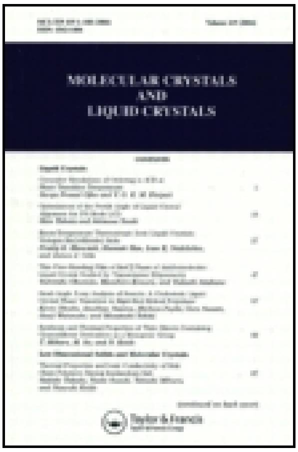

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Structural Investigations of a Non Calamitic Shaped Liquid Crystalline Compound Showing Unusual Phases

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Structural Investigations of a Non Calamitic Shaped Liquid Crystalline Compound Showing Unusual Phases

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X-ray diffraction, birefringence, density and static dielectric permittivity measurements were performed on a calamitic hockey stick shaped mesogen. In addition to SmA phase, this compound exhibits two tilted mesophases – the SmC, synclinic and the SmC$_a$, anticlinic phase. From x-ray diffraction and birefringence data, the orientational order parameters have been determined. The order parameters values drop at the SmC – SmC$_a$ phase boundary. Possible cause for the drop in the order parameter values has been discussed. Interestingly, it has been found that the dielectric anisotropy of this compound changes from positive to negative values in the SmCa phase.

Keywords Dielectric anisotropy; hockey shaped molecule; optical birefringence; orientational order parameter; x-ray diffraction

1. Introduction

Achiral hockey stick shaped compounds are of considerable interest due to the occurrence of titled smectic liquid crystalline phases showing synclinic smectic C (SmC) as well as anticlinic smectic C (SmC$_a$) phases. In our earlier publications [1,2] we have reported the synthesis and detailed structural and conformational investigations from x-ray diffraction and NMR measurements of a hockey stick shaped compound, 4-(3-n-decycloxy phenylimino-methyl) phenyl 4-n-decycloxy-benzoate, comprising of *meta*-alkyloxy substituted three-ring core. In this paper, we report the x-ray diffraction, optical birefringence and static dielectric permittivity measurement of a related hockey stick shaped compound, 4-(3-decyloxyphenyliminomethyl)phenyl 4-decyloxycinnamate (Fig. 1) possessing SmA, SmC (synclinic)

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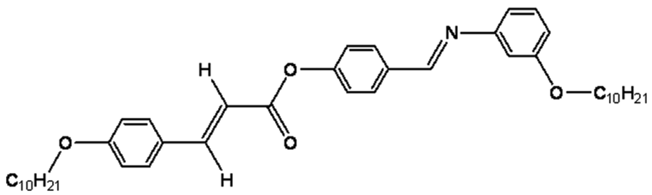


Figure 1. Chemical structure of 4-(3-decyloxyphenyliminomethyl) phenyl 4-decyloxycinnamate.

and SmC_a (anticlinic) phases [3]. Optical transmission (OT) method was used for the identification of the different liquid crystalline phases. The transmitted intensity of a homogeneously aligned sample filled cell was used for the determination of the temperature dependence of birefringence and hence the orientational order parameter. The x-ray diffraction intensities along the outer equatorial arc was analyzed to determine the orientational distribution function and hence the orientational order parameters (OOP's) $\langle P_2 \rangle$ and $\langle P_4 \rangle$, as a function of temperature. Additionally, the dielectric permittivities parallel and perpendicular to the molecular long axis has also been measured.

2. Experimental

2.1. *X-Ray Diffraction Measurements*

X-ray diffraction measurements were done on oriented samples obtained by slow cooling of a drop of the liquid crystal placed on a glass plate. The temperature of the sample was regulated by a temperature controlled heating stage. The x-ray patterns were recorded on a 2-D area detector (HI – Star, Siemens AG) using Ni-filtered Cu K_α radiation. The angular distribution of the x-ray intensity along the outer arc of the diffraction pattern was used to determine the orientational order parameter after necessary background correction. The x-ray diffraction intensity data were analyzed to evaluate order parameters following a procedure described by Bhattacharya and Paul [4]. X-ray diffraction patterns of magnetically aligned samples (magnetic field of about 0.6 T) in the smectic A phase were also recorded on an x-ray film using Ni-filtered Cu Kα radiation of wavelength $\lambda = 1.542$ Å.

