

Acta Crystallographica Section E

Structure Reports

Online

ISSN 1600-5368

(7E)-5-Benzyl-7-(2-chlorobenzylidene)-3-(2-chlorophenyl)-2-phenyl-3,3a,4,5,6,7-hexahydro-2H-pyrazolo[4,3-c]pyridine

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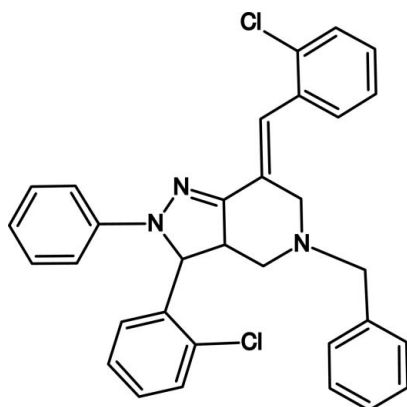
Received 15 June 2010; accepted 16 June 2010

Key indicators: single-crystal X-ray study; $T = 294$ K; mean $\sigma(\text{C}-\text{C}) = 0.004$ Å; R factor = 0.049; wR factor = 0.098; data-to-parameter ratio = 16.3.

In the title 2H-pyrazolo[4,3-c]pyridine derivative, $\text{C}_{32}\text{H}_{27}\text{Cl}_2\text{N}_3$, the dihydropyrazole ring adopts an envelope conformation and the piperidine fused ring a twisted-chair conformation. Two short intramolecular $\text{C}-\text{H}\cdots\text{Cl}$ contacts are observed. The crystal packing is characterized by dimeric $\text{C}-\text{Cl}\cdots\pi$ interactions involving the 5-benzyl ring, with $\text{Cl}\cdots$ centroid and closest atomic $\text{Cl}\cdots\pi$ distances of 3.778 (2) and 3.366 (4) Å, respectively.

Related literature

For the anti-inflammatory activity of 2H-pyrazolo[4,3-c]pyridine derivatives, see Krapcho & Turk (1975). For π -halogen-dimer interactions and their role in host-guest chemistry, see: Noman *et al.* (2004); Nagaraj *et al.* (2005).



Experimental

Crystal data

$\text{C}_{32}\text{H}_{27}\text{Cl}_2\text{N}_3$
 $M_r = 524.47$
Monoclinic, $P2_1/c$
 $a = 13.7117$ (7) Å
 $b = 15.4451$ (6) Å
 $c = 13.6896$ (9) Å
 $\beta = 113.135$ (7)°
 $V = 2666.0$ (2) Å³
 $Z = 4$
Mo $K\alpha$ radiation
 $\mu = 0.27$ mm⁻¹
 $T = 294$ K
 $0.36 \times 0.26 \times 0.22$ mm

Data collection

Oxford Diffraction Xcalibur Eos Gemini diffractometer
Absorption correction: multi-scan (*CrysAlis PRO*; Oxford Diffraction, 2009)
 $T_{\min} = 0.909$, $T_{\max} = 0.943$
11774 measured reflections
5436 independent reflections
2483 reflections with $I > 2\sigma(I)$
 $R_{\text{int}} = 0.049$

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.049$
 $wR(F^2) = 0.098$
 $S = 0.83$
5436 reflections
334 parameters
H-atom parameters constrained
 $\Delta\rho_{\text{max}} = 0.17$ e Å⁻³
 $\Delta\rho_{\text{min}} = -0.23$ e Å⁻³

Table 1

Hydrogen-bond geometry (Å, °).

| $D-H\cdots A$ | $D-H$ | $H\cdots A$ | $D\cdots A$ | $D-H\cdots A$ |
|---|-------|-------------|-------------|---------------|
| $\text{C3}-\text{H3}\cdots\text{Cl1}$ | 0.98 | 2.61 | 3.101 (2) | 111 |
| $\text{C27}-\text{H27}\cdots\text{Cl2}$ | 0.93 | 2.68 | 3.043 (3) | 104 |

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 *PLATON* (Spek, 2009); software used to prepare material for publication: *SHELXL97* and *PLATON*.

The Bioinformatics Infrastructure Facility and the Single Crystal X-ray Diffractometer Facility at the University of Hyderabad are gratefully acknowledged are gratefully acknowledged for computation and data collection. RSR thanks the CSIR, New Delhi, for support under the scientist's pool scheme and NSK thanks the CSIR, New Delhi, for a Senior Research Fellowship.

Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: NG2791).

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supplementary materials

Acta Cryst. (2010). E66, o1734 [doi:10.1107/S1600536810023317]

(7E)-5-Benzyl-7-(2-chlorobenzylidene)-3-(2-chlorophenyl)-2-phenyl-3,3a,4,5,6,7-hexahydro-2H-pyrazolo[4,3-c]pyridine

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Comment

Derivatives of 2H-pyrazolo[4,3-c]pyridine have been tested for anti-inflammatory activity (Krapcho & Turk, 1975). A search in Cambridge Structural Database (version 5.31) for such compounds retrieved zero hits. With a purpose to study hitherto unexplored structures of these compounds, we here report the synthesis and structural investigations on, 5-benzyl-(7E)-7-(2-chlorobenzylidene)-3-(2-chlorophenyl)-2-phenyl- 3,3a,4,5,6,7-hexahydro-2H-pyrazolo[4,3-c]pyridine, (I).

