

## Structure of 1-{[4-(Dimethylamino)phenyl]amino}-4-hydroxy-9,10-anthracenedione

BY JOACHIM KURT FOITZIK, HELMUT PAULUS AND WOLFGANG HAASE

Institut für Physikalische Chemie, Technische Hochschule Darmstadt, Petersenstrasse 20, D-6100 Darmstadt, Federal Republic of Germany

(Received 22 December 1984; accepted 20 September 1985)

**Abstract.**  $C_{22}H_{18}N_2O_3$ ,  $M_r = 358.4$ , triclinic,  $P\bar{1}$ ,  $a = 9.883$  (1),  $b = 9.771$  (1),  $c = 9.623$  (1) Å,  $\alpha = 107.563$  (4),  $\beta = 94.324$  (4),  $\gamma = 100.319$  (4)°,  $V = 863.3$  Å<sup>3</sup>,  $Z = 2$ ,  $D_m = 1.33$  (3),  $D_x = 1.379$  g cm<sup>-3</sup>,  $\lambda(\text{Mo } K\alpha) = 0.71069$  Å,  $\mu = 0.54$  cm<sup>-1</sup>,  $F(000) = 376$ ,  $T = 296$  K, final  $R = 0.0444$  for 2020 unique observed reflections. The torsion angle between the phenyl ring and the anthraquinone part of the molecule is 69.5° and that between the phenyl ring and the dimethylamino group is 14.4°. The crystal packing shows an alternating stacking of phenyl groups and anthraquinone groups respectively.

**Introduction.** The title compound is a pleochroic dye (D-27, according to BDH nomenclature) applicable in guest–host systems for liquid-crystal displays (Pellatt, Roe & Constant, 1980). As part of an investigation concerning properties of liquid crystalline phases (hosts) and non-mesogenic solutes (guests) and interactions between guest and host molecules (Foitzik & Haase, 1983; Foitzik, Paulus & Haase, 1985), the molecular and crystal structure of D-27 has been determined.

**Experimental.** Substance from BDH Chemicals Ltd, no further purification; thin blue needles by slow evaporation of a solution in  $\text{CHCl}_3$ ;  $D_m$  by flotation in  $\text{CCl}_4/1,4$ -dioxane; lattice parameters and e.s.d.'s at 296 K from least-squares refinement of 72 reflections,  $13.0 < 2\theta < 40.2^\circ$ ; Stoe–Siemens AED-2 diffractometer; 4494 intensities measured,  $-11 < h, k, l < 11$ , max.  $\sin\theta/\lambda = 0.5376$  Å<sup>-1</sup>; three standard reflections (131, 210,  $1\bar{1}2$ ), intensity variations <3%; 2247 unique reflections,  $R_{\text{int}} = 0.0329$ , 227 reflections classified as unobserved with  $F_o < 2\sigma(F_o)$ ; no absorption correction; structure solved by direct methods (MULTAN80; Main, Fiske, Hull, Lessinger, Germain, Declercq & Woolfson, 1980); atomic scattering factors from *International Tables for X-ray Crystallography* (1974); all H atoms from difference Fourier map; however, for comparison with other structures of this series (Foitzik, Paulus & Haase, 1986), H atoms bound to C atoms placed at calculated positions (C–H = 1.08 Å), O- and N-bound H atoms refined; all H atoms with isotropic thermal parameters fixed using a factor of  $\approx 1.1$  to the

average value of the diagonal elements of the carrying atom (SHELX76, Sheldrick, 1976); 257 parameters refined on  $F$  giving  $R = 0.0444$ ,  $wR = 0.0488$ ;  $w = k/\sigma^2(F_o)$ , max.  $\Delta/\delta$  0.05; max. 0.14, min.  $-0.17$  e Å<sup>-3</sup> in final difference Fourier synthesis; secondary-extinction coefficient  $4.7 \times 10^{-7}$ ; all calculations performed using the Data General Eclipse S 140 computer and the program package developed in the application laboratory of Stoe & Cie (Darmstadt) and the IBM computer of the Technische Hochschule Darmstadt.

**Discussion.** The atomic coordinates are listed in Table 1.\* Some bond distances and angles for the non-H atoms and H(1N) and H(3O) are shown in Table 2. The D-27 molecule with the atom-numbering scheme is presented in Fig. 1. The anthraquinone system and the phenyl ring are arranged nearly perpendicular to each other with a torsion angle of 69.5° between the best plane through C(1)–C(14), O(1) and O(2) and the best plane through C(15)–C(20). The torsion angle between the phenyl ring and the dimethylamino group is 14.4°. The positions of the atoms H(3O) and H(1N) in the anthraquinone plane and the short contacts of 1.667 [H(3O)···O(1)] and 1.859 Å [H(1N)···O(2)] to the carbonyl O atoms confirm the occurrence of intramolecular hydrogen bonds, which are advantageous for the applicability of these dyes in liquid-crystal displays (Pellatt *et al.*, 1980).

