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Structural and conformational investigations in SmA and different SmC phases of new hockey stick-shaped compounds

B. Das[a]; S. Grande[a]; W. Weissflog[b]; A. Eremin[b]; M. W. Schröder[b]; G. Pelzl[b]; S. Diele[b]; H. Kresse[b]
[a] Universität Leipzig, Fakultät für Physik und Geowissenschaften, Institut für Experimentelle Physik I, Linné Str. 5, D-04103 Leipzig, Germany, [b] Institut für Physikalische Chemie, Martin-Luther-Universität Halle-Wittenberg, Mühlpforte 1, D-06108 Halle, Germany,

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Structural and conformational investigations in SmA and different SmC phases of new hockey stick-shaped compounds

B. DAS, S. GRANDE
Universität Leipzig, Fakultät für Physik und Geowissenschaften,
Institut für Experimentelle Physik I, Linné Str. 5, D-04103 Leipzig, Germany

W. WEISSFLOG*, A. EREMIN, M. W. SCHRÖDER, G. PELZL, S. DIELE and H. KRESSE
Institut für Physikalische Chemie, Martin-Luther-Universität Halle-Wittenberg,
Mühlpforte 1, D-06108 Halle, Germany

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New *meta*-substituted homologous three-ring mesogens, the 4-(3-*n*-decyloxyphenyliminomethyl)phenyl 4-*n*-alkyloxybenzoates, have been synthesized, which are non-linear due only to the attachment of one of the alkyloxy groups in a *meta*-position. The mesophases were studied by optical microscopy, differential scanning calorimetry, NMR spectroscopy, X-ray diffraction, and electro-optical and dielectric measurements. Unusual phase behaviour was observed on varying the length of the terminal chain. The most interesting finding is the occurrence of two polymorphic tilted smectic phases designated as SmC_1 and SmC_2. The existence of these phases was revealed by calorimetric studies and also from the pronounced difference in optical textures. It was shown from NMR measurements that the molecular orientation changes from a synclinic to an anticlinic arrangement in the SmC_1 to SmC_2 phase transition. It has also been shown, using NMR, that the $\mathrm{SmC}_1 \rightarrow \mathrm{SmC}_2$ phase transition in these compounds is accompanied by a conformational change in the molecular fragment containing the aromatic ring with the *meta*-substituted terminal alkyloxy chain. This conformational change is linked to a change in the shape of the molecules and leads to a different packing of the molecules within the layers of the SmC_2 phase. From dielectric measurements an increase by a factor of two was detected in the molecular mobility at the transition into the low temperature SmC_2 phase. This finding supports a change in the packing as result of conformational changes.

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1. Introduction

Bent-shaped mesogens are a topic of considerable recent research interest in the field of liquid crystals. Nevertheless, it should be noted that any bend angle existing in the long axis of the molecules reduces the ability to form mesophases. In order to obtain B-phases from banana-shaped molecules the rigid core contains five or more aromatic rings [1]. The hockey stick compounds described by Samulski *et al.* [2] are non-symmetric with respect to the position of the bend and also consist of five phenyl or heterocyclic moieties. Starting from calamitic three-ring compounds, a fourth aromatic ring can be connected at the *meta*-position, as described recently by Hird *et al.* [3]. Reducing the number of rings further, one terminal phenyl ring of a rod-like three-ring mesogen can be substituted in the *meta*-position by a long chain aliphatic group. In such molecules the bend results only because one terminal group is not linked in a *para*-position. Nematic and smectic phases were reported to occur at relatively low temperatures [4–6]. In the case of the 5-alkyloxy-2,3,4-trifluorophenyl biphenylcarboxylates Hird *et al.* found SmA and SmC phases [3]. The smectic C phase exhibits unusual properties. It spontaneously forms regions of opposite handedness and shows ferroelectric switching, although experimental details were not reported.

In this paper we present *meta*-alkyloxy-substituted three-ring mesogens of a simple chemical structure exhibiting an unusual mesophase behaviour. We will show that these compounds form SmA phases and/or different tilted smectic phases depending on the length of the terminal chains. The mesophases were characterized by differential scanning calorimetry (DSC), polarizing optical microscopy (POM), X-ray diffraction (XRD), NMR studies, and dielectric and electro-optical investigations.

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*Author for correspondence;
e-mail: weissflog@chemie.uni-halle.de

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2. Materials

The new compounds were prepared by the condensation of 4-formylphenyl 4-*n*-alkyloxybenzoates with 3-*n*-decyloxyaniline by heating at reflux in ethanol using a catalytic amount of acetic acid. In the series reported here, the *meta*-alkyloxy chain is unchanged while the length of the *para*-substituent is varied from $n = 8$ to 12 and 16. The transition temperatures and associated transition enthalpies of these compounds are listed in table 1. The numbering of the carbon positions used for assigning the NMR spectra is shown in the structure in table 1. Homologue **8** forms only a SmA phase; lengthening the chain results in a SmA–SmC dimorphism in compound **9**. The homologues **10** and **11** exhibit two tilted smectic phases besides the SmA phase. In homologue **12**, both tilted smectic phases exist in a temperature range sufficiently large to allow for physical measurements; for the longest chain compound **16**, only one smectic C phase could be detected.

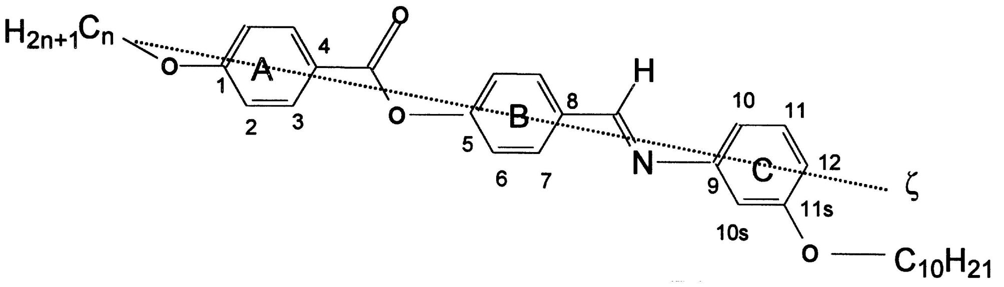
3. Experimental

The phase transition temperatures were determined using a differential scanning calorimeter (DSC-Pyris 1, Perkin Elmer). Textures and the field-induced changes of the textures were examined using a polarising microscope (Leitz Laborlux) equipped with a Linkam hot stage (THM 600/S) and an automatic temperature controller. XRD measurements on non-oriented samples were performed using a Guinier camera as well as a Guinier goniometer (Huber Diffraktionstechnik GmbH). Oriented samples were obtained by slow cooling of a drop of the liquid crystal placed on a glass plate. In this case the X-ray beam was incident parallel to the glass plate. The X-ray patterns were obtained using a 2D area detector (Hi-Star, Siemens AG).

