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Ethyl 3,7-dichloroquinoline-8-carboxylate

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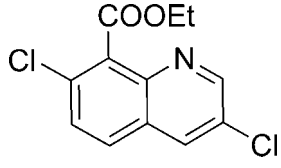
Key indicators: single-crystal X-ray study; T = 296 K; mean σ(C–C) = 0.003 Å; R factor = 0.043; wR factor = 0.117; data-to-parameter ratio = 17.7.

The title compound, $C_{12}H_9Cl_2NO_2$, was prepared by the esterification of 3,7-dichloroquinoline-8-carboxylic acid with triethyl phosphite. The crystal structure is stabilized by aromatic π–π stacking between the benzene and the pyridine rings of neighbouring molecules [centroid–centroid distances = 3.716 (2) and 3.642 (2) Å]. In addition, weak intermolecular C—H···N hydrogen bonds are present in the structure.

Related literature

For the use of 3,7-dichloroquinoline-8-carboxylic acid as a herbicide, see: Nuria *et al.* (1997); Pornprom *et al.* (2006); Sunohara & Matsumoto (2004); Tresch & Grossmann (2002). For the usual preparative route, see: Yang *et al.* (2002). For related complexes, see: An *et al.* (2008); Che *et al.* (2005); Guo (2008); Li *et al.* (2008); Turel *et al.* (2004); Zhang *et al.* (2007). For 3,7-dichloroquinoline-8-carboxylic acid derivatives, see: Liang *et al.* (2006);



Experimental

Crystal data

$C_{12}H_9Cl_2NO_2$
M_r = 270.10
Tetragonal, $I4_1/a$
a = 25.4806 (3) Å
c = 7.3497 (2) Å
V = 4771.87 (15) Å^3
Z = 16
Mo $K\alpha$ radiation
μ = 0.53 mm^{-1}
T = 296 (2) K
0.10 × 0.08 × 0.06 mm

Data collection

Bruker SMART APEX2 diffractometer
Absorption correction: multi-scan (*SADABS*; Bruker, 1999)
T_{min} = 0.950, T_{max} = 0.969
19332 measured reflections
2750 independent reflections
1625 reflections with $I > 2\sigma(I)$
R_{int} = 0.045

Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.043
$wR(F^2)$ = 0.117
S = 1.05
2750 reflections
155 parameters
H-atom parameters constrained
$\Delta\rho_{max}$ = 0.20 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
C11—H11A···N1^{i}	0.97	2.46	3.299 (3)	145

Symmetry code: (i) $-y+\frac{5}{4}, x+\frac{1}{4}, -z+\frac{5}{4}$.

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: *SHELXS97* (Sheldrick, 2008); molecular graphics: *ORTEP-3 for Windows* (Farrugia, 1997); software used to prepare material for publication: *SHELXL97* and *PLATON* (Spek, 2003).

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Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: LX2075).

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supplementary materials

Acta Cryst. (2008). E**64**, o2241 [**doi:10.1107/S1600536808034995**]

Ethyl 3,7-dichloroquinoline-8-carboxylate

F. Zhu, L.-T. An, M. Xia and J.-F. Zhou

Comment

Quinclorac (3,7-dichloroquinoline-8-carboxylic acid) is one of the most effective herbicides (Nuria *et al.*, 1997; Pornprom *et al.*, 2006; Sunohara & Matsumoto, 2004; Tresch & Grossmann, 2002). Usually, it was prepared *via* Skraup cyclization from 2-methyl-3- chloroaniline, followed by chlorination and oxidation (Yang *et al.*, 2002). Furthermore, quinolinecarboxylates can chelate to metal atoms, forming the complexes, such as *trans*-Dimethanolbis(quinoline-8-carboxylato-κ^2N,O)- cobalt(II) (Che *et al.*,2005),*catena*-Poly[nickel(II)-bis(μ-3,7-dichloroquinoline-8-χarboxylato-$\kappa^3N,O:O'$)] (Zhang *et al.*, 2007), *catena*-Poly[cobalt(II)-*bis* (l-3,7-dichloroquinoline-8-carboxylato-$\kappa^3N,O:O'$)] (Li *et al.*, 2008). More recently, we also have reported a Zinc-quinclorac complex (An *et al.*, 2008) and quinclorac (Guo, 2008). But the derivatives of 3,7-dichloroquinoline-8-carboxylic acid have been less reported (Liang *et al.*, 2006). Here we report the crystal structure of the title compound, ethyl 3,7-dichloroquinoline-8-carboxylate (I) (Fig. 1).

