On some liquid crystalline phases exhibited by compounds made of bent-core molecules and their mixtures with rod-like molecules

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Abstract. In most homologous series of compounds made of bent-core (BC) molecules, the B_2, B_1 and B_6 phases occur as the chain length decreases. We have studied binary mixtures of the compound 1,3-phenylene bis[4-(3-methylbenzoyloxy)]4'-n-dodecylbiphenyl 4'-carboxylate (BC12) which exhibits the B_2 phase with the compound 4-biphenylyl 4''-n-undecyloxybenzoate (BO11) made of rod-like (R) molecules. We find the above sequence of occurrence of the B phases with increasing concentration of BO11. In this paper we describe the physical origin for the formation of these phases in both pure compounds and in the mixtures. We have also found the occurrence of the biaxial smectic A phase when the BO11 concentration is increased to 87–95.5 mol%. We also report on another binary system composed of BC12 and 4-n-octyloxy 4'-cyanobiphenyl (8OCB) made of R molecules. This system exhibits the biaxial smectic A phase down to $30°$C. Using polarized infrared spectroscopy we find that the mutual orientation of the R and BC molecules in the SmA_{db} liquid crystal is such that the arrow axes of the BC molecules are along the layer normal of the partial bi-layer smectic structure formed by the rods. We also describe unusual growth patterns obtained when the nematic phase transforms to the SmA_{db} phase in a mixture with 24 mol% of BC12.

Keywords. Mixtures of rod-like and bent-core molecules; biaxial smectic A; B-liquid crystals.

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1. Introduction

Liquid crystals made of rod-like (R) molecules have been known for a long time [1]. The molecules usually lack cylindrical symmetry. However, in most liquid crystals they rotate freely about the long axes resulting in uniaxial media. The possible existence of a biaxial nematic liquid crystal (N_b) was discussed by Freiser [2], for molecules having biaxial shape. But experimentally the biaxial nematic phase has not been established with certainty in thermotropic liquid crystals [3]. Disc-like (D) molecules form another class of liquid crystals, which are known for over 25 years [4]. Such molecules are generally highly symmetric about the short molecular axes. Many theories had also predicted the occurrence of a biaxial nematic liquid crystal by a mutual orientation of R and D molecules in appropriate mixtures [5–7]. However, an experimental investigation of such mixtures showed the coexistence of two uniaxial nematic phases instead of the predicted biaxial phase [8].
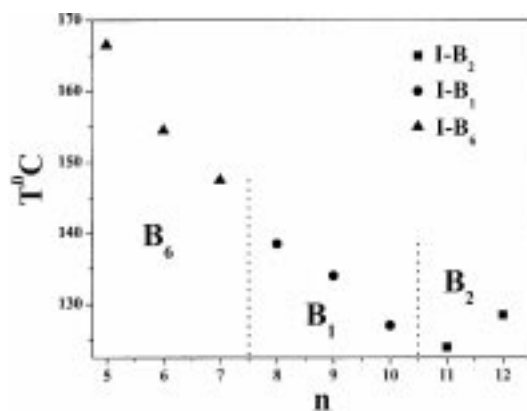
Figure 1. Phase diagram of the homologous series 1,3-phenylene bis[4-(3-methylbenzoyloxy)]4$'$-n-alklybiphenyl 4$'$-carboxylate. Note the occurrence of the B$_6$, B$_1$ and B$_2$ phases as the chain length is increased.

Liquid crystals made of bent-core molecules are currently of considerable interest [9]. Unlike the R molecules, which rotate freely about their long axes, the bent-core (BC) molecules with a large bend angle cannot rotate freely. Compounds composed of these molecules exhibit distinctive liquid crystalline phases (B phases). Usually in a homologous series of symmetrically substituted BC compounds the B$_2$ phase with a lamellar structure, the B$_1$ phase with a rectangular columnar structure and the B$_6$ phase having an intercalated lamellar structure are known to occur with decreasing chain length. For example the homologous series 1,3-phenylene bis[4-(3-methylbenzoyloxy)]4$'$-n-alkylbiphenyl 4$'$-carboxylates exhibit such a sequence [10]. In this series the B$_2$ phase is exhibited for compounds with alkyl chain length $(n) \geq 11$, the B$_1$ phase for $n = 8$–10 and the B$_6$ phase for $n = 5$–7 (figure 1).

