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2,9-Dichloro-5,12-dihydroquino[2,3-*b*]acridine-7,14-dione (red phase)

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Key indicators

Single-crystal X-ray study
T = 93 K
Mean σ(C–C) = 0.005 Å
R factor = 0.056
wR factor = 0.178
Data-to-parameter ratio = 10.2

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

The title compound, $C_{20}H_{10}Cl_2N_2O_2$, is one of the quinacridone derivatives known as a red pigment. The molecule has inversion symmetry. The quinacridone molecules are connected by bifurcated N—H···O hydrogen bonds along [110] to form a two-dimensional hydrogen-bond network.

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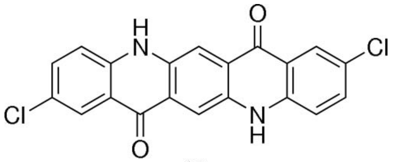
Comment

The title compound, (I), is one of the quinacridone derivatives (QA) known as a red pigment (Pigment Red 202; Herbst & Hunger, 1997) and typically characterized by N—H···O intermolecular hydrogen bonds. Unexpectedly, however, we have recently isolated black crystals that have no intermolecular hydrogen bonds, in contrast with ordinary quinacridone pigments (Senju *et al.*, 2005). The black crystals were obtained from the vapour phase at a lower-temperature region in a sublimation tube. In the same sublimation tube, tiny red crystals were also grown at a higher-temperature region. However, these crystals were too small for structure analysis. Therefore, another approach has been made in the present investigation to grow red crystals from solution, using an autoclave.



(I)

Fig. 1 shows an *ORTEPIII* (Burnett & Johnson, 1996) plot of the molecule. The molecule has inversion symmetry. The quinacridone skeleton is entirely planar, as indicated by the small 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 slightly [0.148 (4) Å] from the least-squares plane of the ring system towards the NH group of a neighbouring molecule for the formation of an N—H···O hydrogen bond. It is also to be noted that there is no ring deformation (C5–C9/N1) in the red phase, while the corresponding plane in the black phase is considerably distorted (Senju *et al.*, 2005).

Fig. 2 shows the molecular arrangement of (I). There are bifurcated N—H···O intermolecular hydrogen bonds between the NH group of one molecule and the O atom of a neighbouring one (Table 2). These interactions form a two-dimensional hydrogen-bond network. In addition, there is a small step of about 0.55 Å between the two molecular planes of the hydrogen-bonded molecules (Fig. 3). This kind of step has also been observed in other hydrogen-bonded pigments, such as 2,9-dimethylquinacridone (Mizuguchi *et al.*, 2002),

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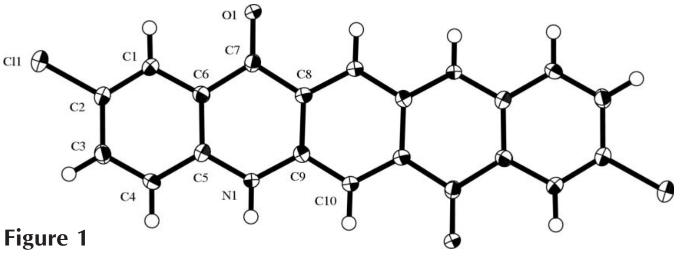

Figure 1
A view of the molecular structure of (I), showing 50% probability displacement ellipsoids for non-H atoms. The unlabelled atoms are related by the symmetry code ($1 - x$, $-y$, $1 - z$).

modifications I and II of dithioketopyrrolopyrroles (Mizuguchi *et al.*, 1990), and thiazine-indigo pigment (Senju & Mizuguchi, 2003).

The above-mentioned layered structure in the red phase provides a striking contrast with the molecular arrangement of the black phase (Senju *et al.*, 2005), in which there are no intermolecular hydrogen bonds and the molecules are arranged in a ‘hunter’s fence’ fashion (*viz*. the molecules form a grid-like structure when viewed from the side). Evidently, these two distinct colours (red and black) are primarily attributed to the difference in molecular arrangement. The correlation between colour and structure is now under investigation and will shortly be reported elsewhere (Senju & Mizuguchi, 2005).

Experimental

The title compound was purchased from Dainippon Ink & Chemicals Inc. and purified twice by sublimation using a two-zone furnace (Mizuguchi, 1981). Single crystals of (I) were grown by gradual cooling of an *N*-methyl-2-pyrrolidone solution prepared at about 473 K. After a week, a number of red platelet single crystals were obtained.

