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Structure of a New Biforked Mesogen Derived from 3-(3,4-Dialkyloxyphenyl)-propanoic Acid

By H. Allouchi, J.-P. Bideau and M. Cotrait

Laboratoire de Cristallographie, URA 144 *du CNRS, Université de Bordeaux* I, 351 *Cours de la Libération, F*-33405 *Talence CEDEX, France*

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Abstract. *p*-Phenylenebis(methyleneamino-*p*-phenyl) bis{3-[3,4-bis(tridecyloxy)phenyl]propanoate}, $C_{90}H_{136}N_2O_8$, monoclinic, $M_r = 1374.0$, $P2_1/c$, $a = 53.518\ (4)$, $b = 8.407\ (1)$, $c = 9.244\ (2)$ Å, $\beta = 93.39\ (1)°$, $V = 4152$ Å^3, $Z = 2$, $D_x = 1.098$ Mg m^{-3}, $\lambda(\mathrm{Cu}\ K\alpha) = 1.5402$ Å, graphite monochromator, $\mu = 0.484$ mm^{-1}, $F(000) = 1508$, $T = 298$ K, $R = 0.074$ for the 2560 observed reflections. The molecules adopt a zigzag form: the polyaromatic central moiety of the molecule is 36.2 Å long; the two alkyloxy chains are stretched (*ttt*) and approximately parallel to the *xy* plane; both chains make an angle close to 120° with the central moiety. Molecules form sheets of about 53 Å thickness and are arranged as in a smectic *C* mesophase; the central cores make a tilt angle of 60° with the normal to the sheet and are quasiparallel to the *xz* plane; interactions between sheets are very weak in the 0*x* direction. An explanation is given of the transition between the crystalline arrangement of the molecule and the hexagonal symmetry of the mesophase for this compound.

Introduction. Since phasmidic, biforked and, more generally, polycatenar mesogens* were first synthesized (Malthete, Levelut & Nguyen, 1985; Nguyen, Destrade, Levelut & Malthete, 1986; Destrade, Nguyen, Roubineau & Levelut, 1988), they have attracted more and more interest in the field of thermotropic liquid crystals. These compounds correspond to hybrids between rod-like and disc-like molecules (Guillon, Skoulios & Malthete, 1987; Malthete, Nguyen & Levelut, 1986), having a classical elongated polyaromatic core (four to six benzene rings), but with the terminal benzene rings possessing more than one terminal chain.

The intense synthetic work in this field is related to the search for new mesomorphic systems and to obtaining an understanding of the correlations between the general shape of a molecule and the symmetry of the induced mesophases. It is well established that this relation is often evident; for instance rod-like molecules form lamellar mesophases whereas disc-like molecules form a rich variety of columnar mesophases (Destrade, Foucher, Gasparoux, Nguyen & Levelut, 1984; Malthete & Collet, 1985).

It is of interest to examine the mesomorphism of hybrid molecules such as polycatenars. A number of different series have already been synthesized. Several molecular variations have been reported, such as variations in the number of benzene rings, the anchoring positions of the paraffinic chains, *etc.* (Nguyen, Malthete & Destrade, 1985; Weissflog, Diele & Demus, 1986).

The most striking behaviour is that some of these compounds, especially tetracatenars, can give lamellar and columnar, as well as hexagonal and cubic mesophases in the same series with respect to the chain length.

It is not surprising *a posteriori* that such hybrid molecules can give lamellar mesophases (rod-like behaviour) and columnar mesophases (disc-like behaviour). However, it is still difficult to find a clear connection between the molecular shape and, for instance, the molecular arrangement. In fact, several molecular models have been proposed to explain the existence of hexagonal symmetry in some of these columnar mesophases (Guillon, Skoulios & Malthete, 1987; Levelut, Malthete, Destrade & Nguyen, 1987; Fang, Levelut & Destrade, 1990); in any case these models emphasize the fundamental role of the supposed molecular associations in the formation of such mesophases. However, the different structural models are unacceptable from the point of view of space filling (Guillon, Skoulios & Malthete, 1987).

Many structural investigations have now been performed on the mesophases of polycatenar mesogens, such as lattice-parameter and symmetry-group determinations (Guillon, Skoulios & Malthete, 1987; Levelut, Malthete, Destrade & Nguyen, 1987; Fang, Levelut & Destrade, 1990). We feel, however, that precise information on the molecular arrangement observed in the crystalline phase could greatly help

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* Polycatenar mesogens from the Latin *catena* (= chain).

