organic compounds

2,4-Dichloro-6-methoxyquinoline

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The title compound, $C_{10}H_7Cl_2NO$, features a planar molecule, excluding the methyl H atoms [maximum deviation = 0.0385 (1) Å]. The crystal packing is stabilized by π–π stacking interactions across inversion centres [centroid-to-centroid distance = 3.736 (3) Å].

Related literature

For general background, see: Fournet *et al.* (1981) and references cited therein; Towers *et al.* (1981); Biavatti *et al.* (2002); McCormick *et al.* (1996); Ziegler & Gelfert, (1959). For related crystal structures, see: Somvanshi *et al.* (2008).
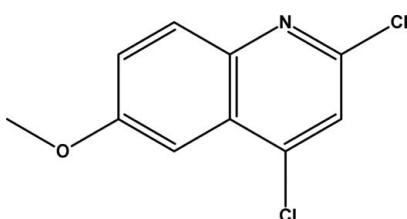
Experimental

Crystal data

$C_{10}H_7Cl_2NO$	γ = 104.150 (14)°
M_r = 228.07	V = 482.5 (3) Å³
Triclinic, $P\bar{1}$	Z = 2
a = 7.431 (2) Å	Mo $K\alpha$ radiation
b = 8.889 (2) Å	μ = 0.63 mm⁻¹
c = 9.083 (4) Å	T = 290 (2) K
α = 116.660 (19)°	0.25 × 0.18 × 0.15 mm
β = 102.301 (2)°	

Data collection

Bruker SMART CCD area-detector diffractometer	5720 measured reflections
Absorption correction: multi-scan (*SADABS*; Sheldrick, 1996)	1782 independent reflections
	1272 reflections with $I > 2\sigma(I)$
T_{min} = 0.811, T_{max} = 0.909	R_{int} = 0.054

Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.065	128 parameters
$wR(F^2)$ = 0.197	H-atom parameters constrained
S = 1.15	$\Delta\rho_{max}$ = 0.38 e Å⁻³
1782 reflections	$\Delta\rho_{min}$ = −0.64 e Å⁻³

Data collection: *SMART* (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: *ORTEP-3* (Farrugia, 1999) and *CAMERON* (Watkin *et al.*, 1993); software used to prepare material for publication: *PLATON* (Spek, 2003).

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supporting information

2,4-Dichloro-6-methoxyquinoline

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S1. Comment

A wide range of medicinal properties have already been identified in compounds containing the quinoline ring system including antiprotozoal (Fournet *et al.*, 1981), antibacterial (Towers *et al.*, 1981), antifungal (Biavatti *et al.*, 2002) and antiviral activities (McCormick *et al.*, 1996). Reaction of aniline with malonic acid in an excess of phosphorus oxychloride at reflux to give 2,4-dichloroquinoline was first reported by Ziegler & Gelfert (1959). A similar derivative of quinoline was synthesized from the mixture of *p*-toluidine and malonic acid in a one-pot reaction from an aryl amine, malonic acid and phosphorous oxychloride and its cytotoxicity has been reported (Somvanshi & Subashini *et al.*, 2008). In continuous of our work, crystal structure of another derivative is reported in this paper.

The crystal packing is stabilized by intermolecular π–π [$Cg1\cdots Cg1$ and $Cg2\cdots Cg2$] stacking interactions with shortest perpendicular distances between isochinoline groups of 3.470 Å and 3.497 Å, the slippages between these ring systems are 1.283 Å and 1.178 Å, the distances between the centroids of the six-membered carbon rings are 3.700 (3) Å and 3.690 (3) Å with the symmetry code (2 - *x*, -*y*, 1 - *z*) and (1 - *x*, -*y*, 1 - *z*), respectively. Further, another intermolecular π–π [$Cg1\cdots Cg2$] stacking interactions with a shortest perpendicular distance of 3.476 Å between the two rings and the distance between the centroids of the six-membered carbon rings is 3.736 (3) Å with the symmetry code (2 - *x*, -*y*, -*z*). $Cg1$ and $Cg2$ are the centroids of N1—C1—C2—C3—C4—C8—C9 ring and C4–C9 ring respectively.

