Structure of 1,5-Bis{[4-(pentyloxy)phenyl]amino}-9,10-anthracenedione

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Abstract. $C_{36}H_{38}N_2O_4$, $M_r = 562.7$, triclinic, $P\bar{1}$, $a = 15.104$ (4), $b = 8.824$ (3), $c = 5.850$ (2) Å, $\alpha = 101.22$ (1), $\beta = 99.46$ (1), $\gamma = 92.58$ (1)°, $V = 751.98$ Å^3, $Z = 1$, $D_x = 1.242$ g cm^{-3}, $\lambda(Mo\ K\alpha) = 0.71069$ Å, $\mu = 0.45$ cm^{-1}, $F(000) = 300$, $T = 297$ K, final $R = 0.0644$ for 1475 unique observed reflections. The torsion angle between the phenyl ring and the anthraquinone part of the molecule is 75.1°. The terminal alkyl chain is fully extended. The torsion angle between the best planes through the anthraquinone ring and the alkyl chain is 18.0°.

Introduction. Structure determinations of pleochroic dyes, applicable for 'guest–host' liquid-crystal displays (GH-LCD), are part of an investigation concerning the interaction of mesogenic and non-mesogenic compounds (Foitzik & Haase, 1983; Foitzik, Paulus & Haase, 1986). The crystal and molecular structure of the title compound (D-43, according to the BDH nomenclature) has been determined and is discussed in relation to the structure of 1-{[4-(dimethyl-amino)phenyl]amino}-4-hydroxy-9,10-anthracenedione (D-27).

Experimental. Substance from BDH, Poole, UK, no further purification; red plates by slow evaporation of a solution in CHCl$_3$/cyclohexane; D_m not determined; $0.800 \times 0.358 \times 0.027$ mm; cell constants and e.s.d.'s at 297 K from least-squares refinement of 42 reflections, $13.0 < 2\theta < 39.2°$; Stoe–Stadi four-circle diffractometer; 2125 intensities measured, $-16 \le h \le 16$, $-9 \le k \le 9$, $-6 \le l \le 0$, max. $\sin\theta/\lambda = 0.5385$ Å^{-1}; two standard reflections (310, 12$\bar{1}$), intensity variation <4%; 1736 unique reflections, $R_{int} = 0.0263$, 261 reflections unobserved with $F_o < 2\sigma(F_o)$; no absorption correction; structure solved by direct methods (*SHELX*76; Sheldrick, 1976); all H atoms but those of the alkyl chain from difference Fourier synthesis; all C-bound H atoms placed at calculated positions (C–H = 1.08 Å) with isotropic thermal parameters, fixed at 1.1 U_{eq} of the appropriate C atom; H(1N) refined with fixed isotropic thermal parameter; 197 parameters refined (on F) giving $R = 0.0644$, $wR = 0.0510$; $w = 1.6771/\sigma^2(F_o)$, max. Δ/σ 0.03; max.

0.19, min. -0.21 e Å^{-3} in final difference Fourier synthesis; secondary-extinction coefficient 3.3×10^{-7}; atomic scattering factors from *International Tables for X-ray Crystallography* (1974); all calculations performed on the IBM 3081K computer of the computing center of the Technische Hochschule Darmstadt.

Discussion. The D-43 molecule is centrosymmetric. The atomic coordinates are listed in Table 1.* Some selected bond distances and angles are shown in Table 2. The D-43 molecule is presented in Fig. 1. The atom-numbering scheme was chosen in accordance with the one selected for D-27. The relatively high R value for this structure in comparison with that for D-27 may be caused by the crystal material and is also an effect of the long terminal alkyl chain. The torsion angle between the best planes through the anthra-quinone ring |C(1)–C(6), C(14), O(1), C(1^i)–C(6^i), C(14^i), O(1^i)| and the phenyl ring is 75.1°, comparable to the value found for D-27 (69.5°). The terminal chain shows a kink at C(27) and is fully extended from C(27) to C(31). This can also be seen from the distance of $\simeq 1.25$ Å between O(4) and the best plane through the chain from C(27) to C(31). The torsion angle between the best planes through the anthraquinone ring and the alkyl chain is 18.0°, both moieties lying nearly perpendicular to the crystallographic *ac* plane.

The ratio of the longest axis to the shorter axes of the molecule is obviously greater than for D-27. Assuming a similar conformation of the molecule when solved in liquid crystalline phases, this would agree with the fact that D-43 has a remarkably higher order parameter than D-27 in a number of nematic hosts (Pellatt, Roe & Constant, 1980; Diot, Foitzik & Haase, 1985; Foitzik & Haase, 1985). Similar to D-27 a hydrogen bond is formed between H(1N) and the adjacent O atom with an O···H distance of 1.863 Å.

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* 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 42511 (13 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

A projection of the crystal structure along [001] is shown in Fig. 2. In the direction of the crystallographic *a* axis an alternating stacking of two alkyl groups and – because of the inversion center in the middle of the anthraquinone system – only one anthraquinone group is found. The shortest distances between non-H atoms of two coplanar anthraquinone rings are $\simeq 3.5$ Å.

A general comparison of some properties of a number of pleochroic anthraquinone dyes including the structural features will be made elsewhere (Foitzik & Haase, 1986).

