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To cite this version:
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(Reçu le 13 octobre 1982, révisé le 20 décembre 1982, accepté le 27 janvier 1983)

Abstract. Microscopical, miscibility and X-ray studies establish the existence of two new mesophases in the two enantiomers of 1 (methyl)-heptyl-terephthalidene bis amino cinnamate. In one of these two mesophases, the two enantiomers do not exhibit a total miscibility range; while for the second the untwisted form observed with the racemic mixture has a higher temperature range of stability than the twisted form observed for the pure enantiomers.

Information about the structures of the two phases is given and a comparison is made with the $S^*_C$ and $S_D$ phases. Nevertheless the location of these two phases in the sequence of the presently known calamitic mesophases is not yet completely established.
structural features that could be deduced from our X-ray diffraction patterns.

2. Thermal analysis and optical observations. — The two enantiomers (+, +) and (−, −) and the racemic mixture (+, +, −, −) have been synthesized [2].

The thermal analysis with a ATD 2 000 Mettler device gives for the pure enantiomers the same result: four endothermal peaks:

\[ T \text{ (°C)} \quad 88.5 \quad 95 \quad 130.5 \quad 133 \]

\[ \Delta H \text{ (kcal/mole)} \quad 0.95 \quad 4.02 \quad 0.285 \quad 0.097 \]

For the racemic mixture, the results of thermal analysis are:

\[ T \text{ (°C)} \quad 112 \quad 158 \]

\[ \Delta H \text{ (kcal/mole)} \quad 0.96 \quad 0.11 \]

Observations of the two enantiomers with a polarizing microscope (Leitz, Panphot) with a heating stage (Mettler, FP 52) indicate a solid-solid transition for the first transition. At 95 °C, melting takes place and a viscous birefringent phase results which exhibits colours due to rotatory power dispersion. At 130.5 °C another viscous phase appears with a mosaic texture (Fig. 2a), rectilinear edges, with a weak rotatory power, and exhibiting a small birefringence. The transition at 133 °C is the clearing point. Supercooling is observed for each transition. All these transformations are first order in accordance with the calorimetric study. These observations show that \( K_1 \) and \( K_2 \) are crystalline phases and \( M_1 \) and \( M_2 \) mesophases.

In a free droplet put upon a glass covered with polysilane [3] the \( M_2 \) mesophase appears on cooling with denticritic contours. In some domains examined with parallel light no birefringence can be detected: this is an optically uniaxial medium. The domains with the optical axis normal to the slide have rectilinear edges and a rectangular form. Consequently the optical axis is only a four-fold symmetry axis.

In the racemate, the \( M_2 \) mesophase disappears and the melting point is observed at 112 °C. The clearing point appears at 158 °C. By cooling the liquid the mesophase displays striated « bâtonnets » and, afterwards, collapsing focal conics or woolly schlieren texture with very mobile disclination lines. In free drops a great number of 1/2 disclination lines are visible (Fig. 2b), excluding, for symmetry reasons, the existence of a smectic C mesophase (1).

3. Miscibility studies. — The isobaric phase diagram of binary mixtures was constructed from microscopic observations of contact preparations [4]. First the mixtures of the two enantiomers are studied (Fig. 3). The mesophases \( M_2 \) exist only in small concentration ranges. If we exclude the blue phases, this is the first example of two enantiomers without total miscibility in a mesomorphic state. An enhance-

Fig. 2. — Optical textures: a) the \( M_2 \) mesophase; b) the \( M_1 \) mesophase for the racemic mixture.

Fig. 3. — Binary diagram of the two enantiomers: (+ +) on the left and (− −) on the right.

(1) This is an observation of Gilles Sigaud from the Paul Pascal Centre at Bordeaux.
ment to 158 °C is observed for the M1 phase of the racemic mixture. In the solid state a racemate exists with a congruent melting point at 112 °C (2). In the contact preparations we can observe that the untwisted M1 mesophase and its texture, obtained by cooling the liquid, is identical to the texture of the racemic mixture obtained directly by synthesis. By a dextrosum rotation for the analyser the isochromatic lines move from the (+ +) enantiomer to the (− −) one. The twisting senses are right handed in the M1 mesophase of (+ +) and left handed in the (− −).

No convergence area is observed in the twisted mixtures: the pitch is, in the M1 phases of pure enantiomers, greater than \( \lambda \sqrt{3/n} \) where \( \lambda \) is the limit for the visible wavelengths and n the averaged refractive index [5]. This is confirmed by the absence of selective reflection for any visible light.

