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Structural study of a smectic C phase of biforked molecules

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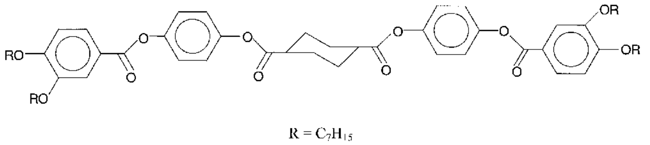
In the framework of a systematic investigation of the molecular organization in different mesophases exhibited by biforked molecules, we present a structural study of the smectic C phase of a biforked compound containing heptyloxy chains. With a combination of dilatometry measurements and X-ray diffraction on polydomain samples, together with a detailed X-ray investigation on oriented samples, it was possible to describe precisely the packing of the molecules within the smectic C layers. The result is a large tilt of the long aromatic cores of about 50°–60° with respect to the normal to the layer planes, whereas the terminal aliphatic chains are close to the normal to the planes with a small tilt angle of about 20°–30°. For the first time, these two angles have been directly observed on the X-ray patterns of oriented samples.

1. Introduction

Among polycatenar mesogens, with their special molecular structure made up of a long aromatic core and several terminal aliphatic chains, biforked molecules give rise to very interesting liquid crystalline systems. Various types of mesophase (nematic, lamellar, columnar, cubic) are formed by these molecules, and quite peculiar polymorphic sequences including lamellar-to-columnar and columnar-to-columnar phase transitions have been reported [1].

Previous studies of biforked compounds using various experimental techniques have shown that in their smectic C phases, the long aromatic cores of the molecules are strongly tilted (about 60°) with respect to the normal to the layers, whereas the aliphatic chains are usually normal to the layers or slightly tilted. Such a molecular arrangement has been deduced from a combination of dilatometry measurements and X-ray diffraction (XRD) studies on powder samples [2, 3]. Nevertheless, a more direct structural characterization can only be obtained by XRD on aligned samples. Naturally, the compatibility of the results obtained through this kind of measurement with those obtained by the method of combining volumetric studies with XRD on powder samples would constitute a clear confirmation of the previous conclusions about the molecular organization of biforked molecules in lamellar phases.

In the present paper, we report a structural study of the smectic C phase of a biforked compound based on two types of experimental results obtained on the one hand by dilatometry experiments combined with XRD on polydomain samples, and on the other, by XRD experiments on monodomain samples. The compound under study belongs to the same homologous series as that studied in [3], with shorter aliphatic chains and exhibits a nematic phase, which may enhance the possibility of aligning the material, giving rise to suitable monodomain samples. The molecular structure and phase sequence of this compound are presented in figure 1.



R = C_7H_{15}

$$\mathrm{Cr} \xrightarrow{137^\circ C} \mathrm{SmC} \xleftrightarrow{167^\circ C} \mathrm{N} \xleftrightarrow{190^\circ C} \mathrm{I}$$

Figure 1. Chemical structure and thermotropic behaviour of the compound studied in this paper.

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2. Experimental

The dilatometry experiments were performed using the Kovacs technique adapted to liquid crystals [4]. For this purpose a high precision computer-controlled, home-built device was used. This system includes automatic data acquisition and allows for a temperature control within ±0.03°C.

The XRD results on powder samples were obtained using an INEL CPS 120 curved counter equipped with a quartz bent monochromator for the $\mathrm{CuK}_{\alpha 1}$ radiation and a computer-controlled oven with a temperature precision within ±0.03°C. In order to improve the angular precision, the XRD data were normalized by comparing the data obtained with the INEL counter with those read with an image plate located in a position coincident with the INEL detector at a temperature of 150°C.

XRD experiments on the aligned mesophase were performed by a simple preparation technique currently reported in [5]. A small drop of the sample was heated on a cleaned glass plate to the isotropic state and cooled slowly to the required temperature of investigation. In this way, a well aligned monodomain could be obtained by surface interaction. The incident X-ray beam was parallel to the glass plate and the scattered intensity was collected on a two-dimensional detector (HI-STAR, Siemens AG, Germany).