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

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

	x	y	z	U_{eq}
C(1)	0·8899 (2)	0·2093 (4)	0·2476 (6)	50
C(2)	0·8392 (2)	0·1536 (4)	0·3991 (7)	59
C(3)	0·8436 (2)	0·0030 (4)	0·4323 (7)	65
C(4)	0·8976 (2)	−0·0966 (4)	0·3142 (6)	52
C(5)	0·9463 (2)	−0·0469 (3)	0·1613 (6)	44
C(6)	1·0027 (2)	−0·1583 (4)	0·0363 (6)	48
C(14)	0·9442 (2)	0·1086 (3)	0·1244 (6)	43
O(1)	1·0024 (2)	−0·2921 (2)	0·0752 (4)	62
N(1)	0·8857 (2)	0·3605 (3)	0·2213 (6)	62
H(1N)	0·9190 (22)	0·3844 (38)	0·1143 (63)	70†
C(15)	0·8298 (2)	0·4665 (4)	0·3354 (7)	52
C(16)	0·7519 (2)	0·5011 (4)	0·2059 (7)	59
C(17)	0·6983 (2)	0·6068 (4)	0·3099 (7)	57
C(18)	0·7237 (2)	0·6783 (4)	0·5461 (7)	52
C(19)	0·8016 (2)	0·6435 (4)	0·6792 (7)	54
C(20)	0·8548 (2)	0·5365 (4)	0·5703 (7)	56
O(4)	0·6668 (2)	0·7853 (3)	0·6306 (5)	67
C(27)	0·6921 (3)	0·8723 (4)	0·8684 (7)	68
C(28)	0·6228 (3)	0·9905 (4)	0·9045 (7)	72
C(29)	0·6282 (3)	1·1120 (4)	0·7517 (7)	72
C(30)	0·5601 (3)	1·2321 (4)	0·7901 (9)	89
C(31)	0·5661 (3)	1·3501 (5)	0·6360 (10)	114

† U_{iso}.

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

C(1)–C(2)	1·404 (4)	N(1)–H(1N)	0·913 (33)
C(1)–C(14)	1·412 (4)	N(1)–C(15)	1·431 (4)
C(1)–N(1)	1·376 (4)	C(18)–O(4)	1·381 (4)
C(2)–C(3)	1·383 (4)	O(4)–C(27)	1·433 (4)
C(3)–C(4)	1·389 (4)	C(27)–C(28)	1·521 (4)
C(4)–C(5)	1·369 (4)	C(28)–C(29)	1·531 (5)
C(5)–C(6)	1·492 (4)	C(29)–C(30)	1·522 (4)
C(5)–C(14)	1·431 (4)	C(30)–C(31)	1·513 (5)
C(6)–O(1)	1·245 (3)		

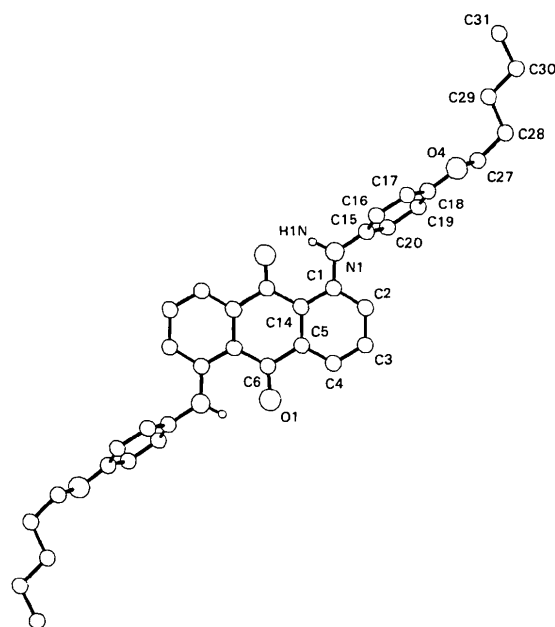|			
N(1)–C(1)–C(2)	119·6 (3)	C(16)–C(15)–N(1)	119·2 (4)
N(1)–C(1)–C(14)	121·1 (3)	C(20)–C(15)–N(1)	120·7 (4)
O(1)–C(6)–C(5)	118·2 (3)	O(4)–C(18)–C(17)	114·9 (3)
H(1N)–N(1)–C(1)	113·1 (2·1)	O(4)–C(18)–C(19)	124·4 (4)
C(15)–N(1)–H(1N)	123·1 (2·1)	C(27)–O(4)–C(18)	118·1 (3)
C(15)–N(1)–C(1)	123·7 (3)	C(28)–C(27)–O(4)	106·6 (3)

Fig. 1. D-43 molecule with labeling scheme. H atoms except H(1N) have been omitted.
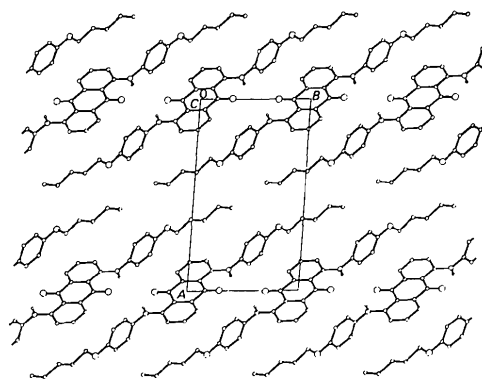

Fig. 2. Crystal structure of D-43 projected along the crystallographic |001| direction. H atoms except H(1N) have been omitted for clarity.

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