We have recently studied [11,12] binary mixtures of the 12th homologue of this series (BC12) exhibiting the B$_2$ phase, with a compound made of R molecules exhibiting the bilayer smectic A phase. In this system (System I) we have found the induction of the B$_1$ and B$_6$ phases with increasing concentration of the compound with R molecules. In addition we have also found the induction of the biaxial smectic A phase in mixtures with relatively low concentrations of the BC compound.

In the present paper, we first discuss the molecular reasons for the formation of the three types of B phases in the homologous series and the induced B phases in mixtures of System I. We have also found the biaxial smectic A phase in mixtures of BC12 and the well-known compound 4-n-octyloxy 4$'$-cyanobiphenyl (8OCB) made of R molecules (System II). We present some experimental results on the biaxial smectic phase of the latter system. 8OCB is known to have a partial bilayer structure. X-ray studies show that even in the mixtures of System II exhibiting the biaxial smectic A phase, the rods form a partial bilayer structure. Investigations on the mutual orientation of the R and BC molecules in the biaxial smectic A (SmA$_{db}$) phase in these mixtures using polarized infrared spectroscopy will be reported. Unusual growth patterns of the SmA$_{db}$ liquid crystal as it separates from the nematic liquid crystal will also be described.

2. Relationship between the formation of the B phase and chain length in a homologous series

The relationship between the formation of a particular type of B liquid crystalline phase and the chain length in a homologous series can be understood in terms of intermolecular interactions and electric polarization which are due to the packing of BC molecules [13].

When the chain length is sufficiently long the molecules have strong biphilicity and there is segregation of the aromatic cores and the aliphatic chains resulting in a layering order of the B_2 phase [14]. In most BC molecules the bend angle (between each arm and the bow axis) is $>60°$. The BC molecules cannot rotate freely about the long (bow) axes, and pack with an in-layer polar order. The aromatic cores are associated with several dipolar groups having components in the molecular plane and these can give rise to a tilting about the arrow axes. This dipolar mechanism is similar to the case of the smectic C liquid crystal formed by R molecules, where the off-axis components of the dipoles can produce tilting of the molecules [15]. Another contributory factor is a larger molecular cross-section of chains compared to the cores, which can also produce tilt [16]. Though the individual molecules are achiral, as a result of the polar ordering of the molecules and the tilt, the layer becomes chiral [17]. The B_2 phase usually has an antiferroelectric interlayer order due to entropic reasons and the medium has no net polarization. However, the layer polarization (P) generates a depolarizing electric field giving rise to a positive self-energy ($\sim P^2$). In ferroelectric crystals the depolarization field is reduced by the formation of domains. To have an equivalent structure in the polarized layers with BC molecules the arrow directions have to reverse sign at the domain interfaces. As this would not be favoured entropically the layers are uniformly polarized in the B_2 phase (figure 2).

The B_1 phase exhibited by the lower homologues has a rectangular columnar structure as shown by X-ray studies (figure 3). This type of domain formation has no net polarization and is also compatible with the geometrical packing of the BC molecules [18]. At the interfaces of these domains the aliphatic chains of molecules of one domain overlap with the aromatic parts of molecules from the neighbouring domains leading to an unfavourable interaction. If the chain length is longer than the arm length of the aromatic core, only the B_2 phase can be stabilized. But if the chain length is shorter than the arm length there is some overlap between the aromatic parts, which has a favourable interaction and the B_1
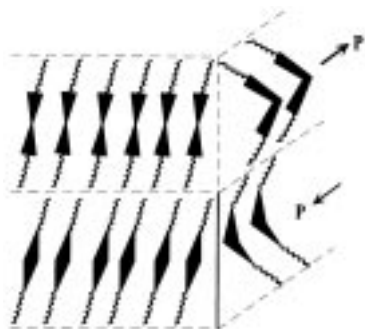
Figure 2. Schematic representation of the structure in the B_2 phase exhibited by compounds made of BC molecules.