2.2. *Optical Birefringence Measurements*

2.2.1. *Thin Prism Method.* Refractive indices (n_o, n_e) for wavelength $\lambda = 632.8$ nm were measured within ±0.0004 by thin prism method. A hollow prism (refracting angle $<2^o$) was constructed by placing the rubbed surfaces inside, with the rubbing direction parallel to the refracting edge of the prism. A light beam from a He-Ne laser in passing through the aligned sample held inside the prism was split into ordinary and extraordinary beams and two spots were thus obtained on a screen. The images of the spots were recorded using a digital camera suitably interfaced with a computer. The high resolution digital images so obtained were further processed to locate the centre of the spots from where the ordinary (n_o) and extraordinary (n_e) refractive indices could be determined [5].

2.2.2. *Optical Transmission Method.* A laser (He-Ne $\lambda = 632.8\,\mathrm{nm}$) beam was directed onto a homogeneously aligned ITO coated LC cell of thickness 8.9 μm (purchased from AWAT PPW, Warsaw, Poland) placed between two crossed linear polarizer. The temperature of the cell was regulated and measured with a temperature controller (Eurotherm PID 2216e) with an accuracy of ±0.1°C by placing the cell in a brass thermostat with glass windows. The birefringence, $\Delta n = n_e - n_o$, where n_e and n_o are the extraordinary and ordinary refractive indices of the liquid crystal medium respectively, was determined by a procedure reported in our earlier publication [6]. This method was previously used to determine birefringence for nematic and SmA phases [6] and is assumed to be valid in SmC phase as well. This method is also used for birefringence measurement of chiral SmA* and SmC* phases [7].

2.3. *Density Measurement*

The density was measured by dilatometric technique with an accuracy of 0.1% and temperature accuracy of ±0.1°C.

2.4. *Dielectric Permittivity Measurements*

The static dielectic permittivities $\varepsilon_{\|}$ and $\varepsilon_{\perp}$ along and perpendicular to the molecular long axis respectively, and hence the dielectric anisotropy $\Delta\varepsilon$ $(=\varepsilon_{\|} - \varepsilon_{\perp})$ were measured at 1 kHz by measuring the capacitance of a liquid crystal cell (thickness 8.9 μm) using a digital LCR-bridge (GW INSTEC LCR 821). The details of the experimental procedure for determining the dielectric permittivities have been reported by us earlier [2,8]. In our measurements the effect of ion conductivity, if present, have been ignored.

3. Results and Discussion

The temperature dependence of the principal refractive indices n_o and n_e in the SmA and SmC phases and the refractive index in the isotropic phase (n_{iso}) at a wavelength of $\lambda = 632.8\,\mathrm{nm}$ were measured (Fig. 2). It has been found that both n_o and n_e changes smoothly at the SmA – SmC transition. However, we were unable to measure the refractive indices in SmC_a phase. Also shown in Figure 2 is the temperature variation of the density of this compound. While the density change is smooth across the SmA-SmC phase boundary, the density changes at the SmA–I as well as SmC – SmC_a phase transition appears to be discontinuous.

The refractive indices (n_o, n_e) and the density data has been utilized to calculate the principal molecular polarizabilities (α_o, α_e) using Vuks method [9]. The orientational order parameter $\langle P_2 \rangle$ can then be evaluated from the relation

$$\langle P_2 \rangle = \frac{\alpha_e - \alpha_o}{\alpha_{\|} - \alpha_{\perp}} = \frac{\Delta\alpha}{\Delta\alpha_0} \tag{1}$$

where α_o and α_e are the effective polarizabilities for the ordinary and extraordinary rays respectively and $\alpha_{\|}$ and $\alpha_{\perp}$ are the polarizabilities parallel and perpendicular to the long axis of the molecule in the solid state. The polarizability anisotropies in the

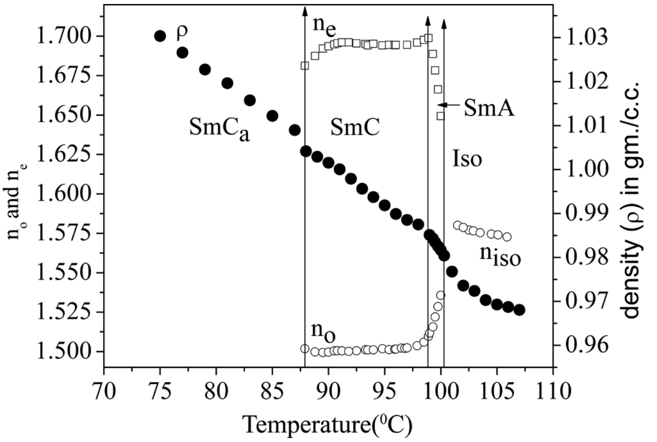


Figure 2. Temperature dependence of the refractive indices n_o and n_e and density values.

perfectly ordered state ($\Delta\alpha_0$) were determined from the well known Haller's [10] extrapolation method.

