Acta Crystallographica Section E
Structure Reports
Online

ISSN 1600-5368

3,10-Dichloro-5,12-dihydroquino[2,3-*b*]-acridine-7,14-dione

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Received 11 November 2005
Accepted 30 November 2005
Online 16 December 2005

The title compound, $C_{20}H_{10}Cl_2N_2O_2$, is one of the quinacridone derivatives known as red pigments. The molecule has inversion symmetry. The quinacridone molecules are connected by N—H$\cdots$O hydrogen bonds along the [1$\overline{1}$0] direction to form a ribbon structure.

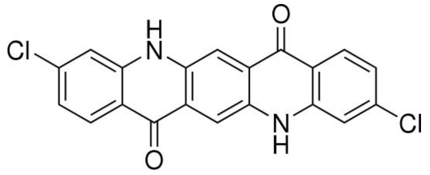
Key indicators

Single-crystal X-ray study
T = 93 K
Mean σ(C–C) = 0.004 Å
R factor = 0.057
wR factor = 0.172
Data-to-parameter ratio = 10.5

For details of how these key indicators were automatically derived from the article, see http://journals.iucr.org/e.

Comment

The title compound, (I), abbreviated to 3,10-DClQA, is one of the quinacridone derivatives on the market which are known as red pigments (Pigment Red 209; Herbst & Hunger, 1997) and typically characterized by N—H$\cdots$O intermolecular hydrogen bonds. 3,10-DClQA exhibits a yellowish–red shade in the solid state, while the colour is bluish–red in 2,9-dichloroquinacridone (2,9-DClQA; Senju *et al.*, 2005), although the solution spectra of both compounds are practically the same. This suggests that intermolecular interactions in the solid state are responsible for the difference in colour. With this background, the structure analysis of (I) has been undertaken.



(I)

Fig. 1 shows a plot of the molecule of (I). The molecule has inversion symmetry. The quinacridine skeleton is entirely planar, as indicated by a small mean deviation of about 0.02 Å from the least-squares plane of the rings defined by atoms C1–C10 and N1. However, the carbonyl O atom deviates by 0.140 (3) Å from the least-squares plane of the ring system towards the NH group of the neighbouring molecule, enabling

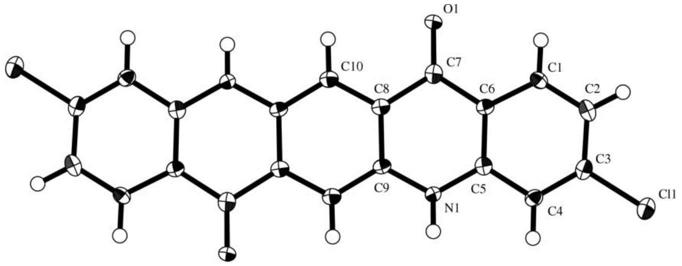


Figure 1
A view of the molecular structure of (I), showing 50% probability displacement ellipsoids. Unlabelled atoms are related by the symmetry code (−*x*, 1 − *y*, 1 − *z*).

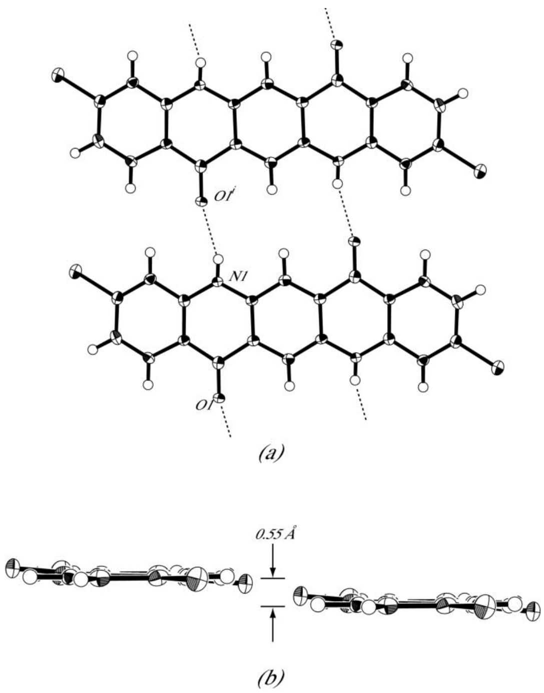


Figure 2
(*a*) Top view of the two hydrogen-bonded molecules. The dotted lines denote hydrogen bonds. [Symmetry code: (i) $1 + x, y - 1, z$.] (*b*) Side view of the two hydrogen-bonded molecules, showing a small step of *ca* 0.55 Å between the molecular planes.

the formation of an N—H···O intermolecular hydrogen bond (Table 2). This tendency was also found in 2,9-DClQA (Senju *et al.*, 2005).

