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Crystal structure of a new biforked mesogen

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The crystal structure of a biforked mesogen derived from 3,4-dialkyloxyphenyl propanoic acid is described. The molecule crystallizes in the $P2_1/c$ space group with two molecules per unit cell: $a = 50{\cdot}740$ (3), $b = 8{\cdot}425$ (2), $c = 9{\cdot}250$ (1) Å, and $\beta = 91{\cdot}340$ (7)°; the final reliability factor is $R = 0{\cdot}086$. Molecules adopt a zig-zag form: the non-aliphatic central moiety is 36·2 Å long; the two alkyloxy chains are stretched (ttt) and are approximately parallel to the xy plane; both chains make an angle close to 120° with the central moiety. Molecules make sheets of about 51 Å thickness; the polyaromatic central core makes an angle close to 60° (tilt angle) with the normal to the sheet and is quasi-parallel to the xy plane; interactions between sheets are very weak. Here, we try to given an explanation of the transition between the crystalline arrangement of molecules and the hexagonal symmetry of the mesophase for this compound.

1. Introduction

Since phasmidic, biforked and more generally polycatenar mesogens have been synthesized [1–3] they have attracted more and more interest in the field of thermotropic liquid crystals. These compounds correspond to hybrid molecules between rod-like and disc-like ones [4, 5] corresponding to a classical elongated polyaromatic core (4 to 6 benzene rings) but the terminal benzene rings possess more than one terminal chain. For instance, the first phasmidic compounds are named hexacatenar while the biforked ones correspond to tetracatenar mesogens.

The intense synthetic work is related to the search for new mesomorphic systems and to the 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 self-evident, for instance rod-like molecules form lamellar mesophases, whereas disc-like and cone-shaped ones form a rich variety of columnar mesophases [6, 7]. It was, of course, of obvious 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 performed such as the number of benzene rings [3], anchoring positions of the paraffinic chains [2, 3, 5] the number and nature of the substituents [5, 8, 9]. Now, some general features can be reviewed, the most striking behaviour of which is that some of these compounds, especially tetracatenars, can give lamellar, columnar and intermediate ribbon mesophases as well as hexagonal and cubic mesophases in the same series with respect to the chain length [2, 3].

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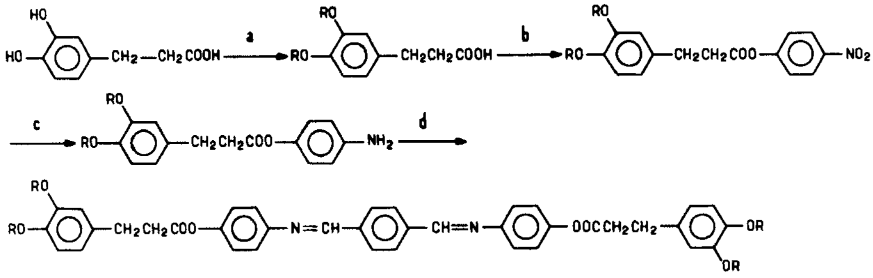
As a matter of fact it is not surprising *a posteriori* that such hybrid molecules can give rise to lamellar (rod-like behaviour) and columnar mesophases (disc-like behaviour). However, it is still difficult to find a clear connection between the molecular shape and for instance the molecular arrangement. In fact, several molecular models have been proposed to explain the evidence of a hexagonal symmetry in some of these columnar mesophases [1, 4, 10, 11], some of these models correspond to groups of several molecules forming clusters surrounded by their paraffinic chains. In any case, all these models emphasize the fundamental role of the supposed molecular associations in the formation of such mesophases and also in the case of lyotropics and neat soaps [12].

Many structural investigations have now been carried out on the mesophases of polycatenar mesogens, such as lattice parameters and symmetry groups [2, 4, 10, 11]. We, however, trust that precise information on the real molecular arrangement directly in the crystalline phase could greatly help the understanding of these molecular associations in the mesophases.

