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Structural studies of a new series of biforked mesogens derived from 3,4 dialkoxy cinnamic acid and 3-(3,4 dialkoxy-phenyl) propanoic acid

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Structural studies of selected homologues of some new series of biforked mesogens have been performed by X-ray diffraction methods. These series exhibit a thermotropic mesomorphism which shows some similarities with lyotropics. We have identified three different mesophases with large three dimensional lattice cells (i.e. body centred cubic, hexagonal and rhombohedral). The occurrence of such mesophases is related to the core flexibility; moreover, the chain to core length ratio is one of the main parameters that drive the thermotropic polymorphism, playing a role similar to that of the solvent concentration in a lyotropic system. However the symmetries as well as the lattice constants, in units of molecular size, appear to be different in the two cases owing to differences in their chemical architecture.

1. Introduction

Since the phasmidic compounds were synthesized by Malthête *et al.* [1] in 1984, they have excited more and more interest in the field of thermotropic liquid crystals. These compounds differ from the usual mesogens because they have more than one aliphatic chain at each terminal phenyl group of an elongated aromatic core; the molecules have therefore an hybrid shape between a rod and a disc. Until the appearance of these new compounds, nearly all of the materials could be classified into two classes of thermotropic mesogens according to their shape, the symmetries of the mesophases being different for these two classes.

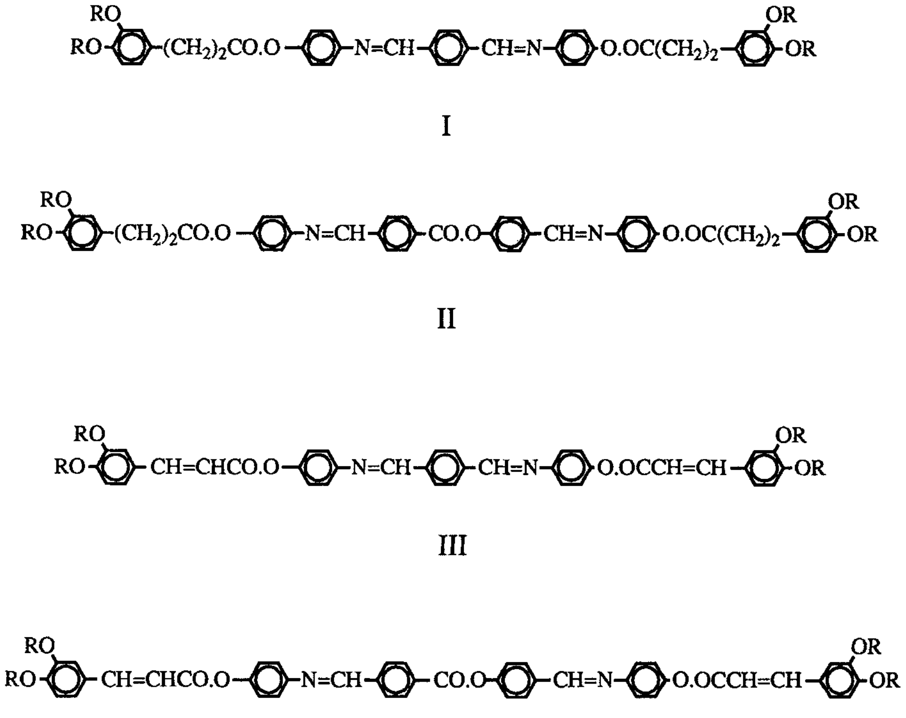
Calamitic molecules are made of an elongated aromatic core with only one chain grafted at each end; these rod-like molecules form nematic and lamellar mesophases (smectic). A very few compounds eventually may also exhibit mesophases with a three dimensional lattice (smectic D). Disc-like molecules constituted of a flat, rigid core surrounded by at least six paraffinic chains form columnar mesophases [2], they stack in cylinders of infinite length forming a two dimensional periodic network. In fact, columnar mesomorphism is more general. As an example, binuclear copper complexes [3] of fatty acids form columnar phases with only four grafted chains. Non-planar (conical) [4] or less rigid (macrocycles) [5] cores can also induce a columnar polymorphism if the number of grafted chains is sufficient. It seems therefore that the symmetry of the mesophases depends of the number of paraffinic chains in comparison to the core size.

Phasmidic molecules having four to six long paraffinic chains are a good example of this idea since they present a smectic and a columnar polymorphism with a large predominence of a hexagonal mesophase for five and six chains. In this case, the column is no longer a stack of individual molecules, but of small clusters of three to five molecules [6]. Each column is still made of a central aromatic core surrounded by a paraffinic external shell but its structure is more similar to the structure of a cylinder in a hexagonal lytotropic mesophase than to that of a column made of rigid disc-like molecules. The phasmidic molecules grafted with four paraffinic chains (also called biforked mesogens) exhibit both smectic and columnar phases. In the same series a transition from a smectic C to a hexagonal phase is obtained by increasing the chain length or the temperature. Between these two phases, mesophases with two dimensional oblique or three dimensional cubic lattices have been already put in evidence [7] underlining the similarities with lyotropic mesomorphism [8]. Recently, new series of biforked molecules have been synthesised and it appears that the polymorphism of a sequence of mesophases beginning with a lamellar S_C and ending with a hexagonal columnar phase is especially rich. As in compounds studied previously the transition between lamellar and columnar phases was obtained by grafting two aliphatic chains at each end of a long rod-like core, the main difference lies in the core flexibility. In a previous paper the synthesis and thermal behaviour including textural observations of four series have been described, [9] and here we present preliminary structural results obtained by the mean of X-ray diffraction methods on the mesophases of some selected compounds.

