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Liquid Crystals

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Phase transitions between smectic A phases as well as smectic C* phases and undulated structures in terminal non-polar compounds

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Phase transitions between smectic A phases as well as smectic C* phases and undulated structures in terminal non-polar compounds†

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Two types of smectic A and smectic C phases, respectively, have been proved by X-ray and DSC methods for compounds that are terminal non-polar, but consist of tuning-fork shaped molecules. The structural models of the phases are discussed on the basis of steric interaction and of a dense packing. The X-ray patterns of oriented samples point to an undulation of the smectic layers in the case of the smectic A and smectic B phase.

1. Introduction

Smectic A and C phases are characterized by long-range translational order in one dimension and liquid-like arrangement of the rod-like molecules in the two other dimensions. In the classical monolayer smectic A phase, the one-dimensional density wave has a periodicity d which is approximately identical with the molecular length. But in substances with a pronounced polar asymmetry, for example, terminal polar substances, the dipolar interaction can lead to a polymorphism of smectic A or smectic C phases where the d value considerably deviates from the molecular length [1–3]. Otherwise, it is also known that the steric asymmetry of molecules can give rise to structural peculiarities of smectic phases. In smectic A phases of swallow-tailed compounds, uncorrelated strings of interdigitated molecules can occur [4]. Smectic A phases of some lateral branched compounds are characterized by an antiparallel alignment of the molecules and a partial intercalation of the terminal chains so that a d value results which is clearly smaller than the molecular length, without any corresponding decrease of the order parameter or the appearance of tilt [5]. Other examples of sterically influenced structure variations are found for terminally fluorinated mesogens [6]. In the smectic A phases of such compounds the layer periodicity exceeds clearly the molecular length ($d/L = 1{\cdot}05$–$1{\cdot}1$). Furthermore, from X-ray investigations a strongly defective modulated layer structure can be derived whereby the position of the areas of shifted layers are not correlated in space [6].

In this paper we show that a special molecular shape not only causes structural peculiarities, but can also lead to different modifications of the smectic A as well as the smectic C* phase—similarly to compounds with polar asymmetry.

2. Materials

The substances under investigation are listed in the table. The synthetic route is described in [7]. It is seen that these substances exhibit a tuning-fork-like molecular shape. The central core is an aromatic ring (A) or a cyclohexane ring (B). In the 1, 3 and 5 positions, rod-like mesogenic moieties R are substituted. It should be noted that compound **BII** contains three different substituents R_1, R_2, and R_3 and therefore their positions are statistical. For all substances listed in the table, the phase transition temperatures are presented and the brackets denote transitions in the supercooled state. The identification of the liquid crystalline phases is anticipated and will be described in § 4.

3. Experimental

The phase transition temperatures (see the table) have been determined, generally, by microscopic and calori-

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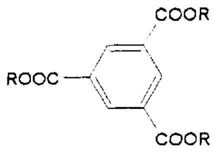
* Author for correspondence.

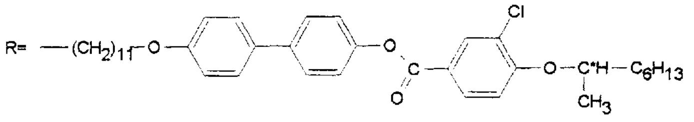
† Dedicated to Prof. Dr A. Saupe on the occasion of his 70th birthday.

Structure and phase behaviour of the compounds under investigation.



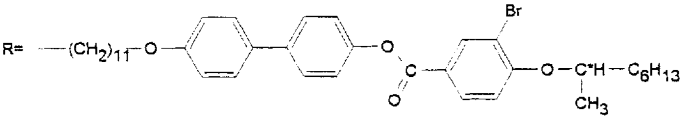
A

AIa

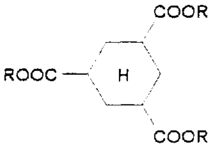


$\mathrm{Cr}(\mathrm{S}^*_{\mathrm{C}1}83)92\mathrm{S}^*_{\mathrm{C}1/2}104\mathrm{Ch}109\mathrm{I}$