The mixtures of one of the enantiomers with two kinds of compounds have been studied in order to compare the new mesophases with known ones:

\[
\begin{align*}
2 & \quad C_nH_{2n+1} - O - \underset{\text{NO}_2}{\text{C}} - \text{OH} \\
3 & \quad C_2H_5 * C -(CH_2)_nO - \underset{\text{CH}_3}{\text{N=CH}} - \underset{\text{H}}{\text{CH}= \text{N}} - O(CH_2)_n \rightarrow C - C_2H_5
\end{align*}
\]

In this paper we use the code letters recommended for the smectic phase [8].

The phase diagram (Fig. 4) of the mixtures of 1-with 2 (\( n = 18 \)) proves that the M2 mesophase is stable at temperatures higher than the smectic D phase [9]. A similar result is obtained by mixing it with the hexadecyl homologue of 2. Moreover figure 4 shows that a large amount of chiral molecules of 1 can be introduced into the smectic D phase. This phase has the symmetry Ia3d with non-chiral molecules and it would be interesting to follow the symmetry characters of the mixtures (2).

The binary diagrams of 1-with 3\((^+)\), \( n = 4 \) and \( n = 3 \) (Fig. 5) show that the S\(_{a}^{c}\) phase is observed at higher temperatures than the M1 mesophase.

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(2) By cooling contact preparations, only a metastable solid form (\( F : 97.2 \, ^\circ C \)) can be observed for the racemate. The lower part of the diagram (Fig. 3) is obtained by observation of contact preparations of the enantiomer with a racemic mixture elaborated by weighting of the two enantiomers, dissolution in dichloromethane and crystallization.

(3) The writers are greatly indebted to the referee who made an excellent remark about the symmetry character of the smectic D phase.
4. X-ray studies. — We have performed X-ray studies on one of the two enantiomers and of mixtures of the two optical antipods at various concentrations. Powder patterns have been obtained with a Guinier camera of high resolution (CoKα) and partially oriented samples held in a Lindemann glass capillary were irradiated by a point focussing X-ray beam (CuKα).

4.1 The M₂ phase. — It is possible to obtain few big domains of the M₂ phase by cooling the sample from the isotropic phase. The X-ray patterns (Fig. 6a) are similar to the patterns of a smectic D phase [9]; several Bragg spots appear at small angles while a quasi-isotropic broad large angle ring is always visible at \( d \approx 4.5 \text{Å} \). We have examined various orientations and checked that we have a tridimensional array of large period superimposed over a local liquid-like order of the neighbouring molecules without any preferential unique direction of the molecules.

Fig. 6. — Diffraction pattern of oriented sample, a) the M₂ mesophase, \( T = 131 \) °C; b) the M₁ mesophase of the racemic mixture, \( T = 154 \) °C.

In order to have a more precise idea of the tridimensional lattice, we have taken powder patterns with rotating samples; we observe seven sharp rings. These rings can be indexed in a tetragonal lattice; the reticular distances are reported in table I. This lattice is body-centred since no reflections \( h + k + l = 2n + 1 \) are seen. If we take into account the chiral symmetry of the molecule only two space groups can fit the observed reflections, the most symmetrical being \( I422 \). A specific gravity of 1 g cm\(^{-3}\) would imply about 340 molecules per unit cell while the lattice parameters are of the order of magnitude of two times the length of a molecule. This lattice is similar to the tetragonal lattice seen by Luzzati et al. in some divalent cation soaps [10].

<table>
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<th>Indices</th>
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<th>Intensity</th>
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4.2 The M₁ phase. — We have taken X-ray patterns of the M₁ phase at various concentrations of the two enantiomers. For the pure compound the transition \( M₂ \rightarrow M₁ \) does not favour the formation of well oriented samples. In this case the diffraction pattern is similar to the pattern of a Sm phase: two small angle rings corresponding to the two first orders of reflection on the layer planes and a broad large angle ring. It is easier to obtain oriented samples by slow cooling of the sample when the M₁ phase is reached from the isotropic liquid. The best oriented samples are obtained in the case of the racemic mixture. Figure 6b shows the diffraction pattern of a sample in which we observed mainly one direction for the layer planes and two directions for the molecular axis. More generally the orientation is not so sharply defined.

