, Y. (1979). *Acta Chim. Sin.* **37**, 129–141.
Sheldrick, G. M. (1996). *SADABS*. University of Göttingen, Germany.
Sheldrick, G. M. (2008). *Acta Cryst.* A**64**, 112–122.

supplementary materials

Acta Cryst. (2010). E**66**, o1839 [**doi:10.1107/S1600536810024566**]

(1*R*,3*S*,4*R*,4a*S*,7*R*,7a*S*,10*R*,12a*R*)-3-Azido-4,7,10-trimethyl-1,10-epidioxyperhydropyrano[4,3-*j*][1,2]benzodioxepine

L. Xie, X. Zhai, J. Zuo, Y. Zhao and P. Gong

Comment

Artemisinin, a sesquiterpene endoperoxide isolated from Artemisia annua *L*, is being widely used to treat drug-resistant malaria (Liu *et al.*, 1979). In addition, Artemisinin and its derivatives also showed potent and broad anticancer properties in different human cancer cell lines and animal models (Efferth *et al.*, 1996). These compounds contain an endoperoxide bridge (R—O—O—*R*) which is required for their biological activities. Recently, there are many reports about significant anticancer activities of artemisinin derivatives, which were expected to be more stable toward the metabolism process (Chadwick *et al.*, 2009; Galal *et al.*, 2009). Herein, we present the synthesis and structure of an artemisinin derivatives, (1*R*,3S,4*R*,4aS,7*R*,7aS,10*R*,12aR)-3-Azido- 4,7,10-trimethyl-1,10-epoxy-decahydro- 12*H*-pyrano[4,3-*j*]-1,2-benzodioxepin.

The crystal structure of the title compound is given in Fig. 1. The bond lengths and angles in the title compound are found to have normal values with respect to highly related compounds (Gul *et al.*, 2009; Jasinski *et al.*, 2008). The six membered rings A, B and C adopt chair, chair and boat conformations, respectively. In the crystal, adjacent molecules are connected by non-classical C—H···N and C—H···O hydrogen bonding, with the distance of 3.628 (6), 3.508 (5) and 3.535 (5) Å (Table 1), respectively.

Experimental

Trimethylchlorosilane (300 mmol, 38.1 ml) was added gradually to a solution of dihydroartemisinin (200 mmol, 56.8 g, diastereomeric mixture with *R* and *S* configuration at C(3)) and sodium azide (300 mmol, 19.5 g) in CH_2Cl_2 (300 ml). Then sodium iodide (20 mmol, 3.0 g) was added to the reaction mixture at low temperature. The reaction mixture was stirred at room temperature for 28 h. The mixture was quenched with a saturated $NaHCO_3$ solution (100 ml) and diluted with CH_2Cl_2. Two phases were separated and the organic phase was washed with brine, dried over $MgSO_4$, filtered, and concentrated under reduced pressure. The crude mixture was purified by column chromatography (silica, 1%-5% EtOAc/hexanes) to furnish the product (94 mmol, 29.0 g) and it's diastereomer with *R* configuration at C(3). Colorless single crystals of the title compound was obtained in CH_2Cl_2 solution after 10 days by slow evaporation at room temperature.

Refinement

In the absence of significant anomalous dispersion effects, Friedel pairs were averaged. All H-atoms were positioned geometrically and refined using a riding model, with C—H = 0.96 Å (CH_3), 0.97 Å (CH_2), 0.98 Å (CH), and U_{iso}(H) =1.2U_{eq}(C).

Figures

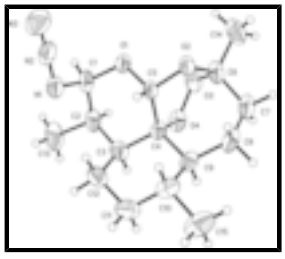


Fig. 1. Molecular structure of the title compound, showing 30% probability displacement ellipsoids and the atom-numbering scheme.

(1*R*,3*S*,4*R*,4a*S*,7*R*,7a*S*,10*R*, 12a*R*)-3-Azido-4,7,10-trimethyl-1,10-epidioxyperhydropyrano[4,3-*j*][1,2]benzodioxepine

Crystal data

$C_{15}H_{23}N_3O_4$	$F(000) = 664$
$M_r = 309.36$	$D_x = 1.275$ Mg m^{-3}
Orthorhombic, $P2_12_12_1$	Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å
Hall symbol: P 2ac 2ab	Cell parameters from 2309 reflections
$a = 7.9938$ (9) Å	$\theta = 2.3$–$21.4°$
$b = 11.207$ (1) Å	$\mu = 0.09$ mm^{-1}
$c = 17.984$ (2) Å	$T = 298$ K
$V = 1611.1$ (3) Å^3	Block, colorless
$Z = 4$	0.50 × 0.40 × 0.38 mm

Data collection

Bruker SMART CCD area-detector diffractometer	1657 independent reflections
Radiation source: fine-focus sealed tube	1130 reflections with $I > 2\sigma(I)$
graphite	$R_{int} = 0.043$
phi and ω scans	$\theta_{max} = 25.0°$, $\theta_{min} = 2.1°$
Absorption correction: multi-scan (*SADABS*; Sheldrick, 1996)	$h = -9\rightarrow7$
$T_{min} = 0.955$, $T_{max} = 0.965$	$k = -13\rightarrow13$
7585 measured reflections	$l = -16\rightarrow21$

Refinement

Refinement on F^2	Primary atom site location: structure-invariant direct methods
Least-squares matrix: full	Secondary atom site location: difference Fourier map
$R[F^2 > 2\sigma(F^2)] = 0.040$	Hydrogen site location: inferred from neighbouring sites
$wR(F^2) = 0.103$	H-atom parameters constrained
$S = 1.09$	$w = 1/[\sigma^2(F_o^2) + (0.0312P)^2 + 0.4488P]$ where $P = (F_o^2 + 2F_c^2)/3$

1657 reflections	$(\Delta/\sigma)_{max} < 0.001$
202 parameters	$\Delta\rho_{max} = 0.12$ e Å^{-3}
0 restraints	$\Delta\rho_{min} = -0.16$ e Å^{-3}

Special details

Experimental. We took dihydroartemisinin (mixture of 3R and 3S isomers of hydroxyl group) as the starting material in our experiment. During the course of synthesis, we got a mixture of two diastereomers with 3S and 3R and all other stereogenic centers are known and still in the configuration as they were in the starting compound. The mixture was separated by silica gel column chromatography and the title compound with 3S was crystallized under our conditions, while the other one (3R) was obtained as amorphous powder.

Geometry. All e.s.d.'s (except the e.s.d. in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell e.s.d.'s are taken into account individually in the estimation of e.s.d.'s in distances, angles and torsion angles; correlations between e.s.d.'s in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell e.s.d.'s is used for estimating e.s.d.'s involving l.s. planes.

Refinement. Refinement of F^2 against ALL reflections. The weighted *R*-factor *wR* and goodness of fit *S* are based on F^2, conventional *R*-factors *R* are based on *F*, with *F* set to zero for negative F^2. The threshold expression of $F^2 > \sigma(F^2)$ is used only for calculating *R*-factors(gt) *etc*. and is not relevant to the choice of reflections for refinement. *R*-factors based on F^2 are statistically about twice as large as those based on *F*, and *R*- factors based on ALL data will be even larger.

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å^2)

	x	*y*	*z*	U_{iso}*/U_{eq}
N1	0.4489 (5)	0.4264 (3)	0.41235 (17)	0.0737 (10)
N2	0.3162 (6)	0.4810 (3)	0.41854 (19)	0.0756 (10)
N3	0.2016 (6)	0.5395 (4)	0.4253 (3)	0.1117 (15)
O1	0.3528 (3)	0.3297 (2)	0.30143 (11)	0.0583 (6)
O2	0.3573 (3)	0.3910 (2)	0.18223 (12)	0.0601 (7)
O3	0.4236 (3)	0.1895 (2)	0.17929 (14)	0.0726 (8)
O4	0.5935 (3)	0.2044 (2)	0.20749 (13)	0.0669 (7)
C1	0.4297 (5)	0.3114 (3)	0.37062 (18)	0.0656 (10)
H1	0.3554	0.2601	0.3999	0.079*
C2	0.5957 (5)	0.2491 (4)	0.3652 (2)	0.0738 (12)
H2	0.5712	0.1695	0.3454	0.089*
C3	0.7131 (5)	0.3075 (4)	0.3087 (2)	0.0670 (11)
H3	0.8021	0.2495	0.2989	0.080*
C4	0.6214 (4)	0.3259 (3)	0.23485 (17)	0.0528 (9)
C5	0.4547 (4)	0.3878 (3)	0.24650 (17)	0.0495 (9)
H5	0.4759	0.4699	0.2627	0.059*
C6	0.3823 (5)	0.2889 (4)	0.13467 (19)	0.0683 (11)
C7	0.5171 (5)	0.3170 (4)	0.0778 (2)	0.0789 (12)
H7A	0.5780	0.2444	0.0667	0.095*
H7B	0.4638	0.3435	0.0322	0.095*
C8	0.6406 (6)	0.4117 (4)	0.1028 (2)	0.0765 (12)
H8A	0.5809	0.4867	0.1075	0.092*
H8B	0.7234	0.4218	0.0639	0.092*
C9	0.7325 (5)	0.3881 (3)	0.1758 (2)	0.0653 (10)

H9	0.8227	0.3319	0.1640	0.078*
C10	0.8171 (5)	0.5007 (4)	0.2052 (2)	0.0798 (12)
H10	0.7293	0.5586	0.2172	0.096*
C11	0.9123 (5)	0.4740 (5)	0.2759 (3)	0.0973 (16)
H11A	0.9621	0.5470	0.2945	0.117*
H11B	1.0020	0.4184	0.2650	0.117*
C12	0.7998 (5)	0.4211 (4)	0.3354 (2)	0.0840 (13)
H12A	0.7159	0.4795	0.3493	0.101*
H12B	0.8661	0.4032	0.3791	0.101*
C13	0.6724 (7)	0.2282 (5)	0.4424 (2)	0.1150 (19)
H13A	0.6936	0.3037	0.4659	0.173*
H13B	0.7756	0.1851	0.4374	0.173*
H13C	0.5960	0.1828	0.4724	0.173*
C14	0.2153 (6)	0.2572 (5)	0.1011 (3)	0.1060 (17)
H14A	0.2293	0.1929	0.0665	0.159*
H14B	0.1704	0.3255	0.0758	0.159*
H14C	0.1398	0.2332	0.1398	0.159*
C15	0.9352 (6)	0.5587 (5)	0.1476 (3)	0.124 (2)
H15A	0.9829	0.6300	0.1683	0.186*
H15B	0.8730	0.5785	0.1036	0.186*
H15C	1.0229	0.5038	0.1351	0.186*

Atomic displacement parameters (Å^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
N1	0.085 (2)	0.083 (2)	0.0530 (19)	−0.002 (2)	0.003 (2)	−0.0156 (19)
N2	0.094 (3)	0.079 (3)	0.055 (2)	−0.016 (2)	0.017 (2)	−0.015 (2)
N3	0.105 (3)	0.112 (3)	0.117 (4)	0.005 (3)	0.021 (3)	−0.037 (3)
O1	0.0652 (14)	0.0705 (16)	0.0393 (12)	−0.0044 (13)	0.0041 (11)	−0.0011 (12)
O2	0.0722 (15)	0.0672 (15)	0.0410 (13)	0.0191 (14)	−0.0084 (13)	−0.0062 (13)
O3	0.101 (2)	0.0608 (16)	0.0560 (14)	−0.0006 (16)	−0.0084 (15)	−0.0067 (15)
O4	0.0912 (19)	0.0523 (15)	0.0572 (14)	0.0182 (14)	0.0006 (14)	−0.0024 (13)
C1	0.095 (3)	0.065 (2)	0.0366 (17)	−0.013 (2)	0.0044 (19)	−0.0005 (19)
C2	0.107 (3)	0.070 (3)	0.044 (2)	0.014 (3)	−0.011 (2)	0.005 (2)
C3	0.068 (2)	0.071 (3)	0.062 (2)	0.019 (2)	−0.010 (2)	0.002 (2)
C4	0.061 (2)	0.051 (2)	0.0465 (18)	0.0126 (19)	0.0015 (17)	−0.0009 (17)
C5	0.058 (2)	0.054 (2)	0.0362 (16)	0.0069 (19)	−0.0015 (18)	−0.0046 (17)
C6	0.094 (3)	0.068 (3)	0.0431 (19)	0.013 (2)	−0.011 (2)	−0.008 (2)
C7	0.111 (3)	0.083 (3)	0.043 (2)	0.025 (3)	0.003 (2)	−0.002 (2)
C8	0.099 (3)	0.082 (3)	0.048 (2)	0.013 (3)	0.022 (2)	0.010 (2)
C9	0.065 (2)	0.068 (2)	0.063 (2)	0.017 (2)	0.016 (2)	−0.001 (2)
C10	0.067 (3)	0.083 (3)	0.090 (3)	−0.003 (2)	0.016 (2)	0.000 (3)
C11	0.063 (3)	0.118 (4)	0.111 (4)	−0.008 (3)	−0.001 (3)	−0.011 (3)
C12	0.076 (3)	0.103 (3)	0.073 (3)	0.007 (3)	−0.018 (2)	−0.006 (3)
C13	0.160 (5)	0.127 (4)	0.057 (3)	0.039 (4)	−0.024 (3)	0.018 (3)
C14	0.120 (4)	0.124 (4)	0.074 (3)	0.003 (4)	−0.035 (3)	−0.030 (3)
C15	0.108 (4)	0.121 (4)	0.143 (5)	−0.028 (4)	0.040 (4)	0.010 (4)

Geometric parameters (Å, °)

N1—N2	1.229 (5)	C7—H7A	0.9700
N1—C1	1.499 (5)	C7—H7B	0.9700
N2—N3	1.133 (5)	C8—C9	1.528 (5)
O1—C1	1.403 (4)	C8—H8A	0.9700
O1—C5	1.437 (4)	C8—H8B	0.9700
O2—C5	1.394 (4)	C9—C10	1.526 (5)
O2—C6	1.442 (4)	C9—H9	0.9800
O3—C6	1.412 (4)	C10—C11	1.511 (6)
O3—O4	1.459 (3)	C10—C15	1.545 (6)
O4—C4	1.464 (4)	C10—H10	0.9800
C1—C2	1.503 (6)	C11—C12	1.518 (6)
C1—H1	0.9800	C11—H11A	0.9700
C2—C3	1.530 (5)	C11—H11B	0.9700
C2—C13	1.536 (5)	C12—H12A	0.9700
C2—H2	0.9800	C12—H12B	0.9700
C3—C12	1.527 (5)	C13—H13A	0.9600
C3—C4	1.531 (4)	C13—H13B	0.9600
C3—H3	0.9800	C13—H13C	0.9600
C4—C5	1.517 (5)	C14—H14A	0.9600
C4—C9	1.550 (5)	C14—H14B	0.9600
C5—H5	0.9800	C14—H14C	0.9600
C6—C14	1.507 (5)	C15—H15A	0.9600
C6—C7	1.518 (5)	C15—H15B	0.9600
C7—C8	1.518 (6)	C15—H15C	0.9600
N2—N1—C1	112.6 (3)	C7—C8—C9	116.5 (3)
N3—N2—N1	174.3 (4)	C7—C8—H8A	108.2
C1—O1—C5	115.3 (3)	C9—C8—H8A	108.2
C5—O2—C6	113.2 (3)	C7—C8—H8B	108.2
C6—O3—O4	108.9 (3)	C9—C8—H8B	108.2
O3—O4—C4	111.4 (2)	H8A—C8—H8B	107.3
O1—C1—N1	111.3 (3)	C10—C9—C8	111.6 (3)
O1—C1—C2	113.4 (3)	C10—C9—C4	112.8 (3)
N1—C1—C2	110.0 (3)	C8—C9—C4	113.0 (3)
O1—C1—H1	107.3	C10—C9—H9	106.3
N1—C1—H1	107.3	C8—C9—H9	106.3
C2—C1—H1	107.3	C4—C9—H9	106.3
C1—C2—C3	112.7 (3)	C11—C10—C9	110.6 (4)
C1—C2—C13	111.4 (3)	C11—C10—C15	109.9 (4)
C3—C2—C13	114.9 (4)	C9—C10—C15	112.7 (4)
C1—C2—H2	105.7	C11—C10—H10	107.9
C3—C2—H2	105.7	C9—C10—H10	107.9
C13—C2—H2	105.7	C15—C10—H10	107.9
C12—C3—C2	115.3 (3)	C10—C11—C12	111.8 (3)
C12—C3—C4	112.2 (3)	C10—C11—H11A	109.3
C2—C3—C4	109.9 (3)	C12—C11—H11A	109.3
C12—C3—H3	106.3	C10—C11—H11B	109.3

C2—C3—H3	106.3	C12—C11—H11B	109.3
C4—C3—H3	106.3	H11A—C11—H11B	107.9
O4—C4—C5	109.7 (3)	C11—C12—C3	111.9 (4)
O4—C4—C3	103.9 (3)	C11—C12—H12A	109.2
C5—C4—C3	111.2 (3)	C3—C12—H12A	109.2
O4—C4—C9	106.0 (3)	C11—C12—H12B	109.2
C5—C4—C9	113.1 (3)	C3—C12—H12B	109.2
C3—C4—C9	112.4 (3)	H12A—C12—H12B	107.9
O2—C5—O1	105.4 (3)	C2—C13—H13A	109.5
O2—C5—C4	112.8 (3)	C2—C13—H13B	109.5
O1—C5—C4	112.7 (3)	H13A—C13—H13B	109.5
O2—C5—H5	108.6	C2—C13—H13C	109.5
O1—C5—H5	108.6	H13A—C13—H13C	109.5
C4—C5—H5	108.6	H13B—C13—H13C	109.5
O3—C6—O2	108.7 (3)	C6—C14—H14A	109.5
O3—C6—C14	104.4 (4)	C6—C14—H14B	109.5
O2—C6—C14	107.5 (3)	H14A—C14—H14B	109.5
O3—C6—C7	112.4 (3)	C6—C14—H14C	109.5
O2—C6—C7	109.5 (3)	H14A—C14—H14C	109.5
C14—C6—C7	114.1 (3)	H14B—C14—H14C	109.5
C8—C7—C6	114.0 (3)	C10—C15—H15A	109.5
C8—C7—H7A	108.7	C10—C15—H15B	109.5
C6—C7—H7A	108.7	H15A—C15—H15B	109.5
C8—C7—H7B	108.7	C10—C15—H15C	109.5
C6—C7—H7B	108.7	H15A—C15—H15C	109.5
H7A—C7—H7B	107.6	H15B—C15—H15C	109.5
C1—N1—N2—N3	−159 (4)	O4—C4—C5—O1	62.1 (3)
C6—O3—O4—C4	44.7 (3)	C3—C4—C5—O1	−52.3 (4)
C5—O1—C1—N1	72.1 (4)	C9—C4—C5—O1	−179.9 (3)
C5—O1—C1—C2	−52.6 (4)	O4—O3—C6—O2	−72.3 (3)
N2—N1—C1—O1	53.7 (4)	O4—O3—C6—C14	173.2 (3)
N2—N1—C1—C2	−179.8 (3)	O4—O3—C6—C7	49.0 (4)
O1—C1—C2—C3	50.7 (4)	C5—O2—C6—O3	30.7 (4)
N1—C1—C2—C3	−74.6 (4)	C5—O2—C6—C14	143.2 (3)
O1—C1—C2—C13	−178.5 (4)	C5—O2—C6—C7	−92.4 (3)
N1—C1—C2—C13	56.2 (5)	O3—C6—C7—C8	−95.2 (4)
C1—C2—C3—C12	78.1 (4)	O2—C6—C7—C8	25.7 (4)
C13—C2—C3—C12	−50.9 (5)	C14—C6—C7—C8	146.2 (4)
C1—C2—C3—C4	−49.8 (4)	C6—C7—C8—C9	56.2 (5)
C13—C2—C3—C4	−178.8 (3)	C7—C8—C9—C10	−165.3 (3)
O3—O4—C4—C5	16.4 (3)	C7—C8—C9—C4	−36.8 (5)
O3—O4—C4—C3	135.4 (3)	O4—C4—C9—C10	−162.7 (3)
O3—O4—C4—C9	−106.0 (3)	C5—C4—C9—C10	77.1 (4)
C12—C3—C4—O4	162.9 (3)	C3—C4—C9—C10	−49.8 (4)
C2—C3—C4—O4	−67.5 (4)	O4—C4—C9—C8	69.6 (4)
C12—C3—C4—C5	−79.1 (4)	C5—C4—C9—C8	−50.7 (4)
C2—C3—C4—C5	50.5 (4)	C3—C4—C9—C8	−177.6 (3)
C12—C3—C4—C9	48.8 (4)	C8—C9—C10—C11	−177.9 (3)
C2—C3—C4—C9	178.4 (3)	C4—C9—C10—C11	53.5 (4)

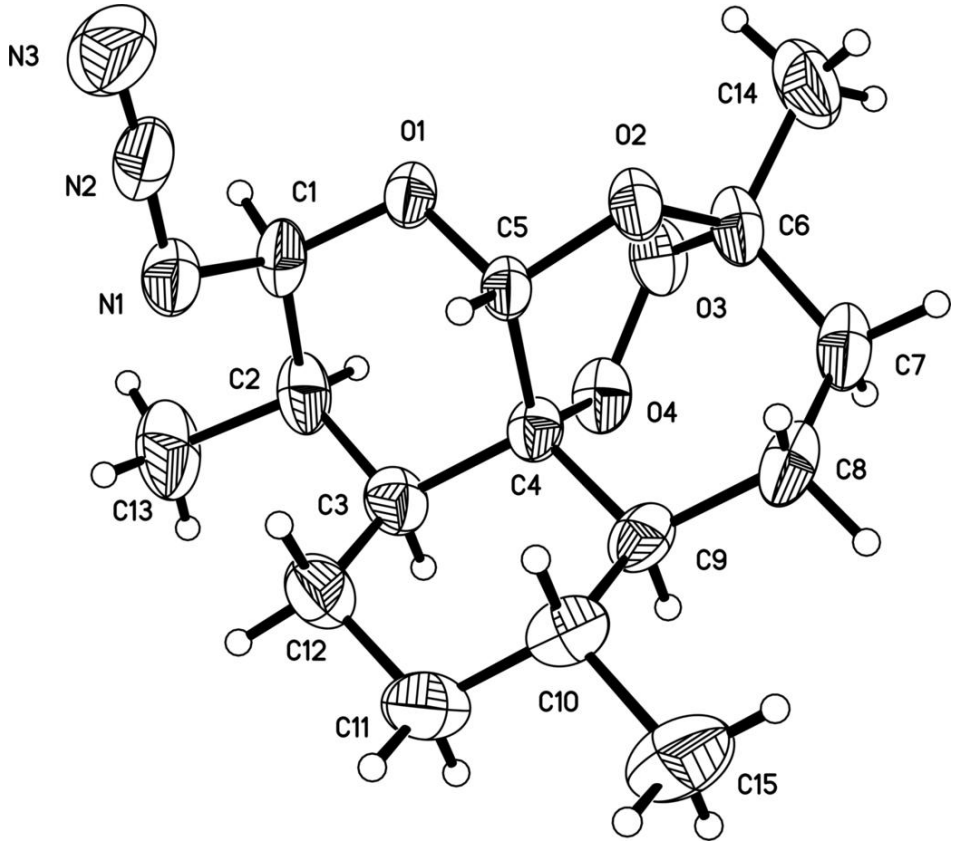
C6—O2—C5—O1	−91.5 (3)	C8—C9—C10—C15	−54.6 (5)
C6—O2—C5—C4	31.9 (4)	C4—C9—C10—C15	176.9 (3)
C1—O1—C5—O2	177.1 (3)	C9—C10—C11—C12	−57.2 (5)
C1—O1—C5—C4	53.7 (4)	C15—C10—C11—C12	177.8 (4)
O4—C4—C5—O2	−57.1 (4)	C10—C11—C12—C3	57.2 (5)
C3—C4—C5—O2	−171.5 (3)	C2—C3—C12—C11	−179.4 (3)
C9—C4—C5—O2	61.0 (4)	C4—C3—C12—C11	−52.6 (4)

Hydrogen-bond geometry (Å, °)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
C7—H7B···N3^{i}	0.97	2.68	3.628 (6)	167
C10—H10···O3^{ii}	0.98	2.67	3.535 (5)	148
C12—H12A···O3^{ii}	0.97	2.65	3.508 (5)	147

Symmetry codes: (i) −*x*+1/2, −*y*+1, *z*−1/2; (ii) −*x*+1, *y*+1/2, −*z*+1/2.

Fig. 1


N3
N2
N1
C1
O1
C5
O2
C14
C6
O3
C7
C2
O4
C8
C13
C3
C4
C9
C12
C10
C11
C15

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N-(1,5-Dimethyl-3-oxo-2-phenyl-2,3-dihydro-1*H*-pyrazol-4-yl)acetamide–naphthalene-2,3-diol (1/1)

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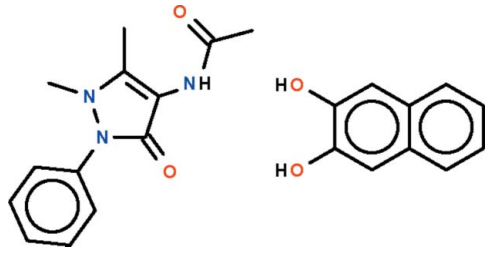
Key indicators: single-crystal X-ray study; T = 100 K; mean σ(C–C) = 0.003 Å; R factor = 0.052; wR factor = 0.131; data-to-parameter ratio = 16.4.

In the reaction of naphthalene-2,3-diol and 4-aminoantipyrine in the presence of acetic acid, the amine function is acetylated and the resulting acetamide co-crystallizes with the diol in the title compound, $C_{13}H_{15}N_3O_2\cdot C_{10}H_8O_2$, with 1:1 molar stoichiometry. The two components are linked by two O–H···O=C hydrogen bonds. One of the hydroxy groups interacts with the pyrazolone carbonyl O atom and the other hydroxy group interacts with the amide O atom of another component, generating a chain motif. Adjacent chains are linked into a layer motif *via* N—H···O interactions involving only the heterocyclic acetamide component.

Related literature

For the crystal structure of 4-acetamido-2,3-dimethyl-1-phenyl-5-pyrazol-3-one, see: Kuznetsov *et al.* (1999). For co-crystals of naphthalene-2,3-diol, see: Fritchie & Johnston (1975); Herbert & Truter (1980); Kuo *et al.* (1974); Nakamatsu *et al.* (2003); Wang *et al.* (2008); Wells *et al.* (1974).



Experimental

Crystal data

$C_{13}H_{15}N_3O_2\cdot C_{10}H_8O_2$
M_r = 405.44
Monoclinic, $P2_1/c$
a = 12.426 (1) Å
b = 14.304 (2) Å
c = 12.959 (1) Å
β = 117.845 (1)°
V = 2036.7 (4) Å^3
Z = 4
Mo $K\alpha$ radiation
μ = 0.09 mm^{-1}
T = 100 K
0.25 × 0.25 × 0.10 mm

Data collection

Bruker SMART APEX diffractometer
19263 measured reflections
4683 independent reflections
3189 reflections with $I > 2\sigma(I)$
R_{int} = 0.061

Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.052
$wR(F^2)$ = 0.131
S = 1.02
4683 reflections
286 parameters
27 restraints
H atoms treated by a mixture of independent and constrained refinement
$\Delta\rho_{max}$ = 0.31 e Å^{-3}
$\Delta\rho_{min}$ = −0.36 e Å^{-3}

Table 1
Hydrogen-bond geometry (Å, °).

D—H···A	D—H	H···A	D···A	D—H···A
N1—H1···O2^{i}	0.87 (1)	2.07 (1)	2.924 (2)	169 (2)
O3—H3···O2	0.85 (3)	1.81 (3)	2.639 (2)	163 (3)
O4—H4···O1^{ii}	0.85 (3)	1.81 (3)	2.646 (2)	168 (3)

Symmetry codes: (i) $-x+1, -y+1, -z+1$; (ii) $x, -y+\frac{3}{2}, z+\frac{1}{2}$.

Data collection: *APEX2* (Bruker, 2009); cell refinement: *SAINT* (Bruker, 2009); data reduction: *SAINT*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *X-SEED* (Barbour, 2001); software used to prepare material for publication: *publCIF* (Westrip, 2010).

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Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: IM2213).

References

Barbour, L. J. (2001). *J. Supramol. Chem.* **1**, 189–191.
Bruker (2009). *APEX2* and *SAINT*. Bruker AXS Inc., Madison, Wisconsin, USA.
Fritchie, C. J. & Johnston, R. M. (1975). *Acta Cryst.* B**31**, 454–461.
Herbert, J. A. & Truter, M. R. (1980). *J. Chem. Soc. Perkin Trans. 2*, pp. 1253–1258.
Kuo, M. C., Dunn, J. B. R. & Fritchie, C. J. (1974). *Acta Cryst.* B**30**, 1766–1771.
Kuznetsov, M. L., Bel'skii, V. K., Dement'ev, A. I., Zaitsev, B. E., Lokshin, B. V. & Zhornik, V. G. (1999). *Russ. Chem. Bull.* **48**, 1274–1280.
Nakamatsu, S., Yoshizawa, K., Toyota, S., Toda, F. & Matijasic, I. (2003). *Org. Biomol. Chem.* **1**, 2231–2234.
Sheldrick, G. M. (2008). *Acta Cryst.* A**64**, 112–122.
Wang, Y.-T., Tang, G.-M. & Wan, W.-Z. (2008). *Acta Cryst.* E**64**, o1754.
Wells, J. L., Trus, B. L., Johnston, R. M., Marsh, R. E. & Fritchie, C. J. (1974). *Acta Cryst.* B**30**, 1127–1134.
Westrip, S. P. (2010). *J. Appl. Cryst.* **43**. Submitted.

supplementary materials

Acta Cryst. (2010). E**66**, o1850 [**doi:10.1107/S1600536810024438**]

N-(1,5-Dimethyl-3-oxo-2-phenyl-2,3-dihydro-1*H*-pyrazol-4-yl)acetamide-naphthalene-2,3-diol (1/1)

A. M. Asiri, S. A. Khan, K. W. Tan and S. W. Ng

Comment

Naphthalene-2,3-diol forms co-crystals with a number of neutral organic compounds (Fritchie & Johnston, 1975; Herbert & Truter, 1980; Kuo *et al.*, 1974; Nakamatsu *et al.*, 2003; Wang *et al.*, 2008; Wells *et al.*, 1974). The attempt to co-crystallize it with the drug 4-aminoantipyrine was sussessful when the reaction was carried out in the presence of acetic acid, but the acetic acid converted the amino group to an acetamido group instead. In the co-crystal (Scheme I, Fig. 1), the acetamide and the diol are linked by two *O*–H···O═C hydrogen bonds. One of the hydroxy groups interacts with the pyrazolyl carbonyl O-atom and the other hydroxy group interacts with the amido O-atom of another component to generate a chain motif. Adjacent chains are linked into a layer motif *via* N–H···O interactions that involves the acetamide component only.

Experimental

Naphthalene-2,3-diol (0.35 g, 2.2 mol) and 4-aminoantipyrine (0.45 g, 2.2 mmol) were heated in methanol (15 ml) for 5 h; three drops of acetic acid were added. Crystals separated from the cool solution when it was set aside for a day.

Refinement

Carbon-bound H-atoms were placed in calculated positions [C–H 0.95 to 0.98 Å, U(H) = 1.2 to 1.5U_{eq}(C)] and were included in the refinement in the riding model approximation. The hydroxy and amino H-atoms were located in a difference Fourier map, and were refined with distance restraints of O–H 0.84±0.01Å and N–H 0.86±0.01 Å. Their temperature factors were freely refined.

The anisotropic temperature factors of C17 to C20 atoms of the naphthalene fused-ring were restrained to be nearly isotropic and with the restraints, the ellipsoids were somewhat elongated.

Figures

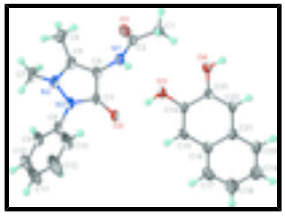


Fig. 1. Thermal ellipsoid plot (Barbour, 2001) of the ($C_{13}H_{15}N_3O_2$)($C_{10}H_8O_2$) co-crystal at the 70% probability level; hydrogen atoms are drawn as spheres of arbitrary radius.

N-(1,5-Dimethyl-3-oxo-2-phenyl-2,3-dihydro-1*H*-pyrazol-4- yl)acetamide–naphthalene-2,3-diol (1/1)

Crystal data

$C_{13}H_{15}N_3O_2 \cdot C_{10}H_8O_2$	$F(000) = 856$
$M_r = 405.44$	$D_x = 1.322$ Mg m^{-3}
Monoclinic, $P2_1/c$	Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å
Hall symbol: -P 2ybc	Cell parameters from 2505 reflections
$a = 12.426$ (1) Å	$\theta = 2.3$–$27.9°$
$b = 14.304$ (2) Å	$\mu = 0.09$ mm^{-1}
$c = 12.959$ (1) Å	$T = 100$ K
$\beta = 117.845$ (1)°	Prism, colorless
$V = 2036.7$ (4) Å^3	0.25 × 0.25 × 0.10 mm
$Z = 4$	

Data collection

Bruker SMART APEX diffractometer	3189 reflections with $I > 2\sigma(I)$
Radiation source: fine-focus sealed tube	$R_{int} = 0.061$
graphite	$\theta_{max} = 27.5°$, $\theta_{min} = 1.9°$
ω scans	$h = -16 \rightarrow 16$
19263 measured reflections	$k = -18 \rightarrow 18$
4683 independent reflections	$l = -16 \rightarrow 16$

Refinement

Refinement on F^2	Primary atom site location: structure-invariant direct methods
Least-squares matrix: full	Secondary atom site location: difference Fourier map
$R[F^2 > 2\sigma(F^2)] = 0.052$	Hydrogen site location: inferred from neighbouring sites
$wR(F^2) = 0.131$	H atoms treated by a mixture of independent and constrained refinement
$S = 1.02$	$w = 1/[\sigma^2(F_o^2) + (0.0544P)^2 + 0.6929P]$ where $P = (F_o^2 + 2F_c^2)/3$
4683 reflections	$(\Delta/\sigma)_{max} = 0.001$
286 parameters	$\Delta\rho_{max} = 0.31$ e Å^{-3}
27 restraints	$\Delta\rho_{min} = -0.35$ e Å^{-3}

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å^2)

	x	*y*	*z*	U_{iso}*/U_{eq}
O1	0.33173 (12)	0.73209 (10)	0.32885 (12)	0.0290 (3)
O2	0.65387 (11)	0.56345 (9)	0.48381 (11)	0.0232 (3)
O3	0.56600 (12)	0.65279 (10)	0.60626 (11)	0.0253 (3)

O4	0.44923 (12)	0.70985 (10)	0.71521 (12)	0.0279 (3)
N1	0.37471 (14)	0.57790 (11)	0.36783 (14)	0.0224 (4)
N2	0.51486 (14)	0.55398 (11)	0.18066 (13)	0.0233 (4)
N3	0.61709 (14)	0.55929 (11)	0.29124 (13)	0.0219 (4)
C1	0.25557 (17)	0.65611 (14)	0.44515 (17)	0.0255 (4)
H1A	0.1879	0.7007	0.4123	0.038*
H1B	0.3105	0.6728	0.5264	0.038*
H1C	0.2237	0.5929	0.4422	0.038*
C2	0.32386 (16)	0.65897 (14)	0.37571 (16)	0.0219 (4)
C3	0.58105 (17)	0.56524 (12)	0.37598 (16)	0.0199 (4)
C4	0.45083 (17)	0.57041 (13)	0.31423 (16)	0.0218 (4)
C5	0.41487 (17)	0.56533 (13)	0.19785 (16)	0.0240 (4)
C6	0.29135 (19)	0.57192 (16)	0.09672 (18)	0.0326 (5)
H6A	0.2302	0.5591	0.1226	0.049*
H6B	0.2835	0.5261	0.0374	0.049*
H6C	0.2788	0.6350	0.0634	0.049*
C7	0.52538 (19)	0.60264 (14)	0.08616 (17)	0.0284 (5)
H7A	0.4540	0.5885	0.0116	0.043*
H7B	0.5992	0.5817	0.0836	0.043*
H7C	0.5300	0.6702	0.1002	0.043*
C8	0.73390 (18)	0.53349 (14)	0.30516 (17)	0.0266 (4)
C9	0.7468 (2)	0.45251 (15)	0.25275 (18)	0.0326 (5)
H9	0.6785	0.4135	0.2091	0.039*
C10	0.8600 (2)	0.4293 (2)	0.2648 (2)	0.0501 (7)
H10	0.8696	0.3745	0.2285	0.060*
C11	0.9594 (2)	0.4857 (2)	0.3296 (3)	0.0681 (10)
H11	1.0371	0.4698	0.3375	0.082*
C12	0.9456 (2)	0.5654 (2)	0.3830 (3)	0.0676 (10)
H12	1.0144	0.6035	0.4284	0.081*
C13	0.8323 (2)	0.59026 (18)	0.3707 (2)	0.0428 (6)
H13	0.8226	0.6452	0.4067	0.051*
C14	0.63471 (17)	0.66192 (13)	0.72372 (15)	0.0202 (4)
C15	0.75639 (18)	0.64515 (14)	0.78429 (17)	0.0266 (4)
H15	0.7987	0.6232	0.7440	0.032*
C16	0.82114 (19)	0.65991 (16)	0.90656 (18)	0.0339 (5)
C17	0.9490 (2)	0.6515 (2)	0.9714 (2)	0.0634 (9)
H17	0.9945	0.6316	0.9335	0.076*
C18	1.0082 (3)	0.6715 (3)	1.0883 (2)	0.0872 (13)
H18	1.0944	0.6674	1.1299	0.105*
C19	0.9427 (2)	0.6980 (3)	1.1467 (2)	0.0719 (10)
H19	0.9845	0.7104	1.2281	0.086*
C20	0.8197 (2)	0.70618 (18)	1.08762 (19)	0.0406 (6)
H20	0.7761	0.7235	1.1285	0.049*
C21	0.75571 (18)	0.68925 (14)	0.96659 (17)	0.0274 (4)
C22	0.62919 (17)	0.70463 (13)	0.90182 (16)	0.0211 (4)
H22	0.5848	0.7235	0.9413	0.025*
C23	0.56923 (16)	0.69285 (12)	0.78342 (16)	0.0198 (4)
H1	0.373 (2)	0.5318 (11)	0.4107 (17)	0.036 (6)*
H3	0.608 (2)	0.6281 (17)	0.577 (2)	0.054 (8)*

H4	0.419 (2)	0.7345 (19)	0.755 (2)	0.067 (9)*

Atomic displacement parameters (Å^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
O1	0.0304 (8)	0.0313 (8)	0.0338 (8)	0.0020 (6)	0.0222 (7)	0.0056 (6)
O2	0.0239 (7)	0.0308 (7)	0.0178 (7)	−0.0018 (6)	0.0121 (6)	−0.0039 (5)
O3	0.0269 (7)	0.0340 (8)	0.0172 (7)	0.0026 (6)	0.0121 (6)	−0.0035 (6)
O4	0.0215 (7)	0.0423 (9)	0.0207 (7)	0.0040 (6)	0.0106 (6)	−0.0036 (6)
N1	0.0230 (8)	0.0287 (9)	0.0210 (9)	−0.0039 (7)	0.0147 (7)	0.0004 (7)
N2	0.0266 (9)	0.0303 (9)	0.0165 (8)	−0.0067 (7)	0.0131 (7)	−0.0030 (7)
N3	0.0238 (8)	0.0281 (9)	0.0175 (8)	−0.0064 (7)	0.0127 (7)	−0.0067 (7)
C1	0.0186 (9)	0.0374 (11)	0.0224 (10)	0.0005 (8)	0.0111 (8)	0.0010 (8)
C2	0.0169 (9)	0.0310 (10)	0.0170 (9)	−0.0037 (8)	0.0073 (8)	−0.0025 (8)
C3	0.0263 (10)	0.0194 (9)	0.0196 (10)	−0.0040 (7)	0.0155 (8)	−0.0036 (7)
C4	0.0246 (10)	0.0240 (10)	0.0214 (10)	−0.0042 (8)	0.0147 (8)	−0.0025 (8)
C5	0.0273 (10)	0.0275 (10)	0.0203 (10)	−0.0063 (8)	0.0137 (8)	−0.0024 (8)
C6	0.0285 (11)	0.0463 (13)	0.0221 (11)	−0.0047 (10)	0.0110 (9)	−0.0027 (9)
C7	0.0387 (12)	0.0323 (11)	0.0211 (10)	−0.0084 (9)	0.0198 (10)	−0.0035 (8)
C8	0.0275 (10)	0.0352 (11)	0.0251 (11)	−0.0061 (8)	0.0191 (9)	−0.0079 (8)
C9	0.0346 (12)	0.0400 (12)	0.0291 (12)	−0.0036 (10)	0.0198 (10)	−0.0093 (9)
C10	0.0452 (15)	0.0678 (18)	0.0458 (15)	0.0041 (13)	0.0284 (13)	−0.0223 (13)
C11	0.0308 (14)	0.117 (3)	0.0654 (19)	−0.0044 (15)	0.0300 (14)	−0.0417 (18)
C12	0.0341 (14)	0.110 (3)	0.071 (2)	−0.0277 (15)	0.0349 (14)	−0.0542 (19)
C13	0.0349 (13)	0.0565 (15)	0.0477 (15)	−0.0169 (11)	0.0282 (12)	−0.0290 (12)
C14	0.0257 (10)	0.0207 (9)	0.0159 (9)	−0.0005 (8)	0.0111 (8)	−0.0022 (7)
C15	0.0262 (10)	0.0348 (11)	0.0247 (11)	0.0040 (8)	0.0169 (9)	−0.0030 (8)
C16	0.0252 (11)	0.0538 (14)	0.0230 (11)	0.0065 (10)	0.0115 (9)	−0.0049 (10)
C17	0.0274 (13)	0.125 (3)	0.0358 (14)	0.0178 (14)	0.0129 (11)	−0.0205 (15)
C18	0.0297 (15)	0.180 (4)	0.0390 (16)	0.0292 (19)	0.0051 (13)	−0.025 (2)
C19	0.0341 (14)	0.142 (3)	0.0275 (14)	0.0191 (16)	0.0041 (11)	−0.0231 (16)
C20	0.0315 (12)	0.0672 (17)	0.0221 (11)	0.0076 (11)	0.0117 (10)	−0.0076 (11)
C21	0.0251 (10)	0.0361 (11)	0.0215 (10)	0.0012 (9)	0.0115 (9)	−0.0030 (8)
C22	0.0259 (10)	0.0235 (9)	0.0186 (9)	−0.0005 (8)	0.0145 (8)	−0.0003 (7)
C23	0.0201 (9)	0.0205 (9)	0.0197 (10)	0.0000 (7)	0.0101 (8)	−0.0004 (7)

Geometric parameters (Å, °)

O1—C2	1.236 (2)	C8—C9	1.389 (3)
O2—C3	1.261 (2)	C9—C10	1.381 (3)
O3—C14	1.360 (2)	C9—H9	0.9500
O3—H3	0.85 (3)	C10—C11	1.383 (4)
O4—C23	1.354 (2)	C10—H10	0.9500
O4—H4	0.85 (3)	C11—C12	1.385 (4)
N1—C2	1.347 (2)	C11—H11	0.9500
N1—C4	1.415 (2)	C12—C13	1.388 (3)
N1—H1	0.868 (10)	C12—H12	0.9500
N2—C5	1.371 (2)	C13—H13	0.9500
N2—N3	1.404 (2)	C14—C15	1.361 (3)