The synthesis and the characterization of the compound have been reported previously [6].

3. Results

3.1. *Molecular volume* V_m

The dilatometry results, presented in figure 2, show a linear increase of the molecular volume V_m with increasing temperature T in the smectic C (SmC), nematic (N) and isotropic (I) phases. The linear fits of V_m as a function of T in the SmC and N phases gave the following results:

for the N phase: $V_\mathrm{m} = 1444.6 + 1.445 \times T$

for the SmC phase: $V_\mathrm{m} = 1463 \times 1.29 \times T$

with V_m in Å^3 and T in °C. It is interesting to note that the thermal expansion coefficients $\alpha = (1/V)(\mathrm{d}V/\mathrm{d}T)$ are 8.8×10^{-4} and $10 \times 10^{-4}\,°\mathrm{C}^{-1}$ in the SmC and N phases, respectively, in agreement with values already reported in the literature for the same phases of other compounds [7]. On the other hand, the SmC–N and N–I phase transitions are characterized by small but significant jumps in the molecular volume within a rather narrow temperature range ($\Delta V/V = 6 \times 10^{-3}$ and 3×10^{-3} for the SmC and N phases, respectively).

3.2. *X-ray diffraction on powder samples*

The XRD patterns obtained for the SmC phase on powder samples are characterized by a sharp Bragg peak in the small angle region corresponding to the smectic layer periodicity, and a diffuse peak in the wide angle region corresponding to the mean lateral distance between neighbouring molecules—the intermolecular interaction distance. Figure 3 presents the variation of the layer spacing d in the SmC phase as a function of temperature. It is interesting to note the small but clear increase in the lamellar periodicity within the temperature range of the smectic C phase, from 30.5 Å at 130°C to 31.3 Å at 165°C.

3.3. *Molecular area S*

Using the values of V_m presented in figure 2 and those of d presented in figure 3, the molecular area S as a function of temperature has been determined. As usual, S is defined as the average area per molecule in the

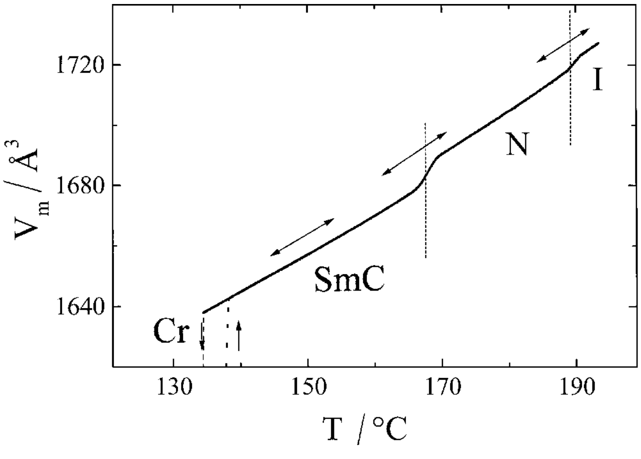

Figure 2. Molecular volume V_m as a function of temperature obtained by dilatometry. Cr, SmC, N and I represent the crystalline, smectic C, nematic and isotropic phases, respectively.

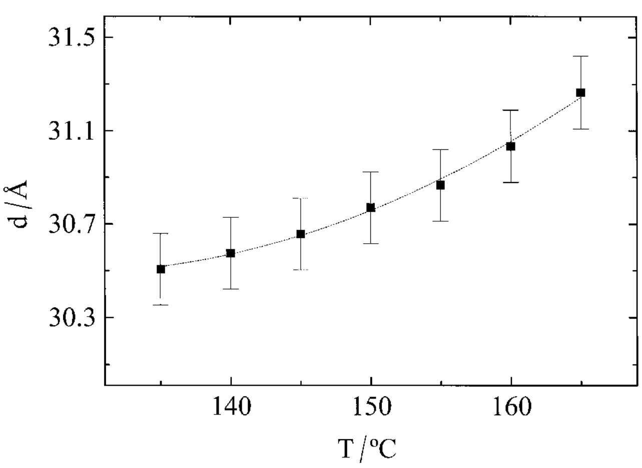

Figure 3. Variation of the layer spacing d with temperature in the SmC phase, as determined from XRD on power samples. The dashed line is a guide for the eye.