2. Experiments

X-ray diffraction data were obtained on unoriented samples held in Lindemann glass tubes rotated around their axis and maintained at a constant temperature to within ± 1°C. We have used a Guinier camera with a diameter of 114·7 mm. The radiation λCuKα_1 comes from a linear fine focus 8 × 0·015 mm and is reflected by a Johannson quartz monochromator. Some experiments have also been performed at LURE using the synchrotron radiation with a Ge(111) monochromator and a collimator with a diameter of 0·3 mm. The wavelength is 1·6 Å, and the film to sample distance of 247 mm allows a better dispersion for the reflections from large three dimensional lattices. The lattice constants were obtained from a least squares fit.

We recall that the four series studied have an original core structure since the two external phenyl rings of a core of five (series I, III) or six (series II, IV) rings are linked to the central part by a flexible -$(CH_2)_2$-linkage (series I, II) or an unsaturated -$(CH)_2$-linkage series (III, IV); see figure 1. We have studied seven different compounds and their polymorphism is reported in table 1. Among these compounds three belong to series I. The shortest derivative (C_9) has three different mesophases as observed by polarizing microscopy, the C_{10} derivative has two mesophases and the last one, C_{14}, only one. Three homologues of series II have also been studied. The C_{10} derivative exhibits four mesophases on heating. The last one is cubic and on cooling the sample from the isotropic liquid, we first see a hexagonal mesophase. This metastable mesophase and the phase which exists just below the cubic phase cannot be studied by X-ray diffraction because of their lack of stability, the C_{12} and C_{14} derivatives have two and one mesophases, respectively. Finally only one compound (C_{12}) with ethylene linkages has been studied (series IV).



I

II

III

IV

Figure 1. The four series of new biforked mesogens [9] ($R = C_nH_{2n+1}$).

Table 1. Phase behaviour of the phasmids.

Compound	C	S_C	?	?	?	Cub	hex2D	I
C_9 (I)	x 109°C	—	x 126°C	x 152°C	x 155°C	—	—	x
C_{10}(I)	x 110°C	—	—	x 150°C	—	—	x 155°C	x
C_{14}(I)	x 111·5°C	—	—	—	—	—	x 154°C	x
C_{10}(II)	x 93°C	x 128°C	x 143°C	x 148°C	—	x	— 207°C	x
C_{12}(II)	x 99°C	—	—	x 130°C	—	—	x 201°C	
C_{14}(II)	x 98°C	—	—	—	—	—	x 195°C	x
C_{12}(IV)	x 143°C	x 176°C	x 204·5°C (*a*)	x 208°C	—	—	—	x

x, the mesophase exists; —, the meosphase does not exist; C = crystal; S_C = smectic C; Cub = cubique; hex2D = hexagonal columnar mesophase; I = isotropic liquid; ?, mesophases identified only by X-ray diffraction methods; (*a*) between 204·5 and 208°C, the C_{12}(III) derivatives present a weakly birefringent shlieren texture which might be that of a nematic mesophase.

These later compounds have high melting points and are chemically less stable than the compounds of series I and II. In the compound studied here, a smectic C phase is obtained just above the melting point, two other mesophases then follow, in fact the last one, above 205°C, is only weakly birefringent.

3. Results

All of the diffraction patterns have sharp rings at small angles and a diffuse halo for a scattering angle of about 20°. Therefore the centres of mass of the molecules have the same kind of order as in a liquid. The sharp rings reveal a periodic organisation in one, two or three dimensions.

We present first the unique derivative of series IV: diffraction patterns cannot be obtained above 200°C since the chemical stability of the compound becomes very low. However, under the action of a magnetic field, we have obtained partially aligned samples of the two mesophases. Just after the melting point we have a lamellar phase with a periodicity of 36·05 Å. This period is small compared to the length of the molecule in an extended conformation ($\sim$65 Å). Therefore, in agreement with the optical observations [9], we have a S_C phase with a tilt angle of the order of 50°. At a higher temperature, the small angle pattern shows six sharp reflections and we can assign these reflections to an oblique two dimensional lattice (see table 2). The lattice constants are $a = 44{\cdot}47$ Å, $c = 39{\cdot}9$ Å, $\beta = 120{\cdot}8°$. The reflection (10) is not of measurable intensity.

