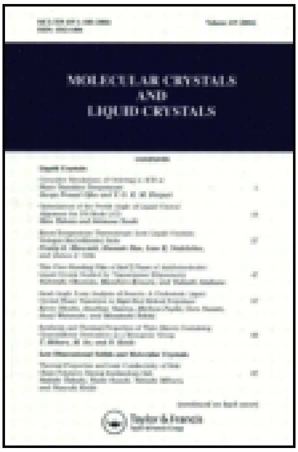

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Physical Properties of Three Liquid Crystals with Negative Dielectric Anisotropy from X-Ray Diffraction and Optical Birefringence Measurements

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Physical Properties of Three Liquid Crystals with Negative Dielectric Anisotropy from X-Ray Diffraction and Optical Birefringence Measurements

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In this work, we report the results of x-ray diffraction, density and birefringence measurements on three fluorinated liquid crystalline compounds having negative dielectric anisotropy. Small angle x-ray diffraction data from aligned samples have been analyzed to determine the orientational order parameter as a function of temperature. The order parameter values were also determined from birefringence measurements and the results were compared with mean field theory. Structural parameters like intermolecular distance and layer thickness (in smectic B phase), apparent molecular length (in nematic phase) have been determined and the order of the phase transition in these compounds has been discussed.

Keywords Birefringence; fluorinated liquid crystals; negative dielectric anisotropy; orientational order parameter; x-ray diffraction

1. Introduction

The order parameter in nematic liquid crystals is one of the most important physical parameters which critically affect its performance in display devices, since, the anisotropies of the dielectric, optical and magnetic properties depend on the order parameter in a more or less straight forward way [1–2]. With this view in mind, we have determined the orientational order parameters of three laterally fluorinated liquid crystalline molecules from x-ray diffraction and optical birefringence measurements. The interesting feature of these molecules is the presence of laterally fluorinated (polar) substituents, which induces a dipole moment perpendicular to the long axes of the molecule, thereby resulting in molecules with negative dielectric anisotropy. The study of the physical properties of these negative dielectric anisotropy materials is becoming increasingly important after the successful development of the Vertical Alignment (VA) technology [3] for active matrix addressed liquid crystal displays.

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Fluorinated nematogens are also promising material from display point of view due to their broad nematic mesophase ranges, low rotational viscosity and high dielectric anisotropy [4]. Moreover, the study of the birefringence, Δn, of these materials is again important so that they may be adjusted to fit the precise display configuration [5].

In this work, three laterally fluorinated compounds, **1-3,** were investigated by x-ray diffraction and refractive index measurements. Of these, two of them have a phenyl bicyclohexane core (compounds **1** and **2**) and the third compound is a terphenyl derivative (compound **3**). Detailed x-ray diffraction measurements were done throughout the mesomorphic range of these three compounds. The orientational order parameters (OOP's), $<P_2>$ and $<P_4>$, apparent molecular length, layer spacing and intermolecular distance were determined as a function of temperature. $<P_2>$ values have also been determined from refractive index measurements using thin prism technique [6]. The ordinary and extraordinary refractive indices as well as the density data have been used to determine the orientational order parameter ($<P_2>$) using the standard Vuks isotropic model [7]. The $<P_2>$ values determined from the refractive index data have been compared with those measured from x-ray diffraction studies. These values have also been compared with the theoretical values of Maier-Saupe [8] for the compound having only nematic phase and McMillan's theory [9] for compounds having both smectic and nematic phases.

2. Experimental

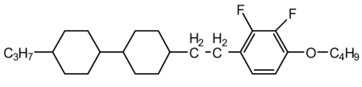
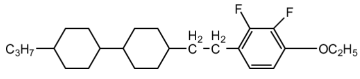
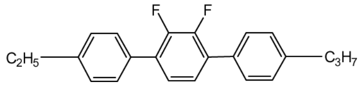
2.1. *Materials*

The compounds were procured from AWAT Co. Ltd., Warsaw, Poland and were used without further purification. The chemical structure and transition temperatures of the compounds are shown in Table 1.

2.2. *Texture Studies*

The transition temperatures and textures were observed using polarizing microscope (Motic BA300) equipped with Mettler Toledo FP900 Hot Stage. Typical thread-like textures characteristic of the nematic phase were observed upon heating for all the compounds. Upon cooling, **1** and **2** exhibited monotropic Smectic B phase with

Table 1. Chemical structure, transition temperatures of compounds **1-3**

Compound no.	Structure	T_m (°C)	$T_{SmB\text{-}N}$ (°C)	T_{NI} (°C)
1		112	(110)	152
2		111	(109)	162
3		73	—	110

() Indicates monotropic transition.

mosaic texture, while **3** showed only nematic phase. All the compounds show large super cooling.

