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Liquid Crystals

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Phasid and biforked mesogens with thiobenzoate end groups

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Phasmid and biforked mesogens with thiobenzoate end groups

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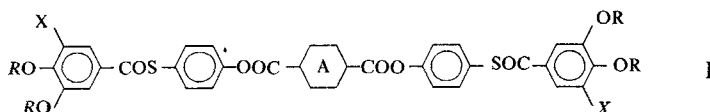
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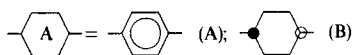
One phasmid and fourteen biforked mesogens with thiobenzoate end groups have been synthesized and studied. The phasmid displays a hexagonal columnar phase with a lattice parameter $a = 45.5 \text{ \AA}$ at 70°C . This phase is not observed for the biforked mesogens which exhibit only a nematic phase, a smectic C phase for short chains and an unknown phase for long chains. The tilt angle of the molecules in the smectic C phase is about 50° (the layer thickness is 38.2 \AA for a molecular length $l = 61 \text{ \AA}$ in the case of **IA** ($n = 12$)). The crystal structure of compound **IB** ($n = 12$) is monoclinic and the molecules adopt a zigzag form.

1. Introduction

Polycatenar mesogens constitute a new class of materials, the molecules of which are formed by a long central aromatic core with several terminal aliphatic chains. Phasמידs (three aliphatic end chains) [1] and biforked mesogens (two aliphatic end chains) [2, 3] have been synthesized and characterized through structural studies [4-15] for a better understanding of the relation between molecular structure and the mesomorphic behaviour. In order to study the influence of the thioester linkage—COS— in comparison with the previously used carboxylate ester group, new series of polycatenar mesogens has been considered; their general chemical formulae are:



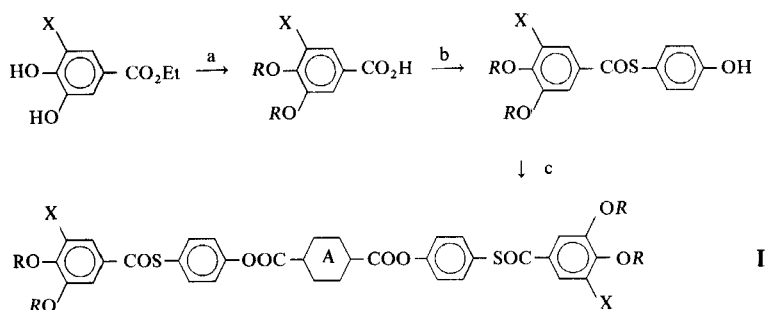
where



$X = \text{H}$; RO , $R = \text{C}_n\text{H}_{2n+1}$

2. Synthesis

The compounds of this series were prepared following the scheme:



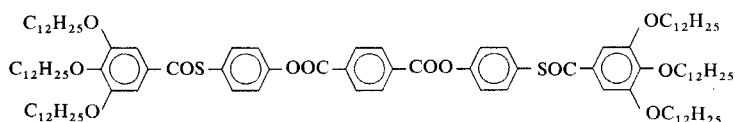
- (a) KOH, EtOH, RBr, HCl,
 (b) SOCl₂, 4-HS-C₆H₄-OH, Et₃N
 (c) HOOC-A-COOH, DCC, DMAP, CH₂Cl₂.

3. Results and discussion

All the compounds prepared are mesomorphic.

3.1. Phasmid or hexacatenar mesogen

Compounds with three chains at each end have enough aliphatic chains to fill the space around the rigid part of the molecules and generally display columnar phases [1, 6, 15]. For this reason we have prepared only one compound with the formula



C 59 ϕ_h 82 I

In fact, it exhibits the hexagonal columnar mesophase between 59°C and 82°C. This less birefringent mesophase has a fan-shaped texture with a wide homeotropic domain. So, it is uniaxial (see figure 1). Its structure was confirmed by X-ray diffraction measurements performed as a function of temperature using a Guinier focusing camera. This was equipped with a bent quartz monochromator (copper K_{α1} radiation from a Philips PW-1009 generator) and a heated sample holder; it was operated under vacuum. The powder patterns of the liquid crystal compound in Lindemann capillaries were recorded photographically.

The X-ray patterns registered contained three sharp Bragg reflections in the small angle region and a diffuse ring at 4.6 Å in the wide angle region. The reciprocal spacings of the sharp reflections were in the ratio 1:√3:√4, indicative of a two dimensional hexagonal lattice. They are in perfect agreement with a conventional columnar structure as suggested by the optical textures observed with a polarizing microscope. The intercolumnar distance deduced is 45.5 Å and does not vary as a function of temperature over the whole stability range of the columnar mesophase. The diffuse ring at 4.6 Å corresponds both to the aliphatic chains and to the rod-like cores of the molecules in the disordered state.

With the assumption of a classical columnar structure for the mesophase of this compound, one can easily calculate the average number n of molecules per unit length of a column, as has already been done for another phasmidic liquid crystal [4]

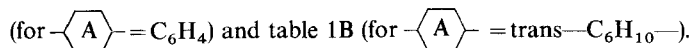
$$n = (\sqrt{3}/2)D^2(N_A/Mv)$$

where D is the distance between the axes of two neighbouring columns, N_A is Avogadro's number, M the molecular weight and v the specific volume. When taking for v an approximate value of $1.05 \text{ cm}^3 \text{ g}^{-1}$, a value comparable to the one measured for a similar phasmidic compound [4], one finds $n = 0.606 \text{ \AA}^{-1}$, which corresponds to 2.8 molecules per 4.6 \AA separation along the axis of the column. Since v is only an approximate value and not a value deduced directly from the experiment, one can consider that the value of n is about 3.