N2—C7	1.466 (2)	C14—C23	1.430 (2)
N3—C3	1.369 (2)	C15—C16	1.418 (3)
N3—C8	1.425 (2)	C15—H15	0.9500
C1—C2	1.498 (2)	C16—C17	1.413 (3)
C1—H1A	0.9800	C16—C21	1.426 (3)
C1—H1B	0.9800	C17—C18	1.369 (4)
C1—H1C	0.9800	C17—H17	0.9500
C3—C4	1.433 (3)	C18—C19	1.398 (4)
C4—C5	1.360 (3)	C18—H18	0.9500
C5—C6	1.484 (3)	C19—C20	1.358 (3)
C6—H6A	0.9800	C19—H19	0.9500
C6—H6B	0.9800	C20—C21	1.409 (3)
C6—H6C	0.9800	C20—H20	0.9500
C7—H7A	0.9800	C21—C22	1.411 (3)
C7—H7B	0.9800	C22—C23	1.367 (3)
C7—H7C	0.9800	C22—H22	0.9500
C8—C13	1.380 (3)		
C14—O3—H3	109.9 (18)	C10—C9—H9	120.4
C23—O4—H4	110.2 (19)	C8—C9—H9	120.4
C2—N1—C4	123.16 (16)	C9—C10—C11	120.1 (2)
C2—N1—H1	117.1 (15)	C9—C10—H10	119.9
C4—N1—H1	118.4 (15)	C11—C10—H10	119.9
C5—N2—N3	106.52 (14)	C10—C11—C12	120.0 (2)
C5—N2—C7	121.38 (17)	C10—C11—H11	120.0
N3—N2—C7	115.82 (15)	C12—C11—H11	120.0
C3—N3—N2	110.07 (14)	C11—C12—C13	120.6 (2)
C3—N3—C8	127.60 (16)	C11—C12—H12	119.7
N2—N3—C8	119.84 (14)	C13—C12—H12	119.7
C2—C1—H1A	109.5	C8—C13—C12	118.7 (2)
C2—C1—H1B	109.5	C8—C13—H13	120.7
H1A—C1—H1B	109.5	C12—C13—H13	120.7
C2—C1—H1C	109.5	O3—C14—C15	125.21 (16)
H1A—C1—H1C	109.5	O3—C14—C23	114.64 (16)
H1B—C1—H1C	109.5	C15—C14—C23	120.15 (17)
O1—C2—N1	122.93 (17)	C14—C15—C16	121.07 (17)
O1—C2—C1	121.01 (17)	C14—C15—H15	119.5
N1—C2—C1	116.05 (17)	C16—C15—H15	119.5
O2—C3—N3	123.60 (17)	C17—C16—C15	123.06 (19)
O2—C3—C4	131.17 (16)	C17—C16—C21	117.99 (19)
N3—C3—C4	105.21 (15)	C15—C16—C21	118.87 (18)
C5—C4—N1	126.85 (17)	C18—C17—C16	121.0 (2)
C5—C4—C3	108.47 (16)	C18—C17—H17	119.5
N1—C4—C3	124.68 (16)	C16—C17—H17	119.5
C4—C5—N2	109.47 (17)	C17—C18—C19	120.5 (2)
C4—C5—C6	130.11 (18)	C17—C18—H18	119.8
N2—C5—C6	120.40 (17)	C19—C18—H18	119.8
C5—C6—H6A	109.5	C20—C19—C18	120.3 (2)
C5—C6—H6B	109.5	C20—C19—H19	119.8
H6A—C6—H6B	109.5	C18—C19—H19	119.8

C5—C6—H6C	109.5	C19—C20—C21	120.9 (2)
H6A—C6—H6C	109.5	C19—C20—H20	119.5
H6B—C6—H6C	109.5	C21—C20—H20	119.5
N2—C7—H7A	109.5	C20—C21—C22	121.83 (18)
N2—C7—H7B	109.5	C20—C21—C16	119.28 (19)
H7A—C7—H7B	109.5	C22—C21—C16	118.82 (18)
N2—C7—H7C	109.5	C23—C22—C21	121.33 (17)
H7A—C7—H7C	109.5	C23—C22—H22	119.3
H7B—C7—H7C	109.5	C21—C22—H22	119.3
C13—C8—C9	121.35 (19)	O4—C23—C22	124.57 (16)
C13—C8—N3	118.83 (18)	O4—C23—C14	115.71 (16)
C9—C8—N3	119.81 (18)	C22—C23—C14	119.71 (17)
C10—C9—C8	119.3 (2)		
C5—N2—N3—C3	5.4 (2)	C8—C9—C10—C11	0.8 (4)
C7—N2—N3—C3	143.68 (16)	C9—C10—C11—C12	0.3 (5)
C5—N2—N3—C8	168.77 (16)	C10—C11—C12—C13	−1.0 (5)
C7—N2—N3—C8	−52.9 (2)	C9—C8—C13—C12	0.5 (4)
C4—N1—C2—O1	5.8 (3)	N3—C8—C13—C12	−179.3 (2)
C4—N1—C2—C1	−174.38 (16)	C11—C12—C13—C8	0.6 (5)
N2—N3—C3—O2	174.23 (16)	O3—C14—C15—C16	177.70 (19)
C8—N3—C3—O2	12.4 (3)	C23—C14—C15—C16	−1.5 (3)
N2—N3—C3—C4	−4.09 (19)	C14—C15—C16—C17	−174.2 (2)
C8—N3—C3—C4	−165.87 (17)	C14—C15—C16—C21	2.5 (3)
C2—N1—C4—C5	−79.6 (3)	C15—C16—C17—C18	176.3 (3)
C2—N1—C4—C3	101.6 (2)	C21—C16—C17—C18	−0.4 (5)
O2—C3—C4—C5	−176.82 (19)	C16—C17—C18—C19	2.0 (6)
N3—C3—C4—C5	1.3 (2)	C17—C18—C19—C20	−1.5 (6)
O2—C3—C4—N1	2.2 (3)	C18—C19—C20—C21	−0.7 (5)
N3—C3—C4—N1	−179.66 (17)	C19—C20—C21—C22	−174.8 (3)
N1—C4—C5—N2	−176.99 (17)	C19—C20—C21—C16	2.3 (4)
C3—C4—C5—N2	2.0 (2)	C17—C16—C21—C20	−1.7 (3)
N1—C4—C5—C6	4.2 (3)	C15—C16—C21—C20	−178.5 (2)
C3—C4—C5—C6	−176.78 (19)	C17—C16—C21—C22	175.4 (2)
N3—N2—C5—C4	−4.4 (2)	C15—C16—C21—C22	−1.4 (3)
C7—N2—C5—C4	−139.91 (18)	C20—C21—C22—C23	176.4 (2)
N3—N2—C5—C6	174.48 (17)	C16—C21—C22—C23	−0.7 (3)
C7—N2—C5—C6	39.0 (3)	C21—C22—C23—O4	−177.26 (18)
C3—N3—C8—C13	−64.6 (3)	C21—C22—C23—C14	1.7 (3)
N2—N3—C8—C13	135.2 (2)	O3—C14—C23—O4	−0.8 (2)
C3—N3—C8—C9	115.5 (2)	C15—C14—C23—O4	178.42 (17)
N2—N3—C8—C9	−44.7 (3)	O3—C14—C23—C22	−179.90 (16)
C13—C8—C9—C10	−1.2 (3)	C15—C14—C23—C22	−0.6 (3)
N3—C8—C9—C10	178.6 (2)		

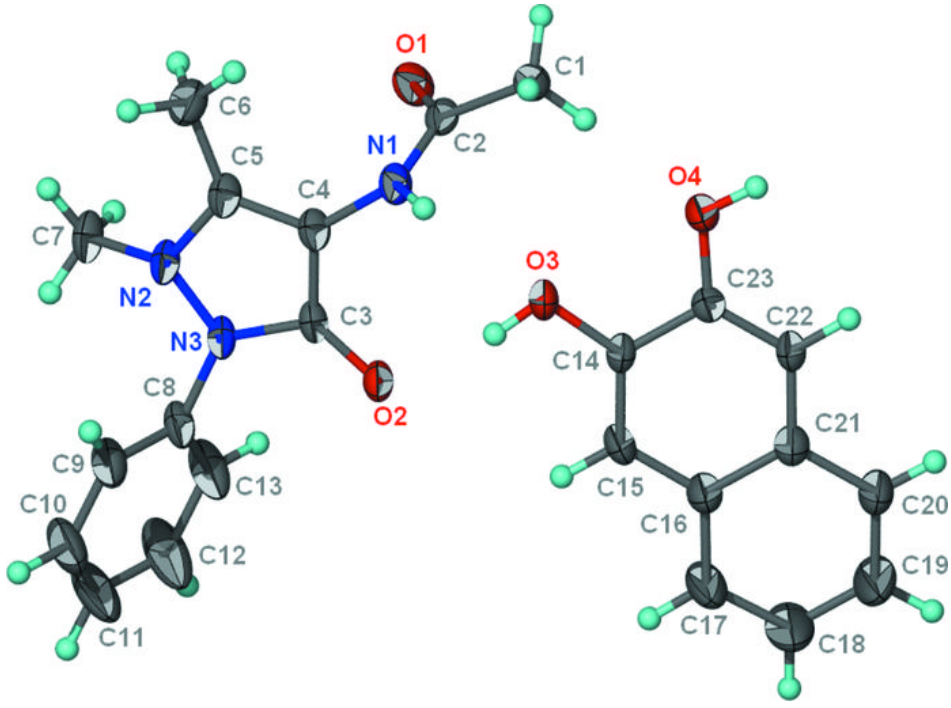
Hydrogen-bond geometry (Å, °)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
N1—H1···O2^{i}	0.87 (1)	2.07 (1)	2.924 (2)	169 (2)
O3—H3···O2	0.85 (3)	1.81 (3)	2.639 (2)	163 (3)

O4—H4···O1^{ii}	0.85 (3)	1.81 (3)	2.646 (2)	168 (3)

Symmetry codes: (i) −*x*+1, −*y*+1, −*z*+1; (ii) *x*, −*y*+3/2, *z*+1/2.

Fig. 1



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Pentaaqua[2-(5-carboxylato-2-oxido-1-pyridinio)acetato]zinc(II) monohydrate

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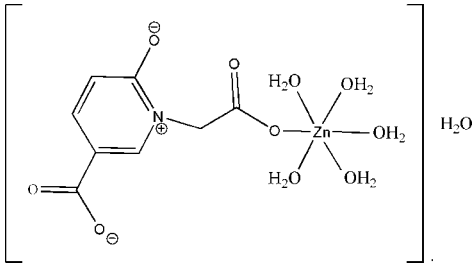
Key indicators: single-crystal X-ray study; T = 293 K; mean σ(C–C) = 0.003 Å; R factor = 0.036; wR factor = 0.084; data-to-parameter ratio = 13.7.

In the title compound, $[Zn(C_8H_5NO_5)(H_2O)_5]\cdot H_2O$, the Zn^{II} atom is coordinated by one O atom from the 2-(5-carboxylato-2-oxidopyridinium-1-yl)acetate ligand and by five water molecules, forming a distorted octahedral geometry. Coordinated and uncoordinated water molecules form O—H···O hydrogen bonds, leading to a three-dimensional framework.

Related literature

For related structures, see: Jiang *et al.* (2009); Szafran *et al.* (2006); Yang *et al.* (2010); Zhang *et al.* (2003); He & Feng (2007).



Experimental

Crystal data

$[Zn(C_8H_5NO_5)(H_2O)_5]\cdot H_2O$
M_r = 368.60
Monoclinic, $P2_1/c$
a = 10.9584 (4) Å
b = 7.5548 (4) Å
c = 16.6510 (7) Å
β = 103.498 (3)°
V = 1340.43 (10) Å^3
Z = 4
Mo $K\alpha$ radiation
μ = 1.89 mm^{-1}
T = 293 K
0.36 × 0.09 × 0.05 mm

Data collection

Bruker APEXII area-detector diffractometer
Absorption correction: multi-scan (*SADABS*; Sheldrick, 1996)
T_{min} = 0.824, T_{max} = 0.918
19343 measured reflections
3086 independent reflections
2233 reflections with $I > 2\sigma(I)$
R_{int} = 0.100

Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.036
$wR(F^2)$ = 0.084
S = 1.00
3086 reflections
226 parameters
18 restraints
H atoms treated by a mixture of independent and constrained refinement
$\Delta\rho_{max}$ = 0.48 e Å^{-3}
$\Delta\rho_{min}$ = −0.80 e Å^{-3}

Table 1
Hydrogen-bond geometry (Å, °).

D—H···A	D—H	H···A	D···A	D—H···A
O1W—H1WA···O2^{i}	0.83 (2)	2.25 (2)	2.972 (3)	145 (3)
O1W—H1WB···O2W^{ii}	0.81 (2)	2.58 (3)	3.118 (3)	125 (3)
O2W—H2WA···O4^{iii}	0.83 (2)	1.89 (2)	2.716 (2)	169 (3)
O2W—H2WB···O2^{i}	0.80 (2)	1.96 (2)	2.742 (2)	163 (2)
O3W—H3WA···O2^{iv}	0.81 (2)	1.89 (2)	2.701 (2)	173 (2)
O3W—H3WB···O4^{v}	0.82 (2)	2.04 (2)	2.849 (2)	170 (3)
O4W—H4WA···O5^{vi}	0.82 (2)	2.02 (2)	2.810 (2)	160 (3)
O5W—H5WA···O1^{iii}	0.82 (2)	1.90 (2)	2.705 (2)	166 (3)
O5W—H5WB···O1^{iv}	0.81 (2)	1.95 (2)	2.742 (2)	164 (3)
O6W—H6WB···O3^{v}	0.82 (2)	1.89 (2)	2.697 (3)	171 (3)

Symmetry codes: (i) $x+1, -y+\frac{1}{2}, z+\frac{1}{2}$; (ii) $-x, -y, -z+1$; (iii) $-x, y-\frac{1}{2}, -z+\frac{1}{2}$; (iv) $x+1, -y+\frac{3}{2}, z+\frac{1}{2}$; (v) $-x, y+\frac{1}{2}, -z+\frac{1}{2}$; (vi) $-x, -y+1, -z+1$.

Data collection: *APEX2* (Bruker, 2006); cell refinement: *SAINT* (Bruker, 2006); data reduction: *SAINT*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *SHELXTL* (Sheldrick, 2008); software used to prepare material for publication: *SHELXTL*.

Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: IS2541).

References

Bruker (2006). *APEX2* and *SAINT*. Bruker AXS Inc., Madison, Wisconsin, USA.
He, Y.-H. & Feng, Y.-L. (2007). *Acta Cryst.* E**63**, o3422.
Jiang, M.-X., Feng, Y.-L., He, Y.-H. & Su, H. (2009). *Inorg. Chim. Acta*, **362**, 2856–2860.
Sheldrick, G. M. (1996). *SADABS*. University of Göttingen, Germany.
Sheldrick, G. M. (2008). *Acta Cryst.* A**64**, 112–122.
Szafran, M., Katrusiak, A., Koput, J. & Dega, S. Z. (2006). *J. Mol. Struct.* **784**, 98–108.
Yang, Q., Zhao, J.-P., Hu, B.-W., Zhang, X.-F. & Bu, X.-H. (2010). *Inorg. Chem.* **49**, 3746–3751.
Zhang, B., Zhu, X.-Q., Lu, J.-Y., He, J., Wang, P. & Cheng, J.-P. (2003). *J. Org. Chem.* **68**, 3295–3298.

supplementary materials

Acta Cryst. (2010). E**66**, m759 [**doi:10.1107/S1600536810017538**]

Pentaaqua[2-(5-carboxylato-2-oxido-1-pyridinio)acetato]zinc(II) monohydrate

J. Chen and Y.-L. Feng

Comment

The pyridinium carboxylate ligands, containing both of carboxylate and quaternary ammonium groups, have been extensively employed to design and construct novel complexes due to its versatile coordination behavior to metal ions (Zhang *et al.*, 2003; Szafran *et al.*, 2006; Yang *et al.*, 2010). Herein, we report the synthesis and crystal structure of a new complex, $[ZnL(H_2O)_5].H_2O$ (LH_2 = 5-carboxy-1-carboxymethyl-2-oxidopyridinium; He & Feng, 2007).

As shown in Fig. 1, the metal center Zn^{II} atom is six-coordinated by one O atom from one L^{2-} ligand [Zn—O 2.1039 (16) Å] and five water molecules [Zn—O 2.0554 (17)–2.0988 (19) Å], to form a distorted octahdral geometry. Notably, only one O atom from the flexible carboxylic groups of L^{2-} ligand coordinates to the Zn^{II} ion. As shown in Fig. 2, the complexes connected with each other by the O—H···O hydrogen bonds generate a three-dimensional structure.

Experimental

All the starting materials and solvents were obtained commercially and were used without further purification. A mixture of *N*-carboxymethyl-2-oxo-pyridine-5-carboxylic acid (0.1972 g, 1 mmol), $ZnNO_3$ (0.1901 g, 1 mmol), and purified water (15 ml) was sealed in a 25 ml stainless steel reactor and kept at 393 K for 3 d. Then, the reactor was cooled to room temperature at a speed of 5 K/h. A large quantity of colorless single crystals were filtered out of the mixture with the yield of 85%.

Refinement

The C-bound H atoms were positioned geometrically and included in the refinement using a riding model, with C—H = 0.93 or 0.97 Å, and with U_{iso}(H) = 1.2U_{eq}(C). The O-bound H atoms was located in a difference Fourier map and refined, with the distance restraint of O—H = 0.82 (2) Å, and with U_{iso}(H) = 1.2U_{eq}(O).

Figures

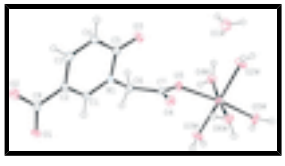


Fig. 1. The molecular structure of the title compound, with 30% probability displacement ellipsoids.

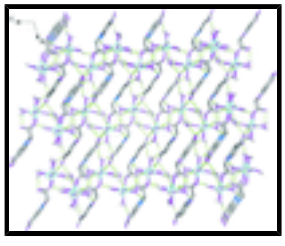


Fig. 2. Three-dimensional framework with hydrogen bonding interactions.

Pentaaqua[2-(5-carboxylato-2-oxido-1-pyridinio)acetato]zinc(II) monohydrate

Crystal data

$[Zn(C_8H_5NO_5)(H_2O)_5]\cdot H_2O$	$F(000) = 760$
$M_r = 368.60$	$D_x = 1.826$ Mg m^{-3}
Monoclinic, $P2_1/c$	Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å
Hall symbol: -P 2ybc	Cell parameters from 6642 reflections
$a = 10.9584$ (4) Å	$\theta = 1.9$–$27.6°$
$b = 7.5548$ (4) Å	$\mu = 1.89$ mm^{-1}
$c = 16.6510$ (7) Å	$T = 293$ K
$\beta = 103.498$ (3)°	Prism, colourless
$V = 1340.43$ (10) Å^3	0.36 × 0.09 × 0.05 mm
$Z = 4$	

Data collection

Bruker APEXII area-detector diffractometer	3086 independent reflections
Radiation source: fine-focus sealed tube	2233 reflections with $I > 2\sigma(I)$
graphite	$R_{int} = 0.100$
ω scans	$\theta_{max} = 27.6°$, $\theta_{min} = 1.9°$
Absorption correction: multi-scan (*SADABS*; Sheldrick, 1996)	$h = -14\rightarrow14$
$T_{min} = 0.824$, $T_{max} = 0.918$	$k = -9\rightarrow8$
19343 measured reflections	$l = -21\rightarrow19$

Refinement

Refinement on F^2	Primary atom site location: structure-invariant direct methods
Least-squares matrix: full	Secondary atom site location: difference Fourier map
$R[F^2 > 2\sigma(F^2)] = 0.036$	Hydrogen site location: inferred from neighbouring sites
$wR(F^2) = 0.084$	H atoms treated by a mixture of independent and constrained refinement
$S = 1.00$	$w = 1/[\sigma^2(F_o^2) + (0.0382P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
3086 reflections	$(\Delta/\sigma)_{max} < 0.001$
226 parameters	$\Delta\rho_{max} = 0.48$ e Å^{-3}
18 restraints	$\Delta\rho_{min} = -0.79$ e Å^{-3}

Special details

Geometry. All esds (except the esd in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell esds are taken into account individually in the estimation of esds in distances, angles and torsion angles; correlations between esds

in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell esds is used for estimating esds involving l.s. planes.

Refinement. Refinement of F^2 against ALL reflections. The weighted *R*-factor wR and goodness of fit *S* are based on F^2, conventional *R*-factors *R* are based on *F*, with *F* set to zero for negative F^2. The threshold expression of $F^2 > \sigma(F^2)$ is used only for calculating *R*-factors(gt) etc. and is not relevant to the choice of reflections for refinement. *R*-factors based on F^2 are statistically about twice as large as those based on *F*, and *R*- factors based on ALL data will be even larger.

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å^2)

	x	*y*	*z*	U_{iso}*/U_{eq}
Zn1	0.14951 (2)	0.39964 (4)	0.404996 (17)	0.02275 (11)
O1	−0.56142 (14)	0.8182 (2)	0.07024 (11)	0.0314 (4)
O1W	0.0969 (2)	0.0417 (3)	0.59084 (15)	0.0564 (6)
H1WA	0.1593 (19)	−0.021 (4)	0.592 (2)	0.068*
H1WB	0.038 (2)	−0.002 (4)	0.5579 (17)	0.068*
O2	−0.70407 (16)	0.6153 (2)	0.01860 (11)	0.0357 (5)
O2W	0.16338 (18)	0.1231 (2)	0.40753 (11)	0.0324 (5)
H2WA	0.149 (2)	0.061 (3)	0.3650 (11)	0.039*
H2WB	0.207 (2)	0.071 (3)	0.4456 (11)	0.039*
O3	−0.30374 (16)	0.1584 (2)	0.26291 (11)	0.0322 (4)
O3W	0.13340 (17)	0.6755 (3)	0.41312 (11)	0.0331 (5)
H3WA	0.183 (2)	0.732 (3)	0.4479 (12)	0.040*
H3WB	0.120 (2)	0.730 (3)	0.3697 (10)	0.040*
O4	−0.08994 (16)	0.4075 (2)	0.22554 (10)	0.0290 (4)
O4W	0.12338 (18)	0.3724 (2)	0.52419 (11)	0.0306 (4)
H4WA	0.092 (2)	0.452 (2)	0.5466 (16)	0.037*
H4WB	0.103 (2)	0.276 (2)	0.5380 (16)	0.037*
O5	−0.04711 (15)	0.3999 (2)	0.36330 (10)	0.0263 (4)
O5W	0.33859 (16)	0.4349 (3)	0.45253 (12)	0.0348 (5)
H5WA	0.400 (2)	0.396 (3)	0.4376 (16)	0.042*
H5WB	0.357 (2)	0.520 (3)	0.4830 (15)	0.042*
O6W	0.17072 (18)	0.3938 (2)	0.28435 (11)	0.0302 (4)
H6WB	0.2178 (19)	0.467 (3)	0.2718 (16)	0.036*
H6WA	0.1020 (16)	0.399 (3)	0.2526 (15)	0.036*
N1	−0.34860 (18)	0.4432 (3)	0.22449 (12)	0.0223 (5)
C1	−0.4197 (2)	0.5668 (3)	0.17514 (15)	0.0233 (6)
H1A	−0.3972	0.6854	0.1826	0.028*
C2	−0.5222 (2)	0.5226 (3)	0.11561 (14)	0.0224 (5)
C3	−0.5541 (2)	0.3417 (3)	0.10731 (15)	0.0287 (6)
H3A	−0.6260	0.3074	0.0687	0.034*
C4	−0.4824 (2)	0.2166 (3)	0.15441 (15)	0.0279 (6)
H4A	−0.5046	0.0981	0.1462	0.033*
C5	−0.3744 (2)	0.2628 (3)	0.21590 (15)	0.0248 (6)
C6	−0.2487 (2)	0.4933 (3)	0.29580 (14)	0.0269 (6)
H6A	−0.2699	0.4489	0.3455	0.032*
H6B	−0.2454	0.6214	0.2996	0.032*
C7	−0.1195 (2)	0.4249 (3)	0.29292 (15)	0.0216 (5)
C8	−0.6009 (2)	0.6622 (3)	0.06435 (14)	0.0240 (6)

Atomic displacement parameters (Å^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Zn1	0.02172 (18)	0.0210 (2)	0.02425 (17)	0.00083 (12)	0.00280 (12)	−0.00019 (12)
O1	0.0270 (10)	0.0199 (11)	0.0432 (11)	−0.0037 (8)	−0.0001 (8)	0.0073 (9)
O1W	0.0464 (15)	0.0551 (16)	0.0705 (17)	0.0124 (12)	0.0194 (12)	0.0136 (13)
O2	0.0303 (11)	0.0272 (11)	0.0393 (11)	−0.0024 (8)	−0.0125 (8)	−0.0002 (8)
O2W	0.0466 (13)	0.0209 (11)	0.0242 (10)	0.0051 (8)	−0.0032 (9)	−0.0027 (8)
O3	0.0332 (10)	0.0268 (11)	0.0346 (10)	0.0082 (8)	0.0040 (8)	0.0064 (8)
O3W	0.0361 (11)	0.0223 (11)	0.0341 (11)	0.0003 (8)	−0.0053 (9)	−0.0004 (8)
O4	0.0275 (10)	0.0371 (11)	0.0215 (9)	0.0010 (8)	0.0042 (8)	0.0006 (8)
O4W	0.0394 (12)	0.0296 (12)	0.0237 (10)	0.0038 (9)	0.0093 (8)	−0.0017 (8)
O5	0.0196 (9)	0.0366 (11)	0.0205 (9)	0.0013 (7)	0.0003 (7)	0.0007 (8)
O5W	0.0203 (10)	0.0372 (13)	0.0448 (12)	0.0009 (8)	0.0036 (9)	−0.0134 (9)
O6W	0.0278 (11)	0.0356 (12)	0.0258 (10)	−0.0059 (8)	0.0035 (8)	0.0019 (8)
N1	0.0183 (11)	0.0221 (13)	0.0242 (11)	0.0009 (9)	0.0002 (8)	−0.0009 (9)
C1	0.0237 (14)	0.0203 (15)	0.0260 (13)	0.0004 (10)	0.0058 (11)	0.0006 (11)
C2	0.0210 (13)	0.0208 (14)	0.0239 (13)	0.0004 (11)	0.0026 (10)	−0.0001 (11)
C3	0.0243 (14)	0.0286 (16)	0.0298 (14)	−0.0037 (11)	−0.0004 (11)	−0.0039 (12)
C4	0.0286 (14)	0.0187 (14)	0.0339 (14)	−0.0023 (11)	0.0025 (11)	−0.0032 (12)
C5	0.0255 (13)	0.0245 (16)	0.0262 (13)	0.0031 (11)	0.0096 (11)	0.0031 (11)
C6	0.0263 (14)	0.0267 (16)	0.0247 (13)	0.0027 (12)	−0.0002 (11)	−0.0034 (11)
C7	0.0221 (13)	0.0142 (14)	0.0267 (13)	−0.0036 (10)	0.0021 (10)	−0.0005 (10)
C8	0.0225 (13)	0.0264 (16)	0.0223 (13)	0.0027 (11)	0.0034 (10)	0.0002 (11)

Geometric parameters (Å, °)

Zn1—O5W	2.0554 (17)	O5W—H5WA	0.821 (16)
Zn1—O6W	2.0759 (18)	O5W—H5WB	0.812 (16)
Zn1—O4W	2.0805 (18)	O6W—H6WB	0.816 (15)
Zn1—O2W	2.0945 (18)	O6W—H6WA	0.814 (16)
Zn1—O3W	2.0988 (19)	N1—C1	1.362 (3)
Zn1—O5	2.1039 (16)	N1—C5	1.392 (3)
O1—C8	1.251 (3)	N1—C6	1.464 (3)
O1W—H1WA	0.829 (17)	C1—C2	1.355 (3)
O1W—H1WB	0.812 (17)	C1—H1A	0.9300
O2—C8	1.257 (3)	C2—C3	1.409 (4)
O2W—H2WA	0.832 (15)	C2—C8	1.498 (3)
O2W—H2WB	0.802 (15)	C3—C4	1.356 (3)
O3—C5	1.246 (3)	C3—H3A	0.9300
O3W—H3WA	0.813 (15)	C4—C5	1.416 (3)
O3W—H3WB	0.816 (15)	C4—H4A	0.9300
O4—C7	1.245 (3)	C6—C7	1.518 (3)
O4W—H4WA	0.823 (15)	C6—H6A	0.9700
O4W—H4WB	0.809 (15)	C6—H6B	0.9700
O5—C7	1.267 (3)		
O5W—Zn1—O6W	92.57 (8)	H6WB—O6W—H6WA	110 (2)

O5W—Zn1—O4W	89.79 (8)	C1—N1—C5	122.35 (19)
O6W—Zn1—O4W	172.96 (8)	C1—N1—C6	121.7 (2)
O5W—Zn1—O2W	93.41 (8)	C5—N1—C6	115.59 (19)
O6W—Zn1—O2W	88.53 (7)	C2—C1—N1	122.1 (2)
O4W—Zn1—O2W	84.70 (7)	C2—C1—H1A	118.9
O5W—Zn1—O3W	86.50 (7)	N1—C1—H1A	118.9
O6W—Zn1—O3W	96.52 (7)	C1—C2—C3	117.1 (2)
O4W—Zn1—O3W	90.25 (7)	C1—C2—C8	120.8 (2)
O2W—Zn1—O3W	174.95 (8)	C3—C2—C8	122.0 (2)
O5W—Zn1—O5	171.74 (7)	C4—C3—C2	121.5 (2)
O6W—Zn1—O5	91.03 (7)	C4—C3—H3A	119.3
O4W—Zn1—O5	87.51 (7)	C2—C3—H3A	119.3
O2W—Zn1—O5	94.10 (7)	C3—C4—C5	121.4 (2)
O3W—Zn1—O5	85.71 (6)	C3—C4—H4A	119.3
H1WA—O1W—H1WB	107 (3)	C5—C4—H4A	119.3
Zn1—O2W—H2WA	123.1 (17)	O3—C5—N1	118.3 (2)
Zn1—O2W—H2WB	122.1 (18)	O3—C5—C4	126.2 (2)
H2WA—O2W—H2WB	111 (2)	N1—C5—C4	115.5 (2)
Zn1—O3W—H3WA	120.8 (18)	N1—C6—C7	114.4 (2)
Zn1—O3W—H3WB	116.6 (19)	N1—C6—H6A	108.7
H3WA—O3W—H3WB	109 (2)	C7—C6—H6A	108.7
Zn1—O4W—H4WA	121.7 (18)	N1—C6—H6B	108.7
Zn1—O4W—H4WB	118.0 (19)	C7—C6—H6B	108.7
H4WA—O4W—H4WB	111 (2)	H6A—C6—H6B	107.6
C7—O5—Zn1	132.66 (16)	O4—C7—O5	125.4 (2)
Zn1—O5W—H5WA	131.2 (19)	O4—C7—C6	120.3 (2)
Zn1—O5W—H5WB	114.9 (18)	O5—C7—C6	114.1 (2)
H5WA—O5W—H5WB	112 (2)	O1—C8—O2	124.0 (2)
Zn1—O6W—H6WB	117.0 (19)	O1—C8—C2	118.4 (2)
Zn1—O6W—H6WA	109.4 (19)	O2—C8—C2	117.6 (2)
O5W—Zn1—O5—C7	103.1 (5)	C1—N1—C5—C4	−2.3 (3)
O6W—Zn1—O5—C7	−12.8 (2)	C6—N1—C5—C4	171.2 (2)
O4W—Zn1—O5—C7	174.1 (2)	C3—C4—C5—O3	178.9 (2)
O2W—Zn1—O5—C7	−101.4 (2)	C3—C4—C5—N1	0.5 (4)
O3W—Zn1—O5—C7	83.6 (2)	C1—N1—C6—C7	−121.4 (2)
C5—N1—C1—C2	1.6 (4)	C5—N1—C6—C7	65.1 (3)
C6—N1—C1—C2	−171.5 (2)	Zn1—O5—C7—O4	21.6 (4)
N1—C1—C2—C3	1.0 (3)	Zn1—O5—C7—C6	−154.06 (16)
N1—C1—C2—C8	177.9 (2)	N1—C6—C7—O4	32.4 (3)
C1—C2—C3—C4	−2.8 (4)	N1—C6—C7—O5	−151.6 (2)
C8—C2—C3—C4	−179.6 (2)	C1—C2—C8—O1	9.1 (3)
C2—C3—C4—C5	2.1 (4)	C3—C2—C8—O1	−174.2 (2)
C1—N1—C5—O3	179.1 (2)	C1—C2—C8—O2	−170.0 (2)
C6—N1—C5—O3	−7.4 (3)	C3—C2—C8—O2	6.7 (3)

Hydrogen-bond geometry (Å, °)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
O1W—H1WA···O2^{i}	0.83 (2)	2.25 (2)	2.972 (3)	145 (3)

O1W—H1WB···O2W^{ii}	0.81 (2)	2.58 (3)	3.118 (3)	125 (3)
O2W—H2WA···O4^{iii}	0.83 (2)	1.89 (2)	2.716 (2)	169 (3)
O2W—H2WB···O2^{i}	0.80 (2)	1.96 (2)	2.742 (2)	163 (2)
O3W—H3WA···O2^{iv}	0.81 (2)	1.89 (2)	2.701 (2)	173 (2)
O3W—H3WB···O4^{v}	0.82 (2)	2.04 (2)	2.849 (2)	170 (3)
O4W—H4WA···O5^{vi}	0.82 (2)	2.02 (2)	2.810 (2)	160 (3)
O5W—H5WA···O1^{iii}	0.82 (2)	1.90 (2)	2.705 (2)	166 (3)
O5W—H5WB···O1^{iv}	0.81 (2)	1.95 (2)	2.742 (2)	164 (3)
O6W—H6WB···O3^{v}	0.82 (2)	1.89 (2)	2.697 (3)	171 (3)

Symmetry codes: (i) *x*+1, −*y*+1/2, *z*+1/2; (ii) −*x*, −*y*, −*z*+1; (iii) −*x*, *y*−1/2, −*z*+1/2; (iv) *x*+1, −*y*+3/2, *z*+1/2; (v) −*x*, *y*+1/2, −*z*+1/2; (vi) −*x*, −*y*+1, −*z*+1.

Fig. 1

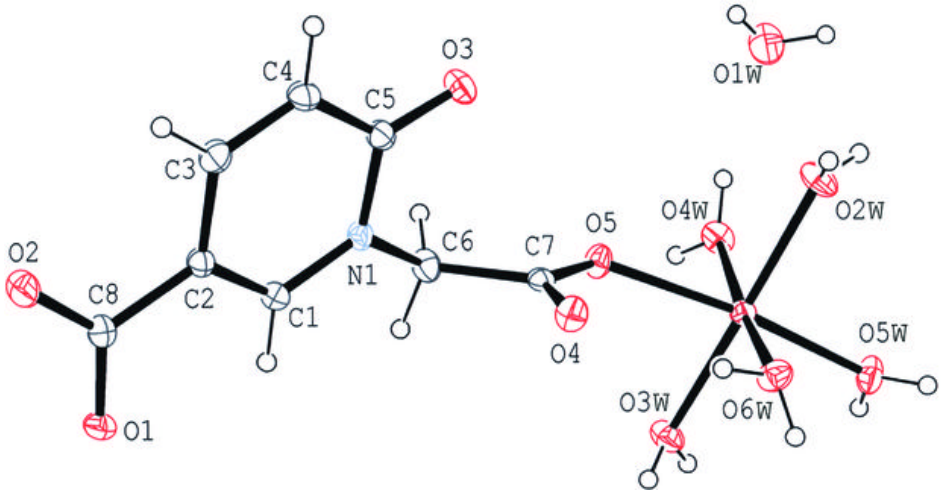
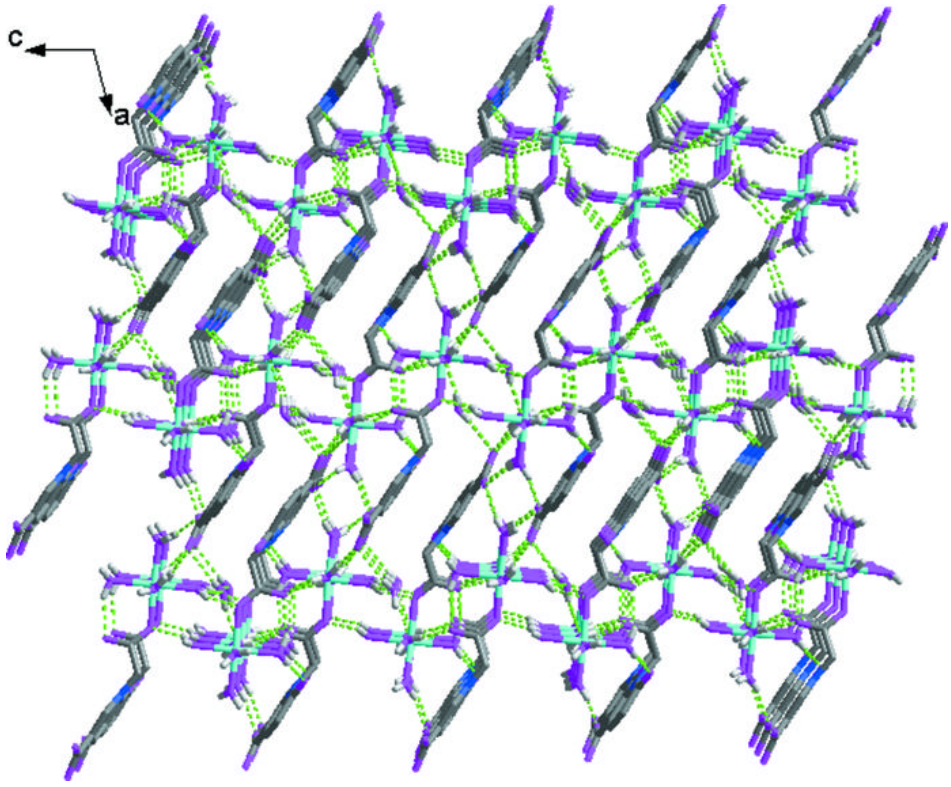


Fig. 2



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catena-Poly[[bis(pyridine-κN)zinc(II)]-μ-benzene-1,4-dicarboxylato-$\kappa^2O^1:O^4$]

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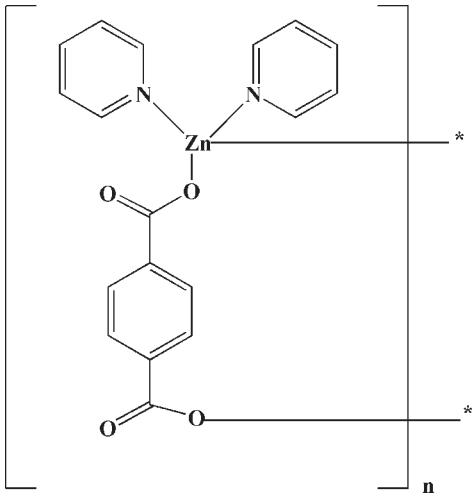
Key indicators: single-crystal X-ray study; T = 173 K; mean σ(C–C) = 0.004 Å; R factor = 0.036; wR factor = 0.082; data-to-parameter ratio = 17.3.

In the title coordination polymer, $[Zn(C_8H_4O_4)(C_5H_5N)_2]_n$, the Zn^{II} atom, located on a twofold rotation axis, is tetracoordinated by two monodentate O atoms from two different carboxylate groups and two pyridyl N atoms, forming a distorted tetrahedral geometry. The Zn^{II} atoms are bridged by terephthalate ligands, generating an infinite zigzag chain along [101].

Related literature

For related structures, see: Li *et al.* (2007); Mori *et al.* (2004).



Experimental

Crystal data

$[Zn(C_8H_4O_4)(C_5H_5N)_2]$
M_r = 387.68
Monoclinic, $C2/c$
a = 20.054 (8) Å
b = 6.299 (2) Å
c = 14.761 (6) Å
β = 111.500 (6)°
V = 1734.9 (11) Å^3
Z = 4
Mo $K\alpha$ radiation
μ = 1.44 mm^{-1}
T = 173 K
0.24 × 0.20 × 0.15 mm

Data collection

Bruker SMART CCD area-detector diffractometer
Absorption correction: numerical (*SADABS*; Bruker, 1998)
T_{min} = 0.724, T_{max} = 0.813
7306 measured reflections
1975 independent reflections
1915 reflections with $I > 2\sigma(I)$
R_{int} = 0.039

Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.036
$wR(F^2)$ = 0.082
S = 1.03
1975 reflections
114 parameters
H-atom parameters constrained
$\Delta\rho_{max}$ = 0.35 e Å^{-3}
$\Delta\rho_{min}$ = −0.22 e Å^{-3}

Data collection: *SMART* (Bruker, 1998); cell refinement: *SAINT* (Bruker, 1998); data reduction: *SAINT*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *SHELXTL* (Sheldrick, 2008); software used to prepare material for publication: *SHELXTL* (Sheldrick, 2008).

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Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: IS2548).

References

Bruker (1998). *SMART*, *SAINT* and *SADABS*. Bruker AXS Inc., Madison, Wisconsin, USA.
Li, J. K., Ma, C. L., He, G. F. & Qiu, L. L. (2007). *J. Coord. Chem.* **61**, 251–261.
Mori, W., Takamizawa, S., Kato, C. N., Ohmura, T. & Sato, T. (2004). *Micropor. Mesopor. Mater.* **73**, 31–46.
Sheldrick, G. M. (2008). *Acta Cryst.* A**64**, 112–122.

supplementary materials

Acta Cryst. (2010). E**66**, m829 [**doi:10.1107/S1600536810022385**]

catena-Poly[[bis(pyridine-κN)zinc(II)]-μ-benzene-1,4-dicarboxylato-$\kappa^2O^1:O^4$]

L.-F. Wang, C.-Q. Li, W.-G. Qiu and H. He

Comment

A great number of the crystal structures of one-dimensional chain complexes have been extensively investigated (Li *et al.* 2007; Mori *et al.* 2004), in most of which interchain hydrogen bonds or π–π interactions connect the chains to produce two-dimensional or three-dimensional structures. Here, we report the synthesis and crystal structure of a new one-dimensional zigzag coordination polymer.

In the title coordination polymer, each Zn(II) atom is four-coordinated. The coordination environment around the Zn(II) ions represents a slightly distorted tetrahedral geometry with two pyridyl N and two monodentate O atoms from two different carboxylates. The Zn centers are interconnected by terephthalate ligands to form an infinite zigzag chain. The Zn—O bond distance between Zn(II) and carboxylate O atom is 1.9622 (18) Å, and the Zn—N bond distance between Zn(II) and the N atom of the pyridine is 2.038 (2) Å.

Experimental

A solution containing a 2:1 molar ratio of 1,4-benzenedicarboxylic acid (0.022 g) and zinc nitrate hexahydrate (0.041 g) in a mixture of pyridine (2 ml) and *N*,*N*-dimethylformamide (2 ml) was sealed in a 5 ml transparent vitreous reactor and kept at 343 K for 5 days, and then cooled to room temperature. The mixture was filtered and colorless crystals suitable for the X-ray investigation were collected.

Refinement

All H atoms were positioned geometrically (C—H = 0.95 Å) and treated as riding, with U_{iso}(H) = 1.2U_{eq}(C).

Figures

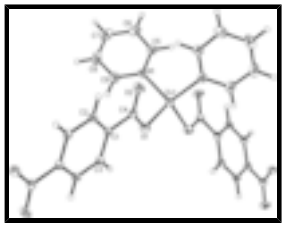


Fig. 1. A view of the molecular structure of the title compound, with displacement ellipsoids drawn at the 30% probability level. Hydrogen atoms have been omitted for clarity.