The structure of (I) with adopted atomic numbering scheme is shown in Fig 1. (I) is a racemic mixture. In the reported model, the stereogenic centers C3 and C3A possess *R*-configurations. The five-membered dihydropyrazole ring (N1/N2/C3/C3A/C7A) adopt an envelope conformation with atom C3 at the flap of the envelope (Ring puckering parameters are: $q_2 = 0.204$ (2) Å, $\varphi_2 = 248.3$ (6)°). The adjacent 6-membered piperidine ring (C3A/C4/N5/C6/C7/C7A) assumes a chair conformation which is substantially twisted from ideal geometry. The puckering parameters are as follows: $q_2 = 0.189$ (2) Å, $q_3 = -0.468$ (2) Å, $\theta = 158.0$ (2)°, $\varphi = 209.5$ (8)°, and total puckering amplitude, $Q = 0.505$ (2) Å.

Two short intra-molecular contacts C3—H3···Cl1 and C27—H27···Cl2 were observed (Table 1). Intermolecular C—Halogen··· π contact stabilizes the dimeric units in (I) (Fig 2). A dimer is formed by C29—Cl2···Cg5ⁱ [symmetry code (i): 1 - x, 1 - y, 1 - z]. The Cl2..Cg5 distance and C29—Cl2···Cg5 angle are 3.778 (2)Å and 141.2 (1)° respectively, whereas the minimum atomic distance in Cl2··· π is 3.366 (4) Å. Cg5 is the centroid of (C21—C26) ring. The C—Halogen··· π dimeric interactions [also referred as PHD; π -halogen-dimer interactions (Noman *et al.* 2004)] have been shown recently, to play an important role in host–guest chemistry (Nagaraj *et al.*, 2005; references therein).

Experimental

1-benzyl-3, 5-dibenzylidenepiperidin-4-one (0.003 mol) and phenyl hydrazine (0.003 mol) were dissolved in 2-propanol. The reaction mixture was refluxed for 1–2 h on a water bath and tested with TLC at regular intervals for completeness of reaction. Following that, the resulting mixture was cooled and poured into crushed ice. The solid so obtained was separated, washed with water and subjected to column chromatography using ethyl acetate and n-hexane. Final yield 89%, m.p. 153–155° C. Suitable single crystals for data collection were grown from ethanol and tetrahydrofuran mixture in 1:1 ratio.

Refinement

H atoms were placed in their stereochemically expected positions and refined with the riding options. The distances with hydrogen atoms are: C(aromatic/*sp*²)—H = 0.93 Å, C(methylene)—H = 0.97 Å, C(methine)—H = 0.98 Å, and $U_{iso} = 1.2 U_{eq}(\text{parent atom})$.

Figures

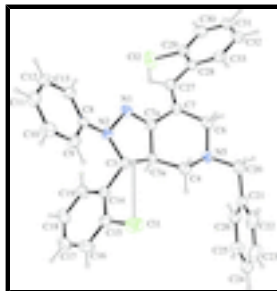


Fig. 1. A view of (I) with non-H atoms shown as probability ellipsoids at 30% levels (Farrugia, 1997). The radii of H atoms are on an arbitrary scale. Dashed lines indicate short intramolecular C—H...Cl contacts.

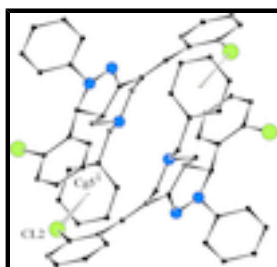


Fig. 2. Dimeric subunits linked by C—Halogen... π interaction in (I). Cg5 is the centroid of (C21—C26) ring.

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Crystal data

$C_{32}H_{27}Cl_2N_3$

$M_r = 524.47$

Monoclinic, $P2_1/c$

Hall symbol: -P 2ybc

$a = 13.7117$ (7) Å

$b = 15.4451$ (6) Å

$c = 13.6896$ (9) Å

$\beta = 113.135$ (7)°

$V = 2666.0$ (2) Å³

$Z = 4$

$F(000) = 1096$

$D_x = 1.307$ Mg m⁻³

Melting point: 427(2) K

Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å

Cell parameters from 2998 reflections

$\theta = 2.6$ – 29.1 °

$\mu = 0.27$ mm⁻¹

$T = 294$ K

Plate, colorless

$0.36 \times 0.26 \times 0.22$ mm

Data collection

Oxford Diffraction Xcalibur Eos Gemini diffractometer

Radiation source: Enhance (Mo) X-ray Source graphite

Detector resolution: 16.3291 pixels mm⁻¹

ω scan

Absorption correction: multi-scan (*Crys.Alis PRO*; Oxford Diffraction, 2009)

$T_{\min} = 0.909$, $T_{\max} = 0.943$

11774 measured reflections

5436 independent reflections

2483 reflections with $I > 2\sigma(I)$

$R_{\text{int}} = 0.049$

$\theta_{\max} = 26.4$ °, $\theta_{\min} = 2.6$ °

$h = -14 \rightarrow 17$

$k = -19 \rightarrow 17$

$l = -15 \rightarrow 17$

Refinement

| | |
|---------------------------------|--|
| Refinement on F^2 | Primary atom site location: structure-invariant direct methods |
| Least-squares matrix: full | Secondary atom site location: difference Fourier map |
| $R[F^2 > 2\sigma(F^2)] = 0.049$ | Hydrogen site location: inferred from neighbouring sites |
| $wR(F^2) = 0.098$ | H-atom parameters constrained |
| $S = 0.83$ | $w = 1/[\sigma^2(F_o^2) + (0.0389P)^2]$ |
| 5436 reflections | where $P = (F_o^2 + 2F_c^2)/3$ |
| 334 parameters | $(\Delta/\sigma)_{\max} < 0.001$ |
| 0 restraints | $\Delta\rho_{\max} = 0.17 \text{ e } \text{\AA}^{-3}$ |
| | $\Delta\rho_{\min} = -0.23 \text{ e } \text{\AA}^{-3}$ |

Special details

Experimental. *CrysAlis PRO*, Oxford Diffraction Ltd., Version 1.171.33.55 (release 05-01-2010 CrysAlis171.NET) Empirical absorption correction using spherical harmonics, implemented in SCALE3 ABSPACK scaling algorithm.