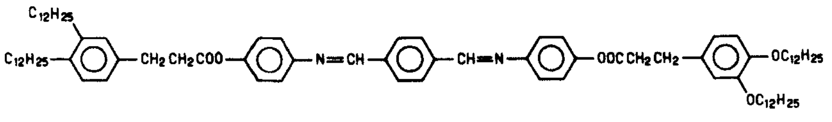
This paper gives the first detailed structural investigation of the crystalline phase of a biforked mesogen derived from 3-(3′,4′-dialkyloxyphenyl) propanoic acid; the polymorphism, the transition temperatures, the enthalpy of transition between phases, studied using polarizing microscopy and differential scanning calorimetry, have recently been published [13].

2. Experimental

The compounds were prepared starting with alkylation of 3,4-dihydroxycinnamic acid, then condensed with 4-nitrophenol, reduction of the nitro group and finally, condensation of the amine with terephtaldehyde. The synthetic route is outlined in the following scheme and full details of the preparation are given in the experimental section of [13].



The formula of the compound currently examined here is the following:



The molecule undergoes the following transitions:

$$C \xrightarrow{112^\circ C} \phi_h \xrightarrow{155^\circ C} I.$$

The symbol ϕ_h is used for the hexagonal columnar phase.

The labelling of atoms of half the molecule is represented in figure 1. Thin crystals have been obtained, with some difficulty, by slow evaporation from toluene solution; they are very fragile and soft and are often twinned. They belong to the monoclinic system with a $P2_1/c$ space group: $a = 50{\cdot}740$ (9), $b = 8{\cdot}425$ (4), $c = 9{\cdot}250$ (4) Å and $\beta = 91{\cdot}34(1)°$ ($V = 3953$ Å^3); the molecular weight is $M_x = 1316$ g; the density is quite low ($d = 1{\cdot}106$ Mg m^{-3}). This corresponds to two molecules ($Z = 2$) per unit cell, so that the asymmetric unit only contains half a molecule: the molecule lies on a centre of symmetry.

The crystal dimensions are $0{\cdot}7 \times 0{\cdot}35 \times 0{\cdot}15$ mm; X-ray diffraction data (λ Cu-K$\alpha = 1{\cdot}5178$ Å) have been collected on a CAD-4 Enraf-Nonius four circle diffractometer with θ between 2° and 60° with the ω-θ mode; absorption has been corrected; 5872 independent reflections have been collected, among which 3922 with $I > 2{\cdot}5\sigma$ (I) have been considered as observed.

The structure has been solved by direct methods, using the Mithril program [14]; x, y, z and thermal parameters were refined with first, isotropic, then anisotropic, thermal scattering factors for C, N and O atoms. At this stage, we could see that the polyaromatic central core has a significantly higher thermal motion than the alkyloxy chains; this is particularly the case for the phenyl ring (atoms C(6) to C(11) and the carboxylic group (atoms O(12) to C(15)). A thorough examination of the electron density showed a delocalization of this latter group, especially for atoms C(15) and C(16); the locations of these atoms can be split statistically into C(15) and C(15′) on the one side, and C(16) and C(16′) on the other, each of them being affected by a weight of 0·5. The refinement was then resumed and hydrogen atoms were located in their theoretical positions [15]; this process leads to better bond lengths and angles.

