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BIFORKED MESOGENS : A NEW TYPE OF THERMOTROPIC LIQUID CRYSTALS

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Résumé
On décrit quelques mésogènes bifourchus dérivant des cinq séries : téréphtalates (IlIa) et trans-cyclohexanedicarboxylates-1,4 (IIIb) de bis-[(dialcoxy-3,4 benzoyloxy)-4' phényle], téréphtalates (IIIc) et trans-cyclohexanedicarboxylates-1,4 (IIId) de bis-[N-(dialcoxy-3,4 benzylidène)amino-4' phényle] et téréphtal-bis-[cycloxy-3,4 benzoyloxy]-4'aniline (IIIe). Ils présentent un polymorphisme original où coexistent phases colonnaires et phases lamellaires à des températures différentes. La phase nématique et/ou la phase smectique C s'observent avec les composés à chaînes courtes, tandis que les composés à chaînes longues présentent une phase colonnaire hexagonale semblable à celle des phasmides (03A6h). Une phase cubique centrée et une phase hexagonale à grand paramètre (égal à deux longueurs moléculaires) sont observées chez un dérivé du cyclohexane.

Abstract
Some biforked mesogens belonging to five series were prepared and studied. They exhibit an interesting polymorphism in which both columnar and lamellar mesomorphic orders coexist at different temperatures. The short chains lead to the classical nematic phase and/or the smectic C phase. The long ones give evidence of a hexagonal columnar mesophase similar to the 03A6h phasmidic phase. One cyclohexane derivative shows a body centered cubic phase and a hexagonal columnar phase with a large lattice parameter corresponding to twice the molecular length.

INTRODUCTION

Two new types of mesogens were recently reported : forked polar mesogens I 1 and phasmids II 2 :

RO

RO

RO

RO

CN NO2

OR

OR

The existence of a partially bilayered SAd phase in series I and columnar phases in series II led us to synthesize a molecular structure intermediate between the classical rod-like liquid crystal architecture and the phasmidic one :

RO

RO

A

OR

in order to obtain both smectic and columnar phases in the same series. (Note that we have arbitrarily drawn one of the possible rotamers of III).

SYNTHESIS

The biforked compounds were prepared following
the schemes I and II:

Scheme I

Scheme II

The five series of biforked mesogens have the general formula:

RESULTS

All the products are mesogenic. Phase transitions were studied by both polarizing microscopy (equipped with a Mettler FP5) and differential scanning calorimetry (Dupont 990). The transition temperatures and types of mesophases are given in Table I.

- Short chains (R = C7H15-)

The compounds IIIc and IIId exhibit only a smectic C phase with a strongly birefringent schlieren texture or a broken-fan shaped texture (Fig. 1).

The compounds IIIa, IIIc and IIIId, in addition to the smectic C phase, exhibit a classical nematic phase with a schlieren texture (Fig. 2).

(*) Compounds III are symmetrical, consequently the linkages are inverted on the right side of cycle A.

- Long chains (R = C11H23, C14H29)

When the chains are very long (C14H29, compounds IIIa, IIIc and IIIId), neither nematic nor smectic C phases are observed, but a hexagonal columnar phase.

| Table I: Transition temperatures(°C) of compounds III |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
|  | X | Y | A | Z | N | Tc | I |  |
| a | C7 | -COO- | -OOC- | - | - | 191 |  | 206 |
| b | " | -COO- | -OOC- | - | - | 155 |  | 187 |
| c | " | -CH = N- | -OOC- | - | - | 195 |  |  |
| d | " | -CH = N- | -OOC- | - | - | 152 |  | 224 |
| e | " | -COO- | -N = CH- | - | - | 139 | 199.5 |  |  |
| a | C11 | -COO- | -OOC- | - | - | 152 | 172 |  |  |
| b | " | -COO- | -OOC- | - | - | 114 | 158 |  |  |
| c | " | -CH = N- | -OOC- | - | - | 155 | 173 |  |  |
| d | " | -CH = N- | -OOC- | - | - | 130 | 155 | 169 | 186 |
|  | C14 | -COO- | -OOC- | - | - | 143 |  | 162 |
| e | " | -CH = N- | -OOC- | - | - | 146 |  | 169 |
| d | " | -CH = N- | -OOC- | - | - | 141 |  | 164 |

