

Structure of 1-Amino-4-hydroxy-2-phenoxy-9,10-anthracenedione

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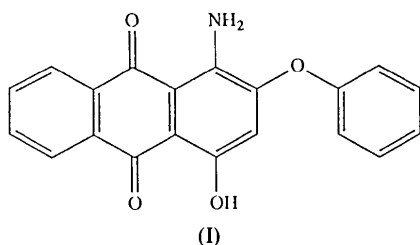
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Abstract. $C_{20}H_{13}NO_4$, $M_r = 331.3$, monoclinic, $P2_1/n$, $a = 14.972$ (3), $b = 5.141$ (1), $c = 19.853$ (3) Å, $\beta = 94.15$ (2)°, $V = 1524$ (1) Å³, $Z = 4$, $D_x = 1.44$ Mg m⁻³, Cu $K\alpha$ radiation, $\lambda = 1.54178$ Å, $\mu = 0.8$ mm⁻¹, $F(000) = 688$, room temperature, $R = 0.043$ for 1575 observed reflections with $|F_o| > 3\sigma(|F_o|)$. The dihedral angle between the phenoxy and anthraquinone rings is 97°. The molecules stack with a 3.4 Å interplanar separation in the **b** direction.

Introduction. As part of a broad study of the crystallization behaviour of dyes, and to provide templates for molecular-modelling studies, the crystal structure of the red dye (I) was determined.



Experimental. Red platey crystals with large {101} faces were grown at room temperature from methylene chloride. Crystal size 0.13 × 0.20 × 0.50 mm. Refined unit-cell parameters obtained from setting angles of 20 reflections with $8 < \theta < 29^\circ$. Nicolet R3m diffractometer. 2257 measured, 1920 independent ($R_{int} = 0.026$) reflections ($\theta < 55^\circ$), Cu $K\alpha$ radiation (graphite monochromator), ω scan. 1575 reflections [$|F_o| > 3\sigma(|F_o|)$] considered observed, index range $h - 15/15$, $k 0/5$, $l 0/21$, two check reflections measured every 50 reflections, no significant decomposition, 5% variation; data brought to uniform scale, Lorentz and polarization corrections. Structure solved by direct methods; non-H atoms refined anisotropically. Positions of the hydroxy H atoms on O(4) and N(1) were located from a ΔF map and refined subject to an O—H and an N—H distance constraint respectively. The posi-

tions of the remaining H atoms were calculated (C—H 0.96 Å) assigned isotropic thermal parameters and allowed to ride on their parent C atoms. An empirical extinction correction was applied [$g = 0.010$ (1)]. Refinement using F magnitudes by block-cascade full-matrix least squares; $R = 0.043$, $wR = 0.048$ [$w^{-1} = \sigma^2(F) + 0.00051F^2$]. $S = 1.54$; 239 refined parameters. $(\Delta/\sigma)_{max} = 0.13$ e Å⁻³; residual electron density in difference map within -0.12 and 0.16 e Å⁻³; atomic scattering factors and dispersion corrections from *International Tables for X-ray Crystallography* (1974, Vol. IV). Computations carried out on an Eclipse S140 computer using the *SHELXTL* program system (Sheldrick, 1983).

Discussion. Table 1* lists the fractional atomic coordinates of the non-H atoms, Table 2 lists bond lengths and angles, and selected torsion angles. The structure of (I) is illustrated in Fig. 1 which includes the atom-numbering scheme. The anthraquinone ring is planar to within 0.063 Å [for C(2)]; O(2) lies 0.10 Å out of this plane. There are notable perturbations in the bonding patterns in the anthraquinone ring. The bonds within the terminal ring *A* are normal for aromatics. With the exception of C(7)—C(12) (1.399 Å), the bonds in the central ring *B* show varying degrees of single-bond character, and there is an appreciable lengthening of the associated C=O distances [1.257 (3) Å for C(6)—O(6) and 1.244 (3) Å for C(13)—O(13)]. In the remaining ring *C* there is a pattern of alternation of bond lengths with C(2)—C(3), C(4)—C(5) and C(1)—C(14) being the shorter. There is an angle of 97° between the anthraquinone plane and the plane of the phenoxy ring (*D*). This

* Lists of structure factors, anisotropic thermal parameters, torsion angles, bond lengths and bond angles involving H atoms, and H-atom parameters have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 54557 (36 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England. [CIF reference: HE0026]