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 (\AA^2)

| | x | y | z | $U_{\text{iso}}^*/U_{\text{eq}}$ |
|-----|--------------|--------------|--------------|----------------------------------|
| C3 | 0.68994 (17) | 0.48100 (13) | 0.39914 (17) | 0.0384 (6) |
| H3 | 0.7343 | 0.4316 | 0.3979 | 0.046* |
| C3A | 0.60177 (16) | 0.44975 (13) | 0.43353 (18) | 0.0372 (6) |
| H3A | 0.5847 | 0.4958 | 0.4735 | 0.045* |
| C4 | 0.62227 (17) | 0.36610 (14) | 0.49646 (19) | 0.0466 (7) |
| H4A | 0.6489 | 0.3225 | 0.4623 | 0.056* |
| H4B | 0.6753 | 0.3756 | 0.5675 | 0.056* |
| C6 | 0.44171 (18) | 0.31461 (13) | 0.39584 (19) | 0.0483 (7) |
| H6A | 0.3770 | 0.2970 | 0.4031 | 0.058* |
| H6B | 0.4665 | 0.2659 | 0.3671 | 0.058* |
| C7 | 0.41706 (18) | 0.38915 (13) | 0.31845 (19) | 0.0399 (6) |
| C7A | 0.51168 (17) | 0.43857 (14) | 0.32849 (19) | 0.0396 (6) |
| C8 | 0.67598 (17) | 0.52120 (13) | 0.21565 (19) | 0.0372 (6) |
| C9 | 0.78552 (18) | 0.51570 (14) | 0.24683 (19) | 0.0440 (6) |
| H9 | 0.8286 | 0.5028 | 0.3170 | 0.053* |
| C10 | 0.8300 (2) | 0.52943 (15) | 0.1736 (2) | 0.0538 (7) |

supplementary materials

| | | | | |
|------|--------------|--------------|--------------|-------------|
| H10 | 0.9033 | 0.5261 | 0.1954 | 0.065* |
| C11 | 0.7685 (2) | 0.54792 (15) | 0.0691 (2) | 0.0565 (7) |
| H11 | 0.7992 | 0.5561 | 0.0202 | 0.068* |
| C12 | 0.6598 (2) | 0.55403 (15) | 0.0385 (2) | 0.0563 (7) |
| H12 | 0.6173 | 0.5671 | -0.0317 | 0.068* |
| C13 | 0.61374 (19) | 0.54113 (14) | 0.1102 (2) | 0.0491 (7) |
| H13 | 0.5406 | 0.5458 | 0.0882 | 0.059* |
| C14 | 0.75983 (17) | 0.55254 (13) | 0.46627 (18) | 0.0371 (6) |
| C15 | 0.86179 (18) | 0.53885 (15) | 0.54037 (19) | 0.0496 (7) |
| C16 | 0.9251 (2) | 0.60585 (19) | 0.5984 (2) | 0.0626 (8) |
| H16 | 0.9935 | 0.5946 | 0.6474 | 0.075* |
| C17 | 0.8869 (2) | 0.68811 (19) | 0.5834 (2) | 0.0629 (8) |
| H17 | 0.9297 | 0.7336 | 0.6211 | 0.075* |
| C18 | 0.7853 (2) | 0.70400 (16) | 0.5126 (2) | 0.0603 (8) |
| H18 | 0.7584 | 0.7601 | 0.5038 | 0.072* |
| C19 | 0.72281 (19) | 0.63714 (15) | 0.4546 (2) | 0.0494 (7) |
| H19 | 0.6542 | 0.6489 | 0.4064 | 0.059* |
| C20 | 0.5425 (2) | 0.25732 (14) | 0.5690 (2) | 0.0565 (7) |
| H20A | 0.5710 | 0.2125 | 0.5381 | 0.068* |
| H20B | 0.4757 | 0.2366 | 0.5688 | 0.068* |
| C21 | 0.6183 (2) | 0.27240 (15) | 0.6818 (2) | 0.0503 (7) |
| C22 | 0.7124 (2) | 0.22752 (18) | 0.7258 (3) | 0.0785 (10) |
| H22 | 0.7295 | 0.1863 | 0.6855 | 0.094* |
| C23 | 0.7823 (3) | 0.2434 (2) | 0.8303 (4) | 0.0997 (14) |
| H23 | 0.8460 | 0.2132 | 0.8594 | 0.120* |
| C24 | 0.7569 (3) | 0.3035 (2) | 0.8899 (3) | 0.0999 (14) |
| H24 | 0.8035 | 0.3141 | 0.9596 | 0.120* |
| C25 | 0.6636 (3) | 0.34798 (18) | 0.8477 (2) | 0.0777 (9) |
| H25 | 0.6462 | 0.3886 | 0.8884 | 0.093* |
| C26 | 0.5955 (2) | 0.33212 (16) | 0.7442 (2) | 0.0601 (8) |
| H26 | 0.5322 | 0.3628 | 0.7156 | 0.072* |
| C27 | 0.32178 (17) | 0.41049 (14) | 0.2455 (2) | 0.0456 (6) |
| H27 | 0.3200 | 0.4618 | 0.2092 | 0.055* |
| C28 | 0.21940 (17) | 0.36564 (15) | 0.21350 (18) | 0.0413 (6) |
| C29 | 0.12329 (18) | 0.41044 (14) | 0.1697 (2) | 0.0454 (6) |
| C30 | 0.02629 (18) | 0.36958 (16) | 0.1313 (2) | 0.0552 (7) |
| H30 | -0.0359 | 0.4017 | 0.1019 | 0.066* |
| C31 | 0.0221 (2) | 0.28080 (17) | 0.1368 (2) | 0.0593 (8) |
| H31 | -0.0429 | 0.2524 | 0.1113 | 0.071* |
| C32 | 0.1142 (2) | 0.23457 (15) | 0.1800 (2) | 0.0570 (8) |
| H32 | 0.1115 | 0.1746 | 0.1845 | 0.068* |
| C33 | 0.21102 (19) | 0.27578 (15) | 0.21688 (19) | 0.0507 (7) |
| H33 | 0.2726 | 0.2428 | 0.2448 | 0.061* |
| N1 | 0.52729 (14) | 0.47054 (11) | 0.24903 (16) | 0.0431 (5) |
| N2 | 0.62818 (14) | 0.51001 (11) | 0.28892 (15) | 0.0403 (5) |
| N5 | 0.52271 (14) | 0.33591 (11) | 0.50228 (15) | 0.0428 (5) |
| Cl1 | 0.91528 (6) | 0.43491 (4) | 0.56217 (7) | 0.0870 (3) |
| Cl2 | 0.12374 (5) | 0.52302 (4) | 0.16351 (7) | 0.0764 (3) |