AIb

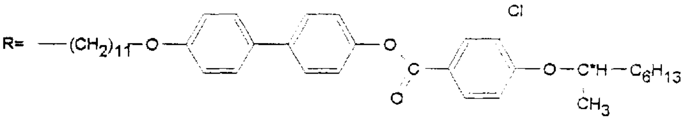


$\mathrm{Cr}(58\mathrm{S}^*_{\mathrm{C}1}74)74\mathrm{S}^*_{\mathrm{C}1/2}93\mathrm{Ch}100.5\mathrm{I}$



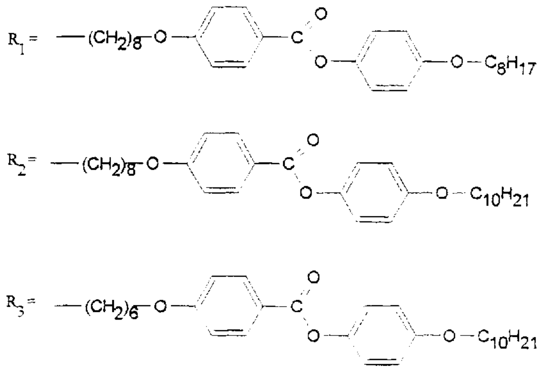
B

BIa



$\mathrm{Cr}82\mathrm{S}^*_{\mathrm{C}1}92\mathrm{S}^*_{\mathrm{C}1/2}112\mathrm{I}$

BII



$\mathrm{Cr}?\mathrm{S}_{\tilde{\mathrm{B}}}33\mathrm{S}_{\tilde{\mathrm{A}}}54\mathrm{S}_{\mathrm{A}1/2}77.5\mathrm{N}82\mathrm{I}$

metric investigations (DSC, Perkin-Elmer). By texture observation, the N and $\mathrm{S_A}$ phase and the cholesteric and S^*_C phase could be identified. The phase transition within the $\mathrm{S_A}$ or S^*_C phase, respectively, has been recognized by X-ray studies using a photographic flat film method for oriented samples and a Guinier goniometer for non-oriented samples. Since the transition temperatures strongly depend on the temperature regime, the values determined by the X-ray measurements are somewhat different from these determined calorimetrically.

4. Results

4.1. *Remarks concerning the nomenclature used*

In the following, it will be shown that there exist transitions within the $\mathrm{S_A}$ and S^*_C phase regions. These phase transitions involve phases with structural similarities to $\mathrm{S_{A1}}$, $\mathrm{S_{A2}}$ and $\mathrm{S}_{\tilde{\mathrm{A}}}$ phases of terminal polar substances, the designation of which is introduced according to the relation $d \cong L$ and $d \cong 2L$, where d and L are the layer thickness and the length of the molecules, respectively [1,3]. In the $\mathrm{S}_{\tilde{\mathrm{A}}}$ phase an undulation of the smectic layers has been proved.

An undulation of the smectic layers has also been found in the low temperature $\mathrm{S_A}$ phase and $\mathrm{S_B}$ phase of the substances **BII**. Therefore the symbols $\mathrm{S}_{\tilde{\mathrm{A}}}$ and $\mathrm{S}_{\tilde{\mathrm{B}}}$ will be used, too, in these cases. In the high temperature $\mathrm{S_A}$ and S^*_C phases, however, the d values correspond to half of the molecular length. Following the designation introduced in the case of polar substances, the symbols $\mathrm{S_{A1/2}}$ and $\mathrm{S}^*_{\mathrm{C}1/2}$ have to be used.

It should be emphasized, that the nomenclature is only based on the structural similarities. The intermolecular interactions leading to the transitions are quite different. Also miscibility studies are still lacking.

4.2. *Phase behaviour of compounds **AIa**, **AIb** and **BIa***

According to the microscopic observations, all three compounds exhibit a smectic C* phase; compounds **AIa** and **AIb** form, in addition, a cholesteric phase. The cholesteric phase commonly appears as a Grandjean texture, whereas the smectic C* phase occurs in a schlieren texture. Because of the chiral centres in the mesogenic units, the smectic C phase is twisted (S^*_C), as indicated by a ferroelectric switching [7]. From electro-optical measurements, a tilt angle of about 40° could be estimated.