2.3. *Refractive Indices Measurements*

Refractive indices (n_o, n_e) for wavelength $\lambda = 632.8\,\text{nm}$ were measured within ±0.0004 by thin prism method as reported by Prasad *et al.* [6]. The temperature of the prism was controlled using a specially constructed heater and Eurotherm 2020 process controller with an accuracy of ±0.1°C. From the density and the refractive indices values, the principal polarizabilities, α_e and α_o, have been calculated using the standard Vuks isotropic model [7].

2.4. *X-Ray Diffraction Measurements*

X-ray diffraction patterns were recorded on an x-ray film using a flat plate camera at several temperatures within the mesomorphic phase, using Ni-filtered Cu K_α radiation of wavelength $\lambda = 1.542\,\text{Å}$. Mono-domain samples were easily obtained by orienting the samples in a magnetic field of about 0.4 T. The experimental set-up and the procedure for orientational order parameter ($<P_2>$ and $<P_4>$) determination from x-ray diffraction studies have been described earlier by Bhattacharjee *et al.* [10].

3. Results and Discussion

3.1. *Density Measurements*

The temperature variation of the density values for **1-3** is shown in Figure 1. There is a discontinuity in the density values at the nematic – smectic B phase transition of **1** and **2**.

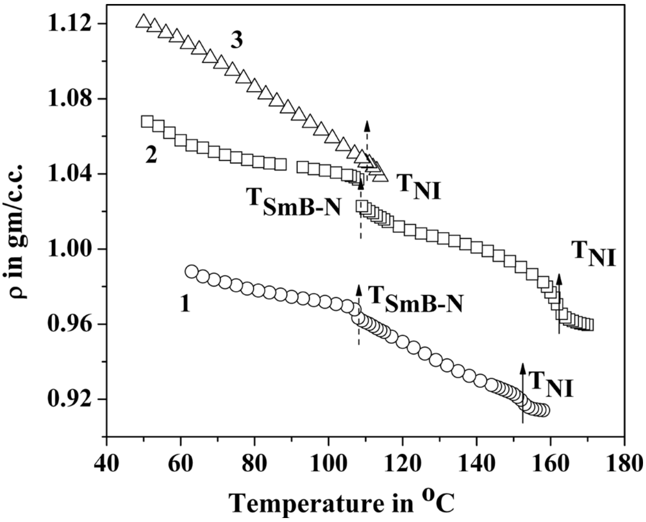


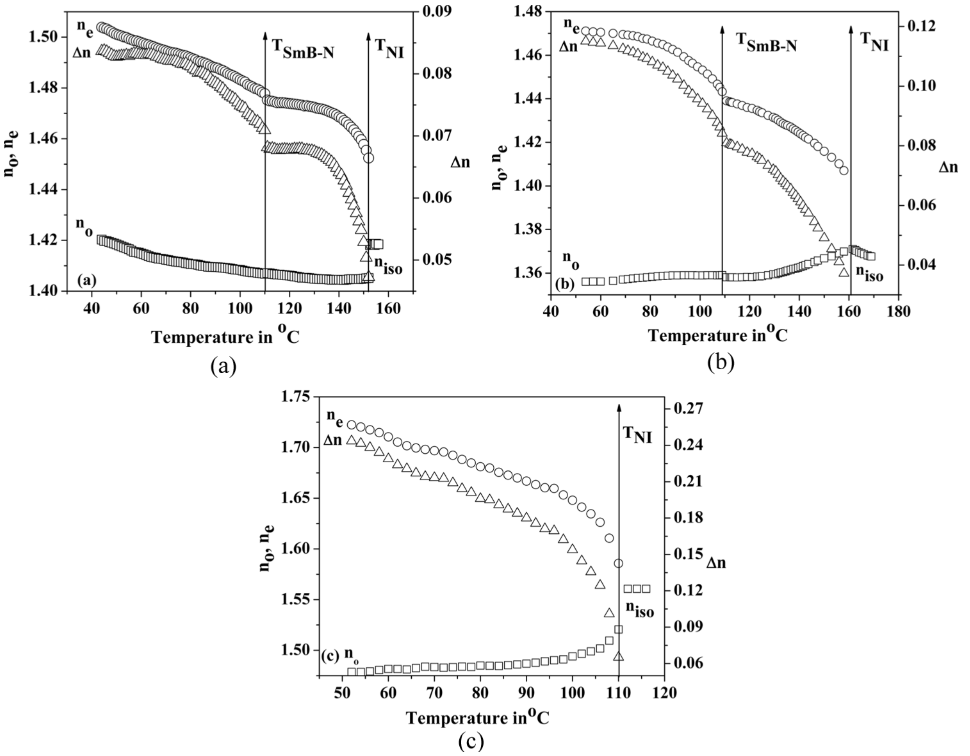
Figure 1. Variation of density values, ρ, as a function of temperature. ○ Comp. **1**; □ Comp. **2**; Δ Comp. **3**. T_{NI} = nematic–isotropic transition temperature; $T_{SmB\text{-}N}$ = smectic B–nematic transition temperature.