plane of the smectic layers:

$$S = \frac{V_m}{d}. \quad (1)$$

The molecular area S is deduced from the projection onto the layer planes of the cross-sectional area of a molecular segment σ measured in the plane perpendicular to the mean molecular axis of that segment.

$$\sigma = S \cos \psi \quad (2)$$

where ψ is the angle between the molecular axis and the normal to the smectic layers (see figure 4). In the present work, the SmC structure has been considered as monolayered, since the molecules are symmetric. Thus, S has been found to be practically constant as a function of temperature with a value of 53.7 ± 0.5 Å^2.

The values of the intermolecular interaction distance D as a function of temperature have been obtained through the analysis of X-ray patterns in the wide angle region. D increases linearly from 4.58 Å at 135°C to 4.63 Å at 165°C. Using these values and considering a local two-dimensional hexagonal arrangement of the molecular segments, the variation of the cross sectional area of the molecular core σ_c [8] as a function of temperature has been calculated and is presented in figure 5.

The cross-sectional area of the aliphatic chains may be obtained by considering the known values for liquid paraffins [9] and taking into account the usual result that the volume of a molten methylene group V_{CH2} does not depend on the compound considered, at a given temperature:

$$V_{CH2} = 26.56 + 0.02023 \times T \quad (3)$$

$$\sigma_{CH2} = V_{CH2}/1.27 \text{ Å} = 20.9146 + 0.0159 \times T. \quad (4)$$

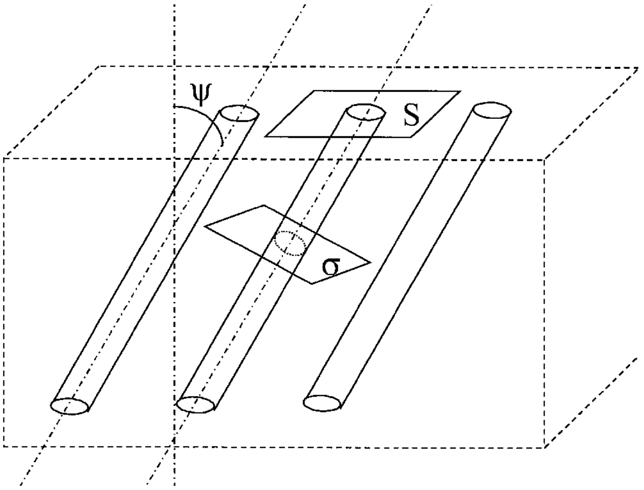

Figure 4. Illustration of the definition of the molecular area S and cross-sectional area σ of a molecular segment.

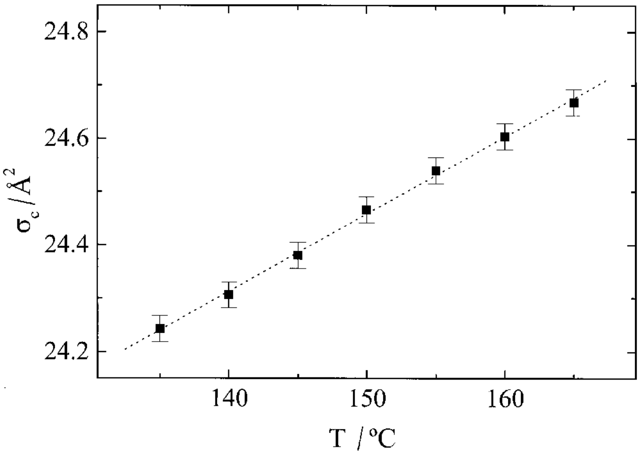

Figure 5. Variation of the cross-sectional area of the molecular core σ_c with temperature. The dashed line is a guide for the eye.