Figure 3. Schematic representation of the structure in the B_1 phase exhibited by compounds made of BC molecules (p2mg symmetry).

Figure 4. Schematic representation of the structure in the B_6 phase exhibited by compounds made of BC molecules.

phase can be stabilized. The lattice parameters in this case correspond to the length of the molecule along the bow axis (=b) and the width of 6–8 molecules (=a) and usually there is no tilting of the molecules. The unfavourable interaction between the chains and the cores appears to be a stabilizing factor of the 2D lattice in the B_1 phase.

If the chains are still shorter the unfavourable interaction is reduced and molecules belonging to neighbouring domains can move freely across the domains to gain entropy and the 2D lattice is destroyed. The B_6 phase with the intercalated structure can then be stabilized (figure 4).

3. Mixtures of BC and R molecules

3.1 *System I*

In our first study [11,12] we used the compound 4-biphenylyl $4''$-*n*-undecyloxybenzoate (BO11) having rod-like molecules. It exhibits the nematic (N) and smectic A_2 (SmA_2) phases. Despite the absence of highly polar end groups, the SmA phase has a bilayer structure. As mentioned earlier, the compound with BC molecules used in the binary mixtures is BC12 exhibiting the lamellar B_2 phase. The molecular structures of these compounds are shown in figure 5 .

A detailed temperature–concentration phase diagram of the binary system composed of BO11 and BC12 is shown in figure 6. Mixtures with a low concentration (<15 mol%) of the rod-like compound exhibit the B_2 phase. With increasing concentration of the rod-like compound, two liquid crystalline phases, distinctive to compounds with BC molecules, are induced. They are the two-dimensional B_1 phase associated with a rectangular lattice (15–63 mol% of BO11) and the B_6 phase having an intercalated structure (63–87 mol% of
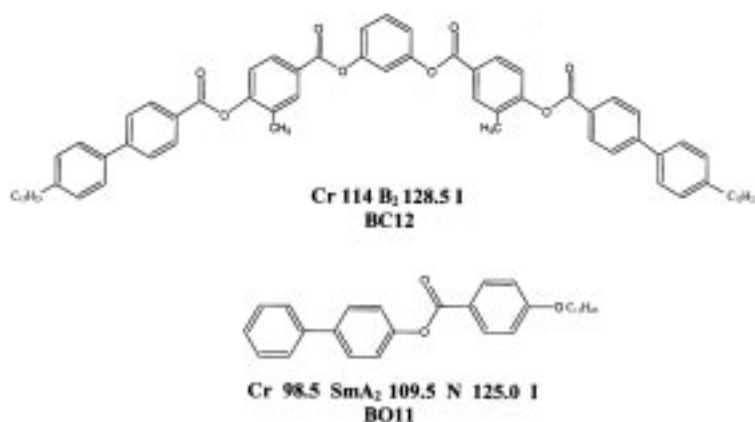
Cr 114 B₂ 128.5 I
BC12

Cr 98.5 SmA₂ 109.5 N 125.0 I
BO11

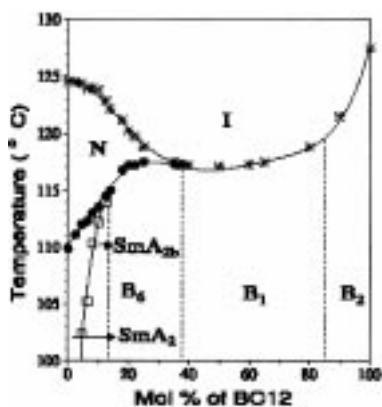**Figure 5.** Molecular structures of the compounds used in System I.

Figure 6. Phase diagram of mixtures of System I.

