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3,7-Dichloroquinoline-8-carboxylic acid

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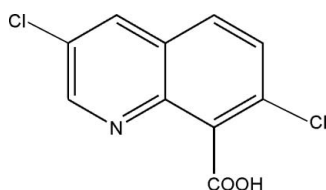
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Key indicators: single-crystal X-ray study; $T = 173$ K; mean $\sigma(\text{C}-\text{C}) = 0.006$ Å; R factor = 0.064; wR factor = 0.141; data-to-parameter ratio = 13.2.

The title compound (trade name: quinclorac), $\text{C}_{10}\text{H}_5\text{Cl}_2\text{NO}_2$, was crystallized from a dimethyl sulfoxide solution. Quinclorac molecules are packed mainly *via* π - π stacking interactions between neighbouring heterocycles (interplanar distance: 3.31 Å) and *via* $\text{O}-\text{H}\cdots\text{N}$ hydrogen bonding.

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 related complexes, see: Li *et al.* (2008); Turel *et al.* (2004); Zhang *et al.* (2007).



Experimental

Crystal data

 $\text{C}_{10}\text{H}_5\text{Cl}_2\text{NO}_2$ $M_r = 242.05$ Triclinic, $P\bar{1}$ $a = 7.5002$ (12) Å $b = 8.4016$ (14) Å $c = 8.732$ (3) Å $\alpha = 102.529$ (6)° $\beta = 93.439$ (6)° $\gamma = 116.479$ (4)° $V = 472.98$ (17) Å³ $Z = 2$ Mo $K\alpha$ radiation $\mu = 0.66$ mm⁻¹ $T = 173$ (2) K

0.26 × 0.22 × 0.20 mm

Data collection

Bruker SMART APEXII diffractometer

Absorption correction: multi-scan (SADABS; Bruker, 1999)

 $T_{\min} = 0.84$, $T_{\max} = 0.88$

5948 measured reflections

1834 independent reflections

1102 reflections with $I > 2\sigma(I)$ $R_{\text{int}} = 0.067$

Refinement

 $R[F^2 > 2\sigma(F^2)] = 0.063$ $wR(F^2) = 0.140$ $S = 1.01$

1834 reflections

139 parameters

H atoms treated by a mixture of independent and constrained refinement

 $\Delta\rho_{\text{max}} = 0.30$ e Å⁻³ $\Delta\rho_{\text{min}} = -0.43$ e Å⁻³

Table 1

Hydrogen-bond geometry (Å, °).

$D-\text{H}\cdots A$	$D-\text{H}$	$\text{H}\cdots A$	$D\cdots A$	$D-\text{H}\cdots A$
$\text{O1}-\text{H1A}\cdots\text{N1}^i$	0.84 (5)	1.91 (5)	2.753 (4)	173 (4)

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

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

Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: ZL2136).

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supplementary materials

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3,7-Dichloroquinoline-8-carboxylic acid

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Comment

Quinlorac (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), and is widely used in agriculture. In addition, as a quinolinecarboxylate derivate, quinlorac could chelate metal ions, forming corresponding complexes (Li *et al.*, 2008; Turel *et al.*, 2004; Zhang *et al.*, 2007). As an extension of these studies, we report herein on the structure of quinlorac.

A quinlorac molecule, which is the asymmetric unit of the structure, is shown in Fig. 1. All the bond distances and bond angles of quinlorac are normal and call for no further comment. Two types of intermolecular interactions are easily found in the structure of quinlorac (Fig. 2). There exists a π - π interaction between adjacent quinin cycles with an inversion center located halfway between the aromatic rings, thus forming stacks along the *a* direction. Quinlorac molecules of adjacent chains are joined through H-bonding of O1—H1 \cdots N1ⁱ (symmetry code: (i) 1 - *x*, 2 - *y*, 1 - *z*) (Table 1) into a triclinic supramolecular architecture (Fig. 2).

Experimental

Quinlorac was obtained from a commercial source and used directly without further purification. Quinlorac (0.5 mmol, 0.121 g) was dissolved in 10 mL DMSO. After ether vapor slowly diffused into the solution at room temperature for several days, colorless prismslike crystals suitable for crystallographic research were obtained.

