Liquid Crystals
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713926090

Ferroelectric switching in a novel bent-shaped mesogen having two non-mesogenic units linked by an alkylene spacer

Veena Prasad; D. S. Shankar Rao; S. Krishna Prasad

To cite this Article Prasad, Veena , Rao, D. S. Shankar and Prasad, S. Krishna(2000) 'Ferroelectric switching in a novel bent-shaped mesogen having two non-mesogenic units linked by an alkylene spacer', Liquid Crystals, 27: 5, 585 — 590
To link to this Article: DOI: 10.1080/026782900202426
URL: http://dx.doi.org/10.1080/026782900202426

LIQUID CRYSTALS, 2000, VOL. 27, NO. 5, 585–590

Ferroelectric switching in a novel bent-shaped mesogen having two non-mesogenic units linked by an alkylene spacer

VEENA PRASAD*, D. S. SHANKAR RAO and S. KRISHNA PRASAD
Centre for Liquid Crystal Research, Jalahalli, Bangalore 560 013, India

(*Received 1 October 1999; accepted 29 November 1999*)

We report the synthesis, X-ray diffraction results and electro-optical switching measurements for a bent-shaped mesogen having two non-mesogenic units linked by an alkylene spacer. The novelty of the molecular structure lies in the carbonyl group of the ester linkage being directly attached to the spacer unit, unlike for banana-shaped molecules reported so far, in which it is one oxygen atom away from the spacer or the central aromatic unit. The compound shows two mesophases: the high temperature mesophase is a tilted smectic phase showing ferroelectric switching characteristics; the low temperature phase is more highly ordered with textural features similar to that of the B_3 banana phase.

1. Introduction

Until recently, only tilted smectic phases of materials comprising chiral molecules were known to exhibit ferro/antiferroelectric properties. A new surge of activity in this field was triggered by the observation of Niori *et al.* [1] of ferroelectric switching in an achiral mesogen. Most of the work in this field has been done on molecules in which the mesogenic groups are linked to the 1- and 3-positions of a phenyl ring through an ester linkage [1–4]. Based on the results obtained from different studies, it has been argued that in smectic phases such molecules can assume a shape referred to as *bow*, *banana* or *bent core*, consequently breaking the symmetry in the plane and leading to the observation of spontaneous polarization [5]. The chemical structure of a representative molecule, compound **1a** exhibiting this type of behaviour is shown in figure 1. Notice that the central part of the molecule has a rigid aromatic ring; initially it was thought that the rigidity of this part was essential for the phenomenon to occur. However, very recently, Watanabe *et al.* [6] observed switching behaviour in a homologous series in which the two mesogenic units are connected to a flexible alkylene spacer through an ester linkage. The molecular structure of such a compound, **1b**, is also given in figure 1. As in other liquid crystalline series, the length of the end chain affects significantly the type of mesophase observed. But a more important role is played by the parity of the alkylene spacer: this is supposed to decide whether or not the molecules take up the bent conformation which, as we have seen above, can lead to the observation of antiferroelectric properties. Experimentally, antiferroelectric type switching behaviour has been obtained [6] for the compound of structure **1b**. A common structural feature of all the non-chiral banana-shaped liquid crystals so far reported is that the central unit—whether aromatic or alkylene spacer—is linked to the oxygen atom of the ester group.

In this paper we report a novel deviation from this structure, in which the alkylene spacer unit is attached to the carbonyl group of the ester linkage. That is, the direction of the ester linkage has been reversed in our compound. We present the synthetic details, X-ray diffraction results and electrical switching properties of the compound with the structural formula **1c** shown in figure 1. The results show ferroelectric behaviour, observed for the first time in a compound with an even parity for the alkylene spacer. Finally, we discuss the type of banana phase observed here, in the light of the recent symmetry analysis by Brand *et al.* [7].