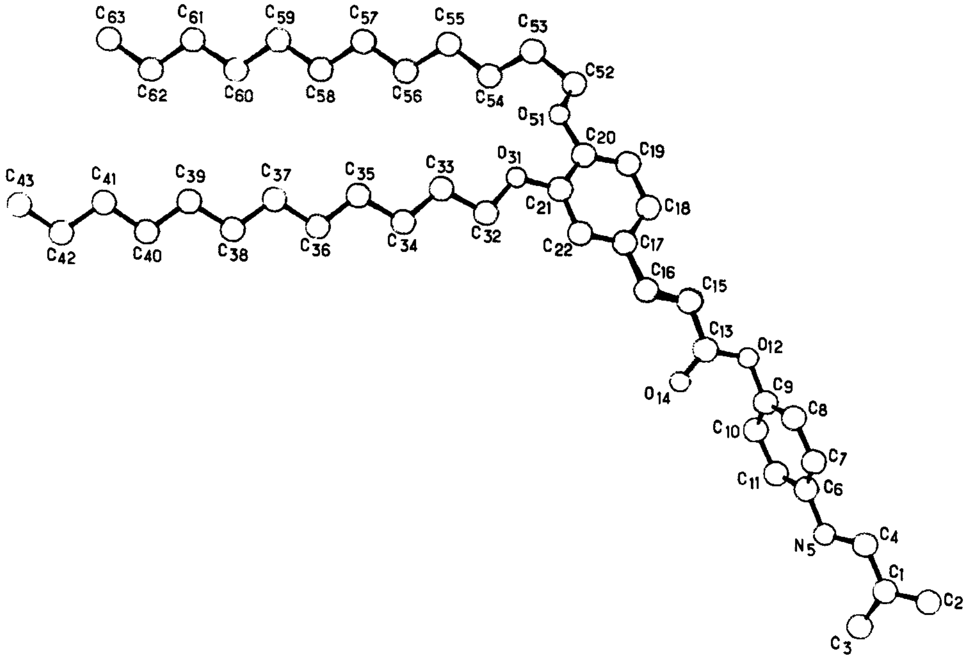


Figure 1. Atomic labelling of the crystallographic asymmetric unit (half the molecule).

Diffusion factors given by Cromer and Waber [16] for non-hydrogen atoms and by Stewart *et al.* [17] for hydrogen atoms were used. The final *R* and weighted *wR* factors are equal to 0·086 and 0·095 respectively. These rather high values can be assigned to the relative disorder of the molecule.

3. Results

3.1. *Description of the molecule*

Atomic parameters (x/a, y/b, z/c and B_{eq}) are given in table 1; the projection of the structure on the xz and xy planes is shown in figures 2 (*a*) and (*b*). Bond lengths and angles with their standard deviations are given in table 2. They are in good agreement with those usually observed for mesogens [18].

Curiously for this type of molecule, the alkyloxy chains are less agitated than the atoms of the polycyclic core of the molecule, particularly for the O(14) atom, as opposed to that generally observed in mesogens [18–20].

The molecule adopts a zig-zag form, as can be seen from the Ortep drawing [21] in figure 3, which is already been observed for a type C smectogen [20]. The significant torsion angles, which entirely define the molecular conformation, are as follows:

C(4)–N(5)–C(6)–C(7) = −37·0(7)°
C(4)–N(5)–C(6)–C(11) = 149·0(6)°
C(8)–C(9)–O(12)–C(13) = −106·2(7)°
C(10)–C(9)–O(12)–C(13) = 78·3(6)°
C(9)–C(12)–C(13)–C(15) = 165·4(7)°
C(9)–C(12)–C(13)–C(15′) = −168·7(6)°
O(12)–C(13)–C(15)–C(16′) = 143·1(7)°
O(12)–C(13)–C(15′)–C(16) = −163·0(7)°
O(14)–C(13)–C(15′)–C(16) = 31·4(8)°
O(14)–C(13)–C(15)–C(16′) = −50(1)°
C(13)–C(15)–C(16′)–C(17) = −174·6(6)°
C(13)–C(15′)–C(16)–C(17) = −170·5(7)°
C(15′)–C(16)–C(17)–C(18) = −18·1(7)°
C(15′)–C(16)–C(17)–C(22) = 173·1(7)°
C(15)–C(16′)–C(17)–C(18) = 67·6(7)°
C(15)–C(16′)–C(17)–C(22) = −131·4(7)°
C(19)–C(20)–O(51)–C(52) = 17·3(4)°
C(21)–C(20)–O(51)–C(52) = −161·4(4)°
C(20)–C(21)–O(31)–C(32) = 166·7(4)°
C(22)–C(21)–O(31)–C(32) = −11·6(4)°
C(20)–C(51)–C(52)–C(53) = −161·0(4)°
O(51)–C(52)–C(53)–C(54) = −63·2(4)°