Fig. 2. An illustration of the zigzag chain formed by bridging terephthalate ligands. H atoms have been omitted.

catena-Poly[[bis(pyridine-κ*N*)zinc(II)]-μ- benzene-1,4-dicarboxylato-κ^2*O*^{1}:*O*^{4}]

Crystal data

$[Zn(C_8H_4O_4)(C_5H_5N)_2]$	$F(000) = 792$
$M_r = 387.68$	$D_x = 1.484$ Mg m^{-3}
Monoclinic, *C*2/*c*	Mo *K*α radiation, λ = 0.71073 Å
Hall symbol: -C 2yc	Cell parameters from 968 reflections
a = 20.054 (8) Å	θ = 2.2–27.5°
b = 6.299 (2) Å	μ = 1.44 mm^{-1}
c = 14.761 (6) Å	*T* = 173 K
β = 111.500 (6)°	Block, colorless
V = 1734.9 (11) Å^3	0.24 × 0.20 × 0.15 mm
Z = 4	

Data collection

Bruker SMART CCD area-detector diffractometer	1975 independent reflections
Radiation source: sealed tube	1915 reflections with $I > 2\sigma(I)$
graphite	$R_{int} = 0.039$
ω scans	$\theta_{max} = 27.5°$, $\theta_{min} = 3.0°$
Absorption correction: numerical (*SADABS*; Bruker, 1998)	$h = -26\rightarrow19$
$T_{min} = 0.724$, $T_{max} = 0.813$	$k = -8\rightarrow8$
7306 measured reflections	$l = -19\rightarrow19$

Refinement

Refinement on F^2	Primary atom site location: structure-invariant direct methods
Least-squares matrix: full	Secondary atom site location: difference Fourier map
$R[F^2 > 2\sigma(F^2)] = 0.036$	Hydrogen site location: inferred from neighbouring sites
$wR(F^2) = 0.082$	H-atom parameters constrained
$S = 1.03$	$w = 1/[\sigma^2(F_o^2) + (0.030P)^2 + 3.5P]$ where $P = (F_o^2 + 2F_c^2)/3$
1975 reflections	$(\Delta/\sigma)_{max} < 0.001$
114 parameters	$\Delta\rho_{max} = 0.35$ e Å^{-3}
0 restraints	$\Delta\rho_{min} = -0.22$ e Å^{-3}

Special details

Geometry. All e.s.d.'s (except the e.s.d. in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell e.s.d.'s are taken into account individually in the estimation of e.s.d.'s in distances, angles and torsion angles; correlations

between e.s.d.'s in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell e.s.d.'s is used for estimating e.s.d.'s involving l.s. planes.

Refinement. Refinement of F^2 against ALL reflections. The weighted *R*-factor *wR* and goodness of fit *S* are based on F^2, conventional *R*-factors *R* are based on *F*, with *F* set to zero for negative F^2. The threshold expression of $F^2 > 2\,\sigma(F^2)$ is used only for calculating *R*-factors (gt) *etc*. and is not relevant to the choice of reflections for refinement. *R*-factors based on F^2 are statistically about twice as large as those based on *F*, and *R*- factors based on ALL data will be even larger.

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å^2)

	x	*y*	*z*	U_{iso}*/U_{eq}
Zn1	0.0000	0.39350 (5)	0.2500	0.02669 (12)
O1	0.07418 (8)	0.5959 (2)	0.32459 (12)	0.0340 (4)
O2	0.12091 (8)	0.3122 (3)	0.41504 (13)	0.0409 (4)
N1	0.04941 (9)	0.1981 (3)	0.18419 (13)	0.0300 (4)
C1	0.18900 (10)	0.6311 (3)	0.44879 (15)	0.0245 (4)
C2	0.24474 (11)	0.5421 (3)	0.52709 (15)	0.0271 (4)
H2	0.2410	0.3996	0.5457	0.032*
C3	0.19468 (11)	0.8406 (3)	0.42210 (15)	0.0265 (4)
H3	0.1570	0.9028	0.3691	0.032*
C4	0.12371 (11)	0.5003 (3)	0.39400 (15)	0.0271 (4)
C5	0.02091 (13)	0.0111 (4)	0.14623 (17)	0.0343 (5)
H5	−0.0249	−0.0258	0.1465	0.041*
C6	0.05508 (15)	−0.1297 (4)	0.10692 (19)	0.0456 (6)
H6	0.0332	−0.2612	0.0809	0.055*
C7	0.12141 (17)	−0.0777 (5)	0.1057 (2)	0.0539 (8)
H7	0.1460	−0.1720	0.0784	0.065*
C8	0.15136 (16)	0.1135 (5)	0.1447 (2)	0.0543 (8)
H8	0.1971	0.1532	0.1447	0.065*
C9	0.11451 (13)	0.2473 (4)	0.18390 (19)	0.0411 (6)
H9	0.1359	0.3783	0.2115	0.049*

Atomic displacement parameters (Å^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Zn1	0.01866 (18)	0.02270 (19)	0.0321 (2)	0.000	0.00149 (14)	0.000
O1	0.0219 (7)	0.0257 (8)	0.0404 (9)	−0.0005 (6)	−0.0049 (6)	0.0005 (7)
O2	0.0300 (8)	0.0289 (9)	0.0483 (10)	−0.0076 (7)	−0.0041 (7)	0.0063 (7)
N1	0.0251 (9)	0.0318 (10)	0.0317 (10)	0.0023 (7)	0.0087 (7)	0.0032 (8)
C1	0.0182 (9)	0.0249 (10)	0.0265 (10)	−0.0011 (7)	0.0036 (8)	−0.0023 (8)
C2	0.0231 (10)	0.0205 (9)	0.0318 (11)	0.0005 (8)	0.0033 (8)	0.0014 (8)
C3	0.0190 (9)	0.0270 (10)	0.0274 (10)	0.0024 (8)	0.0011 (8)	0.0021 (8)
C4	0.0200 (10)	0.0258 (11)	0.0299 (11)	−0.0003 (8)	0.0025 (8)	−0.0010 (9)
C5	0.0328 (12)	0.0342 (12)	0.0334 (12)	0.0020 (9)	0.0090 (10)	−0.0010 (10)
C6	0.0526 (16)	0.0428 (15)	0.0383 (13)	0.0090 (12)	0.0131 (12)	−0.0037 (11)
C7	0.0598 (19)	0.063 (2)	0.0457 (16)	0.0222 (15)	0.0280 (14)	0.0043 (14)
C8	0.0421 (15)	0.075 (2)	0.0576 (18)	0.0072 (14)	0.0328 (14)	0.0088 (16)
C9	0.0349 (13)	0.0465 (15)	0.0450 (14)	−0.0031 (11)	0.0185 (11)	0.0069 (12)

Geometric parameters (Å, °)

Zn1—O1	1.9621 (15)	C3—C2^{i}	1.384 (3)
Zn1—N1	2.0363 (19)	C3—H3	0.9500
O1—C4	1.286 (2)	C5—C6	1.372 (3)
O2—C4	1.231 (3)	C5—H5	0.9500
N1—C5	1.339 (3)	C6—C7	1.377 (4)
N1—C9	1.343 (3)	C6—H6	0.9500
C1—C3	1.394 (3)	C7—C8	1.374 (4)
C1—C2	1.397 (3)	C7—H7	0.9500
C1—C4	1.507 (3)	C8—C9	1.380 (4)
C2—C3^{i}	1.384 (3)	C8—H8	0.9500
C2—H2	0.9500	C9—H9	0.9500
O1—Zn1—O1^{ii}	98.96 (9)	O2—C4—O1	123.93 (19)
O1—Zn1—N1^{ii}	121.77 (8)	O2—C4—C1	120.10 (18)
O1—Zn1—N1	105.02 (8)	O1—C4—C1	115.94 (18)
O1^{ii}—Zn1—N1	121.77 (8)	N1—C5—C6	122.9 (2)
N1^{ii}—Zn1—N1	105.60 (11)	N1—C5—H5	118.6
C4—O1—Zn1	110.39 (13)	C6—C5—H5	118.6
C5—N1—C9	117.9 (2)	C5—C6—C7	119.1 (3)
C5—N1—Zn1	121.59 (15)	C5—C6—H6	120.4
C9—N1—Zn1	120.36 (17)	C7—C6—H6	120.4
C3—C1—C2	119.33 (19)	C8—C7—C6	118.6 (3)
C3—C1—C4	120.72 (18)	C8—C7—H7	120.7
C2—C1—C4	119.95 (19)	C6—C7—H7	120.7
C3^{i}—C2—C1	120.8 (2)	C7—C8—C9	119.5 (3)
C3^{i}—C2—H2	119.6	C7—C8—H8	120.3
C1—C2—H2	119.6	C9—C8—H8	120.3
C2^{i}—C3—C1	119.91 (19)	N1—C9—C8	122.1 (3)
C2^{i}—C3—H3	120.0	N1—C9—H9	119.0
C1—C3—H3	120.0	C8—C9—H9	119.0

Symmetry codes: (i) −*x*+1/2, −*y*+3/2, −*z*+1; (ii) −*x*, *y*, −*z*+1/2.

Fig. 1

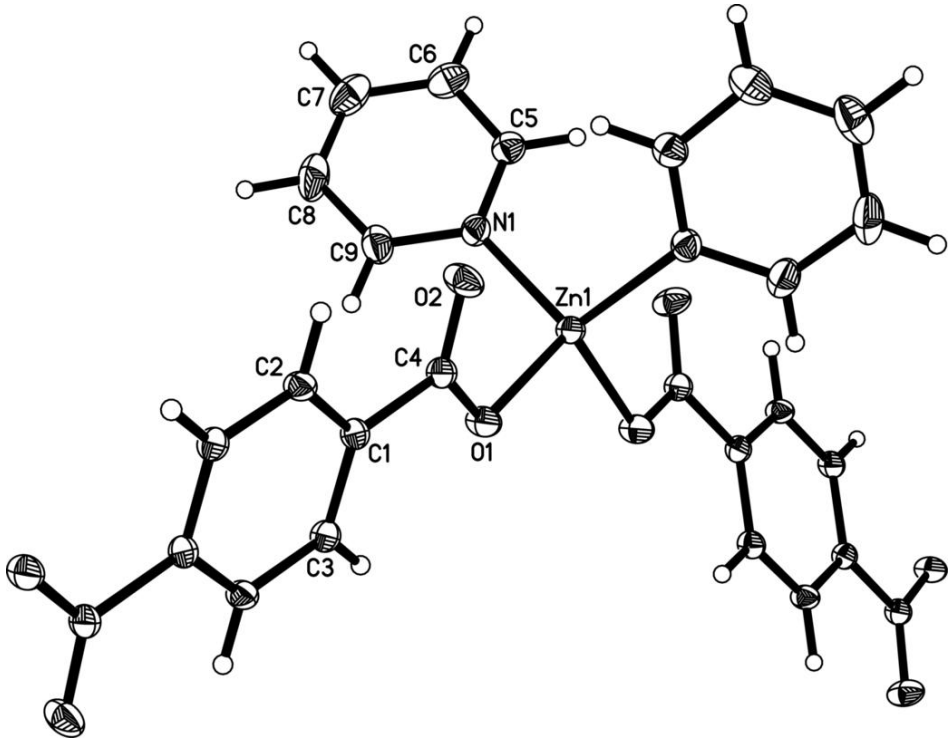
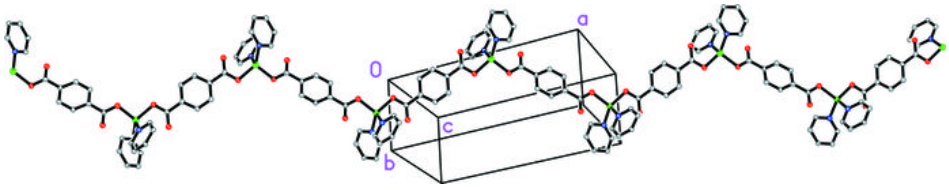


Fig. 2



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(6*S*,7*S*,8*R*,8a*S*)-6-Ethylperhydroindolizine-7,8-diol

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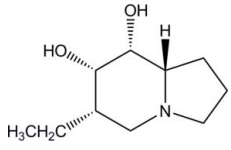
Key indicators: single-crystal X-ray study; T = 298 K; mean σ(C–C) = 0.002 Å; R factor = 0.035; wR factor = 0.099; data-to-parameter ratio = 12.5.

In the title compound, $C_{10}H_{19}NO_2$, the piperidine and pyrrolidine rings of the perhydroindolizine ring system adopt chair and envelope conformations, respectively. In the crystal structure, intermolecular O—H···N and O—H···O hydrogen bonds link the molecules into a chain running along the *a* axis.

Related literature

For indolizine derivatives, see: Bermudez *et al.* (1990); Bonneau *et al.* (2003); Chai *et al.* (2003); Delattre *et al.* (2005); Gundersen *et al.* (2007); Liu *et al.* (2007); Teklu *et al.* (2005); Weide *et al.* (2006). For ring conformations, see: Cremer & Pople (1975); Nardelli (1983). For the synthesis, see: Šafař *et al.* (2010).



Experimental

Crystal data

$C_{10}H_{19}NO_2$
M_r = 185.26
Orthorhombic, $P2_12_12_1$
a = 7.20849 (17) Å
b = 8.83039 (19) Å
c = 15.6656 (4) Å
V = 997.18 (4) Å^3
Z = 4
Mo $K\alpha$ radiation
μ = 0.09 mm^{-1}
T = 298 K
0.51 × 0.29 × 0.09 mm

Data collection

Oxford Diffraction Gemini R CCD diffractometer
Absorption correction: analytical (Clark & Reid, 1995)
T_{min} = 0.950, T_{max} = 0.992
26407 measured reflections
1554 independent reflections
1371 reflections with $I > 2\sigma(I)$
R_{int} = 0.023

Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.035
$wR(F^2)$ = 0.099
S = 1.07
1554 reflections
124 parameters
H atoms treated by a mixture of independent and constrained refinement
$\Delta\rho_{max}$ = 0.17 e Å^{-3}
$\Delta\rho_{min}$ = −0.18 e Å^{-3}

Table 1
Hydrogen-bond geometry (Å, °).

D—H···A	D—H	H···A	D···A	D—H···A
O1—H1*A*···N1^{i}	0.79 (2)	2.104 (19)	2.8619 (16)	160.2 (18)
O12—H12*A*···O1^{i}	0.82 (2)	2.05 (2)	2.8591 (15)	169 (2)

Symmetry code: (i) $x+\frac{1}{2}, -y+\frac{3}{2}, -z+2$.

Data collection: *CrysAlis CCD* (Oxford Diffraction, 2006); cell refinement: *CrysAlis RED* (Oxford Diffraction, 2006); data reduction: *CrysAlis RED*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *DIAMOND* (Brandenburg, 2001); software used to prepare material for publication: *enCIFer* (Allen *et al.*, 2004) and *PLATON* (Spek, 2009).

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Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: IS2552).

References

Allen, F. H., Johnson, O., Shields, G. P., Smith, B. R. & Towler, M. (2004). *J. Appl. Cryst.* **37**, 335–338.
Bermudez, J., Fake, C. S., Joiner, G. F., Joiner, K. A., Km, F. D., Miner, W. D. & Sanger, G. J. (1990). *J. Med. Chem.* **33**, 1924–1929.
Bonneau, R., Collado, D. & Liu, M. T. H. (2003). *J. Photochem. Photobiol. A*, **161**, 43–50.
Brandenburg, K. (2001). *DIAMOND*. Crystal Impact GbR, Bonn, Germany.
Chai, W., Breitenbucher, J. G., Kwok, A., Li, X., Wong, V., Carruthers, N. I., Lovenberg, T. W., Mazur, C., Wilson, S. J., Axe, F. U. & Jones, T. K. (2003). *Bioorg. Med. Chem. Lett.* **13**, 1767–1770.
Clark, R. C. & Reid, J. S. (1995). *Acta Cryst.* A**51**, 887–897.
Cremer, D. & Pople, J. A. (1975). *J. Am. Chem. Soc.* **97**, 1354–1362.
Delattre, F., Woisel, P., Surpateau, G., Cazier, F. & Blach, P. (2005). *Tetrahedron*, **61**, 3939–3945.
Gundersen, L.-L., Charnock, C., Negussie, A. H., Rise, F. & Teklu, S. (2007). *Eur. J. Pharm. Sci.* **30**, 26–30.
Liu, Y., Hu, H.-Y., Liu, Q.-J., Hu, H.-W. & Xu, J.-H. (2007). *Tetrahedron*, **63**, 2024–2033.
Nardelli, M. (1983). *Acta Cryst.* C**39**, 1141–1142.
Oxford Diffraction (2006). *CrysAlis CCD* and *CrysAlis RED*. Oxford Diffraction Ltd, Abingdon, England.
Šafař, P., Žúžiová, J., Marchalín, Š., Prónayová, N., Švorc, Ľ., Vrábel, V., Comesse, S. & Daich, A. (2010). *Tetrahedron Asymmetry*, **21**, 623–630.
Sheldrick, G. M. (2008). *Acta Cryst.* A**64**, 112–122.
Spek, A. L. (2009). *Acta Cryst.* D**65**, 148–155.
Teklu, S., Gundersen, L. L., Larsen, T., Malterud, K. E. & Rise, F. (2005). *Bioorg. Med. Chem.* **13**, 3127–3139.
Weide, T., Arve, L., Prinz, H., Waldmann, H. & Kessler, H. (2006). *Bioorg. Med. Chem. Lett.* **16**, 59–63.

supplementary materials

Acta Cryst. (2010). E**66**, o1666 [**doi:10.1107/S1600536810021240**]

(6*S*,7*S*,8*R*,8a*S*)-6-Ethylperhydroindolizine-7,8-diol

L. Svorc, V. Vrábel, J. Zúziová, S. Marchalín and J. Kozísek

Comment

Bridgehead nitrogen heterocycles are important natural products. Among them, indolizines have received much attention in recent years due to their intriguing molecular structures featured with a 10 *p*-delocalized electrons. They have been extensively examined because of its wide range of potent applications such as biological activities (Bonneau *et al.*, 2003) and a fluorescent probe (Delattre *et al.*, 2005). These molecules have found various pharmaceutical applications as anti-tuberculosis agents (Gundersen *et al.*, 2007), histamine H3 receptor antagonists (Chai *et al.*, 2003), 5-HT3 receptor antagonists (Bermudez *et al.*, 1990), associated with many infectious diseases (Weide *et al.*, 2006) and as 15-lipoxygenase inhibitors (Teklu *et al.*, 2005). Indolizines demonstrate also antifungal, antimycobacterial, antiherpes and antineociceptive properties (Liu *et al.*, 2007). Thus, there is a growing interest in the synthesis and study of crystal and molecular structures of indolizine derivatives.

Based on these facts and in continuation of our interest in developing simple and efficient route for the synthesis of novel monohydroxylated indolizine derivatives, we report here the synthesis, molecular and crystal structure of the title compound, (I). The absolute configuration was established by synthesis and is depicted in the scheme and figure. The expected stereochemistry of atoms C5, C6, C7 and C8 was confirmed as S, R, S and S, respectively (Fig. 1). The central six-membered ring is not planar and adopts a chair conformation (Cremer & Pople, 1975). A calculation of least-squares planes shows that this ring is puckered in such a manner that the four atoms C6, C7, C9 and N1 are coplanar to within 0.019 (2) Å, while atoms C5 and C8 are displaced from this plane on opposite sides, with out-of-plane displacements of -0.720 (2) and 0.636 (1) Å, respectively. In the molecule, the pyrrolidine ring N1/C2–C5 exhibits an envelope conformation with envelope on atom N1 (Nardelli, 1983). The displacement of atom N1 from the mean plane of the remaining four atoms is 0.625 (2) Å. The N1—C2, N1—C5 and N1—C9 bonds are approximately equivalent. Atom N1 is sp^3-hybridized, as evidenced by the sum of the valence angles around it [327.05 (2)°]. Intermolecular O—H···N and O—H···O hydrogen bonds link the neighbouring molecules of (I) into extended chains, which run parallel to the a axis (Fig. 2) and help to stabilize the crystal structure of the compound. Atom N1 (O1) participates as acceptor and atom O1 (O12) as donator in these intermolecular hydrogen bonds.

Experimental

The title compound (6*S*,7*S*,8*R*,8aS)-6-ethylperhydroindolizine-7,8-diol was prepared according literature procedures of Šafař *et al.* (2010).

Refinement

Hydroxyl H atoms were located in a difference Fourier map and their positions were refined freely, with $U_{iso}(H) = 1.2U_{eq}(O)$. Other H atoms were placed in geometrically idealized positions and constrained to ride on their parent atoms, with C—H distances in the range 0.93–0.98 Å, and with $U_{iso}(H) = 1.2U_{eq}(C)$. The absolute configuration could not be reliably determ-

ined for this compound using Mo radiation, and has been assigned according to the synthesis. 1061 total Friedel pairs have been merged.

Figures

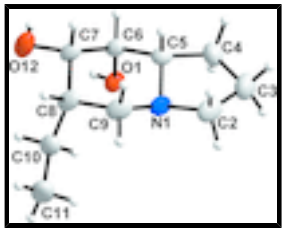


Fig. 1. Molecular structure of (I) with the atomic numbering scheme. Displacement ellipsoids are drawn at the 50% probability level.

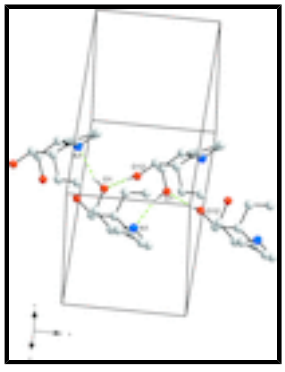


Fig. 2. A partial packing diagram of the molecule of (I), showing a molecular chain along the *a* axis. Hydrogen bonds are indicated by dashed lines. H atoms not involved in the hydrogen bonds have been omitted.

(6*S*,7*S*,8*R*,8a*S*)-6-Ethylperhydroindolizine-7,8-diol

Crystal data

$C_{10}H_{19}NO_2$	$F(000) = 408$
$M_r = 185.26$	$D_x = 1.234$ Mg m^{-3}
Orthorhombic, $P2_12_12_1$	Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å
Hall symbol: P 2ac 2ab	Cell parameters from 17389 reflections
$a = 7.20849$ (17) Å	$\theta = 3.5$–$29.5°$
$b = 8.83039$ (19) Å	$\mu = 0.09$ mm^{-1}
$c = 15.6656$ (4) Å	$T = 298$ K
$V = 997.18$ (4) Å^3	Prism, white
$Z = 4$	0.51 × 0.29 × 0.09 mm

Data collection

Oxford Diffraction Gemini R CCD diffractometer	1554 independent reflections
Radiation source: fine-focus sealed tube	1371 reflections with $I > 2\sigma(I)$
graphite	$R_{int} = 0.023$
Detector resolution: 10.4340 pixels mm^{-1}	$\theta_{max} = 29.5°$, $\theta_{min} = 3.5°$
Rotation method data acquisition using ω and φ scans	$h = -9 \rightarrow 9$
Absorption correction: analytical (Clark & Reid, 1995)	$k = -11 \rightarrow 12$

T_{min} = 0.950, T_{max} = 0.992
26407 measured reflections

l = −21→20

Refinement

Refinement on F^2	Primary atom site location: structure-invariant direct methods
Least-squares matrix: full	Secondary atom site location: difference Fourier map
$R[F^2 > 2\sigma(F^2)]$ = 0.035	Hydrogen site location: inferred from neighbouring sites
$wR(F^2)$ = 0.099	H atoms treated by a mixture of independent and constrained refinement
S = 1.07	$w = 1/[\sigma^2(F_o^2) + (0.0669P)^2 + 0.0442P]$ where $P = (F_o^2 + 2F_c^2)/3$
1554 reflections	$(\Delta/\sigma)_{max} < 0.001$
124 parameters	$\Delta\rho_{max}$ = 0.17 e Å^{-3}
0 restraints	$\Delta\rho_{min}$ = −0.18 e Å^{-3}

Special details

Experimental. (face-indexed; Oxford Diffraction, 2006)

Geometry. All esds (except the esd in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell esds are taken into account individually in the estimation of esds in distances, angles and torsion angles; correlations between esds in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell esds is used for estimating esds involving l.s. planes.

Refinement. Refinement of F^2 against ALL reflections. The weighted *R*-factor wR and goodness of fit *S* are based on F^2, conventional *R*-factors *R* are based on *F*, with *F* set to zero for negative F^2. The threshold expression of $F^2 > \sigma(F^2)$ is used only for calculating *R*-factors(gt) etc. and is not relevant to the choice of reflections for refinement. *R*-factors based on F^2 are statistically about twice as large as those based on *F*, and *R*- factors based on ALL data will be even larger.

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å^2)

	x	*y*	*z*	U_{iso}*/U_{eq}
C2	0.3886 (2)	0.5154 (2)	0.85244 (11)	0.0478 (4)
H2B	0.2624	0.5248	0.8732	0.057*
H2A	0.4043	0.4161	0.8270	0.057*
C3	0.4326 (2)	0.6396 (3)	0.78828 (12)	0.0544 (5)
H3B	0.3442	0.7220	0.7931	0.065*
H3A	0.4284	0.6003	0.7305	0.065*
C4	0.6291 (2)	0.6945 (2)	0.81031 (10)	0.0424 (4)
H4B	0.7087	0.6928	0.7604	0.051*
H4A	0.6266	0.7964	0.8334	0.051*
C5	0.69456 (19)	0.58078 (16)	0.87717 (9)	0.0311 (3)
H5A	0.7393	0.4907	0.8470	0.037*
C6	0.84249 (18)	0.62711 (14)	0.94069 (9)	0.0277 (3)
H6A	0.9566	0.6503	0.9093	0.033*
C7	0.8790 (2)	0.49092 (15)	0.99892 (9)	0.0314 (3)

H7A	0.9272	0.4098	0.9624	0.038*
C8	0.7028 (2)	0.42864 (16)	1.04186 (10)	0.0346 (3)
H8A	0.7353	0.3283	1.0640	0.042*
C9	0.5529 (2)	0.40321 (17)	0.97423 (11)	0.0393 (4)
H9B	0.5893	0.3199	0.9375	0.047*
H9A	0.4376	0.3756	1.0021	0.047*
C10	0.6369 (2)	0.52143 (19)	1.11850 (10)	0.0401 (4)
H10B	0.7403	0.5354	1.1573	0.048*
H10A	0.5987	0.6207	1.0987	0.048*
C11	0.4772 (3)	0.4499 (3)	1.16706 (12)	0.0624 (6)
H11C	0.4429	0.5140	1.2140	0.075*
H11B	0.5147	0.3527	1.1884	0.075*
H11A	0.3730	0.4377	1.1295	0.075*
N1	0.52295 (16)	0.53891 (14)	0.92216 (8)	0.0319 (3)
O1	0.78542 (14)	0.75959 (11)	0.98549 (6)	0.0301 (2)
H1A	0.869 (3)	0.7981 (19)	1.0102 (12)	0.036*
O12	1.01533 (16)	0.51868 (14)	1.06187 (8)	0.0450 (3)
H12A	1.085 (3)	0.582 (2)	1.0417 (14)	0.054*

Atomic displacement parameters (Å^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
C2	0.0338 (7)	0.0584 (10)	0.0512 (9)	−0.0026 (8)	−0.0100 (7)	−0.0214 (8)
C3	0.0466 (9)	0.0696 (12)	0.0471 (9)	0.0076 (9)	−0.0156 (8)	−0.0088 (9)
C4	0.0475 (9)	0.0487 (8)	0.0310 (7)	0.0031 (8)	−0.0053 (7)	−0.0016 (6)
C5	0.0280 (6)	0.0318 (6)	0.0334 (6)	0.0016 (6)	0.0015 (5)	−0.0074 (5)
C6	0.0237 (6)	0.0254 (6)	0.0341 (6)	−0.0005 (5)	0.0016 (5)	−0.0009 (5)
C7	0.0242 (6)	0.0264 (6)	0.0437 (8)	0.0013 (5)	0.0007 (5)	0.0006 (5)
C8	0.0282 (7)	0.0241 (6)	0.0515 (8)	0.0003 (6)	0.0022 (6)	0.0072 (6)
C9	0.0323 (7)	0.0281 (7)	0.0575 (9)	−0.0072 (6)	0.0030 (7)	−0.0038 (6)
C10	0.0360 (7)	0.0458 (8)	0.0385 (7)	0.0043 (7)	0.0019 (6)	0.0102 (6)
C11	0.0378 (8)	0.0995 (16)	0.0500 (9)	0.0001 (10)	0.0066 (8)	0.0219 (11)
N1	0.0242 (5)	0.0326 (6)	0.0387 (6)	−0.0031 (5)	−0.0028 (5)	−0.0084 (5)
O1	0.0274 (5)	0.0244 (4)	0.0385 (5)	−0.0001 (4)	−0.0056 (4)	−0.0038 (4)
O12	0.0305 (6)	0.0498 (7)	0.0548 (7)	−0.0060 (5)	−0.0097 (5)	0.0156 (6)

Geometric parameters (Å, °)

C2—N1	1.4742 (18)	C7—C8	1.5386 (19)
C2—C3	1.521 (3)	C7—H7A	0.9800
C2—H2B	0.9700	C8—C10	1.529 (2)
C2—H2A	0.9700	C8—C9	1.530 (2)
C3—C4	1.536 (2)	C8—H8A	0.9800
C3—H3B	0.9700	C9—N1	1.465 (2)
C3—H3A	0.9700	C9—H9B	0.9700
C4—C5	1.526 (2)	C9—H9A	0.9700
C4—H4B	0.9700	C10—C11	1.518 (2)
C4—H4A	0.9700	C10—H10B	0.9700
C5—N1	1.4710 (17)	C10—H10A	0.9700

C5—C6	1.5148 (18)	C11—H11C	0.9600
C5—H5A	0.9800	C11—H11B	0.9600
C6—O1	1.4250 (16)	C11—H11A	0.9600
C6—C7	1.5322 (18)	O1—H1A	0.79 (2)
C6—H6A	0.9800	O12—H12A	0.82 (2)
C7—O12	1.4137 (18)		
N1—C2—C3	104.54 (13)	O12—C7—H7A	106.7
N1—C2—H2B	110.8	C6—C7—H7A	106.7
C3—C2—H2B	110.8	C8—C7—H7A	106.7
N1—C2—H2A	110.8	C10—C8—C9	113.74 (12)
C3—C2—H2A	110.8	C10—C8—C7	114.10 (12)
H2B—C2—H2A	108.9	C9—C8—C7	109.43 (12)
C2—C3—C4	105.74 (14)	C10—C8—H8A	106.3
C2—C3—H3B	110.6	C9—C8—H8A	106.3
C4—C3—H3B	110.6	C7—C8—H8A	106.3
C2—C3—H3A	110.6	N1—C9—C8	111.68 (11)
C4—C3—H3A	110.6	N1—C9—H9B	109.3
H3B—C3—H3A	108.7	C8—C9—H9B	109.3
C5—C4—C3	103.41 (15)	N1—C9—H9A	109.3
C5—C4—H4B	111.1	C8—C9—H9A	109.3
C3—C4—H4B	111.1	H9B—C9—H9A	107.9
C5—C4—H4A	111.1	C11—C10—C8	113.97 (15)
C3—C4—H4A	111.1	C11—C10—H10B	108.8
H4B—C4—H4A	109.0	C8—C10—H10B	108.8
N1—C5—C6	110.19 (11)	C11—C10—H10A	108.8
N1—C5—C4	103.54 (12)	C8—C10—H10A	108.8
C6—C5—C4	119.40 (13)	H10B—C10—H10A	107.7
N1—C5—H5A	107.7	C10—C11—H11C	109.5
C6—C5—H5A	107.7	C10—C11—H11B	109.5
C4—C5—H5A	107.7	H11C—C11—H11B	109.5
O1—C6—C5	110.00 (11)	C10—C11—H11A	109.5
O1—C6—C7	113.62 (11)	H11C—C11—H11A	109.5
C5—C6—C7	107.46 (11)	H11B—C11—H11A	109.5
O1—C6—H6A	108.5	C9—N1—C5	110.39 (11)
C5—C6—H6A	108.5	C9—N1—C2	113.21 (12)
C7—C6—H6A	108.5	C5—N1—C2	103.45 (11)
O12—C7—C6	113.49 (11)	C6—O1—H1A	112.0 (13)
O12—C7—C8	109.31 (11)	C7—O12—H12A	106.1 (15)
C6—C7—C8	113.52 (12)		
N1—C2—C3—C4	18.32 (17)	O12—C7—C8—C9	178.22 (11)
C2—C3—C4—C5	8.30 (17)	C6—C7—C8—C9	50.40 (15)
C3—C4—C5—N1	−32.09 (15)	C10—C8—C9—N1	76.70 (16)
C3—C4—C5—C6	−154.99 (13)	C7—C8—C9—N1	−52.21 (16)
N1—C5—C6—O1	−63.72 (14)	C9—C8—C10—C11	60.38 (17)
C4—C5—C6—O1	55.85 (16)	C7—C8—C10—C11	−173.12 (12)
N1—C5—C6—C7	60.44 (14)	C8—C9—N1—C5	60.58 (15)
C4—C5—C6—C7	−179.99 (12)	C8—C9—N1—C2	176.00 (12)
O1—C6—C7—O12	−58.02 (16)	C6—C5—N1—C9	−65.22 (14)

C5—C6—C7—O12	−179.95 (11)	C4—C5—N1—C9	165.98 (11)
O1—C6—C7—C8	67.60 (15)	C6—C5—N1—C2	173.37 (12)
C5—C6—C7—C8	−54.33 (14)	C4—C5—N1—C2	44.57 (14)
O12—C7—C8—C10	49.50 (16)	C3—C2—N1—C9	−158.49 (13)
C6—C7—C8—C10	−78.32 (15)	C3—C2—N1—C5	−39.00 (16)

Hydrogen-bond geometry (Å, °)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
O1—H1A···N1^{i}	0.79 (2)	2.104 (19)	2.8619 (16)	160.2 (18)
O12—H12A···O1^{i}	0.82 (2)	2.05 (2)	2.8591 (15)	169 (2)

Symmetry codes: (i) *x*+1/2, −*y*+3/2, −*z*+2.

Fig. 1

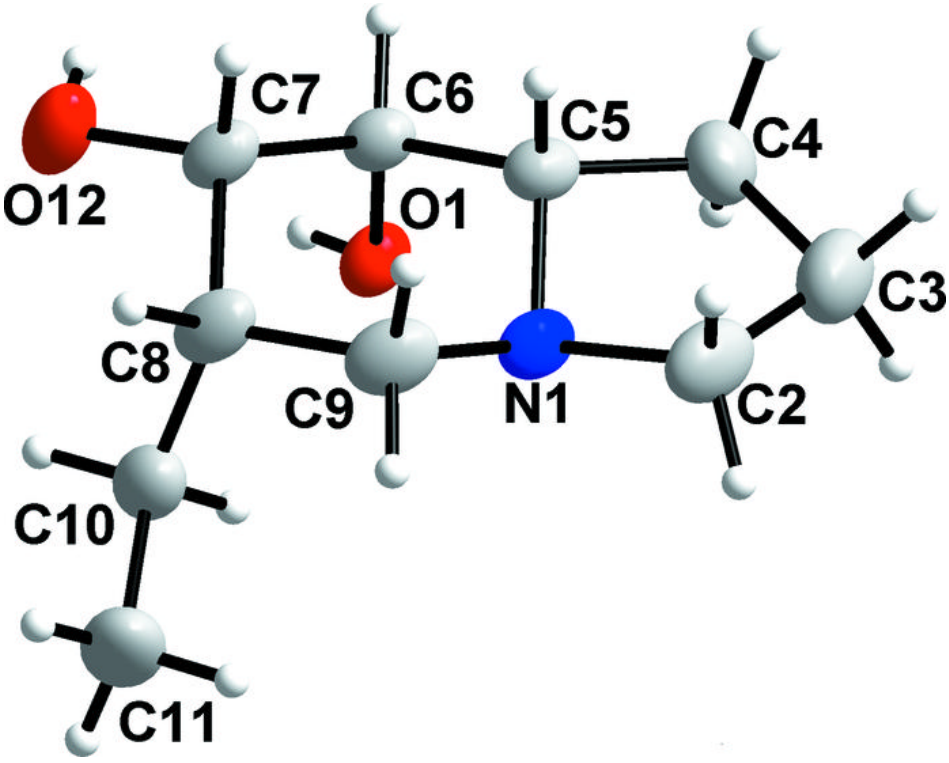
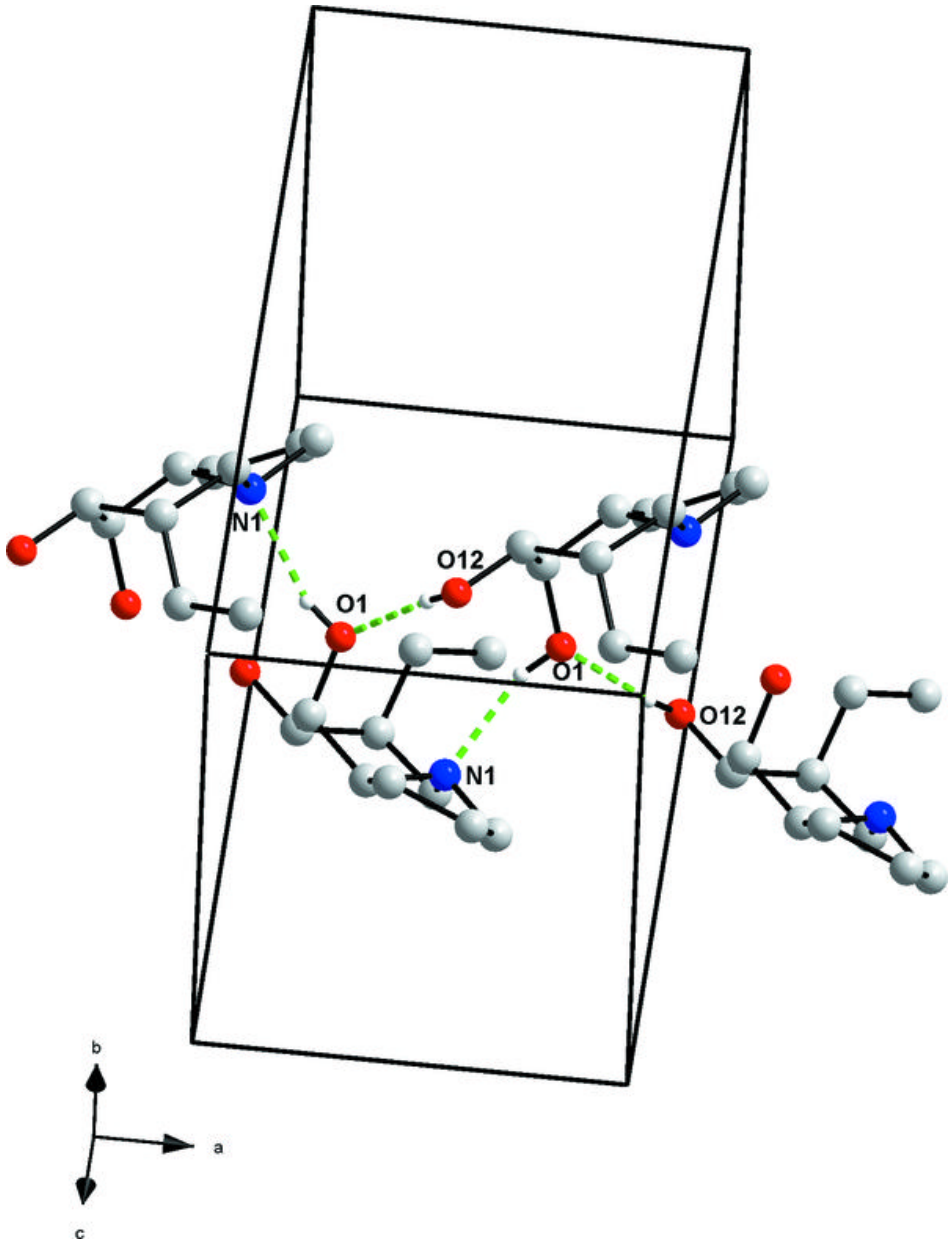


Fig. 2



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4-{(*E*)-[2-(4-Iodobutoxy)benzylidene]amino}-1,5-dimethyl-2-phenyl-1*H*-pyrazol-3(2*H*)-one

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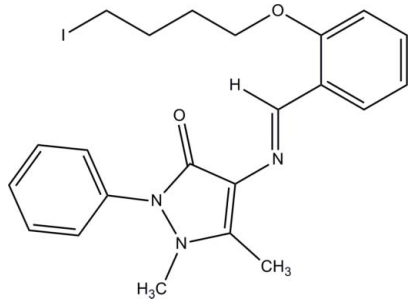
Key indicators: single-crystal X-ray study; T = 100 K; mean σ(C–C) = 0.003 Å; R factor = 0.042; wR factor = 0.159; data-to-parameter ratio = 37.8.

The title Schiff base compound, $C_{22}H_{24}IN_3O_2$, adopts an E configuration about the central C=N bond. The pyrazolone ring makes a dihedral angle of 49.68 (10)° with its attached phenyl ring. The phenolate plane makes dihedral angles of 16.78 (9) and 50.54 (9)°, respectively, with the pyrazolone ring and the terminal phenyl ring. An intramolecular C—H···O hydrogen bond generates an S(6) ring motif. In the crystal structure, an intermolecular C—H···O hydrogen bond is also observed.

Related literature

For background to and applications of Schiff bases, see: Tarafder *et al.* (2002); Silver & Soderlund (2005); Vicini *et al.* (2003); Ozdemir *et al.* (2007); Joshi *et al.* (2004). For background to and the biological activity of 4-aminoantipyrene and its derivatives, see: Jain *et al.* (2003); Filho *et al.* (1998); Sondhi *et al.* (1999); Mishra (1999); Sondhi *et al.* (2001). For related structures, see: Eryigit & Kendi (1998); Manikandan *et al.* (2000). For hydrogen-bond motifs, see: Bernstein *et al.* (1995). For the stability of the temperature controller used in the data collection, see: Cosier & Glazer (1986).



Experimental

Crystal data

$C_{22}H_{24}IN_3O_2$
M_r = 489.34
Monoclinic, $P2_1/c$
a = 11.5235 (10) Å
b = 16.4156 (14) Å
c = 11.2828 (9) Å
β = 94.010 (2)°
V = 2129.1 (3) Å^3
Z = 4
Mo $K\alpha$ radiation
μ = 1.53 mm^{-1}
T = 100 K
0.41 × 0.34 × 0.29 mm

Data collection

Bruker APEXII DUO CCD area-detector diffractometer
Absorption correction: multi-scan (*SADABS*; Bruker, 2009)
T_{min} = 0.571, T_{max} = 0.663
36214 measured reflections
9632 independent reflections
7935 reflections with $I > 2\sigma(I)$
R_{int} = 0.025

Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.042
$wR(F^2)$ = 0.159
S = 1.05
9632 reflections
255 parameters
H-atom parameters constrained
$\Delta\rho_{max}$ = 1.26 e Å^{-3}
$\Delta\rho_{min}$ = −1.68 e Å^{-3}

Table 1
Hydrogen-bond geometry (Å, °).

D—H···A	D—H	H···A	D···A	D—H···A
C10—H10A···O1	0.93	2.30	2.995 (2)	132
C17—H17B···O1^{i}	0.97	2.42	3.193 (2)	137

Symmetry code: (i) $x, -y+\frac{1}{2}, z-\frac{1}{2}$.

Data collection: *APEX2* (Bruker, 2009); cell refinement: *SAINT* (Bruker, 2009); data reduction: *SAINT*; program(s) used to solve structure: *SHELXTL* (Sheldrick, 2008); program(s) used to refine structure: *SHELXTL*; molecular graphics: *SHELXTL*; software used to prepare material for publication: *SHELXTL* and *PLATON* (Spek, 2009).

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Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: IS2554).

‡ Thomson Reuters ResearcherID: A-3561-2009.
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References

Bernstein, J., Davis, R. E., Shimoni, L. & Chang, N.-L. (1995). *Angew. Chem. Int. Ed. Engl.* **34**, 1555–1573.

Bruker (2009). *APEX2*, *SAINT* and *SADABS*. Bruker AXS Inc., Madison, Wisconsin, USA.

Cosier, J. & Glazer, A. M. (1986). *J. Appl. Cryst.* **19**, 105–107.

Eryigit, R. & Kendi, E. (1998). *J. Chem. Crystallogr.* **28**, 145–147.