Therefore, the molecular arrangement in the columnar mesophase in this compound is similar to that described in [4]. It involves groups of three molecules with the aromatic cores parallel to one another and surrounded by the disordered paraffinic chains. Disc-like in shape, these groups are stacked one over one another, as in a conventional columnar mesophase, with an average approach distance of 4.6 \AA . The columns are then assembled in a two dimensional hexagonal lattice.

3.2. Biforked mesogens

The transition temperatures and types of mesophases for compounds I, $X = \text{H}$ are given in table 1A



These compounds with short chains ($n=8$ to 10 or 11) display nematic (N) and smectic C phases. When the chains are long enough, one only obtains the S_C phase. The nematic phase has typical threaded or marbled textures (see figure 2) and the S_C phase has broken fan-shaped or schlieren textures (see figure 3). The most interesting compound is the tetradecyloxy derivative of the central benzene ring series. It displays on cooling from the S_C phase, another and unknown mesophase and has the phase sequence

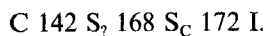
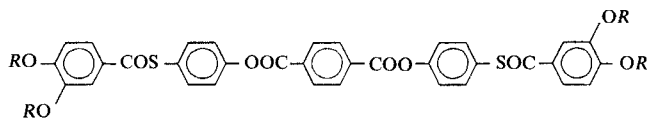


Table 1A. Transition temperatures ($^\circ\text{C}$) of compounds IA.



n		C	S_7		S_C		N	I
8	●	150	—		●	186	●	208
9	●	149	—		●	186	●	199
10	●	146	—		●	181	●	192
11	●	146	—		●	180	●	185
12	●	144	—		●	177	—	●
13	●	145	—		●	175	—	●
14	●	142	●	168	●	172	—	●

●, phase present; —, phase absent.

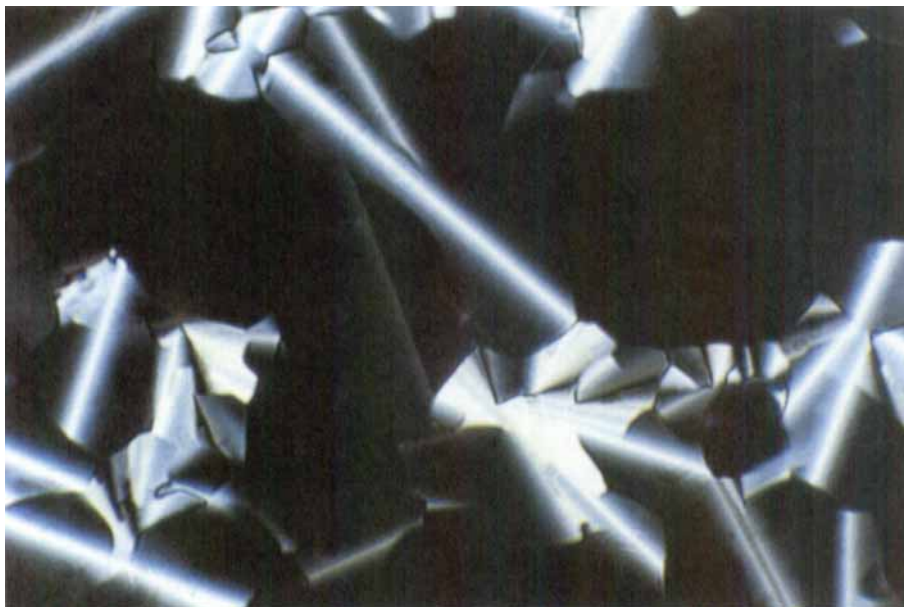


Figure 1. Optical textures of the Φh phase of the plasmid (I, $X = \text{OC}_{12}\text{H}_{2.5}$; central ring = C_6H_4) at 75°C .



Figure 2. Optical textures of the N phase of compound IA ($n = 10$) at 185°C .

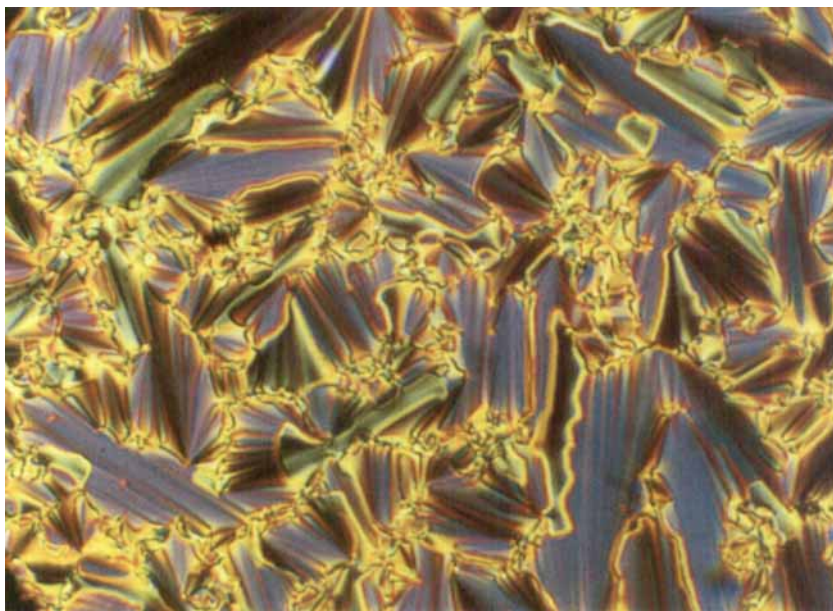


Figure 3. Optical textures of the S_C phase of compound IA ($n=10$) at 160°C.