Refinement

All the non-hydrogen atoms were located from the Fourier maps, and were refined anisotropically. The hydroxyl hydrogen, H1A, was found from the Fourier difference maps and refined isotropically with a fixed O—H bond length. All other H atoms were positioned geometrically. All isotropic vibration parameters of hydrogen atoms were related to the atoms which they are bonded to with $U_{\text{iso}}(\text{H}) = 1.2 U_{\text{eq}}(\text{C}, \text{O})$.

Figures

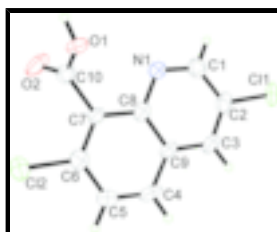


Fig. 1. The asymmetric unit of quinlorac with atom labels and 50% probability displacement ellipsoids for non-H atoms.

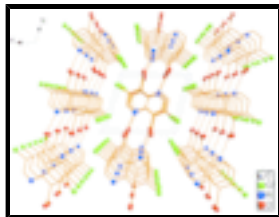


Fig. 2. Packing diagram of quinclorac showing the π - π stacks along the a direction. Inter-molecular H-bonding is indicated via dashed lines.

3,7-Dichloroquinoline-8-carboxylic acid

Crystal data

$C_{10}H_5Cl_2NO_2$	$Z = 2$
$M_r = 242.05$	$F_{000} = 244$
Triclinic, $P\bar{1}$	$D_x = 1.700 \text{ Mg m}^{-3}$
Hall symbol: -P 1	Mo $K\alpha$ radiation
$a = 7.5002 (12) \text{ \AA}$	$\lambda = 0.71073 \text{ \AA}$
$b = 8.4016 (14) \text{ \AA}$	Cell parameters from 958 reflections
$c = 8.732 (3) \text{ \AA}$	$\theta = 2.1\text{--}25.5^\circ$
$\alpha = 102.529 (6)^\circ$	$\mu = 0.66 \text{ mm}^{-1}$
$\beta = 93.439 (6)^\circ$	$T = 173 (2) \text{ K}$
$\gamma = 116.479 (4)^\circ$	Prismlike, colorless
$V = 472.98 (17) \text{ \AA}^3$	$0.26 \times 0.22 \times 0.20 \text{ mm}$

Data collection

Bruker SMART APEXII diffractometer	1834 independent reflections
Radiation source: fine-focus sealed tube	1102 reflections with $I > 2\sigma(I)$
Monochromator: graphite	$R_{\text{int}} = 0.067$
$T = 173(2) \text{ K}$	$\theta_{\text{max}} = 26.0^\circ$
ω scans	$\theta_{\text{min}} = 2.4^\circ$
Absorption correction: multi-scan (SADABS; Bruker, 1999)	$h = -9 \rightarrow 9$
$T_{\text{min}} = 0.84, T_{\text{max}} = 0.88$	$k = -8 \rightarrow 10$
5948 measured reflections	$l = -10 \rightarrow 10$

Refinement

Refinement on F^2	Secondary atom site location: difference Fourier map
Least-squares matrix: full	Hydrogen site location: inferred from neighbouring sites
$R[F^2 > 2\sigma(F^2)] = 0.063$	H atoms treated by a mixture of independent and constrained refinement
$wR(F^2) = 0.140$	$w = 1/[\sigma^2(F_o^2) + (0.062P)^2]$
$S = 1.01$	where $P = (F_o^2 + 2F_c^2)/3$
	$(\Delta/\sigma)_{\text{max}} < 0.001$