Table 2. Powder pattern assignment of the columnar oblique mesophase of the dodecyloxyderivative of series IV at 180°C. Lattice constants: $a = 44{\cdot}47$ Å, $b = 38{\cdot}90$ Å and $\gamma = 120{\cdot}8°$.

h	k	d(calc)/Å	d(meas)/Å
1	0	38·20	—
1	$\bar{1}$	35·83	36·23
0	1	33·42	33·42
2	$\bar{1}$	22·18	—
1	1	20·49	20·56
1	$\bar{2}$	19·38	—
2	0	19·10	19·10
2	$\bar{2}$	17·92	18·05
0	2	16·71	16·59

We now discuss the three derivatives of series I. The C_{14} derivative has a hexagonal columnar mesophase. The lattice spacing decreases with increasing temperature: $a = 54{\cdot}0$ Å at 120°C and 52·6 Å at 140°C.

The high temperature phase of the C_{10} derivative is also a hexagonal columnar mesophase with a lattice spacing of 49·6 Å at 151°C. The low temperature mesophase gives at least twelve sharp rings corresponding to lattice spacings between 60 and 15 Å, the lattice is a three dimensional hexagonal lattice. There are no systematic extinction rules, but a lot of non-forbidden reflections are still missing (see table 3(*a*)). However the powder patterns are reproducible and remain quite unchanged with temperature and so a coexistence of phases induced by impurities is excluded. The lattice parameters decrease simultaneously with increasing temperature, but the ratio c/a is nearly constant (see figure 2(*a*)). At 118°C, $a = 90{\cdot}45$ Å and $c = 145{\cdot}30$ Å. The area of the basal plane of the lattice is nearly three times larger than the lattice area in the hexagonal columnar phase. Indeed the main Fourier component of the electronic density has nearly the same wavevector in the two hexagonal phases, as can be seen on the diffraction pattern of the three dimensional hexagonal phase see (figure 2(*c*)): the visible rings occur in three groups, corresponding roughly to wavevectors q_0, $2q_0$, $3q_0$, with $q_0 = 2\pi/45$ Å.

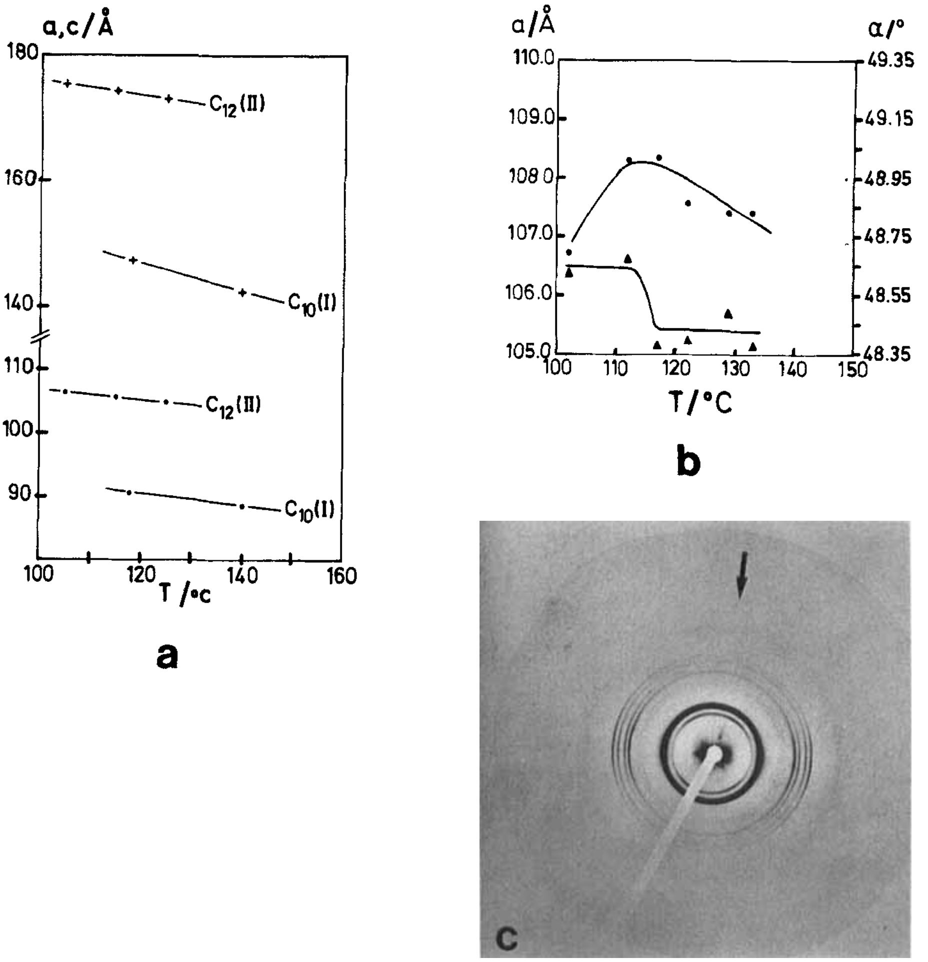


Figure 2. Temperature dependence of the lattice constants for the non- cubic three dimensional mesophases. (*a*) Three dimensional hexagonal mesophases of the C_{10}(I) and C_{12}(II) derivatives; a = ●, c = +. (*b*) Rhombohedral mesophase of the C_9(I) derivative; ● = a, ▲ = α. (*c*) Diffraction pattern of the three dimensional hexagonal mesophase of the C_{10}(I) derivative obtained with the synchrotron source (LURE). T = 118°C; λ = 1·6 Å. Notice the fibre-like textural aspect (fibre axis$\|c$) of the sample, from which a confirmation of the three dimensional character of the lattice is derived.