2. Experimental

2.1. *Synthesis*

The compound **1c**, bis[4-(4-*n*-decyloxyphenyliminomethyl)phenyl] adipate, was synthesized by esterification of adipic acid with 4-(4-*n*-decyloxyphenyliminomethyl)-phenol. The substituted phenol was prepared by condensing 4-*n*-decyloxyaniline with 4-hydroxybenzaldehyde. The detailed synthesis and characterization of these intermediate compounds will be given in a forthcoming paper, but a brief description of the synthesis of **1c** is given below.

---

*Author for correspondence; e-mail: uclcr@giasbg01.vsnl.net.in

Liquid Crystals ISSN 0267-8292 print/ISSN 1366-5855 online © 2000 Taylor & Francis Ltd
http://www.tandf.co.uk/journals

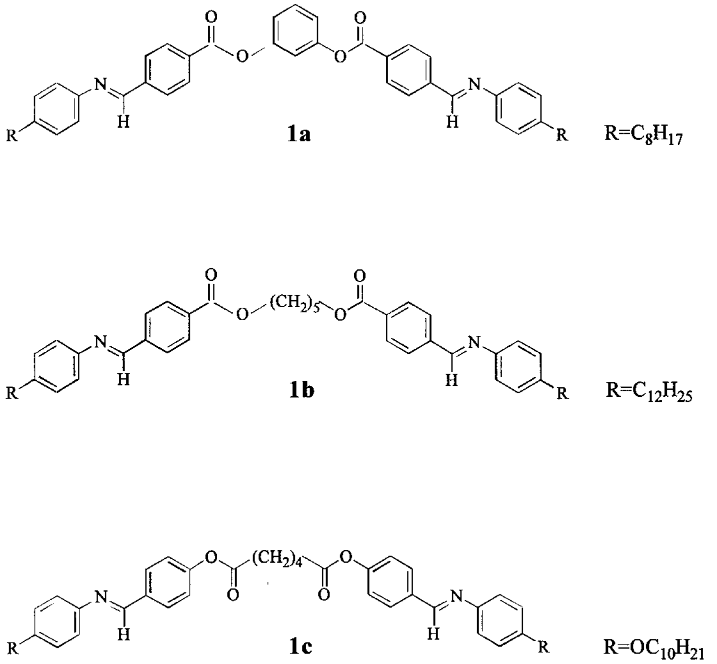


Figure 1. Molecular structures of representative banana-shaped compounds reported in the literature having a central unit which is either a rigid aromatic group (**1a**) or a flexible alkylene spacer (**1b**). **1c** shows the molecular structure of the compound reported in this paper.

Adipic acid (2.0 mmol) and 4-(4-*n*-decyloxyphenyliminomethyl)phenol (4.0 mmol) were dissolved in dichloromethane (100 ml), to which was added dicyclohexylcarbodiimide (5.0 mmol) and a catalytic amount of 4-dimethylaminopyridine. The mixture was then stirred at room temperature for about 24 h, under a nitrogen atmosphere. The dicyclohexylurea formed was filtered off, and the filtrate washed with distilled water (100 ml × 3). The crude product obtained on evaporation of the solvent was purified by flash chromatography on neutral aluminium oxide using CH_2Cl_2 as eluent. Finally the product was recrystallized repeatedly from CH_2Cl_2/C_2H_5OH, yield 57%.

Analytical data obtained for the above compound **1c**: ^1H NMR (200 MHz, $CDCl_3$) δ: 8.46 (s, 2H, –CH=N–), 7.91 (d, $J = 8.6$ Hz, 4H, Ar–H), 7.23 (d, $J = 3.5$ Hz, 4H, Ar–H), 7.19 (d, $J = 3.5$ Hz, 4H, Ar–H), 6.92 (d, $J = 8.6$ Hz, 4H, Ar–H), 3.97 (t, $J = 6.5$ Hz, 4H, $-OCH_2-$), 2.67 (br t, 4H, $-OCOCH_2-$), 1.75–1.91 (m, 8H, $-CH_2-$), 1.27 (m, 28H, $-CH_2-$), 0.88 (br t, 6H, $-CH_3$); FAB Mass: 817 $[MH]^+$ (calculated for $C_{52}H_{68}O_6N_2$).