S2. Experimental

p-Anisidine (10 mmol) and malonic acid (15 mmol) were heated under reflux in phosphorus oxychloride (20 ml), with stirring, for 5 h. The mixture was cooled, poured into crushed ice with vigorous stirring and then made alkaline with 5 *M* sodium hydroxide. Filtration gave the crude product as a brown solid. A Column chromatography (95:5 hexane–EtOAc) yielded the pure dichloroquinoline as off-white needles

S3. Refinement

All the H atoms were positioned geometrically and refined using a riding model [C—H = 0.97 Å and U_{iso}(H) = 1.5U_{eq}(C) for methyl and C—H = 0.93 Å and U_{iso}(H) = 1.2U_{eq}(C) for all other H atoms.
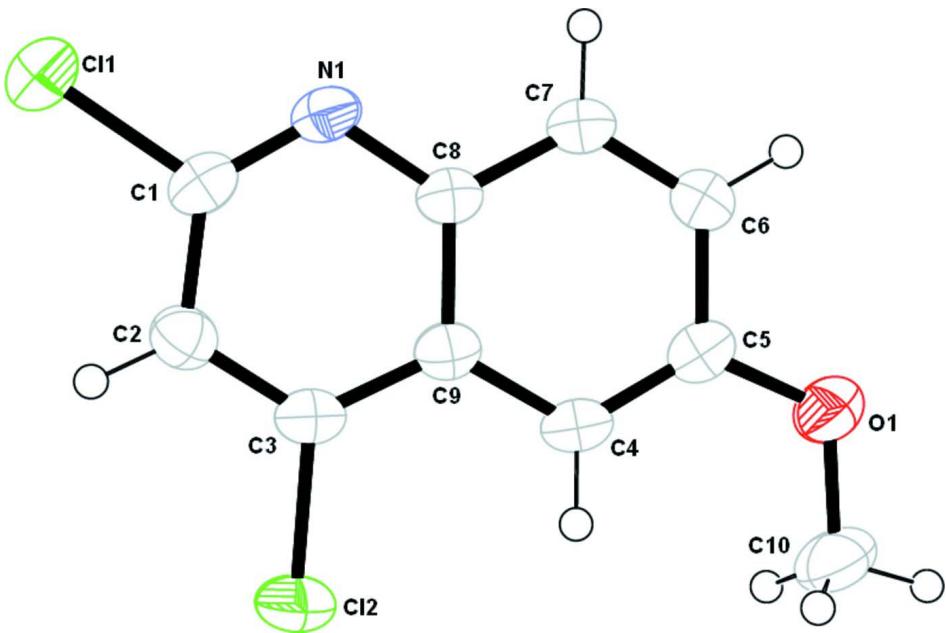
Figure 1
ORTEP diagram of the title compound with 50% probability displacement ellipsoids.
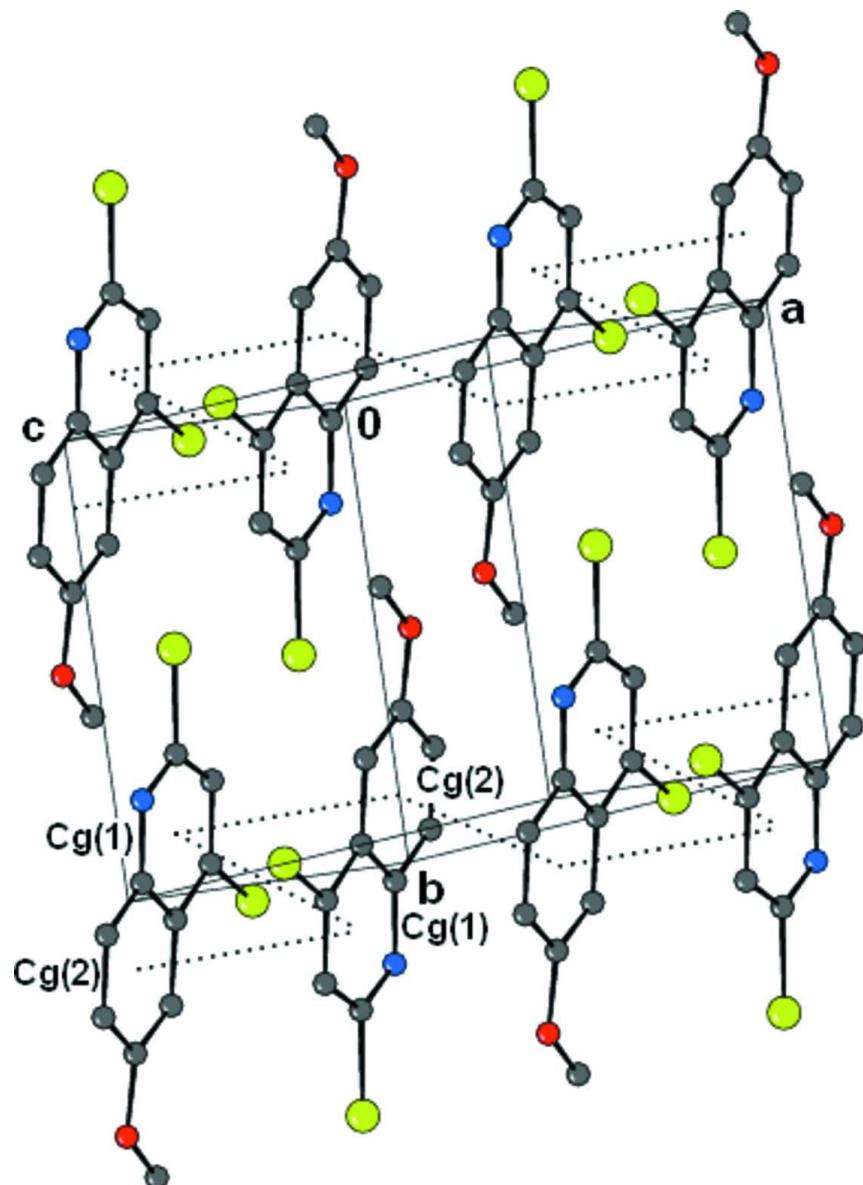
Figure 2