In the title compound (I), as shown in Fig. 1, the plane (O1—C10—O2—C11) is nearly vertical to the quinoline ring, in which the dihedral angel is 86.6 (1). The quinoline unit is essentially planar, with a mean deviation of 0.007 (2) Å from the least-squares plane defined by the ten constituent atoms. The molecular packing (Fig. 2) is stabilized by aromatic π—π stackings between the benzene and the pyridine rings of the adjacent molecules. The $Cg1\cdots Cg2^{ii}$ and $Cg1\cdots Cg2^{iii}$ distances are 3.716 (2) and 3.642 (2) Å (Fig. 2; *Cg*1 and *Cg*2 are the centroids of the C1/C2/C3/C4/C9/C8 benzene ring and the N1/C7/C6/C5/C9/C8 pyridine ring, respectively, symmetry code as in Fig. 2). The crystal structure is further stabilized by intermolecular C11—H11A$\cdots N^{i}$ hydrogen bonds (Fig. 2 and Table 1; symmetry code as in Fig. 2).

Experimental

Ethyl 3,7-dichloroquinoline-8-carboxylate was obtained from the reaction of 3,7-dichloroquinoline-8-carboxylic acid with triethyl phosphite in refluxing condition. After recrystallization from ethanol, then it was dissolved the mixture of acetone/petroleum ether (1:4, V/V). The suitable single-crystal for X-ray analysis was obtained by slow evaporation.

Refinement

All H atoms were geometrically positioned and refined using a riding model, with C—H = 0.93 (aromatic), 0.97 (methylene) and 0.96 Å (methyl) H atoms, and with U_{iso}(H) = 1.2Ueq(C) (aromatic, methylene) and 1.5Ueq(C) (methyl) H atoms.

Figures

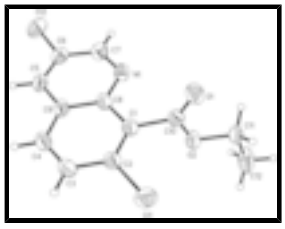


Fig. 1. The molecular structure of the title compound, showing displacement ellipsoids drawn at the 30% probability level.

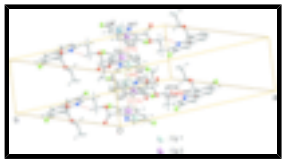


Fig. 2. π—π stackings and C—H···N interactions (dotted lines) in the title compound. Cg denotes ring centroid. [Symmetry code: (i) -y+5/4, x+1/4, -z+5/4; (ii) -x+1, -y+1, -z+2; (iii)-x+1, -y+1, -z+1.]

Ethyl 3,7-dichloroquinoline-8-carboxylate

Crystal data

$C_{12}H_9Cl_2NO_2$	$Z = 16$
$M_r = 270.10$	$F_{000} = 2208$
Tetragonal, $I4_1/a$	$D_x = 1.504$ Mg m^{-3}
Hall symbol: -I_4ad	Melting point: not measured K
$a = 25.4806$ (3) Å	Mo $K\alpha$ radiation $\lambda = 0.71073$ Å
$b = 25.4806$ (3) Å	Cell parameters from 2208 reflections
$c = 7.3497$ (2) Å	$\theta = 1.6$–26.0º
$\alpha = 90$º	$\mu = 0.53$ mm^{-1}
$\beta = 90$º	$T = 296$ (2) K
$\gamma = 90$º	Needle, colorless
$V = 4771.87$ (15) Å^3	0.10 × 0.08 × 0.06 mm