Atomic displacement parameters (Å²)

| | U^{11} | U^{22} | U^{33} | U^{12} | U^{13} | U^{23} |
|-----|-------------|-------------|-------------|--------------|-------------|--------------|
| C3 | 0.0318 (12) | 0.0456 (13) | 0.0375 (14) | 0.0018 (11) | 0.0133 (12) | 0.0007 (12) |
| C3A | 0.0334 (13) | 0.0410 (14) | 0.0401 (14) | -0.0001 (10) | 0.0174 (12) | -0.0006 (12) |
| C4 | 0.0388 (14) | 0.0504 (15) | 0.0494 (16) | -0.0005 (11) | 0.0161 (14) | 0.0036 (13) |
| C6 | 0.0433 (15) | 0.0498 (15) | 0.0512 (17) | -0.0036 (12) | 0.0179 (14) | -0.0057 (13) |
| C7 | 0.0361 (14) | 0.0483 (14) | 0.0384 (15) | -0.0021 (11) | 0.0179 (13) | -0.0016 (12) |
| C7A | 0.0332 (14) | 0.0460 (14) | 0.0429 (16) | 0.0006 (11) | 0.0187 (13) | 0.0023 (12) |
| C8 | 0.0335 (14) | 0.0410 (13) | 0.0380 (14) | -0.0044 (11) | 0.0152 (13) | -0.0030 (12) |
| C9 | 0.0394 (15) | 0.0571 (15) | 0.0380 (15) | 0.0010 (12) | 0.0180 (13) | -0.0014 (12) |
| C10 | 0.0424 (15) | 0.0719 (17) | 0.0555 (18) | -0.0033 (13) | 0.0281 (16) | -0.0068 (15) |
| C11 | 0.0635 (19) | 0.0644 (17) | 0.0556 (19) | -0.0102 (14) | 0.0384 (17) | -0.0052 (15) |
| C12 | 0.0599 (19) | 0.0697 (17) | 0.0403 (16) | -0.0072 (14) | 0.0208 (16) | 0.0048 (14) |
| C13 | 0.0379 (14) | 0.0639 (17) | 0.0440 (16) | -0.0046 (12) | 0.0143 (14) | 0.0015 (14) |
| C14 | 0.0351 (13) | 0.0438 (14) | 0.0352 (14) | -0.0031 (11) | 0.0167 (12) | -0.0005 (12) |
| C15 | 0.0405 (14) | 0.0607 (16) | 0.0414 (15) | -0.0023 (13) | 0.0095 (14) | -0.0021 (13) |
| C16 | 0.0460 (16) | 0.084 (2) | 0.0463 (18) | -0.0079 (16) | 0.0063 (15) | -0.0097 (16) |
| C17 | 0.063 (2) | 0.074 (2) | 0.0553 (19) | -0.0245 (16) | 0.0269 (17) | -0.0207 (16) |
| C18 | 0.070 (2) | 0.0479 (15) | 0.072 (2) | -0.0065 (14) | 0.0376 (19) | -0.0086 (15) |
| C19 | 0.0418 (15) | 0.0516 (16) | 0.0548 (17) | 0.0009 (13) | 0.0187 (14) | -0.0034 (14) |
| C20 | 0.0609 (17) | 0.0449 (15) | 0.0643 (19) | -0.0002 (13) | 0.0252 (17) | 0.0074 (14) |
| C21 | 0.0457 (16) | 0.0430 (15) | 0.0597 (19) | 0.0010 (13) | 0.0179 (16) | 0.0206 (15) |
| C22 | 0.063 (2) | 0.0688 (19) | 0.102 (3) | 0.0148 (16) | 0.031 (2) | 0.037 (2) |
| C23 | 0.051 (2) | 0.090 (3) | 0.130 (4) | 0.010 (2) | 0.007 (3) | 0.064 (3) |
| C24 | 0.073 (3) | 0.095 (3) | 0.090 (3) | -0.032 (2) | -0.013 (2) | 0.049 (2) |
| C25 | 0.083 (2) | 0.077 (2) | 0.057 (2) | -0.0231 (18) | 0.010 (2) | 0.0085 (18) |
| C26 | 0.0543 (18) | 0.0576 (17) | 0.0574 (19) | -0.0043 (14) | 0.0100 (17) | 0.0125 (16) |
| C27 | 0.0397 (15) | 0.0499 (14) | 0.0486 (17) | -0.0030 (12) | 0.0189 (14) | 0.0001 (13) |
| C28 | 0.0369 (14) | 0.0516 (15) | 0.0361 (15) | -0.0030 (12) | 0.0152 (13) | -0.0033 (12) |
| C29 | 0.0399 (15) | 0.0487 (14) | 0.0493 (16) | -0.0047 (12) | 0.0193 (14) | 0.0013 (13) |
| C30 | 0.0377 (15) | 0.0598 (17) | 0.0600 (19) | 0.0001 (12) | 0.0104 (15) | 0.0037 (15) |
| C31 | 0.0448 (16) | 0.0624 (18) | 0.0586 (19) | -0.0144 (14) | 0.0072 (16) | -0.0048 (15) |
| C32 | 0.0527 (17) | 0.0477 (15) | 0.0564 (18) | -0.0077 (13) | 0.0060 (16) | -0.0058 (14) |
| C33 | 0.0448 (16) | 0.0528 (16) | 0.0465 (16) | -0.0005 (12) | 0.0093 (14) | -0.0077 (13) |
| N1 | 0.0299 (11) | 0.0542 (12) | 0.0451 (13) | -0.0051 (9) | 0.0145 (11) | -0.0001 (11) |
| N2 | 0.0287 (11) | 0.0570 (12) | 0.0350 (12) | -0.0049 (9) | 0.0124 (10) | 0.0001 (10) |
| N5 | 0.0400 (12) | 0.0443 (11) | 0.0434 (12) | -0.0051 (9) | 0.0156 (11) | 0.0044 (10) |
| Cl1 | 0.0653 (5) | 0.0766 (5) | 0.0839 (6) | 0.0217 (4) | -0.0087 (5) | 0.0038 (4) |
| Cl2 | 0.0549 (4) | 0.0535 (4) | 0.1194 (7) | 0.0007 (3) | 0.0327 (5) | 0.0127 (4) |