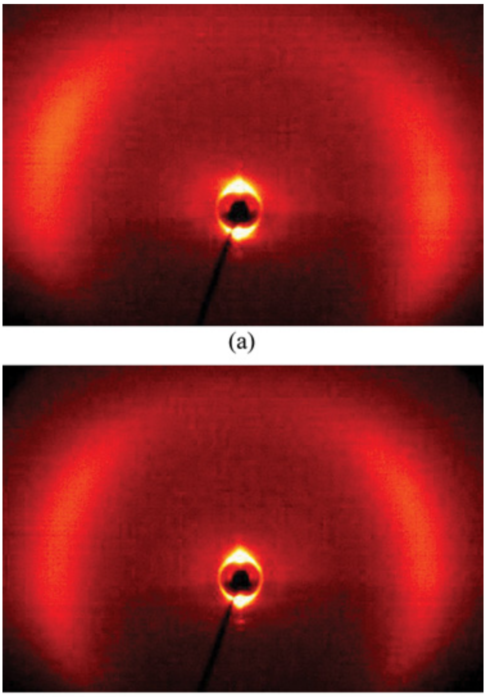
Optical transmission method was also used for identification of the phase transition temperatures of this compound. By studying the transmitted intensity for planar and homeotropic aligned (HT) cells, the phase transition temperatures could easily be identified in both the cases. From the temperature variation of the intensity curve of planar arrangement the existence of three different mesophases were confirmed. Again, from the transmitted intensity data of the HT cells, it was concluded that the two lower temperature mesophases are non-orthogonal in nature i.e., they are tilted as reported in [3].

The optical birefringence data, Δn, obtained from the measured transmitted intensity data of the homogeneously aligned cell [6] of thickness 8.9 μm was utilized to determine the temperature variation of the orientational order parameter in the liquid crystalline phases of this compound. The order parameter is defined as $<P_2> = \Delta n/\Delta n_0$, where Δn_0 is the birefringence in the completely ordered state and was obtained from the temperature dependence of Δn, which can be approximated well for liquid crystals by

$$\Delta n = \Delta n_0 \left(1 - \frac{T}{T_1}\right)^{\beta} \tag{2}$$

where Δn_0, T_1 and β are adjustable parameters ($\Delta n_0 = 0.176$, $T_1 = 336.5\,K$ and $\beta = 0.05$). It may be mentioned here that, for the estimation of Δn_0 the birefringence data was fitted only in the SmA phase.

As already reported in [3], the x-ray diffraction pattern in the SmA phase shows a typical diffuse scattering in the wide angle region, accompanied by sharp reflections in the small angle region indicating the presence of well defined layer structure. In the SmC phase, the two maxima of the outer diffuse scattering rotate out of the equator indicating synclinic arrangement of the molecule (Fig. 3(a)). In the low temperature SmC_a phase the outer diffuse scattering exhibits broader halos centered about the equator (Fig. 3(b)). Analysis of the outer diffuse scattering indicates that



(a)

(b)

Figure 3. X-ray diffraction pattern in (a) SmC phase (93°C) (b) and $\mathrm{SmC_a}$ (70°C) phase. (Figure appears in color online.)