Data collection

Bruker SMART APEX2 diffractometer	2750 independent reflections
Radiation source: fine-focus sealed tube	1625 reflections with $I > 2\sigma(I)$
Monochromator: graphite	$R_{int} = 0.045$
Detector resolution: 10.0 pixels mm^{-1}	$\theta_{max} = 27.5$º
$T = 296(2)$ K	$\theta_{min} = 1.6$º
φ and ω scans	$h = -32 \rightarrow 33$
Absorption correction: multi-scan (SADABS; Bruker, 1999)	$k = -33 \rightarrow 32$
$T_{min} = 0.950$, $T_{max} = 0.969$	$l = -9 \rightarrow 9$
19332 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
$R[F^2 > 2\sigma(F^2)] = 0.043$	H-atom parameters constrained
$wR(F^2) = 0.117$	$w = 1/[\sigma^2(F_o^2) + (0.0469P)^2 + 1.2301P]$ where $P = (F_o^2 + 2F_c^2)/3$
$S = 1.06$	$(\Delta/\sigma)_{max} < 0.001$
2750 reflections	$\Delta\rho_{max} = 0.20$ e Å^{-3}
155 parameters	$\Delta\rho_{min} = -0.25$ e Å^{-3}
Primary atom site location: structure-invariant direct methods	Extinction correction: none

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}
Cl1	0.65771 (2)	0.53635 (3)	0.60570 (9)	0.0725 (2)
Cl2	0.34654 (3)	0.47136 (3)	0.89519 (10)	0.0809 (3)
O1	0.57642 (7)	0.63042 (6)	0.8389 (2)	0.0714 (5)
O2	0.55721 (6)	0.62556 (5)	0.5418 (2)	0.0560 (4)
N1	0.46789 (7)	0.56227 (7)	0.7898 (3)	0.0535 (5)
C1	0.55677 (8)	0.54727 (8)	0.7053 (3)	0.0479 (5)
C2	0.59627 (8)	0.51296 (8)	0.6642 (3)	0.0511 (5)
C3	0.58827 (9)	0.45826 (9)	0.6676 (3)	0.0582 (6)
H3	0.6157	0.4356	0.6390	0.070*
C4	0.54076 (9)	0.43888 (9)	0.7125 (3)	0.0594 (6)
H4	0.5358	0.4027	0.7144	0.071*
C5	0.44775 (9)	0.45445 (8)	0.8039 (3)	0.0574 (6)
H5	0.4405	0.4187	0.8107	0.069*
C6	0.40972 (9)	0.49023 (9)	0.8394 (3)	0.0555 (6)
C7	0.42156 (9)	0.54368 (9)	0.8316 (3)	0.0577 (6)
H7	0.3949	0.5675	0.8577	0.069*
C8	0.50652 (8)	0.52712 (8)	0.7514 (3)	0.0458 (5)
C9	0.49847 (8)	0.47219 (8)	0.7565 (3)	0.0492 (5)

C10	0.56464 (8)	0.60545 (8)	0.7069 (3)	0.0505 (5)
C11	0.56478 (9)	0.68194 (8)	0.5254 (3)	0.0609 (6)
H11A	0.5999	0.6915	0.5639	0.073*
H11B	0.5398	0.7004	0.6015	0.073*
C12	0.55684 (13)	0.69615 (10)	0.3318 (4)	0.0967 (10)
H12A	0.5809	0.6766	0.2574	0.145*
H12B	0.5630	0.7330	0.3160	0.145*
H12C	0.5215	0.6880	0.2967	0.145*