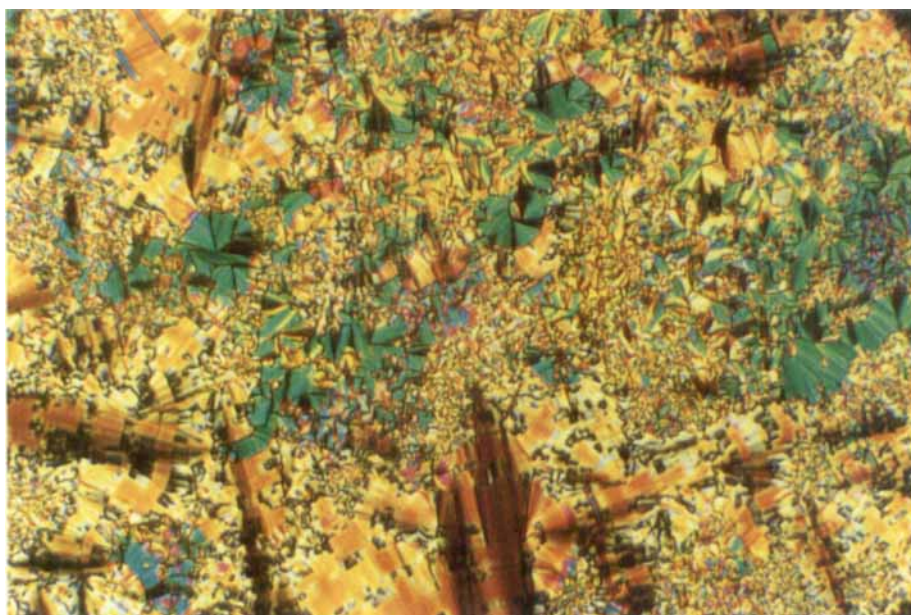
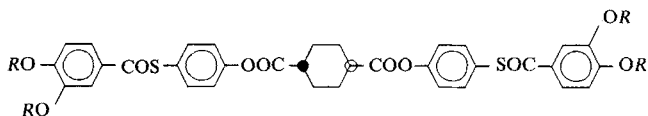


Figure 4. Optical textures of the S_γ phase of compound IA ($n=14$) at 160°C.

Table 1B. Transition temperatures (°C) of compounds **IB**.

n		C		S_C		N	I
8	●	125	●	170	●	183	●
9	●	124	●	169	●	180	●
10	●	122	●	165	●	172	●
11	●	124	●	163	—		●
12	●	122	●	161	—		●
13	●	122	●	159	—		●
14	●	120	●	156	—		●

●, phase present; —, phase absent.

This is the first time one has been able to observe in polycatenar mesogens the occurrence of a mesophase at lower temperatures than the S_C phase (see figure 4). The structural assignment of this phase is in progress.

The compounds with the flexible central cyclohexyl ring display the same mesomorphic properties, but their melting and clearing temperatures are around 20°C lower than those of the central benzene ring compounds.

The smectic C structure of compounds **IA** ($n = 10$ and 12) was characterized by X-ray measurements. The X-ray patterns contain one sharp Bragg reflection in the small angle region and a diffuse ring at 4.65 Å in the wide angle region; they are characteristic of the diffraction of a disordered smectic phase. The layer thicknesses are 36.75 Å and 38.2 Å for $n = 10$ and 12, respectively. In its most extended conformation, the $n = 12$ compound has a molecular length of about 61 Å; the tilt angle of the molecules in the smectic C phase can be estimated to be about 50°. The large value of this angle is probably due to the bulkiness of the paraffinic moiety (two long aliphatic chains attached on each end of the aromatic core), as mentioned previously in another study of biforked mesogens [2].

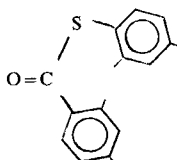
3.3. Comparison between the benzoates and thiobenzoates

The biforked mesogens with two benzoate end groups have been reported and they show a competition between lamellar and columnar mesophases dependent upon the chain length. So we can compare the mesomorphic properties of these mesogens with those of the thiobenzoate series. Let us point out some interesting features:

- The main difference between the benzoate and thiobenzoate derivatives is the existence of the columnar phases in the long chain benzoates [12] ($n = 12-14$). On the other hand, the thiobenzoate with a very long chain ($n = 14$) exhibits an unknown phase (probably a lamellar phase) on cooling from the S_C phase.
- The clarification temperatures of the thiobenzoates are higher than those of the benzoates, but the melting points are the same. The thiobenzoates therefore have wider mesomorphic temperature ranges.