NMR experiments were made in a measuring field of 11.7 T using a Bruker MSL 500 spectrometer operating at 500 MHz for proton resonance. A homogeneous orientation of the molecule long axes is obtained. The samples were held in standard 5 mm tubes, and the temperature was stabilized to within an accuracy of 0.5 K. ^{13}C NMR spectra at 125.6 MHz were recorded in the isotropic state using pulse excitation together with WALTZ decoupling. Proton decoupling in the liquid crystalline phase was achieved by continuous high power irradiation or WALTZ cycles. Both pulse excitation and cross polarization techniques were used to excite the spectra at each temperature. Measurement of the spin-lattice relaxation time, T_1, has been performed as an aid in the assignment of the ^{13}C NMR spectra of the chains.

Dielectric measurements were performed in the frequency range from 1 Hz to 10 MHz using a Solartron

Table 1. Transition temperatures (°C) and associated transition enthalpies [kJ mol^{-1}] for the 4-(3-*n*-decyloxyphenyliminomethyl)-phenyl 4-*n*-alkyloxybenzoates: brackets denotes monotropic phases.



Compound	*n*	Cr		SmC$_2$		SmC$_1$		SmA		I
8	8	•	64 [4.80]	—		—		(•	59) [3.52]	•
9	9	•	57.6 [52.75]	—		(•	52) [0.08]	•	60.5 [3.39]	•
10	10	•	61 [44.4]	(•	57.5 [a]	•	58) [0.18]	•	64 [4.0]	•
11	11	•	57 [61.0]	•	60.5 [0.05]	•	62.5 [0.25][b]	•	63.5 [4.3]	•
12	12	•	65 [55.2]	(•	59) [0.03]	•	66 [5.2]	—		•
16	16	•	69 [79.22]	•	71.6 [6.66]	—		—		•

[a] The DSC peaks are not well resolved for this compound in the SmC$_1$ and SmC$_2$ phases.

[b] This value is only approximate, since this peak could not be well separated from the clearing peak.

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Schlumberger SI 1260 impedance analyser and a Chelsea interface. A brass cell coated with gold (0.05 mm) was used as a capacitor; the calibration was made with cyclohexane. The electro-optical measurements were carried out using commercially available polyimide-coated ITO test cells (EHC).

4. Results

4.1. *Optical textures*

The SmA phase shows a characteristic fan-shaped texture or a homeotropic texture. On cooling the SmA phase (in the case of compound **12** on cooling the isotropic liquid) a broken fan-shaped texture or a schlieren texture appears which is typical for a SmC phase, see figures 1 (*a*) and 1 (*b*). This smectic phase is preliminarily designated as a SmC_1 phase. The transition into the low temperature phase (designated as SmC_2) is accompanied by a clear change of the optical textures. The broken fan-shaped texture is transformed into a smoother fan-shaped texture with irregular stripes across the fans. In addition the birefringence decreases, as indicated by the change of the interference colour, see figure 1 (*c*). The schlieren texture of the SmC_2 phase differs strongly from that of the SmC_1 phase, see figure 1 (*d*). In particular, near the transition the texture becomes strongly fluctuating; furthermore, the disclinations diappear and the texture becomes weakly birefringent.

4.2. *X-ray investigations*

XRD measurements were made on both non-oriented and oriented samples of all the compounds. The XRD patterns of a well oriented monodomain of compound **12** are found to remain unchanged after the transition from the high temperature SmC_1 phase into the low temperature SmC_2 phase. In both cases the patterns exhibit the characteristic features of a SmC phase (figure 2). The

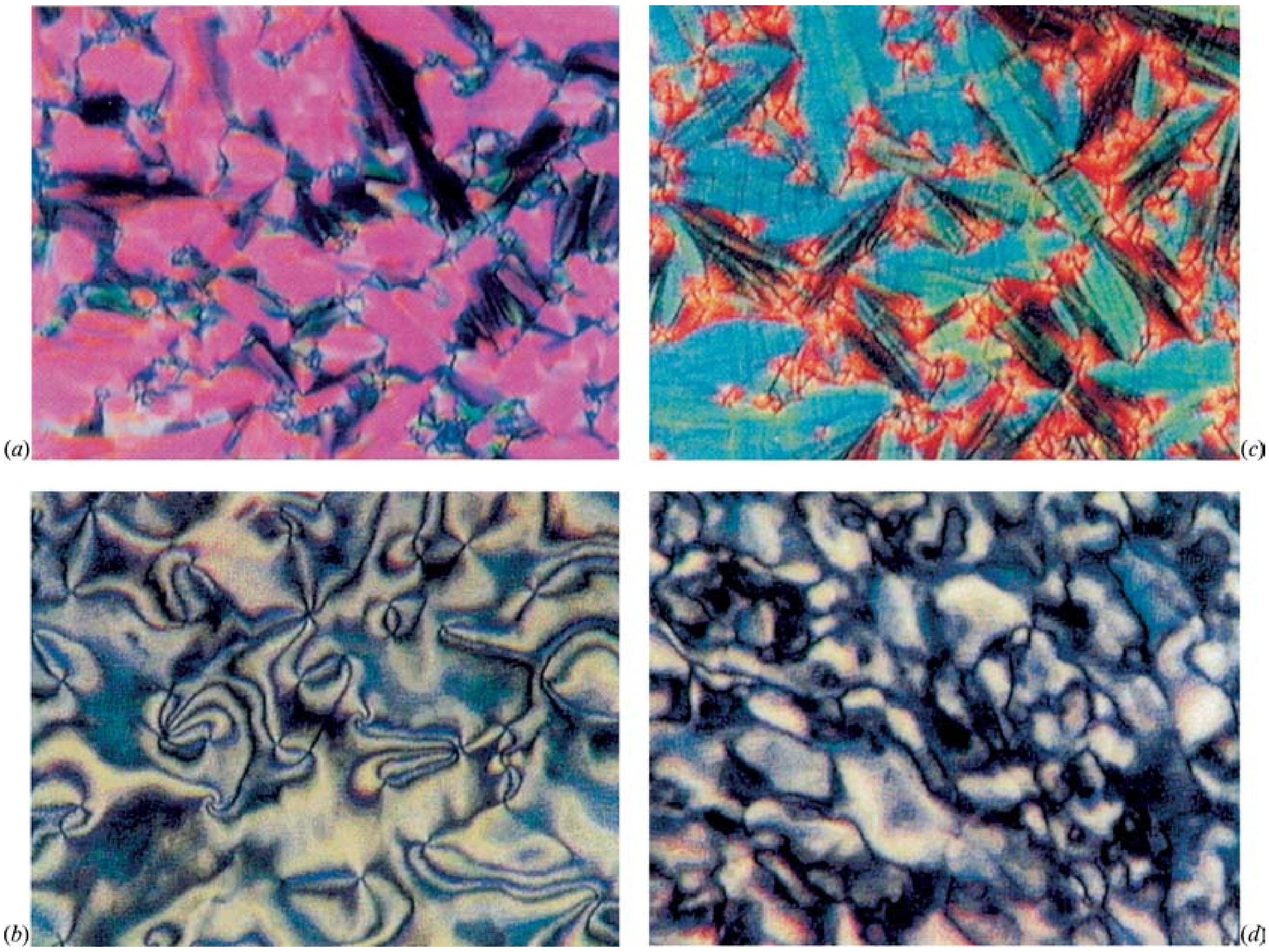

Figure 1. Textures of compound **12**: (*a*) broken fan-shaped texture of the SmC_1 phase (62°C); (*b*) schlieren texture of the SmC_1 phase (59°C); (*c*) smooth fan-shaped texture with irregular stripes across the fans in the SmC_2 phase (58°C); (*d*) schlieren texture of the SmC_2 phase (56°C).