1834 reflections $\Delta\rho_{\max} = 0.30 \text{ e \AA}^{-3}$
 139 parameters $\Delta\rho_{\min} = -0.43 \text{ e \AA}^{-3}$
 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 $F^2 > 2\sigma(F^2)$ 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	$U_{\text{iso}}^*/U_{\text{eq}}$
C1	0.3476 (6)	0.5471 (6)	0.2465 (5)	0.0354 (10)
H1	0.3861	0.5957	0.1583	0.043*
C2	0.2932 (6)	0.3616 (6)	0.2276 (5)	0.0324 (9)
C3	0.2343 (6)	0.2876 (6)	0.3515 (5)	0.0337 (10)
H3	0.1963	0.1613	0.3413	0.040*
C4	0.1686 (6)	0.3342 (6)	0.6269 (5)	0.0369 (10)
H4	0.1286	0.2086	0.6220	0.044*
C5	0.1655 (7)	0.4475 (6)	0.7605 (5)	0.0363 (10)
H5	0.1215	0.4011	0.8489	0.044*
C6	0.2272 (6)	0.6342 (6)	0.7699 (5)	0.0308 (9)
C7	0.2918 (6)	0.7078 (5)	0.6455 (5)	0.0253 (8)
C8	0.2910 (5)	0.5882 (5)	0.5036 (5)	0.0261 (8)
C9	0.2304 (6)	0.4002 (5)	0.4943 (5)	0.0261 (8)
C10	0.3645 (6)	0.9105 (5)	0.6610 (4)	0.0293 (9)
C11	0.29545 (15)	0.22889 (15)	0.04666 (12)	0.0385 (3)
C12	0.23077 (17)	0.77619 (16)	0.94953 (12)	0.0422 (3)
N1	0.3496 (5)	0.6591 (4)	0.3774 (4)	0.0283 (7)
O1	0.5586 (4)	0.9997 (4)	0.6659 (3)	0.0302 (6)
H1A	0.597 (7)	1.106 (7)	0.652 (5)	0.036*
O2	0.2510 (5)	0.9766 (4)	0.6634 (5)	0.0519 (9)

Atomic displacement parameters (\AA^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
C1	0.038 (2)	0.041 (3)	0.032 (2)	0.021 (2)	0.0079 (18)	0.012 (2)
C2	0.027 (2)	0.032 (2)	0.039 (2)	0.0174 (19)	0.0036 (17)	0.0030 (19)
C3	0.033 (2)	0.021 (2)	0.049 (2)	0.016 (2)	0.0051 (19)	0.008 (2)
C4	0.037 (2)	0.025 (2)	0.053 (3)	0.014 (2)	0.006 (2)	0.022 (2)

supplementary materials

C5	0.043 (2)	0.035 (3)	0.036 (2)	0.019 (2)	0.0106 (19)	0.017 (2)
C6	0.0262 (19)	0.035 (2)	0.033 (2)	0.0165 (18)	0.0041 (16)	0.0098 (19)
C7	0.028 (2)	0.020 (2)	0.032 (2)	0.0138 (17)	0.0062 (16)	0.0073 (17)
C8	0.0180 (18)	0.024 (2)	0.034 (2)	0.0095 (16)	0.0014 (15)	0.0050 (17)
C9	0.0258 (18)	0.020 (2)	0.036 (2)	0.0126 (16)	0.0030 (16)	0.0091 (17)
C10	0.034 (2)	0.025 (2)	0.0246 (19)	0.0119 (18)	0.0010 (15)	0.0038 (18)
C11	0.0372 (6)	0.0432 (7)	0.0423 (6)	0.0303 (5)	0.0101 (5)	-0.0006 (5)
C12	0.0548 (7)	0.0433 (7)	0.0343 (6)	0.0280 (6)	0.0144 (5)	0.0089 (5)
N1	0.0318 (18)	0.0235 (18)	0.0295 (17)	0.0130 (15)	0.0066 (13)	0.0069 (15)
O1	0.0319 (16)	0.0189 (15)	0.0364 (16)	0.0071 (13)	0.0056 (12)	0.0120 (13)
O2	0.048 (2)	0.0257 (17)	0.092 (3)	0.0240 (16)	0.0204 (18)	0.0171 (18)

Geometric parameters (\AA , $^\circ$)