Because the phase behaviour of the substances under discussion is quite similar, the principal results of the X-ray investigations will be presented for compound **AIb**. Figure 1 shows the X-ray diagrams of a non-oriented sample as a function of the temperature. At the transition

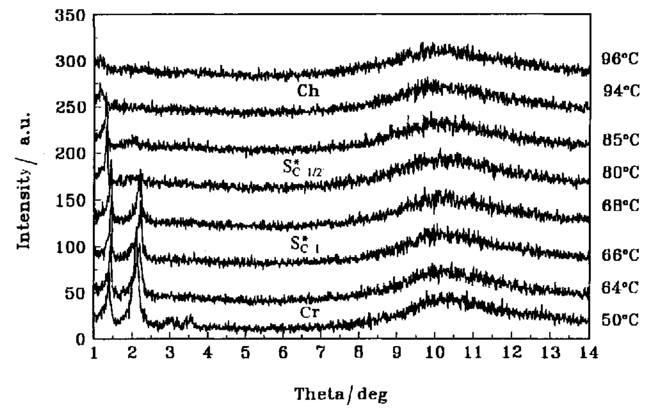


Figure 1. X-ray diffraction pattern of the cholesteric, smectic C* and solid phases of compound **AIb** at different temperatures.

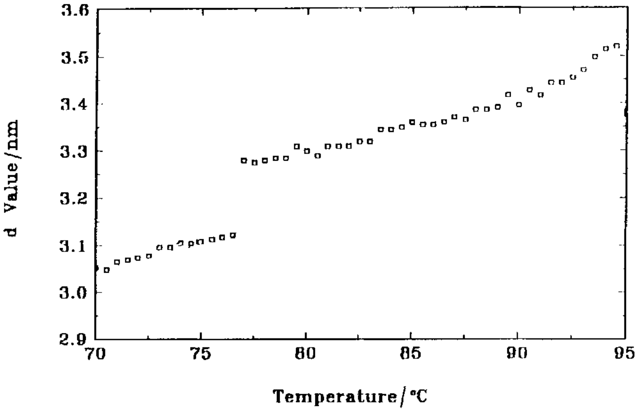


Figure 2. Temperature dependence of the *d* value in the S_{C1}^* and $S_{C1/2}^*$ phases of compounds **AIb**.

of the cholesteric into the smectic C* phase, besides the diffuse outer scattering ($\theta \cong 10°$), a strong reflection at small angles ($\theta = 1{\cdot}26°$) appears, indicating the layer structure.

Regarding the tilt angle, this reflection corresponds to about half of the molecular length ($S_{C1/2}^*$). Whereas the diffuse outer scattering remains unchanged until crystallization occurs at 54°C, below 77°C the position of the small angle reflection is somewhat shifted and an additional strong peak ($\theta = 2{\cdot}1°$) arises (see also figure 1). Figure 2 displays the temperature dependence of the *d* values. The transition is connected with a small jump in the layer thickness.

If the first reflection is designated by a scattering vector q_2 and the second one by q_3, then q_2 is related to q_3 as 2 : 3, and this leads us to index these reflections as (0 0 2) and (0 0 3), respectively, with a consequent doubling of the layer thickness in comparison with the high-temperature smectic C* phase. Considering the tilt angle, the layer thickness now corresponds to the molecular length (S_{C1}^*).

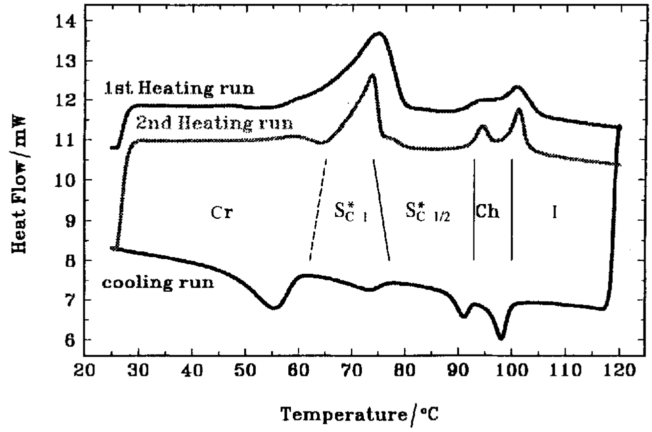


Figure 3. DSC thermograms for heating and cooling runs for compound **AIb**, suggesting the phase sequence indicated in the text.