It seems, from optical observations, that the polymorphism of the C_9 derivative is very similar to that of the C_{10}. In fact, the high temperature mesophase is still columnar phase but six sharp rings are seen and they correspond to an oblique lattice which is slightly distorted from hexagonal symmetry: a = 49·48 Å, b = 47·32 Å, γ = 117·4° (see table 3(*b*)). Assuming a specific gravity of 1 g cm^{-3} we can estimate the mean linear density of molecules along the column axis for the columnar mesophase of the three derivatives. This density is nearly constant and equal to approximately 1 mol/Å; this is comparable to the density of columns of phasmids having the same number of grafted chains and the same core length [6]. Below this mesophase we have seen only a single kind of liquid-crystalline powder pattern. We observe 12 sharp rings at small angles and we can assign a three dimensional hexagonal lattice.

Table 3. Powder pattern assignments of mesophases of series I compounds. (*a*) The three-dimensional hexagonal mesophase of the decyloxy derivative at 118°C. The fourth index $i = -(h + k)$ is omitted in tables (*a*) and (*c*). Lattice constants a = 90·45 Å, c = 145·30 Å. (*b*) The two dimensional oblique lattice of the columnar phase of the nonyloxyderivative at 148°C. a = 49·48 Å, b = 47·31 Å, γ = 117·4°. N.b. the observed rings can be fitted to a centred rectangular lattice a = 87·94 Å, b = 47·75 Å with a least square deviation twice as high; however biforked mesogens generally have only hexagonal or oblique columnar mesophases. (*c*) The rhombohedral R $\bar{3}$ C mesophase of the nonyloxy derivative (hexagonal axes) at 117°C. Lattice constants (*a*) = 88·80 Å, (*c*) = 286·35 Å.

(*a*)

h	*k*	*l*	*d*(calc)/Å	*d*(meas)/Å
0	0	1	145·30	—
1	0	0	78·33	—
0	0	2	72·65	—
1	0	1	68·95	—
1	0	2	53·27	53·27
0	0	3	48·43	—
1	1	0	45·22	45·20
1	1	1	43·18	43·03
1	0	3	41·19	—
2	0	0	39·17	—
1	1	2	38·39	—
2	0	1	37·81	—
0	0	4	36·32	—
2	0	2	34·47	—
1	1	3	33·05	—
1	0	4	32·95	—
2	0	3	30·45	30·53
2	1	0	29·60	—
0	0	5	29·06	29·04
2	1	1	29·01	
1	1	4	28·32	—
2	1	2	27·41	—
1	0	5	27·24	—
2	0	4	26·63	—
3	0	0	26·11	—
3	0	1	25·70	25·63
2	1	3	25·26	—
3	0	2	24·57	—
1	1	5	24·45	24·29
2	0	5	23·34	—
1	0	6	23·14	—
3	0	3	22·98	—
2	1	4	22·95	—
2	2	0	22·61	22·59
2	2	1	22·34	—
3	1	0	21·73	—
2	2	2	21·59	—
3	1	1	21·49	—
3	0	4	21·20	21·26
3	1	2	20·81	—
28 unobserved rings				
4	1	1	16·97	—
1	1	8	16·85	16·87
4	1	2	16·64	—
2	2	6	16·52	—
2	0	8	16·48	16·46
3	2	4	16·46	
3	0	7	16·25	—

Table 3 (*continued*).

(*a*)

h	*k*	*l*	*d*(calc)/Å	*d*(meas)/Å
4	0	5	16·24	—
3	1	6	16·17	—
0	0	9	16·14	—
4	1	3	16·11	—
1	0	9	15·81	15·86

(*b*)

h	*k*	*d*(calc)/Å	*d*(meas)/Å
1	0	43·92	43·78
0	1	42·00	42·06
1	$\bar{1}$	41·30	—
1	1	25·12	25·24
2	$\bar{1}$	24·68	—
1	$\bar{2}$	23·65	23·70
2	0	21·96	21·94
0	2	21·00	20·92
2	$\bar{2}$	20·64	—

(*c*)

h	*k*	*l*	*d*(calc)/Å	*d*(meas)/Å
0	1	1	74·27	—
1	0	2	67·75	—
0	1	4	52·40	52·25
0	0	6	47·73	47·47
1	0	5	45·93	—
1	1	0	44·40	44·15
1	1	3	40·26	4014
2	0	1	38·11	—
0	2	2	37·14	37·41
0	1	7	36·12	35·89
2	0	4	33·87	—
1	1	6	32·51	—
1	0	8	32·45	32·23
0	2	5	31·92	—
1	2	1	28·92	—
2	1	2	28·48	—
2	0	7	28·02	—
1	2	4	26·93	—
0	1	10	26·84	—
0	2	8	26·20	26·36
2	1	5	25·92	—
1	1	9	25·86	25·75
3	0	0	25·63	—
3	0	3	24·76	—
1	0	11	24·66	—
0	0	12	23·86	—
1	2	7	23·69	23·74
2	0	10	22·97	22·84
3	0	6	22·58	—
2	1	8	22·56	—
2	2	0	22·20	22·02