The pattern in figure 6b consists mainly of:

i) four aligned small angle Bragg spots corresponding to the \( \pm 001 \) and \( \pm 002 \) reflections from a layered periodic structure. The layer thickness is equal to 30 Å;

ii) four diffuse spots lying at large angles. These spots are roughly equidistant from the origin and form pairs aligned with this origin. They seem characteristic
of a liquid-like order of parallel molecules in a layer. The transverse extension of these spots is small compared to an ordinary $S_6$ well aligned sample, i.e., the order parameter is higher than in a $S_6$ phase. Figure 6b corresponds to a sample in which two directions of the molecular axis are seen for the same direction of the layer; more generally we observe a distribution of directions. Let us focus our attention on the mean distance between two molecules inside a layer: the diffraction angle corresponding to the maximum of intensity is different for the four diffuse spots and a difference of 6% is observed in the mean distance. Moreover less intense diffuse scattering is observed between the spots and probably corresponds to other molecular and layer orientations. The maximum of intensity lies at a smaller angle. Therefore it appears that the diffuse scattering intensity coming from the « intra-layer molecular interferences » is no longer of circular shape. We can assume an elliptical shape with a 10% ellipticity, the ellipse lying in a plane perpendicular to the long axis of the molecule, the angle between this plane and the layer being $\approx 40^\circ$ (i.e. the tilt angle is $50^\circ$). The ellipse is elongated along the perpendicular to the intersection of the two planes. Therefore the distance between two molecules is smaller in a plane perpendicular to the layer and parallel to the director than in a perpendicular direction. Assuming a coordination number of 6 for the molecules (*) the mean distance should vary between 5.2 and 5.65 Å while the layer thickness 30 Å corresponds to fully extended molecules (46 Å) with a $50^\circ$ tilt angle (Fig. 7).

Our interpretation of the structure of the $M_1$ phase is based on the diffraction pattern on the racemic mixture. In the pure compound we always observe simultaneously many directions for the molecule, while only two directions probably symmetric with respect to the normal to the layer plane are seen in a racemic oriented sample. This difference is due to the chiral character of the pure active compound since in accordance with the optical observation, the director lies on a cone with a helicoidal array; the pitch of this helix is of the order of one micron. In the racemic mixture, the existence of two distinct orientations for the molecules corresponding to one layer direction is surprising and may originate from a segregation of $(++)$ and $(- -)$ molecules in different layers, the orientation of the molecules depending on the sign of the chirality. It will not be possible to decide between an ordered or disordered stacking of layers $(++)$ and $(- -)$, since the periodicity of the electronic density along the normal to the layer is not sensitive to the ordering of $(++)$ and $(- -)$ molecules. Let us underline that the existence of an ordered «racemate» phase would imply a difference between the chiral and the racemic mesophases but no transition line between the two phases has been detected, despite the fact that the stabilization of the racemic mixture is in favour of the existence of a racemate. Moreover we can imagine that $(++)$ and $(- -)$ molecules are in contact

\[ (*) \text{The mean distance } d \text{ between neighbouring molecules is related to the Bragg angle } \theta \text{ corresponding to the maximum intensity and to the X-ray wavelength } \lambda \text{ by the relation } 2d \sin \theta = 1.15 \lambda. \]

![Fig. 7. — Schematic representation of the $M_1$ phase.](image)

![Fig. 8. — Densitometric contour lines of the X-ray pattern of partially oriented samples : a) of the $M_1$ mesophase in the pure active derivative; b) of the p-octyloxybenzoic acid. The circles are put as a guide for the eye.](image)
in each layer and in such a case we can also have either a disordered phase, or a phase with a local ordering (pairing) of optical antipods.

By looking at the large angle diffraction ring we tried to compare the smectic C and the M₁ mesophase: we have compared the anisotropy and the width of the diffraction ring. Figure 8 shows a contour map of the diffraction pattern of partially oriented samples (a) of one of the active components in its M₁ phase and (b) of the Sₖ phase of the octyloxy-benzoic acid (11). The large angle maxima are at the same distance from the origin for all directions of the scattering vector in the case of the Sₖ phase while an anisotropy of 5% is measured for the M₁ phase of the active compound.

In order to compare the width of the Sₖ and M₁ large angle ring we have studied non-oriented samples of mixtures of the (methyl)-heptyl homologue of 3 with 1. Mixtures containing respectively 45 and 55% of this last compound undergo a M₁-Sₖ transition at 143 and 150 °C and a Sₖ-Sₘ transition at about 190 °C. The enthalpies of transition have been measured on a DSC Dupont and the peak is higher for the sample richer in 1.

Microdensitometer traces have been enregistered at different temperatures and we have observed an abrupt increase in the width of the outer ring on going from the M₁ phase to Sₖ and Sₘ phases. The difference is more important when the DSC peak is higher (Fig. 9). We have also plotted for comparison a microdensitometer trace of an X-ray pattern of an F phase (12) which is much narrower. In conclusion, the liquid like character of the in-layer array is evident. Nevertheless this phase M₁ appears to be a new phase compared to the Sₖ.