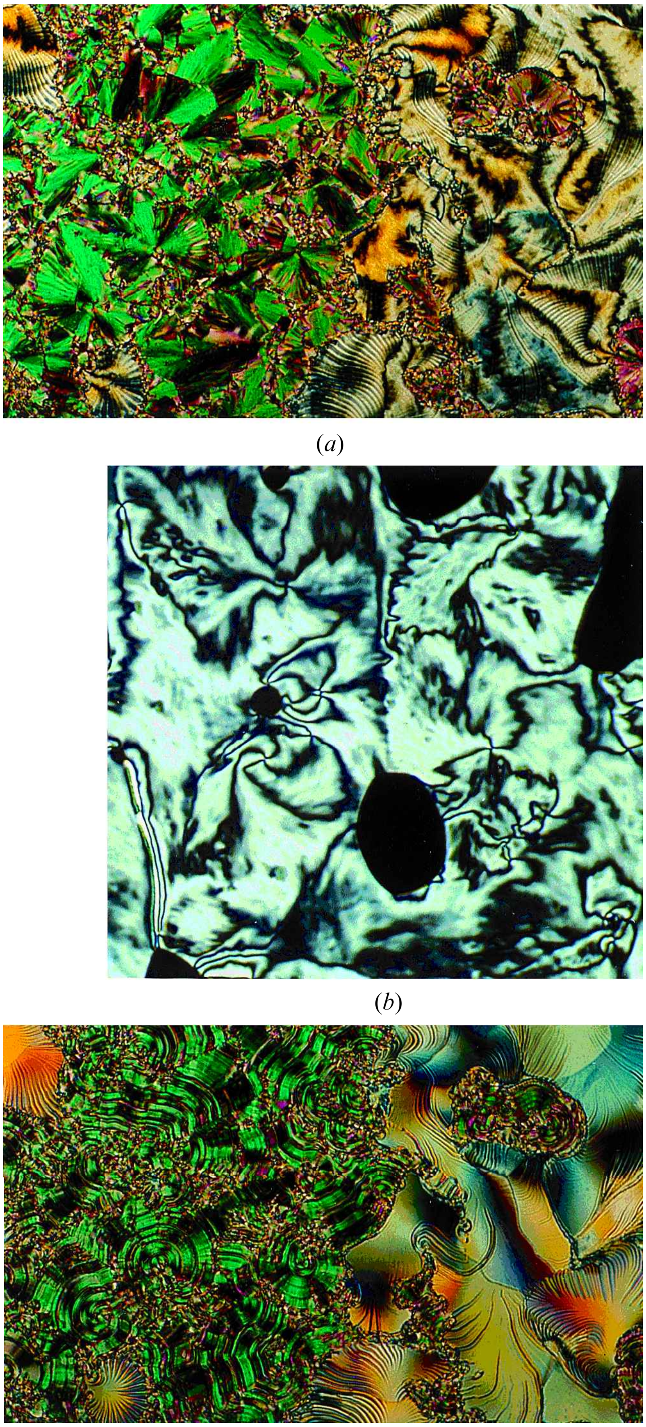
2.2. *Physical studies*

For optical studies, a Leitz DMRXP polarizing microscope in conjunction with a Mettler FP90 hot stage was used. Differential scanning calorimetric scans were taken on a Perkin Elmer DSC 7 apparatus. X-ray measurements were carried out using a MAC Science image plate set-up [8].