With an assignment corresponding to a R$\bar{3}$c rhombohedral space group see (table 3(*c*)) [10]. We have plotted the lattice parameters versus temperature in figure 2(*b*). A slight discontinuity in the angle α of the rhombohedron appears between about 122 and 127°C. Such a discontinuity may correspond to a change in birefringence detected at 127°C with a microscope [9]. At the same temperature, a small anomaly is detected only on heating in the D.S.C. trace (see figure 3).

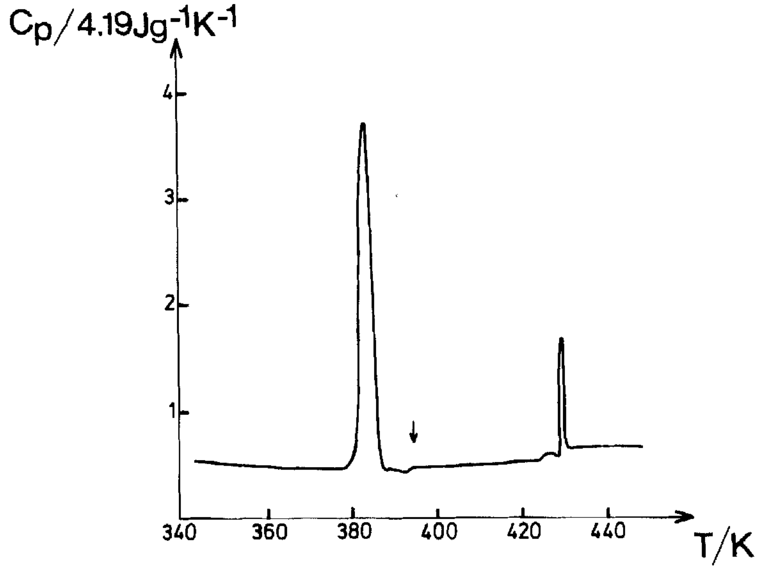


Figure 3. Differential scanning calorimetric trace obtained with a Perkin-Elmer 4 of the C_9(I) derivative (heating rate 10 K/min). The arrow indicates an eventual transition between two rhombohedral mesophases.

The two highest homologues of series II, C_{12} and C_{14}, have the same polymorphism as the C_{10} and C_{14} derivatives of seies I, respectively. The hexagonal columnar phase has a lattice parameter of 57·4 Å for the C_{12} derivative and 59·1 Å for C_{14} at a temperature of about 150°C. The corresponding linear molecular density is 1·2 molecules per Angström of column length; this value is consistent with the linear molecular density in a column of a phasmid, the core of which is made of six phenyl rings [6]. The low temperature mesophase of the C_{12} derivative has a powder pattern entirely similar to that of the low temperature mesophase of the C_{10} derivative of series I. The lattice constant dependence on temperature for the P 6/m m m lattice of the C_{12} derivative of series II is reported in figure 2(*a*).

As we have already pointed out, only three mesophases of the C_{10} derivative have been studied by X-ray diffraction. The S_C phase has a lattice constant of 40·2 Å which is larger than usual for the layer thickness of a S_C phase of phasmids [11]. By heating the sample, the S_C phase transforms into an oblique two dimensional phase with lattice constants: a = 92·3 Å, c = 52·6 Å and β = 97·9°. By comparison with the compound of series IV, it appears that the lattice is more anisometric, and that the reflections ($h\,o$) are still of weak intensity (see Table 4 (*a*)). The diffraction pattern of the cubic phase shows four sharp rings; the corresponding scattering vectors are proportional to the square root of all integers between 6 and 9. We have therefore a body centred cubic lattice (see table 4 (*b*)). The existence of 2 2 2 and 3 3 0–4 1 1 rings

Table 4. Powder pattern assignment of the mesophases of the decyloxy derivative of series II. (*a*) The oblique columnar mesophase at 133°C. Lattice constants = a = 92·3 Å, b = 52·6 Å, γ = 97·9°. (*b*) The body centred cubic lattice at 153°C (a) = 182·63 Å. The five first rings have not been reported in the table since they have not been seen experimentally except for a weak line at the position of the 220 reflection.