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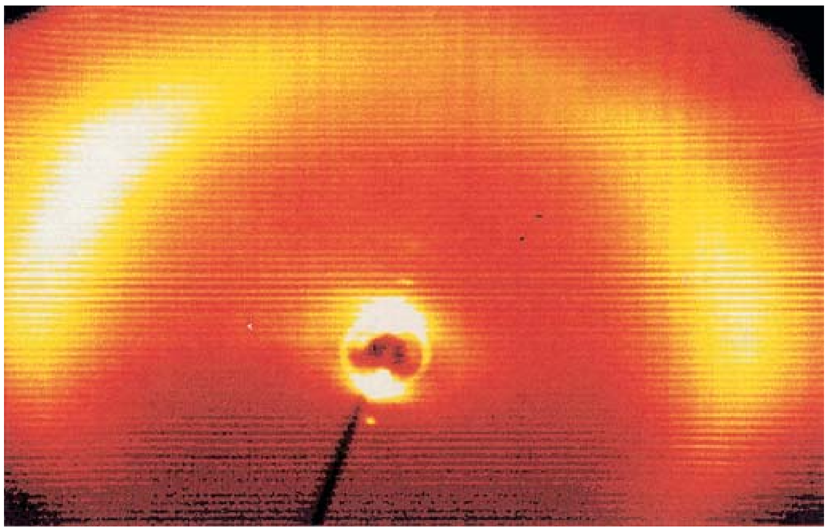

Figure 2. X-ray pattern of an oriented sample of compound **12** in the SmC_2 phase (55°C).

temperature dependence of the d-values as obtained from non-oriented samples are shown in figure 3. For compounds **10** and **11**, the d-values fall at the SmA to SmC phase transition, which is expected for a transition from an orthogonal to a tilted phase. In the SmC_1 and SmC_2 phases the d-values (3.71 nm) remain almost unchanged.

For compound **10**, the tilt angle was determined from the relation $\cos^{-1}(d_{SmC}/d_{SmA})$, where d_{SmC} and d_{SmA} are the layer spacings in the SmA and SmC_2 phases, respectively. The molecular length has been estimated using models to be around 4.0 nm for this molecule. This indicates that the effective molecular length, L_{eff}, in this case is reduced by about 4%. We have applied this reduction factor in the estimation of L_{eff} to the molecular lengths calculated using models of compounds **11** and **12**. These L_{eff} values have been used in place of d_{SmA} to calculate the tilt angles in the smectic phases of these compounds. The tilt angles θ are found to be almost constant at the $SmC_1 \rightarrow SmC_2$ phase transition and have a small temperature dependence within the SmC_2 phase of these compounds (as shown later in figure 9 together with data from NMR studies).

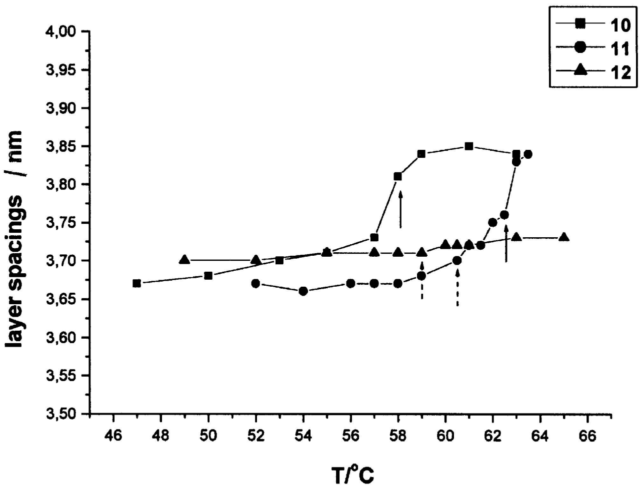

Figure 3. Temperature dependence of the layer spacing in the SmA, SmC_1 and SmC_2 phases of compounds **10**–**12**: ↑ SmA–SmC_1/SmC_2 transition; ⇡ SmC_1–SmC_2 transition. Solid lines are a guide to the eye only.

4.3. *NMR studies*

^{13}C NMR measurements were carried out to obtain a deeper insight into the conformations adopted and the ordering of the molecules in the mesophases. The proton-decoupled ^{13}C NMR spectra in the isotropic and SmC_2 phases for compound **10** are shown in figure 4. All measurements have been taken with decreasing temperature. The transition to the smectic phase is quite sharp and occurs within one degree. Similar spectra have also been obtained for compounds **11** and **12**. The assignment of the lines in the isotropic spectrum rests upon the increment system. The assignment of the lines in the smectic phases have been made by considering the dependence of the line intensity or line widths on the experimental NMR parameters. Further assistance is obtained from a comparison with the spectra of a similar compound. The line shifts are found to have an unusual temperature dependence at the transition to the SmC_2 phase as shown in figure 5 for compound **11**. For further analysis we concentrate on the aromatic part of the spectra having larger anisotropies.

The observed chemical shift δ^i_{zz} is the averaged component of the shift tensor connected with carbon i along the direction of the magnetic field. Its value depends on the orientation of the principal axis system (PAS) in the molecular frame, on the ordering matrix and on the orientation of the director frame in the magnetic field. For the interpretation of our results we use the simple