As shown in Fig. 2(*a*), there are chains of N—H···O intermolecular hydrogen bonds along the $[1\overline{1}0]$ direction. One molecule is bonded to two neighbouring molecules through four hydrogen bonds. There is a small step of about 0.55 Å between the two molecular planes of the hydrogen-bonded molecules, as shown in Fig. 2(*b*). In commercial hydrogen-bonded pigments, there are normally no steps between molecules (Mizuguchi *et al.*, 1992, 1993) and this is a good criterion for strong hydrogen bonds. The existence of the step in (I) indicates a somewhat weaker hydrogen bond. This kind of step has also been found in the following pigments: 2,9-dimethylquinacridone (Mizuguchi *et al.*, 2002), modifications I and II of dithioketopyrrolopyrrole (Mizuguchi *et al.*, 1990), thiazine-indigo (Senju & Mizuguchi, 2003) and 2,9-DClQA (Senju *et al.*, 2005). In the present investigation, no significant difference in structure has been observed between 3,10-DClQA [(I)] and 2,9-DClQA, contrary to our expectation. Further investigation is now in progress in order to elucidate the origin of the difference in colour in the solid state.

Experimental

Compound (I) was purchased form Dainippon Ink & Chemicals Inc. and purified twice by sublimation using a two-zone furnace (Mizuguchi, 1981). Single crystals were grown from the vapour phase in a closed system at about 743 K. After 24 h, a number of red needle-shaped single crystals were obtained.

Crystal data

$C_{20}H_{10}Cl_2N_2O_2$
$M_r = 381.20$
Triclinic, $P\overline{1}$
$a = 3.7635$ (13) Å
$b = 5.853$ (2) Å
$c = 16.746$ (6) Å
$\alpha = 85.20$ (2)°
$\beta = 83.79$ (2)°
$\gamma = 89.32$ (2)°
$V = 365.4$ (2) Å^3

$Z = 1$
$D_x = 1.732$ Mg m^{-3}
Cu $K\alpha$ radiation
Cell parameters from 2796 reflections
$\theta = 10.7$–136.4°
$\mu = 4.17$ mm^{-1}
$T = 93.1$ K
Needle, red
0.10 × 0.05 × 0.02 mm

Data collection

Rigaku R-AXIS RAPID imaging-plate diffractometer
ω scans
Absorption correction: multi-scan (*ABSCOR*; Higashi, 1995)
$T_{\min} = 0.681$, $T_{\max} = 0.921$
3173 measured reflections

1254 independent reflections
1103 reflections with $F^2 > 2\sigma(F^2)$
$R_{\rm int} = 0.046$
$\theta_{\max} = 68.2°$
$h = -4 \rightarrow 4$
$k = -7 \rightarrow 6$
$l = -20 \rightarrow 20$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.057$
$wR(F^2) = 0.172$
$S = 1.13$
1254 reflections
119 parameters
H-atom parameters constrained

$w = 1/[\sigma^2(F_o^2) + (0.1114P)^2 + 0.1855P]$
where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\max} < 0.001$
$\Delta\rho_{\max} = 0.60$ e Å^{-3}
$\Delta\rho_{\min} = -0.38$ e Å^{-3}

Table 1
Selected bond lengths (Å).

Cl1—C3	1.744 (3)	C4—C5	1.414 (4)
O1—C7	1.236 (4)	C5—C6	1.400 (5)
N1—C5	1.371 (4)	C6—C7	1.454 (4)
N1—C9	1.380 (4)	C7—C8	1.482 (4)
C1—C2	1.357 (5)	C8—C10	1.392 (4)
C1—C6	1.421 (4)	C8—C9	1.413 (5)
C2—C3	1.400 (5)	C9—C10ⁱ	1.392 (5)
C3—C4	1.365 (4)		

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*
N1—H1*N*···O1ⁱⁱ	0.79	2.12	2.873 (4)	159

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

The H atom of the NH group was found in a difference density map and fixed in position during the refinement [$U_{\rm iso}$(H) = 0.021 Å^2]. All other H atoms were positioned geometrically and constrained to ride on their parent atoms, with C—H = 0.95 Å and $U_{\rm iso}$(H) = 1.2$U_{\rm eq}$(C).

Data collection: *PROCESS-AUTO* (Rigaku, 1998); cell refinement: *PROCESS-AUTO*; data reduction: *CrystalStructure* (Rigaku/MSC & Rigaku, 2005); program(s) used to solve structure: *SHELXS86* (Sheldrick, 1986); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *ORTEPIII* (Burnett & Johnson, 1996); software used to prepare material for publication: *CrystalStructure*.

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