Since two aliphatic chains are attached to each extremity of the core, the cross-sectional area corresponding to the paraffinic segments is given by:

$$\sigma_{ch} = 2\sigma_{CH2} \quad (5)$$

In equations (3–5) T is in °C, V_{CH2} in Å^3; σ_{CH2} and σ_{ch} are in Å^2.

3.4. *X-ray diffraction on aligned samples*

Several XRD patterns have been registered over the temperature range of the oriented smectic C phase. They are all similar and the image of the XRD pattern obtained at a temperature of 164°C is presented in figure 6 as an example. In the small angle X-ray scattering region (SAXS), the first and second order Bragg peaks corresponding to the lamellar spacing of the SmC phase are observed. These peaks are located on the central (2θ) axis of the pattern, corresponding in reciprocal space to the direction perpendicular to the smectic layers. In the wide angle X-ray scattering region (WAXS), two large diffuse bands are observed which are approximately symmetric with respect to the central axis of the pattern. The value of the angle χ between the centre of these bands and the central 2θ axis determines some average tilt angle in the smectic C phase. Figure 7 represents a schematic for the definition of the 2θ and χ parameters used in the analysis of the XRD patterns on aligned samples.

The analysis of the distribution in 2θ and χ of the diffraction patterns in the SAXS region shows a very narrow peak, which is clear evidence for the excellent orientation of the smectic layers. However, to take into account potential small defects in the orientation, the analysis of the data in the WAXS region was done

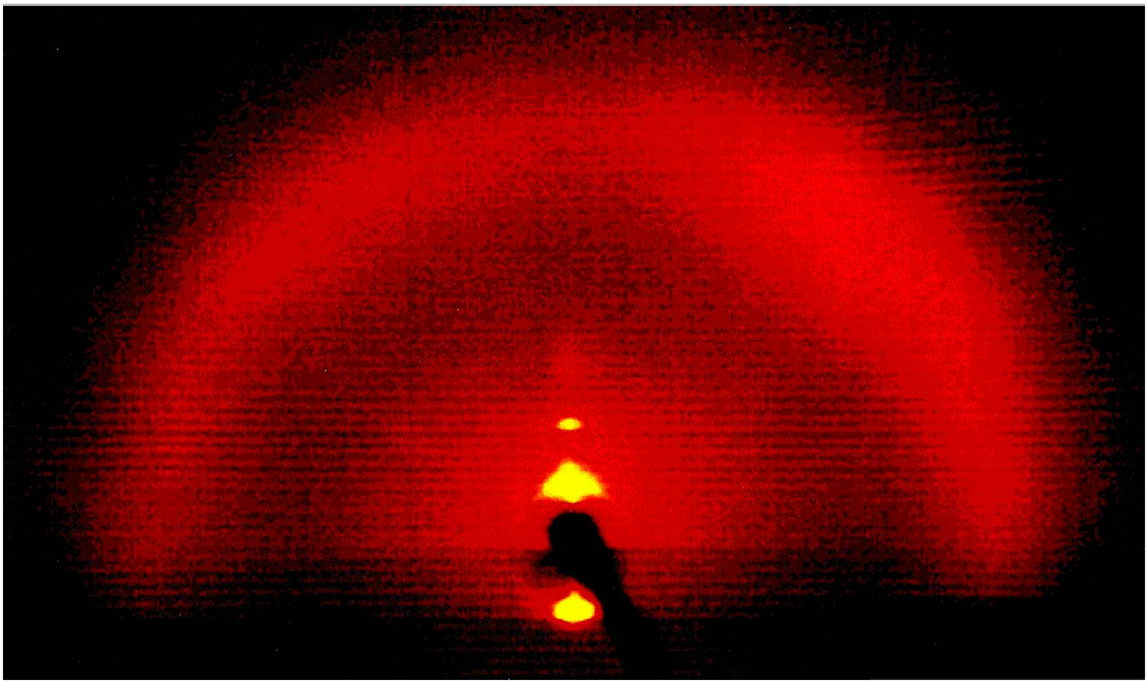

Figure 6. Image of the XRD pattern obtained for the oriented SmC phase at 164°C.