outer halo consists of superposition of two diffraction peaks. This would be in agreement with an anticlinic structure of the lower temperature phase although it is no direct proof. The orientational distribution function $f(\theta)$ and hence the orientational order parameter $\langle P_2\rangle$ and $\langle P_4\rangle$ for this compound has been determined from x-ray intensity data using the method described previously [4]. It is to be noted that to determine the order parameters from x-ray diffraction photographs the x-ray intensity $I\ (\psi)$ vs. azimuthal angle (ψ) curve of the outer diffraction arc for $\psi = 0$ to $\psi = 360^\circ$ was first obtained. The measured intensity distribution $I(\psi)$ was then utilized to determine the orientational distribution function $f(\beta)$ and the order parameters $\langle P_2\rangle$ and $\langle P_4\rangle$. The peak intensity position which corresponds to $\psi = 0$ was determined from the χ – scan. From the values of $I(\psi)$, the distribution function $f(\beta)$, and the order parameters ($\langle P_2\rangle$ and $\langle P_4\rangle$) was calculated following Leadbetter's expression [11]. It may be mentioned here that, for determining the experimental $f(\beta)$ values and hence the order parameters, the azimuthal distribution of the x-ray intensities $I(\psi)$ in one quadrant (from $\psi = 0$ to $\psi = 90^\circ$) is sufficient. However, in case of x-ray patterns on photographic film, the experimental intensity values over the four quadrants are generally measured and the average values of $I(\psi)$ is used to calculate $f(\beta)$. In the present case, due to the shadowing of the picture we concentrate mainly on the non shadowing portion of the diffraction pattern and therefore determine the average values of $I(\psi)$ to calculate $f(\beta)$ and hence $\langle P_2\rangle$ and $\langle P_4\rangle$, from two quadrants only. The temperature variation of $\langle P_2\rangle$ and $\langle P_4\rangle$ from x-ray diffraction measurements from 2D detector are shown in Figure 4. In order to verify our results, we have

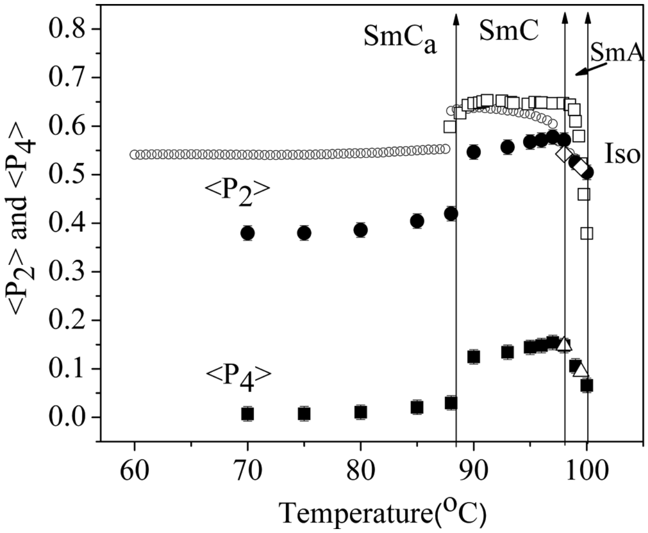


Figure 4. Temperature dependence of the orientational order parameter ⟨P$_2$⟩ from o birefringence measurement (Optical transmission); □ refractive index measurement (thin prism); ● x-ray diffraction measurement (2D detector); ◇ x-ray diffraction measurement (photographic film); ■ ⟨P$_4$⟩ from x-ray diffraction measurement (2D detector); Δ ⟨P$_4$⟩ from x-ray diffraction measurement (photographic film).

also recorded the x-ray diffraction patterns of magnetically aligned sample in the SmA phase on a photographic film and the order parameters obtained from such measurements are shown in the same Figure. The agreement between the two sets of x-ray data seems to be quite good.

The ⟨P$_2$⟩ values obtained from birefringence measurements by thin prism and optical transmission method are also shown in Figure 4. As expected, the ⟨P$_2$⟩ values obtained from both the birefringence and x-ray diffraction measurements increases with decrease in temperature in the SmA phase. The OOP values from x-ray diffraction measurements as well as birefringence measurement by thin prism technique are more or less constant and decreases slightly with decrease in temperature in the SmC phase. On the other hand ⟨P$_2$⟩ values obtained from optical transmission measurement increases with decrease in temperature throughout the SmC mesophase. This is due to the fact that it was possible to obtain a perfectly aligned monodomain in the very thin geometry of the OT measurement in comparison to the thin prism technique. The SmC to SmC$_a$ phase transition is marked by a pronounced drop in the order parameter values as obtained from both the x-ray and birefringence measurements. The re-orientation of the molecules from synclinic arrangement in the SmC phase to anticlinic arrangement in the SmC$_a$ phase causes a broadening of the x-ray distribution function thereby reducing the OOP's. Such a drop in the order parameter values of hockey stick compounds have also been reported by us earlier in other compounds [1,2].