Figure 1: Optical texture of the SC phase of IIIc (C7H15) at 175°C

Figure 2: Optical texture of the N phase of IIId (C7H15) at 170°C
is present (Fig. 3). With an intermediate chain length (C₁₁H₂₃) we only observe for IIIa and IIIb compounds, a smectic C phase, but derivative IIIc exhibits one hexagonal columnar phase. The IIIe derivative (R = C₁₁H₂₃) displays two columnar phases similar to those of phasmids 7. The most interesting case is observed for derivative IIId (R = C₁₁H₂₃) which has the following unusual sequence of mesophases when cycling the temperature:

\[
\begin{align*}
&\text{C}_1\text{C}_1\text{H}_2\text{C}_3 \quad \\
&\text{C}_1\text{C}_1\text{H}_2\text{C}_3\text{O}-\text{CH}=\text{N}-\text{OCO}-\text{COO}-\text{N}=\text{CH}-\text{OC}_1\text{C}_1\text{H}_2\text{C} \\
&\text{OC}_1\text{C}_1\text{H}_2\text{C}
\end{align*}
\]

* Upon heating
- A schlieren texture is established at melting (144°C). The sample is SC.
- T = 146°C, the birefringent texture vanishes completely to give an uniform dark area resulting from the optical isotropy of the cubic structure.
- T = 163°C, the softening of the contours of a free droplet under microscope gives evidence for the clearing point at which point the sample transforms into the isotropic liquid.

* Upon cooling
- T = 158°C, the typical texture of a bidimensional hexagonal columnar phase 3,4 appears. Hence, this mesophase is monotropic (Fig. 4). This behaviour was also observed with 3-nitro-4-alkoxybiphenylcarboxylic acids 5.
- T = 147°C, the hexagonal columnar phase transforms in turn into the cubic stable state by rupture of the metastability.
- T = 140°C, at last the texture becomes birefringent once more when one recovers the Sc phase is reformed.

Four remarks can be underlined regarding the evolution of this polymorphism.
(i) It is clear that the hexagonal columnar phase is only monotropic and metastable with regard to the three dimensional cubic state.
(ii) T = 146°C is the Sc + cubic temperature of transition upon heating.
\[
\begin{align*}
&\text{K} \\ &144^\circ \quad \text{Sc} \\ &8.6^\circ \quad \text{Cubic} \\ &162^\circ \quad \text{I} \\
&140^\circ \\ &\text{Cubic} = 147^\circ \quad \text{Hex} = 158^\circ \\ &0.6^\circ \quad 1.75^\circ \\
&\text{KJ.mol}^{-1}/\text{mol}
\end{align*}
\]

(iii) The examination of free droplets reveals the existence of an atypical, very weakly birefringent texture extending over a few degrees between the isotropic liquid and the hexagonal phase. Whether it is an actual additional phase or only the settlement of the hexagonal texture itself cannot yet be concluded. Accurate experiments have been undertaken on this topic.

The X-ray diffraction methods have been used for the determination of the symmetry properties of the mesophases. Four compounds which exhibit at least one of the three identified mesophases: nematic, smectic or columnar have been chosen for this study. Finally the case of the IIIa compound with C₁₁H₂₃ chains will be discussed. The four first compounds were:

\[
\begin{align*}
&\text{Figure 3 : Optical texture of the }\phi_1\text{ phase of IIIa } \\
&(C_{14}H_{29}) \text{ at } 150^\circ C
\end{align*}
\]

\[
\begin{align*}
&\text{Figure 4 : Optical texture of the hexagonal phase } \\
&(\text{Hex}) \text{ of IIIId } (C_{11}H_{23}) \text{ at } 157^\circ C
\end{align*}
\]

Thus one can imagine that this localized change is the consequence of the heat shock due to a transition from the monotropic hexagonal columnar phase to another monotropic form. This is made unobservable by the immediate switching to the stable cubic state.

(iiii) The examination of free droplets reveals the existence of an atypical, very weakly birefringent texture extending over a few degrees between the isotropic liquid and the hexagonal phase. Whether it is an actual additional phase or only the settlement of the hexagonal texture itself cannot yet be concluded. Accurate experiments have been undertaken on this topic.
IIIc \((R = C_7H_{15})\) which shows a smectic phase

IIIC \((R = C_{11}H_{23})\) which exhibits a columnar phase

IIId \((R = C_7H_{15})\) with a \(N\) - smectic transition

IIle \((R = C_11H_{23})\) which has a low temperature smectic phase and two columnar phases.