Table 1. Atom coordinates ($\times 10^4$) and temperature factors ($\text{\AA}^2 \times 10^3$) with *e.s.d.*'s in parentheses

	<i>x</i>	<i>y</i>	<i>z</i>	<i>U</i> _{eq}
N(1)	7242 (1)	11246 (4)	2002 (1)	60 (1)*
C(1)	7073 (1)	9362 (4)	1531 (1)	51 (1)*
C(2)	6161 (2)	8962 (4)	1289 (1)	54 (1)*
O(2)	5584 (1)	10624 (3)	1576 (1)	71 (1)*
C(3)	5918 (2)	7162 (5)	812 (1)	59 (1)*
C(4)	6576 (2)	5572 (4)	549 (1)	52 (1)*
O(4)	6289 (1)	3809 (3)	80 (1)	67 (1)*
C(5)	7473 (1)	5833 (4)	780 (1)	49 (1)*
C(6)	8129 (2)	4113 (5)	520 (1)	56 (1)*
O(6)	7916 (1)	2456 (4)	71 (1)	73 (1)*
C(7)	9071 (2)	4303 (4)	788 (1)	55 (1)*
C(8)	9704 (2)	2620 (6)	560 (1)	71 (1)*
C(9)	10588 (2)	2762 (6)	810 (1)	78 (1)*
C(10)	10840 (2)	4582 (6)	1293 (1)	80 (1)*
C(11)	10221 (2)	6296 (6)	1533 (1)	72 (1)*
C(12)	9327 (1)	6155 (5)	1281 (1)	56 (1)*
C(13)	8661 (2)	7977 (5)	1546 (1)	54 (1)*
O(13)	8912 (1)	9581 (3)	1989 (1)	69 (1)*
C(14)	7728 (1)	7759 (4)	1281 (1)	47 (1)*
C(15)	4668 (2)	10032 (5)	1533 (1)	59 (1)*
C(16)	4111 (2)	11542 (6)	1126 (1)	73 (1)*
C(17)	3209 (2)	11139 (6)	1110 (2)	87 (1)*
C(18)	2868 (2)	9296 (6)	1501 (2)	86 (1)*
C(19)	3426 (2)	7735 (6)	1910 (2)	92 (1)*
C(20)	4356 (2)	8105 (6)	1927 (1)	78 (1)*

* Equivalent isotropic *U* defined as one third of the trace of the orthogonalized *U*_{*ij*} tensor.

rotation is comprised of torsional rotations about the C(2)—O(2) and O(2)—O(15) bonds of *ca* 18 and 73° respectively.

There are intramolecular hydrogen bonds between the amine hydrogens and O(2) and O(13) [N(1)⋯O(2) 2.58, H(1*a*)⋯O(2) 2.14 Å, N—H⋯O angle 106°; N(1)⋯O(13) 2.65, H(1*b*)⋯O(13) 1.90 Å, N—H⋯O angle 131°] and between the hydroxy oxygen O(4) and the carbonyl oxygen O(6) [O(4)⋯O(6) 2.54, H(4)⋯O(6) 1.64 Å, O—H⋯O angle 149°]. There are no intermolecular hydrogen bonds. The molecular axes lie along the $\langle 110 \rangle$ directions.

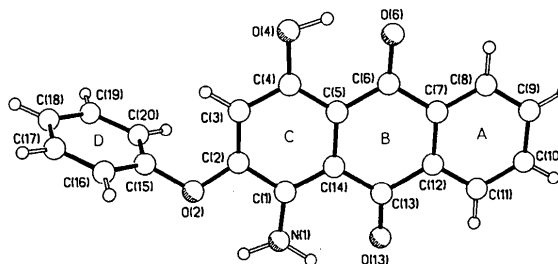


Fig. 1. Ball and stick representation of the structure of (I) showing atom-numbering scheme.