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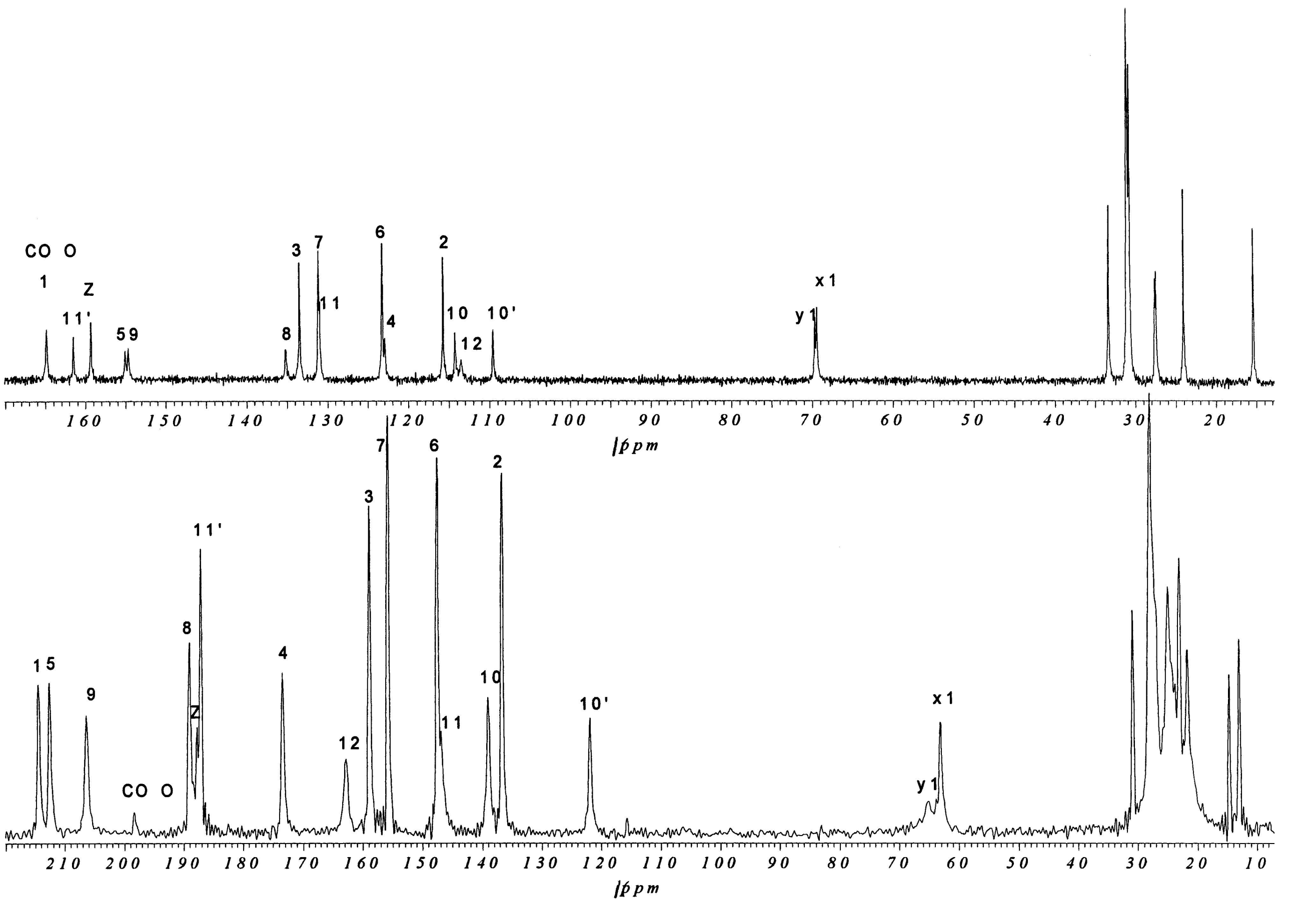

Figure 4. (*a*) Isotropic ^{13}C NMR spectrum of compound **10** at 70°C; (*b*) the ^{13}C NMR spectrum in the SmC$_2$ phase at 52°C using cross polarization and high powder decoupling.

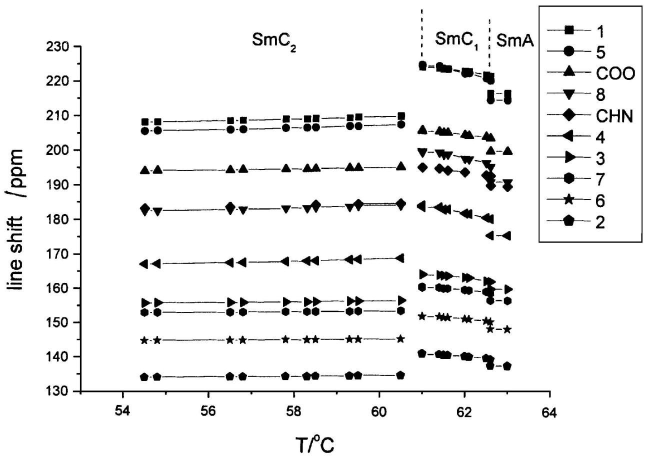

Figure 5. Temperature dependence of the line shifts in the ^{13}C NMR spectrum of compound **11**.

approximation of the separate averaging of order fluctuation described by the order matrix and conformational fluctuations. We assume a fixed orientation of the averaged molecular frame relative to the rings A and B, with the long axis nearly parallel to the *para*-axes, over the liquid crystalline state. This will be supported by the experimental results later. This molecular frame should be the PAS for the order matrix. Further, we approximate the SmC phases by an axial symmetry. The orientational order parameter *S* and biaxiality *D* are then connected with the averaged anisotropic shifts $\delta^i_{\alpha\alpha}$ ($\alpha = \xi, \eta, \zeta$) in the chosen molecular frame by [7, 8]

$$\delta^i_{zz} = \left[S\delta^i_{\zeta\zeta} + \frac{D}{3}\left(\delta^i_{\xi\xi} - \delta^i_{\eta\eta}\right)\right]\left(\frac{3}{2}\cos^2\Phi - \frac{1}{2}\right). \qquad (1)$$

The last bracket expresses the axial symmetric transformation from the director frame to the external magnetic field with an angle Φ to the director. Usually in nematic, SmA and SmC phases the director orients parallel to the field and this bracket has a value of 1.

In reality, using this procedure we determine the local order parameters of the segments under consideration, which agrees approximately with the order of the whole molecule if this part forms the stable rod-like central part of the molecule with minor changes in its shape.

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Chain conformations with higher probability have little effect on the molecular main frame orientation, and fluctuations of the chains should not drastically change over the measured temperature region. We consider the rings A, B and in principle also C, to be the stable central unit, but concede that while a small angle between the *para*-axis and the long axis exists, this is not important in the following discussion.

Justification for the proposed model can be derived from the ratio v^i of the anisotropic shift of positions i relative to C1,

$$v^i = \frac{\delta^i_{zz}}{\delta^{C1}_{zz}} = \frac{\left[S\delta^i_{\zeta\zeta} + \frac{D}{3}(\delta^i_{\xi\xi} - \delta^i_{\eta\eta})\right]}{\left[S\delta^{C1}_{\zeta\zeta} + \frac{D}{3}(\delta^{C1}_{\xi\xi} - \delta^{C1}_{\eta\eta})\right]}. \quad (2)$$

This depends on temperature through D/S and/or the geometry ($\delta_{\zeta\zeta}$). The experimental findings given in figure 6 for compound **12** reveal almost temperature-independent ratios within one phase and at most, small jumps at the transition to the SmC_2 phase. Similar behaviour has been observed for the temperature dependence of the ratios for compounds **10** and **11**. The ratios $i = 2, 3, 6, 7$ are most sensitive since their main frame tensor ($\delta_{11} \approx 38$ ppm, $\delta_{22} \approx 70$ ppm) deviates markedly from C1 ($\delta_{11} \approx 84$ ppm and $\delta_{22} \approx 20$ ppm). The constant v^i at higher temperatures with a stronger variation of S with T suggest strongly a small value of D. We expect typical D values of 0.05 which are nearly constant over the liquid crystalline phases and neglect this contribution in further calculations since its effect corresponds roughly to a renormalisation of $\delta_{\zeta\zeta}$. The almost identical values of v^i for the two phases, where δ^i_{zz} changes strongly, require that $\delta_{\zeta\zeta}$ is constant within 1% and consequently the orientation of the molecular frame varies not more than 3° relative to the *para*-axis of ring A over the whole liquid crystalline region.