Because of the relatively high viscosity, it was impossible to orient the sample by a magnetic field. But in drawn fibres, a preferred direction of the layer normal perpendicular to the fibre axis could be obtained. We found that the reflections with q_2 and q_3 are positioned on a line perpendicular to the fibre axis, which supports the proposed indexing of the scattering maxima. But it should be emphasized that the (0 0 1) reflection has never been observed. Probably the intensity of the (0 0 1) reflection is below the limit of detection caused by the small value of the structure factor at this wavevector.

The transition between these two smectic C* phases indicated by X-ray investigations could be proved by calorimetric measurements. The DSC cooling curve shows a small, but clear transition peak corresponding to a transition heat of the order of $1{\cdot}5\,\mathrm{J\,g^{-1}}$ (see figure 3). It should be mentioned that such a transition peak for $S_{C1}^* \rightarrow S_{C1/2}^*$ was also observed for the compounds **AIa** and **BIa**.

Looking for a structure model for both smectic C* phases, we have to take into account the layer periodicity, the molecular length, the tilt angle and the space filling conditions. Near the phase transition $S_{C1/2}^* \rightarrow S_{C1}^*$ the experimental *d* value was 3·28 nm for the $S_{C1/2}^*$ phase and 6·3 nm for the S_{C1}^* phase. The overall length of the molecule is about 8·4 nm, whereas the length of the mesogenic moieties is about 4 nm. In addition, from dielectric measurements it follows that an essential part of the molecules must be aligned antiparallel in both smectic C* phases.

Figures 4 (*a*)–(*d*) present four packing models which fulfil the conditions mentioned above. In model I, the parallel aligned molecules are shifted by half a molecular length so that a layer periodicity $d = \frac{1}{2}(L\cos\beta)$ (β = tilt angle) results. Model II is characterized by an antiparallel alignment with a layer spacing $d = L\cos\beta$. In model III,