![Fig. 9. — Plot of the relative scattering intensity versus the scattering vector Q = \(4 \pi \sin \theta / \lambda\) for the M₁ and Sₖ mesophases of a binary mixture of 45% terephthalidene-bis-methyl-heptoxy aniline — 55% terephthalidene-bis-methyl heptylaminocinnamate, and for the Sₖ phase of the terephthalidene-bis-decylaniline.](image)

5. Discussion. — The two mesophases M₁ and M₂ appear to be new ones: the M₁ mesophase consists of a tridimensional tetragonal lattice superimposed upon a short range liquid order of the centre of mass. Until now, in thermotropic liquid crystals, only the Sₖ and the blue phases had these characteristics but the lattice is cubic in these two cases [11, 16]. Let us note that the M₂ phase only appears in compounds or mixtures which have optical activity, while the similar tetragonal thermotropic phase seen in anhydrous soaps [10] occurs with non-active molecules.

Let us discuss the position of these two new mesophases among the other known calamitic (i.e. mesophases made of rodlike non-lipid molecules (5)). A general sequence which gives the order in which the different mesophases could appear on decreasing the temperature from that corresponding to the isotropic liquid to that corresponding to the crystalline phases was established. Despite the fact that things appear more and more complex as we progress in the understanding of the mesomorphic state, we can refer to this general scheme:

— first, one finds either the nematic (N) or the cholesteric phase in which no periodic translational order of the molecules has been detected;

— after, this we have the differing layered structures: in smectic A and C, each layer is a two-dimensional liquid in which the molecules are normal to the layer in a Sₐ and tilted in a Sₖ and there is a one-dimensional periodicity along the normal to the layers. Some discontinuous change of the layer thickness could occur in the Sₐ range leading to Sₐ-Sₖ transition or to N-Sₐ-N-Sₐ sequences [13].

Below these disordered smectic phases, stacks of two-dimensional crystalline (or quasi crystalline) layers have been found in which the molecules may or may not be tilted. Examples are the hexatic B, Smectic F smectic I phases. Lastly we found 3d crystals in which a positional correlation is established between the 2d layers: Sₖ-Sₐ-Sₙ-Sₐ-Sₖ-Sₙ-Sₖ [14].

In a third group of mesophases a periodic structure with a 2d or 3d lattice is established but the local order of the molecules is liquid-like at least in some directions and the periodic order is an order of points, lines or walls of singularity. The mesophases of these types appear as intermediate stages between either two lamellar phases such as the smectic D phases which is a cubic phase (space group Ia3d) and the 2d ribbon phases with centred rectangular or oblique lattices [15], or just before the isotropic phase such as the blue phases. Some of the blue phases have a cubic lattice of very large lattice constant [16]. Our M₂ phase belongs to this last group and appears at higher temperatures than the Sₖ phase and it is shown in figure 4 that the Sₖ ↔ M₂ transition occurs over a wide range of concentration. A structural study of this transition may yield new information about the nature of the two
phases. Moreover the virtual transition temperature (M$_2$-L for 2 octadecyl homologue) obtained by extrapolation of the spindle M$_2$-L is 192 ± 2°C: this temperature is equal to the temperature of the monotropic transition S$_4$-L (6) in 2 (octadecyl homologue) while a reversible monotropic S$_4$-S$_A$ transition is observed in the hexadecyl homologue of 2. Therefore M$_2$ has to be inserted between S$_D$ and S$_A$.

The M$_1$ phase is a disordered lamellar phase which appears distinct from S$_C$ and S$_A$ structures. At the transition S$_C$ $\rightarrow$ M$_1$ no change of the layer thickness is involved and it appears that the difference between S$_C$ and M$_1$ comes from the anisotropy of the surroundings of a molecule in the layer. This anisotropy is larger in the M$_1$ phase which appears at lower temperature than the S$_C$ phase (Fig. 5). Finally, the position of the M$_1$ phase with respect to the ordered two- or three-dimensional phases is not known.

In order to be consistent with the usual code letters and to avoid ambiguity with different letters such as L (Liquid), M (mesophase) etc., we suggest the denomination S$_0$ for the M$_1$ phase and S$_Q$ for the M$_2$ mesophase.

Acknowledgments. — We are indebted to Mrs A. Beguin and Dr. J. C. Dubois for the elaboration of coated glasses, to Dr. D. Demus for the compounds 2 used in the miscibility studies and to Mrs M. F. Achard for measuring the enthalpies of transitions for the racemic compound.

References