The difference between the physical properties of these materials may be due to resonance effects or steric hindrance. As a matter of fact, the bond length $X-C_{Ar}$ is longer with S but the angle $C(=O)-X-C_{Ar}$ is lower with S. These values in table 2 [16] explain:

- The existence of an interaction between the two H in the *ortho*-positions of the two benzene rings in the bent conformation. This favours the planar *trans*-arrangement and the lengthening of the molecules:



- The increase in resonance in these thiobenzoates in which the *trans*-conformation is more stable and again, lengthening of the molecules is favoured. On the other hand, the larger dipole moment observed for the thiobenzoates than that for the benzoates, would favour formation of smectic phases [17].

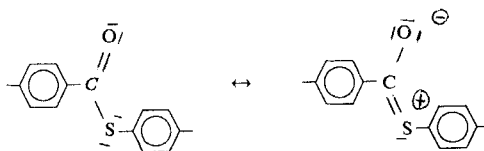


Table 2. Physical data for O and S molecular units.

	Molecular unit or atom	O	S
Angle	$C-X-C_{Ar}$	110°	104°
Bond	$X-C_{Ar}$	1.43 \AA	1.81 \AA
Electronegativity	X	3.5	2.5
IR	$COX-Ar$	1730 cm^{-1}	1670 cm^{-1}

4. Crystal structure analysis

4.1. Experimental

The compound studied is **IB** ($n=12$), whose molecular formula is $C_{82}H_{124}O_{10}S_2$ ($M_w = 1334.0 \text{ g cm}^{-3}$). It crystallizes from toluene solution: monoclinic system, space group P_{21}/c ($Z=2$); therefore the molecule lies on a centre of symmetry; the asymmetric unit corresponds to half the molecule. The crystal dimensions are $0.4 \times 0.225 \times 0.15 \text{ mm}$. The unit cell parameters were precisely determined from a least-squares fit of the setting angles for 25 centred reflections with $15 < \theta < 26^\circ$: $a = 50.674(7)$, $b = 9.943(1)$, $c = 8.254(1)$ and $\beta = 92.83(1)^\circ$. The data were collected on an Enraf-Nonius CAD-4 four-circle diffractometer, equipped with a graphite monochromator with $\sin \theta/\lambda < 0.50$ and an ω - 2θ scan mode. The radiation used was CuK_α ($\lambda = 1.54018 \text{ \AA}$). Reflections with

$\theta < 25^\circ$ have been measured twice and averaged. An empirical absorption correction was applied: the transmission factors were between 0.94 and 0.98. 4062 independent reflections were measured, out of which 2782 are observed ($I < 3\sigma(I)$). The structure was solved by direct methods using a Mithril package [18] and refined by least-squares refinement of $\Sigma w(F_o - F_c)^2$ with $w = 1/\sigma(F)^2$. All non-hydrogen atoms were refined with anisotropic thermal factors. Because of the high thermal motion of most non-hydrogen atoms, hydrogen atoms were placed in their theoretical position [19]. The refinement was then resumed. Diffusion factors for non-hydrogen atoms [20] and for hydrogens [21] were used.

The final reliability factors were $R = 0.076$ and $wR = 0.085$; $s = 2.85$; residual electronic density between -0.4 and $0.3 \text{ e}\text{\AA}^{-3}$; $(\Delta/\sigma)_{\text{max}} = 0.3$.

4.2. Results

Because the molecule lies on a centre of symmetry (P_{21}/c with $Z = 2$), the asymmetric unit corresponds to half the molecule. The labelling of the atoms is shown in figure 5.

Atomic parameters are given in table 3; the projection of the structure along the b axis is shown in figure 6. Bond lengths and bond angles, and their standard deviations are given in tables 4 and 5. They are in good agreement with those usually observed for similar compounds [13, 22]. Nevertheless, the bond lengths and angles relating to the ends of both alkyl chains are affected by large uncertainties resulting from the large thermal scattering factors of the corresponding atoms.

As expected, the polyaromatic central core atoms involve significantly smaller thermal motions than those of the alkyloxy chains: O(31) to C(43) and O(51) to C(63), respectively, especially for the octyl terminal groups, as can be seen from the Ortep drawing [23] in figure 7. The molecule adopts a zigzag form, as observed in

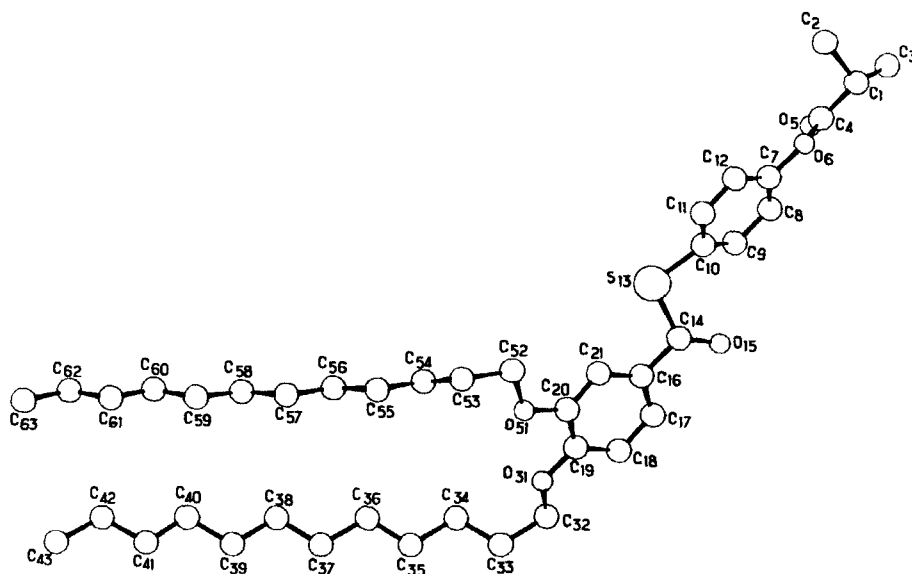


Figure 5. Labelling of atoms.