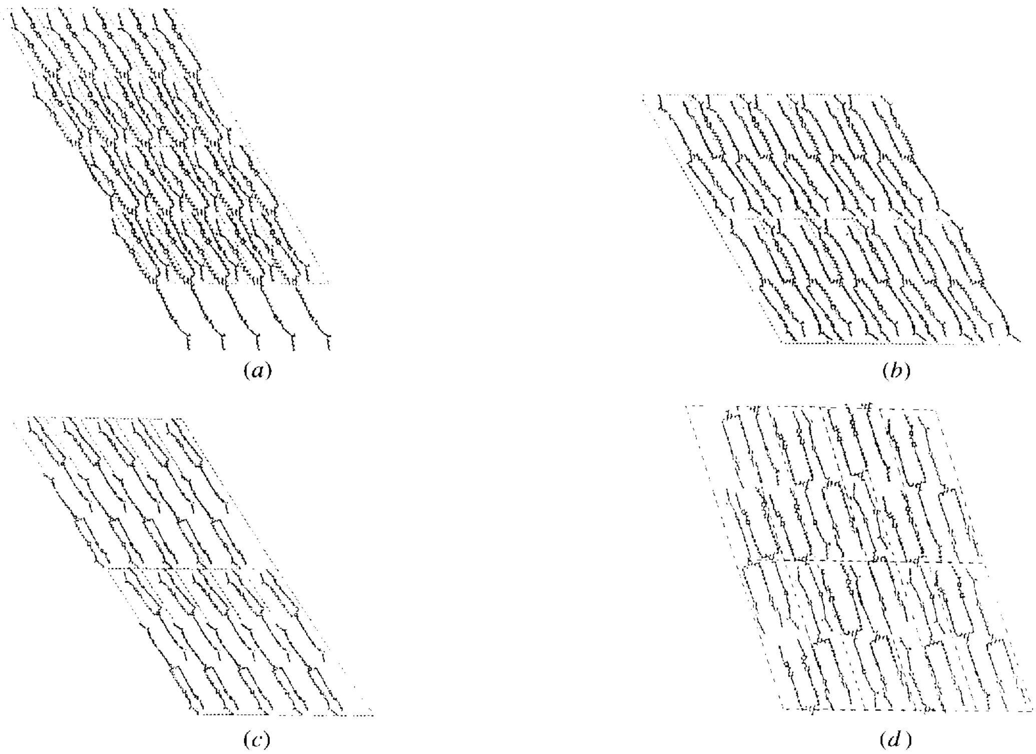


Figure 4. (*a*) Packing model I: layer period $d = 1/2(L\cos\beta)$. (*b*) Packing model II: layer period $d = L\cos\beta$. (*c*) Packing model III: layer period $d = 3/2(L\cos\beta)$. (*d*) Packing model IV: layer period $d = 1/2(L\cos\beta)$.

the molecules are also antiparallel but they are shifted by a half molecular length. From this structure a layer period $d = \frac{3}{2}(L\cos\beta)$ can be deduced. Model IV is a combination of model II and III which gives rise to a d value $d = \frac{1}{2}(L\cos\beta)$.

It is seen that model III contradicts the experimental results. The experimental d value of the S_{C1}^* phase is only fulfilled by model II with the antiparallel alignment of molecules. The transition from S_{C1}^* into the $S_{C1/2}^*$ phase is connected with a halving of the layer period, which can be explained either by model I or model IV. Otherwise, a transition from the structure of model I to model II should be accompanied by a clear change in the dielectric permittivity parallel to the director ($\varepsilon_{\|}$); this could not be observed [8]. Furthermore, this transition would demand the rotation of about 50 per cent of the molecules around the short axes which should be reflected in a greater transition enthalpy as experimentally observed. For this reason model IV seems to be the most plausible structure model of the $S_{C1/2}^*$ phase and this which would satisfy the space filling condition, the experimental d value and the results of the dielectric measurements.

4.3. *Phase behaviour of the compounds* ***BII***

By microscopic observation, besides the nematic phase, a smectic A phase was found which maintained a homeotropic or fan-shaped texture until the crystallization. But as seen from the calorimetric curve, a very weak transition peak at 54°C ($\Delta H \cong 0{\cdot}16\,\mathrm{J\,g^{-1}}$) and a pronounced peak at 28°C ($\Delta H = 9{\cdot}85\,\mathrm{J\,g^{-1}}$) was detected (see figure 5). X-ray investigations give evidence that the first peak is caused by a transition between different smectic A

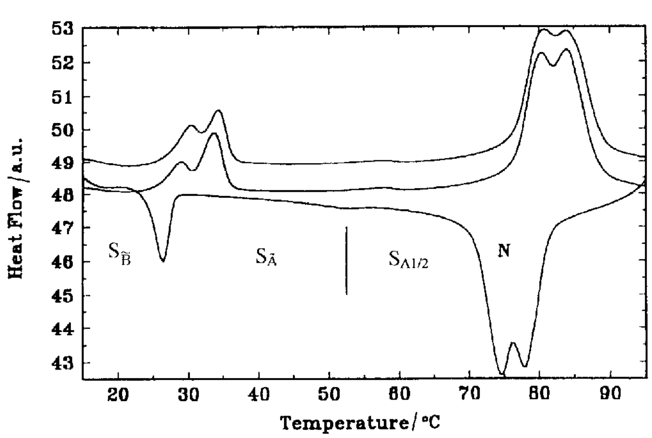


Figure 5. DSC thermograms for heating and cooling of compounds **BII** suggesting the phase sequence indicated in the text.

phases, whereas the second one corresponds to a transition from smectic A to smectic B.