3. Results and discussion

3.1. *Mesomorphic properties*

The compound shows two enantiotropic mesophases. On cooling from the isotropic phase, at 222.5°C, some regions show the appearance of bâtonnets, while in other regions a hazy grey birefringence can be seen. Further cooling results in the bâtonnets coalescing to a broken fan-shaped texture and the grey regions show the four-brush schlieren texture characteristic of a tilted smectic phase, figures 2 (*a*) and 2 (*b*). Shearing the sample does not result in a 'pseudo-isotropic' texture. These features are similar to the observations [3] for the M2 phase of a compound with a non-Schiff's base banana-shaped molecule. We observed no fringe pattern superposed on the fan-shaped texture, but in certain regions strands were seen over the schlieren texture. The appearance of all these features for the same phase makes it difficult to associate the phase with any of the known banana phases reported in the literature. For this reason, we will just refer to it as the X_1 phase. A second transition appears at 173.5°C, accompanied by a drastic textural change. The regions that have the schlieren texture in the X_1 phase show a mosaic texture and those with the broken fan pattern exhibit fringes superposed on the fans, figure 2 (*c*). Further, as we shall see from the X-ray studies, this phase is a highly ordered phase and this therefore makes it comparable [9] to the Hex B_b or B_3 banana phases observed in, for example, compound **1a**. But for the sake of uniformity we refer to it as the X_2 phase. The DSC thermograms obtained in both



(*a*)

(*b*)

(*c*)

Figure 2. Microphotographs taken (at 190°C) in the X_1 phase showing (*a*) the broken fan-shaped texture and the four-brush schlieren texture. The schlieren texture is shown on an enlarged scale in (*b*); dark regions are air bubbles. The photograph taken (at 165°C) in the X_2 phase (*c*) is of the same region as (*a*) for the X_1 phase. The schlieren texture region of the X_1 phase has a mosaic pattern and fringes appear on the broken fan-shaped texture.

the heating and cooling modes (both at a rate of 10°C min^{-1}), and shown in figure 3, corroborate these observations. The values of the enthalpies obtained for the isotropic–X_1 and X_1–X_2 transitions are 27.5 and 12.3 J g^{-1}, respectively. These values are comparable to those obtained for other banana-shaped compounds [1, 9].

3.2. *X-ray studies*

The samples showed a weak but spontaneous alignment of the molecules perpendicular to the walls of the capillary tube. In the X_1 phase in the small angle region, a sharp Bragg reflection and a broad halo are seen, see figure 4 (*a*). In the wide angle region, a diffuse ring is seen around $2\theta \sim 20°$ pointing to a smectic structure without any long range positional order within the layers. The layer reflections were seen on the equator, but the diffuse scattering at wide angles had maxima off the meridional direction. In fact, by keeping 2θ fixed at the peak value of 19.2° and plotting the intensity as a function of the χ angle, we obtained the pattern shown in the inset of figure 4 (*a*). The pattern of the four peaks as a function of χ, along with the layer reflections on the equatorial axis, are similar to those for the B_2 banana phase of a chlorine-substituted banana-shaped compound by Pelzl *et al.* [10]. From the angular separation between the peaks shown in the inset, one obtains a value of about 36° for the tilt of the molecules, or equivalently that the two parts of the molecules are tilted with respect to each other with an angle of 108° between them. This is comparable to the value of a 37° tilt for the B_2 phase reported by Pelzl *et al.* [10]. In the X_2 phase at low angles, an additional peak appears whose *d*-spacing is exactly half of the most intense lowest