One of the alkyloxy chains (atoms 21 to 43), i.e. chain 1, is completely stretched with C–C–C–C angles diverging from 0° or 180° by less than 5°. The other one (atoms C(52) to C(63)), i.e. chain 2, is partly extended with a torsion angle around the C(52)–C(53) bond close to −60°; the linear part starting with atom C(52) is 14·0 Å long; the length of chain 1, starting with the C(21) atoms of the phenyl ring, is 16·3 Å long. Chains 1 and 2 are not parallel, as can be seen from figure 2 (*a*) but make an angle of 38° between them (see figure 2 (*b*)), however both chains are parallel to the xy plane.

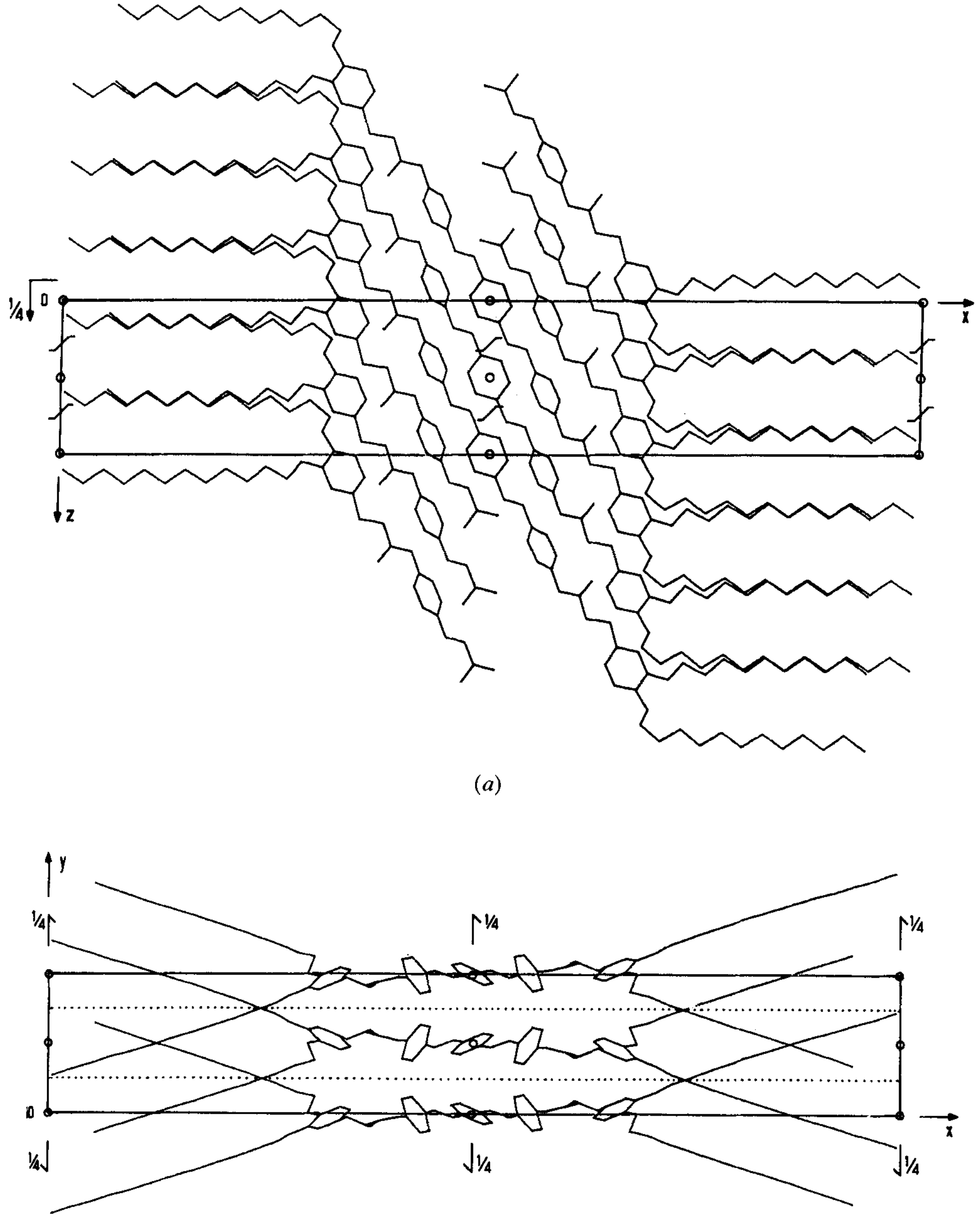
Table 1. Final atomic coordinates and equivalent isotropic thermal parameters B_{eq} (Å^2), where $B_{eq}=\frac{4}{3}\Sigma_i\Sigma_j\beta_{ij}\alpha_i\cdot\alpha_j$.