Geometric parameters (Å, °)

| | | | |
|---------|-----------|---------|-----------|
| C3—N2 | 1.480 (3) | C17—C18 | 1.372 (3) |
| C3—C14 | 1.514 (3) | C17—H17 | 0.9300 |
| C3—C3A | 1.537 (3) | C18—C19 | 1.377 (3) |
| C3—H3 | 0.9800 | C18—H18 | 0.9300 |
| C3A—C7A | 1.493 (3) | C19—H19 | 0.9300 |

supplementary materials

| | | | |
|-------------|-------------|---------------|-------------|
| C3A—C4 | 1.517 (3) | C20—N5 | 1.478 (3) |
| C3A—H3A | 0.9800 | C20—C21 | 1.503 (3) |
| C4—N5 | 1.474 (3) | C20—H20A | 0.9700 |
| C4—H4A | 0.9700 | C20—H20B | 0.9700 |
| C4—H4B | 0.9700 | C21—C26 | 1.373 (3) |
| C6—N5 | 1.481 (3) | C21—C22 | 1.377 (3) |
| C6—C7 | 1.510 (3) | C22—C23 | 1.397 (4) |
| C6—H6A | 0.9700 | C22—H22 | 0.9300 |
| C6—H6B | 0.9700 | C23—C24 | 1.368 (5) |
| C7—C27 | 1.337 (3) | C23—H23 | 0.9300 |
| C7—C7A | 1.464 (3) | C24—C25 | 1.364 (4) |
| C7A—N1 | 1.287 (3) | C24—H24 | 0.9300 |
| C8—C13 | 1.392 (3) | C25—C26 | 1.379 (3) |
| C8—C9 | 1.393 (3) | C25—H25 | 0.9300 |
| C8—N2 | 1.408 (3) | C26—H26 | 0.9300 |
| C9—C10 | 1.379 (3) | C27—C28 | 1.470 (3) |
| C9—H9 | 0.9300 | C27—H27 | 0.9300 |
| C10—C11 | 1.375 (3) | C28—C33 | 1.395 (3) |
| C10—H10 | 0.9300 | C28—C29 | 1.398 (3) |
| C11—C12 | 1.383 (3) | C29—C30 | 1.376 (3) |
| C11—H11 | 0.9300 | C29—C12 | 1.741 (2) |
| C12—C13 | 1.375 (3) | C30—C31 | 1.376 (3) |
| C12—H12 | 0.9300 | C30—H30 | 0.9300 |
| C13—H13 | 0.9300 | C31—C32 | 1.367 (3) |
| C14—C15 | 1.383 (3) | C31—H31 | 0.9300 |
| C14—C19 | 1.388 (3) | C32—C33 | 1.376 (3) |
| C15—C16 | 1.383 (3) | C32—H32 | 0.9300 |
| C15—C11 | 1.741 (2) | C33—H33 | 0.9300 |
| C16—C17 | 1.359 (3) | N1—N2 | 1.411 (2) |
| C16—H16 | 0.9300 | | |
| N2—C3—C14 | 111.73 (17) | C18—C17—H17 | 120.1 |
| N2—C3—C3A | 101.74 (17) | C17—C18—C19 | 120.2 (2) |
| C14—C3—C3A | 115.45 (19) | C17—C18—H18 | 119.9 |
| N2—C3—H3 | 109.2 | C19—C18—H18 | 119.9 |
| C14—C3—H3 | 109.2 | C18—C19—C14 | 121.5 (2) |
| C3A—C3—H3 | 109.2 | C18—C19—H19 | 119.2 |
| C7A—C3A—C4 | 110.32 (17) | C14—C19—H19 | 119.2 |
| C7A—C3A—C3 | 101.19 (18) | N5—C20—C21 | 113.11 (18) |
| C4—C3A—C3 | 116.68 (18) | N5—C20—H20A | 109.0 |
| C7A—C3A—H3A | 109.4 | C21—C20—H20A | 109.0 |
| C4—C3A—H3A | 109.4 | N5—C20—H20B | 109.0 |
| C3—C3A—H3A | 109.4 | C21—C20—H20B | 109.0 |
| N5—C4—C3A | 109.35 (17) | H20A—C20—H20B | 107.8 |
| N5—C4—H4A | 109.8 | C26—C21—C22 | 118.0 (3) |
| C3A—C4—H4A | 109.8 | C26—C21—C20 | 120.6 (2) |
| N5—C4—H4B | 109.8 | C22—C21—C20 | 121.5 (3) |
| C3A—C4—H4B | 109.8 | C21—C22—C23 | 120.5 (3) |
| H4A—C4—H4B | 108.3 | C21—C22—H22 | 119.8 |
| N5—C6—C7 | 113.30 (17) | C23—C22—H22 | 119.8 |