This model now allows for the calculation of a S_{eff} characterizing approximately the order and orientation of the whole molecule using the relationship

$$\frac{\delta^i_{zz}}{\delta^i_{\zeta\zeta}} = S_{\text{eff}} = S\left(\frac{3}{2}\cos^2\Phi - \frac{1}{2}\right) \quad \text{for } i = 1, 4, 5, 8. \quad (3)$$

We calculate the effective order parameter from the carbon atoms in the *para*-positions 1, 4, 5 and 8. The $\delta_{\zeta\zeta}$ are taken from measured rod-like reference molecules (also after neglecting D) and fitted by their ratios (84.5, 85.75, 97.49 and 91.30 ppm for $i = 1$, 4, 5 and 8, respectively). The temperature dependence of S_{eff} is shown in figure 7. The order increases in all materials within the first phase and decreases in the last phase. For compound **10** the decrease has already begun in the first phase. The order at the clearing point is clearly higher for compound **12** and the temperature dependence is steeper for compound **11**.

We always measure the product of the two terms in equation (3), but, from the numerical values of S_{eff}, its increase at the SmA–SmC_1 transition (in compounds **10** and **11**) and the strong orientational forces in the large external field, we require that $\Phi = 0$ in the SmC_1 phase. The director orients parallel to the magnetic field and the layer normal is tilted, and we have $S_{\text{eff}} = S$.

The sudden decrease of the effective S at the transition to the low temperature SmC_2 phase reflects our opinion of a change in Φ. A decrease in S is generally not forbidden, but the temperature dependence contradicts common theoretical models. The explanation of the

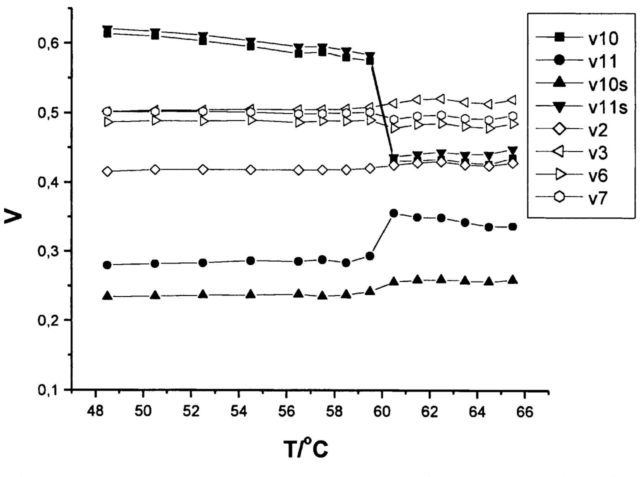

Figure 6. Temperature dependence of the v ratios for compound **12**.

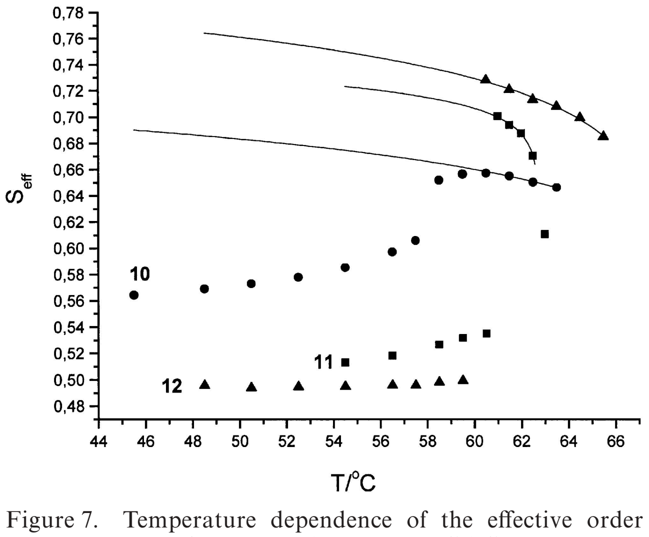

Figure 7. Temperature dependence of the effective order parameter of compounds **10**–**12**. Solid lines represent theoretical curves.

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drastic decrease of δ^i_{zz} for all the carbons i of the three aromatic rings as arising from a change in the conformation of the molecule ($\delta_{\zeta\zeta}$) can be excluded given the temperature dependence of the ratios v^i (figure 6).

The identification of Φ with an extra tilt θ in the SmC$_2$ phase is in contradiction to the observed tilt angle temperature dependence from XRD measurements, for which almost constant tilt angles at the SmC$_1 \rightarrow$ SmC$_2$ phase transition are found. Thus the only possible explanation is a change in the molecular organization. The alignment of the director parallel to the external field in the SmC$_1$ phase changes to an arrangement where the director is tilted with an angle $\theta \approx \Phi$, see figure 8. In the low temperature SmC$_2$ phase, the molecules are tilted and the layer normals are parallel to the external field.

For the calculations of Φ according to equation (3) the order parameter S must be known. We assume a continuous increase of S_{eff} in the SmC$_2$ phase as shown by the extrapolated curves in figure 7. This is a simple approximation to get approximate numerical values for the tilt angle. The error is of the same order of magnitude as the simplifications in equation (1). The evaluated tilt angles θ in the SmC$_2$ phases are shown in figure 9. They are found to be in fairly good agreement with those calculated from XRD measurements regardless of the assumptions in the NMR model and in the molecular lengths. The proposed change in the director orientation appears to us as the only explanation of the experimental findings, and is strongly supported by the agreement of the tilt angles within the homologues series.

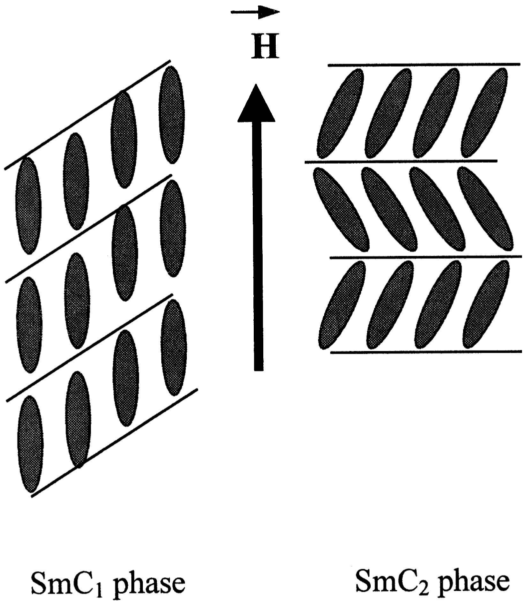

Figure 8. Sketch of the molecular alignment with respect to the magnetic field in the NMR experiment in the SmC$_1$ and SmC$_2$ phases.