Atom	x/a	y/b	z/c	B_{eq}/Å^2
C(1)	0·98980	0·51388	2·35912	5·784
C(2)	1·01399	0·57676	2·39492	6·427
C(3)	0·97575	0·43597	2·46720	7·186
C(4)	0·97867	0·52691	2·21315	6·151
N(5)	0·95634	0·47639	2·17788	6·045
C(6)	0·94598	0·49383	2·03569	5·939
C(7)	0·95017	0·62648	1·95111	7·473
C(8)	0·93896	0·64019	1·81277	6·780
C(9)	0·92316	0·52432	1·76226	6·714
C(10)	0·91763	0·39339	1·84803	6·739
C(11)	0·92896	0·37771	1·98536	6·934
O(12)	0·91348	0·52547	1·62063	7·425
C(13)	0·88971	0·55819	1·59139	5·199
O(14)	0·87569	0·58456	1·68909	9·048
C(15)	0·88075	0·59740	1·44006	5·013
C(15′)	0·88136	0·52252	1·43802	4·323
C(16)	0·85693	0·60683	1·40199	5·206
C(16′)	0·85307	0·52677	1·41393	4·078
C(17)	0·84475	0·55287	1·25275	4·599
C(18)	0·85780	0·47371	1·14521	4·921
C(19)	0·84642	0·45607	1·00756	4·432
C(20)	0·82166	0·51638	0·97796	3·257
C(21)	0·80848	0·60089	1·08402	3·226
C(22)	0·81965	0·61706	1·22102	4·733
O(31)	0·78439	0·65989	1·04389	3·515
C(32)	0·76745	0·71718	1·15341	3·545
C(33)	0·74239	0·77021	1·07537	3·528
C(34)	0·72092	0·82043	1·17630	4·267
C(35)	0·69591	0·87151	1·09139	4·148
C(36)	0·67325	0·91924	1·18553	4·588
C(37)	0·64882	0·96452	1·09881	4·250
C(38)	0·62531	1·01000	1·18931	4·670
C(39)	0·60110	1·05773	1·09904	4·958
C(40)	0·57720	1·09440	1·19047	5·175
C(41)	0·55299	1·14354	1·09760	5·726
C(42)	0·52898	1·18316	1·18843	6.613
C(43)	0·50532	1·23361	1·10001	8·421
O(51)	0·80784	0·49835	0·84968	3·568
C(52)	0·81605	0·37677	0·75443	4·160
C(53)	0·79301	0·34301	0·64935	3·549
C(54)	0·76914	0·28013	0·72488	3·984
C(55)	0·74628	0·23364	0·62319	3·861
C(56)	0·72208	0·18151	0·70509	4·207
C(57)	0·69849	0·13545	0·60847	4·418
C(58)	0·67460	0·08642	0·69249	4·385
C(59)	0·65068	0·04237	0·59821	4·569
C(60)	0·62691	−0·00320	0·68838	5·077
C(61)	0·60282	−0·05217	0·59256	5·309
C(52)	0·57927	−0·09861	0·68236	5·906
C(63)	0·55549	−0·14667	0·58472	7·450

Table 2. Bond lengths (Å) and angles (°) with standard deviations in parentheses.