(*a*)

h	*k*	*d*(calc)/Å	*d*(meas)/Å
1	0	92·62	—
0	1	52·29	51·51
1	$\bar{1}$	48·80	48·12
2	0	46·31	45·71
1	1	42·85	43·54
2	$\bar{1}$	37·61	38·10
2	1	32·32	32·65
1	$\bar{2}$	26·22	—
0	2	26·15	26·12

(*b*)

h	*k*	*l*	*d*(calc)/Å	*d*(meas)/Å
2	2	2	52·72	52·75
3	2	1	48·81	49·11
4	0	0	45·66	45·40
4	1	1	43·05	43·00
3	3	0		

ruled out the presence of a diamond glide mirror. Therefore an isomorphy with the smectic D phase (space group I a$\bar{3}$d) [12] is excluded. This cubic phase is analogous to that already discovered with another phasmid [5]. The powder patterns of the two compounds exhibit the same rings of high intensity but in [5] ten different scattering vectors proportional to the square roots of 3, 5, 6, 7, 8, 9, 10, 13, 19, 25 have been measured. Here the lattice constant, a = 182·63 Å, is slightly higher than in the first phasmid studied. Among the seven possible space groups, we have only kept the centrosymmetric ones since presently there is no evidence of a chirality in any phasmidic mesophase. Three possibilities can thus be considered: I m $\bar{3}$, I $\bar{4}$ 3 m and I m $\bar{3}$ m.

4. Discussion

The preliminary structural results obtained on these compounds have two aspects: on the one hand, the structural features of the smectic C and the hexagonal columnar phases are very similar to those of all phasmids; on the other hand, the transition between the lamellar and the columnar phase through new mesophases can take different aspects depending of the chemical architecture of the compounds. The same kind of remarks can be made about the mesomorphism of amphiphilic molecules which usually form lyotropic phases. In this case, a change in the symmetry of the mesophases corresponds to a modification of the curvature of the interface between hydrophobic and hydrophilic media. This curvature, most often driven by the water concentration, is introduced to counterbalance the misfit between the equilibrium areas of the two amphipatic parts of the molecule. The liquid-crystalline behaviour can then be described as an organisation of films (water and paraffinic ones) in which the role of a single molecule is without any clear meaning. We have already underlined that the interface between aromatic cores and paraffinic chains is fundamental for the description of the phasmidic mesophases while the behaviour of a single molecule cannot be followed [6]. Since the curvature of the aromatic-paraffinic medium interface depends on the number of paraffinic chains grafted onto a core and of the relative thickness of the two films let us introduce a parameter $B = n_c/n_\phi$ where n_c is the number of carbon atoms of the paraffinic moïety of a molecule and n_ϕ the number of phenyl rings forming the core. Phasmidic compounds studied here exhibit only a columnar hexagonal phase for $B > 9$ and a smectic C nematic sequence for $B < 6$. This statement holds also for phasmids studied previously at least if the core is sufficiently long (five phenyl rings and more) and if a long chain is grafted in paraposition on each external core ring [6]. If we show the polymorphism of the series I and II on a plane (B versus temperature), the domains of stability of the different mesophases are the same except a difference in the temperature scale for the two series (see figure 4).

This schematic representation of the phase diagram is very crude, firstly because the temperature scale is dependent of the core size (n_ϕ) and because B is not the only relevant parameter describing the chemical structure; secondly because no information is given about the real shape of the domains and of the possible sequence of mesophases. However, we have a synthetic view of the topology of the phase diagram and this can help us in making a comparison with lyotropic systems where B is replaced by the water concentration. As an example, a very rich sequence of mesophases have been found in the binary system, sodium dodecyl sulphate-water [13], and with an increasing amount of water lamellar L_α, tetragonal (three dimensional), cubic (I m $\bar{3}$ m) rhombohedral, oblique (2D) and hexagonal (2D) symmetries are encountered successively.

At a first glance the similarities between this sequence and the phasmidic polymorphism obviously appear. Assuming that in our case the frontiers between cubic, oblique and rhombohedral phases are not well defined, a path can be drawn which goes successively through the domains of lamellar, rhombohedral, cubic, oblique and hexagonal columnar mesophases. However, if we consider the symmetries, the differences are obvious. The lamellar phase of phasmidic molecules is of smectic C type while the L_α phase can be compared to an S_A phase, as a consequence, the oblique phase appears to be different. In figure 4, there are, in fact, two domains for the oblique phase: close to the S_C domain, the relation between the lamellar phase and the two dimensional phase is obvious. In fact, the lamellae break into finite ribbons (see figure 5(*a*)); moreover, there is no important modulation of the density along the width of a ribbon since (*h o*) reflections have a very weak intensity. A second domain corresponds to the distortion of the hexagonal structure and no feature of the lamellar phase remains at this stage (see figure 5(*b*)). But a continuity between the two domains can be found for a more rigid central part (hatched zone of figure 4) as illustrated previously by some phasmids [7]) and here by the compound of series IV. The flexibility of the core can be enhanced by the introduction of a saturated part (ring or ethylene group), with consequently the appearance of a cubic phase.

