

2,9-Dichloro-5,12-dihydroquino[2,3-*b*]acridine-7,14-dioneTakatoshi Senju, Tomonori Hoki
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Key indicators

Single-crystal X-ray study
 $T = 93\text{ K}$
Mean $\sigma(\text{C}-\text{C}) = 0.012\text{ \AA}$
 R factor = 0.100
 wR factor = 0.350
Data-to-parameter ratio = 10.3For details of how these key indicators were
automatically derived from the article, see
<http://journals.iucr.org/e>.

The title compound, $\text{C}_{20}\text{H}_{10}\text{Cl}_2\text{N}_2\text{O}_2$, is an industrially important red pigment. The molecule has inversion symmetry. The molecule is not entirely planar, as shown by the dihedral angle of $176.7(3)^\circ$ between the planes of the benzene ring at the center and that at the extremity. The molecules are stacked in a 'hunter's fence' fashion (*i.e.* when viewed from the side, the molecules cross one another with an angle of about 50° in a grid-like structure) along the a axis.

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Comment

The title compound, (I), is known as a red pigment (Pigment Red 202; Herbst & Hunger, 1997). The present pigment is widely used in practice, side by side with 2,9-dimethylquinacridone (Pigment Red 122). The structure of PR122 was analyzed by Mizuguchi *et al.* (2002) and was found to possess a two-dimensional hydrogen-bond network based on $\text{N}-\text{H}\cdots\text{O}$ intermolecular hydrogen bonds between the NH group of one molecule and the carbonyl O atom of the neighboring one. This structure is quite different from the ordinary three-dimensional hydrogen-bond network of quinacridones, as characterized by a 'hunter's fence' structure, whereby one quinacridone molecule forms hydrogen bonds to four neighboring atoms. In the present paper, we report the structure of (I). Interestingly, the color of the single crystals of (I) is not red but black. In addition, the structure is very rare, because there are none of the intermolecular hydrogen bonds normally found in quinacridone pigments.

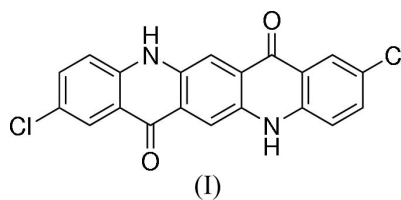


Fig. 1 shows an *ORTEP* (Burnett & Johnson, 1996) plot of the molecule, which has inversion symmetry. The C5–C9/N1 ring (ring *B*) is significantly deformed, as shown by the bond lengths and angles given in Table 1. This deformation exerts a profound influence on the benzene rings adjacent to ring *B* (rings *A* and *A'*). The dihedral angle between the planes of rings *A* and *B* is $177.9(3)^\circ$, while there is an angle of $176.7(3)^\circ$ between the planes of ring *A* and the C8/C9/C10ⁱ/C8ⁱ/C9ⁱ/C10 ring [ring *C*; symmetry code: (i) $2 - x, -y, 1 - z$]. This tendency can also be recognized in the dimethyl analog (PR122). The extent of the deformation is, however, much less and the molecule is almost planar (Mizuguchi *et al.*, 2002).

Fig. 2 shows the molecular packing, characterized by a 'hunter's fence' structure. The planes of the molecules form an

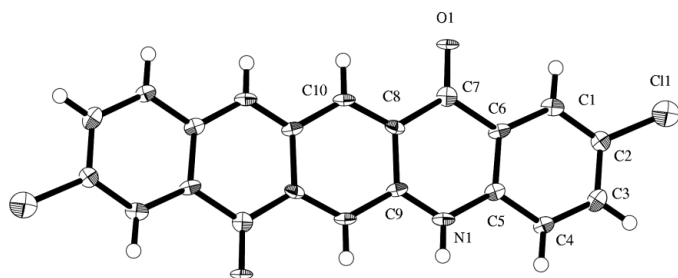


Figure 1
A view of the molecular structure of (I), showing 50% probability displacement ellipsoids for non-H atoms. The unlabeled atoms are related to the labeled atoms by the symmetry code (2 - x, -y, 1 - z).

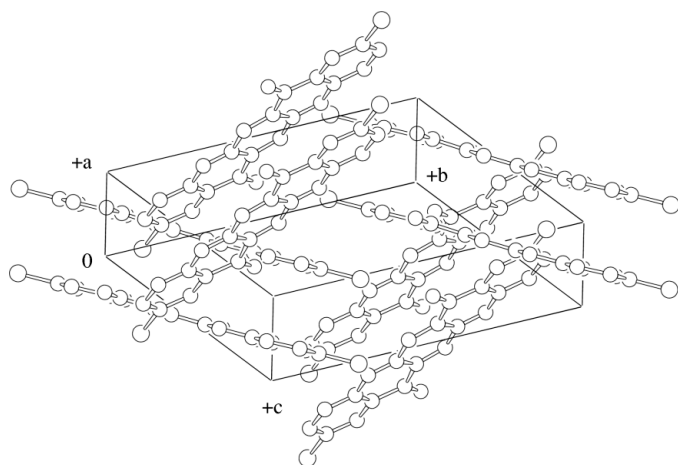


Figure 2
The molecular arrangement of (I). The molecules are arranged in a 'hunter's fence' fashion.