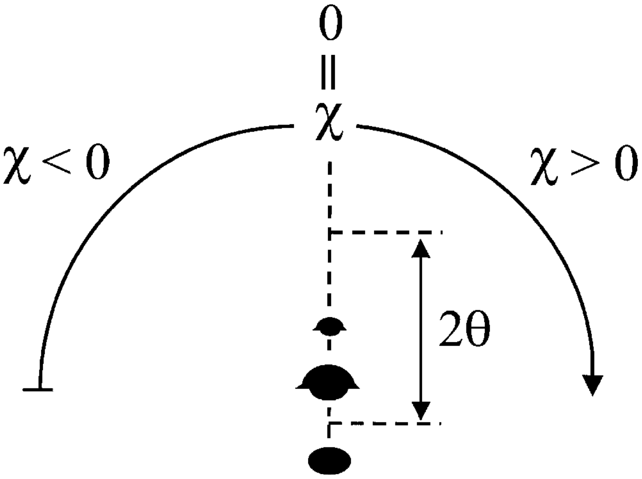

Figure 7. Definition of the 2θ and χ parameters used in the analysis of XRD patterns on aligned samples.

considering the distribution of the intensity $I(\psi)$ given by

$$I(\psi) = I(\chi) + I(-\chi) \qquad (6)$$

where $I(\chi)$ is obtained by integration in 2θ for constant χ (along a radial direction) in the WAXS region, and

$$\psi = 90° - |\chi_{\mathrm{WAXS}}| \qquad (7)$$

is the tilt angle of the molecules defined in expression (2). The plot of the distribution $I(\psi)$ for $T = 138°C$ is presented in figure 8.

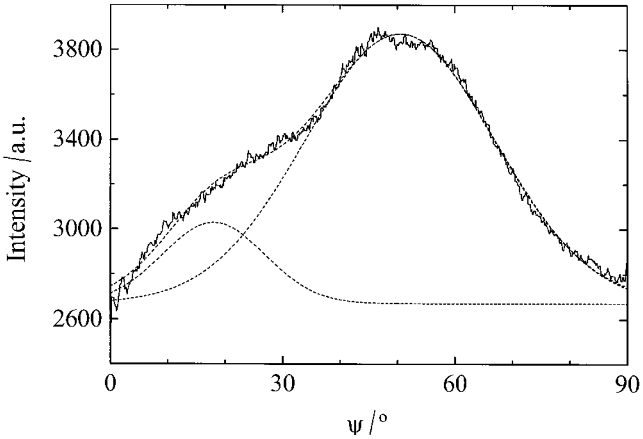

Figure 8. Distribution $I(\psi)$ (full line) in the WAXS region at $T = 138°C$. Fit of $I(\psi)$ (dashed line) in the WAXS region with two gaussian curves (dashed lines), centred at $\psi = 18°$ and $\psi = 51°$ corresponding to the average tilt angles of the chains and of the core, respectively, at $T = 138°C$.

4. Discussion and structural model

Using the results for S and σ_c and equation (2), the values of the tilt angle of the core ψ_c as a function of the temperature are obtained and presented in figure 9. The tilt angle decreases slightly with increasing temperature, thus inducing the small increase of the total layer thickness as observed in figure 3. However, it can be considered that the values of ψ_c are around 63° for the whole temperature range of the smectic C phase. Taking

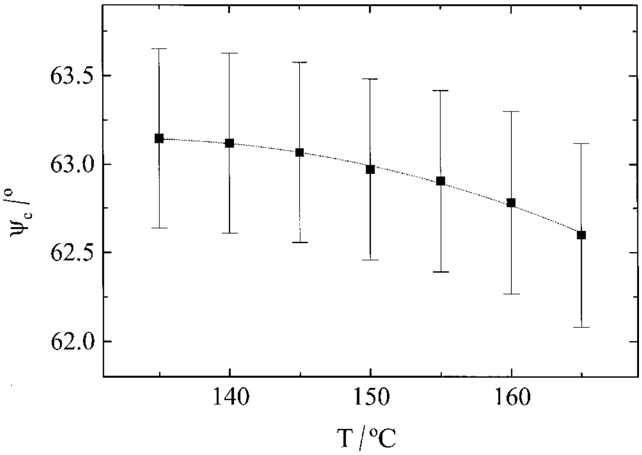

Figure 9. Tilt angle of the core ψ_c as a function of the temperature T, obtained by the analysis of XRD data on powder samples combined with dilatometry. The dashed line is a guide for the eye.