BO11). Thus increasing the concentration of the rods has the same effect as the shortening of the chain length in the homologous series of the BC compound. The aromatic moieties of the rods are attracted to the aromatic parts of the BC molecules and this is exploited by the medium to reduce the electrostatic energy of the polarized layers of the B_2 phase. In the proposed model of the induced B_1 phase, the rods lie at the interfaces between neighbouring domains (figure 7). The aromatic parts of the rods partly overlap with the aromatic cores of the BC molecules at the interface of both the domains, enhancing the attractive interaction between the domains. The rods aid in holding the domain structure together, thus acting like glue. As the concentration of rods is increased they are no longer confined to the interfaces between the domains and beyond about 63 mol% of the rods, the 2D lattice structure gets disrupted resulting in the B_6 phase (figure 8) as in the case of short homologues.

The most interesting part of the phase diagram is for concentration of rods in the range of 87–95.5 mol%. Homeotropically aligned samples exhibit a Schlieren texture on cooling from the uniaxial smectic A phase, having defects of both strengths ± 1 and $\pm 1/2$. Cono-

scopic observations on field aligned samples show evidence for biaxiality. X-ray studies reveal that the rods form a bilayer structure [12]. Based on the experimental studies we concluded that the induced liquid crystalline phase, in this concentration range, corresponds to the orthogonal biaxial smectic A phase. This type of liquid crystalline phase [1] had been proposed theoretically and first found in a polymeric system [19]. More recently there are reports of the observation of the biaxial smectic A phase in other systems [20].

Various possible mutual orientations of the R and BC molecules in this concentration range have been considered [12] in order to account for the experimental observations like the formation of defects with strength $\pm 1/2$. A model in which the arrow axes of the BC molecules point along the layer normal of the bilayer smectic structure has been proposed [12]. The origin of the biaxial phase has been interpreted as an orientational transition of the BC molecules in a background anisotropic matrix of a smectic A liquid crystal made of R molecules [11]. We have now carried out experiments to obtain direct information about the mutual orientation of R and BC molecules using polarized infrared radiation in a second system exhibiting the biaxial smectic A phase.

3.2 *System II*

The biaxial smectic A phase obtained in System I (see figure 6) occurs at temperatures of the order of $\sim 100°C$. We found that mixtures composed of 8OCB (figure 9) and 10–24 mol% of BC12 (System II) exhibit the biaxial smectic A(SmA$_{db}$) phase down to about 30°C. The detailed temperature–concentration phase diagram will be published elsewhere.

As mentioned earlier, X-ray studies show that the rods form a partial bilayer structure in the SmA$_{db}$ phase in these mixtures. We therefore propose that the mutual orientation of the R and BC molecules are as shown in figure 10. We describe an experiment in which polarized infrared radiation has been used to probe the mutual orientation of R and BC molecules to confirm the structure.
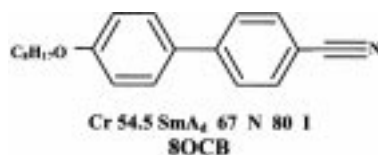

Figure 7. Schematic representation of the structure in the B$_1$ phase exhibited by mixtures of compounds made R and BC molecules.

Figure 8. Schematic representation of the structure in the B$_6$ phase exhibited by mixtures of compounds made of R and BC molecules.

Some liquid crystalline phases

Cr 54.5 SmA$_d$ 67 N 80 I
8OCB

Figure 9. Molecular structure of the rod-like compound used in System II.

Figure 10. Schematic representation of the structure in the SmA$_{db}$ liquid crystal.

3.3 *Studies with polarized infrared radiation*

Polarized infrared (IR) spectroscopy is a convenient technique for obtaining orientational information about molecules if the transition moments associated with different chemical bonds in the molecules are well-defined. This method involves studying the angular dependence of peak absorbance related with different chemical bonds, using incident polarized IR radiation. For a uniaxial medium the absorbance is given by

$$A(\alpha, \omega) = k\{(S/2)\sin^2\alpha + (S/2)(2 - 3\sin^2\alpha)\cos^2\omega + (1 - S)/3\}, \qquad (1)$$