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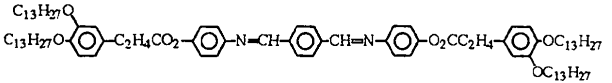
the understanding of these molecular associations in the mesophases.

This paper gives the detailed structural investigation of the crystalline phase of a biforked mesogen derived from 3-(3,4-dialkyloxyphenyl)propanoic acid: the polymorphism, the transition temperatures and the enthalpy of transition between phases, studied using polarizing microscopy and differential scanning calorimetry, have been published recently (Destrade, Nguyen, Alstermark, Lindsten, Nilsson & Otterholm, 1990).

Experimental. Compound (I) was prepared following the procedure described by Destrade, Nguyen, Alstermark, Lindsten, Nilsson & Otterholm (1990).



(I)

The molecule undergoes the following transitions:

$$K \xrightarrow{385\ \text{K}} \varnothing_h \xrightarrow{428\ \text{K}} I.$$

The symbol $\varnothing_h$ is used for the hexagonal columnar phase; the labelling of the atoms is represented in Fig. 1.

Thin crystals were obtained from toluene solution; crystal dimensions 0.4 × 0.225 × 0.15 mm. Unit-cell parameters were determined by least-squares fit of 25 reflections with θ 19–47°. Scan range $(1.6 + 0.15\tan\theta)°$, detector width $(2.2 + 1.1\tan\theta)$ mm, Nonius CAD-4 diffractometer, graphite monochromator, with $\sin\theta/\lambda < 0.56$ Å^{-1} ($-65 < h < 65$, $k < 11$, $l < 10$) and ω–2θ scans; reflections with $\theta < 25°$ were measured twice and averaged; experimental absorption correction applied, transmission factors between 0.93 and 0.99; three reflections (17,2,2, $8\bar{4}2$, 712) were monitored every 200 reflections. 7871 independent reflections measured, only 2560 observed [$I > 3\sigma(I)$]. The structure was solved by direct methods using *MITHRIL* (Gilmore, 1984), refined by block-diagonal least squares on F with anisotropic factors for non-H atoms, minimizing $w(|F_o| - |F_c|)^2$ [$w = 1/\sigma^2(F)$].

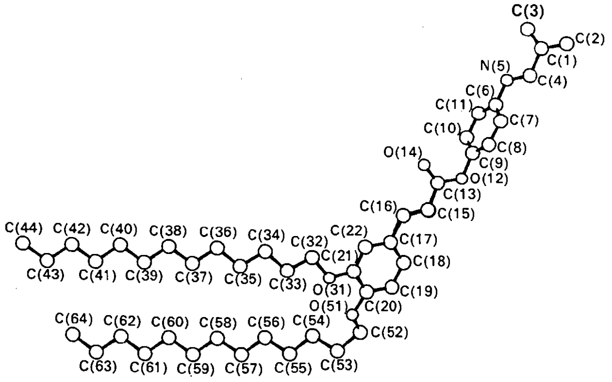


Fig. 1. Atomic labelling of the crystallographic asymmetric unit (half the molecule).

At this stage, the polyaromatic central core atoms were found to have significantly higher thermal motions than those of the alkyloxy chains; a thorough examination showed a delocalization of electronic density for a few atoms, especially C(15) and C(16); their positions can be statistically split into C(15) and C(15′) on the one side, C(16) and C(16′) on the other side, each of them having an occupancy factor of 0.5.

It was not possible to find two positions for the central core of the molecule from a difference Fourier synthesis. Attempts to refine the structure using two positions for the core failed. The refinement was resumed and H atoms located in their theoretical positions (Lehman, Koetzle & Hamilton, 1972); this process led to improved bond lengths and angles.

Scattering factors of Cromer & Waber (1974) for non-H atoms and of Stewart Davidson & Simpson (1965) for H atoms were used. The final reliability factors were $R = 0.074$ and $wR = 0.096$; $S = 1.45$; residual electron density between -0.4 and 0.3 e Å^{-3}; $(\Delta/\sigma)_{\max} = 0.3$; 424 parameters. The relatively high reliability factor can be attributed to the disorder of the central core of the molecule.