The transition within the smectic A region was obvious from the X-ray pattern of a non-oriented sample. The X-ray pattern above 54°C shows one strong small angle reflection which corresponds to a layer period $d_2 = 3{\cdot}56$ nm, whereas the molecular length obtained by a molecular model amounts to about 7·0 nm. Below 54°C, a second strong small angle reflection occurs, the d value of which (d') is nearly twice d_2 found for the high-temperature phase $S_{A1/2}$ (see figure 6). It follows from figure 7 that the full width at half maximum (FWHM) of the diffuse outer scattering remains unchanged up to 33°C. Then, a pronounced drop occurs which is due to the transition of the S_A phase into a smectic phase with order within the layers. The nematic phase of compounds **BII** could be homogeneously oriented by a magnetic field. This orientation was preserved also in the smectic state. X-ray patterns of oriented samples give additional information about the structure of the phases under discussion (see figure 8).

According to figure 8, the high-temperature phase $S_{A1/2}$ exhibits the (0 0 1) reflection on the meridian of the pattern parallel to the magnetic field. In addition, a very weak diffuse scattering is observed at nearly the half Bragg angle. This diffuse scattering condenses at the transition into the low temperature S_A phase. The second reflection in the small angle region is split off as shown schematically in figure 9. The splitting means that the intensity distribution exhibits maxima definitely out of the merid-

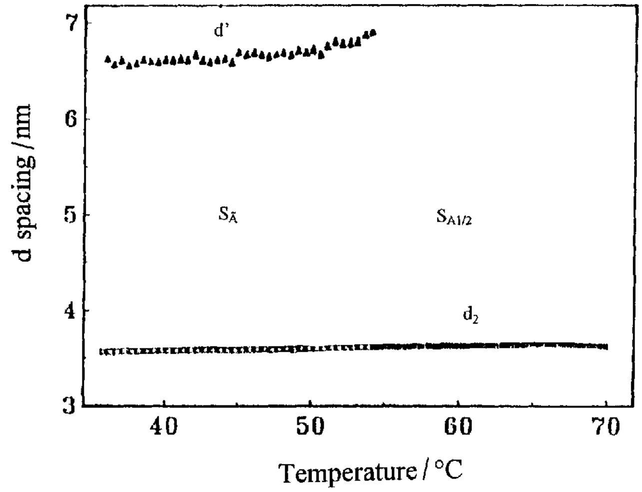


Figure 6. Temperature dependence of d values for the $S_{\tilde{A}}$ and $S_{A1/2}$ phases of the compounds **BII**.

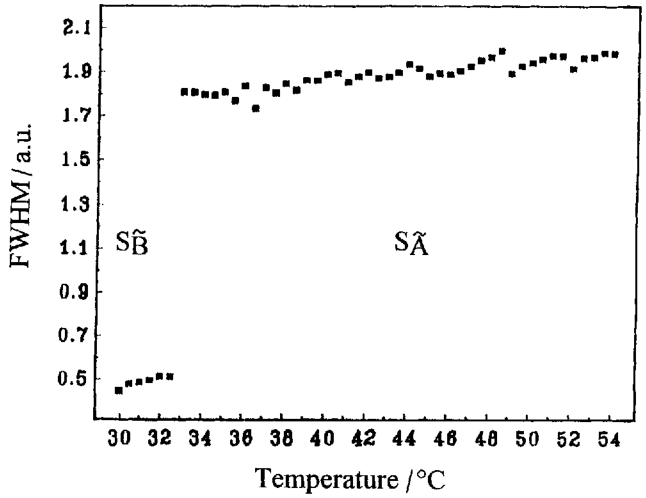


Figure 7. The full width of the half maximum (FWHM) of the outer scattering (~10°) in the $S_{\tilde{A}}$ and $S_{\tilde{B}}$ phase of compound **BII**.