The crystal packing diagram of the title compound. The dotted lines indicate π–π interactions. All H atoms have been omitted for clarity.

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Crystal data

$C_{10}H_7Cl_2NO$	$\gamma = 104.150\ (14)°$
$M_r = 228.07$	$V = 482.5\ (3)\ Å^3$
Triclinic, $P\overline{1}$	$Z = 2$
Hall symbol: -P 1	$F(000) = 232$
$a = 7.431\ (2)\ Å$	$D_x = 1.570\ Mg\ m^{-3}$
$b = 8.889\ (2)\ Å$	Mo $K\alpha$ radiation, $\lambda = 0.71073\ Å$
$c = 9.083\ (4)\ Å$	Cell parameters from 856 reflections
$\alpha = 116.660\ (19)°$	$\theta = 1.9$–$20.7°$
$\beta = 102.301\ (2)°$	$\mu = 0.63\ mm^{-1}$

T = 290 K

Block, colourless

$0.25 \times 0.18 \times 0.15$ mm

Data collection

Bruker SMART CCD area-detector diffractometer	5720 measured reflections
Radiation source: fine-focus sealed tube	1782 independent reflections
Graphite monochromator	1272 reflections with $I > 2\sigma(I)$
φ and ω scans	R_{int} = 0.054
Absorption correction: multi-scan (*SADABS*; Sheldrick, 1996)	θ_{max} = 25.5°, θ_{min} = 2.7°
	$h = -5 \rightarrow 8$
	$k = -10 \rightarrow 10$
T_{min} = 0.811, T_{max} = 0.909	$l = -11 \rightarrow 11$