Atomic displacement parameters (Å^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Cl1	0.0602 (4)	0.0814 (5)	0.0760 (5)	0.0005 (3)	0.0113 (3)	−0.0024 (3)
Cl2	0.0661 (4)	0.1000 (5)	0.0765 (5)	−0.0247 (4)	−0.0006 (3)	0.0114 (4)
O1	0.0916 (13)	0.0584 (10)	0.0642 (12)	−0.0132 (9)	−0.0061 (9)	−0.0109 (8)
O2	0.0650 (10)	0.0406 (8)	0.0624 (11)	−0.0065 (7)	−0.0037 (8)	0.0032 (7)
N1	0.0524 (11)	0.0480 (10)	0.0601 (12)	0.0009 (9)	−0.0024 (9)	0.0023 (8)
C1	0.0560 (13)	0.0447 (12)	0.0430 (13)	−0.0014 (10)	−0.0049 (10)	0.0001 (9)
C2	0.0580 (13)	0.0529 (13)	0.0424 (12)	0.0009 (10)	−0.0021 (10)	−0.0015 (10)
C3	0.0704 (16)	0.0530 (14)	0.0511 (14)	0.0128 (11)	−0.0018 (11)	−0.0042 (10)
C4	0.0804 (17)	0.0423 (12)	0.0555 (15)	0.0022 (12)	−0.0030 (12)	−0.0035 (10)
C5	0.0778 (17)	0.0462 (12)	0.0483 (14)	−0.0158 (12)	−0.0057 (11)	0.0036 (10)
C6	0.0584 (14)	0.0637 (15)	0.0445 (13)	−0.0129 (11)	−0.0065 (10)	0.0043 (10)
C7	0.0557 (14)	0.0595 (14)	0.0578 (15)	0.0034 (11)	−0.0035 (11)	0.0037 (11)
C8	0.0567 (13)	0.0418 (12)	0.0389 (12)	0.0007 (10)	−0.0072 (9)	0.0002 (9)
C9	0.0667 (15)	0.0412 (12)	0.0397 (13)	−0.0033 (10)	−0.0077 (10)	0.0014 (9)
C10	0.0456 (12)	0.0497 (13)	0.0562 (15)	−0.0038 (10)	0.0016 (10)	−0.0020 (11)
C11	0.0583 (14)	0.0392 (12)	0.0851 (18)	−0.0080 (10)	0.0071 (12)	0.0011 (11)
C12	0.139 (3)	0.0547 (16)	0.097 (2)	−0.0178 (17)	−0.0243 (19)	0.0215 (15)

Geometric parameters (Å, °)

Cl1—C2	1.729 (2)	C4—H4	0.9300
Cl2—C6	1.730 (2)	C5—C6	1.356 (3)
O1—C10	1.198 (2)	C5—C9	1.413 (3)
O2—C10	1.331 (2)	C5—H5	0.9300
O2—C11	1.454 (2)	C6—C7	1.396 (3)
N1—C7	1.309 (3)	C7—H7	0.9300
N1—C8	1.360 (2)	C8—C9	1.415 (3)
C1—C2	1.367 (3)	C11—C12	1.482 (3)
C1—C8	1.420 (3)	C11—H11A	0.9700
C1—C10	1.496 (3)	C11—H11B	0.9700
C2—C3	1.409 (3)	C12—H12A	0.9600
C3—C4	1.348 (3)	C12—H12B	0.9600
C3—H3	0.9300	C12—H12C	0.9600
C4—C9	1.409 (3)		
C10—O2—C11	115.91 (17)	C6—C7—H7	118.1
C7—N1—C8	117.60 (18)	N1—C8—C9	122.72 (19)

C2—C1—C8	119.03 (18)	N1—C8—C1	117.63 (17)
C2—C1—C10	122.47 (18)	C9—C8—C1	119.65 (19)
C8—C1—C10	118.49 (18)	C4—C9—C5	124.3 (2)
C1—C2—C3	121.5 (2)	C4—C9—C8	118.6 (2)
C1—C2—Cl1	120.06 (16)	C5—C9—C8	117.1 (2)
C3—C2—Cl1	118.45 (17)	O1—C10—O2	124.7 (2)
C4—C3—C2	119.8 (2)	O1—C10—C1	124.5 (2)
C4—C3—H3	120.1	O2—C10—C1	110.81 (18)
C2—C3—H3	120.1	O2—C11—C12	107.63 (19)
C3—C4—C9	121.5 (2)	O2—C11—H11A	110.2
C3—C4—H4	119.3	C12—C11—H11A	110.2
C9—C4—H4	119.3	O2—C11—H11B	110.2
C6—C5—C9	119.07 (19)	C12—C11—H11B	110.2
C6—C5—H5	120.5	H11A—C11—H11B	108.5
C9—C5—H5	120.5	C11—C12—H12A	109.5
C5—C6—C7	119.6 (2)	C11—C12—H12B	109.5
C5—C6—Cl2	121.59 (18)	H12A—C12—H12B	109.5
C7—C6—Cl2	118.82 (19)	C11—C12—H12C	109.5
N1—C7—C6	123.9 (2)	H12A—C12—H12C	109.5
N1—C7—H7	118.1	H12B—C12—H12C	109.5

Hydrogen-bond geometry (Å, °)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
C11—H11A···N1^{i}	0.97	2.46	3.299 (3)	145

Symmetry codes: (i) −*y*+5/4, *x*+1/4, −*z*+5/4.