Discussion. Atomic parameters are given in Table 1* and the numbering of the atoms is presented in Fig. 1. Projections of the structure along the b and c axes are shown in Fig. 2. Bond lengths and angles are given in Table 2. They are in good agreement with those usually observed for mesogens (Cotrait, Marsau & Pesquer, 1979; Cotrait, Sy & Ptak, 1975; Cotrait, Gaultier, Polycarpe, Giroud & Mueller-Westerhoff, 1983).

Curiously, the alkyloxy chains are less agitated than the polycyclic core, contrary to what is generally observed in mesogens.

The molecule adopts a zigzag form, as can be seen from the *ORTEP* drawing (Johnson, 1965) in Fig. 3, as already observed for a few type *C* smectogens. The significant torsion angles, which define the molecular conformation, are given in Table 2.

One of the alkyloxy chains [atoms C(32) to C(44), chain 1] is completely extended with C—C—C—C angles deviating from 180° by less than 5°. The other

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* Lists of structure factors, anisotropic thermal parameters and H-atom parameters have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 54704 (52 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 1. *Fractional atomic coordinates and equivalent isotropic temperature factors* (Å^2) *with e.s.d.'s in parentheses*

$$B_{eq} = (4/3)\sum_i\sum_j \beta_{ij}\mathbf{a}_i.\mathbf{a}_j.$$

	x	*y*	*z*	B_{eq}
C(1)	0.9903 (1)	0.0115 (12)	−0.8657 (8)	7.9 (4)
C(2)	1.0135 (1)	0.0789 (14)	−0.8853 (8)	9.2 (5)
C(3)	0.9768 (1)	−0.0676 (12)	−0.9758 (8)	8.4 (5)
C(4)	0.9797 (1)	0.0267 (13)	−0.7202 (7)	8.5 (5)
N(5)	0.9583 (1)	−0.0258 (10)	−0.6980 (6)	8.3 (4)
C(6)	0.9482 (1)	−0.0024 (13)	−0.5628 (7)	8.0 (4)
C(7)	0.9531 (2)	0.1216 (14)	−0.4704 (9)	9.9 (6)
C(8)	0.9422 (2)	0.1369 (15)	−0.3410 (9)	11.1 (6)
C(9)	0.9270 (1)	0.0274 (15)	−0.2990 (7)	10.1 (5)
C(10)	0.9213 (1)	−0.1094 (13)	−0.3846 (8)	8.8 (5)
C(11)	0.9321 (2)	−0.1199 (13)	−0.5188 (8)	9.5 (5)
O(12)	0.9174 (1)	0.0281 (11)	−0.1593 (5)	12.6 (4)
C(13)	0.8949 (1)	0.0518 (12)	−0.1418 (7)	7.4 (4)
O(14)	0.8818 (1)	0.0833 (13)	−0.2447 (6)	14.5 (5)
C(15)	0.8862 (2)	0.0931 (18)	0.0034 (11)	5.5 (6)
C(15′)	0.8868 (2)	0.0226 (18)	0.0067 (13)	6.1 (7)
C(16)	0.8636 (3)	0.1046 (20)	0.0299 (16)	8.3 (9)
C(16′)	0.8615 (2)	0.0198 (21)	0.0241 (11)	6.2 (7)
C(17)	0.8519 (1)	0.0502 (10)	0.1758 (6)	5.9 (3)
C(18)	0.8645 (1)	−0.0260 (10)	0.2899 (6)	5.9 (3)
C(19)	0.8536 (1)	−0.0408 (8)	0.4218 (6)	4.5 (3)
C(20)	0.8301 (1)	0.0167 (7)	0.4411 (5)	3.9 (2)
C(21)	0.8177 (1)	0.0989 (8)	0.3264 (6)	4.2 (3)
C(22)	0.8282 (1)	0.1142 (8)	0.1950 (6)	4.8 (3)
O(31)	0.7947 (1)	0.1579 (6)	0.3558 (4)	5.2 (2)
C(32)	0.7785 (1)	0.2138 (8)	0.2388 (6)	4.2 (3)
C(33)	0.7549 (1)	0.2617 (8)	0.3051 (6)	4.4 (3)
C(34)	0.7340 (1)	0.3150 (8)	0.1946 (6)	4.7 (3)
C(35)	0.7102 (1)	0.3599 (8)	0.2673 (6)	4.6 (3)
C(36)	0.6886 (1)	0.4081 (8)	0.1619 (6)	4.9 (3)
C(37)	0.6652 (1)	0.4509 (8)	0.2392 (6)	5.0 (3)
C(38)	0.6429 (1)	0.4948 (9)	0.1410 (6)	5.2 (3)
C(39)	0.6197 (1)	0.5388 (9)	0.2211 (7)	5.9 (3)
C(40)	0.5971 (1)	0.5782 (9)	0.1208 (7)	5.8 (3)
C(41)	0.5737 (1)	0.6150 (11)	0.2052 (7)	6.6 (4)
C(42)	0.5513 (1)	0.6607 (10)	0.1094 (7)	6.6 (4)
C(43)	0.5280 (1)	0.6893 (13)	0.1922 (9)	9.1 (5)
C(44)	0.5050 (1)	0.7426 (17)	0.0932 (11)	12.2 (7)
O(51)	0.8170 (1)	−0.0020 (5)	0.5617 (4)	4.4 (2)
C(52)	0.8246 (1)	−0.1247 (8)	0.6622 (6)	4.6 (3)
C(53)	0.8030 (1)	−0.1545 (7)	0.7572 (5)	4.0 (3)
C(54)	0.7799 (1)	−0.2164 (8)	0.6690 (6)	4.7 (3)
C(55)	0.7582 (1)	−0.2610 (9)	0.7602 (6)	5.0 (3)
C(56)	0.7348 (1)	−0.3103 (8)	0.6675 (6)	4.8 (3)
C(57)	0.7126 (1)	−0.3544 (8)	0.7535 (6)	5.0 (3)
C(58)	0.6899 (1)	−0.4039 (9)	0.6586 (6)	5.3 (3)
C(59)	0.6670 (1)	−0.4444 (8)	0.7407 (6)	5.1 (3)
C(60)	0.6442 (1)	−0.4895 (9)	0.6432 (6)	5.7 (3)
C(61)	0.6213 (1)	−0.5294 (9)	−0.7243 (6)	5.7 (3)
C(62)	0.5987 (1)	−0.5752 (10)	0.6250 (7)	6.1 (3)
C(63)	0.5754 (1)	−0.6168 (11)	0.7038 (8)	7.1 (4)
C(64)	0.5531 (1)	−0.6676 (13)	0.6027 (10)	9.2 (5)