C(1)-C(2)	1·37(1)	C(15)-C(16′)	1·53(1)	C(37)-C(38)	1·523(7)
C(1)-C(3)	1·41(1)	C(15′)-C(16)	1·46(1)	C(38)-C(39)	1·523(8)
C(2)-C(3′)	1·369(9)	C(16)-C(17)	1·56(1)	C(39)-C(40)	1·527(8)
C(1)-N(4)	1·455(9)	C(16′)-C(17)	1·56(1)	C(40)-C(41)	1·539(8)
C(4)-N(5)	1·250(9)	C(17)-C(18)	1·378(8)	C(41)-C(42)	1·532(9)
N(5)-C(6)	1·412(8)	C(17)-C(22)	1·410(7)	C(42)-C(43)	1·50(1)
C(6)-C(7)	1·37(1)	C(18)-C(19)	1·393(7)	O(51)-C(52)	1·422(6)
C(6)-C(11)	1·376(9)	C(19)-C(20)	1·377(6)	C(52)-C(53)	1·530(7)
C(7)-C(8)	1·39(1)	C(20)-C(21)	1·395(7)	C(53)-C(54)	1·509(7)
C(8)-C(9)	1·34(1)	C(20)-O(51)	1·373(5)	C(54)-C(55)	1·527(7)
C(9)-C(10)	1·39(1)	C(21)-C(22)	1·383(7)	C(55)-C(56)	1·522(7)
C(9)-O(12)	1·39(1)	C(21)-O(31)	1·363(5)	C(56)-C(57)	1·527(7)
C(10)-C(11)	1·39(1)	O(31)-C(32)	1·424(6)	C(57)-C(58)	1·513(7)
O(12)-C(13)	1·262(8)	C(32)-C(33)	1·515(7)	C(58)-C(59)	1·524(7)
C(13)-O(14)	1·184(8)	C(33)-C(34)	1·511(7)	C(59)-C(60)	1·532(8)
C(13)-C(15)	1·50(1)	C(34)-C(35)	1·538(7)	C(60)-C(61)	1·550(8)
C(13)-C(15′)	1·50(1)	C(35)-C(36)	1·513(7)	C(61)-C(62)	1·520(8)
		C(36)-C(37)	1·510(7)	C(62)-C(63)	1·55(1)