Table 2. Bond lengths (Å), bond angles (°) and selected torsion angles (°) with *e.s.d.*'s in parentheses

N(1)—C(1)	1.357 (3)	C(1)—C(2)	1.429 (3)
C(1)—C(14)	1.399 (3)	C(2)—O(2)	1.369 (3)
C(2)—C(3)	1.355 (3)	O(2)—C(15)	1.402 (3)
C(3)—C(4)	1.409 (3)	C(4)—O(4)	1.348 (3)
C(4)—C(5)	1.394 (3)	C(5)—C(6)	1.444 (3)
C(5)—C(14)	1.436 (3)	C(6)—O(6)	1.257 (3)
C(6)—C(7)	1.475 (3)	C(7)—C(8)	1.384 (4)
C(7)—C(12)	1.399 (3)	C(8)—C(9)	1.382 (3)
C(9)—C(10)	1.372 (4)	C(10)—C(11)	1.388 (4)
C(11)—C(12)	1.397 (3)	C(12)—C(13)	1.492 (3)
C(13)—O(13)	1.244 (3)	C(13)—C(14)	1.461 (3)
C(15)—C(16)	1.362 (3)	C(15)—C(20)	1.365 (4)
C(16)—C(17)	1.364 (4)	C(17)—C(18)	1.348 (4)
C(18)—C(19)	1.380 (4)	C(19)—C(20)	1.403 (4)

N(1)—C(1)—C(2)	117.4 (2)	N(1)—C(1)—C(14)	124.4 (2)
C(2)—C(1)—C(14)	118.2 (2)	C(1)—C(2)—O(2)	112.7 (2)
C(1)—C(2)—C(3)	122.4 (2)	O(2)—C(2)—C(3)	124.9 (2)
C(2)—O(2)—C(15)	118.9 (2)	C(2)—C(3)—C(4)	119.6 (2)
C(3)—C(4)—O(4)	116.7 (2)	C(3)—C(4)—C(5)	120.4 (2)
O(4)—C(4)—C(5)	122.9 (2)	C(4)—C(5)—C(6)	119.2 (2)
C(4)—C(5)—C(14)	119.7 (2)	C(6)—C(5)—C(14)	121.1 (2)
C(5)—C(6)—O(6)	121.6 (2)	C(5)—C(6)—C(7)	119.2 (2)
O(6)—C(6)—C(7)	119.2 (2)	C(6)—C(7)—C(8)	120.0 (2)
C(6)—C(7)—C(12)	120.3 (2)	C(8)—C(7)—C(12)	119.7 (2)
C(7)—C(8)—C(9)	120.6 (2)	C(8)—C(9)—C(10)	119.7 (3)
C(9)—C(10)—C(11)	121.1 (2)	C(10)—C(11)—C(12)	119.4 (2)
C(7)—C(12)—C(11)	119.5 (2)	C(7)—C(12)—C(13)	121.2 (2)
C(11)—C(12)—C(13)	119.3 (2)	C(12)—C(13)—O(13)	119.3 (2)
O(13)—C(13)—C(14)	118.1 (2)	O(13)—C(13)—C(14)	122.6 (2)
C(1)—C(14)—C(5)	119.7 (2)	C(1)—C(14)—C(13)	120.2 (2)
C(5)—C(14)—C(13)	120.1 (2)	O(2)—C(15)—C(16)	117.9 (2)
O(2)—C(15)—C(20)	119.7 (2)	C(16)—C(15)—C(20)	122.3 (2)
C(15)—C(16)—C(17)	119.3 (3)	C(16)—C(17)—C(18)	120.5 (3)
C(17)—C(18)—C(19)	120.7 (3)	C(18)—C(19)—C(20)	119.5 (3)
C(15)—C(20)—C(19)	117.7 (2)		

C(3)—C(2)—O(2)—C(15)	18.8 (3)	C(2)—O(2)—C(15)—C(20)	74.6 (3)
C(1)—C(2)—O(2)—C(15)	-163.0 (2)	C(2)—O(2)—C(15)—C(16)	-109.6 (3)