into account the value of the molecular length of the rigid core as found by molecular simulation, 30.5 Å, the aromatic sublayer thickness is found to be 14.1 Å. From the value of the layer spacing, 31 Å, determined experimentally at 155°C (see figure 3), the aliphatic sublayer on each side of the aromatic cores is deduced to have a thickness of 8.4 Å. Comparing this latter value with the theoretical length of the chains (9.4 Å, measured in a zigzag planar conformation), the average tilt angle of the terminal chains is deduced to be about 27°. It is interesting also to calculate the average tilt angle of the aliphatic chains through the relation σ_{ch}/S. For example, at $T = 160°C$, such a tilt angle is found to be about 29°, in full agreement with the value (27°) deduced above from the aliphatic sublayer.

Considering the results presented in the previous section, the packing model within the SmC phase is illustrated in figure 10. Note that the representation of the (molten) chains is simply illustrating the average tilting. In this model, the molecular cores present a tilt angle relative to the normal to the smectic layers of about 63°, and the molten aliphatic chains are on average tilted at an angle close to 25°–30°. It is worthwhile noticing that the tilt angle of the aromatic core, having a much higher value than the average tilt angle of the chains, is justified by the greater cross sectional area of the set of the two end chains of the molecule compared with that of the core (for instance $\sigma_{ch} = 46.6\,\text{Å}^2$ and $\sigma_c = 24.5\,\text{Å}^2$ at 150°C). The tilt angle of the cores determined in this study is close to values previously found for similar compounds in [2] and [3] of about 60° and 66°, respectively. As previously reported [2], these angles are also close to those found in the crystal phases of these substances, which agrees with an interpretation of the crystal-to-smectic C phase transition as involving a loss of positional order, but not a significant change of the orientational order of each part of the molecules.

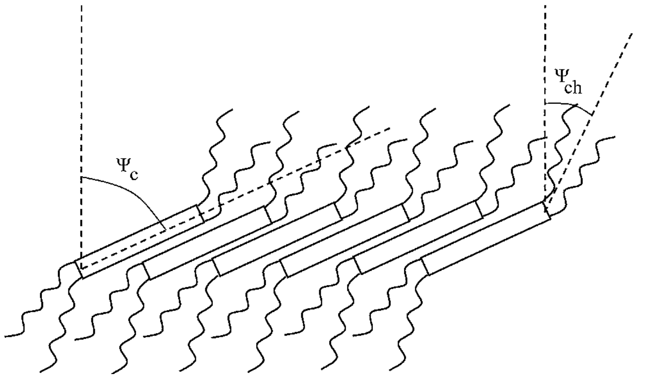

Figure 10. Molecular organization of the biforked molecules within the SmC layers. Rectangles stand for the long aromatic cores of the molecules, and wavy lines for the disorganized terminal aliphatic chains.

Let us now consider in more detail the XRD pattern recorded with the oriented sample, and more particularly the wide angle region (figure 8). It seems to be characterized by a very large band centred around 50°–60°, with a pronounced shoulder at about 20°–30°. Indeed, the scattering intensity curve as a function of χ is easily fitted with two distinct gaussian curves, one being centred at 18° and the other at 51° (figure 8). Even if these values are slightly smaller than those obtained by the indirect method combining XRD and dilatometry experiments, there is no doubt that these two gaussian curves correspond to the average tilt angle of the aromatic cores, ψ_c, and of the aliphatic chains, ψ_{ch}, respectively. The analysis of the $I(\psi)$ profile at different temperatures shows no significant change of the angles ψ_c and ψ_{ch} over the whole temperature range of the smectic C phase.