Fig. 2 shows a projection of the crystal structure along [001]. The phenyl rings are oriented almost parallel to the  $c$  axis. The anthraquinone parts of the molecules – necessarily coplanar because of the inversion center in  $\frac{1}{2}, 0, \frac{1}{2}$  – are arranged in pairs along the  $b$  axis. The shortest distances between non-H atoms of the adjoining anthraquinone rings are about 3.5 Å. Similarly two phenyl rings of two other molecules are stacked parallel to each other across the center of

\* Lists of structure factors, anisotropic thermal parameters, H-atom coordinates, least-squares planes and bond distances and angles have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 42510 (16 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

symmetry at 0,0,0 with shortest intermolecular distances of again 3.5 Å. Therefore a stacking of phenyl and anthraquinone pairs is found respectively, in the direction of the *b* axis and an alternation of phenyl and anthraquinone layers in the [100] direction.

Table 1. Atomic positional parameters and equivalent isotropic temperature factors ( $\text{\AA}^2 \times 10^3$ ) with e.s.d.'s in parentheses

$$U_{eq} = \frac{1}{3} [U_{11}(aa^*)^2 + U_{22}(bb^*)^2 + U_{33}(cc^*)^2 + 2U_{12}aa^*bb^*\cos\gamma + 2U_{13}aa^*cc^*\cos\beta + 2U_{23}bb^*cc^*\cos\alpha].$$

	<i>x</i>	<i>y</i>	<i>z</i>	$U_{eq}$
C(1)	0.2666 (2)	0.0988 (2)	0.6158 (2)	47
C(2)	0.3069 (2)	0.2546 (2)	0.6627 (2)	52
C(3)	0.3856 (2)	0.3258 (2)	0.5867 (2)	55
C(4)	0.4297 (2)	0.2466 (2)	0.4561 (2)	53
C(5)	0.3926 (2)	0.0945 (2)	0.4050 (2)	45
C(6)	0.4385 (2)	0.0152 (2)	0.2687 (2)	49
C(7)	0.3949 (2)	-0.1454 (2)	0.2112 (2)	45
C(8)	0.4318 (2)	-0.2221 (2)	0.0766 (2)	53
C(9)	0.3929 (2)	-0.3728 (2)	0.0237 (2)	58
C(10)	0.3175 (2)	-0.4493 (2)	0.1029 (2)	61
C(11)	0.2795 (2)	-0.3736 (2)	0.2358 (2)	57
C(12)	0.3178 (2)	-0.2207 (2)	0.2907 (2)	46
C(13)	0.2743 (2)	-0.1414 (2)	0.4323 (2)	50
C(14)	0.3099 (2)	0.0168 (2)	0.4851 (2)	44
O(1)	0.5132 (2)	0.0818 (2)	0.2001 (2)	68
O(2)	0.2070 (2)	-0.2151 (2)	0.4990 (2)	74
O(3)	0.5076 (2)	0.3245 (2)	0.3857 (2)	78
H(3O)	0.5282 (23)	0.2565 (26)	0.3022 (26)	80†
N(1)	0.1900 (2)	0.0314 (2)	0.6972 (2)	62
H(1N)	0.1768 (21)	-0.0713 (23)	0.6639 (22)	65†
C(15)	0.1445 (2)	0.1036 (2)	0.8330 (2)	54
C(16)	0.1993 (2)	0.0869 (2)	0.9615 (2)	57
C(17)	0.1531 (2)	0.1501 (2)	1.0931 (2)	57
C(18)	0.0496 (2)	0.2310 (2)	1.0999 (2)	53
C(19)	-0.0044 (2)	0.2481 (2)	0.9688 (2)	58
C(20)	0.0426 (2)	0.1838 (2)	0.8372 (2)	61
N(3)	0.0007 (2)	0.2897 (2)	1.2319 (2)	68
C(27)	0.0791 (2)	0.3003 (3)	1.3686 (2)	70
C(28)	-0.1034 (3)	0.3757 (3)	1.2386 (3)	81

†  $U_{iso}$ .