| | | | |
|----------------|--------------|-----------------|-------------|
| N5—C6—H6A | 108.9 | C24—C23—C22 | 119.8 (3) |
| C7—C6—H6A | 108.9 | C24—C23—H23 | 120.1 |
| N5—C6—H6B | 108.9 | C22—C23—H23 | 120.1 |
| C7—C6—H6B | 108.9 | C25—C24—C23 | 120.3 (3) |
| H6A—C6—H6B | 107.7 | C25—C24—H24 | 119.8 |
| C27—C7—C7A | 120.7 (2) | C23—C24—H24 | 119.8 |
| C27—C7—C6 | 126.6 (2) | C24—C25—C26 | 119.3 (3) |
| C7A—C7—C6 | 112.69 (19) | C24—C25—H25 | 120.4 |
| N1—C7A—C7 | 123.8 (2) | C26—C25—H25 | 120.4 |
| N1—C7A—C3A | 114.9 (2) | C21—C26—C25 | 122.1 (3) |
| C7—C7A—C3A | 121.2 (2) | C21—C26—H26 | 119.0 |
| C13—C8—C9 | 118.6 (2) | C25—C26—H26 | 119.0 |
| C13—C8—N2 | 119.9 (2) | C7—C27—C28 | 130.2 (2) |
| C9—C8—N2 | 121.5 (2) | C7—C27—H27 | 114.9 |
| C10—C9—C8 | 120.0 (2) | C28—C27—H27 | 114.9 |
| C10—C9—H9 | 120.0 | C33—C28—C29 | 115.5 (2) |
| C8—C9—H9 | 120.0 | C33—C28—C27 | 122.7 (2) |
| C11—C10—C9 | 121.4 (2) | C29—C28—C27 | 121.6 (2) |
| C11—C10—H10 | 119.3 | C30—C29—C28 | 122.9 (2) |
| C9—C10—H10 | 119.3 | C30—C29—C12 | 117.43 (18) |
| C10—C11—C12 | 118.5 (3) | C28—C29—C12 | 119.63 (17) |
| C10—C11—H11 | 120.7 | C31—C30—C29 | 119.4 (2) |
| C12—C11—H11 | 120.7 | C31—C30—H30 | 120.3 |
| C13—C12—C11 | 121.1 (3) | C29—C30—H30 | 120.3 |
| C13—C12—H12 | 119.5 | C32—C31—C30 | 119.6 (2) |
| C11—C12—H12 | 119.5 | C32—C31—H31 | 120.2 |
| C12—C13—C8 | 120.4 (2) | C30—C31—H31 | 120.2 |
| C12—C13—H13 | 119.8 | C31—C32—C33 | 120.7 (2) |
| C8—C13—H13 | 119.8 | C31—C32—H32 | 119.6 |
| C15—C14—C19 | 116.5 (2) | C33—C32—H32 | 119.6 |
| C15—C14—C3 | 123.4 (2) | C32—C33—C28 | 121.9 (2) |
| C19—C14—C3 | 120.10 (19) | C32—C33—H33 | 119.1 |
| C16—C15—C14 | 122.2 (2) | C28—C33—H33 | 119.1 |
| C16—C15—C11 | 117.7 (2) | C7A—N1—N2 | 107.59 (19) |
| C14—C15—C11 | 120.18 (18) | C8—N2—N1 | 115.95 (18) |
| C17—C16—C15 | 119.7 (2) | C8—N2—C3 | 121.56 (17) |
| C17—C16—H16 | 120.2 | N1—N2—C3 | 110.18 (17) |
| C15—C16—H16 | 120.2 | C4—N5—C20 | 110.11 (18) |
| C16—C17—C18 | 119.9 (2) | C4—N5—C6 | 111.69 (18) |
| C16—C17—H17 | 120.1 | C20—N5—C6 | 108.06 (17) |
| N2—C3—C3A—C7A | 18.3 (2) | C26—C21—C22—C23 | -0.6 (4) |
| C14—C3—C3A—C7A | 139.43 (18) | C20—C21—C22—C23 | 179.1 (2) |
| N2—C3—C3A—C4 | 137.96 (19) | C21—C22—C23—C24 | 0.5 (5) |
| C14—C3—C3A—C4 | -100.9 (2) | C22—C23—C24—C25 | 0.0 (5) |
| C7A—C3A—C4—N5 | -52.9 (2) | C23—C24—C25—C26 | -0.4 (5) |
| C3—C3A—C4—N5 | -167.63 (18) | C22—C21—C26—C25 | 0.2 (4) |
| N5—C6—C7—C27 | -141.8 (2) | C20—C21—C26—C25 | -179.5 (2) |
| N5—C6—C7—C7A | 39.4 (3) | C24—C25—C26—C21 | 0.3 (4) |
| C27—C7—C7A—N1 | -36.8 (3) | C7A—C7—C27—C28 | 172.6 (2) |