Table 3. Atomic coordinates and $\text{Beq} (\text{\AA}^2) = \frac{4}{3} \sum_i \sum_j \beta_{ij} a_i \cdot a_j$ for **IB** ($n=12$).

	X	Y	Z	$\text{Beq}/\text{\AA}^2$
C(1)	0.4901(2)	0.0023(8)	0.1638(9)	2.8(4)
C(2)	0.4736(2)	0.0628(9)	0.0212(9)	3.4(4)
C(3)	0.5073(2)	-0.1196(9)	0.1116(9)	3.6(4)
C(4)	0.4710(1)	-0.0534(9)	0.2860(9)	2.8(4)
O(5)	0.4649(1)	-0.1725(6)	0.3088(7)	4.4(3)
O(6)	0.4615(1)	0.0582(6)	0.3711(6)	3.7(3)
C(7)	0.4410(2)	0.0393(9)	0.4811(9)	3.3(4)
C(8)	0.4418(2)	-0.0703(9)	0.5925(10)	3.7(5)
C(9)	0.4218(2)	-0.0761(9)	0.7045(9)	3.3(4)
C(10)	0.4036(1)	0.0302(9)	0.7075(9)	2.4(4)
C(11)	0.4040(2)	0.1415(9)	0.5953(9)	3.5(4)
C(12)	0.4223(2)	0.1452(8)	0.4800(10)	3.4(4)
S(13)	0.3758(1)	0.0279(3)	0.8334(2)	3.5(1)
C(14)	0.3897(2)	-0.0195(9)	1.0298(9)	3.4(4)
O(15)	0.4125(1)	-0.0485(9)	1.0575(7)	6.0(4)
C(16)	0.3694(1)	-0.0247(9)	1.1576(9)	2.9(4)
C(17)	0.3749(2)	-0.1044(9)	1.2956(9)	3.0(4)
C(18)	0.3566(2)	-0.1161(9)	1.4110(9)	3.3(4)
C(19)	0.3324(1)	-0.0476(9)	1.3921(9)	3.0(4)
C(20)	0.3272(2)	0.0385(10)	1.2572(9)	3.3(4)
C(21)	0.3455(2)	0.0491(9)	1.1386(9)	3.5(4)
O(31)	0.3131(1)	-0.0509(6)	1.5016(6)	3.9(3)
C(32)	0.3149(2)	-0.1592(10)	1.6273(9)	3.9(5)
C(33)	0.2896(2)	-0.1442(11)	1.7177(10)	4.6(5)
C(34)	0.2653(2)	-0.1692(11)	1.6144(11)	4.7(5)
C(35)	0.2392(2)	-0.1422(13)	1.6990(11)	6.0(6)
C(36)	0.2148(2)	-0.1555(13)	1.5980(12)	6.0(6)
C(37)	0.1893(2)	-0.1249(14)	1.6806(13)	6.8(7)
C(38)	0.1642(2)	-0.1399(15)	1.5785(14)	8.0(8)
C(39)	0.1388(2)	-0.1177(15)	1.6590(16)	8.7(8)
C(40)	0.1137(2)	-0.1364(18)	1.5589(16)	9.8(9)
C(41)	0.0896(2)	-0.1109(18)	1.6372(18)	10.5(10)
C(42)	0.0654(2)	-0.1351(26)	1.5412(22)	15.5(14)
C(43)	0.0400(3)	-0.1098(29)	1.6138(26)	18.0(17)
O(51)	0.3033(1)	0.1050(7)	1.2516(6)	4.3(3)
C(52)	0.2971(2)	0.1894(11)	1.1110(10)	4.6(5)
C(53)	0.2691(2)	0.2472(12)	1.1316(11)	5.4(6)
C(54)	0.2477(2)	0.1379(12)	1.1301(12)	5.5(6)
C(55)	0.2209(2)	0.2037(14)	1.1489(12)	6.7(7)
C(56)	0.1974(2)	0.1097(15)	1.1368(14)	8.1(8)
C(57)	0.1707(2)	0.1788(18)	1.1504(16)	9.7(9)
C(58)	0.1459(3)	0.0889(18)	1.1294(17)	10.5(10)
C(59)	0.1200(2)	0.1666(18)	1.1382(18)	10.7(10)
C(60)	0.0962(2)	0.0905(21)	1.1060(20)	12.7(12)
C(61)	0.0717(2)	0.1609(20)	1.1247(22)	12.7(12)
C(62)	0.0474(3)	0.0815(30)	1.0932(26)	18.7(18)
C(63)	0.0229(4)	0.1487(32)	1.1153(35)	22.9(23)

similar compounds. The significant torsion angles of the polyaromatic central core are as follows:

C(3)–C(1)–C(4)–O(5)	–18.4(6)
C(2)–C(1)–C(4)–O(6)	–78.3(6)
C(1)–C(4)–O(6)–C(7)	–7.5(7)
C(4)–O(6)–C(7)–C(8)	46.6(7)
C(9)–C(10)–S(13)–C(14)	48.3(6)
S(13)–C(14)–C(16)–C(17)	157.9(6)
C(18)–C(19)–O(31)–C(32)	–15.6(7)
C(21)–C(20)–O(51)–C(52)	0.6(7)
C(19)–O(31)–C(32)–C(33)	–174.7(7)
C(20)–O(51)–C(52)–C(53)	178.2(7)
O(31)–C(32)–C(33)–C(34)	61.4(7)
O(51)–C(52)–C(53)–C(54)	–65.6(8)

Both alkyloxy chains are extended with C–C–C angles lying apart at 180°, within less than 10°.