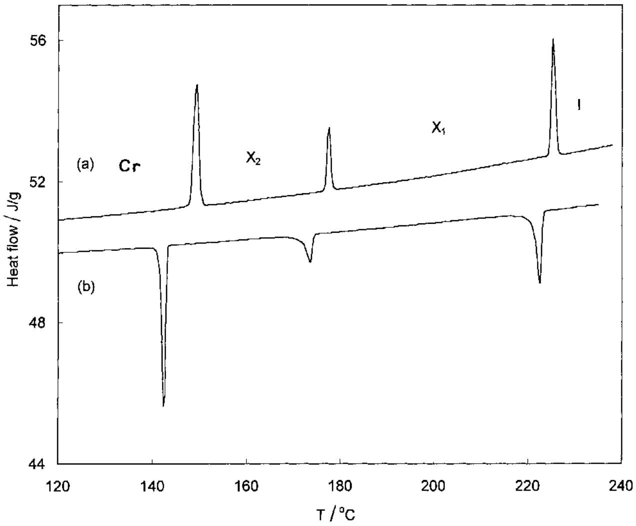
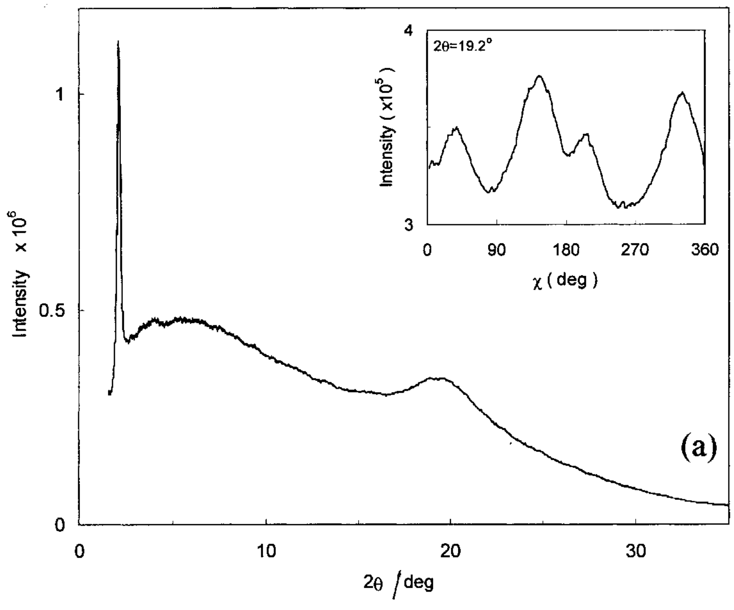


Figure 3. DSC scans for the heating (*a*) and cooling (*b*) modes at a rate of 10°C min^{-1}.



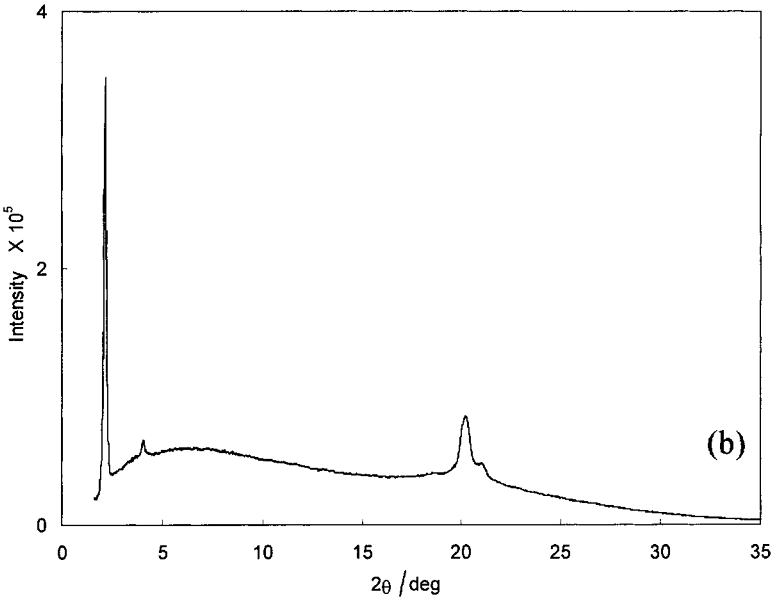


Figure 4. One dimensional cut of the X-ray diffraction pattern obtained in the (*a*) X_1 phase and (*b*) X_2 phase showing the χ-averaged intensity plotted as a function of 2θ angle. The inset in figure 4 (*a*) is the intensity profile as a function of χ with 2θ fixed at the peak value (= 19.2°) of the diffuse wide angle peak.

angle peak, indicating that it is a second order reflection. The wide angle ring becomes very sharp in the 2θ direction, figure 4 (*b*), and also shows a shoulder at higher angles. It may be recalled that such a pattern was seen for the Hex B_b or B_3 banana phase of compound **1a**.