Filho, V. C., Correa, R., Vaz, Z., Calixto, J. B., Nunes, R. J., Pinheiro, T. R., Andrcopulo, A. D. & Yunes, R. A. (1998). *Farmaco*, **53**, 55–58.

Jain, S. C., Sinha, S., Bhagat, S., Errington, W. & Olsen, C. E. (2003). *Synth. Commun.* **33**, 563–577.

Joshi, S., Khosla, N. & Tiwari, P. (2004). *Bioorg. Med. Chem.* **12**, 571–576.

Manikandan, P., Justin Thomas, K. R. & Manoharan, P. T. (2000). *Acta Cryst.* C**56**, 308–309.

Mishra, A. P. (1999). *J. Indian Chem. Soc.* **76**, 35–37.

Ozdemir, A., Turan-Zitouni, G., Kaplancikli, Z., Revial, G. & Guven, K. (2007). *Eur. J. Med.* **42**, 403–409.

Sheldrick, G. M. (2008). *Acta Cryst.* A**64**, 112–122.

Silver, K. & Soderlund, D. M. (2005). *Neuro Toxicol.* **26**, 397–406.

Sondhi, S. M., Sharma, V. K., Verma, R. P., Singhal, N., Shukla, R., Raghubir, R. & Dubey, M. P. (1999). *Synthesis*, pp. 878–884.

Sondhi, S. M., Singhal, N., Verma, R. P., Arora, S. K. & Dastidar, S. G. (2001). *Indian J. Chem. Sect. B*, **40**, 113–119.

Spek, A. L. (2009). *Acta Cryst.* D**65**, 148–155.

Tarafder, M. T., Kasbollah, A., Saravan, N., Crouse, K. A., Ali, A. M. & Tin, O. K. (2002). *J. Biochem. Mol. Biol. Biophys.* **6**, 85–91.

Vicini, P., Geronikaki, A., Incerti, M., Busonera, B., Poni, G., Kabras, C. A. & Colla, P. L. (2003). *Bioorg. Med. Chem.* **11**, 4785–4789.

supplementary materials

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4-{(*E*)-[2-(4-Iodobutoxy)benzylidene]amino}-1,5-dimethyl-2-phenyl-1*H*-pyrazol-3(2*H*)-one

H.-K. Fun, M. Hemamalini, A. M. Asiri and S. A. Khan

Comment

Schiff bases are generally synthesized from the condensation of primary amines and active carbonyl group. Various heterocyclic ring containing Schiff bases were reported to possess cytotoxic (Tarafder *et al.*, 2002), anticonvulsant (Silver & Soderlund, 2005), antiproliferative (Vicini *et al.*, 2003), anticancer and antifungal activities (Ozdemir *et al.*, 2007). It's also used as ligands for the complexes synthesis (Joshi *et al.*, 2004). As evident from the literature, it was noted that a lot of research has been carried out on Schiff bases but no work has been done on the long chain Schiff base. 4-Aminoantipyrene, which contain pyrazolone ring, is an important compound in the class analgesic agent in otic solutions in combination with other analgesic such as benzocaine and phenylephrine. Pyrazolone is a five-membered lactam ring compound containing two N atoms and ketone in the same molecule. Lactam structure is an active nucleus in pharmacological activity, especially in the class of nonsteroidal antiinflammatory agents used in the treatment of arthritis and other musculo skeletal and joint disorders. Pyrazolone derivatives, as lactam structure related compounds, are also widely used in preparing dyes and pigments. 4-Aminoantipyrene and its derivatives have potential biological activities (Jain *et al.*, 2003). Analgesic and antiinflammatory activities of the 4-aminoantipyrene complexes were extensively studied and reported (Filho *et al.*, 1998; Sondhi *et al.*, 1999). Apart from that, antimicrobial and anticancer activity of the 4-aminoantipyrine derivatives and their metal complexes caught the attention of many researchers during last decade (Mishra, 1999; Sondhi *et al.*, 2001). In this paper we report the synthesis and the crystal structure of a mono Schiff base bearing butyl iodide side chain. It is noteworthy that the alkylating agent used in this reaction is dibromo butyl, and after obtaining the *O*-alkylation product, the charge transfer catalyst used caused the free bromide atom to be substituted by an iodide atom.

The title compound (I) is shown in Fig. 1. The molecule adopts a trans configuration about the central C10═N3 double bond. The C—N bond lengths of N1—C6 [1.422 (2) Å], N1—C9 [1.398 (2) Å], N2—C21 [1.459 (3) Å], N2—C7 [1.365 (2) Å] and N3—C8 [1.389 (2) Å] are normal for C—N single-bond distances. The distance between C10—N3 [1.290 (2) Å] is typical for a C═ N double-bond distance. These bonds are comparable with those in *N*-(1*H*-benzoimidazol-2-ylmethyl)-*N*-(2,6-dichlorophenyl) amine (Eryigit & Kendi, 1998). The N1—N2 [1.403 (2) Å] single-bond length is comparable with that in 2,6-bis(3,5-dimethylpyrazol-1-ylmethyl)pyridine (Manikandan *et al.*, 2000).

Atom O1 deviates from the pyrazoline mean plane by 0.028 (1) Å. The pyrazolone ring (C7–C9/N1/N2) is almost planar, with maximum deviation of 0.045 (2) Å for atom N2. It makes a dihedral angle of 49.68 (10)° with its attached phenyl ring (C1–C6). The phenolate residue (C11–C16/O2) is essentially planar, with maximum deviation of 0.031 (2) Å for O2. This plane makes dihedral angles of 16.78 (9) and 50.54 (9)°, respectively, with the pyrazolone ring (C7–C9/N1/N2) and the terminal (C1–C6) phenyl ring. The N2-N1-C6-C5 and C1-C6-N1-C9 torsion angles are -147.45 (18) and -116.1 (2)°, respectively.

In the crystal structure (Fig. 2), intramolecular C10—H10A···O1 hydrogen bond interactions generate an *S*(6) ring motif (Bernstein *et al.*, 1995). The crystal packing is consolidated by weak non-classical intermolecular C17—H17B···O1 hydrogen bonds (Table 1). The combination of both intra and intermolecular C—H···O hydrogen bonds stabilize the crystal

structure. There exists an unusual short contact between atoms I1 and C8 with a distance of 3.3606 (17) Å, which is shorter than the sum of their van der Waals radii.

Experimental

The title compound was synthesized by the reaction of mono Schiff base (1 g, 0.0032 mol) with dibromo butane (0.0016 mol) in the presence of freshly heated K_2CO_3 (0.0097 mol) and tetrabutylamonium iodide (PTC) (0.0004 mol) in dry acetone with continuous stirring at 40 °C for 8h. After the completion of the reaction, the product obtained was purified by passing through silica-gel column (60-120 mesh) and further crystallized from methanol. Yield: 65 %; m. p. 136 °C. IR (KBr) ν_{max} cm^{-1}: 3014 (C–H aromatic), 1666 (C═O), 1571 (HC═N), 1299 (C–O), 1108 (C–N). ^{1}H-NMR ($CDCl_3$) δ: 10.13 (s, 1H, C–H olefinic), 8.22-6.96 (m, 9H, C–H aromatic), 3.57 (s, O–CH_2CH_2), 3.33 (s, N–CH_3), 2.92 (s, I–CH_2), 2.22 (s,-CH_3), 2.11 (s, 2×CH_2).

Refinement

All hydrogen atoms were positioned geometrically (C–H = 0.93–0.97 Å) and were refined using a riding model, with U_{iso}(H) = 1.2 or 1.5U_{eq}(C). A rotating group model was used for the methyl group. The highest peak of 1.26 eÅ^3 was found at a distance of 0.70 Å from I1 and the deepest hole of -1.68 eÅ^3 was at a distance of 0.54 Å from I1.

Figures

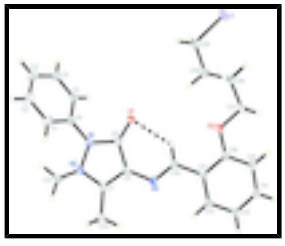


Fig. 1. The asymmetric unit of the title compound, showing 50% probability displacement ellipsoids and the atom-numbering scheme. An intramolecular hydrogen bond is shown as dashed line.

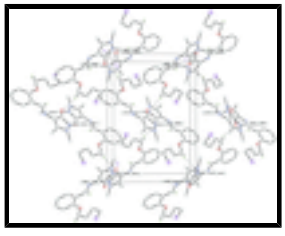


Fig. 2. The crystal packing of the title compound, showing hydrogen-bonded (dashed lines) network. H atoms not involved in the hydrogen bond interactions are omitted for clarity.

4-{(*E*)-[2-(4-Iodobutoxy)benzylidene]amino}- 1,5-dimethyl-2-phenyl-1*H*-pyrazol-3(2*H*)-one

Crystal data

$C_{22}H_{24}IN_3O_2$	$F(000) = 984$
$M_r = 489.34$	$D_x = 1.527$ Mg m^{-3}
Monoclinic, $P2_1/c$	Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å
Hall symbol: -P 2ybc	Cell parameters from 9944 reflections

a = 11.5235 (10) Å	θ = 2.7–35.4°
b = 16.4156 (14) Å	μ = 1.53 mm^{-1}
c = 11.2828 (9) Å	T = 100 K
β = 94.010 (2)°	Blcok, yellow
V = 2129.1 (3) Å^3	0.41 × 0.34 × 0.29 mm
Z = 4	

Data collection

Bruker APEXII DUO CCD area-detector diffractometer	9632 independent reflections
Radiation source: fine-focus sealed tube	7935 reflections with $I > 2\sigma(I)$
graphite	R_{int} = 0.025
φ and ω scans	θ_{max} = 35.6°, θ_{min} = 2.2°
Absorption correction: multi-scan (*SADABS*; Bruker, 2009)	h = −16→18
T_{min} = 0.571, T_{max} = 0.663	k = −26→26
36214 measured reflections	l = −17→18

Refinement

Refinement on F^2	Primary atom site location: structure-invariant direct methods
Least-squares matrix: full	Secondary atom site location: difference Fourier map
$R[F^2 > 2\sigma(F^2)]$ = 0.042	Hydrogen site location: inferred from neighbouring sites
$wR(F^2)$ = 0.159	H-atom parameters constrained
S = 1.05	$w = 1/[\sigma^2(F_o^2) + (0.1027P)^2 + 1.5532P]$ where $P = (F_o^2 + 2F_c^2)/3$
9632 reflections	$(\Delta/\sigma)_{max}$ = 0.001
255 parameters	$\Delta\rho_{max}$ = 1.26 e Å^{-3}
0 restraints	$\Delta\rho_{min}$ = −1.68 e Å^{-3}

Special details

Experimental. The crystal was placed in the cold stream of an Oxford Cryosystems Cobra open-flow nitrogen cryostat (Cosier & Glazer, 1986) operating at 100.0 (1) K.

Geometry. All s.u.'s (except the s.u. in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell s.u.'s are taken into account individually in the estimation of s.u.'s in distances, angles and torsion angles; correlations between s.u.'s in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell s.u.'s is used for estimating s.u.'s involving l.s. planes.

Refinement. Refinement of F^2 against ALL reflections. The weighted R-factor wR and goodness of fit S are based on F^2, conventional R-factors R are based on F, with F set to zero for negative F^2. The threshold expression of $F^2 > 2\sigma(F^2)$ is used only for calculating R-factors(gt) etc. and is not relevant to the choice of reflections for refinement. R-factors based on F^2 are statistically about twice as large as those based on F, and R- factors based on ALL data will be even larger.

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters ($Å^2$)

	x	*y*	*z*	U_{iso}*/U_{eq}
I1	0.290561 (14)	0.362436 (10)	0.802978 (17)	0.03475 (7)
O1	0.68399 (13)	0.05872 (8)	0.94462 (12)	0.0192 (2)
O2	0.71122 (14)	0.22745 (9)	0.66181 (13)	0.0206 (2)
N1	0.76696 (14)	−0.05557 (10)	1.03829 (14)	0.0182 (3)
N2	0.87138 (14)	−0.09878 (10)	1.03161 (15)	0.0200 (3)
N3	0.89080 (14)	0.03071 (9)	0.78003 (13)	0.0163 (2)
C1	0.78638 (19)	−0.05051 (15)	1.25448 (18)	0.0266 (4)
H1A	0.8669	−0.0531	1.2531	0.032*
C2	0.7339 (2)	−0.04626 (17)	1.36239 (19)	0.0315 (5)
H2A	0.7798	−0.0461	1.4336	0.038*
C3	0.6135 (2)	−0.04230 (14)	1.3637 (2)	0.0275 (4)
H3A	0.5791	−0.0395	1.4357	0.033*
C4	0.54450 (18)	−0.04253 (12)	1.25739 (19)	0.0232 (3)
H4A	0.4640	−0.0392	1.2586	0.028*
C5	0.59526 (17)	−0.04769 (11)	1.14967 (18)	0.0199 (3)
H5A	0.5492	−0.0490	1.0786	0.024*
C6	0.71592 (17)	−0.05082 (11)	1.14923 (16)	0.0186 (3)
C7	0.92082 (16)	−0.07340 (11)	0.93152 (15)	0.0172 (3)
C8	0.85924 (15)	−0.00877 (10)	0.88180 (15)	0.0156 (3)
C9	0.75980 (16)	0.00540 (10)	0.95158 (15)	0.0161 (3)
C10	0.82737 (16)	0.09014 (10)	0.73798 (15)	0.0166 (3)
H10A	0.7665	0.1092	0.7803	0.020*
C11	0.85006 (16)	0.12799 (10)	0.62451 (15)	0.0160 (3)
C12	0.93106 (16)	0.09552 (11)	0.55089 (16)	0.0184 (3)
H12A	0.9768	0.0516	0.5775	0.022*
C13	0.94457 (18)	0.12744 (12)	0.43891 (17)	0.0209 (3)
H13A	0.9995	0.1057	0.3912	0.025*
C14	0.87488 (18)	0.19228 (12)	0.39885 (16)	0.0210 (3)
H14A	0.8814	0.2124	0.3226	0.025*
C15	0.79573 (17)	0.22751 (11)	0.47051 (16)	0.0195 (3)
H15A	0.7510	0.2717	0.4432	0.023*
C16	0.78371 (16)	0.19599 (10)	0.58414 (15)	0.0167 (3)
C17	0.64112 (18)	0.29607 (12)	0.62471 (18)	0.0224 (3)
H17A	0.5886	0.2813	0.5572	0.027*
H17B	0.6902	0.3403	0.6010	0.027*
C18	0.57265 (18)	0.32256 (11)	0.72692 (19)	0.0229 (3)
H18A	0.5220	0.3673	0.7010	0.027*
H18B	0.6262	0.3426	0.7905	0.027*
C19	0.49946 (19)	0.25498 (12)	0.7752 (2)	0.0244 (3)
H19A	0.4505	0.2319	0.7103	0.029*
H19B	0.5506	0.2122	0.8072	0.029*
C20	0.4233 (2)	0.28321 (15)	0.8710 (2)	0.0301 (4)
H20A	0.4709	0.3111	0.9327	0.036*
H20B	0.3884	0.2362	0.9066	0.036*
C21	0.8675 (2)	−0.18482 (14)	1.0635 (2)	0.0313 (5)

H21A	0.9438	−0.2080	1.0613	0.047*
H21B	0.8147	−0.2129	1.0080	0.047*
H21C	0.8414	−0.1902	1.1421	0.047*
C22	1.02298 (18)	−0.11555 (13)	0.88815 (18)	0.0223 (3)
H22A	1.0828	−0.1196	0.9515	0.033*
H22B	1.0517	−0.0852	0.8236	0.033*
H22C	1.0008	−0.1692	0.8612	0.033*

Atomic displacement parameters (Å^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
I1	0.02522 (9)	0.03191 (10)	0.04766 (12)	0.00818 (5)	0.00638 (7)	0.01372 (6)
O1	0.0219 (6)	0.0172 (5)	0.0185 (5)	0.0063 (4)	0.0021 (4)	0.0012 (4)
O2	0.0269 (7)	0.0163 (5)	0.0188 (5)	0.0067 (5)	0.0033 (5)	0.0036 (4)
N1	0.0186 (6)	0.0191 (6)	0.0169 (6)	0.0048 (5)	0.0018 (5)	0.0040 (5)
N2	0.0181 (6)	0.0195 (6)	0.0224 (7)	0.0051 (5)	0.0023 (5)	0.0069 (5)
N3	0.0184 (6)	0.0155 (6)	0.0147 (6)	0.0014 (5)	−0.0003 (4)	0.0013 (4)
C1	0.0213 (8)	0.0392 (11)	0.0191 (8)	−0.0067 (7)	0.0002 (6)	0.0047 (7)
C2	0.0296 (10)	0.0457 (13)	0.0192 (8)	−0.0092 (9)	0.0020 (7)	0.0032 (8)
C3	0.0321 (10)	0.0283 (9)	0.0232 (8)	−0.0054 (8)	0.0091 (7)	−0.0004 (7)
C4	0.0233 (8)	0.0184 (7)	0.0288 (9)	0.0010 (6)	0.0076 (7)	0.0021 (6)
C5	0.0197 (7)	0.0165 (7)	0.0234 (8)	0.0014 (5)	0.0012 (6)	0.0012 (6)
C6	0.0200 (7)	0.0182 (7)	0.0177 (7)	−0.0004 (5)	0.0020 (5)	0.0031 (5)
C7	0.0181 (7)	0.0169 (6)	0.0162 (6)	0.0029 (5)	−0.0003 (5)	0.0028 (5)
C8	0.0174 (6)	0.0146 (6)	0.0145 (6)	0.0020 (5)	−0.0001 (5)	0.0010 (5)
C9	0.0190 (7)	0.0143 (6)	0.0149 (6)	0.0017 (5)	−0.0002 (5)	0.0008 (5)
C10	0.0206 (7)	0.0139 (6)	0.0151 (6)	0.0016 (5)	0.0005 (5)	0.0006 (5)
C11	0.0187 (7)	0.0137 (6)	0.0153 (6)	−0.0002 (5)	−0.0008 (5)	0.0002 (5)
C12	0.0204 (7)	0.0184 (7)	0.0162 (6)	0.0021 (6)	−0.0001 (5)	−0.0001 (5)
C13	0.0223 (8)	0.0235 (8)	0.0169 (7)	−0.0005 (6)	0.0027 (6)	0.0009 (6)
C14	0.0227 (8)	0.0232 (8)	0.0169 (7)	−0.0017 (6)	0.0007 (6)	0.0042 (6)
C15	0.0209 (7)	0.0187 (7)	0.0186 (7)	−0.0012 (6)	−0.0009 (6)	0.0050 (5)
C16	0.0199 (7)	0.0138 (6)	0.0162 (6)	−0.0010 (5)	−0.0001 (5)	0.0006 (5)
C17	0.0257 (8)	0.0170 (7)	0.0245 (8)	0.0053 (6)	0.0026 (6)	0.0055 (6)
C18	0.0246 (8)	0.0137 (6)	0.0304 (9)	0.0020 (6)	0.0024 (7)	0.0009 (6)
C19	0.0252 (8)	0.0172 (7)	0.0310 (9)	0.0018 (6)	0.0025 (7)	0.0036 (6)
C20	0.0298 (10)	0.0298 (10)	0.0314 (10)	0.0106 (8)	0.0063 (8)	0.0122 (8)
C21	0.0305 (10)	0.0227 (9)	0.0418 (12)	0.0084 (8)	0.0110 (9)	0.0154 (8)
C22	0.0210 (8)	0.0219 (7)	0.0243 (8)	0.0062 (6)	0.0031 (6)	0.0024 (6)

Geometric parameters (Å, °)

I1—C20	2.111 (2)	C11—C12	1.398 (3)
O1—C9	1.235 (2)	C11—C16	1.410 (2)
O2—C16	1.355 (2)	C12—C13	1.387 (3)
O2—C17	1.432 (2)	C12—H12A	0.9300
N1—C9	1.398 (2)	C13—C14	1.390 (3)
N1—N2	1.403 (2)	C13—H13A	0.9300
N1—C6	1.422 (2)	C14—C15	1.387 (3)

N2—C7	1.365 (2)	C14—H14A	0.9300
N2—C21	1.459 (3)	C15—C16	1.398 (2)
N3—C10	1.289 (2)	C15—H15A	0.9300
N3—C8	1.389 (2)	C17—C18	1.506 (3)
C1—C6	1.391 (3)	C17—H17A	0.9700
C1—C2	1.398 (3)	C17—H17B	0.9700
C1—H1A	0.9300	C18—C19	1.518 (3)
C2—C3	1.390 (3)	C18—H18A	0.9700
C2—H2A	0.9300	C18—H18B	0.9700
C3—C4	1.392 (3)	C19—C20	1.512 (3)
C3—H3A	0.9300	C19—H19A	0.9700
C4—C5	1.388 (3)	C19—H19B	0.9700
C4—H4A	0.9300	C20—H20A	0.9700
C5—C6	1.392 (3)	C20—H20B	0.9700
C5—H5A	0.9300	C21—H21A	0.9600
C7—C8	1.374 (2)	C21—H21B	0.9600
C7—C22	1.478 (3)	C21—H21C	0.9600
C8—C9	1.454 (2)	C22—H22A	0.9600
C10—C11	1.463 (2)	C22—H22B	0.9600
C10—H10A	0.9300	C22—H22C	0.9600
C16—O2—C17	118.14 (15)	C14—C13—H13A	120.4
C9—N1—N2	109.46 (14)	C15—C14—C13	121.23 (17)
C9—N1—C6	124.67 (15)	C15—C14—H14A	119.4
N2—N1—C6	118.95 (15)	C13—C14—H14A	119.4
C7—N2—N1	107.41 (14)	C14—C15—C16	119.45 (17)
C7—N2—C21	121.40 (17)	C14—C15—H15A	120.3
N1—N2—C21	115.78 (16)	C16—C15—H15A	120.3
C10—N3—C8	118.86 (15)	O2—C16—C15	123.87 (16)
C6—C1—C2	118.8 (2)	O2—C16—C11	115.96 (15)
C6—C1—H1A	120.6	C15—C16—C11	120.17 (17)
C2—C1—H1A	120.6	O2—C17—C18	108.56 (15)
C3—C2—C1	120.3 (2)	O2—C17—H17A	110.0
C3—C2—H2A	119.9	C18—C17—H17A	110.0
C1—C2—H2A	119.9	O2—C17—H17B	110.0
C2—C3—C4	120.08 (19)	C18—C17—H17B	110.0
C2—C3—H3A	120.0	H17A—C17—H17B	108.4
C4—C3—H3A	120.0	C17—C18—C19	113.44 (16)
C5—C4—C3	120.3 (2)	C17—C18—H18A	108.9
C5—C4—H4A	119.9	C19—C18—H18A	108.9
C3—C4—H4A	119.9	C17—C18—H18B	108.9
C4—C5—C6	119.19 (18)	C19—C18—H18B	108.9
C4—C5—H5A	120.4	H18A—C18—H18B	107.7
C6—C5—H5A	120.4	C20—C19—C18	113.41 (18)
C1—C6—C5	121.36 (18)	C20—C19—H19A	108.9
C1—C6—N1	119.94 (18)	C18—C19—H19A	108.9
C5—C6—N1	118.69 (17)	C20—C19—H19B	108.9
N2—C7—C8	109.87 (15)	C18—C19—H19B	108.9
N2—C7—C22	121.27 (16)	H19A—C19—H19B	107.7
C8—C7—C22	128.82 (16)	C19—C20—I1	111.76 (15)

C7—C8—N3	122.69 (16)	C19—C20—H20A	109.3
C7—C8—C9	107.86 (15)	I1—C20—H20A	109.3
N3—C8—C9	129.42 (15)	C19—C20—H20B	109.3
O1—C9—N1	123.96 (16)	I1—C20—H20B	109.3
O1—C9—C8	131.28 (16)	H20A—C20—H20B	107.9
N1—C9—C8	104.73 (14)	N2—C21—H21A	109.5
N3—C10—C11	120.79 (16)	N2—C21—H21B	109.5
N3—C10—H10A	119.6	H21A—C21—H21B	109.5
C11—C10—H10A	119.6	N2—C21—H21C	109.5
C12—C11—C16	118.64 (16)	H21A—C21—H21C	109.5
C12—C11—C10	121.71 (16)	H21B—C21—H21C	109.5
C16—C11—C10	119.52 (16)	C7—C22—H22A	109.5
C13—C12—C11	121.30 (17)	C7—C22—H22B	109.5
C13—C12—H12A	119.3	H22A—C22—H22B	109.5
C11—C12—H12A	119.3	C7—C22—H22C	109.5
C12—C13—C14	119.12 (18)	H22A—C22—H22C	109.5
C12—C13—H13A	120.4	H22B—C22—H22C	109.5
C9—N1—N2—C7	−8.6 (2)	C6—N1—C9—O1	−21.4 (3)
C6—N1—N2—C7	−160.89 (17)	N2—N1—C9—C8	6.5 (2)
C9—N1—N2—C21	−147.91 (19)	C6—N1—C9—C8	156.82 (17)
C6—N1—N2—C21	59.8 (2)	C7—C8—C9—O1	175.93 (19)
C6—C1—C2—C3	−0.1 (4)	N3—C8—C9—O1	−6.2 (3)
C1—C2—C3—C4	0.0 (4)	C7—C8—C9—N1	−2.11 (19)
C2—C3—C4—C5	0.8 (3)	N3—C8—C9—N1	175.74 (17)
C3—C4—C5—C6	−1.4 (3)	C8—N3—C10—C11	−173.62 (16)
C2—C1—C6—C5	−0.5 (3)	N3—C10—C11—C12	7.8 (3)
C2—C1—C6—N1	−179.6 (2)	N3—C10—C11—C16	−176.25 (17)
C4—C5—C6—C1	1.3 (3)	C16—C11—C12—C13	−1.8 (3)
C4—C5—C6—N1	−179.60 (17)	C10—C11—C12—C13	174.17 (18)
C9—N1—C6—C1	−116.1 (2)	C11—C12—C13—C14	−0.9 (3)
N2—N1—C6—C1	31.7 (3)	C12—C13—C14—C15	2.6 (3)
C9—N1—C6—C5	64.8 (3)	C13—C14—C15—C16	−1.6 (3)
N2—N1—C6—C5	−147.45 (18)	C17—O2—C16—C15	1.2 (3)
N1—N2—C7—C8	7.2 (2)	C17—O2—C16—C11	−179.42 (17)
C21—N2—C7—C8	143.72 (19)	C14—C15—C16—O2	178.16 (18)
N1—N2—C7—C22	−170.71 (17)	C14—C15—C16—C11	−1.2 (3)
C21—N2—C7—C22	−34.2 (3)	C12—C11—C16—O2	−176.58 (16)
N2—C7—C8—N3	178.79 (16)	C10—C11—C16—O2	7.4 (2)
C22—C7—C8—N3	−3.5 (3)	C12—C11—C16—C15	2.8 (3)
N2—C7—C8—C9	−3.2 (2)	C10—C11—C16—C15	−173.23 (17)
C22—C7—C8—C9	174.55 (19)	C16—O2—C17—C18	−177.32 (16)
C10—N3—C8—C7	178.99 (17)	O2—C17—C18—C19	−55.7 (2)
C10—N3—C8—C9	1.4 (3)	C17—C18—C19—C20	−175.30 (18)
N2—N1—C9—O1	−171.71 (17)	C18—C19—C20—I1	67.8 (2)

Hydrogen-bond geometry (Å, °)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
C10—H10A···O1	0.93	2.30	2.995 (2)	132

C17—H17B···O1^{i}	0.97	2.42	3.193 (2)	137

Symmetry codes: (i) *x*, −*y*+1/2, *z*−1/2.

Fig. 1

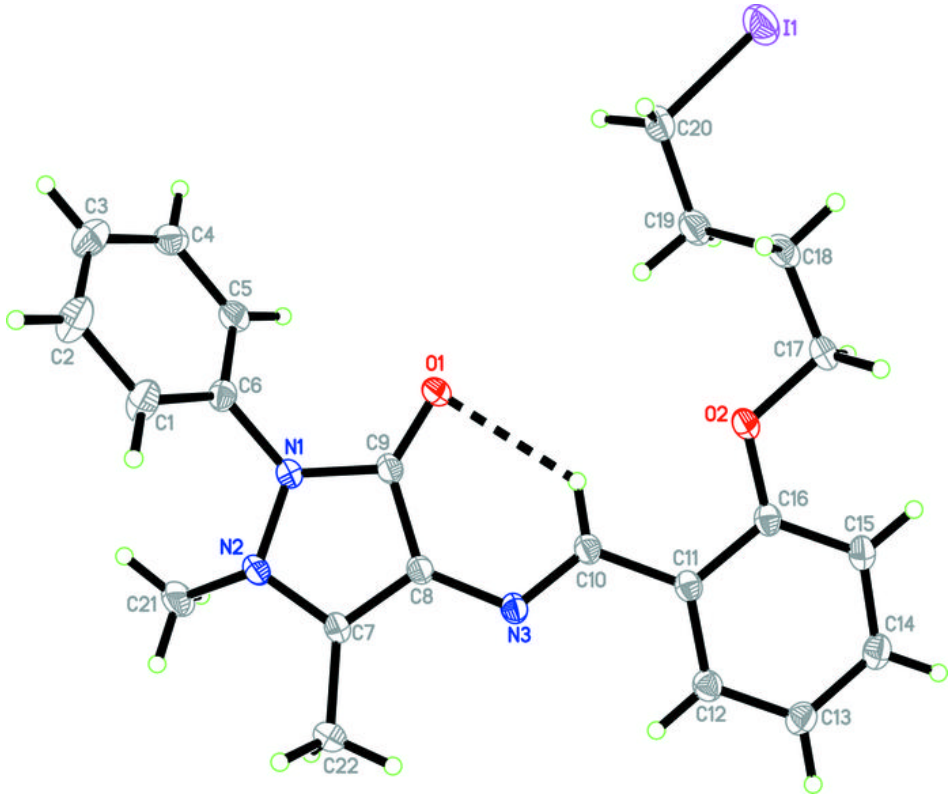
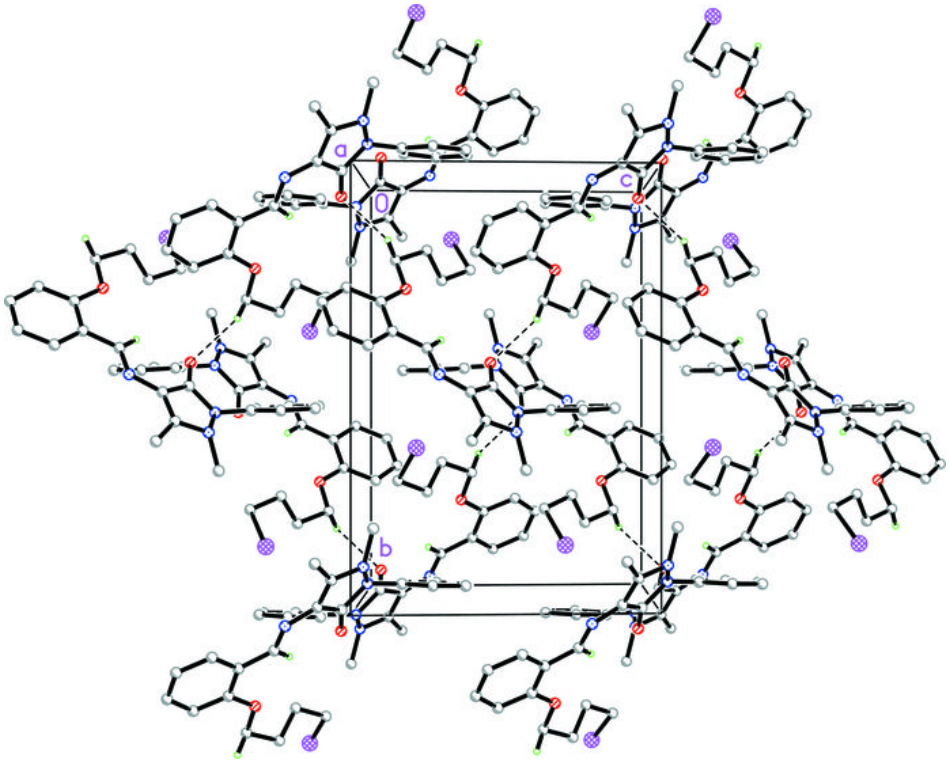


Fig. 2



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3-Chloro-*N*-(4-sulfamoylphenyl)-propanamide

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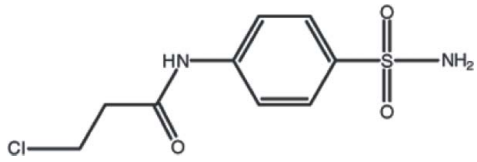
Key indicators: single-crystal X-ray study; T = 296 K; mean σ(C–C) = 0.003 Å; R factor = 0.038; wR factor = 0.106; data-to-parameter ratio = 15.0.

In the title compound, $C_9H_{11}ClN_2O_3S$, the dihedral angle between the benzene ring and the amido –NHCO– plane is 15.0 (2)°. An intramolecular C—H···O hydrogen bond generates an S(6) ring motif. In the crystal structure, the amino NH_2 group is involved in intermolecular N—H···O hydrogen bonds, which connect the molecules into a double layer structure expanding parallel to the *bc* plane. The layers are further linked by an amido N—H···O hydrogen bond. Between the layers, a weak π–π interaction with a centroid–centroid distance of 3.7447 (12) Å is also observed.

Related literature

For the antibacterial and pharmacological properties of sulfonamides and their derivatives, see: Albala *et al.* (1994); Mann & Keilin (1940); Maren (1976); Pastorekova *et al.* (2004); Reynolds (1996); Silverman (1992); Supuran & Scozzafava (2001, 2002); Supuran *et al.* (2003, 2004); Türkmen *et al.* (2005). For graph-set notation, see: Bernstein *et al.* (1995).



Experimental

Crystal data

$C_9H_{11}ClN_2O_3S$
M_r = 262.72
Monoclinic, $P2_1/c$
a = 7.7554 (4) Å
b = 14.8191 (8) Å
c = 9.7482 (5) Å
β = 94.181 (4)°
V = 1117.36 (10) Å^3
Z = 4
Mo $K\alpha$ radiation
μ = 0.52 mm^{-1}
T = 296 K
0.78 × 0.45 × 0.22 mm

Data collection

Stoe IPDS2 diffractometer
Absorption correction: integration (*X-RED32*; Stoe & Cie, 2002)
T_{min} = 0.754, T_{max} = 0.892
6023 measured reflections
2294 independent reflections
2007 reflections with $I > 2\sigma(I)$
R_{int} = 0.040

Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.038
$wR(F^2)$ = 0.106
S = 1.08
2294 reflections
153 parameters
2 restraints
H atoms treated by a mixture of independent and constrained refinement
$\Delta\rho_{max}$ = 0.28 e Å^{-3}
$\Delta\rho_{min}$ = −0.44 e Å^{-3}

Table 1
Hydrogen-bond geometry (Å, °).

D—H···A	D—H	H···A	D···A	D—H···A
N1—H1A···O1^{i}	0.859 (18)	2.14 (2)	2.926 (2)	151 (3)
N1—H1B···O3^{ii}	0.85 (2)	2.12 (3)	2.923 (2)	158 (3)
N2—H2A···O2^{iii}	0.86	2.13	2.991 (2)	175
C3—H3···O3	0.93	2.32	2.889 (3)	120

Symmetry codes: (i) $x, -y+\frac{3}{2}, z-\frac{1}{2}$; (ii) $-x, -y+1, -z+1$; (iii) $-x+1, y-\frac{1}{2}, -z+\frac{1}{2}$.

Data collection: *X-AREA* (Stoe & Cie, 2002); cell refinement: *X-AREA* (Stoe & Cie, 2002); data reduction: *X-RED32* (Stoe & Cie, 2002); program(s) used to solve structure: *SIR97* (Altomare *et al.*, 1999); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *ORTEP-3* (Farrugia, 1997); software used to prepare material for publication: *WinGX* (Farrugia, 1999).

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Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: IS2555).

References

Albala, D. M., Prien, E. L. & Galal, H. A. (1994). *J. Endourol.* **8**, 401–403.
Altomare, A., Burla, M. C., Camalli, M., Cascarano, G. L., Giacovazzo, C., Guagliardi, A., Moliterni, A. G. G., Polidori, G. & Spagna, R. (1999). *J. Appl. Cryst.* **32**, 115–119.
Bernstein, J., Davis, R. E., Shimoni, L. & Chang, N.-L. (1995). *Angew. Chem. Int. Ed. Engl.* **34**, 1555–1573.
Farrugia, L. J. (1997). *J. Appl. Cryst.* **30**, 565.
Farrugia, L. J. (1999). *J. Appl. Cryst.* **32**, 837–838.
Mann, T. & Keilin, D. (1940). *Nature* (London), **164**, 146–148.
Maren, T. H. (1976). *Annu. Rev. Pharmacol. Toxicol.* **16**, 309–327.
Pastorekova, S., Parkkila, S., Pastorek, J. & Supuran, C. T. J. (2004). *J. Enzyme Inhib. Med. Chem.* **19**, 199–229.
Reynolds, J. E. F. (1996). Editor. *Martindale: The Extra Pharmacopoeia*, 31st ed. London: The Royal Pharmaceutical Society.
Sheldrick, G. M. (2008). *Acta Cryst.* A**64**, 112–122.
Silverman, R. B. (1992). *The Organic Chemistry of Drug Design and Drug Action*. London: Academic.
Stoe & Cie (2002). *X-AREA* and *X-RED32*. Stoe & Cie, Darmstadt, Germany.
Supuran, C. T. & Scozzafava, A. (2001). *Curr. Med. Chem. Immunol. Endocrinol. Metab. Agent.* **1**, 61–97.
Supuran, C. T. & Scozzafava, A. (2002). *Expert Opin. Ther. Patents*, **12**, 217–242.
Supuran, C. T., Scozzafava, A. & Casini, A. (2003). *Med. Res. Rev.* **23**, 146–189.

Supuran, C. T., Vullo, D., Manole, G., Casini, A. & Scozzafava, A. (2004). *Curr. Med. Chem. Cardiovasc. Hematol. Agents*, **2**, 49–68.

Türkmen, H., Durgun, M., Yılmaztekin, S., Emul, M., Innocenti, A., Vullo, D., Scozzafava, A. & Supuran, C. T. (2005). *Bioorg. Med. Chem. Lett.* **15**, 367–372.

supplementary materials

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3-Chloro-*N*-(4-sulfamoylphenyl)propanamide

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Comment

Sulfanilamide is a sulfonamide antibacterial. Chemically, it is a molecule containing the sulfonamide functional group attached to an aniline. As an antibiotic, it functions by competitively inhibiting (*i.e*, by acting as a substrate analogue) enzymatic reactions involving. Inhibition of the zinc enzyme carbonic anhydrase (CA, EC 4.2.1.1) with sulfonamides may be exploited clinically for the treatment and prevention of a multitude of diseases (Pastorekova *et al.*, 2004; Supuran *et al.*, 2004; Mann & Keilin, 1940). With the early report that sulfanilamide acts as an inhibitor of CA, a great scientific adventure initiated, leading to the development of several classes of drugs based on the sulfonamide motif.

Sulfonamides and their derivatives have been the subject of investigation for many reasons. The amides are important constituent of many biologically significant compounds. The chemistry of sulfonamides is of interest as they show distinct physical, chemical and biological properties. The sulfonamide derivatives are known for their numerous pharmacological activities, antibacterial, antitumor, insulin-release stimulation and antithyroid properties (Maren, 1976). In addition, the unsubstituted aromatic/heterocyclic sulfonamides act as carbonic anhydrase inhibitors (Supuran & Scozzafava, 2001; Türkmen *et al.*, 2005; Supuran *et al.*, 2003) whereas other types of derivatives show diuretic activity (high-ceiling diuretics or thiadiazine diuretics), hypoglycemic activity and anti- cancer properties (Supuran & Scozzafava, 2002). Although sulfonamides are best known as bacteriostatic (Silverman, 1992) and antimalarial agents (Albala *et al.*, 1994), there is now a range of drugs, possessing very different pharmacological activities, in which the sulfonamide group is present (Reynolds, 1996). Due to their significant pharmacology applications and widespread use in medicine, these compounds have gained attention in bio-inorganic and metal-based drug chemistry. In this work we report the crystal structure of 3-chloro-*N*-(4-sulfamoylphenyl)propanamide.

In the title molecule (I), (Fig. 1), the S═O distances [1.4302 (14) and 1.4349 (16) Å] and the O═S═O angle [118.21 (9)°] are within the normal range as the values of the other geometric parameters of the molecule. The dihedral angle between the benzene ring and the amido –NHCO– plane is 15.0 (2)°.

The crystal structure is stabilized by N—H···O type hydrogen bonds (Table 1, Fig. 2). N1—H1A···O1 and N1—H1B···O3 generate the two-dimensional network (double layer structure), but N2—H2A···O2 links the layers into a three-dimensional network. An intramolecular hydrogen contact C3—H3···O3 generates a ring of graph-set motif S(6) (Bernstein *et al.*, 1995) (Table 1). Furthermore, crystal packing is influenced by weak π–π stacking interactions between nearby aromatic rings of the adjacent molecules, [$Cg\cdots Cg^{iv}$ = 3.7447 (12) Å; *Cg* is the centroid of the C1–C6 ring; symmetry code: (iv) 1 - *x*, 1 - *y*, 1 - *z*].

Experimental

Sulfanilamide (2.00 g, 0.011 mol) and *N*-ethylmaleimide (NEM) (1.566 g, 0.016 mol) were stirred in tetrahydrofuran (THF) (200 ml) until most of the starting material had dissolved. 3-Chloropropanoylchloride (1.782 g, 0.014 mol) in THF was slowly added to the reaction mixture. The reaction was stirred at 258 K for 4 h under anhydrous conditions. After warming to room temperature the white precipitate of NEM/HCl salt filtered off. The THF was removed in *vacuo* and the resulting

white solid dissolved in ethyl acetate. The organic extract was washed with 3*M* hydrochloric acid (20 ml) then with saturated sodium bicarbonate solution (20 ml) and finally with brine. Drying over magnesium sulfate and evaporation yielded a white solid which was recrystallized from water to give the title compound (yield: 70%, m.p: 501–503 K).

Refinement

The H-atoms of the NH_2 group were located in a difference Fourier map, and were refined with distance restraints of N—H = 0.86 (2) Å; their temperature factors were freely refined. The other H-atoms were placed in calculated positions with C—H = 0.93–0.97 Å and N—H = 0.86 Å, and were included in the refinement in the riding model approximation, with U_{iso}(H) = 1.2U_{eq}(C, N).

Figures

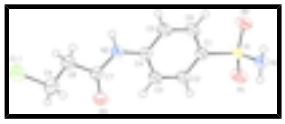


Fig. 1. The title molecule with the atom numbering scheme. Displacement ellipsoids for non-H atoms are drawn at the 50% probability level.

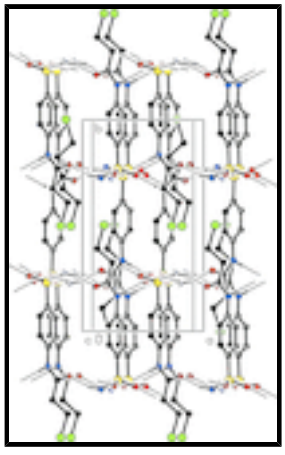


Fig. 2. The packing of the molecules of (I) linked by of N—H···O hydrogen bonds, viewed down the *c* axis. All hydrogen atoms not involved in hydrogen bonding have been omitted for clarity. Hydrogen bonds are indicated by dotted lines.