The two chains are labelled as follows: chain 1 corresponds to atoms C(32) to C(43), chain 2 corresponds to atoms C(52) to C(63).

The O–C–C–C angle, at the beginning of each alkyloxy chain, differs from 180°: 61°, –66° for chains 1 and 2. The lengths of aliphatic chains 1 and 2 are about the same: 13.93 and 13.90 Å, respectively. The salient feature is that the mean planes of

Table 4. Bond lengths in Å and standard deviations in parentheses; the C₃' atom is the analogue (1–x, –y, –z) of the C(3) atom through the centre of symmetry. Compound **IB** (n = 12).

Bond	Length/Å	Bond	Length/Å
C(1)–C(2)	1.52(1)	O(31)–C(32)	1.46(1)
C(1)–C(3)	1.52(1)	C(32)–C(33)	1.52(1)
C(1)–C(4)	1.53(1)	C(33)–C(34)	1.48(1)
C(4)–O(5)	1.19(1)	C(34)–C(35)	1.55(1)
C(4)–O(6)	1.37(1)	C(35)–C(36)	1.46(2)
O(6)–C(7)	1.42(1)	C(36)–C(37)	1.52(2)
C(7)–C(8)	1.39(1)	C(37)–C(38)	1.50(2)
C(7)–C(12)	1.38(1)	C(38)–C(39)	1.49(2)
C(8)–C(9)	1.40(1)	C(39)–C(40)	1.49(2)
C(9)–C(10)	1.36(1)	C(40)–C(41)	1.43(2)
C(10)–C(11)	1.40(1)	C(41)–C(42)	1.44(2)
C(10)–S(13)	1.792(8)	C(42)–C(43)	1.47(3)
C(11)–C(12)	1.36(1)	O(51)–C(52)	1.43(1)
S(13)–C(14)	1.793(9)	C(52)–C(53)	1.54(1)
C(14)–O(15)	1.20(1)	C(53)–C(54)	1.50(1)
C(14)–C(16)	1.51(1)	C(54)–C(55)	1.51(2)
C(16)–C(17)	1.38(1)	C(55)–C(56)	1.49(2)
C(16)–C(21)	1.40(1)	C(56)–C(57)	1.51(2)
C(17)–C(18)	1.37(1)	C(57)–C(58)	1.52(2)
C(18)–C(19)	1.39(1)	C(58)–C(59)	1.51(2)
C(19)–C(20)	1.40(1)	C(59)–C(60)	1.42(2)
C(19)–O(31)	1.36(1)	C(60)–C(61)	1.42(2)
C(20)–C(21)	1.38(1)	C(61)–C(62)	1.45(3)
C(20)–O(51)	1.36(1)	C(62)–C(63)	1.41(4)
C(2)–C(3)	1.59(1)		

Table 5. Bond angles in ($^{\circ}$) and standard deviations in parenthesis; the C'(2) and C'(3) atoms are the analogues (1-x, -y, -z) of the C(2) and C(3) atoms through the centre of symmetry; for **IB** ($n=12$).

Bonds	Angle/ $^{\circ}$	Bonds	Angle/ $^{\circ}$
C(2)-C(1)-C(3)	111.5(7)	C(19)-C(20)-C(21)	119.8(8)
C(2)-C(1)-C(4)	107.4(6)	C(19)-C(20)-O(51)	115.4(7)
C(3)-C(1)-C(4)	108.5(6)	C(21)-C(20)-O(51)	124.8(7)
C(1)-C(4)-O(5)	127.7(7)	C(16)-C(21)-C(20)	119.5(8)
C(1)-C(4)-O(6)	108.9(6)	C(19)-O(31)-C(32)	117.8(6)
O(5)-C(4)-O(6)	123.4(7)	O(31)-C(32)-C(33)	105.1(7)
C(4)-O(6)-C(7)	121.1(6)	C(32)-C(33)-C(34)	113.3(8)
O(6)-C(7)-C(8)	121.3(7)	C(33)-C(34)-C(35)	114.5(8)
O(6)-C(7)-C(12)	115.3(7)	C(34)-C(35)-C(36)	116.4(9)
C(8)-C(7)-C(12)	123.0(8)	C(35)-C(36)-C(37)	116.2(9)
C(7)-C(8)-C(9)	117.9(8)	C(36)-C(37)-C(38)	117(1)
C(8)-C(9)-C(10)	119.6(7)	C(37)-C(38)-C(39)	118(1)
C(9)-C(10)-C(11)	120.6(7)	C(38)-C(39)-C(40)	118(1)
C(9)-C(10)-S(13)	123.6(6)	C(39)-C(40)-C(41)	117(1)
C(11)-C(10)-S(13)	115.4(6)	C(40)-C(41)-C(42)	117(1)
C(10)-C(11)-C(12)	120.9(8)	C(41)-C(42)-C(43)	119(2)
C(7)-C(12)-C(11)	117.9(8)	C(20)-O(51)-C(52)	116.2(6)
C(10)-S(13)-C(14)	104.0(4)	O(51)-C(52)-C(53)	105.9(7)
S(13)-C(14)-O(15)	124.2(7)	C(52)-C(53)-C(54)	115.2(8)
S(13)-C(14)-C(16)	112.9(6)	C(53)-C(54)-C(55)	111.7(9)
O(15)-C(14)-C(16)	122.9(8)	C(54)-C(55)-C(56)	118(1)
C(14)-C(16)-C(17)	118.5(7)	C(55)-C(56)-C(57)	117(1)
C(14)-C(16)-C(21)	121.4(7)	C(56)-C(57)-C(58)	119(1)
C(17)-C(16)-C(21)	120.1(7)	C(57)-C(58)-C(59)	116(1)
C(16)-C(17)-C(18)	120.2(8)	C(58)-C(59)-C(60)	118(1)
C(17)-C(18)-C(19)	120.7(8)	C(59)-C(60)-C(61)	119(1)
C(18)-C(19)-C(20)	119.6(7)	C(60)-C(61)-C(62)	119(2)
C(18)-C(19)-O(31)	124.9(7)	C(61)-C(62)-C(63)	119(2)
C(20)-C(19)-O(31)	115.4(7)	C(1)-C(2)-C'(3)	109.3(7)
		C(1)-C(2)-C'(2)	108.1(7)