Compound **3** however shows normal temperature dependence. It is also observed that the entropy change associated with the nematic – smectic B transition (N -Sm B) for **2** are much higher than those observed at the nematic-isotropic (N-I) transition. On the contrary, there is a smaller entropy change at the N -Sm B transition for **1**, in comparison to the N-I transition.

3.2. *Refractive Index Measurements*

The temperature dependence of the principal refractive indices n_o and n_e and the refractive index in the isotropic phase (n_{iso}) at a wavelength of $\lambda = 632.8$ nm for the three compounds were measured and are shown in Figures 2(a)–(c). Also shown in the same figure is the birefringence Δn of the compounds as a function of temperature. Similar to the density values, there is an abrupt jump in the birefringence values at the N-SmB transition for **1** and **2**. Compound **3** shows the highest birefringence of around 0.24 at 50°C. This is due to the presence of conjugated π-bond in the rigid core of the terphenyl derivative **3.** It may be mentioned that recent efforts are being made to synthesize such high birefringence materials which also combine the necessary rotational viscosity and polarity, to facilitate reduction in the cell gap for display devices [11].

Using the refractive indices (n_o, n_e) and the density values, the principal molecular polarizabilities (α_o, α_e) and hence the polarizability anisotropy ($\Delta\alpha$) were



(a) (b)

(c)

Figure 2. Experimental values of refractive indices n_o and n_e and birefringence ($\Delta n = n_e - n_o$) as a function of temperature for: (a) Comp. **1**; (b) Comp. **2**; (c) Comp. **3**. T_{NI} = nematic – isotropic transition temperature; $T_{SmB\text{-}N}$ = smectic B– nematic transition temperature.

Table 2. Values of adjustable parameters $\Delta\alpha_0$, T* and β

Sample name	$\Delta\alpha_0$	T*	β
1	7.93 ± 0.18	425.9 ± 0.5	0.11 ± 0.008
2	10.87 ± .41	425.9 ± 0.4	0.24 ± 0.018
3	16.31 ± 0.14	382.1 ± 0.2	0.20 ± 0.003

calculated using Vuks method [7]. The orientational order parameter $<P_2>$ can be determined from the relation

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

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 perfectly ordered state ($\Delta\alpha_0$) were determined from the Haller's extrapolation method [12] using the equation,

$$\Delta\alpha = \Delta\alpha_0\left(1 - \frac{T}{T^*}\right)^{\beta} \tag{2}$$

where $\Delta\alpha_0$, T* and β are adjustable parameters. The calculated values of $\Delta\alpha_0$, T* and β are listed in Table 2. It may be mentioned that for **1** and **2** we have fitted equation (2) by taking the values of Δn only in the higher temperature nematic phase.