Refinement

Refinement on F^2	Secondary atom site location: difference Fourier map
Least-squares matrix: full	
$R[F^2 > 2\sigma(F^2)]$ = 0.065	Hydrogen site location: inferred from neighbouring sites
$wR(F^2)$ = 0.197	
S = 1.15	H-atom parameters constrained
1782 reflections	$w = 1/[\sigma^2(F_o^2) + (0.0844P)^2 + 0.6982P]$ where $P = (F_o^2 + 2F_c^2)/3$
128 parameters	
0 restraints	$(\Delta/\sigma)_{max} < 0.001$
Primary atom site location: structure-invariant direct methods	$\Delta\rho_{max}$ = 0.38 e Å^{-3}
	$\Delta\rho_{min}$ = −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}
Cl1	0.3126 (2)	1.55448 (15)	0.76004 (16)	0.0555 (4)
Cl2	0.2701 (2)	0.98994 (16)	0.84707 (16)	0.0592 (5)
N1	0.2689 (5)	1.2373 (5)	0.5081 (5)	0.0400 (9)
O1	0.2020 (5)	0.5198 (4)	0.1887 (4)	0.0517 (8)
C1	0.2837 (6)	1.3262 (5)	0.6714 (6)	0.0383 (10)
C2	0.2849 (6)	1.2594 (5)	0.7862 (5)	0.0382 (9)
H2	0.2972	1.3312	0.9031	0.046*
C3	0.2666 (6)	1.0805 (6)	0.7130 (5)	0.0378 (9)
C4	0.2323 (6)	0.7880 (5)	0.4545 (6)	0.0380 (9)
H4	0.2318	0.7305	0.5184	0.046*
C5	0.2168 (6)	0.6950 (5)	0.2814 (6)	0.0392 (10)
C6	0.2134 (7)	0.7815 (6)	0.1824 (6)	0.0422 (10)
H6	0.1994	0.7169	0.0641	0.051*
C7	0.2302 (7)	0.9572 (6)	0.2591 (6)	0.0421 (10)

H7	0.2294	1.0119	0.1926	0.051*
C8	0.2489 (6)	1.0586 (5)	0.4363 (5)	0.0350 (9)
C9	0.2491 (6)	0.9716 (5)	0.5361 (5)	0.0344 (9)
C10	0.2067 (8)	0.4245 (7)	0.2807 (7)	0.0573 (13)
H10A	0.3330	0.4855	0.3778	0.086*
H10B	0.1897	0.3014	0.2006	0.086*
H10C	0.1007	0.4228	0.3254	0.086*

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Cl1	0.0789 (9)	0.0407 (6)	0.0592 (8)	0.0310 (6)	0.0316 (6)	0.0293 (6)
Cl2	0.0927 (11)	0.0533 (7)	0.0488 (7)	0.0298 (7)	0.0288 (6)	0.0383 (6)
N1	0.049 (2)	0.0396 (19)	0.046 (2)	0.0226 (17)	0.0195 (17)	0.0300 (17)
O1	0.070 (2)	0.0391 (16)	0.0490 (18)	0.0252 (16)	0.0202 (16)	0.0246 (15)
C1	0.038 (2)	0.035 (2)	0.047 (2)	0.0168 (18)	0.0141 (19)	0.0248 (19)
C2	0.038 (2)	0.044 (2)	0.038 (2)	0.0176 (19)	0.0164 (18)	0.0234 (19)
C3	0.040 (2)	0.042 (2)	0.041 (2)	0.0169 (18)	0.0150 (18)	0.0284 (19)
C4	0.039 (2)	0.039 (2)	0.044 (2)	0.0151 (18)	0.0138 (19)	0.0295 (19)
C5	0.039 (2)	0.035 (2)	0.045 (2)	0.0148 (18)	0.0130 (19)	0.0232 (19)
C6	0.053 (3)	0.045 (2)	0.036 (2)	0.023 (2)	0.0185 (19)	0.0234 (19)
C7	0.055 (3)	0.044 (2)	0.042 (2)	0.025 (2)	0.020 (2)	0.030 (2)
C8	0.036 (2)	0.037 (2)	0.038 (2)	0.0151 (17)	0.0127 (17)	0.0239 (18)
C9	0.032 (2)	0.036 (2)	0.039 (2)	0.0127 (17)	0.0127 (17)	0.0235 (18)
C10	0.070 (3)	0.048 (3)	0.074 (3)	0.028 (2)	0.030 (3)	0.043 (3)