where ω is the angle between the polarization direction of incident radiation and the symmetry axis (director), α the angle made by the chemical bond with the molecular axis which orients along the director [21] and S the orientational order parameter. For the smectic phase S can be expected to be large and therefore for comparing dichroisms we assume $S = 1$. For obtaining information about the mutual orientation of R and BC molecules, two chemical bonds which are infrared active, and mutually exclusive in the two types of molecules are required. We have made use of the C≡N bond of 8OCB and the C=O bond of BC12 (there are four such bonds in each BC molecule). The C≡N bond is along the long axis of the 8OCB molecule which is along the axis of symmetry, i.e., $\alpha = 0°$. In the case of the BC molecule all the four C=O bonds are orthogonal to the bow axis but make different angles with the arrow axis. This is suggested by the molecular structure as determined by a 3D optimization procedure based on molecular mechanics [22] on the aromatic core of the BC12 molecule.

The experiment has been carried out for the mixture with 11 mol% of BC12 (Mix11) and exhibiting the following phase sequence on cooling from the isotropic phase

I 85 N 57.8 SmA$_d$ 40.3 SmA$_{db}$ (temperatures in °C).

Planar aligned samples were obtained by oblique deposition of SiO on CaF$_2$ plates, which are transparent in the infrared region. The cell with a thickness of ∼15 μm was taken in a suitable heater and the alignment of the sample checked in the nematic and smectic phases using a polarizing microscope. A wire grid polarizer (IGP 227) from Moletron Detector Inc. was used to obtain polarized infrared radiation. The polarized spectra
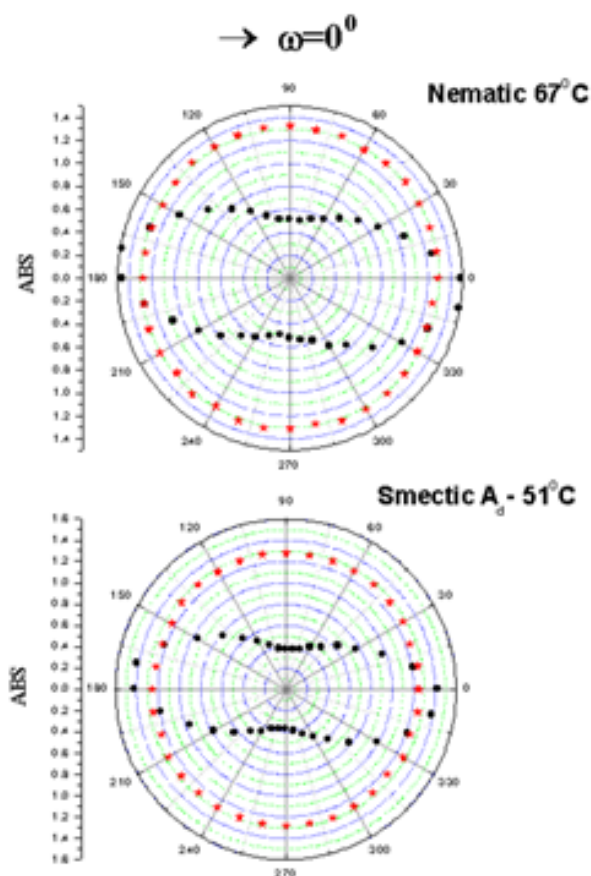
Figure 11. Polar plots of absorbance as a function of polarizer angle, sample: Mix11. • corresponds to C≡N bond and ⋆ corresponds to C=O bond.

were recorded for different settings of the polarizer angle using the Shimadzu FTIR 8400 spectrophotometer.

The polar plots of absorbance as functions of the polarizer angle in the nematic and smectic phases are shown in figure 11. The peak absorbance corresponding to the C≡N bond from 8OCB shows a maximum when $\omega = 0$ and $180°$. But in the case of the C=O bond there is no significant angular dependence.