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

C(1)—C(2)	1.38 (1)	C(21)—C(22)	1.378 (9)
C(1)—C(3)	1.38 (1)	C(21)—O(31)	1.368 (8)
C(2)—C′(3)	1.42 (1)	O(31)—C(32)	1.428 (8)
C(3)—C′(2)	1.42 (1)	C(32)—C(33)	1.493 (9)
C(1)—C(4)	1.49 (1)	C(33)—C(34)	1.537 (9)
C(4)—N(5)	1.25 (1)	C(34)—C(35)	1.522 (9)
N(5)—C(6)	1.41 (1)	C(35)—C(36)	1.520 (9)
C(6)—C(7)	1.35 (1)	C(36)—C(37)	1.52 (1)
C(6)—C(11)	1.40 (1)	C(37)—C(38)	1.51 (1)
C(7)—C(8)	1.37 (2)	C(38)—C(39)	1.53 (1)
C(8)—C(9)	1.30 (1)	C(39)—C(40)	1.52 (1)
C(9)—C(10)	1.40 (1)	C(40)—C(41)	1.54 (1)
C(9)—O(12)	1.42 (1)	C(41)—C(42)	1.50 (1)
C(10)—C(11)	1.40 (1)	C(42)—C(43)	1.52 (1)
O(12)—C(13)	1.24 (1)	C(43)—C(44)	1.55 (2)
C(13)—O(14)	1.18 (1)	O(51)—C(52)	1.435 (8)
C(13)—C(15)	1.48 (2)	C(52)—C(53)	1.518 (9)
C(13)—C(15′)	1.47 (2)	C(53)—C(54)	1.535 (9)
C(15)—C(16′)	1.49 (2)	C(54)—C(55)	1.516 (9)
C(15′)—C(16)	1.45 (2)	C(55)—C(56)	1.535 (9)
C(16)—C(17)	1.58 (2)	C(56)—C(57)	1.519 (9)
C(16′)—C(17)	1.54 (2)	C(57)—C(58)	1.51 (1)
C(17)—C(18)	1.37 (1)	C(58)—C(59)	1.52 (1)
C(17)—C(22)	1.40 (1)	C(59)—C(60)	1.52 (1)
C(18)—C(19)	1.39 (1)	C(60)—C(61)	1.52 (1)
C(19)—C(20)	1.363 (9)	C(61)—C(62)	1.52 (1)
C(20)—C(21)	1.400 (9)	C(62)—C(63)	1.53 (1)
C(20)—O(51)	1.366 (7)	C(63)—C(64)	1.53 (1)