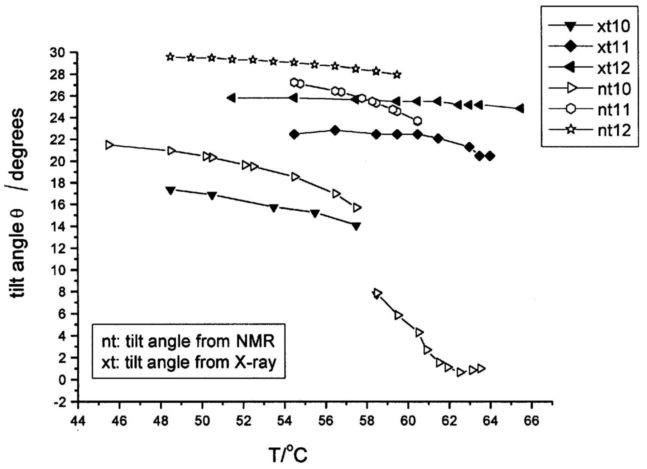

Figure 9. Temperature dependence of the tilt angle θ in the SmC$_2$ phase (from NMR) and in the SmC$_1$ and SmC$_2$ phase (from XRD) of compounds **10**–**12**.

Ring C was excluded from the preceding discussion. The numerical values of v^i for $i = 10, 10\mathrm{s}, 11, 11\mathrm{s}$ agree with those of $i = 2, 3, 6, 7$, in the SmC$_1$ phase but they show a remarkable temperature dependence in the SmC$_2$ phase (figure 6). The $\delta^i_{\zeta\zeta}$ changes with temperature at a fixed orientation of the molecular system. An increase in v^i is observed for diagonal carbons $i = 10, 11\mathrm{s}$ and a decrease for $i = 10\mathrm{s}, 11$. This is explained by the absence of fast 180° flips averaging the tensors for the rings A and B. The different temperature dependence requires a small tilt between the *para*-axis and the molecular long axis. From the behaviour of the rings A and B we have derived almost constant tilt angles. The bond to ring C via the –C(H)=N– segment allows no change in the angle between the essentially parallel *para*-axes of rings B and C. There remains only a change in the torsion angle of the plane of ring C relative to that of ring A (which defines the molecular frame) for the interpretation of the temperature dependence of the ratios.

For a more detailed consideration we use the connection between the tensor components in the molecular frame (ξ, η, ζ) and the *para*-axis frame (δ^{p}_{11} parallel to the *para*-axis, δ^{p}_{22} perpendicular) according to:

$$\delta_{\zeta\zeta} = \langle \delta^{\mathrm{p}}_{11} - (\delta^{\mathrm{p}}_{11} - \delta^{\mathrm{p}}_{22}) \sin^2 \varepsilon - (\delta^{\mathrm{p}}_{11} + 2\delta^{\mathrm{p}}_{22}) \sin^2 \varepsilon \sin^2 \varphi + \delta^{\mathrm{p}}_{12} \cos \varphi \sin 2\varepsilon \rangle. \tag{4}$$

Here ε is the tilt angle between the *para*-axis (corresponds to the direction of δ^{p}_{11}) and the molecular axis ζ and φ describes the rotation of the ring plane against the $\zeta\xi$-plane. δ^{p}_{12} is the non-diagonal element in the case of the non-flipping aromatric ring. Diagonal positions in ring C form identical angles ε with the long axis, positive for $i = 10, 11\mathrm{s}$ and negative for the other two. This explains the observed tendency at low temperatures if φ is small. The two groups approach each other in the tensor values if φ goes to 90° (of course $\pm\varphi$ give identical values). This behaviour is observed at high temperatures. Although we do not have precise knowledge of the PAS tensor components of the four carbons considered (positions 10, 10s, 11 and 11s), nonetheless from the temperature dependence of the ratios it doubtlessly follows that there is a discontinuous change in the torsion angle of ring C at the $\mathrm{SmC_1} \rightarrow \mathrm{SmC_2}$ transition and a further decrease of the torsion angle within the $\mathrm{SmC_2}$ phase. Like the tilt angle, the amount of change increases from compound **10** to compound **12**.

More quantitative values are in principal available from the six observed shifts from ring C, but this requires knowledge of the six PAS tensors. For approximate values we assume typical components obtained from the comparison of this ring with the *para*-substituted ring A of bent molecules [9]. With $\varepsilon = 8°$ to $10°$ we obtain for φ a decrease of 60° to 80°, that means from perhaps 80° at high temperatures to about 0°–20° at low temperatures. The calculated values of the tensor components are given in table 2 together with the experimentally determined $\delta_{\zeta\zeta}$ values at the highest and lowest temperatures.

A variable torsion angle of the ring-plane in benzilidenaniline was found in different investigations [10]. The conformational change is also reflected in the observed shifts of the first methylene group after the oxygen ($\mathrm{O{-}CH_2}$). The anisotropies can be resolved and they behave quite differently. Assuming an identical PAS tensor, this must be caused entirely by a different geometry with respect to the molecular frame. Figure 10 shows the usual increase of $\delta_{\zeta\zeta}$ for the first segment of the left chain (y1) for all the three compounds **10**, **11** and **12** with decreasing temperature due to growing probability of the all-*trans*-conformation. The $\delta_{\zeta\zeta}$ of the first segment of the right chain (x1) bonded to ring C decreases at the $\mathrm{SmC_1} \rightarrow \mathrm{SmC_2}$ transition at lower temperatures.

Table 2. Comparison of the calculated and experimental $\delta_{\zeta\zeta}$ values for the carbons in ring C. The two values in the last three columns are taken at the highest and lowest temperatures.

Carbon atom	δ_{11}/δ_{22} assumed	$\delta_{\zeta\zeta}$ calc	$\delta_{\zeta\zeta}$ exp 10	11	12
C9	88/15		86.1 88.8	86.0 89.86	85.59 91.11
C10	90/24	37 49	37.05 44.25	36.75 47.23	35.96 51.07
C10s	75/10	21.6 19.1	21.59 19.94	21.73 20.25	21.58 19.68
C11	87/16	29.5 26	29.45 25.44	29.43 24.80	29.66 23.65
C11s	92/25	38.3 50.4	38.28 45.72	38.01 48.86	37.24 52.76
C12	94/25		83.15 84.72	83.14 85.74	82.62 86.02

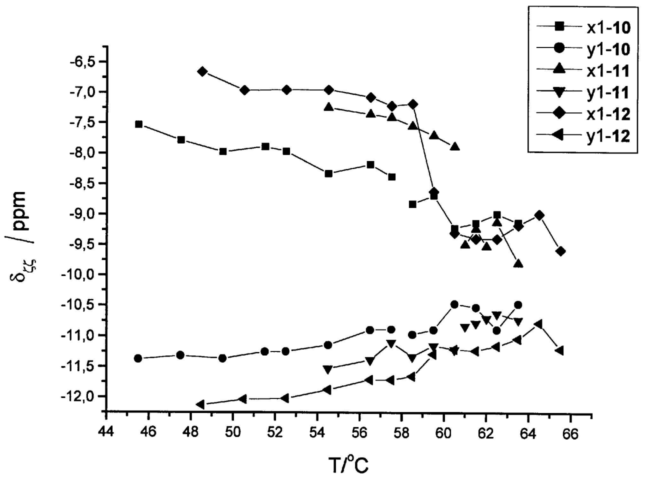

Figure 10. Temperature dependence of $\delta_{\zeta\zeta}$ from the first segment of the right (x) and left (y) chains of compounds **10**–**12**.