3.3. *X-Ray Diffraction Measurements*

X-ray diffraction patterns were recorded throughout the entire mesomorphic range of all the compounds. X-ray diffraction photographs of sample **1** in the nematic

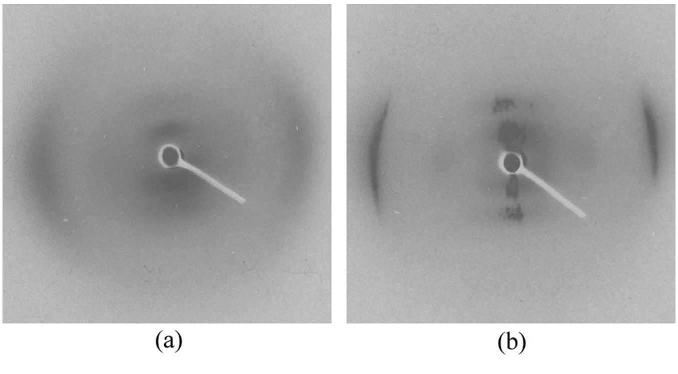
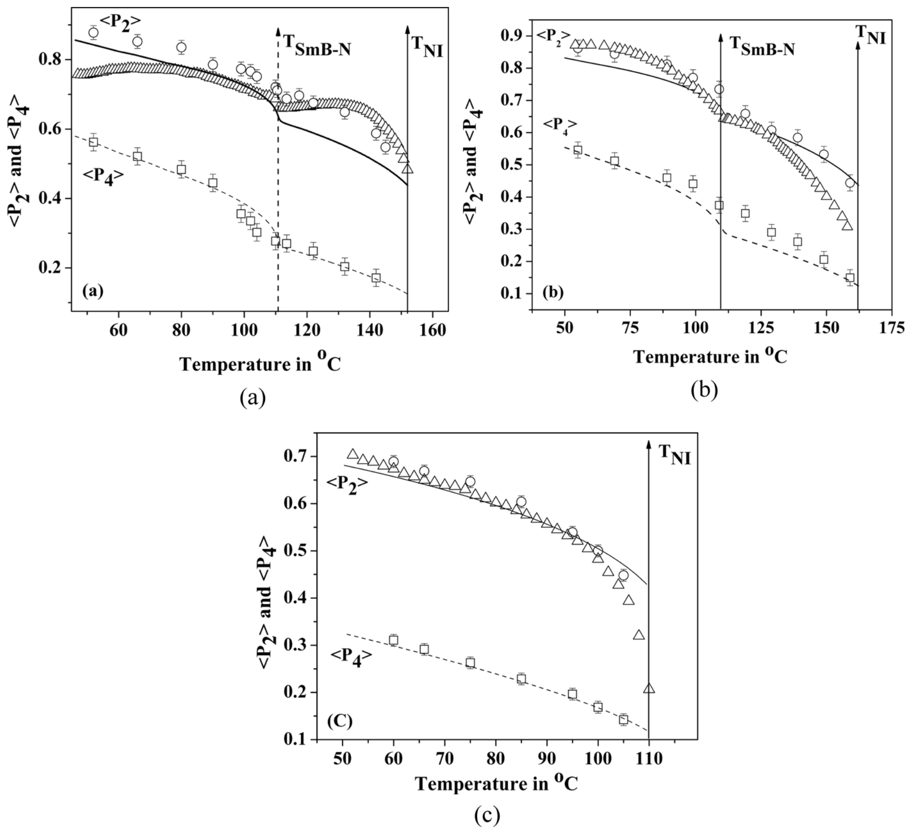

(a) (b)

Figure 3. X-ray diffraction photographs from aligned sample of sample 1 in: (a) Nematic (114°C) and (b) Smectic B (82°C) phases.

(114°C) and smectic B (82°C) phases are shown in Figures 3(a)–(b). In the nematic phase, the outer halo is split into two crescents for each of which the intensity is maximum in the equatorial direction, whereas in the smectic B phase, this halo is replaced by sharp crescents of relatively intense diffuse scattering on both sides of the equatorial maxima. In the meridional direction second order reflections are observed both in the nematic and smectic B phases. The angular distribution of the x-ray diffraction intensities of well – oriented monodomain samples of **1, 2** and **3** were utilized to obtain the orientational distribution function f(θ), and hence the orientational order parameters (OOP) $<P_2>$ and $<P_4>$, following a procedure reported by Bhattacharya *et al.* [10].