C(1)-C(2)-C(3′)	120·9(7)	C(17)-C(18)-C(19)	121·0(5)
C(1)-C(3)-C(2′)	120·6(6)	C(18)-C(19)-C(20)	119·9(5)
C(2)-C(1)-C(3)	118·5(6)	C(19)-C(20)-C(21)	119·9(4)
C(2)-C(1)-C(4)	121·3(6)	C(19)-C(20)-O(51)	125·2(4)
C(3)-C(1)-C(4)	120·2(6)	C(21)-C(20)-C(51)	114·9(4)
C(1)-C(4)-N(5)	123·1(6)	C(20)-C(21)-C(22)	120·9(4)
C(4)-N(5)-C(6)	121·5(6)	C(20)-C(21)-O(31)	115·9(4)
N(5)-C(6)-C(7)	123·6(6)	C(22)-C(21)-O(31)	124·0(4)
N(5)-C(6)-C(11)	117·2(6)	C(17)-C(22)-C(21)	120·1(5)
C(7)-C(6)-C(11)	119·0(6)	C(21)-O(31)-C(32)	118·8(3)
C(6)-C(7)-C(8)	121·6(7)	O(31)-C(32)-C(33)	105·9(4)
C(7)-C(8)-C(9)	119·1(7)	C(32)-C(33)-C(34)	113·4(4)
C(8)-C(9)-C(10)	120·5(7)	C(33)-C(34)-C(35)	111·2(4)
C(8)-C(9)-O(12)	121·3(7)	C(34)-C(35)-C(36)	114·2(4)
C(10)-C(9)-C(12)	118·0(6)	C(35)-C(36)-C(37)	112·8(4)
C(9)-C(10)-C(11)	120·4(7)	C(36)-C(37)-C(38)	114·6(4)
C(6)-C(11)-C(10)	119·3(6)	C(37)-C(38)-C(39)	113·4(4)
C(9)-C(12)-C(13)	121·2(6)	C(38)-C(39)-C(40)	113·0(4)
O(12)-C(13)-O(14)	117·8(6)	C(39)-C(40)-C(41)	112·3(5)
O(12)-C(13)-C(15)	121·2(6)	C(40)-C(41)-C(42)	112·7(5)
O(12)-C(13)-C(15′)	113·9(6)	C(41)-C(42)-C(43)	113·6(6)
O(14)-C(13)-C(15)	119·8(7)	C(20)-O(51)-C(52)	117·7(4)
O(14)-C(13)-C(15′)	127·1(6)	O(51)-C(52)-C(53)	107·3(4)
C(13)-C(15′)-C(16)	109·8(8)	C(52)-C(53)-C(54)	112·4(4)
C(13)-C(15)-C(16′)	108·7(7)	C(53)-C(54)-C(55)	114·3(4)
C(15′)-C(16)-C(17)	111·9(7)	C(54)-C(55)-C(56)	112·1(4)
C(15)-C(16′)-C(17)	108·8(7)	C(55)-C(56)-C(57)	114·2(4)
C(16)-C(17)-C(18)	126·4(6)	C(56)-C(57)-C(58)	113·3(4)
C(16′)-C(17)-C(18)	120·0(6)	C(57)-C(58)-C(59)	114·2(4)
C(16)-C(17)-C(22)	113·9(6)	C(58)-C(59)-C(60)	112·1(4)
C(16′)-C(17)-C(18)	118·8(5)	C(59)-C(60)-C(61)	112·1(4)
C(18)-C(17)-C(22)	118·8(5)	C(61)-C(62)-C(63)	111·1(5)
		C(60)-C(61)-C(62)	112·0(5)



(*a*)

(*b*)

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

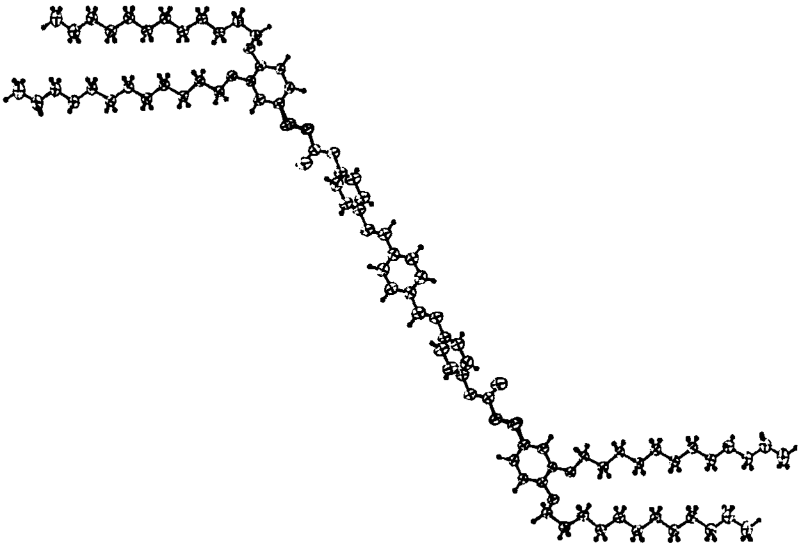


Figure 3. Ortep drawing of the molecule considered.

The angle between the polyaromatic central core and both alkyloxy chains is close to 120°. This polyaromatic moiety is 33·2 Å long (the distance between C(20) and its homologue C′(20)) relative to the centre of symmetry, which coincides with the centre of the molecule, or 36·2 Å (the distance between O(51) and its homologue O′(51)).