angle of about 50° when viewed from the side. There are short intermolecular contacts [H1 \cdots H1N($x, \frac{1}{2} - y, \frac{1}{2} + z$) of 1.99 Å and Cl1 \cdots O1($1 - x, \frac{1}{2} + y, \frac{3}{2} - z$) of 3.084 (6) Å]. The former interaction corresponds to the contact in which two molecules (each of which stems from a different column) cross each other when viewed from the side. The latter interaction occurs on the extended vector of the C—Cl bond toward the neighboring molecule in the next column. There are none of the N—H \cdots O intermolecular hydrogen bonds normally found in quinacridone pigments.

The crystal of (I) is black in color, largely because of excitonic interactions in the solid state, which are closely correlated with the molecular arrangement. The present interactions are typical of dyestuffs or pigments in which the extinction coefficient of the component molecule is high and the molecules are arranged periodically in the solid state (Mizuguchi & Shikamori, 2004). Details on the correlation between the structure and the black color of the crystal of (I) will be published shortly elsewhere (Senju & Mizuguchi, 2005).

Experimental

Compound (I) was purchased from Dainippon Ink and Chemicals Inc. and purified twice by sublimation using a two-zone furnace

(Mizuguchi, 1981). Single crystals were grown from the vapor phase in a closed system at about 773 K. After 24 h, a number of black needle-shaped crystals were obtained.

Crystal data

C₂₀H₁₀Cl₂N₂O₂
M_r = 381.20
Monoclinic, P2₁/c
a = 3.782 (1) Å
b = 14.840 (4) Å
c = 12.942 (3) Å
β = 91.93 (2)°
V = 726.0 (3) Å³
Z = 2

D_x = 1.744 Mg m⁻³
Cu Kα radiation
Cell parameters from 4881 reflections
θ = 3.0–68.1°
μ = 4.20 mm⁻¹
T = 93.1 K
Needle, black
0.40 × 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} = 0.677, T_{max} = 0.919
6026 measured reflections
1222 independent reflections
745 reflections with F² > 2σ(F²)
R_{int} = 0.078
θ_{max} = 68.2°
h = -3 → 3
k = -17 → 17
l = -15 → 15

Refinement

Refinement on F²
R(F) = 0.100
wR(F²) = 0.350
S = 1.14
1222 reflections
119 parameters
H-atom parameters constrained

w = 1/[σ²(F_o²) + (0.1985P)² + 2.3331P]
where P = (F_o² + 2F_c²)/3
(Δσ)_{max} < 0.001
Δρ_{max} = 0.56 e Å⁻³
Δρ_{min} = -0.93 e Å⁻³

Table 1

Selected geometric parameters (Å, °).

Cl1—C2	1.691 (9)	C4—C5	1.39 (1)
O1—C7	1.24 (1)	C5—C6	1.44 (1)
N1—C5	1.39 (1)	C6—C7	1.48 (1)
N1—C9	1.30 (1)	C7—C8	1.47 (1)
C1—C2	1.39 (1)	C8—C9	1.47 (1)
C1—C6	1.39 (1)	C8—C10	1.36 (1)
C2—C3	1.40 (1)	C9—C10 ⁱ	1.43 (1)
C3—C4	1.39 (1)		
Cl1—C2—C1	121.5 (7)	C1—C6—C5	119.6 (8)
Cl1—C2—C3	117.6 (7)	C2—C3—C4	119.5 (8)
O1—C7—C6	121.5 (8)	C3—C4—C5	120.8 (8)
O1—C7—C8	122.8 (8)	C4—C5—C6	119.0 (8)
N1—C5—C6	123.4 (7)	C5—C6—C7	118.5 (7)
N1—C5—C4	117.6 (7)	C6—C7—C8	115.7 (7)
C9—N1—C5	119.4 (7)	C7—C8—C10	121.7 (7)
N1—C9—C8	123.9 (7)	C7—C8—C9	118.9 (7)
N1—C9—C10 ⁱ	118.3 (7)	C10—C8—C9	119.3 (7)
C1—C2—C3	120.9 (8)	C8—C9—C10 ⁱ	117.7 (7)
C6—C1—C2	120.1 (8)	C8—C10—C9 ⁱ	123.0 (7)
C1—C6—C7	121.9 (7)		

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

All H atoms were positioned geometrically and included in the riding-model approximation [C—H = 0.93 Å, N—H = 0.86 Å and U_{iso}(H) = 1.2U_{eq}(C)].

Data collection: *PROCESS-AUTO* (Rigaku Corporation, 1998); cell refinement: *PROCESS-AUTO*; data reduction: *CrystalStructure* (Rigaku/MSK & Rigaku Corporation, 2004); program(s) used to solve structure: *SIR2002* (Burla *et al.*, 2003); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *ORTEP III* (Burnett & Johnson, 1996); software used to prepare material for publication: *CrystalStructure*.

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