two adjacent aliphatic chains are roughly perpendicular, as can be seen in figure 5. This probably corresponds to a close contact between both chains, as observed in similar structures [13, 22].

The angle between the axis of the central core and the direction of the alkyloxy chains is close to 130° . The core is 33.1 \AA long. The central cyclohexyl ring φ_0 , defined by atoms C(1) to C(3) and their analogues through the centre of symmetry, its adjacent cycle φ_1 , defined by atoms C(7) to C(12), the following one φ_2 , defined by atoms C(16) to C(21) and both the (C-COO) and C-COS) groups characterize the geometry of the polyaromatic central core.

The C-COO group makes an angle of 38° with the φ_1 cycle; the latter makes an angle of 42° with the C-COS group, which in turn, makes an angle of 22° with the φ_2 cycle; the angle between the φ_1 and φ_2 groups is 21° .

The cohesion in the crystal is almost entirely due to van der Waals forces; this is in agreement with the rather low density: 1.121. There are few intramolecular contacts, particularly between contiguous alkyloxy chains. There are very few intermolecular

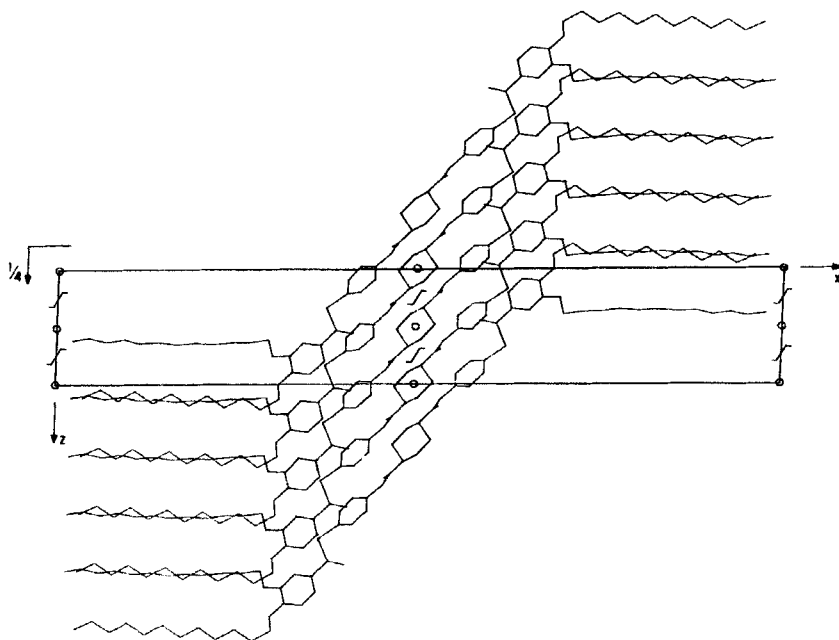


Figure 6. Projection of the structure along the *b* axis.

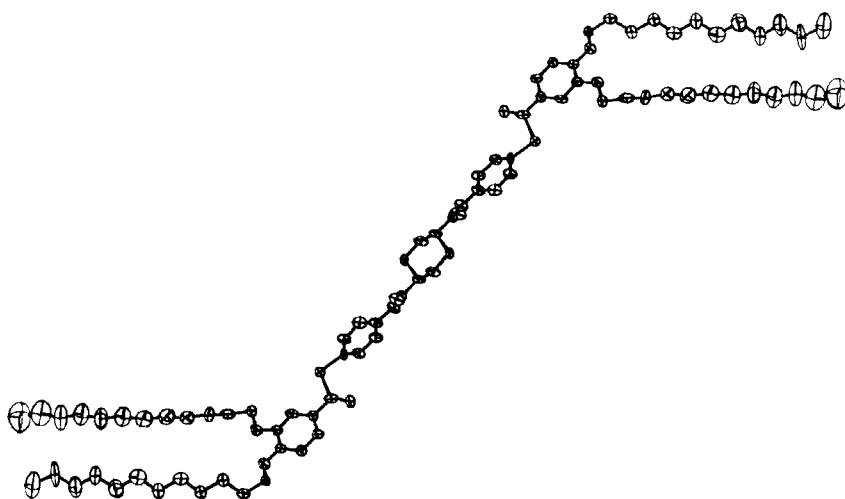


Figure 7. Ortep drawing of the molecule **IB**.

contacts between the parent molecule and its neighbours through the c glide plane and the 2_1 axes, involving particularly the central polyaromatic cores.