supplementary materials

| | | | |
|-----------------|-------------|-----------------|--------------|
| C6—C7—C7A—N1 | 142.1 (2) | C6—C7—C27—C28 | -6.1 (4) |
| C27—C7—C7A—C3A | 147.8 (2) | C7—C27—C28—C33 | -31.2 (4) |
| C6—C7—C7A—C3A | -33.3 (3) | C7—C27—C28—C29 | 153.8 (3) |
| C4—C3A—C7A—N1 | -135.4 (2) | C33—C28—C29—C30 | -0.6 (4) |
| C3—C3A—C7A—N1 | -11.3 (2) | C27—C28—C29—C30 | 174.7 (2) |
| C4—C3A—C7A—C7 | 40.4 (3) | C33—C28—C29—C12 | 178.85 (18) |
| C3—C3A—C7A—C7 | 164.53 (19) | C27—C28—C29—C12 | -5.9 (3) |
| C13—C8—C9—C10 | -0.4 (3) | C28—C29—C30—C31 | 0.9 (4) |
| N2—C8—C9—C10 | -178.2 (2) | C12—C29—C30—C31 | -178.6 (2) |
| C8—C9—C10—C11 | -0.6 (4) | C29—C30—C31—C32 | -0.2 (4) |
| C9—C10—C11—C12 | 1.1 (4) | C30—C31—C32—C33 | -0.8 (4) |
| C10—C11—C12—C13 | -0.6 (4) | C31—C32—C33—C28 | 1.1 (4) |
| C11—C12—C13—C8 | -0.3 (4) | C29—C28—C33—C32 | -0.4 (4) |
| C9—C8—C13—C12 | 0.8 (3) | C27—C28—C33—C32 | -175.6 (2) |
| N2—C8—C13—C12 | 178.6 (2) | C7—C7A—N1—N2 | -177.40 (19) |
| N2—C3—C14—C15 | -140.5 (2) | C3A—C7A—N1—N2 | -1.7 (3) |
| C3A—C3—C14—C15 | 103.9 (3) | C13—C8—N2—N1 | 35.8 (3) |
| N2—C3—C14—C19 | 39.0 (3) | C9—C8—N2—N1 | -146.42 (19) |
| C3A—C3—C14—C19 | -76.6 (3) | C13—C8—N2—C3 | 174.33 (19) |
| C19—C14—C15—C16 | -1.5 (4) | C9—C8—N2—C3 | -7.9 (3) |
| C3—C14—C15—C16 | 178.0 (2) | C7A—N1—N2—C8 | 158.2 (2) |
| C19—C14—C15—C11 | 179.33 (19) | C7A—N1—N2—C3 | 15.1 (2) |
| C3—C14—C15—C11 | -1.2 (3) | C14—C3—N2—C8 | 74.5 (2) |
| C14—C15—C16—C17 | 0.3 (4) | C3A—C3—N2—C8 | -161.78 (18) |
| C11—C15—C16—C17 | 179.5 (2) | C14—C3—N2—N1 | -144.89 (18) |
| C15—C16—C17—C18 | 1.3 (4) | C3A—C3—N2—N1 | -21.2 (2) |
| C16—C17—C18—C19 | -1.8 (4) | C3A—C4—N5—C20 | -176.51 (18) |
| C17—C18—C19—C14 | 0.6 (4) | C3A—C4—N5—C6 | 63.4 (2) |
| C15—C14—C19—C18 | 1.1 (4) | C21—C20—N5—C4 | 61.7 (3) |
| C3—C14—C19—C18 | -178.5 (2) | C21—C20—N5—C6 | -176.1 (2) |
| N5—C20—C21—C26 | 59.8 (3) | C7—C6—N5—C4 | -56.7 (2) |
| N5—C20—C21—C22 | -119.9 (2) | C7—C6—N5—C20 | -178.0 (2) |

Hydrogen-bond geometry (\AA , $^\circ$)

| <i>D</i> —H \cdots <i>A</i> | <i>D</i> —H | H \cdots <i>A</i> | <i>D</i> \cdots <i>A</i> | <i>D</i> —H \cdots <i>A</i> |
|-------------------------------|-------------|---------------------|----------------------------|-------------------------------|
| C3—H3 \cdots C11 | 0.98 | 2.61 | 3.101 (2) | 111 |
| C27—H27 \cdots C12 | 0.93 | 2.68 | 3.043 (3) | 104 |