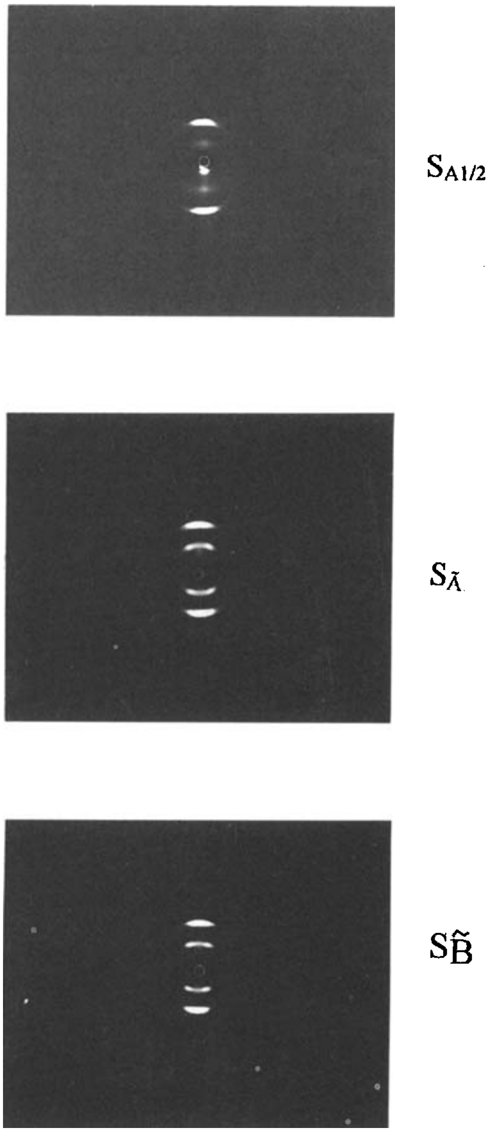


Figure 8. Small angle X-ray patterns of oriented samples of the $S_{\tilde{A}}$, $S_{A1/2}$ and $S_{\tilde{B}}$ phases of compounds **BII**.

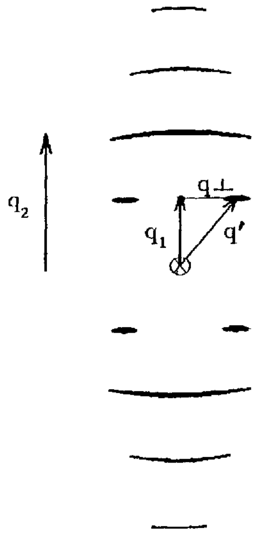


Figure 9. Schematic representation of the X-ray diffraction pattern in the small angle region in the $S_{\tilde{A}}$ phase of compounds **BII** (q_1, q_2, q', $q_\perp$: scattering vectors).

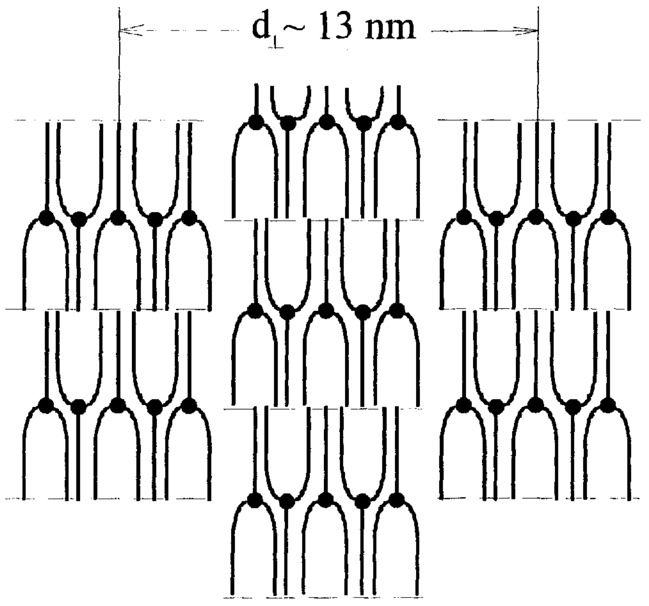


Figure 10. Schematic representation of the undulation of the layers in the $S_{\tilde{A}}$ and $S_{\tilde{B}}$ phases of compounds **BII**.

ian. This kind of pattern can be explained by an undulation of the smectic layers perpendicular to the layer normal (see figure 10) which has been found in the $S_{\tilde{A}}$ phase of terminal polar substances [9, 10]. The splitting of the reflection and the corresponding undulation remain unchanged in the smectic B phase.