The central cycle $\varphi 0$, defined by atoms C(1), C(2) and C(3) and their homologues C′(1), C′(2) and C′(3), makes an angle of 66° with the following cycle $\varphi 1$ (atoms C(6) to C(11)), which in its turn makes an angle close to 47° with the next cycle $\varphi 2$ (atoms C(17) to C(22)); the angle between $\varphi 2$ and $\varphi 0$ is close to 72°. Finally the line defined by C(1) to O(51), that is to say the polycyclic core axis, is quasi-linear.

3.2. *Molecular packing*

The cohesion in the crystal is assumed to be almost uniquely due to van der Waals forces; this is in agreement with the very low density of 1·108. There are few intramolecular contacts, particularly between alkyloxy chains. There are very weak intermolecular contacts between the whole molecule and its homologues through the centres of symmetry; such contacts are only between methyl terminal groups. On the contrary, there are numerous interactions between one molecule and its homologues through the *c* glide plane and the 2_1 axes: on the one side, between chain 1 of one molecule and chain 2 of neighbouring ones; on the other side between neighbouring polyaromatic central cores.

Molecules form two-dimensional sheets parallel to the $y0z$ plane, whose thickness is about 51 Å, which is the length of the *a* axis, as can be seen in figure 2(*a*).

4. Discussion

The molecular arrangement, represented in figure 1(*a*) is typical of a lamellar structure with segregation of the aliphatic chains and of the central polyaromatic core. It is then possible to define molecular sheets as they are in smectic phases.

The aliphatic chains 1 and 2, are roughly perpendicular to the sheet plane. The polyaromatic cores are also linear and parallel to each other and to the *xz* plane; the average distance between core axes is close to 4·9 Å; they make an angle close to 60° (tilt angle) with the director perpendicular to the sheets.

This kind of arrangement, although concerning the solid state, is perfectly characteristic of a smectic C phase structure. As we recall such mesophases have been observed in another family of biforked mesogens for short lengths of alkyloxy chains [11]; moreover it is worthy to compare the above parameters to these, directly measured on the smectic C mesophase of a similar compound [13]. In this latter case we again find a molecular tilt angle of 60°. However the lattice spacing of the columnar mesophase is about 49·6 and 52·6 Å for the $C_{10}H_{21}$ and the $C_{14}H_{29}$ alkyloxy derivatives respectively (however we are presently in the solid state, where alkyl chains are fully or largely stretched).

In fact, for the present compound, the mesomorphic phase observed above the crystalline phase is not a smectic C phase but shows a hexagonal symmetry and probably a ϕ_h columnar structure [13]. The correlation between the symmetry of the crystal structure and the mesophase symmetry is not obvious. However it is noteworthy that the 60° tilt angle in the solid phase is in agreement with a hexagonal symmetry. The problem is then to find in which direction and where the loss of symmetry will happen, which corresponds to the crystal (3D)→hexagonal and eventually columnar mesophase transition; this is really a difficult task.

Interactions are very weak perpendicular to the *xz* plane, with a thickness of 51 Å, in the 0*x* direction and indefinite length in the 0*y* and 0*z* directions. There is no definitive proof of the existence of well-defined columns in the mesophase: under these conditions, we only have to understand the hexagonal symmetry in the mesophase but not the existence of the columns. Most of the molecular models [4, 5, 11] proposed for the hexagonal mesophase should be rejected from the point of view of filling space.

It is noteworthy that the crystal–mesophase transition enthalpy is not considerable [13] and may essentially correspond to the melting of chains, without a great intra- and intermolecular rearrangement. To support this hypothesis it should be noted, that for these compounds, the temperature of crystallization is very close to the temperature of melting. In such a case the structural invariant element could be the zig-zag conformation as found in the crystal. But even for this hypothesis the correlation between the crystal and the mesophase structures cannot be definitively assessed. In any case, the crystal structure has now been achieved and we have shown that more precise information should be obtained directly from the mesophase. Some high-resolution X-ray measurements are in progress.

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