In the case of the compound with R molecules as $\alpha = 0°$ the maximum absorbance due to the cyano bond is expected to be obtained when $\omega = 0$ and $180°$. This is experimentally observed. In the case of the compound with BC molecules there are two possibilities. The orientation of the BC molecule can be such that the bow axis is parallel to the layer normal, i.e., along the axis of symmetry. As the C=O bonds are orthogonal to the bow axis, $\alpha = 90°$. Then the absorbance due to the C=O bond should be maximum when $\omega = 90$ and $270°$ (eq. (1)). The dichroism would be opposite to that observed for the C≡N bond and would be clearly observed in the experiment. However, we do not see any evidence for such a behaviour experimentally. On the other hand in our model the arrow axes of the BC

(a) (b)
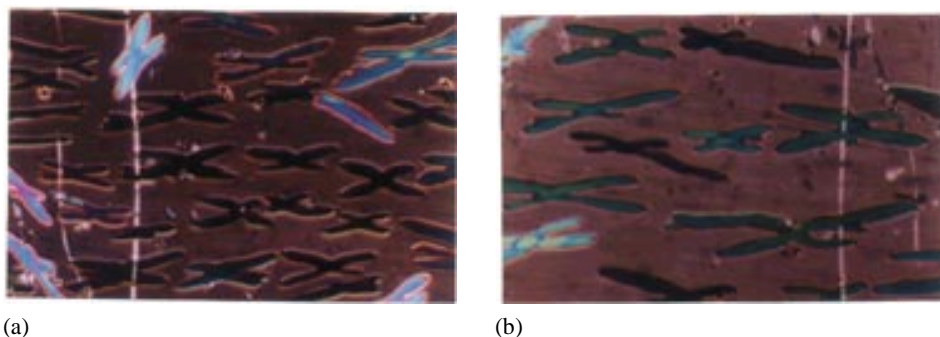
Figure 12. (**a**) Growth of SmA_{db} liquid crystal from the nematic liquid crystal in Mix24, planar aligned cell, crossed polarizers, rubbing direction parallel to lower edge of the photograph ($\times$400). (**b**) Similar sample as in figure 12. Vertical electric field (10 kHz, 5 V/μm) applied to align nematic homeotropically, crossed polarizers at 45° to the rubbing direction ($\times$400).
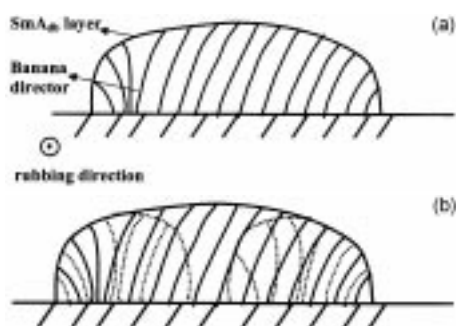
Figure 13. (**a**) Cross-section of a SmA_{db} domain (Mix24). (**b**) Growth of new layers (dotted lines) on the same SmA_{db} layer shown in figure 13a.

molecule orient along the layer normal of the partial bilayer structure of the rods. As the four C=O bonds make different angles with the arrow axis α can average out to make the angular dependence on ω negligible (eq. (1)). Such a behavior is observed experimentally. Therefore, we conclude that the arrow axes of the BC molecules are along the layer normal of the smectic structure formed by the rods, in conformity with our proposed model.

The BC molecules which are orientationally disordered in the uniaxial SmA phase, become orientationally ordered with the background matrix of rods remaining intact, at the transition from the uniaxial SmA phase into the biaxial SmA phase. The dichroisms of the C≡N and C=O groups are similar in both the uniaxial and biaxial smectic phases.

4. Growth patterns of the SmA_{db} liquid crystal from the nematic liquid crystal

Growth patterns of the SmA_{db} phase in a mixture with 24 mol% of BC12 in System II (Mix24) having a direct nematic (N) to SmA_{db} transition have been studied in planar

aligned samples. Instead of the batonnets with focal-conic domains usually seen with uni-axial smectics, the SmA_{db} liquid crystal separates as forked structures (figure 12a) from the nematic liquid crystal.