3-Chloro-*N*-(4-sulfamoylphenyl)propanamide

Crystal data

$C_9H_{11}ClN_2O_3S$	$F(000)$ = 544
M_r = 262.72	D_x = 1.562 Mg m^{-3}
Monoclinic, $P2_1/c$	Mo $K\alpha$ radiation, λ = 0.71073 Å
Hall symbol: -P 2ybc	Cell parameters from 8775 reflections
a = 7.7554 (4) Å	θ = 2.1–28.0°
b = 14.8191 (8) Å	μ = 0.52 mm^{-1}
c = 9.7482 (5) Å	*T* = 296 K
β = 94.181 (4)°	Prism, colourless
V = 1117.36 (10) Å^3	0.78 × 0.45 × 0.22 mm
Z = 4	

Data collection

Stoe IPDS2 diffractometer	2294 independent reflections
Radiation source: sealed X-ray tube, 12 x 0.4 mm long-fine focus	2007 reflections with $I > 2\sigma(I)$
plane graphite	$R_{int} = 0.040$
Detector resolution: 6.67 pixels mm^{-1}	$\theta_{max} = 26.5°$, $\theta_{min} = 2.5°$
ω scans	$h = -8 \rightarrow 9$
Absorption correction: integration (*X-RED32*; Stoe & Cie, 2002)	$k = -16 \rightarrow 18$
$T_{min} = 0.754$, $T_{max} = 0.892$	$l = -12 \rightarrow 12$
6023 measured reflections	

Refinement

Refinement on F^2	Primary atom site location: structure-invariant direct methods
Least-squares matrix: full	Secondary atom site location: difference Fourier map
$R[F^2 > 2\sigma(F^2)] = 0.038$	Hydrogen site location: inferred from neighbouring sites
$wR(F^2) = 0.106$	H atoms treated by a mixture of independent and constrained refinement
$S = 1.08$	$w = 1/[\sigma^2(F_o^2) + (0.0602P)^2 + 0.351P]$ where $P = (F_o^2 + 2F_c^2)/3$
2294 reflections	$(\Delta/\sigma)_{max} < 0.001$
153 parameters	$\Delta\rho_{max} = 0.28$ e Å^{-3}
2 restraints	$\Delta\rho_{min} = -0.44$ e Å^{-3}

Special details

Geometry. Bond distances, angles *etc*. have been calculated using the rounded fractional coordinates. All su's are estimated from the variances of the (full) variance-covariance matrix. The cell e.s.d.'s are taken into account in the estimation of distances, angles and torsion angles

Refinement. Refinement on F^2 for ALL reflections except those flagged by the user for potential systematic errors. Weighted *R*-factors *wR* and all goodnesses of fit *S* are based on F^2, conventional *R*-factors *R* are based on *F*, with *F* set to zero for negative F^2. The observed criterion of $F^2 > \sigma(F^2)$ is used only for calculating -*R*-factor-obs *etc*. and is not relevant to the choice of reflections for refinement. *R*-factors based on F^2 are statistically about twice as large as those based on *F*, and *R*-factors based on ALL data will be even larger.

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å^2)

	x	*y*	*z*	U_{iso}*/U_{eq}
Cl1	0.18392 (12)	−0.00186 (4)	0.38004 (9)	0.0791 (3)
S1	0.31196 (6)	0.73280 (3)	0.40392 (4)	0.0330 (1)
O1	0.2882 (2)	0.75787 (10)	0.54296 (14)	0.0471 (5)
O2	0.4665 (2)	0.76199 (10)	0.34461 (15)	0.0445 (5)

O3	0.1258 (2)	0.28706 (10)	0.52407 (19)	0.0571 (6)
N1	0.1520 (2)	0.77368 (12)	0.31092 (18)	0.0398 (5)
N2	0.3009 (2)	0.33382 (11)	0.36141 (18)	0.0419 (5)
C1	0.3044 (2)	0.61415 (12)	0.39403 (17)	0.0331 (5)
C2	0.2424 (3)	0.56420 (15)	0.4978 (2)	0.0499 (7)
C3	0.2372 (4)	0.47119 (15)	0.4898 (2)	0.0530 (7)
C4	0.2965 (2)	0.42797 (13)	0.37652 (19)	0.0360 (5)
C5	0.3592 (3)	0.47919 (15)	0.2722 (2)	0.0508 (7)
C6	0.3617 (3)	0.57169 (15)	0.2792 (2)	0.0488 (7)
C7	0.2202 (3)	0.27011 (13)	0.4329 (2)	0.0389 (6)
C8	0.2583 (3)	0.17489 (14)	0.3889 (2)	0.0448 (6)
C9	0.1263 (4)	0.10957 (16)	0.4265 (4)	0.0725 (10)
H1A	0.153 (4)	0.7665 (17)	0.2235 (18)	0.053 (7)*
H1B	0.055 (3)	0.7636 (17)	0.342 (3)	0.051 (7)*
H2	0.20340	0.59310	0.57430	0.0600*
H2A	0.36310	0.31400	0.29840	0.0500*
H3	0.19400	0.43770	0.56030	0.0640*
H5	0.40020	0.45050	0.19620	0.0610*
H6	0.40150	0.60550	0.20760	0.0590*
H8A	0.26540	0.17370	0.29000	0.0540*
H8B	0.36990	0.15670	0.43140	0.0540*
H9A	0.01560	0.12520	0.38000	0.0870*
H9B	0.11490	0.11230	0.52490	0.0870*

Atomic displacement parameters (Å^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Cl1	0.1120 (6)	0.0337 (3)	0.0982 (6)	−0.0094 (3)	0.0520 (5)	−0.0065 (3)
S1	0.0424 (3)	0.0302 (2)	0.0276 (2)	−0.0060 (2)	0.0106 (2)	−0.0011 (2)
O1	0.0702 (10)	0.0434 (8)	0.0294 (7)	−0.0105 (7)	0.0146 (6)	−0.0057 (5)
O2	0.0459 (8)	0.0452 (8)	0.0440 (8)	−0.0140 (6)	0.0142 (6)	0.0000 (6)
O3	0.0628 (10)	0.0383 (8)	0.0757 (11)	−0.0035 (7)	0.0427 (9)	−0.0018 (7)
N1	0.0471 (10)	0.0372 (9)	0.0367 (9)	0.0024 (7)	0.0131 (7)	0.0019 (7)
N2	0.0504 (10)	0.0315 (8)	0.0466 (9)	0.0014 (7)	0.0233 (7)	−0.0011 (7)
C1	0.0382 (10)	0.0295 (9)	0.0323 (8)	0.0002 (7)	0.0075 (7)	0.0012 (6)
C2	0.0740 (15)	0.0352 (10)	0.0443 (11)	0.0005 (10)	0.0310 (10)	0.0001 (8)
C3	0.0814 (16)	0.0348 (11)	0.0473 (11)	0.0008 (11)	0.0354 (11)	0.0060 (9)
C4	0.0383 (10)	0.0315 (9)	0.0394 (9)	0.0021 (8)	0.0116 (8)	0.0022 (7)
C5	0.0732 (15)	0.0387 (10)	0.0447 (11)	−0.0035 (10)	0.0323 (11)	−0.0041 (9)
C6	0.0712 (15)	0.0377 (10)	0.0410 (10)	−0.0061 (10)	0.0278 (10)	0.0009 (8)
C7	0.0385 (10)	0.0335 (10)	0.0461 (11)	−0.0008 (8)	0.0126 (8)	0.0004 (8)
C8	0.0500 (12)	0.0344 (10)	0.0520 (11)	−0.0010 (9)	0.0176 (9)	−0.0027 (8)
C9	0.0714 (18)	0.0328 (11)	0.118 (2)	−0.0020 (12)	0.0382 (17)	−0.0012 (13)

Geometric parameters (Å, °)

Cl1—C9	1.778 (3)	C3—C4	1.384 (3)
S1—O1	1.4302 (14)	C4—C5	1.385 (3)
S1—O2	1.4349 (16)	C5—C6	1.373 (3)

S1—N1	1.6012 (17)	C7—C8	1.510 (3)
S1—C1	1.7617 (18)	C8—C9	1.475 (4)
O3—C7	1.218 (3)	C2—H2	0.9300
N2—C4	1.404 (3)	C3—H3	0.9300
N2—C7	1.354 (3)	C5—H5	0.9300
N1—H1A	0.859 (18)	C6—H6	0.9300
N1—H1B	0.85 (2)	C8—H8A	0.9700
N2—H2A	0.8600	C8—H8B	0.9700
C1—C2	1.369 (3)	C9—H9A	0.9700
C1—C6	1.385 (3)	C9—H9B	0.9700
C2—C3	1.381 (3)		
Cl1···N1^{i}	3.3993 (19)	C3···O3	2.889 (3)
Cl1···C9^{ii}	3.543 (3)	C7···O2^{vi}	3.173 (3)
Cl1···H9B^{ii}	3.0400	C8···O2^{vi}	3.372 (3)
S1···O1^{iii}	3.5128 (14)	C9···Cl1^{ii}	3.543 (3)
O1···N1^{iv}	2.926 (2)	C7···H3	2.7900
O1···S1^{iv}	3.5128 (14)	C8···H6^{x}	3.0400
O1···O2^{iv}	3.171 (2)	H1A···O1^{iii}	2.14 (2)
O2···N2^{v}	2.992 (2)	H1A···H2^{iii}	2.5800
O2···C8^{vi}	3.372 (3)	H1B···O3^{vii}	2.12 (3)
O2···O1^{iii}	3.171 (2)	H2···O1	2.5500
O2···C7^{vi}	3.173 (3)	H2···H1A^{iv}	2.5800
O3···N1^{vii}	2.923 (2)	H2A···H5	2.2800
O3···C3	2.889 (3)	H2A···H8A	2.2100
O1···H6^{iv}	2.6900	H2A···O2^{x}	2.1300
O1···H1A^{iv}	2.14 (2)	H3···O3	2.3200
O1···H2	2.5500	H3···C7	2.7900
O2···H8A^{v}	2.8600	H5···H2A	2.2800
O2···H6	2.7100	H6···O2	2.7100
O2···H2A^{v}	2.1300	H6···C8^{v}	3.0400
O2···H8B^{vi}	2.7200	H6···H8B^{v}	2.4300
O3···H9A	2.8800	H6···O1^{iii}	2.6900
O3···H9B	2.5900	H8A···H2A	2.2100
O3···H3	2.3200	H8A···O2^{x}	2.8600
O3···H1B^{vii}	2.12 (3)	H8A···O3^{xi}	2.8000
O3···H8A^{viii}	2.8000	H8B···H6^{x}	2.4300
N1···Cl1^{ix}	3.3993 (19)	H8B···O2^{vi}	2.7200
N1···O3^{vii}	2.923 (2)	H9A···O3	2.8800
N1···O1^{iii}	2.926 (2)	H9B···O3	2.5900
N2···O2^{x}	2.991 (2)	H9B···Cl1^{ii}	3.0400
O1—S1—O2	118.21 (9)	N2—C7—C8	113.46 (18)
O1—S1—N1	106.87 (9)	O3—C7—C8	122.71 (18)
O1—S1—C1	107.76 (8)	C7—C8—C9	112.9 (2)

O2—S1—N1	107.05 (9)	Cl1—C9—C8	110.8 (2)
O2—S1—C1	107.72 (8)	C1—C2—H2	120.00
N1—S1—C1	108.98 (9)	C3—C2—H2	120.00
C4—N2—C7	128.58 (17)	C2—C3—H3	120.00
S1—N1—H1A	117 (2)	C4—C3—H3	120.00
S1—N1—H1B	113.8 (19)	C4—C5—H5	120.00
H1A—N1—H1B	114 (3)	C6—C5—H5	119.00
C4—N2—H2A	116.00	C1—C6—H6	120.00
C7—N2—H2A	116.00	C5—C6—H6	120.00
S1—C1—C2	120.76 (14)	C7—C8—H8A	109.00
S1—C1—C6	119.09 (14)	C7—C8—H8B	109.00
C2—C1—C6	120.15 (18)	C9—C8—H8A	109.00
C1—C2—C3	120.56 (19)	C9—C8—H8B	109.00
C2—C3—C4	119.8 (2)	H8A—C8—H8B	108.00
N2—C4—C5	117.07 (17)	Cl1—C9—H9A	109.00
C3—C4—C5	119.15 (19)	Cl1—C9—H9B	109.00
N2—C4—C3	123.77 (18)	C8—C9—H9A	110.00
C4—C5—C6	121.01 (19)	C8—C9—H9B	109.00
C1—C6—C5	119.32 (19)	H9A—C9—H9B	108.00
O3—C7—N2	123.84 (18)		
O1—S1—C1—C2	14.47 (18)	C2—C1—C6—C5	−1.5 (3)
O2—S1—C1—C2	143.03 (16)	C6—C1—C2—C3	0.4 (3)
N1—S1—C1—C2	−101.16 (17)	C1—C2—C3—C4	0.6 (4)
O1—S1—C1—C6	−165.74 (15)	C2—C3—C4—N2	178.1 (2)
O2—S1—C1—C6	−37.18 (17)	C2—C3—C4—C5	−0.5 (3)
N1—S1—C1—C6	78.63 (17)	N2—C4—C5—C6	−179.24 (19)
C7—N2—C4—C3	15.1 (3)	C3—C4—C5—C6	−0.6 (3)
C7—N2—C4—C5	−166.4 (2)	C4—C5—C6—C1	1.6 (3)
C4—N2—C7—O3	1.0 (3)	O3—C7—C8—C9	21.5 (3)
C4—N2—C7—C8	−178.99 (18)	N2—C7—C8—C9	−158.5 (2)
S1—C1—C2—C3	−179.80 (19)	C7—C8—C9—Cl1	−177.00 (18)
S1—C1—C6—C5	178.75 (17)		

Symmetry codes: (i) *x*, *y*−1, *z*; (ii) −*x*, −*y*, −*z*+1; (iii) *x*, −*y*+3/2, *z*−1/2; (iv) *x*, −*y*+3/2, *z*+1/2; (v) −*x*+1, *y*+1/2, −*z*+1/2; (vi) −*x*+1, −*y*+1, −*z*+1; (vii) −*x*, −*y*+1, −*z*+1; (viii) *x*, −*y*+1/2, *z*+1/2; (ix) *x*, *y*+1, *z*; (x) −*x*+1, *y*−1/2, −*z*+1/2; (xi) *x*, −*y*+1/2, *z*−1/2.

Hydrogen-bond geometry (Å, °)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
N1—H1A···O1^{iii}	0.859 (18)	2.14 (2)	2.926 (2)	151 (3)
N1—H1B···O3^{vii}	0.85 (2)	2.12 (3)	2.923 (2)	158 (3)
N2—H2A···O2^{x}	0.86	2.13	2.991 (2)	175
C3—H3···O3	0.93	2.32	2.889 (3)	120

Symmetry codes: (iii) *x*, −*y*+3/2, *z*−1/2; (vii) −*x*, −*y*+1, −*z*+1; (x) −*x*+1, *y*−1/2, −*z*+1/2.

Fig. 1

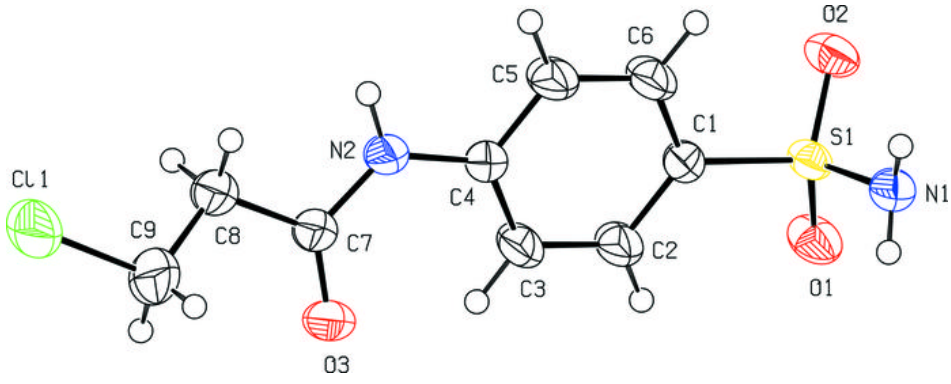
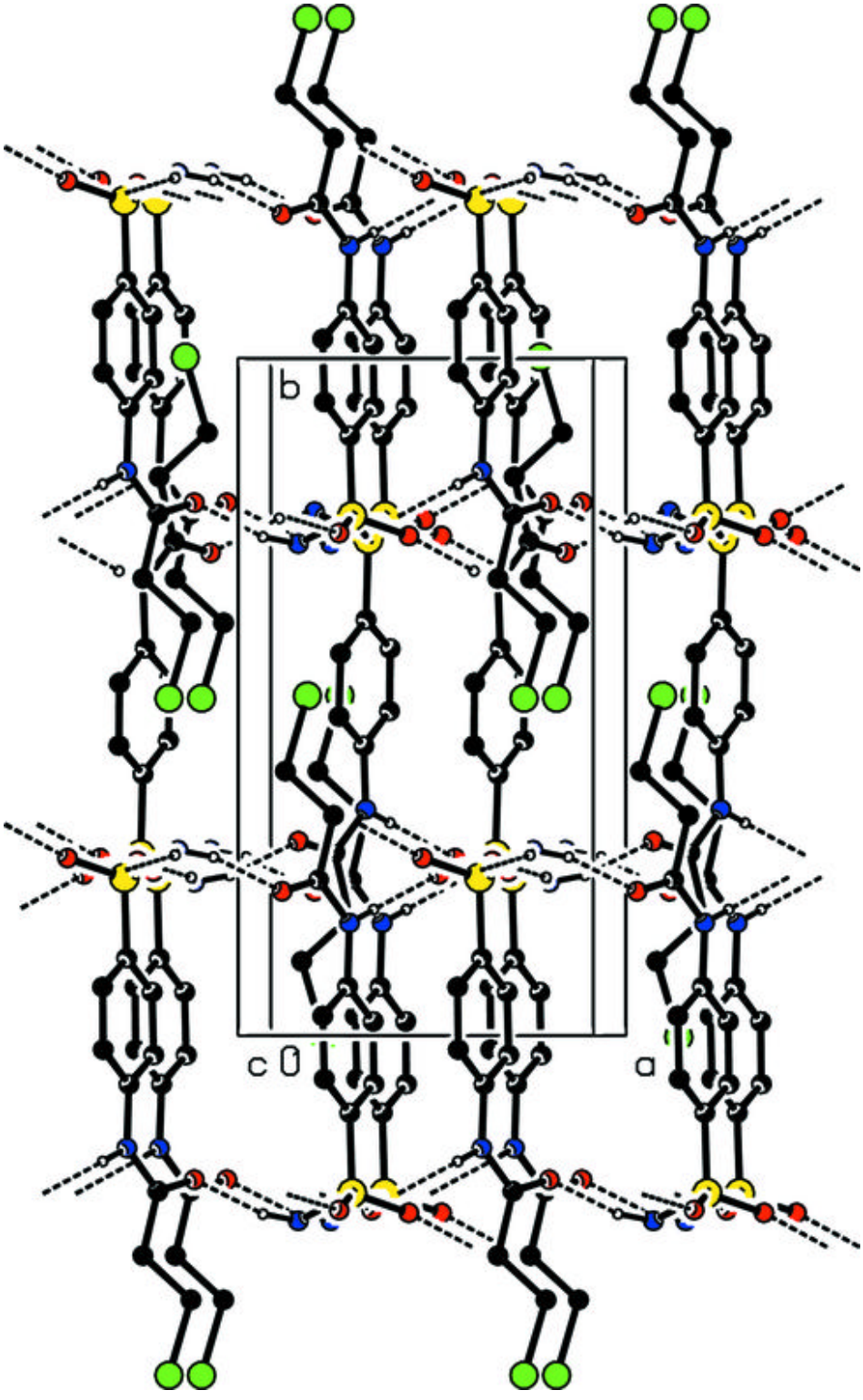


Fig. 2



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Diaquabis(hydrogen tartrato)copper(II) dihydrate

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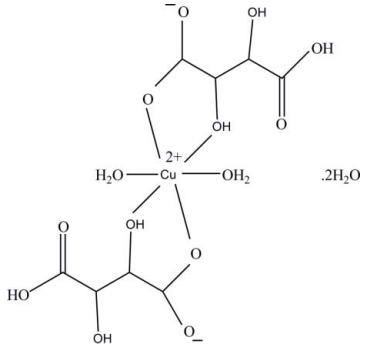
Key indicators: single-crystal X-ray study; T = 100 K; mean σ(C–C) = 0.001 Å; R factor = 0.023; wR factor = 0.082; data-to-parameter ratio = 27.3.

The title complex, $[Cu(C_4H_5O_6)_2(H_2O)_2]\cdot 2H_2O$, contains a Cu^{II} ion lying on an inversion centre. The coordination geometry of the Cu^{II} ion is a distorted octahedron with four O atoms from two hydrogen tartrate ions occupying the equatorial positions and two O atoms from two coordinated water molecules occupying the axial positions. In the crystal structure, intermolecular O—H···O and C—H···O hydrogen bonds link the molecules into a three-dimensional network.

Related literature

For background to coordination polymers, see: Stang & Olenyuk (1997); Aakeroy & Seddon (1993); Munakata *et al.* (1999); Fujita *et al.* (1994); Hagrman *et al.* (1997). For the optical activity of tartaric acid, see: Synoradzki *et al.* (2008). For related structures, see: Jian *et al.* (2005). For the stability of the temperature controller used for the data collection, see: Cosier & Glazer (1986).



Experimental

Crystal data

$[Cu(C_4H_5O_6)_2(H_2O)_2]\cdot 2H_2O$
M_r = 433.76
Monoclinic, $P2_1/c$
a = 7.1577 (8) Å
b = 14.0989 (14) Å
c = 7.8910 (8) Å
β = 109.136 (2)°
V = 752.32 (14) Å^3
Z = 2
Mo $K\alpha$ radiation
μ = 1.54 mm^{-1}
T = 100 K
0.42 × 0.15 × 0.08 mm

Data collection

Bruker APEXII DUO CCD area-detector diffractometer
Absorption correction: multi-scan (*SADABS*; Bruker, 2009)
T_{min} = 0.563, T_{max} = 0.885
12361 measured reflections
3298 independent reflections
3001 reflections with $I > 2\sigma(I)$
R_{int} = 0.023

Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.023
$wR(F^2)$ = 0.082
S = 1.20
3298 reflections
121 parameters
H atoms treated by a mixture of independent and constrained refinement
$\Delta\rho_{max}$ = 0.68 e Å^{-3}
$\Delta\rho_{min}$ = −0.45 e Å^{-3}

Table 1
Hydrogen-bond geometry (Å, °).

D—H···A	D—H	H···A	D···A	D—H···A
O4—H4···O1W^{i}	0.82	1.91	2.7200 (12)	170
O2—H5···O2W^{ii}	0.72 (3)	1.82 (3)	2.5331 (12)	170 (3)
O6—H6···O3^{iii}	0.82	1.70	2.5092 (12)	167
O1W—H11···O5^{iv}	0.91	1.91	2.8119 (11)	175 (1)
O1W—H12···O4	0.96	1.85	2.8091 (11)	177
O2W—H21···O1^{v}	0.90	1.94	2.8298 (12)	173
O2W—H22···O5^{i}	0.89	1.98	2.8100 (12)	154
C2—H2···O6^{ii}	0.98	2.43	3.2727 (12)	143
C3—H3···O4^{i}	0.98	2.46	3.4160 (13)	166

Symmetry codes: (i) $x, -y+\frac{1}{2}, z+\frac{1}{2}$; (ii) $-x+2, -y, -z+1$; (iii) $x+1, y, z$; (iv) $x-1, -y+\frac{1}{2}, z-\frac{1}{2}$; (v) $-x+1, -y, -z+1$.

Data collection: *APEX2* (Bruker, 2009); cell refinement: *SAINT* (Bruker, 2009); data reduction: *SAINT*; program(s) used to solve structure: *SHELXTL* (Sheldrick, 2008); program(s) used to refine structure: *SHELXTL*; molecular graphics: *SHELXTL*; software used to prepare material for publication: *SHELXTL* and *PLATON* (Spek, 2009).

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Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: IS2556).

References

Aakeroy, C. B. & Seddon, K. R. (1993). *Chem. Soc. Rev.* **6**, 397–407.
Bruker (2009). *APEX2*, *SAINT* and *SADABS*. Bruker AXS Inc., Madison, Wisconsin, USA.
Cosier, J. & Glazer, A. M. (1986). *J. Appl. Cryst.* **19**, 105–107.
Fujita, M., Kwon, Y. J., Miyazawa, M. & Ogura, K. (1994). *J. Chem. Soc. Chem. Commun.* **17**, 1997–1998.

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§ Thomson Reuters ResearcherID: A-3561-2009.

Hagrman, D., Zubieta, C., Rose, D. J., Zubieta, J. & Haushalter, R. C. (1997). *Angew. Chem. Int. Ed. Engl.* **35**, 873–877.
Jian, F. F., Zhao, P. & Wang, Q. (2005). *J. Coord. Chem.* **58**, 1133–1138.
Munakata, M., Wu, L. P. & Kuroda-sowa, T. (1999). *Inorg. Chem.* **46**, 17–3.
Sheldrick, G. M. (2008). *Acta Cryst.* A**64**, 112–122.
Spek, A. L. (2009). *Acta Cryst.* D**65**, 148–155.
Stang, P. J. & Olenyuk, B. (1997). *Acc. Chem. Res.* **30**, 502–518.
Synoradzki, L., Bernas, U. & Ruskowski, P. (2008). *Org. Prep. Proced. Int.* **40**, 163–200.

supplementary materials

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Diaquabis(hydrogen tartrato)copper(II) dihydrate

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Comment

In recent years, there has been great interest in the study of coordination polymers with network structures due to their possible chemical and physical properties (Stang & Olenyuk, 1997; Aakeroy & Seddon, 1993; Munakata *et al.*, 1999). A number of unique networks have been obtained by reactions between transition metal ions and rationally designed organic ligands (Fujita *et al.*, 1994; Hagrman *et al.*, 1997). Tartaric acid has been used as building blocks to construct 1D, 2D and 3D frameworks due to the diversity of binding modes of the carboxyl group and hydroxyl group in the tartaric acid. It has many applications such as in making silver mirrors, in the manufacture of soft drinks, to provide tartness to foods, in tanning leather, and in making blueprints. Tartaric acid also has optical activity (Synoradzki *et al.*, 2008). We report the crystal structure of (I).

(I) consists of a copper ion lying on a crystallographic inversion centre, two hydrogen tartrate ions, two coordinated water molecules and two uncoordinated water molecules (Fig. 1). The environment about the copper(II) ion is a distorted octahedron with four oxygen atoms from two hydrogen tartrate ions and two oxygen atoms from the coordinated water molecules completing the coordination. All the four oxygen atoms from the two hydrogen tartrate anions occupy equatorial positions and the oxygen atoms from the water molecules occupy in the axial positions. The equatorial and axial distances of Cu—O [Cu—O1 = 1.9327 (7) Å; Cu—O2 = 1.9637 (7) Å and Cu—O1W = 2.4651 (8) Å] agree with those reported for similar systems (Jian *et al.*, 2005).

In the crystal structure, intermolecular O1W—H12···O4, O4—H4···O1W, O2—H5···O2W, O6—H6···O3, O1W—H11···O5, O2W—H21···O1, O2W—H22···O5, C2—H2···O6 and C3—H3···O4 hydrogen bonds (Table 1) link the molecules into a three-dimensional network.

Experimental

DL-Tartaric acid (0.02 mol, 3.0 g) was dissolved in distilled water in a flat bottom flask with magnetic stirrer. $CuCl_2$ (0.01 mol, 1.45 g) was added in small portions with continuous stirring for three hours at room temperature. The blue crystals formed were washed with *N,N*-dimethylformamide then with methanol and dried at 353 K.

Refinement

Atom H5 was located in a difference Fourier map and refined freely. The remaining H atoms, excepting the water H atoms, were positioned geometrically (C—H = 0.98 Å and O—H = 0.82 Å) and were refined using a riding model, with U_{iso}(H) = 1.2U_{eq}(C) or 1.5U_{eq}(O). The water H atoms were located in the difference map and then treated as riding atoms on the parent O atoms, with O—H = 0.8936–0.9551 Å and U_{iso}(H) = 1.5U_{eq}(O).

Figures

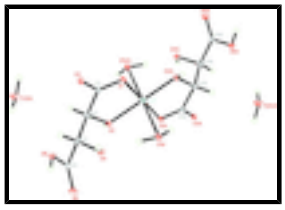


Fig. 1. The molecular structure of the title compound, showing 50% probability displacement ellipsoids and the atom-numbering scheme. C1A–C4A/O1A–O6A/O1WA/O2WA are generated by the symmetry code 1-*x*, -*y*, -*z*.

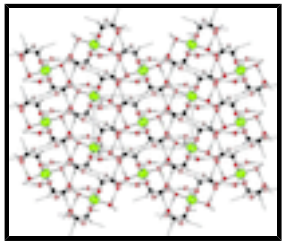


Fig. 2. The crystal packing of the title compound, showing hydrogen-bonded (dashed lines) network.

Diaquabis(hydrogen tartrato)copper(II) dihydrate

Crystal data

$[Cu(C_4H_5O_6)_2(H_2O)_2]\cdot 2H_2O$	$F(000) = 446$
$M_r = 433.76$	$D_x = 1.915$ Mg m^{-3}
Monoclinic, $P2_1/c$	Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å
Hall symbol: -P 2ybc	Cell parameters from 6852 reflections
$a = 7.1577$ (8) Å	$\theta = 3.6$–$35.0°$
$b = 14.0989$ (14) Å	$\mu = 1.54$ mm^{-1}
$c = 7.8910$ (8) Å	$T = 100$ K
$\beta = 109.136$ (2)°	Plate, blue
$V = 752.32$ (14) Å^3	0.42 × 0.15 × 0.08 mm
$Z = 2$	

Data collection

Bruker APEXII DUO CCD area-detector diffractometer	3298 independent reflections
Radiation source: fine-focus sealed tube	3001 reflections with $I > 2\sigma(I)$
graphite	$R_{int} = 0.023$
φ and ω scans	$\theta_{max} = 35.0°$, $\theta_{min} = 2.9°$
Absorption correction: multi-scan (*SADABS*; Bruker, 2009)	$h = -11 \rightarrow 11$
$T_{min} = 0.563$, $T_{max} = 0.885$	$k = -21 \rightarrow 22$
12361 measured reflections	$l = -12 \rightarrow 12$

Refinement

Refinement on F^2	Primary atom site location: structure-invariant direct methods
Least-squares matrix: full	Secondary atom site location: difference Fourier map

$R[F^2 > 2\sigma(F^2)] = 0.023$	Hydrogen site location: inferred from neighbouring sites
$wR(F^2) = 0.082$	H atoms treated by a mixture of independent and constrained refinement
$S = 1.20$	$w = 1/[\sigma^2(F_o^2) + (0.0456P)^2 + 0.1293P]$ where $P = (F_o^2 + 2F_c^2)/3$
3298 reflections	$(\Delta/\sigma)_{max} = 0.001$
121 parameters	$\Delta\rho_{max} = 0.68$ e Å^{-3}
0 restraints	$\Delta\rho_{min} = -0.45$ e Å^{-3}

Special details

Experimental. The crystal was placed in the cold stream of an Oxford Cryosystems Cobra open-flow nitrogen cryostat (Cosier & Glazer, 1986) operating at 100.0 (1) K.

Geometry. All s.u.'s (except the s.u. in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell s.u.'s are taken into account individually in the estimation of s.u.'s in distances, angles and torsion angles; correlations between s.u.'s in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell s.u.'s is used for estimating s.u.'s involving l.s. planes.

Refinement. Refinement of F^2 against ALL reflections. The weighted R-factor wR and goodness of fit S are based on F^2, conventional R-factors R are based on F, with F set to zero for negative F^2. The threshold expression of $F^2 > 2\sigma(F^2)$ is used only for calculating R-factors(gt) etc. and is not relevant to the choice of reflections for refinement. R-factors based on F^2 are statistically about twice as large as those based on F, and R- factors based on ALL data will be even larger.

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å^2)

	x	*y*	*z*	U_{iso}*/U_{eq}
Cu1	0.5000	0.0000	0.0000	0.00746 (6)
O1	0.39754 (10)	0.03576 (5)	0.18906 (9)	0.00912 (12)
O2	0.75259 (11)	0.04633 (5)	0.16577 (9)	0.00829 (12)
O3	0.48127 (11)	0.11064 (5)	0.45343 (10)	0.00963 (12)
O4	0.69066 (11)	0.24378 (5)	0.22934 (10)	0.00920 (12)
H4	0.6209	0.2764	0.2705	0.014*
O5	1.08144 (12)	0.25669 (5)	0.29938 (12)	0.01450 (14)
O6	1.13354 (11)	0.12193 (5)	0.45912 (10)	0.01096 (13)
H6	1.2407	0.1230	0.4424	0.016*
C1	0.52178 (13)	0.07526 (6)	0.32500 (12)	0.00733 (14)
C2	0.73709 (13)	0.08036 (6)	0.33188 (11)	0.00687 (14)
H2	0.8181	0.0405	0.4303	0.008*
C3	0.80915 (13)	0.18289 (6)	0.36467 (12)	0.00714 (14)
H3	0.8008	0.2036	0.4805	0.009*
C4	1.02337 (14)	0.19094 (6)	0.37032 (12)	0.00806 (14)
O1W	0.46452 (11)	0.16624 (5)	−0.10244 (10)	0.01087 (13)
H11	0.3385	0.1878	−0.1356	0.016*
H12	0.5389	0.1917	0.0120	0.016*
O2W	0.94287 (12)	0.05593 (6)	0.78307 (13)	0.01680 (16)
H21	0.8316	0.0315	0.7943	0.025*
H22	0.9492	0.1191	0.7909	0.025*

H5	0.832 (5)	0.0119 (17)	0.174 (4)	0.034 (7)*

Atomic displacement parameters (Å^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Cu1	0.00525 (8)	0.00959 (9)	0.00761 (8)	−0.00150 (5)	0.00221 (6)	−0.00224 (4)
O1	0.0068 (3)	0.0113 (3)	0.0093 (3)	−0.0019 (2)	0.0027 (2)	−0.0022 (2)
O2	0.0063 (3)	0.0096 (3)	0.0089 (3)	0.0004 (2)	0.0025 (2)	−0.0024 (2)
O3	0.0082 (3)	0.0113 (3)	0.0103 (3)	−0.0005 (2)	0.0042 (2)	−0.0021 (2)
O4	0.0084 (3)	0.0086 (3)	0.0103 (3)	0.0030 (2)	0.0026 (2)	0.0020 (2)
O5	0.0092 (3)	0.0115 (3)	0.0228 (4)	−0.0008 (2)	0.0052 (3)	0.0063 (3)
O6	0.0064 (3)	0.0098 (3)	0.0168 (3)	0.0018 (2)	0.0041 (2)	0.0043 (2)
C1	0.0068 (3)	0.0063 (3)	0.0089 (3)	0.0001 (3)	0.0026 (3)	0.0008 (3)
C2	0.0055 (3)	0.0071 (3)	0.0080 (3)	−0.0003 (2)	0.0021 (3)	−0.0006 (3)
C3	0.0061 (3)	0.0068 (3)	0.0083 (3)	0.0001 (3)	0.0019 (3)	0.0002 (2)
C4	0.0071 (3)	0.0073 (3)	0.0093 (3)	−0.0003 (3)	0.0021 (3)	−0.0010 (3)
O1W	0.0090 (3)	0.0101 (3)	0.0127 (3)	0.0002 (2)	0.0024 (2)	0.0003 (2)
O2W	0.0104 (3)	0.0101 (3)	0.0321 (4)	0.0008 (2)	0.0098 (3)	0.0007 (3)

Geometric parameters (Å, °)

Cu1—O1	1.9327 (7)	O5—C4	1.2239 (12)
Cu1—O1^{i}	1.9327 (7)	O6—C4	1.3027 (11)
Cu1—O2^{i}	1.9637 (7)	O6—H6	0.8200
Cu1—O2	1.9637 (7)	C1—C2	1.5259 (13)
Cu1—O1W	2.4651 (8)	C2—C3	1.5281 (13)
Cu1—O1W^{i}	2.4651 (8)	C2—H2	0.9800
O1—C1	1.2753 (11)	C3—C4	1.5235 (13)
O2—C2	1.4339 (11)	C3—H3	0.9800
O2—H5	0.73 (3)	O1W—H11	0.9051
O3—C1	1.2461 (11)	O1W—H12	0.9551
O4—C3	1.4152 (11)	O2W—H21	0.8982
O4—H4	0.8200	O2W—H22	0.8936
O1—Cu1—O1W	88.90 (3)	O3—C1—C2	116.99 (8)
O1—Cu1—O1W^{i}	91.11 (3)	O1—C1—C2	117.92 (8)
O1W—Cu1—O2	82.85 (3)	O2—C2—C1	109.36 (7)
O1W—Cu1—O1W^{i}	180	O2—C2—C3	110.39 (7)
O1W—Cu1—O2	82.85 (3)	C1—C2—C3	109.36 (7)
O1W^{i}—Cu1—O2^{i}	82.85 (3)	O2—C2—H2	109.2
O1^{i}—Cu1—O1W^{i}	88.90 (3)	C1—C2—H2	109.2
O1—Cu1—O1^{i}	180.00 (6)	C3—C2—H2	109.2
O1—Cu1—O2^{i}	95.83 (3)	O4—C3—C4	108.99 (7)
O1^{i}—Cu1—O2^{i}	84.17 (3)	O4—C3—C2	111.13 (7)
O1—Cu1—O2	84.17 (3)	C4—C3—C2	110.86 (7)
O1^{i}—Cu1—O2	95.83 (3)	O4—C3—H3	108.6
O2^{i}—Cu1—O2	180.0	C4—C3—H3	108.6

C1—O1—Cu1	115.26 (6)	C2—C3—H3	108.6
C2—O2—Cu1	112.96 (5)	O5—C4—O6	125.12 (9)
C2—O2—H5	116 (2)	O5—C4—C3	122.17 (8)
Cu1—O2—H5	111 (2)	O6—C4—C3	112.71 (8)
C3—O4—H4	109.5	H11—O1W—H12	110.0
C4—O6—H6	109.5	H21—O2W—H22	113.7
O3—C1—O1	125.09 (9)		
$O2^{i}$—Cu1—O1—C1	−176.70 (7)	O3—C1—C2—O2	−173.54 (8)
O2—Cu1—O1—C1	3.30 (7)	O1—C1—C2—O2	6.20 (11)
O1—Cu1—O2—C2	0.36 (6)	O3—C1—C2—C3	−52.55 (10)
$O1^{i}$—Cu1—O2—C2	−179.64 (6)	O1—C1—C2—C3	127.19 (8)
O1W—Cu1—O1—C1	−79.64 (6)	O2—C2—C3—O4	62.36 (9)
$O1W^{i}$—Cu1—O1—C1	100.37 (6)	C1—C2—C3—O4	−58.01 (9)
O1W—Cu1—O2—C2	89.98 (6)	O2—C2—C3—C4	−59.01 (9)
$O1W^{i}$—Cu1—O2—C2	−90.02 (6)	C1—C2—C3—C4	−179.37 (7)
Cu1—O1—C1—O3	173.56 (7)	O4—C3—C4—O5	16.25 (12)
Cu1—O1—C1—C2	−6.17 (10)	C2—C3—C4—O5	138.88 (9)
Cu1—O2—C2—C1	−3.22 (9)	O4—C3—C4—O6	−164.52 (8)
Cu1—O2—C2—C3	−123.59 (6)	C2—C3—C4—O6	−41.90 (10)

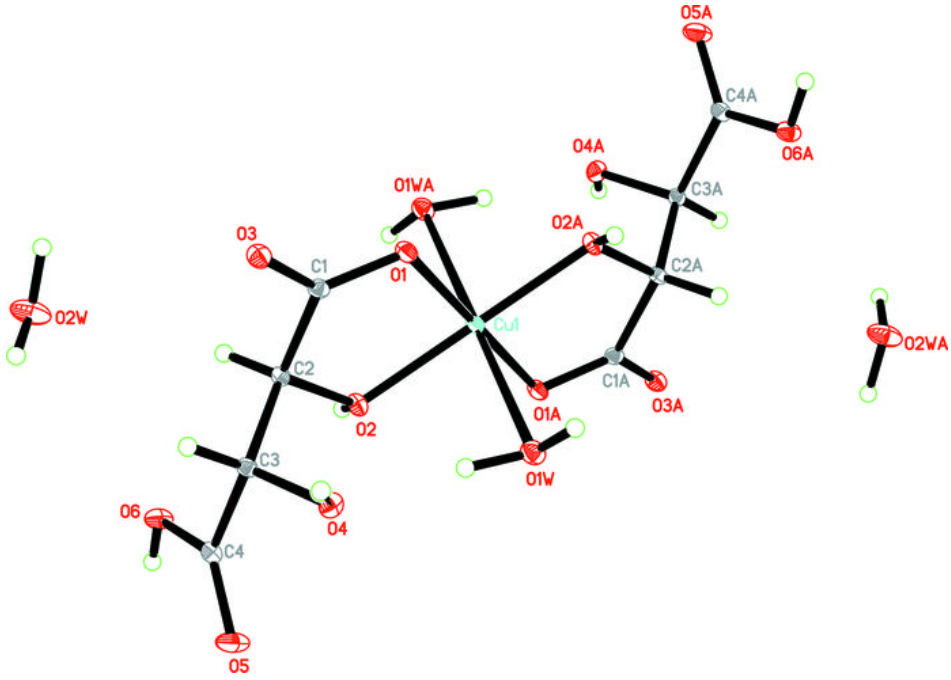
Symmetry codes: (i) −*x*+1, −*y*, −*z*.

Hydrogen-bond geometry (Å, °)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
O4—H4···$O1W^{ii}$	0.82	1.91	2.7200 (12)	170
O2—H5···$O2W^{iii}$	0.72 (3)	1.82 (3)	2.5331 (12)	170 (3)
O6—H6···$O3^{iv}$	0.82	1.70	2.5092 (12)	167
O1W—H11···$O5^{v}$	0.91	1.91	2.8119 (11)	175 (1)
O1W—H12···O4	0.96	1.85	2.8091 (11)	177
O2W—H21···$O1^{vi}$	0.90	1.94	2.8298 (12)	173
O2W—H22···$O5^{ii}$	0.89	1.98	2.8100 (12)	154
C2—H2···$O6^{iii}$	0.98	2.43	3.2727 (12)	143
C3—H3···$O4^{ii}$	0.98	2.46	3.4160 (13)	166

Symmetry codes: (ii) *x*, −*y*+1/2, *z*+1/2; (iii) −*x*+2, −*y*, −*z*+1; (iv) *x*+1, *y*, *z*; (v) *x*−1, −*y*+1/2, *z*−1/2; (vi) −*x*+1, −*y*, −*z*+1.