Crystal data

$C_{20}H_{10}Cl_2N_2O_2$
$M_r = 381.22$
Triclinic, $P\bar{1}$
$a = 3.7819$ (11) Å
$b = 5.8314$ (16) Å
$c = 16.754$ (4) Å
$\alpha = 94.956$ (16)°
$\beta = 95.136$ (17)°
$\gamma = 90.660$ (18)°
$V = 366.56$ (17) Å^3

$Z = 1$
$D_x = 1.727$ Mg m^{-3}
Cu $K\alpha$ radiation
Cell parameters from 2754 reflections
$\theta = 10.6$–136.1°
$\mu = 4.16$ mm^{-1}
$T = 93.1$ K
Platelet, red
$0.60 \times 0.40 \times 0.05$ mm

Data collection

Rigaku R-AXIS RAPID imaging-plate diffractometer
ω scans
Absorption correction: multi-scan (*ABSCOR*; Higashi, 1995)
$T_{\min} = 0.179$, $T_{\max} = 0.812$
3027 measured reflections

1217 independent reflections
1057 reflections with $F^2 > 2\sigma(F^2)$
$R_{\rm int} = 0.042$
$\theta_{\max} = 68.1°$
$h = -4 \rightarrow 4$
$k = -7 \rightarrow 7$
$l = -20 \rightarrow 20$

Refinement

Refinement on F^2
$R(F) = 0.056$
$wR(F^2) = 0.178$
$S = 1.14$
1217 reflections
119 parameters
H-atom parameters constrained

$w = 1/[\sigma^2(F_o^2) + (0.116P)^2 + 0.1655P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\max} < 0.001$
$\Delta\rho_{\max} = 0.50$ e Å^{-3}
$\Delta\rho_{\min} = -0.40$ e Å^{-3}

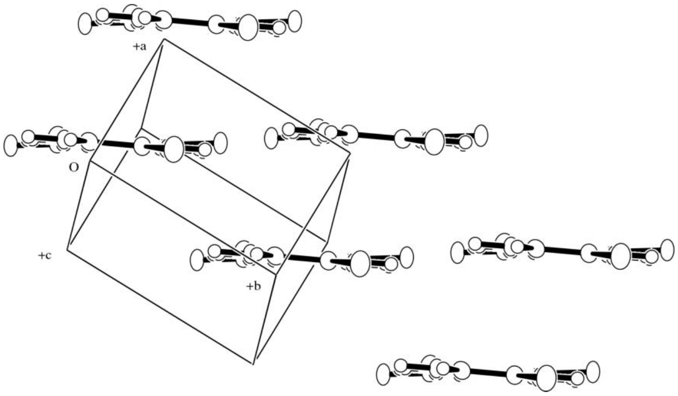

Figure 2
The packing arrangement of (I).

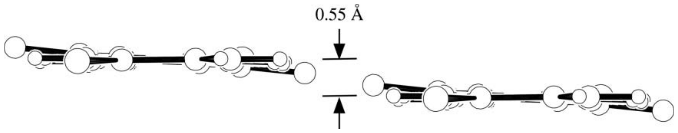

Figure 3
Side view of two hydrogen-bonded molecules. There is a small step of about 0.55 Å between the two molecular planes of the hydrogen-bonded molecules.

Table 1
Selected geometric parameters (Å, °).

Cl1—C2	1.743 (3)	C4—C5	1.411 (4)
O1—C7	1.243 (4)	C5—C6	1.412 (5)
N1—C5	1.369 (4)	C6—C7	1.459 (4)
N1—C9	1.377 (4)	C7—C8	1.466 (4)
C1—C2	1.360 (5)	C8—C10$^{\rm i}$	1.400 (5)
C1—C6	1.404 (4)	C8—C9	1.421 (5)
C2—C3	1.410 (5)	C9—C10	1.386 (5)
C3—C4	1.362 (4)		
C5—N1—C9	122.6 (3)	C5—C6—C7	120.7 (3)
C2—C1—C6	120.4 (3)	O1—C7—C6	122.3 (3)
C1—C2—C3	120.9 (3)	O1—C7—C8	121.8 (3)
C1—C2—Cl1	119.7 (3)	C6—C7—C8	115.8 (3)
C3—C2—Cl1	119.4 (3)	C10$^{\rm i}$—C8—C9	119.4 (3)
C4—C3—C2	119.6 (3)	C10$^{\rm i}$—C8—C7	120.1 (3)
C3—C4—C5	120.9 (3)	C9—C8—C7	120.5 (3)
N1—C5—C4	120.7 (3)	N1—C9—C10	120.4 (3)
N1—C5—C6	120.4 (3)	N1—C9—C8	119.9 (3)
C4—C5—C6	118.9 (3)	C10—C9—C8	119.7 (3)
C1—C6—C5	119.2 (3)	C9—C10—C8$^{\rm i}$	120.9 (3)
C1—C6—C7	120.1 (3)		

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

Table 2
Hydrogen-bonding geometry (Å, °).

D—H$\cdots A$	D—H	H$\cdots A$	$D\cdots A$	D—H$\cdots A$
N1—H1N$\cdots$O1$^{\rm ii}$	0.88	2.03	2.869 (3)	159

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

All H atoms were positioned geometrically and constrained to ride on their parent atoms with C—H = 0.95 Å and N—H = 0.88 Å, and $U_{\rm iso}({\rm H}) = 1.2U_{\rm eq}$(parent atom).

Data collection: *PROCESS-AUTO* (Rigaku, 1998); cell refinement: *PROCESS-AUTO*; data reduction: *CrystalStructure* (Rigaku/MSC, 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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