C1—N1	1.308 (5)	C5—H5	0.9500
C1—C2	1.391 (6)	C6—C7	1.373 (6)
C1—H1	0.9500	C6—C12	1.743 (4)
C2—C3	1.362 (6)	C7—C8	1.414 (5)
C2—C11	1.731 (4)	C7—C10	1.510 (5)
C3—C9	1.403 (6)	C8—N1	1.369 (5)
C3—H3	0.9500	C8—C9	1.417 (5)
C4—C5	1.345 (6)	C10—O2	1.206 (5)
C4—C9	1.405 (5)	C10—O1	1.299 (5)
C4—H4	0.9500	O1—H1A	0.84 (5)
C5—C6	1.405 (6)		
N1—C1—C2	124.6 (4)	C7—C6—C12	119.9 (3)
N1—C1—H1	117.7	C5—C6—C12	118.0 (3)
C2—C1—H1	117.7	C6—C7—C8	117.8 (4)
C3—C2—C1	118.9 (4)	C6—C7—C10	121.0 (3)
C3—C2—C11	121.5 (3)	C8—C7—C10	121.2 (3)
C1—C2—C11	119.6 (3)	N1—C8—C7	118.2 (4)
C2—C3—C9	119.2 (4)	N1—C8—C9	121.6 (3)
C2—C3—H3	120.4	C7—C8—C9	120.2 (4)
C9—C3—H3	120.4	C3—C9—C4	122.9 (4)
C5—C4—C9	120.5 (4)	C3—C9—C8	118.0 (4)
C5—C4—H4	119.7	C4—C9—C8	119.1 (3)
C9—C4—H4	119.7	O2—C10—O1	125.4 (4)
C4—C5—C6	120.2 (4)	O2—C10—C7	122.5 (3)
C4—C5—H5	119.9	O1—C10—C7	112.1 (3)
C6—C5—H5	119.9	C1—N1—C8	117.7 (3)
C7—C6—C5	122.1 (4)	C10—O1—H1A	113 (3)

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

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
O1—H1A \cdots N1 ⁱ	0.84 (5)	1.91 (5)	2.753 (4)	173 (4)

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

Fig. 1

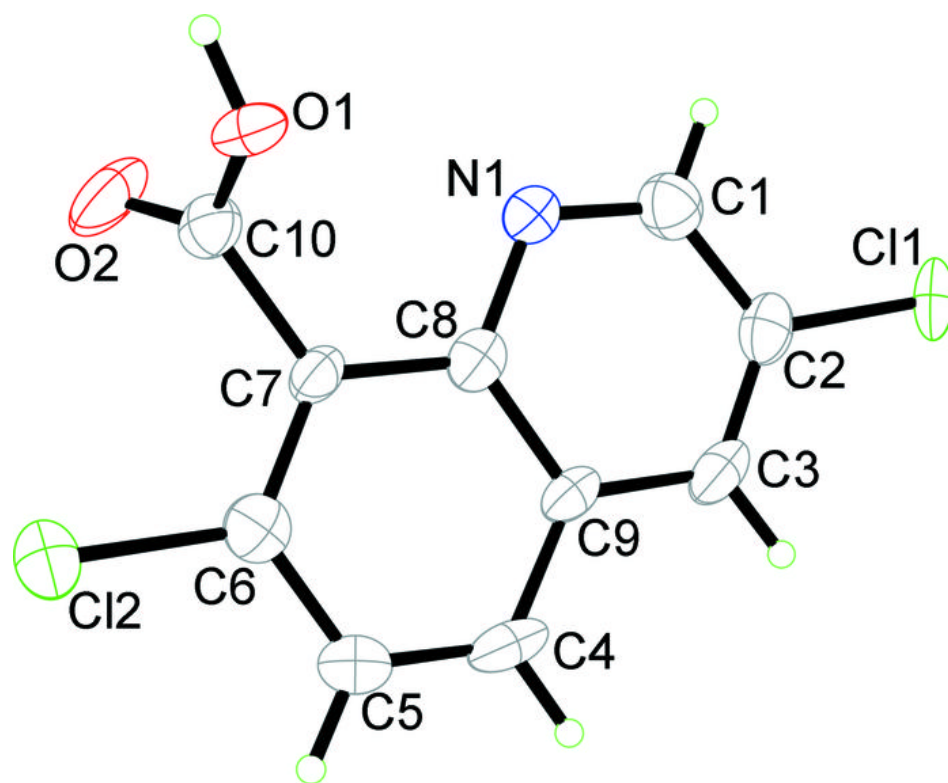


Fig. 2