Molecules give two dimensional sheets, parallel to the yz plane, whose thickness is about 50 \AA , the length of the a axis. Interactions between sheets, through the terminal methyl groups are very weak.

4.3. Discussion

The molecular arrangement, represented in figure 5, 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 exist in smectic phases.

Both aliphatic chains are roughly perpendicular to the sheet plane. The polyaromatic cores are also linear and parallel to each other and to the xz plane; they make a tilt angle close to 70° with the director perpendicular to the sheets.

This kind of arrangement, although it concerns the solid state, is perfectly characteristic of a smectic C structure. Such mesophases have been observed in another family of biforked mesogens, for short lengths of the alkyloxy chains [7]; moreover it is noteworthy to compare the above parameters with these directly measured on the smectic C mesophase of a similar compound [3].

5. Conclusion

We have prepared two new series of biforked mesogens (tetracatenar and one phasmid (hexacatenar) with the $-\text{COS}-$ linkage. The latter displays a hexagonal columnar phase like the benzoates, but the former have a different behaviour from the benzoates. They only exhibit N and smectic C phases. One crystal structure has been obtained with the compound **IB** ($n = 12$). It is monoclinic and the molecules adopt a zigzag form: the polyaromatic central moiety of the molecules is almost linear and the two alkyloxy chains are extended. The mean axis of these chains make an angle close to 130° with the polyaromatic central core. The important bulkiness of the aliphatic chains induces a large tilt angle of the polyaromatic central cores of the molecules; the same feature is also observed in the smectic C phase. It is interesting to analyse the role of the aliphatic bulkiness in the special case of the phasmidic compound. Columnar mesophases are often observed with phasmids, instead of smectic C phases with biforked mesogens. This behaviour is probably due to crowding in the aliphatic medium; in the case of the phasmids, the smectic C layers are destabilized, the interactions between the aromatic cores becoming too weak. As a consequence, the smectic layers are broken into ribbons, which can then arrange themselves according to a two dimensional lattice. It could be useful to analyse the evolution of the molecular area in the smectic C phases of compounds exhibiting both smectic and columnar mesophases; work is in progress in that direction.

6. Experimental

The infrared spectra were recorded using a Perkin-Elmer 783 spectrophotometer and the NMR spectra with a Bruker 270 MHz instrument.

General procedure for the preparation of 4-hydroxyphenyl-3,4-dialkoxythiobenzoates: a solution of 3,4-dialkoxybenzoyl chloride (25 mmol) (prepared from the corresponding acid and an excess of thionyl chloride) [12] in CH_2Cl_2 (50 ml) was added dropwise over one hour to a cold solution (ice bath) of 4-hydroxythiophenol [24] (30 mmol) in CH_2Cl_2 (50 ml) and Et_3N (30 mmol). The reaction mixture was

stirred at room temperature overnight, the solvent was removed by rotary evaporation and the residual solid was transferred to a separatory funnel containing ethyl acetate (300 ml) and water (200 ml). The phases were separated and the organic phase was dried over anhydrous Na_2SO_4 , filtered through a pad of silica gel and concentrated by rotary evaporation. The solid was recrystallized from methanol. Yield: 70–92 per cent.

IR (Nujol, cm^{-1}): 3420, 1655, 1600, 1220, 1140.

NMR (CDCl_3 , d): 6.9–7.7 (m, 6 H), 6.8–7.45 (2d, 4 H), 5.65 (s, 1 H, OH), 4.05 (m, 4H, 2- CH_2O), 1.85 (m, 4H), 1.25–1.55 (m, 12–44 H), 0.9 (m, 12 H).

General procedure for the preparation of bis-3,4-dialkoxythiobenzoyloxyphenyl terephthalate: 4-hydroxyphenyl-3,4-dialkoxythiobenzoate (22 mmol), terephthalic acid (0.21 g, 1 mmol), dicyclohexylcarbodiimide (DDC) (0.21 g, 1 mmol), and 4-*N,N*-dimethylaminopyridine (DMAP) (20 mg) were mixed in CH_2Cl_2 (30 ml). The mixture was stirred at room temperature overnight. After filtration, the solvent was removed and the residue was chromatographed on silica gel with CH_2Cl_2 as eluent. The desired derivative was recrystallized from a toluene–ethanol (1:1) mixture. Yield 35–60 per cent.

IR (Nujol, cm^{-1}): 2930, 1735, 1675, 1595, 1200, 840

NMR(CDCl_3 , d): 8.4 (s, 4 H), 6.9–7.7 (m, 6 H), 7.35–7.6 (2d, 4 H), 4.05 (m, 8 H, 4- CH_2O), 1.85 (m, 8 H), 1.25–1.55 (m, 24–88 H), 0.88 (m, 12 H)

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