The cubic phase of the phasmid may belong to the I m $\bar{3}$ m space group. Models with this symmetry have been proposed for lyotropic systems: they consist of an array of cylinders parallel to [1 0 0] directions and linked three by three at the centre and the corners of the cube. A recent description of the cubic lattices encountered in lyotropic systems involves the concept of a minimal surface [14]. For the I m $\bar{3}$ m group, the

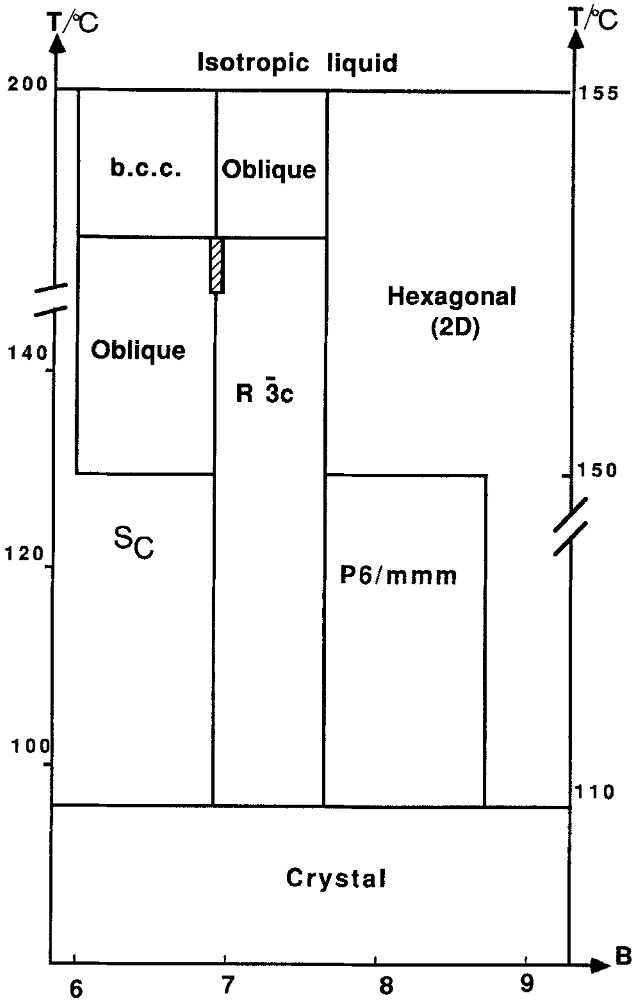


Figure 4. Phase diagram of the phasmidic compounds. The two scales in temperature correspond to different series; on the left side series II and IV and on the right side series I. The hatched zone manages an eventual continuity between different kinds of oblique lattices. *B* is the ratio of the number of phenyl rings over the number of the carbon atoms in the paraffinic chains.

surface is a Schwartz type P surface (see figure 6). The minimal surface divides the space into two equivalent subspaces; these two subspaces form interwoven labyrinths, a backbone of + 1 disclination lines is located in each subspace on the four fold axes and − 1/2 lines, normal to the minimal surface, are on threefold axes. In our case, because of the large lattice constant the mean distance between two equivalent points is of the order of two molecular lengths and we must consider that the constitutive cylinders have a complex structure: the + 1 singularity lines and the minimal surface are both centred in aromatic zones while a double layer of paraffinic chains lies in between (see figure 7(*a*)). As the number of layers located between two equivalent singularities increases the periodic organization can be more and more easily described as a regular textural network, in which the curvature stress applied to a molecule varies with its distance from the nearest singularity. However the wavelength

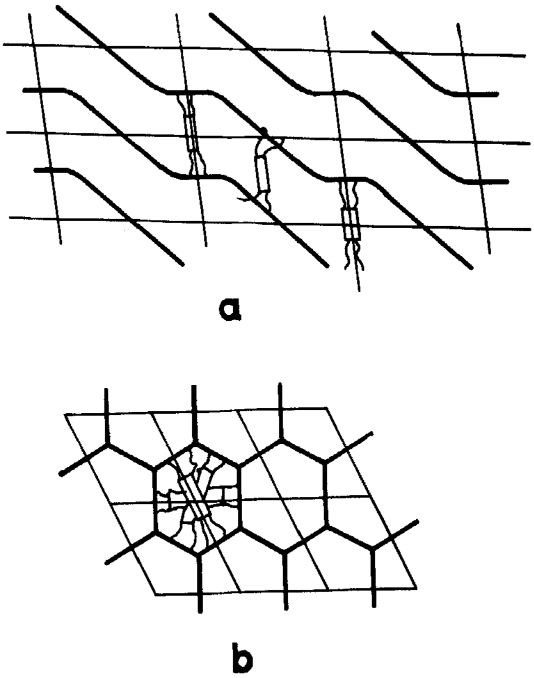


Figure 5. Two aspects of the oblique phase. (*a*) The ribbon structure which exists in the neighbouring lamellar phase. (*b*) A distorsion of the hexagonal columnar mesophase. Methyl end groups of the molecules are located on the surface represented here by a thick line.