3.3. *Electro-optic behaviour*

Figure 5 shows the current response to an applied triangular wave in the X_1 phase at 185°C with a 100 Hz, 14 V μm^{-1} field. Only one current peak is seen during one half period of the applied waveform, pointing to a ferroelectric switching. With this type of measurement, it is difficult to differentiate between ferroelectric switching and dielectric switching. Therefore, we used the Diamant bridge technique to look for hysteresis loops. Figure 6 shows such a loop obtained for the X_1 phase at 185°C with a 30 Hz, 8 V μm^{-1} sine wave field, and confirms that the switching is indeed of the ferroelectric type. Even when the frequency was reduced to 1 Hz, the profile remained the same, probably ruling out antiferroelectric order. The spontaneous polarization calculated

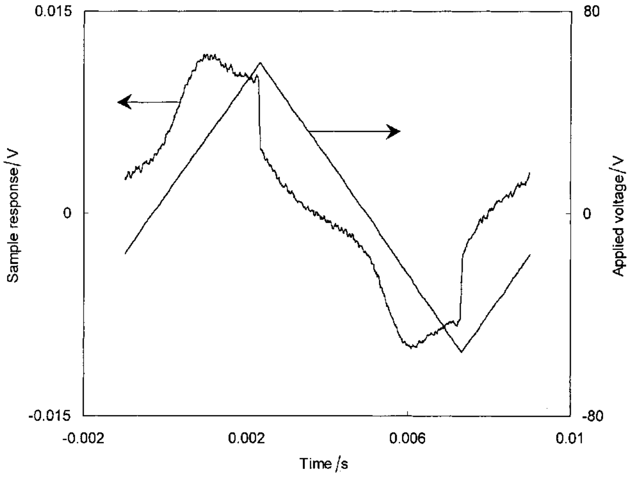


Figure 5. Switching current response in the X_1 phase at 185°C obtained by applying an electric field of triangular waveform (100 Hz, 14 V μm^{-1}). A calibrated resistance of 1 kΩ was used to convert the sample current to a voltage signal.

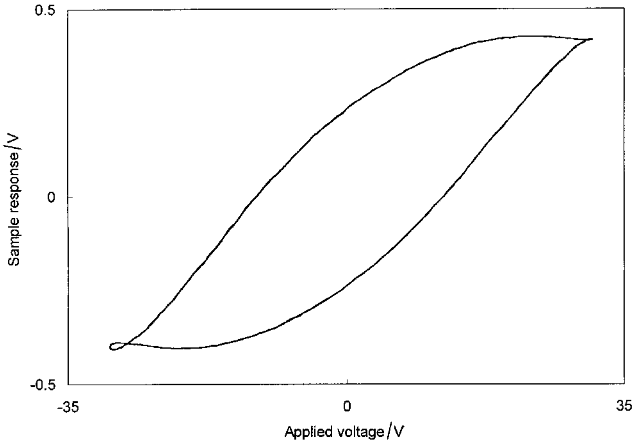


Figure 6. Electric polarization vs. applied voltage hysteresis loop obtained at 185°C for the X_1 phase.

from either of the methods gave a value of 42 nC cm^{-2} at 185°C and has a weak temperature dependence. This value is much smaller than that obtained for compound **1b**, which exhibits an antiferroelectric phase [6]. Optically, the equilibrium states for the opposite signs of the field appear identical, with only a transient change. This is to be expected as the tip of the bent-shaped molecules point towards the field, resulting in hardly any change in the birefringence on applying the field.