Fig. 1

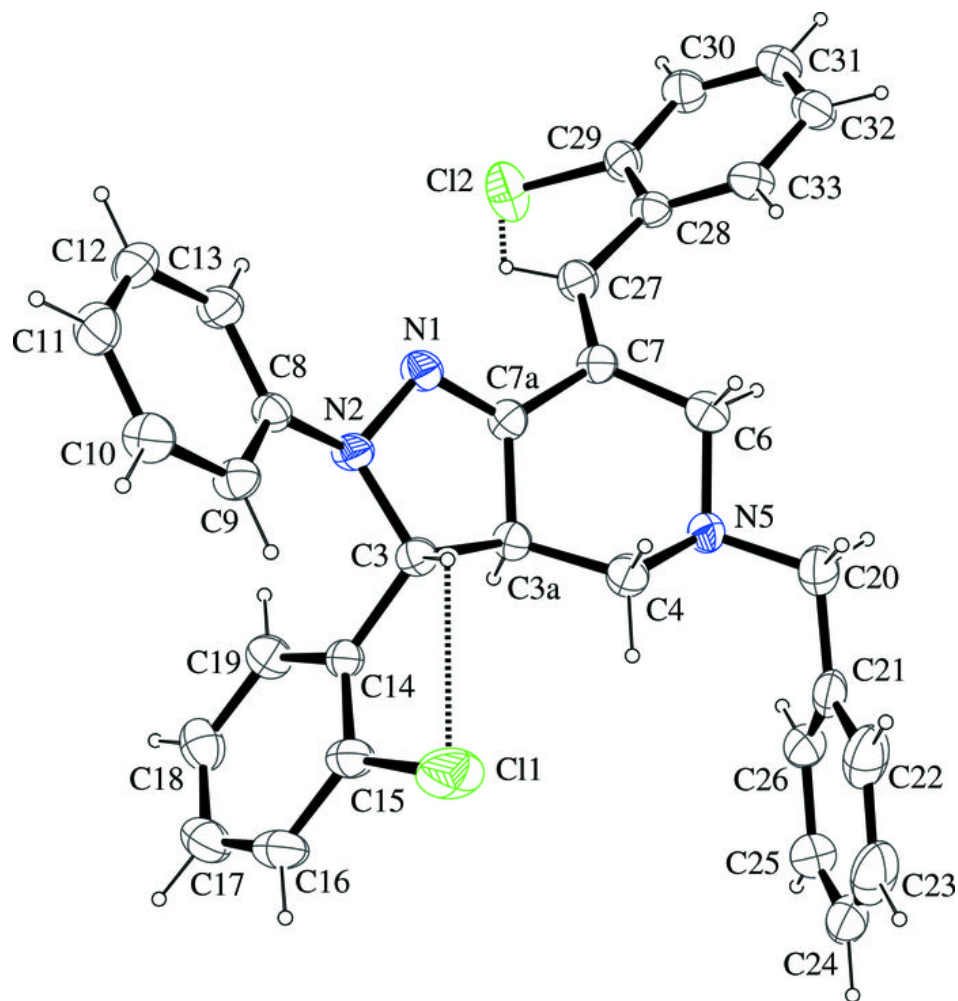
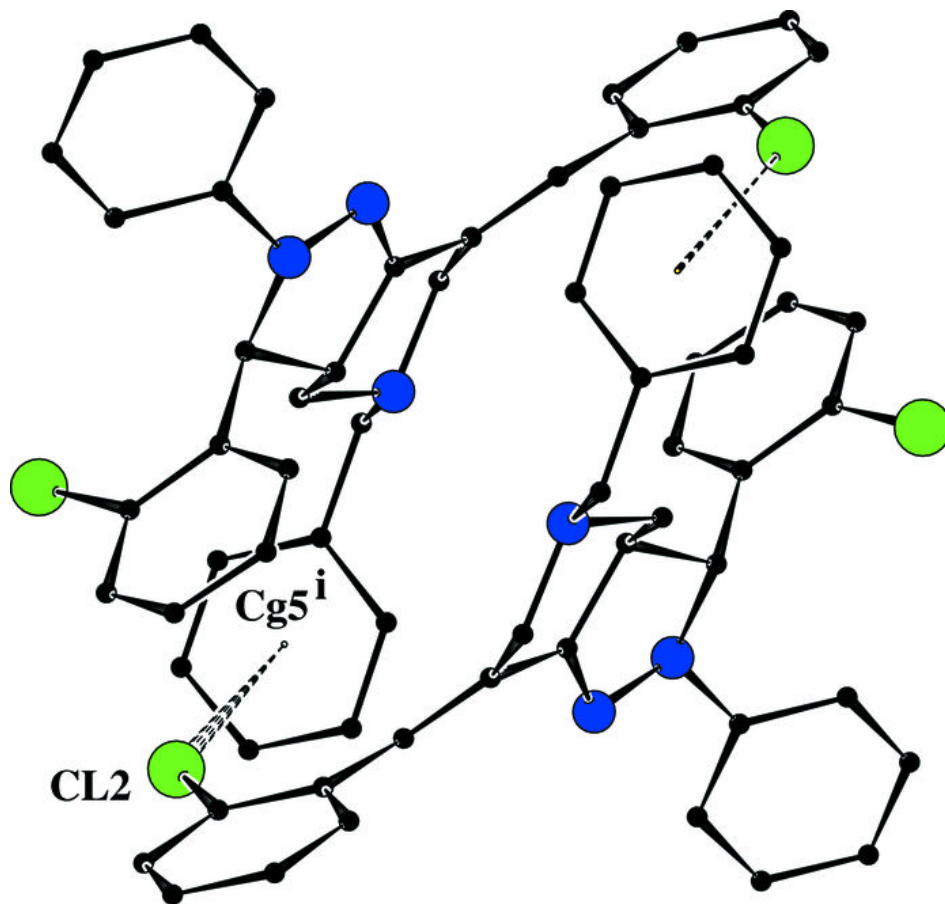


Fig. 2



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