The splitting of the (0 0 1) reflection can also explain why, in the X-ray pattern of non-oriented samples (see figure 6), d_2 of the $S_{A1/2}$ phase is not exactly half value of d' in the $S_{\tilde{A}}$ phase. As seen from figure 9, the layer spacing in $S_{\tilde{A}}$ calculated on the basis of the scattering vector q' must be smaller than twice d_2. The pattern of oriented samples proves that q_2 is twice q_1. Apart from the undulation of the layers, the transition $S_{A1/2} \rightarrow S_{\tilde{A}}$ should be accompanied by a reorganization of the molecules which is probably analogous to that of the $S^*_{\tilde{C}1/2} \rightarrow S^*_{\tilde{C}1}$ transition; this means that in the $S_{\tilde{A}}$ phase the antiparallel packing of the tuning-fork-like molecules must be dominant. In the $S_{A1/2}$ phase there is obviously a combination of pairs of antiparallel aligned molecules which are shifted by half the molecular length.

5. Discussion

In the compounds under investigation the mesogenic moieties are decoupled from the central core by a flexible spacer so that they are able to align parallel to each other and to form smectic layer structures. The relative flexibility of the mesogenic units is also indicated by the electro-optical behaviour of the $S^*_{\tilde{C}1/2}$ phases. It could be shown [7] that the ferroelectric switching is relatively fast, so that polymeric foils of these materials can be obtained as switchable elements.

The main structural feature of the tuning-fork-like molecules is a pronounced difference of the cross-sections in different parts of the molecules. The steric repulsions associated with the steric asymmetry of the molecules obviously give rise to the occurrence of different types of smectic A as well as smectic C phases. For molecules with polar asymmetry, the different kinds of smectic layering were theoretically treated by Prost *et al.* [11, 12], who postulated the competition between two incommensurable length scales. Because of the polar asymmetry, not only should the density modulation determine the smectic layering, but also the position of the molecular dipoles with respect to the layers. In this way two characteristic lengths occur—the molecular length L and the length L' corresponding to the formation of spatial associates which lead to the repetition of the local polar groups.

As discussed by de Jeu *et al.* [13], and Ostrowski [6], molecules with steric asymmetry should in principle also be able to form different smectic A or C phases. As in the case of terminal polar substances, the whole tuning-fork-shaped molecule can be presented by a vector indicating the steric dipole. Obviously the antiparallel correlation of molecules indicated by dielectric measurements is energetically favourable. Depending on the temperature-dependent flexibility of the spacers and the terminal alkyl chains and because of the lateral cohesion between the mesogenic units, the space filling condition can be realized in different ways, so that, in spite of the same point group symmetry, different modifications are possible which are distinguished by the packing of the molecules. Unlike terminal-polar compounds, in the high temperature smectic A and C phases, the layer period corresponds to half of the molecular length, whereas in the low temperature phases, the *d* value agrees with the full molecular length. It is known that in smectic A phases of terminal-polar compounds, the small angle reflections can be observed out of the meridian, which points to an additional periodic density modulation in the plane of the smectic layers [1, 10, 11]. In this case, the position of bilayers with antiparallel arranged dipoles is shifted periodically in the direction of the layer normal so that a modulation of the layer planes occurs. These smectic phases were designated as $S_{\tilde{A}}$ or $S_{\tilde{C}}$ phases. Recently Ostrowski [14] reported an example of a terminal non-polar compound possessing a pronounced steric asymmetry which also shows such undulation of the layers. Therefore it is not surprising that the tuning-fork-like molecules which show a strong tendency to antiparallel order are able to form smectic $\tilde{A}$ phases. As shown by our structure models (see § 4), the antiparallel aligned 'steric dipole' of the tuning-fork-like molecules can also change periodically from layer to layer giving rise to the observed in-plane modulation (see figure 10). The period of modulation $d = 2\pi/q_\perp$ was found to be about 13 nm. It is remarkable that this modulation persists in the smectic B phase, too. The transition from the $S_{\tilde{A}}$ into the $S_{A1/2}$ phase can be explained then by a loss of the segregation of the antiparallel arranged dipoles leading to the undulation, so that the structure of the $S_{A1/2}$ phase consists more or less of pairs of antiparallel molecules which are shifted by a half of the molecular length. The results presented in this paper give further evidence for the role of steric repulsion associated with the steric asymmetry of molecules on the polymorphism of smectic A or C* phases.

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