It is also observed from Figure 4 that the order parameters obtained from optical birefringence measurement are larger than those from x-ray diffraction by about 15% in SmC phase and 25% in SmC$_a$ phases. This is due to the fact that birefringence measurements were made on the rigid 3-ring core of the molecule,

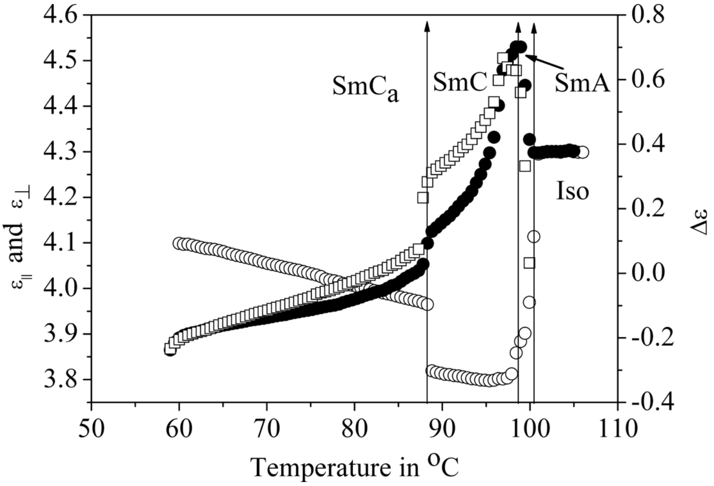


Figure 5. Variation of electric permittivities $\varepsilon_{||}$, $\varepsilon_{\perp}$ and dielectric anisotropy ($\Delta\varepsilon$) as a function of temperature. Key to symbols: ■, $\varepsilon_{||}$; o $\varepsilon_{\perp}$; □ $\Delta\varepsilon$.

whereas the x-ray diffraction pattern is obtained essentially from whole of the molecule including the chain parts, which causes lowering of the order parameter. As observed by us from our previous NMR measurements on a similar hockey stick shaped compound [1,2], it is likely that, in the anticlinic SmC$_a$ phase, the plane of the meta substituted third benzene ring of this compound, rotate to a more parallel position, giving rise to a bent hockey shape, which reduces the orientational order parameter further.

The temperature dependence of the dielectric permittivities $\varepsilon_{||}$ and $\varepsilon_{\perp}$ and dielectric anisotropy ($\Delta\varepsilon = \varepsilon_{||} - \varepsilon_{\perp}$) is shown in Figure 5. From the Figure it is evident that the dielectric anisotropy increases with decrease of temperature in the SmA phase, as expected. In the SmC phase, the $\Delta\varepsilon$ values show a reverse trend. The $\Delta\varepsilon$ values drops abruptly again in SmC – SmC$_a$ phase transition. This drop further continues within the SmC$_a$ phase and goes over to negative values ($\varepsilon_{||} < \varepsilon_{\perp}$) with further decrease in temperature. The bent hockey stick shape in the SmC$_a$ phase becomes clearly dominant with decrease in temperature and thereby affecting a cross-over from positive dielectric anisotropy to negative dielectric anisotropy.

4. Conclusions

Orientational order parameter values in the SmA, SmC and SmC$_a$ phases of a hockey stick shaped compound have been determined from x-ray diffraction studies and compared with those obtained from birefringence measurements. OOP's determined from birefringence measurement are larger than those from x-ray diffraction because birefringence measurements are made on the rigid 3-ring core of the molecule in comparison to x-ray diffraction pattern which is obtained essentially from the electron density distribution of the whole molecule including the chain parts. This along with the non-perfect alignment of the layers within the sample reduces the order parameters calculated from X-ray diffraction measurements. From earlier investigations on similar hockey stick shaped compounds it has been found that the molecular shape assumes a rod like form in the high temperature SmC phase giving rise to a synclininc arrangement and changes to a hockey stick shape in the low temperature SmC_a phase therefore favouring. an anticlinic arrangement of the molecules. This reorientation of the molecules affects a drop in the OOP values at the SmC – SmC_a phase transition. The molecular shape in the SmC_a phase in the form of a bent hockey stick shape perhaps promotes a changeover of the dielectric anisotropy of this compound from positive to negative values.

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