Geometric parameters (Å, º)

Cl1—C1	1.749 (4)	C4—C9	1.415 (5)
Cl2—C3	1.734 (4)	C4—H4	0.9300
N1—C1	1.293 (5)	C5—C6	1.422 (6)
N1—C8	1.372 (5)	C6—C7	1.352 (6)
O1—C5	1.359 (5)	C6—H6	0.9300
O1—C10	1.433 (5)	C7—C8	1.402 (6)
C1—C2	1.412 (5)	C7—H7	0.9300
C2—C3	1.377 (6)	C8—C9	1.432 (5)
C2—H2	0.9300	C10—H10A	0.9600
C3—C9	1.411 (6)	C10—H10B	0.9600
C4—C5	1.370 (6)	C10—H10C	0.9600
C1—N1—C8	117.4 (3)	C7—C6—H6	119.8
C5—O1—C10	117.2 (4)	C5—C6—H6	119.8
N1—C1—C2	126.7 (4)	C6—C7—C8	121.6 (4)
N1—C1—Cl1	116.3 (3)	C6—C7—H7	119.2
C2—C1—Cl1	117.0 (3)	C8—C7—H7	119.2
C3—C2—C1	115.3 (4)	N1—C8—C7	119.1 (3)
C3—C2—H2	122.3	N1—C8—C9	122.6 (4)
C1—C2—H2	122.3	C7—C8—C9	118.3 (4)

C2—C3—C9	122.4 (3)	C3—C9—C4	125.0 (4)
C2—C3—Cl2	117.9 (3)	C3—C9—C8	115.5 (3)
C9—C3—Cl2	119.6 (3)	C4—C9—C8	119.5 (4)
C5—C4—C9	120.1 (4)	O1—C10—H10A	109.5
C5—C4—H4	120.0	O1—C10—H10B	109.5
C9—C4—H4	120.0	H10A—C10—H10B	109.5
O1—C5—C4	125.8 (4)	O1—C10—H10C	109.5
O1—C5—C6	114.1 (4)	H10A—C10—H10C	109.5
C4—C5—C6	120.0 (4)	H10B—C10—H10C	109.5
C7—C6—C5	120.5 (4)		
C8—N1—C1—C2	1.2 (6)	C1—N1—C8—C9	−1.6 (6)
C8—N1—C1—Cl1	179.1 (3)	C6—C7—C8—N1	178.9 (4)
N1—C1—C2—C3	−0.6 (6)	C6—C7—C8—C9	−0.2 (7)
Cl1—C1—C2—C3	−178.5 (3)	C2—C3—C9—C4	179.2 (4)
C1—C2—C3—C9	0.4 (6)	Cl2—C3—C9—C4	0.4 (6)
C1—C2—C3—Cl2	179.2 (3)	C2—C3—C9—C8	−0.8 (6)
C10—O1—C5—C4	−1.2 (6)	Cl2—C3—C9—C8	−179.6 (3)
C10—O1—C5—C6	179.3 (4)	C5—C4—C9—C3	−179.8 (4)
C9—C4—C5—O1	179.3 (4)	C5—C4—C9—C8	0.3 (6)
C9—C4—C5—C6	−1.3 (6)	N1—C8—C9—C3	1.5 (6)
O1—C5—C6—C7	−178.9 (4)	C7—C8—C9—C3	−179.5 (4)
C4—C5—C6—C7	1.6 (7)	N1—C8—C9—C4	−178.6 (4)
C5—C6—C7—C8	−0.8 (7)	C7—C8—C9—C4	0.5 (6)
C1—N1—C8—C7	179.3 (4)		