The X-ray pattern of magnetically aligned samples of the IIIe (C7) compound is that of a usual neematic phase of elongated molecules with evidence of tilted cybotactic group 6, the apparent length of the molecule is 51.3 Å and the tilt angle reaches 60° near the N - smectic transition. On cooling one obtains a smectic phase with an unique orientation of the director and a conical texture of the layer planes. In IIIc (C7) the smectic planes are oriented by the capillary walls. For the two compounds with short chains we are able to orient the director under the action of a magnetic field, starting from a given texture for the smectic layers the molecules minimize their angle with the field keeping their tilted orientation versus the layer planes. In the case of the IIIe (C11) a lamellar phase exists at low temperature but we were not able to obtain any orientation of the molecules. The layer thickness is respectively 31.6 Å, 28.9 Å and 34.1 Å for IIIc (C7), IIIe (C7) and IIIe (C11). The tilt angle can be measured separately only in IIIe (C7) and is of = 60°. Probably the value of this angle is high (50 - 60°) in the three cases and therefore is consistent with a fully extended configuration of the molecules. Nevertheless a zig-zag configuration with chains normal to the layer planes and cores making a 120° angle with them should ensure a mean area per chain equal to the core mean area. Such a model would imply a shortest apparent chain length but is still consistent with the X-ray data.

The C7 derivatives of both series IIIc and IIIe present columnar hexagonal phases. We have not obtained oriented samples, the lattice constants are respectively equal to 46.4 Å and 46.9 Å for IIIc (C11) and IIIe (C11). We can compare to the lattice constant of the hexagonal \(h\) phase of a phasmid with the same core of IIIc substituted by six \(C_{12}H_{25}\) chains (46.0 Å). The distance between two columns does not depend on the molecular weight and seems to be only a function of the largest molecular dimension. The scattering diagrams apparently show that the average stacking distance between the rigid cores is the same in both cases. The IIIc (C11) derivative has a mesophase between the smectic and the hexagonal phase, the structure of which is that of a ribbon phase like \(c_{ob}\) with a 2D oblique lattice \(a = 33.4\) Å, \(c = 59.5\) Å; \(\beta = 145°\). The thickness of a ribbon can be equal to the layer thickness of the smectic low temperature phase and the density arguments led to a width of the ribbon of about two molecules. The area of the hexagonal lattice is not far from twice the area of the oblique lattice in this compound.

At last let us examine the mesophase of the IIId (C11) derivative: A first experiment performed on this compound does not allow any structural analysis:

i. The smectic phase is not seen because of a coexistence either with a crystalline phase or with the cubic one.

ii. For the two other mesophases cubic and hexagonal the number of reflections at small angle is high and a classical analysis of the patterns obtained with our usual set up is impossible.

In order to have reliable data we use a monochromatic parallel beam obtained with the synchrotron source LURE, a Ge (111) bent crystal and a collimator of 2mm of diameter. The film to sample distance is 250 mm. The diffraction pattern of a sample heated in the cubic phase is made of sharp dotted rings (Fig. 5). The corresponding scattering vector length are proportional to square roots of integers \(n = 3,5,6,7,8,9,10,13,19,25\) between \(n = 10\) and \(n = 25\) few other rings are seen but cannot be unambiguously pointed up since they are of low intensity. The lattice is \(b c c\) with \(a = 161.2\) Å, but we note the absence of three low angle rings (\(n = 1,2,4\)) nevertheless we cannot determine the space group. By heating this mesophase we obtained a pattern of an isotropic liquid and after a further cooling the hexagonal phase grows in large domains, the lattice is a 2D lattice with \(a = 135\) Å. There is a relation between the size of the cubic lattice and that of the hexagonal 2D lattice since the reciprocal 111 plane of the cubic phase is identical to the unique reciprocal hexagonal plane of the columnar mesophase.

Moreover a comparison between the length of the molecule \((\sim 63\) Å) and the size of the hexagonal lattice favours a complex hexagonal structure 7 in which the core and the external shell of each column are paraffinic while the intermediate zone is made of the aromatic part of the molecules*. Further diffraction experiments especially on single crystals are needed for a better description of the structure of these two mesophases.

CONCLUSION

The recent discovery of phasmedi with a rod-like core and half disk ends, shows the existence of intermediate phase between columnar and lamellar phases 6,9.

*Columns in which aromatic moieties are in the axial part and at the external part will also correspond to the description of the hexagonal phase.
With the new biforked mesogen family having an intermediate architecture between rod-like liquid crystals and phasmids, we obtain both lamellar and columnar mesophases in the same series. Moreover, evidence of a centered cubic phase and of a hexagonal columnar phase with a large lattice parameter are given. The final interesting fact is the existence of a nematic phase and probably of an atypical very weakly birefringent phase. So, like phasmids, the biforked mesogens show potential to the thermotropic analogues of the lyotropic biaxial nematic 10.

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