Figure 4(a)–(c) show the variation of the experimentally determined OOP's with temperature for all the three samples studied. The experimental $<P_2>$ and $<P_4>$ values are found to be discontinuous across the N-Sm B phase transition for **1** and **2**. Also, these values are found to be relatively high in the smectic B phase of **1** and **2**, showing the phase to be much more orientationally ordered than the



(a)

(b)

(c)

Figure 4. Temperature variation of orientational order parameters $<P_2>$ and $<P_4>$ for: (a) Comp. **1**; (b) Comp. **2**; (c) Comp **3**. ○ = x-ray data for $<P_2>$, □ = x-ray data for $<P_4>$, Δ refractive index data for $<P_2>$, —— $<P_2>$ from McMillan's theory (or Maier Saupe theory), ······ $<P_4>$ from McMillan's theory (or Maier- Saupe theory). T_{NI} = nematic – isotropic transition temperature, T_{SmB-N} = smectic B – nematic transition temperature.

neighbouring nematic phase. It may be mentioned that although the approximation used for calculating $<P_L>$ ($L = 2, 4$) is not valid for $<P_2> > 0.8$, we are still reporting the OOP values since at least qualitatively they show a degree of order of these fluorinated molecules possessing smectic B phase for which such values are rare. We have fitted our experimental data with those calculated from the McMillan's theory for Smectic A [9] for **1** and **2** using the potential parameters α and δ as two adjustable constants, due to lack of other alternatives. In the calculation using McMillan's model, the parameter α which varies with the chain length has been varied keeping the parameter, δ fixed ($\delta = 0.25$). The best fitted theoretical curves were obtained for α equal to 0.55 and 0.52 for compounds **1** and **2** respectively. The agreement between the experimental and theoretical values seems to be fair for **1** and fairly good for **2**. For **3,** a very good agreement is observed between the experimental $<P_2>$ and $<P_4>$ values and theoretical Maier – Saupe values. Also shown in Figure 4(a)–(c) are the $<P_2>$ values determined from refractive index measurements on **1, 2** and **3**. The experimental $<P_2>$ values obtained from refractive index and x-rays agree fairly well for both **1** and **2,** except very near the N-I transition, in spite of the fact that two different techniques have been employed to determine the orientational order parameters of these compounds. Lower values of the order parameter from refractive index measurement near the N-I transitions may be due to strong thermal fluctuations of the chain part of the molecules.

The temperature variation of the layer spacing, d, or apparent molecular length, l, for all the compounds is shown in Figure 5. For both **1** and **2**, the values of the smectic layer spacing, d remains almost constant in the Smectic B phase. The apparent molecular length, l increases slightly with increase in temperature in the nematic phase of both **1** and **2.** This is probably due to the increased thermal vibrations of the chain parts just before the transition. It was found that the intermolecular distance (D), increases with increasing temperature, caused once again by the increasing thermal vibrations of the molecules.

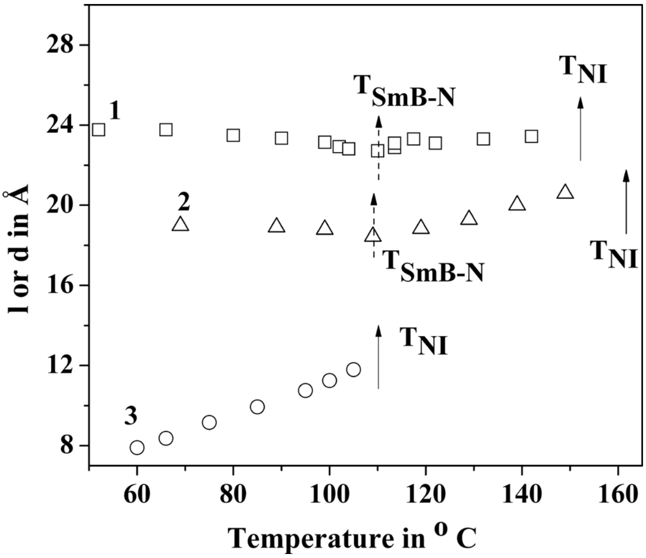


Figure 5. Temperature dependences of l or d values for: □ Comp. **1**; Δ Comp **2**; ○ Comp. **3**.

4. Conclusions

The physical properties of three laterally fluorinated liquid crystalline compound **1, 2** and **3**, have been studied by different experimental techniques. From density, refractive index and $<P_2>$ values determined from the x-ray diffraction and refractive index measurements, the order of the N-Sm B phase transition is found to be discontinuous for both **1** and **2**. Fairly good agreement is observed between the experimental and theoretically calculated $<P_2>$ and $<P_4>$ values for **1** and **2**, even though the McMillan model is strictly valid for the Smectic A phase. $<P_2>$ values determined from x-ray diffraction measurements are found to be in fairly good agreement with those obtained from refractive index measurements even after considering the different assumptions and approximations involved in the order parameter determination from x-ray diffraction and refractive index measurements.

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