Fig. 1

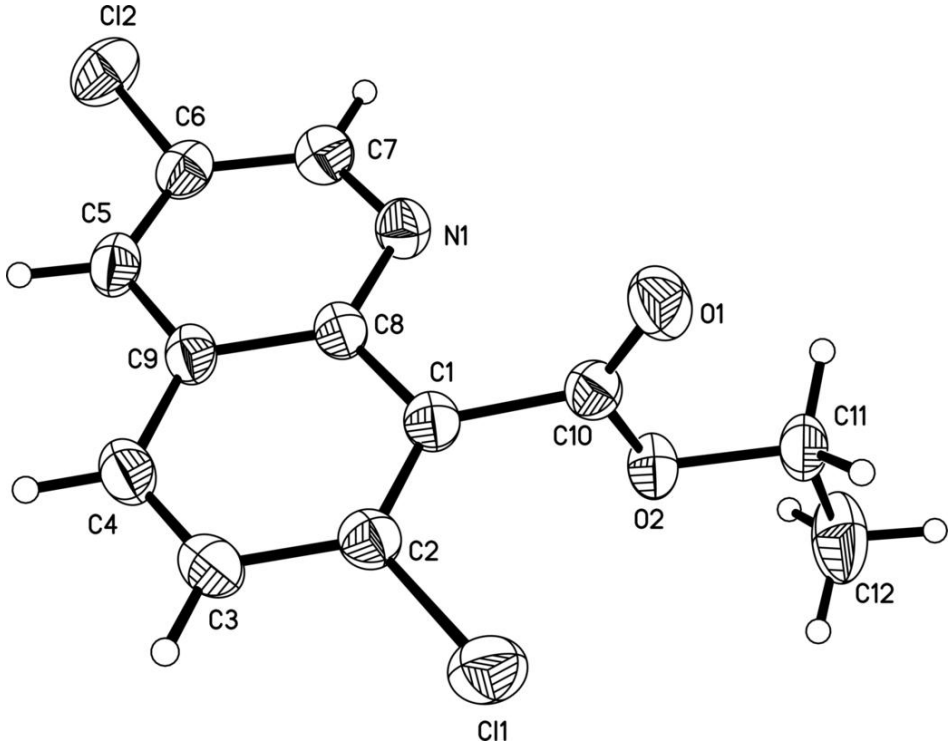
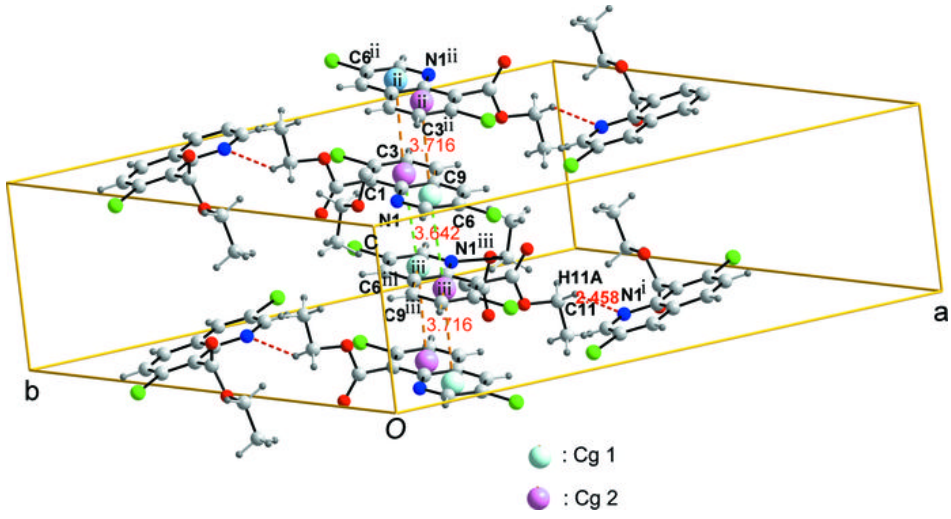


Fig. 2


C6ii
N1ii
C3ii
C3i
3.716
C9
C1
N1
C6
3.642
N1iii
C6iii
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3.716
H11A
2.458
C11
N1i
a
b
O
: Cg 1
: Cg 2