Planar aligned samples were prepared between polyimide coated and rubbed glass plates. As the sample is cooled from the nematic phase, the SmA_{db} domains first form as elliptic objects, which are elongated along the nematic director. The smectic layer normal is along the rubbing direction. With decrease in temperature as the SmA_{db} domain widens, the tip splits, and the two branches grow with different rates. Sometimes a further splitting can also be observed (figure 12b). A possible origin of the branching can be described as follows: the SmA_{db} liquid crystal appears to partially wet the rubbed poly-imide layer used for the planar alignment. The banana director is likely to make a large angle with the SmA_{db}–N interface in a direction orthogonal to the layer normal. The cross-section of the SmA_{db} domain would be as shown in figure 13a. As new layers form they preferentially nucleate near the two edges to reduce curvature distortion energy. If the area of the underlying layer is large enough, two new layers can grow independently (figure 13b) giving rise to the two branches.

5. Conclusion

Molecular reasons for the formation of the B_2, B_1 and B_6 phases in a homologous se-ries of compounds made of BC molecules and their mixtures with compounds made of R molecules have been discussed. A second binary system composed of R and BC molecules exhibiting the biaxial smectic A phase at a temperature convenient for several experiments has been found. Polarized infrared radiation has been used to probe the mutual orientation of the R and BC molecules in the SmA_d and SmA_{db} phases in this system. The results suggest that the arrow axes of the BC molecules are along the layer normal of the partial bilayer smectic structure formed by the rods in agreement with the model proposed earlier. Growth patterns of the SmA_{db} phase from the N phase in planar aligned samples have been studied.

References

[1] P G de Gennes and J Prost, *The physics of liquid crystals*, 2nd ed (Clarendon Press, Oxford, 1995)
[2] M J Freiser, *Phys. Rev. Lett.* **24**, 1041 (1970)
[3] K Praefcke, *Mol. Cryst. Liq. Cryst.* **364**, 15 (2001)
[4] S Chandrasekhar, B K Sadashiva and K A Suresh, *Pramana – J. Phys.* **9**, 471 (1977)
[5] R Alben, *J. Chem. Phys.* **59**, 4299 (1973)
[6] Y Rabin, W E McMullen and W M Gelbart, *Mol. Cryst. Liq. Cryst.* **89**, 67 (1982)
[7] Z Y Chen and J M Deutch, *J. Chem. Phys.* **80**, 2151 (1984)
[8] R Pratibha and N V Madhusudana, *Mol. Cryst. Liq. Cryst. Lett.* **1**, 111 (1985)
[9] G Pelzl, S Diele and W Weissflog, *Adv. Mater.* **11**, 707 (1999)
[10] B K Sadashiva, V A Raghunathan and R Pratibha, *Ferroelectrics* **243**, 249 (2000)
[11] R Pratibha, N V Madhusudana and B K Sadashiva, *Science* **288**, 2184 (2000)
[12] R Pratibha, N V Madhusudana and B K Sadashiva, *Mol. Cryst. Liq. Cryst.* **365**, 755 (2001)

[13] N V Madhusudana, Presented at the Boulder FLC Workshop, University of Colorado, 21–24 August 2002 (http://anni.colorado.edu/bananas)

[14] T Niori, T Sekine, J Watanabe, T Furukawa and H Takezoe, *J. Mater. Chem.* **6**, 1231 (1996)

[15] A S Govind and N V Madhusudana, *Euro. Phys. J.* **E9**, 107 (2002)

[16] Y Lansac, N A Clark and M A Glaser, *Poster presented at the 19th International Liquid Crystal Conference*, Edinburgh, UK, 30 June–5 July 2002

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

[18] J Watanabe, T Niori, T Sekine and H Takezoe, *Jpn. J. Appl. Phys.* **37**, L139 (1998)

[19] H F Leube and H Finkelmann, *Makromol. Chem.* **192**, 1317 (1991)

[20] T Hegmann, J Kain, S Diele, G Pelzl and C Tschierske, *Angew. Chem. Int. Ed.* **40**, 887 (2001)

[21] K H Kim, K Ishikawa, H Takezoe and A Fukuda, *Phys. Rev.* **E51**, 2166 (1995)

[22] ACD/Chemsketch software from Advanced Chemistry Development Inc.