Fig. 1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C4A
06A
04A
C3A
01WA
02A
03
C1
01
C2A
02W
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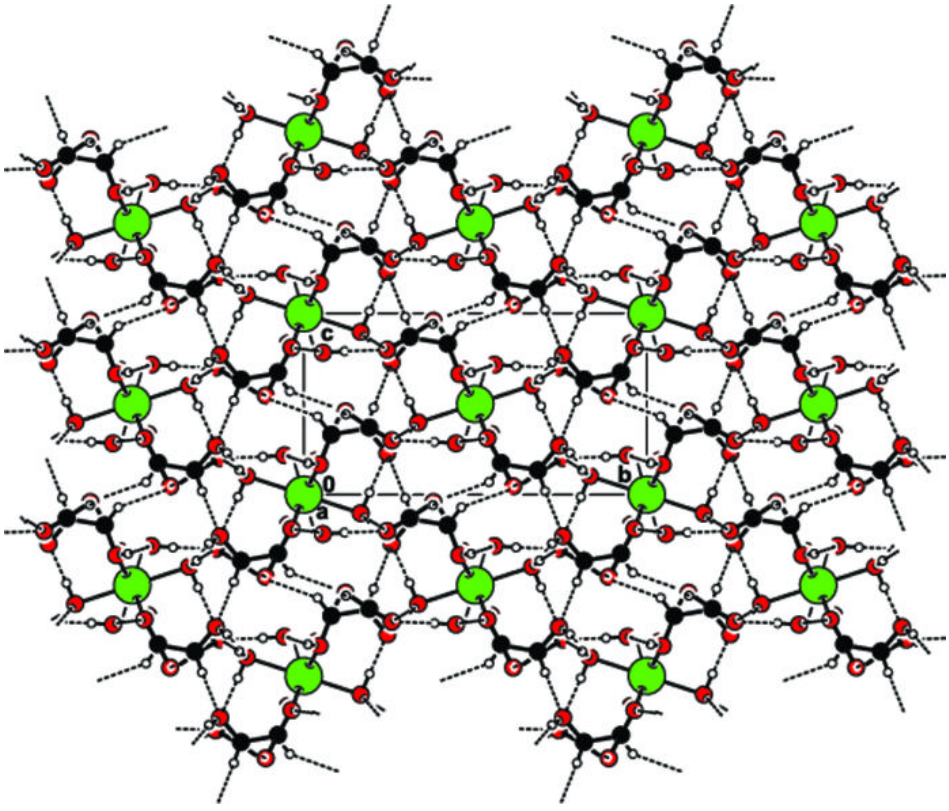
02
C3
01W
06
04
C4
05

Fig. 2



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(*Z*)-3-(2-{2-[1-(4-Hydroxyphenyl)ethylidene]hydrazin-1-yl}-1,3-thiazol-4-yl)-2*H*-chromen-2-one

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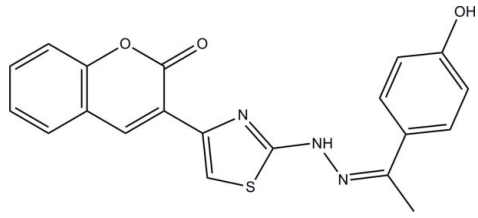
Key indicators: single-crystal X-ray study; T = 100 K; mean σ(C–C) = 0.003 Å; R factor = 0.045; wR factor = 0.161; data-to-parameter ratio = 15.6.

In the title compound, $C_{20}H_{15}N_3O_3S$, an intramolecular C—H···O hydrogen bond generates an S(6) ring motif. The chromene ring system is inclined at dihedral angles of 14.21 (9) and 9.91 (10)°, respectively, with respect to the thiazole and benzene rings. The thiazole ring makes a dihedral angle of 24.06 (11)° with the benzene ring. In the crystal structure, O—H···O hydrogen bonds link the molecules into a zigzag chain along [20$\bar{1}$]. Weak N—H···O and C—H···O interactions connect the chains into a three-dimensional network. π–π stacking interactions with a centroid–centroid distance of 3.4209 (14) Å are also observed between the chains.

Related literature

For a related structure, see: Arshad *et al.* (2010). For the synthesis, see: Siddiqui *et al.* (2009); Liu *et al.* (2008). For general background to and the biological activity of coumarin derivatives, see: Anderson *et al.* (2002); Finn *et al.* (2004); Hofmanova *et al.* (1998). For the biological activity of aminothiazole derivatives, see: Hiremath *et al.* (1992); Gursoy & Karah (2000); Jayashree *et al.* (2005); Patt *et al.* (1992). For bond-length data, see: Allen *et al.* (1987). For the stability of the temperature controller used for the data collection, see: Cosier & Glazer (1986). For hydrogen-bond motifs, see: Bernstein *et al.* (1995).



Experimental

Crystal data

$C_{20}H_{15}N_3O_3S$
M_r = 377.41
Monoclinic, $P2_1/c$
a = 9.1117 (16) Å
b = 16.225 (3) Å
c = 12.113 (2) Å
β = 104.657 (3)°
V = 1732.5 (5) Å^3
Z = 4
Mo $K\alpha$ radiation
μ = 0.21 mm^{-1}
T = 100 K
0.38 × 0.06 × 0.05 mm

Data collection

Bruker SMART APEXII DUO CCD area-detector diffractometer
Absorption correction: multi-scan (*SADABS*; Bruker, 2009)
T_{min} = 0.922, T_{max} = 0.990
16535 measured reflections
3957 independent reflections
2932 reflections with $I > 2\sigma(I)$
R_{int} = 0.060

Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.045
$wR(F^2)$ = 0.161
S = 1.10
3957 reflections
253 parameters
H atoms treated by a mixture of independent and constrained refinement
$\Delta\rho_{max}$ = 0.40 e Å^{-3}
$\Delta\rho_{min}$ = −0.41 e Å^{-3}

Table 1
Hydrogen-bond geometry (Å, °).

D—H···A	D—H	H···A	D···A	D—H···A
N2—H12*N*···O3^{i}	0.88 (2)	2.36 (2)	3.213 (3)	164 (2)
O3—H13*O*···O2^{ii}	0.89 (4)	1.87 (4)	2.743 (3)	169 (3)
C5—H5*A*···O3^{iii}	0.93	2.46	3.386 (3)	173
C11—H11*A*···O2	0.93	2.39	2.915 (3)	115

Symmetry codes: (i) $-x+1, y-\frac{1}{2}, -z-\frac{1}{2}$; (ii) $x+1, -y+\frac{1}{2}, z-\frac{1}{2}$; (iii) $x-1, y-1, z$.

Data collection: *APEX2* (Bruker, 2009); cell refinement: *SAINT* (Bruker, 2009); data reduction: *SAINT*; program(s) used to solve structure: *SHELXTL* (Sheldrick, 2008); program(s) used to refine structure: *SHELXTL*; molecular graphics: *SHELXTL*; software used to prepare material for publication: *SHELXTL* and *PLATON* (Spek, 2009).

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§ Thomson Reuters ResearcherID: A-5525-2009.
¶ Thomson Reuters ResearcherID: A-3561-2009.

Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: IS2557).

References

Allen, F. H., Kennard, O., Watson, D. G., Brammer, L., Orpen, A. G. & Taylor, R. (1987). *J. Chem. Soc. Perkin Trans. 2*, pp. S1–19.

Anderson, D. M., Shelley, S., Crick, N. & Buraglio, L. (2002). *J. Clin. Pharmacol.* **42**, 1358–1365.

Arshad, A., Osman, H., Lam, C. K., Quah, C. K. & Fun, H.-K. (2010). *Acta Cryst.* E**66**, o1446–o1447.

Bernstein, J., Davis, R. E., Shimoni, L. & Chang, N.-L. (1995). *Angew. Chem. Int. Ed. Engl.* **34**, 1555–1573.

Bruker (2009). *APEX2*, *SAINT* and *SADABS*. Bruker AXS Inc., Madison, Wisconsin, USA.

Cosier, J. & Glazer, A. M. (1986). *J. Appl. Cryst.* **19**, 105–107.

Finn, G. J., Creaven, B. S. & Egan, D. A. (2004). *Cancer Lett.* **214**, 43–54.

Gursoy, A. & Karah, N. (2000). *Arzneim. Forsch.* **50**, 167–172.

Hiremath, S. P., Swamy, K. M. K. & Mrnthyunjayaswamy, B. H. M. (1992). *J. Indian Chem. Soc.* **69**, 87–89.

Hofmanova, J., Kozubik, A., Dusek, L. & Pachernik, J. (1998). *Eur. J. Pharmacol.* **350**, 273–284.

Jayashree, B. S., Anuradha, D. & Venugopala, N. K. (2005). *Asian J. Chem.* **17**, 2093–2097.

Liu, J., Yei, W., Wan, Y., Ma, L. & Song, H. (2008). *Bioorg. Med. Chem.* **16**, 1096–1102.

Patt, W. C., Hamilton, H. W., Taylor, M. D., Ryan, M. J., Taylor, D. G., Conolly, C. J. C., Doherty, A. M., Klutchko, S. R., Sircar, I., Steinbaugh, B. A., Batley, B. L., Painchaud, C. A., Rapundalo, S. T., Michniewicz, B. M. & Olson, S. C. (1992). *J. Med. Chem.* **35**, 2562–2572.

Sheldrick, G. M. (2008). *Acta Cryst.* A**64**, 112–122.

Siddiqui, N., Faiz, M. A. & Suroor, A. K. (2009). *Acta Pol. Pharm. Drug Research*, **66**, 161–167.

Spek, A. L. (2009). *Acta Cryst.* D**65**, 148–155.

supplementary materials

Acta Cryst. (2010). E**66**, o1632-o1633 [**doi:10.1107/S1600536810021604**]

(*Z*)-3-(2-{2-[1-(4-Hydroxyphenyl)ethylidene]hydrazin-1-yl}-1,3-thiazol-4-yl)-2*H*-chromen-2-one

A. Arshad, H. Osman, C. K. Lam, C. K. Quah and H.-K. Fun

Comment

Aminothiazole ring is found to be associated with diverse pharmacological activities such as antifungal (Hiremath *et al.*, 1992), anti-tuberculosis (Gursoy & Karah, 2000), anti-inflammation (Jayashree *et al.*, 2005) and antihypertensive (Patt *et al.*, 1992). In addition, coumarin and its derivatives also exhibit significant enzyme inhibition (Hofmanova *et al.*, 1998), anticoagulant (Anderson *et al.*, 2002) and free radical scavenging (Finn *et al.*, 2004) activities. The title compound is a new derivative of thiazolyl coumarin. We present here its crystal structure.

Bond lengths (Allen *et al.*, 1987) and the angles of the title compound (Fig. 1), are within the normal range and comparable with a related structure (Arshad *et al.*, 2010). The molecular structure is stabilized by intramolecular C11—H11A···O2 hydrogen bond which generates an *S*(6) ring motif (Bernstein *et al.*, 1995). The chromene (O1/C1–C9) ring system and thiazole (S1/N1/C10–C12) ring are approximately planar, with the maximum deviation of 0.021 (2) Å for atom O1 and 0.008 (2) Å for atom C10. The chromene ring system is inclined at angles of 14.21 (9) and 9.91 (10)° with respect to the thiazole and benzene (C14–C19) rings, respectively. The thiazole ring makes a dihedral angle of 24.06 (11)° with the benzene ring.

In the crystal packing (Fig.2), the N2—H12N···O3 and C5—H5A···O3 interactions form a pair of bifurcated acceptor bonds which together with O3—H13O···O2 interactions link the independent molecules into a three-dimensional network. The short intermolecular distance [3.4209 (14) Å] between symmetry-related S1/N1/C10–C12 (centroid *Cg*1) and O1/C1/C2/C7–C9 (centroid *Cg*2) rings [symmetry code: -*x*, -*y*, -*z*] indicates the existence of π–π stacking interaction.

Experimental

4-Hydroxyacetophenone thiosemicarbazone (Liu *et al.*, 2008) and 3-[ω-bromoacetyl coumarin] (Siddiqui *et al.*, 2009) were synthesized as reported in the literature. The title compound was obtained by the cyclocondensation of 4-hydroxyacetophenone thiosemicarbazone with 3-[ω-bromoacetyl coumarin]. A solution of 3-[ω-bromoacetyl coumarin] (2.5 mmol) and 4-hydroxyacetophenone thiosemicarbazone (2.5 mmol) in chloroform-ethanol (2:1) was refluxed for 45 minutes at 60 °C to get dense yellow precipitates. The reaction mixture was cooled in ice bath and basified with ammonia to pH 7–8. The title compound was recrystallized from ethanol-chloroform (3:2) as yellow needle-like crystals.

Refinement

Atoms H12N and H13O were located in a difference Fourier map and allowed to be refined freely. The rest of H atoms were positioned geometrically and refined using a riding model, with C—H = 0.93–0.96 Å, and with U_{iso}(H) = 1.2 U_{eq}(C) or 1.5 U_{eq}(C). A rotating-group model was applied for the methyl groups.

Figures

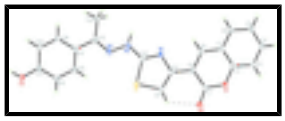


Fig. 1. The molecular structure of the title compound showing 50% probability displacement ellipsoids for non-H atoms and the atom-numbering scheme. Intramolecular interaction is shown by a dashed line.

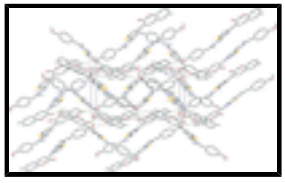


Fig. 2. The crystal structure of the title compound viewed along the *c* axis. H atoms not involved in intermolecular interactions (dashed lines) have been omitted for clarity.

(*Z*)-3-(2-{2-[1-(4-Hydroxyphenyl)ethylidene]hydrazin-1-yl}-1,3- thiazol-4-yl)-2*H*-chromen-2-one

Crystal data

$C_{20}H_{15}N_3O_3S$	$F(000) = 784$
$M_r = 377.41$	$D_x = 1.447$ Mg m^{-3}
Monoclinic, $P2_1/c$	Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å
Hall symbol: -P 2ybc	Cell parameters from 2347 reflections
$a = 9.1117$ (16) Å	$\theta = 2.8$–$27.3°$
$b = 16.225$ (3) Å	$\mu = 0.21$ mm^{-1}
$c = 12.113$ (2) Å	$T = 100$ K
$\beta = 104.657$ (3)°	Needle, yellow
$V = 1732.5$ (5) Å^3	0.38 × 0.06 × 0.05 mm
$Z = 4$	

Data collection

Bruker SMART APEXII DUO CCD area-detector diffractometer	3957 independent reflections
Radiation source: fine-focus sealed tube	2932 reflections with $I > 2\sigma(I)$
graphite	$R_{int} = 0.060$
φ and ω scans	$\theta_{max} = 27.5°$, $\theta_{min} = 2.1°$
Absorption correction: multi-scan (*SADABS*; Bruker, 2009)	$h = -11 \rightarrow 11$
$T_{min} = 0.922$, $T_{max} = 0.990$	$k = -21 \rightarrow 21$
16535 measured reflections	$l = -15 \rightarrow 15$

Refinement

Refinement on F^2	Primary atom site location: structure-invariant direct methods
Least-squares matrix: full	Secondary atom site location: difference Fourier map
$R[F^2 > 2\sigma(F^2)] = 0.045$	Hydrogen site location: inferred from neighbouring sites
$wR(F^2) = 0.161$	H atoms treated by a mixture of independent and constrained refinement

S = 1.10	$w = 1/[\sigma^2(F_o^2) + (0.0927P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
3957 reflections	$(\Delta/\sigma)_{max} = 0.001$
253 parameters	$\Delta\rho_{max} = 0.40$ e Å^{-3}
0 restraints	$\Delta\rho_{min} = -0.41$ e Å^{-3}

Special details

Experimental. The crystal was placed in the cold stream of an Oxford Cyrosystems Cobra open-flow nitrogen cryostat (Cosier & Glazer, 1986) operating at 100.0 (1) K.

Geometry. All e.s.d.'s (except the e.s.d. in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell e.s.d.'s are taken into account individually in the estimation of e.s.d.'s in distances, angles and torsion angles; correlations between e.s.d.'s in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell e.s.d.'s is used for estimating e.s.d.'s involving l.s. planes.

Refinement. Refinement of F^2 against ALL reflections. The weighted *R*-factor *wR* and goodness of fit *S* are based on F^2, conventional *R*-factors *R* are based on *F*, with *F* set to zero for negative F^2. The threshold expression of $F^2 > \sigma(F^2)$ is used only for calculating *R*-factors(gt) *etc*. and is not relevant to the choice of reflections for refinement. *R*-factors based on F^2 are statistically about twice as large as those based on *F*, and *R*- factors based on ALL data will be even larger.

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å^2)

	x	*y*	*z*	U_{iso}*/U_{eq}
S1	0.38934 (7)	0.12646 (3)	0.08727 (5)	0.01862 (18)
O1	−0.03963 (18)	−0.12925 (9)	0.20648 (14)	0.0161 (4)
O2	0.05580 (19)	−0.00659 (10)	0.25771 (15)	0.0200 (4)
O3	0.8063 (2)	0.48865 (10)	−0.15666 (16)	0.0223 (4)
N1	0.2563 (2)	−0.00002 (11)	−0.02742 (17)	0.0157 (4)
N2	0.4034 (2)	0.07847 (12)	−0.12284 (19)	0.0180 (4)
N3	0.4819 (2)	0.15129 (11)	−0.11761 (17)	0.0153 (4)
C1	0.0479 (3)	−0.06337 (13)	0.1917 (2)	0.0155 (5)
C2	−0.0638 (2)	−0.19722 (13)	0.1346 (2)	0.0148 (5)
C3	−0.1574 (3)	−0.25933 (14)	0.1574 (2)	0.0181 (5)
H3A	−0.2042	−0.2544	0.2170	0.022*
C4	−0.1785 (3)	−0.32860 (14)	0.0888 (2)	0.0198 (5)
H4A	−0.2406	−0.3708	0.1025	0.024*
C5	−0.1085 (3)	−0.33653 (14)	−0.0009 (2)	0.0212 (5)
H5A	−0.1237	−0.3838	−0.0458	0.025*
C6	−0.0166 (3)	−0.27378 (14)	−0.0225 (2)	0.0190 (5)
H6A	0.0295	−0.2789	−0.0825	0.023*
C7	0.0075 (2)	−0.20265 (13)	0.0454 (2)	0.0152 (5)
C8	0.1015 (3)	−0.13536 (13)	0.0300 (2)	0.0147 (5)
H8A	0.1499	−0.1381	−0.0289	0.018*
C9	0.1230 (2)	−0.06783 (13)	0.0976 (2)	0.0146 (5)
C10	0.2180 (2)	0.00109 (13)	0.07732 (19)	0.0138 (5)
C11	0.2764 (3)	0.06418 (14)	0.1475 (2)	0.0194 (5)
H11A	0.2582	0.0730	0.2188	0.023*

C12	0.3457 (2)	0.06236 (13)	−0.0311 (2)	0.0151 (5)
C13	0.5341 (3)	0.17206 (13)	−0.2030 (2)	0.0160 (5)
C14	0.6101 (2)	0.25398 (13)	−0.1918 (2)	0.0150 (5)
C15	0.5766 (3)	0.31265 (14)	−0.1168 (2)	0.0184 (5)
H15A	0.5077	0.2996	−0.0745	0.022*
C16	0.6444 (3)	0.38995 (14)	−0.1045 (2)	0.0207 (5)
H16A	0.6213	0.4280	−0.0541	0.025*
C17	0.7469 (3)	0.41031 (13)	−0.1679 (2)	0.0177 (5)
C18	0.7836 (3)	0.35256 (13)	−0.2415 (2)	0.0159 (5)
H18A	0.8541	0.3655	−0.2826	0.019*
C19	0.7150 (3)	0.27562 (13)	−0.2536 (2)	0.0166 (5)
H19A	0.7392	0.2377	−0.3038	0.020*
C20	0.5172 (3)	0.12174 (14)	−0.3094 (2)	0.0208 (5)
H20A	0.4122	0.1084	−0.3403	0.031*
H20B	0.5749	0.0718	−0.2914	0.031*
H20C	0.5537	0.1528	−0.3644	0.031*
H12N	0.364 (3)	0.0512 (15)	−0.186 (2)	0.016 (7)*
H13O	0.894 (4)	0.491 (2)	−0.176 (3)	0.060 (11)*

Atomic displacement parameters (Å^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
S1	0.0201 (3)	0.0173 (3)	0.0188 (3)	−0.0056 (2)	0.0057 (3)	−0.0023 (2)
O1	0.0168 (8)	0.0155 (8)	0.0185 (9)	−0.0017 (6)	0.0093 (7)	−0.0006 (6)
O2	0.0204 (9)	0.0213 (8)	0.0198 (9)	−0.0021 (6)	0.0081 (8)	−0.0047 (7)
O3	0.0233 (10)	0.0163 (8)	0.0321 (11)	−0.0043 (7)	0.0162 (9)	−0.0022 (7)
N1	0.0157 (10)	0.0157 (9)	0.0173 (11)	−0.0020 (7)	0.0070 (9)	0.0005 (7)
N2	0.0210 (11)	0.0158 (9)	0.0193 (12)	−0.0052 (8)	0.0089 (9)	−0.0005 (8)
N3	0.0126 (9)	0.0149 (9)	0.0176 (11)	−0.0022 (7)	0.0023 (8)	0.0020 (7)
C1	0.0134 (11)	0.0169 (10)	0.0156 (12)	0.0005 (8)	0.0024 (9)	0.0012 (9)
C2	0.0131 (11)	0.0149 (10)	0.0152 (12)	0.0017 (8)	0.0016 (9)	0.0007 (8)
C3	0.0165 (11)	0.0222 (11)	0.0162 (12)	0.0000 (9)	0.0053 (10)	0.0032 (9)
C4	0.0169 (12)	0.0190 (11)	0.0236 (14)	−0.0052 (9)	0.0050 (10)	0.0024 (9)
C5	0.0224 (13)	0.0186 (11)	0.0213 (14)	−0.0040 (9)	0.0033 (11)	−0.0030 (10)
C6	0.0200 (12)	0.0212 (11)	0.0162 (13)	−0.0018 (9)	0.0055 (10)	−0.0020 (9)
C7	0.0141 (11)	0.0162 (10)	0.0143 (12)	0.0013 (8)	0.0017 (9)	0.0010 (8)
C8	0.0144 (11)	0.0188 (11)	0.0114 (12)	0.0017 (8)	0.0041 (9)	0.0018 (8)
C9	0.0122 (11)	0.0164 (10)	0.0161 (12)	0.0010 (8)	0.0054 (9)	0.0020 (9)
C10	0.0109 (11)	0.0170 (10)	0.0127 (12)	0.0016 (8)	0.0018 (9)	0.0028 (8)
C11	0.0227 (12)	0.0187 (11)	0.0194 (13)	−0.0024 (9)	0.0100 (11)	0.0000 (9)
C12	0.0129 (11)	0.0161 (10)	0.0159 (12)	0.0014 (8)	0.0029 (9)	0.0017 (9)
C13	0.0129 (11)	0.0174 (11)	0.0178 (13)	0.0009 (8)	0.0041 (10)	0.0027 (9)
C14	0.0127 (11)	0.0179 (11)	0.0140 (12)	0.0011 (8)	0.0027 (9)	0.0037 (9)
C15	0.0174 (12)	0.0202 (11)	0.0207 (13)	−0.0025 (9)	0.0106 (10)	0.0015 (9)
C16	0.0243 (13)	0.0168 (11)	0.0246 (14)	−0.0010 (9)	0.0127 (12)	−0.0037 (9)
C17	0.0183 (12)	0.0125 (10)	0.0233 (14)	−0.0009 (8)	0.0073 (10)	0.0027 (9)
C18	0.0139 (11)	0.0193 (11)	0.0162 (12)	0.0004 (8)	0.0067 (10)	0.0028 (9)
C19	0.0166 (11)	0.0188 (11)	0.0149 (12)	0.0033 (8)	0.0049 (10)	0.0015 (9)

C20	0.0208 (12)	0.0223 (12)	0.0198 (13)	−0.0039 (9)	0.0061 (11)	−0.0015 (10)

Geometric parameters (Å, °)

S1—C11	1.730 (2)	C6—H6A	0.9300
S1—C12	1.735 (2)	C7—C8	1.429 (3)
O1—C1	1.372 (3)	C8—C9	1.352 (3)
O1—C2	1.388 (3)	C8—H8A	0.9300
O2—C1	1.210 (3)	C9—C10	1.472 (3)
O3—C17	1.375 (3)	C10—C11	1.351 (3)
O3—H13O	0.89 (4)	C11—H11A	0.9300
N1—C12	1.307 (3)	C13—C14	1.489 (3)
N1—C10	1.399 (3)	C13—C20	1.500 (3)
N2—C12	1.369 (3)	C14—C19	1.400 (3)
N2—N3	1.374 (3)	C14—C15	1.401 (3)
N2—H12N	0.88 (3)	C15—C16	1.389 (3)
N3—C13	1.288 (3)	C15—H15A	0.9300
C1—C9	1.471 (3)	C16—C17	1.391 (3)
C2—C3	1.393 (3)	C16—H16A	0.9300
C2—C7	1.397 (3)	C17—C18	1.391 (3)
C3—C4	1.382 (3)	C18—C19	1.387 (3)
C3—H3A	0.9300	C18—H18A	0.9300
C4—C5	1.397 (3)	C19—H19A	0.9300
C4—H4A	0.9300	C20—H20A	0.9600
C5—C6	1.385 (3)	C20—H20B	0.9600
C5—H5A	0.9300	C20—H20C	0.9600
C6—C7	1.402 (3)		
C11—S1—C12	87.85 (11)	C11—C10—C9	128.6 (2)
C1—O1—C2	122.81 (18)	N1—C10—C9	115.73 (19)
C17—O3—H13O	112 (2)	C10—C11—S1	110.99 (18)
C12—N1—C10	108.79 (19)	C10—C11—H11A	124.5
C12—N2—N3	115.41 (19)	S1—C11—H11A	124.5
C12—N2—H12N	117.1 (17)	N1—C12—N2	123.1 (2)
N3—N2—H12N	124.5 (17)	N1—C12—S1	116.75 (18)
C13—N3—N2	118.8 (2)	N2—C12—S1	120.13 (17)
O2—C1—O1	116.5 (2)	N3—C13—C14	114.7 (2)
O2—C1—C9	126.0 (2)	N3—C13—C20	124.7 (2)
O1—C1—C9	117.55 (19)	C14—C13—C20	120.6 (2)
O1—C2—C3	117.3 (2)	C19—C14—C15	117.8 (2)
O1—C2—C7	120.29 (19)	C19—C14—C13	122.7 (2)
C3—C2—C7	122.4 (2)	C15—C14—C13	119.5 (2)
C4—C3—C2	117.9 (2)	C16—C15—C14	121.3 (2)
C4—C3—H3A	121.1	C16—C15—H15A	119.4
C2—C3—H3A	121.1	C14—C15—H15A	119.4
C3—C4—C5	121.4 (2)	C15—C16—C17	119.8 (2)
C3—C4—H4A	119.3	C15—C16—H16A	120.1
C5—C4—H4A	119.3	C17—C16—H16A	120.1
C6—C5—C4	119.7 (2)	O3—C17—C16	117.8 (2)
C6—C5—H5A	120.1	O3—C17—C18	122.3 (2)

C4—C5—H5A	120.1	C16—C17—C18	119.8 (2)
C5—C6—C7	120.5 (2)	C19—C18—C17	120.0 (2)
C5—C6—H6A	119.8	C19—C18—H18A	120.0
C7—C6—H6A	119.8	C17—C18—H18A	120.0
C2—C7—C6	118.1 (2)	C18—C19—C14	121.3 (2)
C2—C7—C8	117.6 (2)	C18—C19—H19A	119.4
C6—C7—C8	124.3 (2)	C14—C19—H19A	119.4
C9—C8—C7	122.7 (2)	C13—C20—H20A	109.5
C9—C8—H8A	118.7	C13—C20—H20B	109.5
C7—C8—H8A	118.7	H20A—C20—H20B	109.5
C8—C9—C1	119.0 (2)	C13—C20—H20C	109.5
C8—C9—C10	121.0 (2)	H20A—C20—H20C	109.5
C1—C9—C10	120.02 (19)	H20B—C20—H20C	109.5
C11—C10—N1	115.6 (2)		
C12—N2—N3—C13	−177.2 (2)	C8—C9—C10—N1	12.9 (3)
C2—O1—C1—O2	177.4 (2)	C1—C9—C10—N1	−166.16 (19)
C2—O1—C1—C9	−2.4 (3)	N1—C10—C11—S1	−1.4 (3)
C1—O1—C2—C3	−178.8 (2)	C9—C10—C11—S1	176.69 (18)
C1—O1—C2—C7	2.9 (3)	C12—S1—C11—C10	0.95 (18)
O1—C2—C3—C4	−177.9 (2)	C10—N1—C12—N2	180.0 (2)
C7—C2—C3—C4	0.3 (4)	C10—N1—C12—S1	−0.4 (2)
C2—C3—C4—C5	0.0 (4)	N3—N2—C12—N1	173.3 (2)
C3—C4—C5—C6	−0.4 (4)	N3—N2—C12—S1	−6.3 (3)
C4—C5—C6—C7	0.4 (4)	C11—S1—C12—N1	−0.31 (19)
O1—C2—C7—C6	177.9 (2)	C11—S1—C12—N2	179.3 (2)
C3—C2—C7—C6	−0.3 (3)	N2—N3—C13—C14	176.85 (19)
O1—C2—C7—C8	−1.6 (3)	N2—N3—C13—C20	−0.7 (3)
C3—C2—C7—C8	−179.8 (2)	N3—C13—C14—C19	158.3 (2)
C5—C6—C7—C2	−0.1 (3)	C20—C13—C14—C19	−24.1 (3)
C5—C6—C7—C8	179.4 (2)	N3—C13—C14—C15	−21.8 (3)
C2—C7—C8—C9	−0.1 (3)	C20—C13—C14—C15	155.9 (2)
C6—C7—C8—C9	−179.6 (2)	C19—C14—C15—C16	0.4 (4)
C7—C8—C9—C1	0.5 (3)	C13—C14—C15—C16	−179.6 (2)
C7—C8—C9—C10	−178.6 (2)	C14—C15—C16—C17	0.4 (4)
O2—C1—C9—C8	−179.2 (2)	C15—C16—C17—O3	177.3 (2)
O1—C1—C9—C8	0.7 (3)	C15—C16—C17—C18	−1.4 (4)
O2—C1—C9—C10	−0.1 (4)	O3—C17—C18—C19	−177.0 (2)
O1—C1—C9—C10	179.81 (19)	C16—C17—C18—C19	1.6 (4)
C12—N1—C10—C11	1.2 (3)	C17—C18—C19—C14	−0.9 (4)
C12—N1—C10—C9	−177.19 (19)	C15—C14—C19—C18	−0.1 (3)
C8—C9—C10—C11	−165.2 (2)	C13—C14—C19—C18	179.8 (2)
C1—C9—C10—C11	15.7 (4)		

Hydrogen-bond geometry (Å, °)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
N2—H12N···O3^{i}	0.88 (2)	2.36 (2)	3.213 (3)	164 (2)
O3—H13O···O2^{ii}	0.89 (4)	1.87 (4)	2.743 (3)	169 (3)

C5—H5A···O3^{iii}	0.93	2.46	3.386 (3)	173.
C11—H11A···O2	0.93	2.39	2.915 (3)	115.

Symmetry codes: (i) −*x*+1, *y*−1/2, −*z*−1/2; (ii) *x*+1, −*y*+1/2, *z*−1/2; (iii) *x*−1, *y*−1, *z*.

Fig. 1

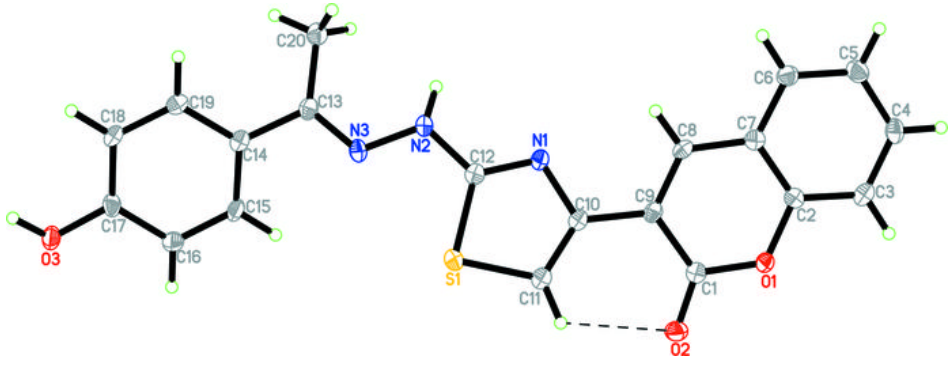
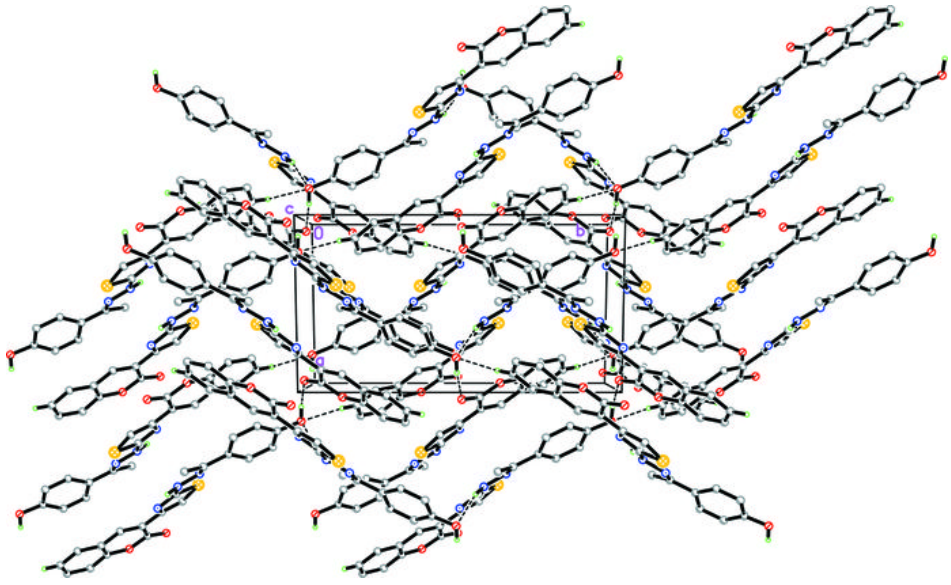

C20
C13
C18
C19
C14
N3
N2
C12
N1
C10
C9
C8
C7
C6
C5
C4
C3
C2
C15
C17
C16
O3
S1
C11
C1
O1
O2

Fig. 2



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Cholest-5-en-7-one

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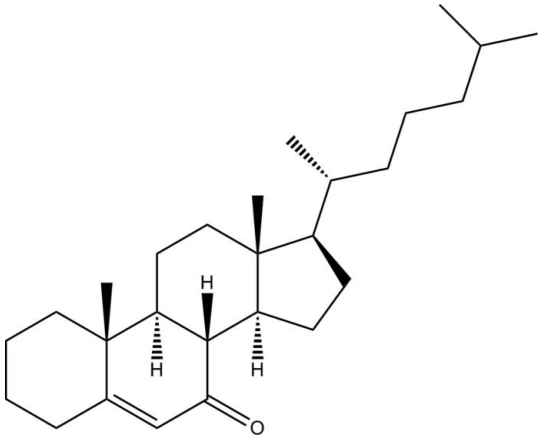
Key indicators: single-crystal X-ray study; T = 100 K; mean σ(C–C) = 0.004 Å; R factor = 0.051; wR factor = 0.132; data-to-parameter ratio = 13.9.

In the decahydrophenanthrenone ring system of the title compound, $C_{27}H_{44}O$, the two cyclohexane rings adopt chair conformations, whereas the cyclohexene ring adopts an envelope conformation. The cyclopentane ring is twisted. In the crystal structure, molecules are stacked along the a axis, but no significant intermolecular interactions are observed.

Related literature

For general background to and the biological activity of steroid derivatives, see: Drach *et al.* (2000); Grover *et al.* (2007); Khan & Yusuf (2009). For the synthesis of title compound, see: Dauben & Takemura (1953); Ruiz (1958). For the stability of the temperature controller used for the data collection, see: Cosier & Glazer (1986). For details of ring conformations, see: Cremer & Pople (1975). For bond-length data, see: Allen *et al.* (1987).



Experimental

Crystal data

$C_{27}H_{44}O$
M_r = 384.62
Monoclinic, $P2_1$
a = 6.3468 (13) Å
b = 11.517 (3) Å
c = 15.678 (3) Å
β = 91.470 (5)°
V = 1145.6 (4) Å^3
Z = 2
Mo $K\alpha$ radiation
μ = 0.07 mm^{-1}
T = 100 K
0.25 × 0.18 × 0.03 mm

Data collection

Bruker SMART APEXII DUO CCD area-detector diffractometer
Absorption correction: multi-scan (*SADABS*; Bruker, 2009)
T_{min} = 0.984, T_{max} = 0.998
13066 measured reflections
3512 independent reflections
2776 reflections with $I > 2\sigma(I)$
R_{int} = 0.058

Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.051
$wR(F^2)$ = 0.132
S = 1.04
3512 reflections
252 parameters
1 restraint
H-atom parameters constrained
$\Delta\rho_{max}$ = 0.51 e Å^{-3}
$\Delta\rho_{min}$ = −0.44 e Å^{-3}

Data collection: *APEX2* (Bruker, 2009); cell refinement: *SAINT* (Bruker, 2009); data reduction: *SAINT*; program(s) used to solve structure: *SHELXTL* (Sheldrick, 2008); program(s) used to refine structure: *SHELXTL*; molecular graphics: *SHELXTL*; software used to prepare material for publication: *SHELXTL* and *PLATON* (Spek, 2009).

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Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: IS2558).

References

Allen, F. H., Kennard, O., Watson, D. G., Brammer, L., Orpen, A. G. & Taylor, R. (1987). *J. Chem. Soc. Perkin Trans. 2*, pp. S1–19.
Bruker (2009). *APEX2*, *SAINT* and *SADABS*. Bruker AXS Inc., Madison, Wisconsin, USA.
Cosier, J. & Glazer, A. M. (1986). *J. Appl. Cryst.* **19**, 105–107.
Cremer, D. & Pople, J. A. (1975). *J. Am. Chem. Soc.* **97**, 1354–1358.
Dauben, W. G. & Takemura, K. H. (1953). *J. Am. Chem. Soc.* **75**, 6302–6304.
Drach, S. V., Litvinovskaya, R. P. & Kripach, V. A. (2000). *Chem. Heterocycl. Compd*, **36**, 233–255.
Grover, V. K., Babu, R. & Bedi, S. P. S. (2007). *Indian J. Anaesth.* **51**, 389–393.
Khan, S. A. & Yusuf, M. (2009). *Eur. J. Med. Chem.* **44**, 2597–2600.
Ruiz, H. J. (1958). *Chem. Abstr.* **52**, 10126a.
Sheldrick, G. M. (2008). *Acta Cryst.* A**64**, 112–122.
Spek, A. L. (2009). *Acta Cryst.* D**65**, 148–155.

‡ Thomson Reuters ResearcherID: A-5525-2009.
§ Thomson Reuters ResearcherID: A-3561-2009.

supplementary materials

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Cholest-5-en-7-one

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Comment

Steroids are compounds of biological origin and play an important role in biological systems. The dramatic expansion of steroidal chemistry came with the discovery of steroidal hormones. The discovery of several steroids with their wide application in therapy have brought about an increasing interest (Grover *et al.*, 2007). During the last decade, the major efforts of the chemists were directed towards the modification of the structures of steroids in order to enhance their biologically activity (Khan & Yusuf, 2009; Drach *et al.*, 2000).

The bond lengths (Allen *et al.*, 1987) and angles in the title compound (Fig. 1) are within normal ranges. The cyclopentane ring, C1/C14–C17 is twisted about the C1–C14 with the puckering parameters (Cremer & Pople, 1975) Q = 0.442 (3) Å and φ = 191.8 (3)°. In the tetradecahydrophenanthrene ring system, two cyclohexane rings, C5—C10 and C1—C4/C13/C14 adopt chair conformations with the puckering parameters Q = 0.539 (3) Å, Θ = 170.8 (3)° and φ = 320 (2)°; and Q = 0.585 (3) Å, Θ = 173.3 (3)° and φ = 150 (2) °, respectively, whereas C4/C5/C10—C13 adopts an envelope conformation with atom C4 deviating by 0.317 (2) Å from the mean plane through the remaining atoms, puckering parameters Q = 0.456 (3) Å, Θ = 51.6 (4)° and φ = 343.4 (4)°. The butyl (C19—C22) substituent at C18 is nearly planar, this plane lying almost perpendicular to the least-squares plane of the cyclopentane ring. The maximum deviation of the atoms C19, C20, C21 and C22 from their mean plane is 0.002 (3) Å for atoms C19, C21 and C22; and the dihedral angle between the plane of the butyl group and the least-squares plane through cyclopentane ring is 80.0 (2)°. In the crystal packing (Fig. 2), the molecules are stacked along the crystallographic *a* axis.

Experimental

A solution of butyl chromate [*tert*-butyl alcohol (60 ml), CrO_3 (20 g), acetic acid (84 ml) and acetic anhydride (10 ml)] (Ruiz, 1958) was added at 0 °C to a solution of cholest-5-ene (8 g) in CCl_4 (150 ml), acetic acid (30 ml) and acetic anhydride (10 ml). The contents were refluxed for 3 h and then diluted with water. The organic layer was washed with sodium bicarbonate solution (5%) and water; and then dried over anhydrous sodium sulfate. Evaporation of the solvents under reduced pressure provided cholest-5-en-7-one which was crystallized from methanol (3.1 g), *m.p.* 128 °C (reported, *m.p.* 125–129 °C; Dauben & Takemura, 1953).

Refinement

All H atoms were positioned geometrically and refined using a riding model, with C—H = 0.93–0.98 Å and U_{iso}(H) = 1.2 or 1.5 U_{eq}(C). A rotating-group model was applied for the methyl groups. The highest residual electron density peak is located at 0.07 Å from C24 and the deepest hole is located at 0.60 Å from C24. In the absence of significant anomalous dispersion, 2670 Friedel pairs were merged in the final refinement.

Figures

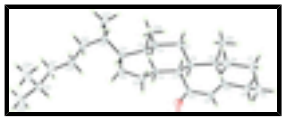


Fig. 1. The molecular structure of the title compound, showing 50% probability displacement ellipsoids for non-H atoms and the atom-numbering scheme.

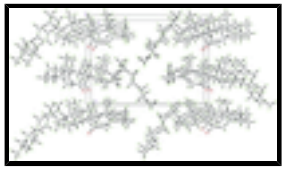


Fig. 2. The crystal structure of the title compound viewed along the *a* axis.

Cholest-5-en-7-one

Crystal data

$C_{27}H_{44}O$	$F(000) = 428$
$M_r = 384.62$	$D_x = 1.115$ Mg m^{-3}
Monoclinic, $P2_1$	Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å
Hall symbol: P 2yb	Cell parameters from 2115 reflections
$a = 6.3468$ (13) Å	$\theta = 2.2$–$27.8°$
$b = 11.517$ (3) Å	$\mu = 0.07$ mm^{-1}
$c = 15.678$ (3) Å	$T = 100$ K
$\beta = 91.470$ (5)°	Plate, colourless
$V = 1145.6$ (4) Å^3	0.25 × 0.18 × 0.03 mm
$Z = 2$	

Data collection

Bruker SMART APEXII DUO CCD area-detector diffractometer	3512 independent reflections
Radiation source: fine-focus sealed tube	2776 reflections with $I > 2\sigma(I)$
graphite	$R_{int} = 0.058$
φ and ω scans	$\theta_{max} = 30.2°$, $\theta_{min} = 1.3°$
Absorption correction: multi-scan (*SADABS*; Bruker, 2009)	$h = -8 \rightarrow 8$
$T_{min} = 0.984$, $T_{max} = 0.998$	$k = -16 \rightarrow 16$
13066 measured reflections	$l = -21 \rightarrow 22$

Refinement

Refinement on F^2	Primary atom site location: structure-invariant direct methods
Least-squares matrix: full	Secondary atom site location: difference Fourier map
$R[F^2 > 2\sigma(F^2)] = 0.051$	Hydrogen site location: inferred from neighbouring sites
$wR(F^2) = 0.132$	H-atom parameters constrained
$S = 1.04$	$w = 1/[\sigma^2(F_o^2) + (0.0534P)^2 + 0.3776P]$

	where $P = (F_o^2 + 2F_c^2)/3$
3512 reflections	$(\Delta/\sigma)_{max} = 0.001$
252 parameters	$\Delta\rho_{max} = 0.51$ e Å^{-3}
1 restraint	$\Delta\rho_{min} = -0.44$ e Å^{-3}

Special details

Experimental. The crystal was placed in the cold stream of an Oxford Cyrosystems Cobra open-flow nitrogen cryostat (Cosier & Glazer, 1986) operating at 100.0 (1) K.

Geometry. All e.s.d.'s (except the e.s.d. in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell e.s.d.'s are taken into account individually in the estimation of e.s.d.'s in distances, angles and torsion angles; correlations between e.s.d.'s in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell e.s.d.'s is used for estimating e.s.d.'s involving l.s. planes.