There exists a strong correlation between the rearrangement of the director and the change of conformation. At high temperatures in the SmA or $\mathrm{SmC_1}$ phase the plane of ring C is oriented more or less perpendicular to the other ring planes and this also involves the first segments of the chain. The molecular shape is then more rod-like. At low temperatures in the $\mathrm{SmC_2}$ phase the planes of the three rings are nearly parallel, forming a planar molecule including the first elements of the chain at ring C.

4.4. *Electro-optical and dielectric investigations*

Applying an electric field above a threshold of about 1.7 V μm^{-1}, the interference colour of the fan-shaped texture of the $\mathrm{SmC_1}$ phase is changed (figure 11). In the $\mathrm{SmC_2}$ phase the threshold increases (~2.5 V μm^{-1}) but the optical picture is quite different compared with the $\mathrm{SmC_1}$ phase. As seen in figure 12, above the threshold not only is the colour of the fans changed but also the stripes disappear. In both SmC phases, the textures of the switched states are independent of the polarity of the applied field. Current response measurements provide no evidence for a polar (ferroelectric or antiferroelectric) structure for the $\mathrm{SmC_1}$ or $\mathrm{SmC_2}$ phases. Therefore, it can be assumed that the field-induced switching corresponds to a Fréedericksz transition [11] driven by the dielectric anisotropy.

In the dielectric spectrum of the smectic phases of compound **12** one absorption maximum in the MHz region was observed which is due to the reorientation about the short molecular axis. The relaxation time τ_1 corresponding to this reorientation is shown in figure 13 for the $\mathrm{SmC_1}$ and $\mathrm{SmC_2}$ phases of compound **12**. τ_1 is of

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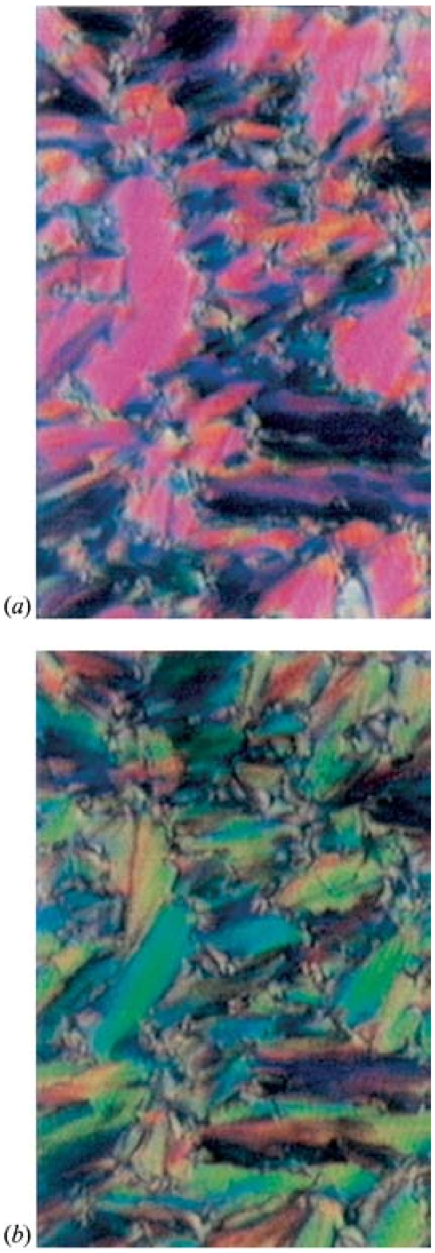

Figure 11. Broken fan-shaped texture of the SmC_1 phase of compound **12** (63°C, sample thickness 6 μm): (*a*) 0 V; (*b*) ±20 V.

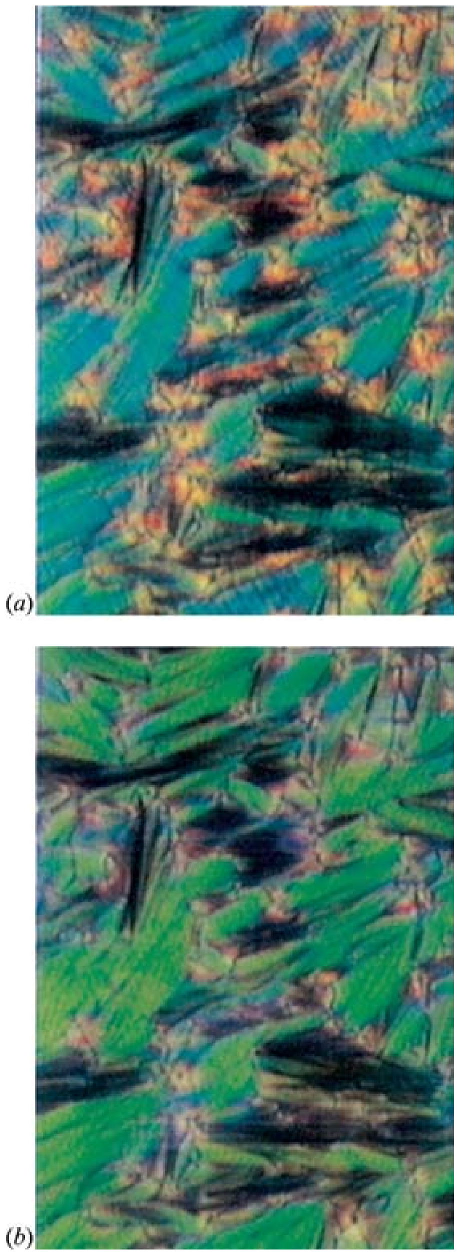

Figure 12. Fan-shaped texture of the SmC_2 phase of compound **12** (55°C, sample thickness 6 μm): (*a*) 0 V; (*b*) ±50 V.

the same order of magnitude as for calamitic three-ring compounds. This is also true for the jump in τ_1 observed at the transition from the isotropic to the SmC_1 phase. The magnitude of the static dielectric constant does not support the presence of ferroelectric short range order, as observed for example for the B_2 phase [12]. However, a quite unexpected result is the increase of the molecular mobility (decrease of τ) by a factor of two at the transition into the low temperature SmC_2 phase. This finding supports a change in the packing resulting from conformational changes.