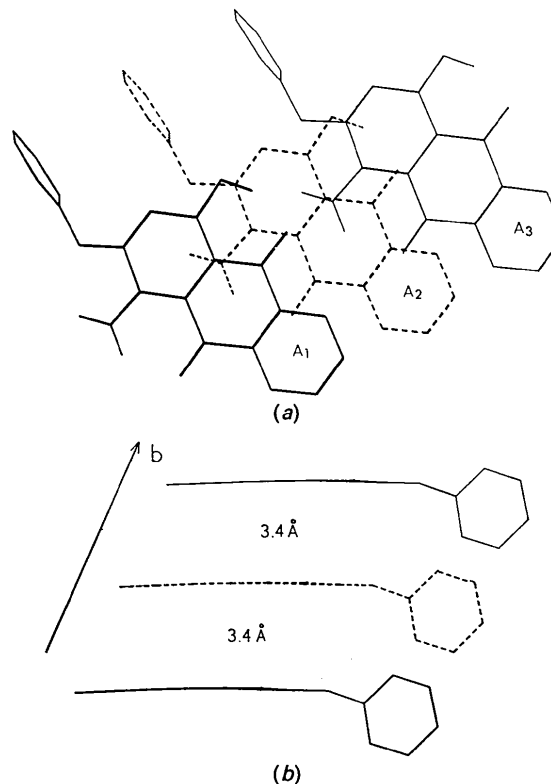


Fig. 2. (a) Plan and (b) elevation, of the molecular stacking in the *b* direction in the crystals. The sequence within the stack is *A*₁, *A*₂, *A*₃.

The molecules form stacks in the crystallographic **b** direction (Figs. 2*a,b*) with an interplanar separation of 3.4 Å.

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Structure of 1-Butyl-5-[(4-chlorophenyl)azo]-1,2,5,6-tetrahydro-4-methyl-2,6-dioxo-3-pyridinecarbonitrile

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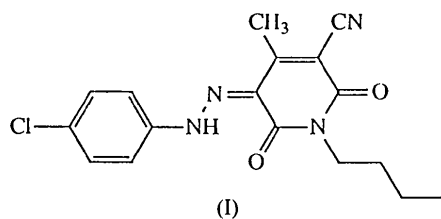
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Abstract. C₁₇H₁₇ClN₄O₂, *M_r* = 344.8, monoclinic, *P*2₁/*c*, *a* = 7.586 (2), *b* = 11.429 (4), *c* = 19.592 (8) Å, β = 93.52 (3)°, *V* = 1695 (1) Å³, *Z* = 4, *D_x* = 1.35 Mg m⁻³, Cu *K*α radiation, λ = 1.54178 Å, μ = 2.19 mm⁻¹, *F*(000) = 776, room temperature, *R* = 0.045 for 1499 observed reflections with |*F_o*| > 3σ(|*F_o*|). The molecule has an essentially planar and highly conjugated geometry reinforced by an intramolecular NH⋯O hydrogen bond. The molecules form parallel overlapping stacks in the crystal.

Introduction. As part of a general study of the crystal chemistry of dyes and to provide templates for molecular-modelling studies, the crystal structure of the yellow dye (I) was determined.



Experimental. Orange acicular single crystals, bounded by {011} faces, suitable for X-ray crystallography were grown at room temperature from methyl ethyl ketone. Crystal size 0.09 × 0.01 × 0.50 mm. Refined unit-cell parameters obtained from setting angles of 18 reflections with 9 < θ < 30°. Nicolet *R3m* diffractometer. 2030 measured, 1748 independent (*R_{int}* = 0.053) reflections (θ < 50°), Cu *K*α radiation (graphite monochromator), ω scan. 1499 reflections [|*F_o*| > 3σ(|*F_o*|)] considered observed, index range *h* -7/7, *k* 0/11, *l* 0/19, two check reflections measured every 50 reflections, no

significant decomposition, 5% variation; data brought to uniform scale, Lorentz and polarization corrections, numerical absorption correction, minimum and maximum transmission factors 0.67 and 0.83. Structure solved by direct methods; non-H atoms refined anisotropically; position of H atom on N(11) and orientation of methyl hydrogens on C(18) determined from a Δ*F* map. H atom on N(11) refined isotropically subject to an N—H distance constraint; remaining H-atom positions calculated (C—H 0.96 Å), assigned isotropic thermal parameters and allowed to ride on their parent C atoms. Methyl groups refined as rigid bodies. An empirical extinction correction was applied [*g* = 0.0036 (7)]. Refinement using *F* magnitudes by block-cascade full-matrix least squares; *R* = 0.045, *wR* = 0.49 [*w*⁻¹ = σ²(*F*) + 0.00068*F*²]. *S* = 1.56; 228 refined parameters. (Δ/σ)_{max} = 0.017 e Å⁻³; residual electron density in difference map within -0.17 and 0.21 e Å⁻³; atomic scattering factors and dispersion corrections from *International Tables for X-ray Crystallography* (1974, Vol. IV). Computations carried out on an Eclipse S140 computer using the *SHELXTL* program system (Sheldrick, 1983).

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