C(2)—C(1)—C(3)	122.6 (8)	C(19)—C(20)—O(51)	126.0 (6)
C(1)—C(2)—C(3′)	118.1 (8)	C(21)—C(20)—O(51)	115.2 (5)
C(1)—C(3)—C(2′)	119.6 (8)	C(20)—C(21)—C(22)	120.7 (6)
C(2)—C(1)—C(4)	117.9 (8)	C(20)—C(21)—O(31)	115.7 (7)
C(3)—C(1)—C(4)	119.5 (8)	C(22)—C(21)—O(31)	124.2 (6)
C(1)—C(4)—N(5)	120.9 (8)	C(17)—C(22)—C(21)	119.7 (6)
C(4)—N(5)—C(6)	119.8 (8)	C(21)—O(31)—C(32)	118.8 (5)
N(5)—C(6)—C(7)	126.7 (8)	C(31)—C(32)—C(33)	105.6 (5)
N(5)—C(6)—C(11)	115.7 (8)	O(32)—C(33)—C(34)	113.8 (5)
C(7)—C(6)—C(11)	117.6 (9)	C(33)—C(34)—C(35)	111.9 (5)
C(6)—C(7)—C(8)	123 (1)	C(34)—C(35)—C(36)	114.1 (5)
C(7)—C(8)—C(9)	120 (1)	C(35)—C(36)—C(37)	112.1 (6)
C(8)—C(9)—C(10)	122 (1)	C(36)—C(37)—C(38)	114.7 (6)
C(8)—C(9)—O(12)	122.2 (9)	C(37)—C(38)—C(39)	113.7 (6)
C(10)—C(9)—O(12)	115.3 (8)	C(38)—C(39)—C(40)	113.6 (6)
C(9)—C(10)—C(11)	116.9 (8)	C(39)—C(40)—C(41)	112.3 (6)
C(6)—C(11)—C(10)	120.6 (9)	C(40)—C(41)—C(42)	113.1 (6)
C(9)—C(12)—C(13)	122.1 (8)	C(41)—C(42)—C(43)	113.5 (7)
O(12)—C(13)—O(14)	117.3 (9)	C(42)—C(43)—C(44)	114.0 (8)
O(12)—C(13)—C(15)	121.8 (9)	C(20)—O(51)—C(52)	117.9 (5)
O(14)—C(13)—C(15)	117.7 (9)	O(51)—C(52)—C(53)	107.0 (5)
O(14)—C(13)—C(15′)	126 (1)	C(52)—C(53)—C(54)	111.7 (5)
C(13)—C(15)—C(16′)	111 (1)	C(53)—C(54)—C(55)	113.9 (5)
C(13)—C(15′)—C(16)	112 (1)	C(54)—C(55)—C(56)	112.1 (5)
C(15)—C(16′)—C(17)	113 (1)	C(55)—C(56)—C(57)	114.5 (5)
C(15′)—C(16)—C(17)	113 (1)	C(57)—C(58)—C(59)	114.6 (6)
C(16′)—C(17)—C(18)	116.4 (8)	C(58)—C(59)—C(60)	113.6 (6)
C(16′)—C(17)—C(22)	121.9 (8)	C(59)—C(60)—C(61)	114.0 (6)
C(18)—C(17)—C(22)	119.5 (7)	C(60)—C(61)—C(62)	113.4 (6)
C(17)—C(18)—C(19)	120.2 (7)	C(61)—C(62)—C(63)	114.4 (6)
C(18)—C(19)—C(20)	121.0 (6)	C(62)—C(63)—C(64)	113.6 (7)
C(19)—C(20)—C(21)	118.8 (6)		