Table 2. Selected bond distances (Å) and angles (°) with e.s.d.'s in parentheses

C(1)–C(2)	1.422 (3)	C(9)–C(10)	1.387 (3)
C(1)–C(14)	1.415 (3)	C(10)–C(11)	1.387 (3)
C(1)–N(1)	1.357 (2)	C(11)–C(12)	1.395 (3)
C(2)–C(3)	1.350 (3)	C(12)–C(13)	1.487 (3)
C(3)–C(4)	1.408 (3)	C(13)–C(14)	1.441 (3)
C(4)–C(5)	1.387 (3)	C(13)–O(2)	1.243 (2)
C(4)–O(3)	1.346 (2)	O(3)–H(3O)	0.938 (23)
C(5)–C(6)	1.459 (3)	N(1)–H(1N)	0.937 (21)
C(5)–C(14)	1.437 (2)	N(1)–C(15)	1.434 (2)
C(6)–C(7)	1.468 (3)	C(18)–N(3)	1.388 (2)
C(6)–O(1)	1.251 (2)	N(3)–C(27)	1.441 (3)
C(7)–C(8)	1.398 (3)	N(3)–C(28)	1.435 (3)
C(7)–C(12)	1.391 (3)		
C(8)–C(9)	1.376 (3)		
N(1)–C(1)–C(2)	120.0 (2)	H(1N)–N(1)–C(1)	114.1 (1.3)
N(1)–C(1)–C(14)	121.3 (2)	C(15)–N(1)–H(1N)	119.7 (1.3)
O(3)–C(4)–C(3)	117.3 (2)	C(16)–C(15)–N(1)	119.2 (2)
O(3)–C(4)–C(5)	122.6 (2)	C(20)–C(15)–N(1)	121.5 (2)
O(1)–C(6)–C(5)	121.2 (2)	N(3)–C(18)–C(17)	120.7 (2)
O(1)–C(6)–C(7)	119.7 (2)	N(3)–C(18)–C(19)	121.7 (2)
O(2)–C(13)–C(12)	118.3 (2)	C(27)–N(3)–C(18)	119.7 (2)
O(2)–C(13)–C(14)	122.8 (2)	C(28)–N(3)–C(18)	120.4 (2)
H(3O)–O(3)–C(4)	106.8 (1.4)	C(28)–N(3)–C(27)	117.7 (2)
C(15)–N(1)–C(1)	125.7 (2)		

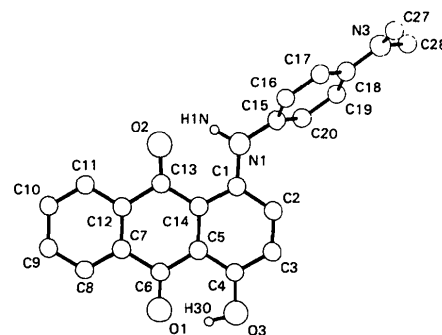


Fig. 1. D-27 molecule with labeling scheme. H atoms except H(1N) and H(3O) have been omitted.

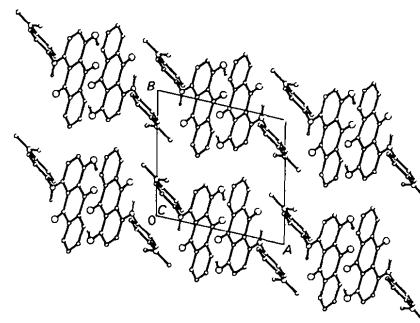


Fig. 2. Crystal structure of D-27 projected along the crystallographic [001] line.

## References

- FOITZIK, J. K. & HAASE, W. (1983). *Mol. Cryst. Liq. Cryst.* **97**, 231–240.
- FOITZIK, J. K., PAULUS, H. & HAASE, W. (1985). *Mol. Cryst. Liq. Cryst. Lett.* **1**, 1–7.
- FOITZIK, J. K., PAULUS, H. & HAASE, W. (1986). *Acta Cryst.* **C42**, 108–109.
- International Tables for X-ray Crystallography* (1974). Vol. IV. Birmingham: Kynoch Press. (Present distributor D. Reidel, Dordrecht.)
- MAIN, P., FISKE, S. J., HULL, S. E., LESSINGER, L., GERMAIN, G., DECLERCQ, J.-P. & WOOLFSON, M. M. (1980). *MULTAN80. A System of Computer Programs for the Automatic Solution of Crystal Structures from X-ray Diffraction Data*. Univ. of York, England, and Louvain, Belgium.
- PELLATT, M. G., ROE, I. H. C. & CONSTANT, J. (1980). *Mol. Cryst. Liq. Cryst.* **59**, 299–316.
- SHELDRICK, G. M. (1976). *SHELX76*. Program for crystal structure determination. Univ. of Cambridge, England.