5. Summary

The homologous hockey stick-shaped compounds described in this paper form three smectic phases, a SmA phase and two distinct SmC phases (SmC_1 and SmC_2). The occurrence of these two SmC phases is the most interesting and surprising result of these experimental studies. X-ray patterns of oriented samples show no significant differences between the SmC_1 and SmC_2 phases; the layer spacings and the tilt angles are nearly identical. On the other hand, the transition between the SmC_1 and SmC_2 phases is revealed by a small calorimetric signal

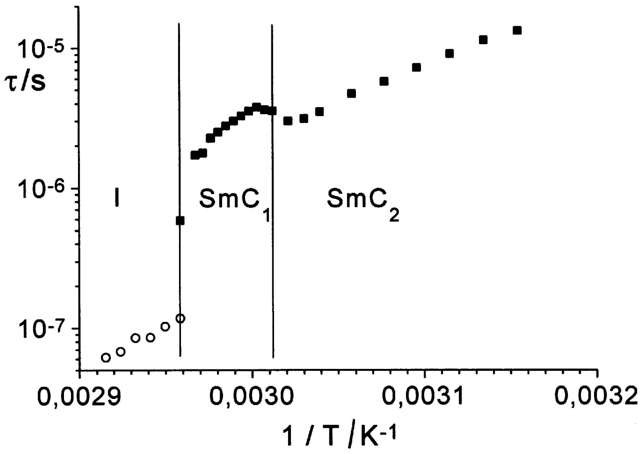

Figure 13. Relaxation times τ of compound **12** for the reorientation about the short molecular axes.

and by a pronounced change in the optical textures. Also the electro-optical behaviour of the two smectic C phases is quite different, but there was no evidence to support a polar structure as suggested by Stannarius *et al.* [13] for the compound **12** on the basis of electro-optical investigations on free-standing films. The polar switching in the bulk phase of 2,3,4-trifluorophenyl biphenylcarboxylates [3], which has a similar molecular structure, could be related to the presence of the fluoro-substituents in these compounds. Furthermore, it is remarkable for the substances under study that according to dielectric measurements the relaxation time of the rotation of the molecules about the short axis decreases by a factor of 2 at the transition from the SmC_1 to the SmC_2 phase.

Detailed NMR measurements give information about the structural changes which take place at the phase transition $SmC_1 \rightarrow SmC_2$. At the transition to the SmC_2 phase, the director becomes tilted with respect to the torque of the magnetic field which must be driven by strong interactions giving rise to a helical superstructure or, more probably, to an alternating tilt. The resulting anticlinic structure of the SmC_2 phase (see figure 8) is compatible with the smooth SmA-like texture and the results obtained for free-standing films [13]. The X-ray pattern obtained using conventional techniques cannot differentiate between the two structures. The pattern of a rotationally disordered synclinic packing is the same as that of an anticlinic packing. As found by NMR

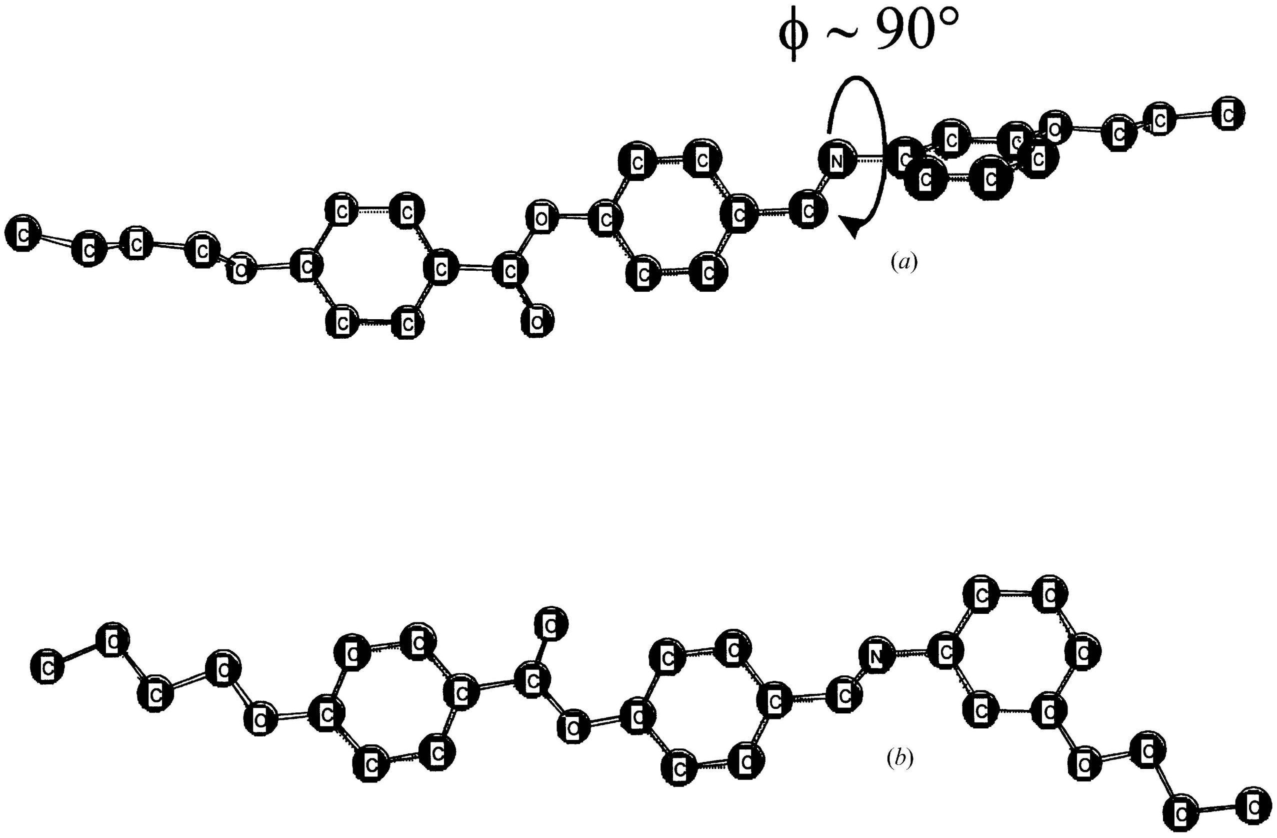

Figure 14. Model of the molecular conformation in the SmC_1 and SmC_2 phases. (*a*) The plane of the ring C is nearly perpendicular with respect to the plane of the rings A and B in the SmC_1 phase corresponding to a torsion angle $\varphi \sim 90°$; (*b*) the plane of ring C rotates to a more parallel position ($\varphi = 0°$) in the low temperature SmC_2 phase.

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measurements, the structural changes at the transition SmC_1–SmC_2 are obviously a result of the change of the conformation of the molecules. Whereas in the high temperature SmC_1 phase the molecules can be regarded as relatively extended, the molecules in the low temperature SmC_2 phase adopt a bent shape in the form of a hockey stick (see figure 14) which favours anticlinic packing. It should be noted that in a chiral bimesogenic liquid crystal containing a siloxane moiety as the central part, a transition from a synclinic high temperature phase (SmC*) into an anticlinic low temperature phase (SmC_A^*) was reported [14]. In this case the phase transition is also the result of a conformational change of the molecules from an elongated into a bent shape which favours an anticlinic packing. Therefore conformational changes are obviously responsible for the different packing of the molecules in the two SmC phases.

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