C(4)—N(5)—C(6)—C(7)	29.6 (9)	C(15)—C(16′)—C(17)—C(18)	−71 (1)
C(4)—N(5)—C(6)—C(11)	−149.2 (8)	C(15′)—C(16)—C(17)—C(18)	18 (1)
C(8)—C(9)—O(12)—C(13)	112 (1)	C(15′)—C(16)—C(17)—C(22)	−174 (1)
C(9)—C(12)—C(13)—C(15)	−163.6 (9)	C(15)—C(16′)—C(17)—C(22)	126 (1)
C(9)—C(12)—C(13)—C(15′)	170.2 (9)	C(16)—C(17)—C(18)—C(19)	168.5 (9)
C(10)—C(9)—O(12)—C(13)	−74.8 (9)	C(19)—C(20)—O(51)—C(52)	−18.1 (6)
C(12)—C(13)—C(15)—C(16′)	−144 (1)	C(21)—C(20)—O(51)—C(52)	160.2 (5)
C(12)—C(13)—C(15′)—C(16)	160 (1)	C(20)—C(21)—O(31)—C(32)	−167.1 (5)
O(14)—C(13)—C(15)—C(16′)	57 (1)	C(22)—C(21)—O(31)—C(32)	12.2 (6)
O(14)—C(13)—C(15′)—C(16)	−26 (1)	C(20)—C(51)—C(52)—C(53)	−162.4 (5)
C(13)—C(15′)—C(16)—C(17)	170 (1)	O(51)—C(52)—C(53)—C(54)	63.2 (5)

one [atoms C(52) to C(64), chain 2] is partly extended with a torsion angle around the C(52)—C(53) bond close to 60°. The lengths of chains 1 and 2 are 17.6 and 16.1 Å respectively. These chains are not parallel, as might be inferred from Fig. 2(*a*) but make an angle of about 40° with each other (Fig. 2*b*); however, both chains are parallel to the *xy* plane.

The angle between the central core and both alkyloxy chains is close to 120°. This core is 36.2 Å long [distance between O(51) and its homologue O′(51) relative to the centre of symmetry].

The central ring φ_0, defined by atoms C(1), C(2), C(3) and their homologues C′(1), C′(2) and C′(3), makes an angle of 30° with the following ring, φ_1 [atoms C(6) to C(11)], which in turn makes an angle close to 90° with the next ring, φ_2 [atoms C(17) to C(22)]; the angle between φ_2 and φ_0 is close to 60°.

The cohesion in the crystal is almost uniquely a result of van der Waals forces; this is in agreement with the very low density: 1.098 Mg m^{-3}. There are no intramolecular contacts, particularly between alkyloxy chains. There are very few intermolecular contacts between the whole molecule and its homologues through the centres of symmetry, only between methyl terminal groups. On the contrary, there are numerous interactions between homologues through the *c* glide plane and the 2_1 axis: on one side, between chain 1 of one molecule and chain 2 of neighbouring molecules; on the other side between neighbouring polyaromatic central cores. Parallel cores are 4.9 Å apart and are arranged in a quasi-hexagonal array.

The molecules are arranged in two-dimensional sheets, parallel to the *yz* plane, whose thickness is about 53 Å, the length of the *a* axis. Interactions between sheets, *i.e.* between the terminal methyl groups at $x \simeq 0$ and 1, are very weak.

The molecular arrangement (Fig. 2*a*) is typical of a lamellar structure with segregation of the aliphatic chains and of the central polyaromatic cores. It is then possible to define molecular sheets as they are in smectic phases.

Both aliphatic chains are approximately perpendicular to the sheet plane. The polyaromatic cores are aligned and parallel to each other and to the *xz* plane; they make a tilt angle close to 60° with the normal to the sheets. This kind of arrangement, although concerning the solid state, is perfectly characteristic of a smectic *C* structure. Such mesophases have been observed in another family of biforked mesogens for short alkyloxy chain lengths (Fang, Levelut & Destrade, 1990). Moreover, it is worth comparing the above parameters to these, directly measured on the smectic *C* mesophase of a similar compound (Destrade, Nguyen, Roubineau & Levelut, 1988). In this latter case, the lattice spacing of the columnar mesophase is about 49.6 and 52.6 Å for the $C_{10}H_{21}$ and $C_{14}H_{29}$ alkyloxy derivatives, respectively (Fang, Levelut & Destrade, 1990). In fact, for the present compound, the mesomorphic phase observed above the crystalline phase is not a smectic *C* phase but has hexagonal symmetry and probably has a $\varnothing_h$ columnar structure (Destrade, Nguyen, Alstermark, Lindsten, Nilsson & Otterholm, 1990). The correlation between the crystal structure and the mesophase symmetries is not obvious. The problem is to find in which direction and where the loss of symmetry that corresponds to the crystal three-dimensional→two-dimensional hexagonal columnar transition will occur.