Refinement. Refinement of F^2 against ALL reflections. The weighted *R*-factor *wR* and goodness of fit *S* are based on F^2, conventional *R*-factors *R* are based on *F*, with *F* set to zero for negative F^2. The threshold expression of $F^2 > \sigma(F^2)$ is used only for calculating *R*-factors(gt) *etc*. and is not relevant to the choice of reflections for refinement. *R*-factors based on F^2 are statistically about twice as large as those based on *F*, and *R*- factors based on ALL data will be even larger.

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å^2)

	x	*y*	*z*	U_{iso}*/U_{eq}
O1	−0.4772 (3)	0.33629 (19)	1.00165 (15)	0.0316 (5)
C1	−0.0378 (3)	0.1067 (2)	0.87139 (16)	0.0161 (5)
C2	0.1540 (4)	0.0845 (2)	0.92977 (16)	0.0201 (5)
H2A	0.2407	0.1539	0.9323	0.024*
H2B	0.2376	0.0224	0.9061	0.024*
C3	0.0906 (4)	0.0514 (2)	1.02042 (17)	0.0225 (5)
H3A	0.2171	0.0426	1.0559	0.027*
H3B	0.0194	−0.0232	1.0185	0.027*
C4	−0.0544 (4)	0.1409 (2)	1.06179 (16)	0.0185 (5)
H4A	0.0278	0.2126	1.0678	0.022*
C5	−0.1179 (4)	0.1052 (2)	1.15351 (16)	0.0196 (5)
C6	0.0827 (4)	0.1099 (3)	1.21199 (18)	0.0283 (6)
H6A	0.1757	0.0470	1.1963	0.034*
H6B	0.1558	0.1823	1.2016	0.034*
C7	0.0402 (5)	0.1007 (3)	1.30742 (18)	0.0344 (7)
H7A	−0.0224	0.0259	1.3196	0.041*
H7B	0.1719	0.1067	1.3399	0.041*
C8	−0.1088 (5)	0.1976 (3)	1.33392 (19)	0.0382 (7)
H8A	−0.1375	0.1906	1.3942	0.046*
H8B	−0.0432	0.2725	1.3246	0.046*
C9	−0.3134 (5)	0.1899 (3)	1.28214 (18)	0.0292 (6)
H9A	−0.3867	0.1193	1.2975	0.035*
H9B	−0.4024	0.2551	1.2965	0.035*
C10	−0.2795 (4)	0.1900 (2)	1.18697 (17)	0.0210 (5)
C11	−0.3927 (4)	0.2611 (2)	1.13562 (17)	0.0225 (5)
H11A	−0.4862	0.3119	1.1610	0.027*

C12	−0.3792 (4)	0.2643 (2)	1.04303 (17)	0.0200 (5)
C13	−0.2455 (4)	0.1700 (2)	1.00234 (16)	0.0171 (5)
H13A	−0.3321	0.1000	0.9958	0.021*
C14	−0.1667 (4)	0.2043 (2)	0.91427 (16)	0.0163 (5)
H14A	−0.0687	0.2690	0.9239	0.020*
C15	−0.3230 (4)	0.2445 (2)	0.84445 (16)	0.0222 (5)
H15A	−0.3637	0.3247	0.8531	0.027*
H15B	−0.4485	0.1964	0.8432	0.027*
C16	−0.1995 (4)	0.2306 (2)	0.76141 (17)	0.0219 (5)
H16A	−0.1674	0.3062	0.7377	0.026*
H16B	−0.2826	0.1874	0.7195	0.026*
C17	0.0071 (4)	0.1643 (2)	0.78416 (16)	0.0176 (5)
H17A	0.1178	0.2224	0.7941	0.021*
C18	0.0752 (4)	0.0879 (2)	0.70931 (16)	0.0196 (5)
H18A	−0.0375	0.0310	0.6992	0.024*
C19	0.0939 (4)	0.1585 (3)	0.62657 (16)	0.0233 (5)
H19A	0.1268	0.1053	0.5808	0.028*
H19B	−0.0427	0.1924	0.6128	0.028*
C20	0.2579 (4)	0.2556 (2)	0.62794 (17)	0.0221 (5)
H20A	0.2318	0.3072	0.6754	0.027*
H20B	0.3971	0.2223	0.6366	0.027*
C21	0.2520 (4)	0.3250 (3)	0.54552 (19)	0.0320 (7)
H21A	0.1114	0.3567	0.5371	0.038*
H21B	0.2772	0.2725	0.4985	0.038*
C22	0.4102 (5)	0.4243 (3)	0.5418 (2)	0.0320 (7)
H22A	0.4035	0.4667	0.5958	0.038*
C23	0.3563 (6)	0.5096 (4)	0.4707 (3)	0.0520 (7)
H23A	0.4624	0.5689	0.4693	0.078*
H23B	0.2219	0.5445	0.4810	0.078*
H23C	0.3504	0.4694	0.4171	0.078*
C24	0.6329 (5)	0.3824 (4)	0.5333 (3)	0.0520 (7)
H24A	0.7271	0.4476	0.5350	0.078*
H24B	0.6459	0.3422	0.4801	0.078*
H24C	0.6680	0.3307	0.5796	0.078*
C25	−0.1682 (4)	−0.0043 (2)	0.85817 (18)	0.0228 (5)
H25A	−0.0796	−0.0649	0.8371	0.034*
H25B	−0.2809	0.0104	0.8176	0.034*
H25C	−0.2257	−0.0278	0.9115	0.034*
C26	−0.2164 (5)	−0.0170 (2)	1.15541 (19)	0.0270 (6)
H26A	−0.3263	−0.0224	1.1124	0.040*
H26B	−0.2743	−0.0307	1.2105	0.040*
H26C	−0.1099	−0.0739	1.1446	0.040*
C27	0.2764 (4)	0.0194 (2)	0.72725 (18)	0.0234 (5)
H27A	0.3139	−0.0225	0.6769	0.035*
H27B	0.2542	−0.0343	0.7730	0.035*
H27C	0.3882	0.0719	0.7432	0.035*

Atomic displacement parameters (Å^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
O1	0.0336 (11)	0.0294 (11)	0.0322 (11)	0.0148 (9)	0.0057 (8)	0.0012 (9)
C1	0.0144 (10)	0.0140 (10)	0.0201 (12)	0.0000 (9)	0.0035 (8)	0.0013 (10)
C2	0.0156 (10)	0.0227 (12)	0.0222 (12)	0.0014 (9)	0.0048 (9)	0.0033 (11)
C3	0.0207 (12)	0.0259 (13)	0.0213 (13)	0.0073 (10)	0.0054 (10)	0.0053 (11)
C4	0.0184 (11)	0.0179 (11)	0.0192 (12)	0.0001 (9)	0.0030 (9)	0.0024 (10)
C5	0.0222 (11)	0.0170 (11)	0.0199 (12)	0.0015 (10)	0.0064 (9)	0.0022 (10)
C6	0.0264 (13)	0.0351 (15)	0.0235 (13)	0.0030 (12)	0.0012 (10)	0.0034 (13)
C7	0.0378 (16)	0.0427 (18)	0.0226 (14)	0.0050 (15)	0.0003 (12)	0.0029 (14)
C8	0.0532 (19)	0.0413 (18)	0.0203 (14)	0.0078 (16)	0.0044 (13)	−0.0032 (14)
C9	0.0379 (15)	0.0256 (13)	0.0245 (14)	0.0041 (12)	0.0090 (11)	0.0016 (12)
C10	0.0232 (12)	0.0159 (11)	0.0243 (13)	−0.0019 (10)	0.0065 (10)	−0.0012 (10)
C11	0.0229 (12)	0.0188 (12)	0.0263 (13)	0.0007 (10)	0.0079 (10)	−0.0013 (11)
C12	0.0179 (11)	0.0167 (11)	0.0255 (13)	−0.0007 (9)	0.0046 (9)	−0.0007 (10)
C13	0.0150 (10)	0.0170 (11)	0.0196 (11)	−0.0003 (9)	0.0039 (8)	0.0004 (10)
C14	0.0149 (10)	0.0144 (10)	0.0199 (12)	−0.0024 (9)	0.0037 (8)	0.0015 (10)
C15	0.0188 (11)	0.0236 (13)	0.0244 (13)	0.0078 (10)	0.0029 (9)	0.0017 (11)
C16	0.0187 (11)	0.0242 (12)	0.0229 (13)	0.0020 (10)	0.0019 (9)	0.0041 (11)
C17	0.0138 (10)	0.0163 (11)	0.0228 (12)	−0.0024 (9)	0.0025 (9)	0.0011 (10)
C18	0.0185 (11)	0.0193 (12)	0.0212 (12)	−0.0025 (9)	0.0036 (9)	−0.0020 (10)
C19	0.0213 (12)	0.0304 (14)	0.0181 (12)	0.0022 (11)	0.0003 (10)	0.0009 (11)
C20	0.0245 (12)	0.0232 (13)	0.0187 (12)	0.0020 (10)	0.0018 (9)	0.0025 (11)
C21	0.0226 (13)	0.0477 (18)	0.0258 (15)	0.0027 (13)	0.0029 (11)	0.0120 (14)
C22	0.0381 (16)	0.0290 (14)	0.0294 (16)	0.0061 (13)	0.0145 (13)	0.0078 (13)
C23	0.0340 (11)	0.0552 (16)	0.0672 (17)	0.0041 (11)	0.0088 (11)	0.0357 (15)
C24	0.0340 (11)	0.0552 (16)	0.0672 (17)	0.0041 (11)	0.0088 (11)	0.0357 (15)
C25	0.0240 (12)	0.0151 (11)	0.0297 (14)	−0.0007 (10)	0.0080 (10)	0.0009 (11)
C26	0.0386 (15)	0.0168 (12)	0.0260 (14)	−0.0028 (11)	0.0102 (12)	0.0037 (11)
C27	0.0260 (12)	0.0212 (12)	0.0232 (13)	0.0030 (10)	0.0065 (10)	0.0006 (11)

Geometric parameters (Å, °)

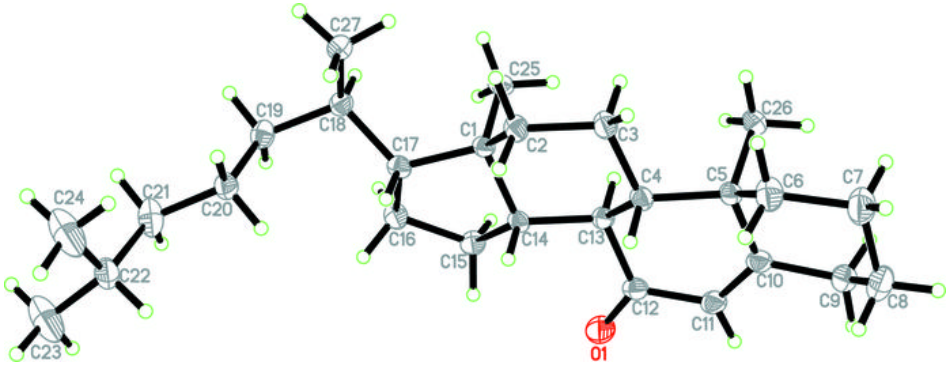
O1—C12	1.215 (3)	C15—H15A	0.9700
C1—C2	1.526 (3)	C15—H15B	0.9700
C1—C25	1.534 (3)	C16—C17	1.551 (3)
C1—C17	1.553 (3)	C16—H16A	0.9700
C1—C14	1.554 (3)	C16—H16B	0.9700
C2—C3	1.535 (3)	C17—C18	1.537 (3)
C2—H2A	0.9700	C17—H17A	0.9800
C2—H2B	0.9700	C18—C27	1.521 (4)
C3—C4	1.537 (3)	C18—C19	1.538 (4)
C3—H3A	0.9700	C18—H18A	0.9800
C3—H3B	0.9700	C19—C20	1.528 (4)
C4—C13	1.547 (3)	C19—H19A	0.9700
C4—C5	1.558 (3)	C19—H19B	0.9700
C4—H4A	0.9800	C20—C21	1.519 (4)

C5—C10	1.519 (3)	C20—H20A	0.9700
C5—C26	1.541 (4)	C20—H20B	0.9700
C5—C6	1.550 (4)	C21—C22	1.524 (5)
C6—C7	1.531 (4)	C21—H21A	0.9700
C6—H6A	0.9700	C21—H21B	0.9700
C6—H6B	0.9700	C22—C24	1.502 (4)
C7—C8	1.527 (5)	C22—C23	1.518 (5)
C7—H7A	0.9700	C22—H22A	0.9800
C7—H7B	0.9700	C23—H23A	0.9600
C8—C9	1.516 (5)	C23—H23B	0.9600
C8—H8A	0.9700	C23—H23C	0.9600
C8—H8B	0.9700	C24—H24A	0.9600
C9—C10	1.513 (4)	C24—H24B	0.9600
C9—H9A	0.9700	C24—H24C	0.9600
C9—H9B	0.9700	C25—H25A	0.9600
C10—C11	1.344 (4)	C25—H25B	0.9600
C11—C12	1.457 (4)	C25—H25C	0.9600
C11—H11A	0.9300	C26—H26A	0.9600
C12—C13	1.528 (3)	C26—H26B	0.9600
C13—C14	1.532 (3)	C26—H26C	0.9600
C13—H13A	0.9800	C27—H27A	0.9600
C14—C15	1.530 (4)	C27—H27B	0.9600
C14—H14A	0.9800	C27—H27C	0.9600
C15—C16	1.545 (3)		
C2—C1—C25	111.2 (2)	C16—C15—H15A	111.0
C2—C1—C17	115.98 (18)	C14—C15—H15B	111.0
C25—C1—C17	110.3 (2)	C16—C15—H15B	111.0
C2—C1—C14	106.4 (2)	H15A—C15—H15B	109.0
C25—C1—C14	111.92 (18)	C15—C16—C17	107.5 (2)
C17—C1—C14	100.51 (18)	C15—C16—H16A	110.2
C1—C2—C3	111.90 (19)	C17—C16—H16A	110.2
C1—C2—H2A	109.2	C15—C16—H16B	110.2
C3—C2—H2A	109.2	C17—C16—H16B	110.2
C1—C2—H2B	109.2	H16A—C16—H16B	108.5
C3—C2—H2B	109.2	C18—C17—C16	111.0 (2)
H2A—C2—H2B	107.9	C18—C17—C1	119.3 (2)
C2—C3—C4	113.4 (2)	C16—C17—C1	103.87 (18)
C2—C3—H3A	108.9	C18—C17—H17A	107.4
C4—C3—H3A	108.9	C16—C17—H17A	107.4
C2—C3—H3B	108.9	C1—C17—H17A	107.4
C4—C3—H3B	108.9	C27—C18—C17	114.0 (2)
H3A—C3—H3B	107.7	C27—C18—C19	110.3 (2)
C3—C4—C13	111.1 (2)	C17—C18—C19	111.7 (2)
C3—C4—C5	112.6 (2)	C27—C18—H18A	106.8
C13—C4—C5	113.32 (19)	C17—C18—H18A	106.8
C3—C4—H4A	106.4	C19—C18—H18A	106.8
C13—C4—H4A	106.4	C20—C19—C18	116.3 (2)
C5—C4—H4A	106.4	C20—C19—H19A	108.2
C10—C5—C26	107.6 (2)	C18—C19—H19A	108.2

C10—C5—C6	109.0 (2)	C20—C19—H19B	108.2
C26—C5—C6	110.3 (2)	C18—C19—H19B	108.2
C10—C5—C4	110.0 (2)	H19A—C19—H19B	107.4
C26—C5—C4	111.9 (2)	C21—C20—C19	111.8 (2)
C6—C5—C4	108.0 (2)	C21—C20—H20A	109.3
C7—C6—C5	114.4 (2)	C19—C20—H20A	109.3
C7—C6—H6A	108.7	C21—C20—H20B	109.3
C5—C6—H6A	108.7	C19—C20—H20B	109.3
C7—C6—H6B	108.7	H20A—C20—H20B	107.9
C5—C6—H6B	108.7	C20—C21—C22	115.2 (3)
H6A—C6—H6B	107.6	C20—C21—H21A	108.5
C8—C7—C6	109.9 (3)	C22—C21—H21A	108.5
C8—C7—H7A	109.7	C20—C21—H21B	108.5
C6—C7—H7A	109.7	C22—C21—H21B	108.5
C8—C7—H7B	109.7	H21A—C21—H21B	107.5
C6—C7—H7B	109.7	C24—C22—C23	109.8 (3)
H7A—C7—H7B	108.2	C24—C22—C21	112.6 (3)
C9—C8—C7	109.8 (3)	C23—C22—C21	112.2 (3)
C9—C8—H8A	109.7	C24—C22—H22A	107.3
C7—C8—H8A	109.7	C23—C22—H22A	107.3
C9—C8—H8B	109.7	C21—C22—H22A	107.3
C7—C8—H8B	109.7	C22—C23—H23A	109.5
H8A—C8—H8B	108.2	C22—C23—H23B	109.5
C10—C9—C8	112.7 (2)	H23A—C23—H23B	109.5
C10—C9—H9A	109.0	C22—C23—H23C	109.5
C8—C9—H9A	109.0	H23A—C23—H23C	109.5
C10—C9—H9B	109.0	H23B—C23—H23C	109.5
C8—C9—H9B	109.0	C22—C24—H24A	109.5
H9A—C9—H9B	107.8	C22—C24—H24B	109.5
C11—C10—C9	120.3 (2)	H24A—C24—H24B	109.5
C11—C10—C5	122.7 (2)	C22—C24—H24C	109.5
C9—C10—C5	117.0 (2)	H24A—C24—H24C	109.5
C10—C11—C12	124.6 (2)	H24B—C24—H24C	109.5
C10—C11—H11A	117.7	C1—C25—H25A	109.5
C12—C11—H11A	117.7	C1—C25—H25B	109.5
O1—C12—C11	120.5 (2)	H25A—C25—H25B	109.5
O1—C12—C13	123.0 (2)	C1—C25—H25C	109.5
C11—C12—C13	116.5 (2)	H25A—C25—H25C	109.5
C12—C13—C14	113.0 (2)	H25B—C25—H25C	109.5
C12—C13—C4	109.7 (2)	C5—C26—H26A	109.5
C14—C13—C4	109.24 (18)	C5—C26—H26B	109.5
C12—C13—H13A	108.3	H26A—C26—H26B	109.5
C14—C13—H13A	108.3	C5—C26—H26C	109.5
C4—C13—H13A	108.3	H26A—C26—H26C	109.5
C15—C14—C13	120.13 (19)	H26B—C26—H26C	109.5
C15—C14—C1	104.36 (19)	C18—C27—H27A	109.5
C13—C14—C1	113.01 (19)	C18—C27—H27B	109.5
C15—C14—H14A	106.1	H27A—C27—H27B	109.5
C13—C14—H14A	106.1	C18—C27—H27C	109.5

C1—C14—H14A	106.1	H27A—C27—H27C	109.5
C14—C15—C16	103.77 (19)	H27B—C27—H27C	109.5
C14—C15—H15A	111.0		
C25—C1—C2—C3	−64.6 (3)	C5—C4—C13—C12	55.4 (3)
C17—C1—C2—C3	168.2 (2)	C3—C4—C13—C14	−52.3 (3)
C14—C1—C2—C3	57.4 (3)	C5—C4—C13—C14	179.8 (2)
C1—C2—C3—C4	−55.3 (3)	C12—C13—C14—C15	−53.9 (3)
C2—C3—C4—C13	51.4 (3)	C4—C13—C14—C15	−176.4 (2)
C2—C3—C4—C5	179.7 (2)	C12—C13—C14—C1	−177.8 (2)
C3—C4—C5—C10	−173.8 (2)	C4—C13—C14—C1	59.7 (3)
C13—C4—C5—C10	−46.6 (3)	C2—C1—C14—C15	166.22 (19)
C3—C4—C5—C26	−54.2 (3)	C25—C1—C14—C15	−72.2 (2)
C13—C4—C5—C26	72.9 (3)	C17—C1—C14—C15	44.9 (2)
C3—C4—C5—C6	67.4 (3)	C2—C1—C14—C13	−61.6 (2)
C13—C4—C5—C6	−165.5 (2)	C25—C1—C14—C13	60.0 (3)
C10—C5—C6—C7	49.0 (3)	C17—C1—C14—C13	177.14 (19)
C26—C5—C6—C7	−68.9 (3)	C13—C14—C15—C16	−161.7 (2)
C4—C5—C6—C7	168.5 (3)	C1—C14—C15—C16	−33.7 (2)
C5—C6—C7—C8	−57.5 (4)	C14—C15—C16—C17	9.3 (3)
C6—C7—C8—C9	58.3 (3)	C15—C16—C17—C18	147.7 (2)
C7—C8—C9—C10	−54.5 (3)	C15—C16—C17—C1	18.4 (3)
C8—C9—C10—C11	−131.4 (3)	C2—C1—C17—C18	83.6 (3)
C8—C9—C10—C5	49.8 (3)	C25—C1—C17—C18	−43.9 (3)
C26—C5—C10—C11	−104.0 (3)	C14—C1—C17—C18	−162.2 (2)
C6—C5—C10—C11	136.3 (3)	C2—C1—C17—C16	−152.2 (2)
C4—C5—C10—C11	18.1 (3)	C25—C1—C17—C16	80.2 (2)
C26—C5—C10—C9	74.6 (3)	C14—C1—C17—C16	−38.0 (2)
C6—C5—C10—C9	−45.0 (3)	C16—C17—C18—C27	−179.6 (2)
C4—C5—C10—C9	−163.2 (2)	C1—C17—C18—C27	−59.0 (3)
C9—C10—C11—C12	−177.1 (3)	C16—C17—C18—C19	54.5 (3)
C5—C10—C11—C12	1.5 (4)	C1—C17—C18—C19	175.1 (2)
C10—C11—C12—O1	−175.3 (3)	C27—C18—C19—C20	−65.8 (3)
C10—C11—C12—C13	7.4 (4)	C17—C18—C19—C20	62.2 (3)
O1—C12—C13—C14	25.7 (3)	C18—C19—C20—C21	−175.9 (2)
C11—C12—C13—C14	−157.1 (2)	C19—C20—C21—C22	179.7 (2)
O1—C12—C13—C4	147.9 (2)	C20—C21—C22—C24	71.8 (4)
C11—C12—C13—C4	−34.9 (3)	C20—C21—C22—C23	−163.7 (3)
C3—C4—C13—C12	−176.7 (2)		

Fig. 1


C27
C25
C19
C18
C1
C2
C3
C26
C17
C4
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C6
C7
C24
C21
C20
C16
C15
C14
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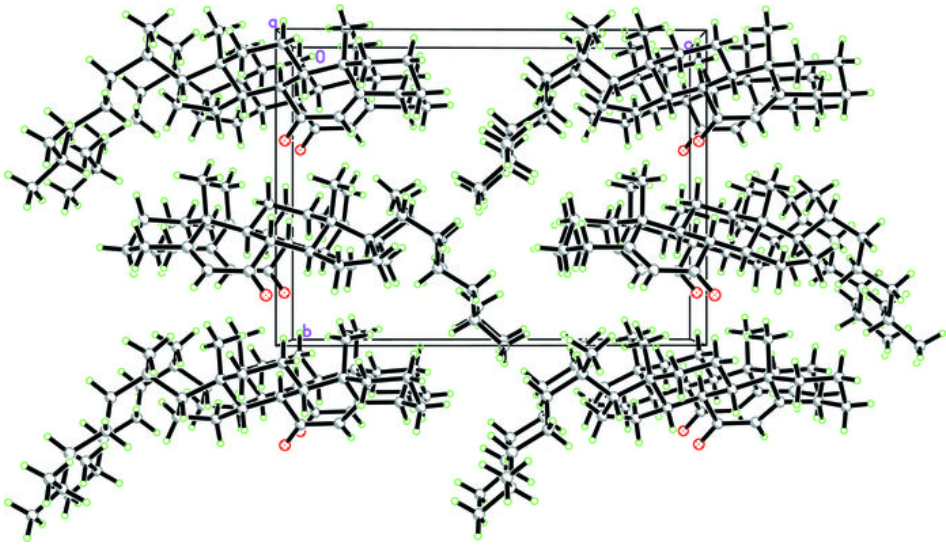
C22
C10
C12
C11
C9
C8
C23
O1

Fig. 2



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2′-Ethoxy-1,3,3-trimethylspiro[indoline-2,3′-3*H*-naphtho[2,1-*b*][1,4]oxazine]

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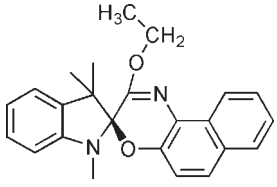
Key indicators: single-crystal X-ray study; T = 293 K; mean σ(C–C) = 0.002 Å; R factor = 0.043; wR factor = 0.085; data-to-parameter ratio = 17.3.

In the title compound, $C_{24}H_{24}N_2O_2$, the five-membered ring of the indoline ring system adopts an envelope conformation with the spiro C atom at the flap. The dihedral angle between the benzene ring of the indoline ring system and the naphthalene ring system is 71.70 (7)°. In the crystal structure, pair of weak C—H···O hydrogen bonds link the molecules into centrosymmetric dimers.

Related literature

For applications of spirooxazines, see: Chibisov & Gardner (1999); Khairutdinov *et al.* (1998); Pozzo *et al.* (1993); Tan *et al.* (2005); Zhang *et al.* (2008). For related structures, see: Lin *et al.* (2009); Uznanski *et al.* (2001).



Experimental

Crystal data

$C_{24}H_{24}N_2O_2$
M_r = 372.45
Monoclinic, $P2_1/c$
a = 8.6105 (4) Å
b = 22.9239 (8) Å
c = 10.2022 (5) Å
β = 93.516 (4)°
V = 2009.98 (15) Å^3
Z = 4
Mo $K\alpha$ radiation
μ = 0.08 mm^{-1}
T = 293 K
0.34 × 0.30 × 0.20 mm

Data collection

Oxford Xcalibur Gemini ultra diffractometer
Absorption correction: multi-scan (*CrysAlis PRO RED*; Oxford Diffraction, 2009)
T_{min} = 0.974, T_{max} = 0.984
12650 measured reflections
4449 independent reflections
2198 reflections with $I > 2\sigma(I)$
R_{int} = 0.033

Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.043
$wR(F^2)$ = 0.085
S = 0.98
4449 reflections
257 parameters
H-atom parameters constrained
$\Delta\rho_{max}$ = 0.16 e Å^{-3}
$\Delta\rho_{min}$ = −0.18 e Å^{-3}

Table 1
Hydrogen-bond geometry (Å, °).

D—H···A	D—H	H···A	D···A	D—H···A
C18—H18···O1^{i}	0.93	2.60	3.5014 (18)	164

Symmetry code: (i) $-x, -y+1, -z+1$.

Data collection: *CrysAlis PRO CCD* (Oxford Diffraction, 2009); cell refinement: *CrysAlis PRO CCD*; data reduction: *CrysAlis PRO RED* (Oxford Diffraction, 2009); program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *SHELXTL* (Sheldrick, 2008); software used to prepare material for publication: *SHELXTL*.

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Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: IS2559).

References

Chibisov, A. K. & Gardner, H. (1999). *J. Phys. Chem. A*, **103**, 5211–5216.
Khairutdinov, R. F., Giertz, K., Hurst, J. K., Voloshina, E. N., Voloshin, N. A. & Minkin, V. I. (1998). *J. Am. Chem. Soc.* **49**, 12707–12713.
Lin, J., Chai, W., Song, L., Qin, L. & Shu, K. (2009). *Acta Cryst.* C**65**, o621–o623.
Oxford Diffraction (2009). *CrysAlis PRO CCD* and *CrysAlis PRO RED*. Oxford Diffraction Ltd, Yarnton, England.
Pozzo, J. L., Samat, A., Guglielmetti, R. & Keukeleireb, D. D. (1993). *J. Chem. Soc. Perkin Trans. 2*, pp. 1327–1332.
Sheldrick, G. M. (2008). *Acta Cryst.* A**64**, 112–122.
Tan, T.-F., Chen, P.-L., Huang, H.-M. & Meng, J.-B. (2005). *Tetrahedron*, **61**, 8192–8198.
Uznanski, P., Amiens, C., Donnadieu, B., Coppel, Y. & Chaudret, B. (2001). *New J. Chem.* **25**, 1486–1494.
Zhang, C.-R., Zhang, Z.-B., Fan, M.-G. & Yan, W.-P. (2008). *Dyes Pigm.* **76**, 832–835.

supplementary materials

Acta Cryst. (2010). E**66**, o1695 [**doi:10.1107/S1600536810022890**]

2'-Ethoxy-1,3,3-trimethylspiro[indoline-2,3'-3*H*-naphtho[2,1-*b*][1,4]oxazine]

J. Lin, W. Chai, Y. Yang, J. He and K. Shu

Comment

Serve as an organic photochromic, spirooxazines have real or potential applications in many field, such as protection, decoration, display, memory, switches, photography, photometry and photomechanics (Chibisov & Gardner, 1999). For further approach to real applications, numerous types of spirooxazine derivatives have been reported over the past several decades (Pozzo *et al.*, 1993; Khairutdinov *et al.*, 1998; Zhang *et al.*, 2008). Traditionally, synthesis of spirooxazines is based on a thermal condensation reaction of the corresponding alkylidene heterocycle or its conjugate acid with *ortho*-hydroxynitroso aromatic derivatives in most polar organic solvents. To be notice, alkylidene heterocycle, such as: 1,3,3-trimethyl-2- methyleneindoline derivatives, were not stable in the air at room temperature, so they must be purified by vacuum distillation before use (Tan *et al.*, 2005). This brings to a big problem that we have to re-synthesis alkylidene heterocycle part if we want to get a novel spirooxazine with different substituents at alkylidene heterocycle moiety. According to our previous work (Lin *et al.*, 2009) in which we reported a new strategy to get a 2'-position substituted spirooxazine, a new derivative, 1,3,3-trimethyl-2'-ethoxy-1,3-dihydrospiro(indole-2,3'-naphtho(2,1-b) (1,4)oxazine), (II), has been synthesized and its crystal structure is reported here.

Since we synthesized an unexpected new organic photochromic compound, (2*S*)-2'-ethoxy-1,3,3-trimethyl-6'-(piperidin-1-yl) spiro[indoline-2,3'-3'H-naphtho[2,1-*b*][1,4]oxazine], we studied on the possibility of the ethoxy reaction at the 2'-position of spirooxazine using another spirooxazine derivative, $C_{22}H_{20}N_2O$, (I). The title compound, $C_{24}H_{24}N_2O_2$, (II), was synthesized successfully (Fig. 1), which testified it is a general method to fabricate ethoxy-substituted (may be alkoxy-substituted) spirooxazines at the C2'carbon atom of the C2'=N1' bond.

The title compound, $C_{24}H_{24}N_2O_2$, consists of an ethoxy group bonded to parent molecule (I) at the 2'-position crystallizing with a molecule in the asymmetric unit (Fig. 2). The five-membered ring C1/N2/C6–C8 adopts an envelope conformation with the flap at C8. The dihedral angle between the benzene ring (atoms C1–C6) and the naphthalene ring (atoms C10–C19) is 71.70 (7)°. For the other 2'-position substituted derivatives ($C_{23}H_{22}N_2O_2$, $C_{27}H_{24}N_2O_2$ and $C_{29}H_{33}N_3O_2$), the corresponding dihedral angles are 74.2 (1), 76.5 (6) and 71.6 (2)/72.7 (2)°, respectively (Uznanski *et al.*, 2001; Lin *et al.*, 2009). The bond lengths and angles around the spiro carbon in (II) are similar to those in the other photochromic spirooxazines.

Experimental

Potassium iodide (17 mg, 0.1 mmol) and the parent spirooxazine, 1,3,3-trimethylspiro[indoline-2,3'-[3H]-naphth[2,1-*b*][1,4]oxazine] (33 mg, 0.1 mmol) were heated in a Teflon-lined stainless steel autoclave with ethanol (10 ml) at 393 K. Block-shaped colorless crystals of (II), were obtained by slow evaporation from the filtrated reaction solution at room temperature. Yield: 45% (with reaction solution left). m.p.: 418–419 K. IR (KBr, cm^{-1}): 3053, 2982, 2964, 2888, 1724, 1714, 1637, 1609, 1577, 1508, 1490, 1466, 1398, 1383, 1367, 1321, 1296, 1267, 1252, 1232, 1198, 1188, 1153, 1140, 1101, 1086, 1037, 1024, 993, 977, 952, 895, 862, 816, 781, 750, 743, 683, 655, 632, 606, 566, 551, 516, 499, 437. ^{1}H NMR ($CDCl_3$): δ

6.56–8.47 (10*H*, ArH), 4.58 (2*H*, CH_2), 2.94 (3*H*, CH_3), 1.42 (3*H*, CH_3), 1.22 (6*H*, CH_3). Analysis found (calculated) for $C_{24}H_{24}N_2O_2$: C 77.35 (77.39), H 6.60 (6.49), N 7.50% (7.52%).

Refinement

The H atoms were placed in their calculated positions (C—H = 0.93–0.97 Å) and included in the refinement using the riding model, with U_{iso}(H) = 1.2 or 1.5U_{eq}(C).

Figures

Fig. 1. Synthesis of the title compound, (II).

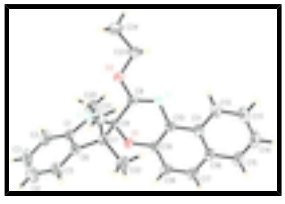


Fig. 2. The structure of (II), showing the atom-labeling scheme of the asymmetric unit. Displacement ellipsoids are drawn at the 30% probability level and H atoms are shown as small spheres of arbitrary radii.

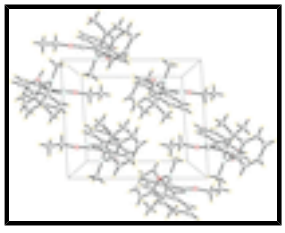


Fig. 3. A packing diagram of (II), viewed along the *a* axis.

2'-Ethoxy-1,3,3-trimethylspiro[indoline-2,3'-3*H*- naphtho[2,1-*b*][1,4]oxazine]

Crystal data

$C_{24}H_{24}N_2O_2$	$F(000)$ = 792
M_r = 372.45	D_x = 1.231 Mg m^{-3}
Monoclinic, $P2_1/c$	Melting point: 418 K
Hall symbol: -P 2ybc	Mo $K\alpha$ radiation, λ = 0.71073 Å
a = 8.6105 (4) Å	Cell parameters from 3384 reflections
b = 22.9239 (8) Å	θ = 3.2–27.3°
c = 10.2022 (5) Å	μ = 0.08 mm^{-1}
β = 93.516 (4)°	T = 293 K
V = 2009.98 (15) Å^3	Block, colorless
Z = 4	0.34 × 0.30 × 0.20 mm

Data collection

Oxford Xcalibur Gemini ultra diffractometer	4449 independent reflections
Radiation source: fine-focus sealed tube	2198 reflections with $I > 2\sigma(I)$
graphite	R_{int} = 0.033

Detector resolution: 10.3592 pixels mm^{-1}

ω scans

Absorption correction: multi-scan (*CrysAlis PRO RED*; Oxford Diffraction, 2009)

T_{min} = 0.974, T_{max} = 0.984

12650 measured reflections

θ_{max} = 27.3°, θ_{min} = 3.3°

h = −11→10

k = −29→28

l = −13→13

Refinement

Refinement on F^2

Least-squares matrix: full

$R[F^2 > 2\sigma(F^2)]$ = 0.043

$wR(F^2)$ = 0.085

S = 0.98

4449 reflections

257 parameters

0 restraints

Primary atom site location: structure-invariant direct methods

Secondary atom site location: difference Fourier map

Hydrogen site location: inferred from neighbouring sites

H-atom parameters constrained

$w = 1/[\sigma^2(F_o^2) + (0.030P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$

$(\Delta/\sigma)_{max} < 0.001$

$\Delta\rho_{max}$ = 0.16 e $Å^{-3}$

$\Delta\rho_{min}$ = −0.18 e $Å^{-3}$

Special details

Geometry. All e.s.d.'s (except the e.s.d. in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell e.s.d.'s are taken into account individually in the estimation of e.s.d.'s in distances, angles and torsion angles; correlations between e.s.d.'s in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell e.s.d.'s is used for estimating e.s.d.'s involving l.s. planes.

Refinement. Refinement of F^2 against ALL reflections. The weighted *R*-factor *wR* and goodness of fit *S* are based on F^2, conventional *R*-factors *R* are based on *F*, with *F* set to zero for negative F^2. The threshold expression of $F^2 > \sigma(F^2)$ is used only for calculating *R*-factors(gt) *etc*. and is not relevant to the choice of reflections for refinement. *R*-factors based on F^2 are statistically about twice as large as those based on *F*, and *R*- factors based on ALL data will be even larger.

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters ($Å^2$)

	x	*y*	*z*	U_{iso}*/U_{eq}
O1	0.10563 (10)	0.53152 (4)	0.31415 (9)	0.0480 (3)
O2	0.22203 (12)	0.57809 (4)	0.00532 (9)	0.0593 (3)
N1	0.23974 (13)	0.48659 (5)	0.09366 (11)	0.0489 (3)
N2	0.09544 (13)	0.62319 (5)	0.21564 (12)	0.0482 (3)
C1	0.13539 (18)	0.66314 (6)	0.31558 (15)	0.0487 (4)
C2	0.0555 (2)	0.71249 (7)	0.3510 (2)	0.0713 (5)
H2	−0.0378	0.7234	0.3069	0.086*
C3	0.1210 (3)	0.74527 (7)	0.4557 (2)	0.0930 (7)
H3	0.0704	0.7789	0.4814	0.112*
C4	0.2579 (3)	0.72923 (9)	0.5217 (2)	0.0945 (7)
H4	0.2972	0.7511	0.5929	0.113*
C5	0.3369 (2)	0.68093 (7)	0.48276 (17)	0.0704 (5)

H5	0.4308	0.6704	0.5263	0.085*
C6	0.27635 (18)	0.64807 (6)	0.37867 (14)	0.0473 (4)
C7	0.34049 (16)	0.59543 (6)	0.31284 (14)	0.0450 (4)
C8	0.19045 (15)	0.57223 (5)	0.23417 (13)	0.0410 (3)
C9	0.21867 (16)	0.54118 (6)	0.10658 (13)	0.0454 (4)
C10	0.22059 (15)	0.45194 (5)	0.20565 (14)	0.0416 (3)
C11	0.26861 (15)	0.39259 (6)	0.20617 (15)	0.0441 (4)
C12	0.34693 (17)	0.36818 (6)	0.10200 (16)	0.0568 (4)
H12	0.3668	0.3910	0.0296	0.068*
C13	0.39369 (19)	0.31155 (7)	0.1063 (2)	0.0715 (5)
H13	0.4463	0.2961	0.0372	0.086*
C14	0.3635 (2)	0.27640 (7)	0.2132 (2)	0.0758 (6)
H14	0.3962	0.2377	0.2150	0.091*
C15	0.2869 (2)	0.29814 (6)	0.31467 (19)	0.0671 (5)
H15	0.2666	0.2741	0.3850	0.081*
C16	0.23744 (16)	0.35707 (6)	0.31460 (16)	0.0498 (4)
C17	0.16004 (19)	0.38141 (6)	0.41846 (16)	0.0620 (5)
H17	0.1372	0.3580	0.4891	0.074*
C18	0.11748 (17)	0.43869 (6)	0.41815 (15)	0.0575 (4)
H18	0.0670	0.4542	0.4883	0.069*
C19	0.15037 (16)	0.47384 (5)	0.31146 (14)	0.0438 (4)
C20	−0.06197 (19)	0.61855 (7)	0.15824 (19)	0.0748 (5)
H20A	−0.1290	0.6046	0.2232	0.112*
H20B	−0.0643	0.5918	0.0857	0.112*
H20C	−0.0971	0.6562	0.1277	0.112*
C21	0.46191 (17)	0.61472 (6)	0.21791 (16)	0.0620 (5)
H21A	0.4164	0.6429	0.1573	0.093*
H21B	0.4962	0.5815	0.1703	0.093*
H21C	0.5492	0.6319	0.2667	0.093*
C22	0.4158 (2)	0.55129 (6)	0.40929 (17)	0.0717 (5)
H22A	0.5025	0.5691	0.4574	0.108*
H22B	0.4513	0.5182	0.3618	0.108*
H22C	0.3408	0.5388	0.4693	0.108*
C23	0.2486 (2)	0.55342 (7)	−0.12201 (15)	0.0756 (5)
H23A	0.1723	0.5234	−0.1445	0.091*
H23B	0.3516	0.5362	−0.1213	0.091*
C24	0.2344 (2)	0.60208 (8)	−0.21924 (17)	0.0930 (6)
H24A	0.1314	0.6182	−0.2204	0.139*
H24B	0.2537	0.5875	−0.3050	0.139*
H24C	0.3090	0.6319	−0.1949	0.139*

Atomic displacement parameters (Å^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
O1	0.0591 (6)	0.0358 (5)	0.0510 (6)	0.0043 (5)	0.0201 (5)	0.0047 (4)
O2	0.0940 (8)	0.0462 (6)	0.0382 (6)	−0.0067 (5)	0.0094 (5)	0.0066 (5)
N1	0.0654 (8)	0.0389 (7)	0.0436 (8)	−0.0023 (6)	0.0126 (6)	−0.0006 (6)
N2	0.0505 (8)	0.0390 (7)	0.0543 (8)	0.0086 (6)	−0.0031 (6)	0.0064 (6)

C1	0.0630 (10)	0.0305 (8)	0.0545 (10)	0.0000 (7)	0.0183 (8)	0.0056 (7)
C2	0.0823 (12)	0.0414 (10)	0.0938 (15)	0.0106 (9)	0.0344 (11)	0.0083 (10)
C3	0.1261 (19)	0.0404 (10)	0.1195 (19)	−0.0058 (12)	0.0634 (16)	−0.0214 (12)
C4	0.1252 (19)	0.0703 (14)	0.0921 (17)	−0.0293 (13)	0.0388 (15)	−0.0338 (12)
C5	0.0889 (13)	0.0617 (11)	0.0616 (12)	−0.0206 (10)	0.0123 (10)	−0.0123 (9)
C6	0.0604 (10)	0.0366 (8)	0.0458 (9)	−0.0056 (7)	0.0099 (8)	0.0008 (7)
C7	0.0509 (9)	0.0378 (8)	0.0460 (9)	0.0027 (7)	0.0004 (7)	0.0055 (7)
C8	0.0486 (9)	0.0349 (7)	0.0401 (9)	0.0017 (7)	0.0076 (7)	0.0061 (6)
C9	0.0567 (10)	0.0419 (9)	0.0381 (9)	−0.0045 (7)	0.0063 (7)	0.0043 (7)
C10	0.0487 (9)	0.0344 (8)	0.0426 (9)	−0.0033 (6)	0.0088 (7)	0.0003 (7)
C11	0.0401 (8)	0.0364 (8)	0.0557 (10)	−0.0027 (7)	0.0026 (7)	−0.0040 (7)
C12	0.0566 (10)	0.0454 (9)	0.0688 (12)	0.0018 (8)	0.0064 (9)	−0.0114 (8)
C13	0.0694 (12)	0.0547 (11)	0.0904 (15)	0.0075 (9)	0.0040 (10)	−0.0217 (10)
C14	0.0750 (13)	0.0415 (10)	0.1086 (18)	0.0119 (9)	−0.0133 (12)	−0.0127 (11)
C15	0.0749 (12)	0.0407 (9)	0.0841 (14)	−0.0019 (8)	−0.0092 (11)	0.0060 (9)
C16	0.0506 (10)	0.0356 (8)	0.0629 (11)	−0.0028 (7)	0.0004 (8)	0.0021 (8)
C17	0.0761 (12)	0.0466 (10)	0.0646 (12)	−0.0051 (8)	0.0152 (9)	0.0186 (8)
C18	0.0722 (11)	0.0476 (9)	0.0555 (11)	0.0025 (8)	0.0262 (8)	0.0082 (8)
C19	0.0493 (9)	0.0328 (8)	0.0503 (10)	0.0007 (7)	0.0117 (7)	0.0039 (7)
C20	0.0609 (12)	0.0686 (11)	0.0928 (14)	0.0078 (9)	−0.0135 (10)	0.0146 (10)
C21	0.0533 (10)	0.0603 (10)	0.0734 (12)	−0.0029 (8)	0.0120 (9)	−0.0050 (8)
C22	0.0805 (12)	0.0560 (10)	0.0748 (13)	0.0045 (9)	−0.0259 (10)	0.0107 (9)
C23	0.1160 (15)	0.0711 (11)	0.0406 (11)	−0.0154 (10)	0.0133 (10)	−0.0001 (9)
C24	0.1305 (17)	0.1011 (15)	0.0468 (12)	−0.0337 (13)	0.0011 (11)	0.0163 (10)