We were unable to get a good brush pattern, but obtained only a randomly oriented focal-conic fan-shaped texture. On application of the electric field, a very small decrease in birefringence was noticed, but no fringes were observed, as was reported for the B_2 phase [10]. A similar feature has been noticed by Choi *et al.* [6] in a compound with a flexible central linkage. The extinction direction of the focal-conics seems to depend on the polarity of the field, although the change in the angle was very small.

In the X_2 phase, even with a 14 V μm^{-1} field, a very weak switching current signal was seen only near the transition to the X_1 phase. Perhaps a much larger field could provide a full switching in this phase, but our samples were not able to withstand higher voltages.

Recently, Brand *et al.* [7] have proposed a molecular model to explain the possibility of a variety of tilted smectic phases with fluid layers, with emphasis on banana phases, and are able to account for the observation of macroscopic handedness in achiral molecules. What is more interesting from an experimental point of view, is that it associates the different phases with easily obtained experimental signatures, such as the defect texture involving the in-plane director, the type of electro-optic response and the presence/absence of left and right hand helices. For example, the conventional banana phase, reported for example by Sekine *et al.* [9], is supposed to be a good candidate for what is termed a C_G or C_{B2} phase. In the light of this model, let us recall the features of the X_1 phase that we have observed. It shows only integer strength defects for the in-plane director (homeotropic geometry), the hysteresis loop is of the ferroelectric type, and the left and right helices expected for the C_G or C_{B2} phase are absent. According to the model, only one phase, namely the C_{B1} phase, has all these three features. Therefore, it is tempting to say that the X_1 phase may correspond to the C_{B1} phase of the model.

In summary, we have reported a novel compound whose molecular structure deviates from known materials exhibiting banana phases. Optical, electro-optical and X-ray measurements have been carried out on the two mesophases observed. The high temperature phase is a tilted smectic exhibiting integer strength defects and ferroelectric switching. The low temperature phase is a more highly ordered phase having textural and X-ray features of the B_3 banana phase.

We are indebted to Prof. S. Chandrasekhar for his keen interest in this work and for many useful discussions.

References

[1] Niori, T., Sekine, F., Watanabe, J., Furukawa, T., and Takezoe, H., 1996, *J. mater. Chem.*, **6**, 1231.

[2] Jakli, A., Rauch, S., Lotzsch, D., and Heppke, G., 1998, *Phys. Rev. E*, **57**, 6737.

[3] Shen, D., Diele, S., Wirth, I., and Tschierske, C., 1998, *Chem. Commun.*, 2573.

[4] Shen, D., Diele, S., Pelzl, G., Wirth, I., and Tschierske, C., 1999, *J. mater. Chem.*, **9,** 661.

[5] Link, D. R., Natale, G., Shao, R., Maclennan, J. E., Clark, N. A., Korblova, E., and Walba, D. M., 1997, *Science*, **278,** 1924.

[6] Watanabe, J., Niori, T., Choi, S.-W., Takanishi, Y., and Takezoe, H., 1998, *Jpn. J. appl. Phys.*, **37,** L401; Choi, S.-W., Zennyoji, M., Takanishi, Y., Takezoe, H., Niori, T., and Watanabe, J., 1999, *Mol. Cryst. liq. Cryst.*, **328,** 185.

[7] Brand, H. R., Cladis, P. E., and Pleiner, H., 1998, *Eur. Phys. J.*, **B6**, 347.

[8] Kumar, S., Shankar Rao, D. S., and Krishna Prasad, S., 1999, *J. mater. Chem.*, **9,** 2751.

[9] Sekine, T., Niori, T., Sone, M., Watanabe, J., Choi, S.-W., Takanishi, Y., and Takezoe, H., 1997, *Jpn. J. appl. Phys.*, **36,** 6455.

[10] Pelzl, G., Diele, S., Grande, S., Jakli, A., Lischka, C. H., Kresse, H., Schmalfuss, H., Wirth, I., and Weissflog, W., 1999, *Liq. Cryst.*, **26,** 401.