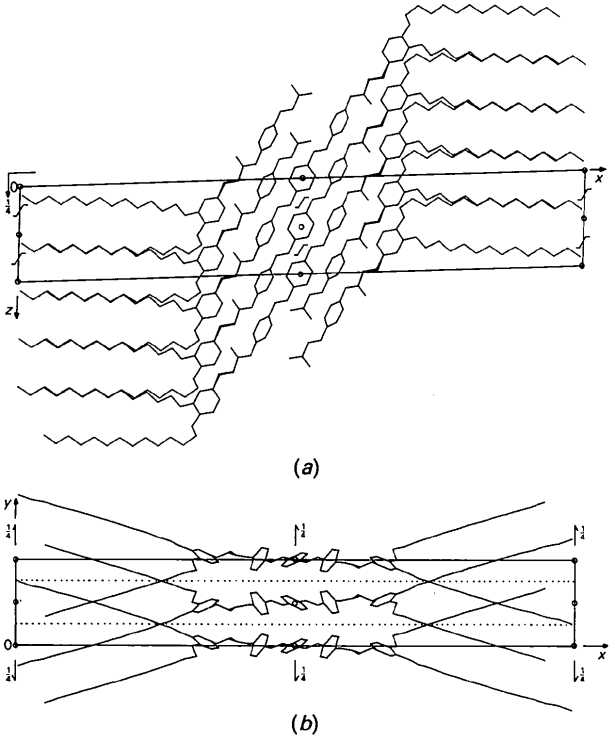

Fig. 2. Projections of the structure on the (*a*) *xz* and (*b*) *xy* planes.

Interactions between sheets are very weak in the 0*x* direction. Moreover if we suppose that interactions between chains of neighbouring molecules are weakened by heating, we can imagine that two-dimensional (011) sheets can rotate around the perpendicular to the (011) plane through 60° steps, to give rise to a hexagonal columnar phase. If there was no melting or shrinking of alkyloxy chains, such columns should have a radius of about 29 Å, *i.e.* 58 Å between neighbouring columns.

Another hypothesis can be formulated: there is no definitive proof of the existence of well-defined columns in the mesophase; we then have only to understand the hexagonal symmetry in the mesophase but not the existence of columns.

We know that the crystal→mesophase transition enthalpy is not significant and may essentially correspond to the melting of chains. This hypothesis is supported by the fact that these compounds have their temperature of crystallization very close to the

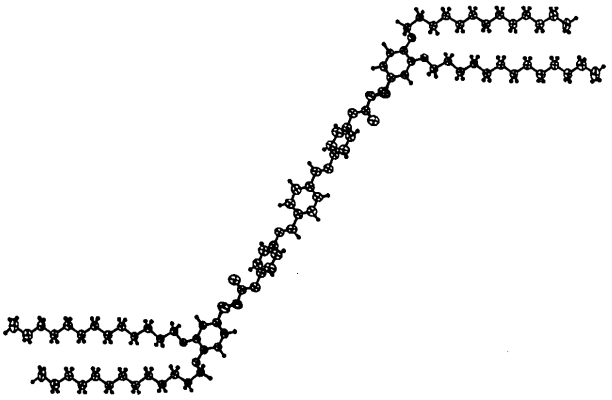

Fig. 3. *ORTEP* drawing (Johnson, 1965) of the molecule.

temperature of melting. In these conditions the structural invariant element could be the zigzag conformation as found in the crystal. If we now suppose that, at the transition, the two-dimensional organization is conserved in the (011) plane, one can easily imagine not a columnar structure, but a lamellar structure in hexagonal network.

References

Cotrait, M., Gaultier, J., Polycarpe, C., Giroud, A. M. & Mueller-Westerhoff, U. T. (1983). *Acta Cryst.* **C39**, 833–835.

Cotrait, M., Marsau, P. & Pesquer, M. (1979). *Acta Cryst.* **B35**, 1102–1107.

Cotrait, M., Sy, D. & Ptak, M. (1975). *Acta Cryst.* **B31**, 1869–1874.

Cromer, D. T. & Waber, J. T. (1974). *International Tables for X-ray Crystallography*, Vol. IV. Birmingham: Kynoch Press. (Present distributor Kluwer Academic Publishers, Dordrecht.)

Destrade, C., Foucher, P., Gasparoux, H., Nguyen, H. T. & Levelut, A. M. (1984). *Mol. Cryst. Liq. Cryst.* **106**, 121–125.