It is important to note here that the two gaussian curves have a relatively large width, corresponding to very large fluctuations of orientation of each part of the molecules. If we take into account these large orientational fluctuations, these results are in good agreement with the tilt angles found by the method combining powder XRD and dilatometry. However, it is worth pointing out that this is the first time that the two different average orientations of the aromatic cores and of the aliphatic chains of biforked compounds have been directly observed in smectic C phases.

5. Conclusion

This work shows that, in the smectic C phase of biforked molecules, the long rigid aromatic cores are strongly tilted (about 50°–60° for ψ_c) with respect to the normal to the layer planes, whereas the average tilt angle of the aliphatic chains is only 20°–30° (ψ_{ch}), as reported in previous studies on this kind of compound [2, 3]. The difference in the values of ψ_c and ψ_{ch} is because the cross sectional area of the aliphatic part of a biforked molecule is nearly double that of the aromatic core. It is important to stress that, in the frame of the method that combines the XRD results on powder samples with very precise volumetric studies, the values of ψ_c are uniquivocally determined by the measurements of the molecular volume V_m, of the smectic layer spacing d, and of the molecular cross sectional area σ_c.

A detailed analysis in the wide angle region of the XRD patterns for oriented samples shows that the broad signal observed can be decomposed into two distinct bands. These correspond to the diffraction of molecular segments tilted at about 20° and 50° with respect to the layer planes. Indeed, the corresponding molecular segments are the terminal aliphatic chains and the long aromatic cores. Thus, for the first time with polycatenar compounds, the tilt of each part of the molecules is directly observed on the X-ray pattern for the smectic phase. Despite a wide orientational distribution of the molecular segments, it can be considered that there is a fairly good agreement between the tilts thus measured and those deduced from the combined analysis of dilatometry measurements and XRD patterns of powder samples which has been used so far for such types of material.

All these experimental results point out the validity of the model of the molecular organization within the smectic C phase of biforked molecules. It is characterized by a very large tilt angle of the long aromatic cores and a much smaller tilt of the terminal aliphatic chains. It is interesting to remember that such an organization has already been found to exist in the crystalline phases of such compounds. These results clearly indicate that the transition between the crystalline phase and the smectic C phase occurs with the loss of positional order of the aromatic cores and melting of the aliphatic chains, but with no significant change of the average orientation of each molecular segment.

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References

[1] Nguyen, H. T., Destrade, C., and Malthête, J., 1997, *Adv. Mater.*, **9,** 375 and references therein.

[2] Allouchi, H., Cotrait, M., Guillon, D., Heinrich, B., and Nguyen, H. T., 1995, *Chem. Mater.*, **7,** 2252.

[3] Guillon, D., Heinrich, B., Ribeiro, A. C., Cruz, C., and Nguyen, H. T., 1998, *Mol. Cryst. liq. Cryst.*, **317,** 51.

[4] Kovacs, A. J., 1955, *Ric. Sci. Suppl.*, **25,** 668; Guillon, D., and Skoulios, A., 1977, *Mol. Cryst. liq. Cryst.*, **39,** 139.

[5] Diele, S., Grande, S., Kain, J., Pelzl, G., and Weissflog, W., 2001, *Mol. Cryst. liq. Cryst.*, **362,** 111.

[6] Nguyen, H. T., Destrade, C., and Malthête, J., 1990, *Liq. Cryst.*, **8,** 797.

[7] Guillon, D., and Skoulios, A., 1976, *J. Physique*, **37,** 797; Poeti, G., Fanelli, E., Torquati, G., and Guillon, D., 1983, *Il Nuovo Cimento, 1*, **2D,** 1335.

[8] Marcos, M., Gimènez, F., Serrano, J. L., Donnio, B., Heinrich, B., and Guillon, D., 2001, *Chem. Eur. J.*, **7,** 1006.

[9] Doolittle, A. K., 1951, *J. Appl. Phys.*, **22,** 1471.