Geometric parameters (Å, °)

O1—C19	1.3780 (14)	C12—C13	1.3591 (19)
O1—C8	1.4640 (15)	C12—H12	0.9300
O2—C9	1.3371 (15)	C13—C14	1.393 (2)
O2—C23	1.4478 (18)	C13—H13	0.9300
N1—C9	1.2724 (16)	C14—C15	1.356 (2)
N1—C10	1.4095 (16)	C14—H14	0.9300
N2—C1	1.3977 (18)	C15—C16	1.417 (2)
N2—C8	1.4320 (16)	C15—H15	0.9300
N2—C20	1.4471 (18)	C16—C17	1.402 (2)
C1—C6	1.3823 (19)	C17—C18	1.3631 (19)
C1—C2	1.383 (2)	C17—H17	0.9300
C2—C3	1.397 (3)	C18—C19	1.3971 (19)
C2—H2	0.9300	C18—H18	0.9300
C3—C4	1.372 (3)	C20—H20A	0.9600
C3—H3	0.9300	C20—H20B	0.9600
C4—C5	1.371 (3)	C20—H20C	0.9600
C4—H4	0.9300	C21—H21A	0.9600
C5—C6	1.378 (2)	C21—H21B	0.9600
C5—H5	0.9300	C21—H21C	0.9600
C6—C7	1.5025 (19)	C22—H22A	0.9600
C7—C22	1.5278 (18)	C22—H22B	0.9600
C7—C21	1.5332 (19)	C22—H22C	0.9600

C7—C8	1.5713 (18)	C23—C24	1.493 (2)
C8—C9	1.5163 (18)	C23—H23A	0.9700
C10—C19	1.3649 (19)	C23—H23B	0.9700
C10—C11	1.4218 (17)	C24—H24A	0.9600
C11—C12	1.409 (2)	C24—H24B	0.9600
C11—C16	1.4125 (19)	C24—H24C	0.9600
C19—O1—C8	116.81 (10)	C14—C13—H13	119.7
C9—O2—C23	117.27 (11)	C15—C14—C13	120.53 (16)
C9—N1—C10	116.47 (12)	C15—C14—H14	119.7
C1—N2—C8	108.97 (11)	C13—C14—H14	119.7
C1—N2—C20	121.73 (13)	C14—C15—C16	120.68 (17)
C8—N2—C20	120.44 (11)	C14—C15—H15	119.7
C6—C1—C2	121.30 (15)	C16—C15—H15	119.7
C6—C1—N2	110.22 (12)	C17—C16—C11	118.98 (13)
C2—C1—N2	128.46 (15)	C17—C16—C15	122.42 (15)
C1—C2—C3	117.11 (17)	C11—C16—C15	118.60 (15)
C1—C2—H2	121.4	C18—C17—C16	121.46 (14)
C3—C2—H2	121.4	C18—C17—H17	119.3
C4—C3—C2	121.72 (18)	C16—C17—H17	119.3
C4—C3—H3	119.1	C17—C18—C19	119.34 (14)
C2—C3—H3	119.1	C17—C18—H18	120.3
C5—C4—C3	120.08 (19)	C19—C18—H18	120.3
C5—C4—H4	120.0	C10—C19—O1	120.43 (12)
C3—C4—H4	120.0	C10—C19—C18	121.66 (12)
C4—C5—C6	119.59 (18)	O1—C19—C18	117.88 (13)
C4—C5—H5	120.2	N2—C20—H20A	109.5
C6—C5—H5	120.2	N2—C20—H20B	109.5
C5—C6—C1	120.14 (15)	H20A—C20—H20B	109.5
C5—C6—C7	130.64 (15)	N2—C20—H20C	109.5
C1—C6—C7	109.21 (12)	H20A—C20—H20C	109.5
C6—C7—C22	113.40 (13)	H20B—C20—H20C	109.5
C6—C7—C21	109.53 (11)	C7—C21—H21A	109.5
C22—C7—C21	108.61 (12)	C7—C21—H21B	109.5
C6—C7—C8	100.77 (11)	H21A—C21—H21B	109.5
C22—C7—C8	114.07 (11)	C7—C21—H21C	109.5
C21—C7—C8	110.25 (12)	H21A—C21—H21C	109.5
N2—C8—O1	107.05 (10)	H21B—C21—H21C	109.5
N2—C8—C9	112.96 (11)	C7—C22—H22A	109.5
O1—C8—C9	106.91 (10)	C7—C22—H22B	109.5
N2—C8—C7	103.68 (10)	H22A—C22—H22B	109.5
O1—C8—C7	110.71 (10)	C7—C22—H22C	109.5
C9—C8—C7	115.30 (11)	H22A—C22—H22C	109.5
N1—C9—O2	122.16 (13)	H22B—C22—H22C	109.5
N1—C9—C8	125.60 (12)	O2—C23—C24	107.05 (14)
O2—C9—C8	112.23 (11)	O2—C23—H23A	110.3
C19—C10—N1	120.89 (12)	C24—C23—H23A	110.3
C19—C10—C11	119.45 (13)	O2—C23—H23B	110.3
N1—C10—C11	119.60 (13)	C24—C23—H23B	110.3
C12—C11—C16	118.97 (13)	H23A—C23—H23B	108.6

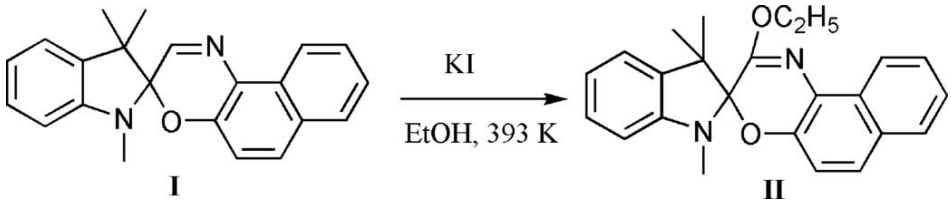
C12—C11—C10	121.99 (14)	C23—C24—H24A	109.5
C16—C11—C10	119.04 (13)	C23—C24—H24B	109.5
C13—C12—C11	120.65 (16)	H24A—C24—H24B	109.5
C13—C12—H12	119.7	C23—C24—H24C	109.5
C11—C12—H12	119.7	H24A—C24—H24C	109.5
C12—C13—C14	120.55 (17)	H24B—C24—H24C	109.5
C12—C13—H13	119.7		

Hydrogen-bond geometry (Å, °)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
C18—H18···O1^{i}	0.93	2.60	3.5014 (18)	164.

Symmetry codes: (i) −*x*, −*y*+1, −*z*+1.

Fig. 1



I **II**

Fig. 2

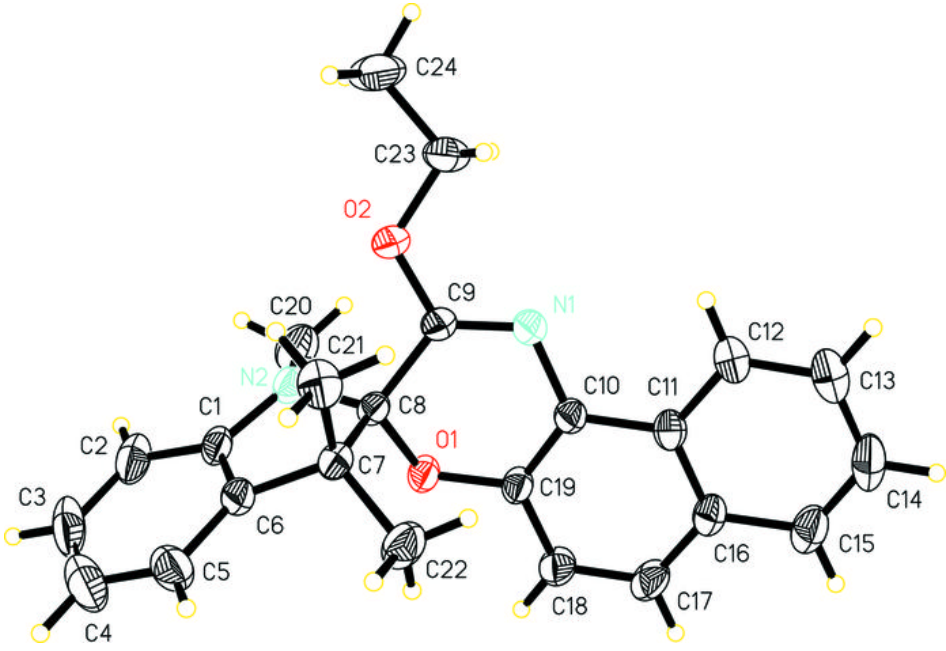
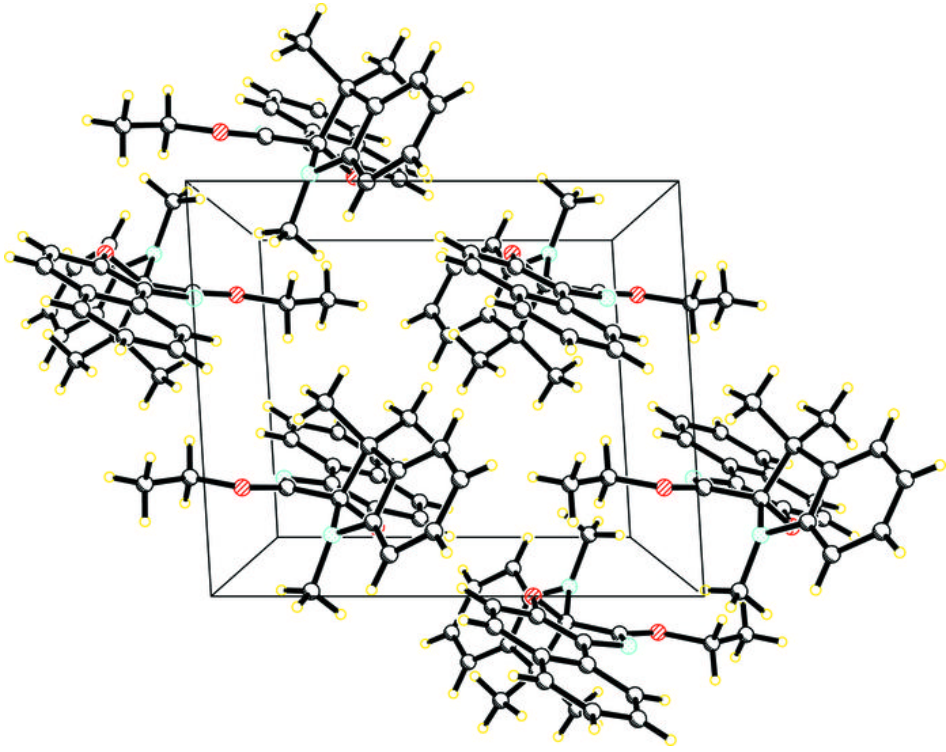

C24
C23
O2
C9
N1
C20
C21
N2
C1
C8
C10
C11
C12
C13
C2
O1
C7
C19
C14
C3
C6
C16
C15
C5
C22
C18
C17
C4

Fig. 3



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4-Methyl-5-phenyl-1*H*-pyrazol-3-ol

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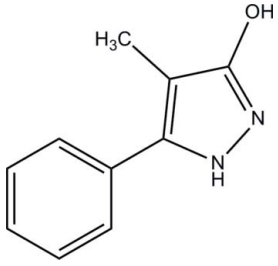
Key indicators: single-crystal X-ray study; T = 100 K; mean σ(C–C) = 0.003 Å; R factor = 0.059; wR factor = 0.204; data-to-parameter ratio = 21.6.

The title compound, $C_{10}H_{10}N_2O$, crystallizes with two independent molecules in the asymmetric unit, having closely comparable geometries. The dihedral angles between the 1*H*-pyrazole and benzene rings in the two molecules are 39.57 (14) and 41.95 (13)°. The two molecules are each connected to neighbouring molecules by pairs of intermolecular O—H···N hydrogen bonds, forming dimers with $R_2^2(8)$ ring motifs. These dimers are further linked into $R_4^4(10)$ ring motifs by intermolecular N—H···O hydrogen bonds, forming chains along [101]. The crystal structure is further stabilized by a C—H···π interaction.

Related literature

For the biological activity of 4-methyl-3-phenyl-1*H*-pyrazol-5-ol, see: Brogden (1986); Gursoy *et al.* (2000); Ragavan *et al.* (2009, 2010); Watanabe *et al.* (1984); Kawai *et al.* (1997); Wu *et al.* (2002). For related structures, see: Shahani *et al.* (2009, 2010*a*,*b*,*c*). For hydrogen-bond motifs, see: Bernstein *et al.* (1995). For bond-length data, see: Allen *et al.* (1987). For the stability of the temperature controller used for the data collection, see: Cosier & Glazer (1986).



Experimental

Crystal data

$C_{10}H_{10}N_2O$
M_r = 174.20
Monoclinic, $C2/c$
a = 26.4082 (19) Å
b = 11.0972 (8) Å
c = 14.1245 (10) Å
β = 118.996 (1)°
V = 3620.4 (4) Å^3
Z = 16
Mo $K\alpha$ radiation
μ = 0.09 mm^{-1}
T = 100 K
0.35 × 0.14 × 0.08 mm

Data collection

Bruker APEXII DUO CCD area-detector diffractometer
Absorption correction: multi-scan (*SADABS*; Bruker, 2009)
T_{min} = 0.970, T_{max} = 0.993
19166 measured reflections
5255 independent reflections
2907 reflections with $I > 2\sigma(I)$
R_{int} = 0.049

Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.059
$wR(F^2)$ = 0.204
S = 1.13
5255 reflections
243 parameters
H atoms treated by a mixture of independent and constrained refinement
$\Delta\rho_{max}$ = 0.33 e Å^{-3}
$\Delta\rho_{min}$ = −0.26 e Å^{-3}

Table 1
Hydrogen-bond geometry (Å, °).

*Cg*1 is the centroid of the C1*B*–C6*B* benzene ring.

D—H···A	D—H	H···A	D···A	D—H···A
O1*A*—H1*OA*···N2*A*^{i}	0.83	1.85	2.673 (2)	171
O1*B*—H1*OB*···N2*B*^{ii}	0.83	1.84	2.670 (2)	177
N1*B*—H1*NB*···O1*A*^{iii}	1.00 (3)	1.85 (3)	2.836 (3)	171 (3)
N1*A*—H1*NA*···O1*B*^{iv}	0.97 (3)	1.88 (3)	2.844 (2)	173 (2)
C10*A*—H10*C*···*Cg*1^{v}	0.96	2.77	3.575 (3)	142

Symmetry codes: (i) $-x+\frac{1}{2}, -y+\frac{5}{2}, -z+1$; (ii) $-x, y, -z-\frac{1}{2}$; (iii) $-x+\frac{1}{2}, y-\frac{1}{2}, -z+\frac{1}{2}$; (iv) $-x, -y+2, -z$; (v) $x, -y, z-\frac{1}{2}$.

Data collection: *APEX2* (Bruker, 2009); cell refinement: *SAINT* (Bruker, 2009); data reduction: *SAINT*; program(s) used to solve structure: *SHELXTL* (Sheldrick, 2008); program(s) used to refine structure: *SHELXTL*; molecular graphics: *SHELXTL*; software used to prepare material for publication: *SHELXTL* and *PLATON* (Spek, 2009).

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Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: IS2561).

References

Allen, F. H., Kennard, O., Watson, D. G., Brammer, L., Orpen, A. G. & Taylor, R. (1987). *J. Chem. Soc. Perkin Trans. 2*, pp. S1–19.
Bernstein, J., Davis, R. E., Shimoni, L. & Chang, N.-L. (1995). *Angew. Chem. Int. Ed. Engl.* **34**, 1555–1573.
Brogden, R. N. (1986). *Pyrazolone Derivatives Drugs*, **32**, 60–70.
Bruker (2009). *APEX2*, *SAINT* and *SADABS*. Bruker AXS Inc., Madison, Wiscosin, USA.
Cosier, J. & Glazer, A. M. (1986). *J. Appl. Cryst.* **19**, 105–107.

‡ Thomson Reuters ResearcherID: A-3561-2009.

Gursoy, A., Demirayak, S., Capan, G., Erol, K. & Vural, K. (2000). *Eur. J. Med. Chem.* **35**, 359–364.
Kawai, H., Nakai, H., Suga, M., Yuki, S., Watanabe, T. & Saito, K. I. (1997). *J. Pharmcol. Exp. Ther.* **281**, 921–927.
Ragavan, R. V., Vijayakumar, V. & Kumari, N. S. (2009). *Eur. J. Med. Chem.* **44**, 3852–3857.
Ragavan, R. V., Vijayakumar, V. & Kumari, N. S. (2010). *Eur. J. Med. Chem.* **45**, 1173–1180.
Shahani, T., Fun, H.-K., Ragavan, R. V., Vijayakumar, V. & Sarveswari, S. (2009). *Acta Cryst.* E**65**, o3249–o3250.
Shahani, T., Fun, H.-K., Ragavan, R. V., Vijayakumar, V. & Sarveswari, S. (2010*a*). *Acta Cryst.* E**66**, o142–o143.
Shahani, T., Fun, H.-K., Ragavan, R. V., Vijayakumar, V. & Sarveswari, S. (2010*b*). *Acta Cryst.* E**66**, o1357–o1358.
Shahani, T., Fun, H.-K., Ragavan, R. V., Vijayakumar, V. & Sarveswari, S. (2010*c*). *Acta Cryst.* E**66**, o1482–o1483.
Sheldrick, G. M. (2008). *Acta Cryst.* A**64**, 112–122.
Spek, A. L. (2009). *Acta Cryst.* D**65**, 148–155.
Watanabe, T., Yuki, S., Egawa, M. & Nishi, H. (1984). *J. Pharmacol. Exp. Ther.* **268**, 1597–1604.
Wu, T. W., Zeng, L. H., Wu, J. & Fung, K. P. (2002). *Life Sci.* **71**, 2249–2255.

supplementary materials

Acta Cryst. (2010). E**66**, o1697-o1698 [**doi:10.1107/S1600536810022828**]

4-Methyl-5-phenyl-1*H*-pyrazol-3-ol

T. Shahani, H.-K. Fun, R. V. Ragavan, V. Vijayakumar and S. Sarveswari

Comment

Pyrazolone derivatives have a broad spectrum of biological activities being used as analgesic, antipyretic and anti-inflammatory therapeutical drugs (Brogden, 1986; Gursoy *et al.*, 2000). A class of new compounds with the pyrazolone moiety was synthesized and reported for their antibacterial and antifungal activities by Ragavan *et al.* (2009, 2010). A new pyrazolone derivative, edaravone (3-methyl-1-phenyl-2-pyrazoline-5-one), is being used as a drug in clinical practice for brain ischemia (Watanabe *et al.*, 1984; Kawai *et al.*, 1997) and the same has been found to be effective against myocardial ischemia (Wu *et al.*, 2002).

There are two independent molecules (A and B) in the asymmetric unit (Fig. 1). The maximum deviations in 1*H*-pyrazole ring (N1/N2/C7–C9) for molecules A and B are 0.006 (2) and 0.011 (2) Å, respectively, at atoms C6A and C6B. The dihedral angles formed between the 1*H*-pyrazole ring and benzene ring in molecules A and B are 39.57 (14) and 41.95 (13)°, respectively. The bond lengths (Allen *et al.*, 1987) and angles are within normal ranges and comparable to those closely related structures (Shahani *et al.*, 2009, 2010*a*–*c*).

In the crystal packing (Fig. 2), pairs of intermolecular O1A—H1OA···N2A and O1B—H1OB···N2B hydrogen bonds (Table 1) form dimers with neighbouring molecules, generating $R_2^2(8)$ ring motifs (Bernstein *et al.*, 1995). These dimers are further linked into $R_4^4(10)$ ring motifs by additional intermolecular N1A—H1NA···O1B and N1B—H1NB···O1A hydrogen bonds (Table 1), forming one dimensional chains along the [101] direction. The crystal structure is further stabilized by C—H···π interaction (Table 1), involving the C1B—C6B benzene ring (centroid *Cg*1).

Experimental

The compound 4-methyl-5-phenyl-1-*H*-pyrazol-3-ol has been synthesized using the method available in the literature (Ragavan *et al.*, 2009, 2010) and recrystallized using the ethanol (white solid). *m.p.* 278.5–493 K.

Refinement

The H atoms bound to O atoms were located in a difference map and constrained to ride with their parent atoms, with U_{iso}(H) = 1.5U_{eq}(O) (O—H = 0.83 Å). The H atoms bound to N atoms were located in a difference map and were refined freely [refined N—H lengths, 1.00 (3) and 0.97 (2) Å]. All other H atoms were positioned geometrically (C—H = 0.93–0.96 Å], with U_{iso}(H) = 1.2 or 1.5U_{eq}(C).

Figures

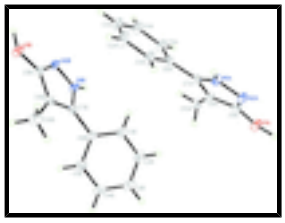


Fig. 1. The molecular structure of the title compound, showing 20% probability displacement ellipsoids and the atom numbering scheme.

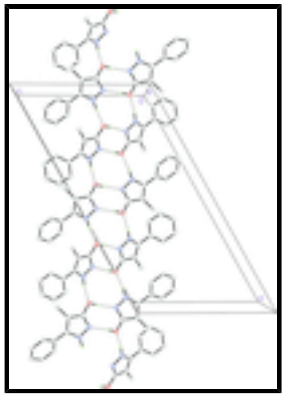


Fig. 2. The crystal packing of the title compound, viewed approximately along the *b* axis, showing a one-dimensional chain.

4-Methyl-5-phenyl-1*H*-pyrazol-3-ol

Crystal data

$C_{10}H_{10}N_2O$	$F(000) = 1472$
$M_r = 174.20$	$D_x = 1.278$ Mg m^{-3}
Monoclinic, *C*2/*c*	Mo *K*α radiation, λ = 0.71073 Å
Hall symbol: -C 2yc	Cell parameters from 3052 reflections
a = 26.4082 (19) Å	θ = 3.3–27.2°
b = 11.0972 (8) Å	μ = 0.09 mm^{-1}
c = 14.1245 (10) Å	*T* = 100 K
β = 118.996 (1)°	Block, colourless
V = 3620.4 (4) Å^3	0.35 × 0.14 × 0.08 mm
Z = 16	

Data collection

Bruker APEXII DUO CCD area-detector diffractometer	5255 independent reflections
Radiation source: fine-focus sealed tube	2907 reflections with $I > 2\sigma(I)$
graphite	$R_{int} = 0.049$
φ and ω scans	$\theta_{max} = 30.0°$, $\theta_{min} = 2.0°$
Absorption correction: multi-scan (*SADABS*; Bruker, 2009)	$h = -37 \rightarrow 28$
$T_{min} = 0.970$, $T_{max} = 0.993$	$k = -15 \rightarrow 13$
19166 measured reflections	$l = -19 \rightarrow 19$

Refinement

Refinement on F^2	Primary atom site location: structure-invariant direct methods
Least-squares matrix: full	Secondary atom site location: difference Fourier map
$R[F^2 > 2\sigma(F^2)] = 0.059$	Hydrogen site location: inferred from neighbouring sites
$wR(F^2) = 0.204$	H atoms treated by a mixture of independent and constrained refinement
$S = 1.13$	$w = 1/[\sigma^2(F_o^2) + (0.0985P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
5255 reflections	$(\Delta/\sigma)_{max} = 0.001$
243 parameters	$\Delta\rho_{max} = 0.33$ e Å^{-3}
0 restraints	$\Delta\rho_{min} = -0.26$ e Å^{-3}

Special details

Experimental. The crystal was placed in the cold stream of an Oxford Cyrosystems Cobra open-flow nitrogen cryostat (Cosier & Glazer, 1986) operating at 100.0 (1) K.

Geometry. All e.s.d.'s (except the e.s.d. in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell e.s.d.'s are taken into account individually in the estimation of e.s.d.'s in distances, angles and torsion angles; correlations between e.s.d.'s in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell e.s.d.'s is used for estimating e.s.d.'s involving l.s. planes.

Refinement. Refinement of F^2 against ALL reflections. The weighted *R*-factor *wR* and goodness of fit *S* are based on F^2, conventional *R*-factors *R* are based on *F*, with *F* set to zero for negative F^2. The threshold expression of $F^2 > \sigma(F^2)$ is used only for calculating *R*-factors(gt) *etc*. and is not relevant to the choice of reflections for refinement. *R*-factors based on F^2 are statistically about twice as large as those based on *F*, and *R*- factors based on ALL data will be even larger.

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å^2)

	x	*y*	*z*	U_{iso}*/U_{eq}
O1A	0.30484 (5)	1.15234 (15)	0.48624 (10)	0.0513 (4)
H1OA	0.3021	1.1865	0.5356	0.077*
N1A	0.17011 (7)	1.19165 (16)	0.26752 (12)	0.0419 (4)
N2A	0.21137 (6)	1.22060 (17)	0.36985 (11)	0.0416 (4)
C1A	0.09436 (9)	1.0463 (3)	0.07114 (18)	0.0643 (7)
H1AA	0.0772	1.0599	0.1142	0.077*
C2A	0.06077 (11)	1.0113 (3)	−0.0353 (2)	0.0835 (10)
H2AA	0.0211	1.0019	−0.0634	0.100*
C3A	0.08503 (12)	0.9902 (3)	−0.09985 (19)	0.0704 (8)
H3AA	0.0621	0.9665	−0.1715	0.084*
C4A	0.14342 (12)	1.0042 (3)	−0.05821 (19)	0.0676 (7)
H4AA	0.1603	0.9906	−0.1017	0.081*
C5A	0.17726 (10)	1.0384 (3)	0.04793 (17)	0.0605 (6)
H5AA	0.2170	1.0462	0.0758	0.073*
C6A	0.15335 (8)	1.06126 (19)	0.11381 (14)	0.0412 (4)

C7A	0.18926 (8)	1.10453 (19)	0.22525 (14)	0.0386 (4)
C8A	0.24504 (8)	1.07398 (19)	0.30334 (14)	0.0406 (4)
C9A	0.25656 (7)	1.1493 (2)	0.39179 (14)	0.0404 (4)
C10A	0.28424 (9)	0.9785 (2)	0.30003 (17)	0.0526 (5)
H10A	0.2662	0.9409	0.2300	0.079*
H10B	0.2914	0.9190	0.3545	0.079*
H10C	0.3202	1.0143	0.3135	0.079*
O1B	−0.05992 (5)	0.70768 (16)	−0.21038 (10)	0.0515 (4)
H1OB	−0.0528	0.7049	−0.2616	0.077*
N1B	0.08261 (7)	0.69465 (18)	−0.01528 (12)	0.0468 (4)
N2B	0.04080 (6)	0.70277 (17)	−0.12057 (12)	0.0455 (4)
C1B	0.14424 (9)	0.7478 (2)	0.21872 (16)	0.0564 (6)
H1BA	0.1524	0.8034	0.1787	0.068*
C2B	0.17998 (11)	0.7390 (3)	0.32909 (18)	0.0725 (8)
H2BA	0.2123	0.7887	0.3631	0.087*
C3B	0.16837 (12)	0.6580 (3)	0.38904 (18)	0.0708 (8)
H3BA	0.1925	0.6531	0.4635	0.085*
C4B	0.12108 (10)	0.5843 (3)	0.33917 (17)	0.0630 (7)
H4BA	0.1134	0.5285	0.3797	0.076*
C5B	0.08471 (9)	0.5923 (2)	0.22872 (16)	0.0520 (5)
H5BA	0.0524	0.5426	0.1954	0.062*
C6B	0.09620 (8)	0.67397 (19)	0.16757 (14)	0.0409 (4)
C7B	0.05896 (8)	0.68061 (19)	0.04958 (14)	0.0400 (4)
C8B	−0.00068 (8)	0.6800 (2)	−0.01460 (14)	0.0411 (5)
C9B	−0.00976 (8)	0.69654 (19)	−0.12047 (14)	0.0406 (4)
C10B	−0.04620 (9)	0.6615 (3)	0.01754 (18)	0.0598 (6)
H10D	−0.0283	0.6528	0.0947	0.090*
H10E	−0.0679	0.5901	−0.0167	0.090*
H10F	−0.0717	0.7298	−0.0047	0.090*
H1NB	0.1235 (11)	0.687 (3)	0.0001 (19)	0.073 (8)*
H1NA	0.1316 (11)	1.224 (2)	0.2420 (18)	0.064 (7)*

Atomic displacement parameters (Å^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
O1A	0.0298 (6)	0.0806 (12)	0.0370 (7)	0.0088 (6)	0.0112 (5)	−0.0066 (7)
N1A	0.0321 (7)	0.0554 (11)	0.0348 (7)	0.0049 (7)	0.0134 (6)	−0.0018 (7)
N2A	0.0299 (7)	0.0569 (11)	0.0336 (7)	0.0034 (7)	0.0120 (6)	−0.0038 (7)
C1A	0.0429 (11)	0.093 (2)	0.0548 (12)	−0.0142 (12)	0.0221 (10)	−0.0223 (12)
C2A	0.0463 (13)	0.126 (3)	0.0661 (15)	−0.0210 (15)	0.0174 (12)	−0.0364 (17)
C3A	0.0739 (17)	0.079 (2)	0.0488 (12)	−0.0139 (14)	0.0223 (12)	−0.0220 (12)
C4A	0.0755 (16)	0.082 (2)	0.0516 (12)	−0.0043 (14)	0.0357 (12)	−0.0183 (12)
C5A	0.0478 (11)	0.0854 (19)	0.0496 (11)	−0.0037 (12)	0.0245 (10)	−0.0106 (12)
C6A	0.0393 (9)	0.0436 (12)	0.0394 (9)	−0.0020 (8)	0.0180 (8)	−0.0021 (8)
C7A	0.0342 (8)	0.0461 (12)	0.0385 (9)	−0.0015 (8)	0.0199 (7)	−0.0007 (8)
C8A	0.0330 (8)	0.0515 (13)	0.0383 (9)	0.0012 (8)	0.0181 (7)	−0.0002 (8)
C9A	0.0295 (8)	0.0549 (13)	0.0363 (9)	0.0031 (8)	0.0157 (7)	0.0020 (8)
C10A	0.0426 (10)	0.0601 (15)	0.0530 (11)	0.0109 (10)	0.0214 (9)	−0.0005 (10)

O1B	0.0298 (6)	0.0862 (12)	0.0357 (7)	0.0068 (7)	0.0135 (6)	−0.0007 (6)
N1B	0.0305 (8)	0.0740 (14)	0.0338 (7)	−0.0012 (8)	0.0139 (6)	0.0038 (7)
N2B	0.0291 (7)	0.0713 (13)	0.0316 (7)	0.0007 (7)	0.0113 (6)	0.0029 (7)
C1B	0.0556 (12)	0.0620 (16)	0.0418 (10)	−0.0101 (11)	0.0160 (9)	0.0013 (10)
C2B	0.0650 (15)	0.088 (2)	0.0436 (12)	−0.0171 (14)	0.0097 (11)	−0.0075 (12)
C3B	0.0685 (16)	0.102 (2)	0.0352 (10)	0.0073 (15)	0.0196 (11)	0.0036 (12)
C4B	0.0648 (14)	0.0853 (19)	0.0455 (11)	0.0113 (13)	0.0320 (11)	0.0194 (11)
C5B	0.0494 (11)	0.0626 (15)	0.0466 (10)	0.0015 (10)	0.0253 (9)	0.0098 (10)
C6B	0.0398 (9)	0.0474 (12)	0.0349 (8)	0.0043 (8)	0.0176 (8)	0.0034 (8)
C7B	0.0369 (9)	0.0481 (12)	0.0351 (9)	−0.0006 (8)	0.0174 (8)	0.0021 (8)
C8B	0.0338 (9)	0.0519 (13)	0.0384 (9)	−0.0004 (8)	0.0180 (8)	0.0009 (8)
C9B	0.0308 (8)	0.0524 (13)	0.0363 (9)	0.0002 (8)	0.0145 (7)	−0.0011 (8)
C10B	0.0405 (11)	0.0886 (19)	0.0561 (12)	0.0052 (11)	0.0280 (10)	0.0070 (12)

Geometric parameters (Å, °)

O1A—C9A	1.326 (2)	O1B—C9B	1.323 (2)
O1A—H1OA	0.8273	O1B—H1OB	0.8317
N1A—C7A	1.356 (3)	N1B—C7B	1.345 (2)
N1A—N2A	1.3612 (19)	N1B—N2B	1.359 (2)
N1A—H1NA	0.97 (2)	N1B—H1NB	1.00 (3)
N2A—C9A	1.337 (2)	N2B—C9B	1.338 (2)
C1A—C2A	1.380 (3)	C1B—C2B	1.380 (3)
C1A—C6A	1.381 (3)	C1B—C6B	1.384 (3)
C1A—H1AA	0.9300	C1B—H1BA	0.9300
C2A—C3A	1.365 (4)	C2B—C3B	1.368 (4)
C2A—H2AA	0.9300	C2B—H2BA	0.9300
C3A—C4A	1.367 (4)	C3B—C4B	1.368 (4)
C3A—H3AA	0.9300	C3B—H3BA	0.9300
C4A—C5A	1.375 (3)	C4B—C5B	1.383 (3)
C4A—H4AA	0.9300	C4B—H4BA	0.9300
C5A—C6A	1.378 (3)	C5B—C6B	1.383 (3)
C5A—H5AA	0.9300	C5B—H5BA	0.9300
C6A—C7A	1.470 (2)	C6B—C7B	1.470 (2)
C7A—C8A	1.388 (2)	C7B—C8B	1.385 (2)
C8A—C9A	1.409 (3)	C8B—C9B	1.407 (3)
C8A—C10A	1.498 (3)	C8B—C10B	1.491 (3)
C10A—H10A	0.9600	C10B—H10D	0.9600
C10A—H10B	0.9600	C10B—H10E	0.9600
C10A—H10C	0.9600	C10B—H10F	0.9600
C9A—O1A—H1OA	115.1	C9B—O1B—H1OB	106.7
C7A—N1A—N2A	111.00 (15)	C7B—N1B—N2B	110.74 (15)
C7A—N1A—H1NA	130.4 (15)	C7B—N1B—H1NB	130.8 (14)
N2A—N1A—H1NA	117.7 (14)	N2B—N1B—H1NB	117.7 (14)
C9A—N2A—N1A	105.76 (15)	C9B—N2B—N1B	106.09 (15)
C2A—C1A—C6A	120.2 (2)	C2B—C1B—C6B	120.0 (2)
C2A—C1A—H1AA	119.9	C2B—C1B—H1BA	120.0
C6A—C1A—H1AA	119.9	C6B—C1B—H1BA	120.0
C3A—C2A—C1A	120.9 (2)	C3B—C2B—C1B	120.7 (2)

C3A—C2A—H2AA	119.5	C3B—C2B—H2BA	119.7
C1A—C2A—H2AA	119.5	C1B—C2B—H2BA	119.7
C2A—C3A—C4A	119.3 (2)	C4B—C3B—C2B	119.8 (2)
C2A—C3A—H3AA	120.3	C4B—C3B—H3BA	120.1
C4A—C3A—H3AA	120.3	C2B—C3B—H3BA	120.1
C3A—C4A—C5A	120.1 (2)	C3B—C4B—C5B	120.2 (2)
C3A—C4A—H4AA	119.9	C3B—C4B—H4BA	119.9
C5A—C4A—H4AA	119.9	C5B—C4B—H4BA	119.9
C4A—C5A—C6A	121.3 (2)	C4B—C5B—C6B	120.3 (2)
C4A—C5A—H5AA	119.4	C4B—C5B—H5BA	119.9
C6A—C5A—H5AA	119.4	C6B—C5B—H5BA	119.9
C5A—C6A—C1A	118.19 (18)	C1B—C6B—C5B	119.03 (18)
C5A—C6A—C7A	120.97 (18)	C1B—C6B—C7B	120.16 (18)
C1A—C6A—C7A	120.81 (18)	C5B—C6B—C7B	120.79 (18)
N1A—C7A—C8A	107.63 (16)	N1B—C7B—C8B	108.12 (15)
N1A—C7A—C6A	121.31 (16)	N1B—C7B—C6B	120.11 (16)
C8A—C7A—C6A	131.04 (18)	C8B—C7B—C6B	131.71 (17)
C7A—C8A—C9A	104.45 (17)	C7B—C8B—C9B	104.41 (16)
C7A—C8A—C10A	129.14 (17)	C7B—C8B—C10B	129.08 (17)
C9A—C8A—C10A	126.32 (17)	C9B—C8B—C10B	126.47 (17)
O1A—C9A—N2A	122.24 (17)	O1B—C9B—N2B	121.95 (16)
O1A—C9A—C8A	126.60 (17)	O1B—C9B—C8B	127.43 (17)
N2A—C9A—C8A	111.16 (15)	N2B—C9B—C8B	110.60 (15)
C8A—C10A—H10A	109.5	C8B—C10B—H10D	109.5
C8A—C10A—H10B	109.5	C8B—C10B—H10E	109.5
H10A—C10A—H10B	109.5	H10D—C10B—H10E	109.5
C8A—C10A—H10C	109.5	C8B—C10B—H10F	109.5
H10A—C10A—H10C	109.5	H10D—C10B—H10F	109.5
H10B—C10A—H10C	109.5	H10E—C10B—H10F	109.5
C7A—N1A—N2A—C9A	−0.7 (2)	C7B—N1B—N2B—C9B	1.5 (2)
C6A—C1A—C2A—C3A	0.3 (5)	C6B—C1B—C2B—C3B	−0.2 (4)
C1A—C2A—C3A—C4A	0.0 (5)	C1B—C2B—C3B—C4B	0.4 (5)
C2A—C3A—C4A—C5A	0.4 (5)	C2B—C3B—C4B—C5B	−0.7 (4)
C3A—C4A—C5A—C6A	−1.2 (4)	C3B—C4B—C5B—C6B	0.8 (4)
C4A—C5A—C6A—C1A	1.4 (4)	C2B—C1B—C6B—C5B	0.2 (4)
C4A—C5A—C6A—C7A	−176.4 (2)	C2B—C1B—C6B—C7B	−178.2 (2)
C2A—C1A—C6A—C5A	−1.0 (4)	C4B—C5B—C6B—C1B	−0.5 (3)
C2A—C1A—C6A—C7A	176.8 (3)	C4B—C5B—C6B—C7B	178.0 (2)
N2A—N1A—C7A—C8A	0.7 (2)	N2B—N1B—C7B—C8B	−0.3 (2)
N2A—N1A—C7A—C6A	−177.51 (17)	N2B—N1B—C7B—C6B	−177.91 (18)
C5A—C6A—C7A—N1A	138.9 (2)	C1B—C6B—C7B—N1B	39.6 (3)
C1A—C6A—C7A—N1A	−38.9 (3)	C5B—C6B—C7B—N1B	−138.8 (2)
C5A—C6A—C7A—C8A	−38.9 (3)	C1B—C6B—C7B—C8B	−137.3 (2)
C1A—C6A—C7A—C8A	143.3 (2)	C5B—C6B—C7B—C8B	44.2 (3)
N1A—C7A—C8A—C9A	−0.5 (2)	N1B—C7B—C8B—C9B	−0.9 (2)
C6A—C7A—C8A—C9A	177.5 (2)	C6B—C7B—C8B—C9B	176.3 (2)
N1A—C7A—C8A—C10A	176.4 (2)	N1B—C7B—C8B—C10B	177.0 (2)
C6A—C7A—C8A—C10A	−5.6 (4)	C6B—C7B—C8B—C10B	−5.9 (4)
N1A—N2A—C9A—O1A	−179.23 (17)	N1B—N2B—C9B—O1B	176.63 (19)

N1A—N2A—C9A—C8A	0.4 (2)	N1B—N2B—C9B—C8B	−2.1 (2)
C7A—C8A—C9A—O1A	179.64 (19)	C7B—C8B—C9B—O1B	−176.7 (2)
C10A—C8A—C9A—O1A	2.7 (3)	C10B—C8B—C9B—O1B	5.3 (4)
C7A—C8A—C9A—N2A	0.1 (2)	C7B—C8B—C9B—N2B	1.9 (2)
C10A—C8A—C9A—N2A	−176.89 (19)	C10B—C8B—C9B—N2B	−176.1 (2)

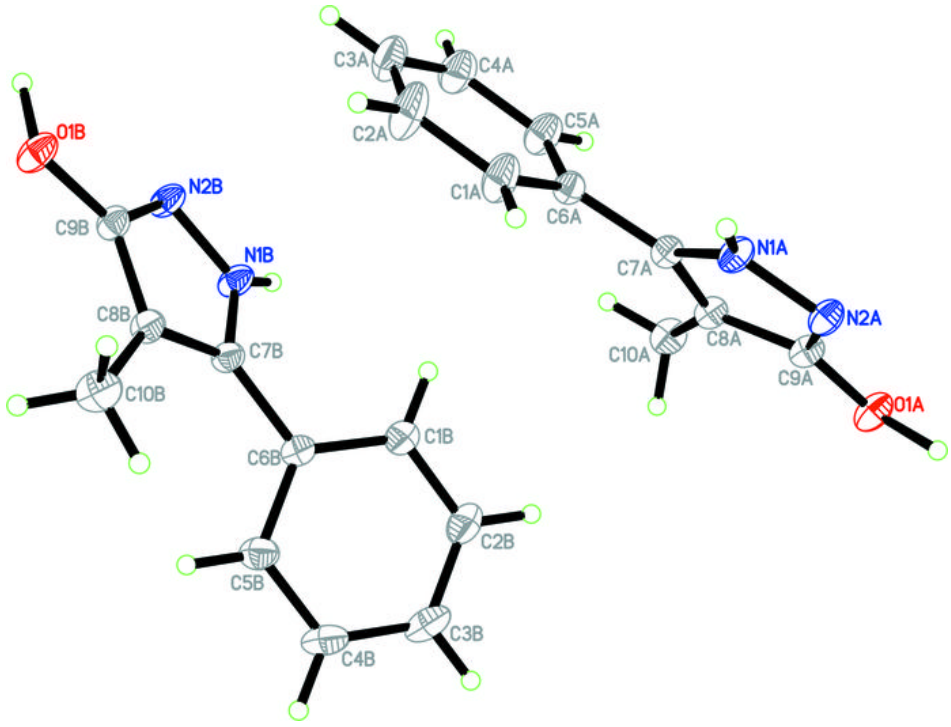
Hydrogen-bond geometry (Å, °)

Cg1 is the centroid of the C1B–C6B benzene ring.

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
O1A—H1OA···N2A^{i}	0.83	1.85	2.673 (2)	171
O1B—H1OB···N2B^{ii}	0.83	1.84	2.670 (2)	177
N1B—H1NB···O1A^{iii}	1.00 (3)	1.85 (3)	2.836 (3)	171 (3)
N1A—H1NA···O1B^{iv}	0.97 (3)	1.88 (3)	2.844 (2)	173 (2)
C10A—H10C···Cg1^{v}	0.96	2.77	3.575 (3)	142

Symmetry codes: (i) −*x*+1/2, −*y*+5/2, −*z*+1; (ii) −*x*, *y*, −*z*−1/2; (iii) −*x*+1/2, *y*−1/2, −*z*+1/2; (iv) −*x*, −*y*+2, −*z*; (v) *x*, −*y*, *z*−1/2.

Fig. 1


C3A
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C5A
C2A
C1A
C6A
N1A
C7A
N2A
C8A
C10A
C9A
O1A
O1B
N2B
C9B
N1B
C8B
C7B
C10B
C1B
C6B
C2B
C5B
C3B
C4B

Fig. 2