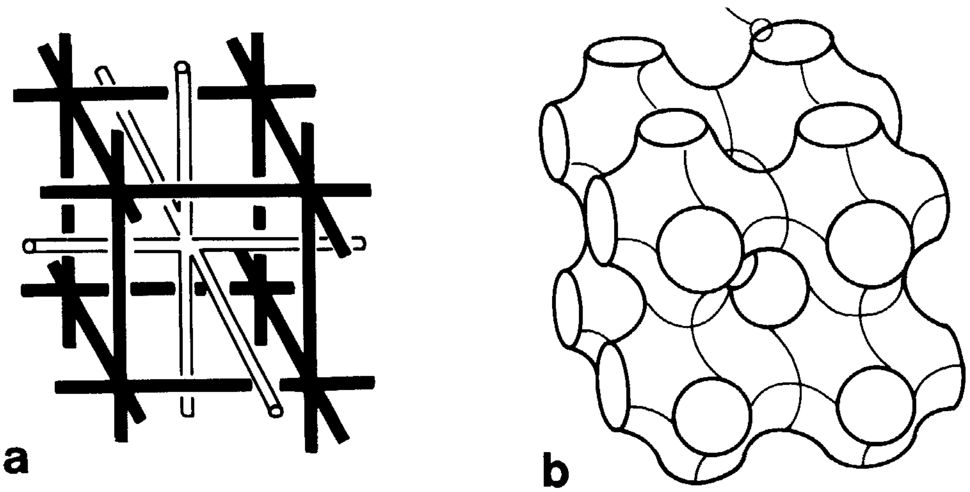


Figure 6. Schematic representation of the cubic $\mathrm{Im}\bar{3}$ mesophase. (*a*) The two networks of cylinders intersecting at each corner and at the centre of the cube. The black and white networks are equivalent. (*b*) The periodic Schwarz minimal surface of *P* type equidistant of the two networks of cylinders.

spectrum of the electronic density profile is focussed around the single layer thickness. This fact may explain why the first visible diffraction rings correspond to lattice spacings of the order of the diameter of a column in the normal two dimensional hexagonal phase.

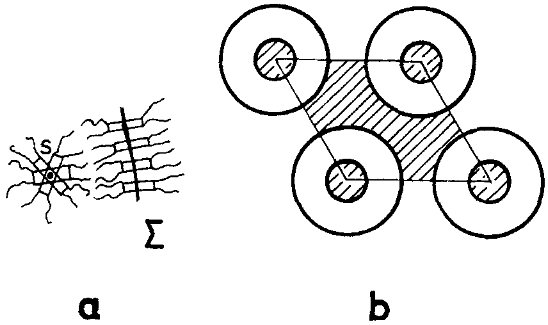


Figure 7. Representation of a complex structure of cylinders. (*a*) A section of the molecular organization going from $a + 1$ singularity line S to the minimal surface Σ. (*b*) A columnar hexagonal mesophase. The hatched areas contain the aromatic moieties of the molecules. There are at least two unequivalent aromatic areas with a double layer of paraffinic chains in between (white areas).

The presence of a rhombohedral phase close to the cubic phase cannot be considered in the same way in lyotropic and thermotropic systems. There is a difference in the symmetry since we have a non-symmorphic space group moreover the rhombohedron is very oblate compared to rhombohedral lattices in lyotropics. In face, at low temperatures with increasing B, we have a sequence S_C, $R\bar{3}c$, $P6/mmm$ (3D), columnar hexagonal, which appears specific to these systems. The three uniaxial phases appear to be closely related. The modulation of the electronic density has nearly the same period in the three phases, but the period in a direction perpendicular to the optical axis is $\sqrt{3}$ times higher in the three dimensional phases than it is in the columnar phase. In fact, in all of the three dimensional phases, the lattice constants are large compared to the molecular size and simultaneously the first reflections are of very low intensity. A possible explanation of these features can be found by looking at the metastable two dimensional hexagonal phase with a large lattice size [6]. This phase is made of complex cylinders made of more than one layer of molecules. It can also be considered as a regular array of focal conics with one $+1$ singularity lines and two $-1/2$ lines per unit cell (see figure 7(*b*)). Interaction between lines might destabilize such an array of infinite parallel lines. A description of the molecular organization of the three dimensional hexagonal mesophase is easily derived from that of the complex two dimensional hexagonal one by adding a modulation of the director orientation along the line, which induces point defects. A comparison of the hexagonal lattice of the rhombohedral network and that of the hexagonal one in the same series shows that they a differ only by their period c. Indeed all the defect lines become equivalent in the rhombohedral phase and, due to the $\bar{3}c$ symmetry, the density of point defects remains the same while the period c is two times larger. At this state of our knowledge we do not want to give a more precise description of these new mesophases with three dimensional networks. A lot of further experimental observations are needed in order to complete our preliminary investigations into these problems. However, this crude analysis of the polymorphism of phasmids has pointed out the existence of phase transformations induced by a curvature change in thermotropic liquid crystals as well as in lyotropics. The transition between the lamellar mesophase and the columnar one occurs through a sequence of intermediate phases of similar symmetries in both thermotropic and lyotropic systems. However, we have indicated some differences in the details of these sequences. These differences are due to the fact that the interactions between long rod-like cores cannot be compared to the usual interactions that mainly drive the behaviour of the hydrophilic/hydrophobic interface in lyotropic systems.

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