Destrade, C., Nguyen, H. T., Alstermark, C., Lindsten, G., Nilsson, M. & Otterholm, B. (1990). *Mol. Cryst. Liq. Cryst.* **180**, 265–280.

Destrade, C., Nguyen, H. T., Roubineau, A. & Levelut, A. M. (1988). *Mol. Cryst. Liq. Cryst.* **159**, 163–171.

Fang, Y., Levelut, A. M. & Destrade, C. (1990). *Liq. Cryst.* **7**, 265–278.

Gilmore, C. J. (1984). *J. Appl. Cryst.* **17**, 42–46.

Guillon, D., Skoulios, A. & Malthete, J. (1987). *Europhys. Lett.* **3**, 67–72.

Johnson, C. K. (1965). *ORTEP*. Report ORNL-3794. Oak Ridge National Laboratory, Tennessee, USA.

Lehman, M. S., Koetzle, T. F. & Hamilton, W. C. (1972). *J. Am. Chem. Soc.* **94**, 2657–2660.

Levelut, A. M., Malthete, J., Destrade, C. & Nguyen, H. T. (1987). *Liq. Cryst.* **2**, 877–888.

Malthete, J. & Collet, A. (1985). *Nouv. J. Chim.* **9**, 151–155.

Malthete, J., Levelut, A. M. & Nguyen, H. T. (1985). *J. Phys. (Paris) Lett.* **46**, L875–L880.

Malthete, J., Nguyen, H. T. & Levelut, A. M. (1986). *J. Chem. Soc. Chem. Commun.* pp. 1548–1553.

Nguyen, H. T., Destrade, C., Levelut, A. M. & Malthete, J. (1986). *J. Phys. (Paris)*, **47**, 453–457.

Nguyen, H. T., Malthete, J. & Destrade, C. (1985). *Mol. Cryst. Liq. Cryst. Lett.* **2**(5), 133–138.

Stewart, R. F., Davidson, E. R. & Simpson, W. T. (1965). *J. Chem. Phys.* **42**, 3175–3187.

Weissflog, W., Diele, S. & Demus, D. (1986). *Mater. Chem. Phys.* **15**, 475–480.

Acta Cryst. (1992). **C48**, 1041–1043

Structure of Butanedione Bis(methylphenylhydrazone)

By Gabriele Bocelli and Andrea Cantoni

Centro di Studio per la Strutturistica Diffrattometrica del CNR, Viale delle Scienze, I-43100 Parma, Italy

and Giorgio Tosi

Dipartimento di Scienze dei Materiali e della Terra, Università degli Studi di Ancona, Via Brecce Bianche, I-60131 Ancona, Italy

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Abstract. $C_{18}H_{22}N_4$, $M_r = 294.40$, monoclinic, $P2_1/c$, $a = 13.490\,(3)$, $b = 7.734\,(2)$, $c = 8.211\,(3)$ Å, $\beta = 97.60\,(4)°$, $V = 849.6\,(4)$ Å^3, $Z = 2$, $D_x = 1.15$ g cm^{-3}, Mo $K\alpha$, $\lambda = 0.71069$ Å, $\mu = 0.66$ cm^{-1}, $F(000) = 316$, room temperature, $R = 0.052$, $wR = 0.053$ for 639 independent observed reflections. A π delocalization is observed between the aromatic ring and the aliphatic chain. Steric hindrance between the methyl groups and between methyl groups and the adjacent H atoms of the ring is avoided by rotation of the chain and by the enlargement of some angles.

Introduction. In the past ten years hydrazones have been considered as donors in complexes with a variety of π^*-organic acceptors (Bruni, Cardellini, Conti, Giorgini & Tosi, 1990, and references therein). Molecular complexes (MC) of different stability have been obtained in solution and the moderately weak interactions discussed in terms of ionization potentials, transition energies and thermodynamic properties.

Except with large-size acceptors (*e.g.* 9-dicyanomethylene-2,4,7-trinitrofluorene) (Bruni, Cardillo, Giorgini, Tosi, Bocelli & Rizzoli, 1990), we were unable to obtain crystalline complexes in order to verify the hypothesis (supported by spectroscopic results) that the hydrazono group C═N—N can be considered the active donor centre (Bruni, Cardellini & Tosi, 1988).

All the experimental results were in agreement with the hypothesis that the factor which determines the spectroscopic and structural features (and conse-

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