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Induction of B_1, B_6 and Biaxial Smectic A Phases in Binary Mixtures of Compounds with Rod-Like and Bent-Core Molecules

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We have studied a binary mixture of compounds, one of which has rod-like molecules and the other bent-core molecules. The rod-like molecules are biphilic in nature with a long alkoxy chain attached to an aromatic moeity only at one end, and exhibit the bilayer SmA_2 phase, even though they do not have the highly polar cyano or nitro groups. The compound with bent-core molecules exhibit the B_2 phase which has polarized layers with tilted molecules. Three liquid crystalline phases are induced in the binary mixtures, depending on the concentration: the 2-dimensionally ordered B_1 phase for compositions with 15 to 63 mol % of the rod-like molecules and the B_6 phase for 63 to 87 mol %. The sequence obtained on increasing the concentration of rod-like molecules is the same as that seen on shortening the chain length of the BC molecules. Between 87 to 95.5 mol % of the rod-like molecules, a new biaxial smectic A_2 (SmA_{2b}) phase is induced. On the basis of several observations, we argue that it corresponds to a structure in which the BC molecules are reoriented with their arrow directions pointed along the layer normal. The SmA_2 to SmA_{2b} transition corresponds to an orientational transition of the bent-core molecules in the anisotropic SmA_2 background medium.

Keywords: Biaxial smectic A; bilayer smectic A; induced phases; binary mixtures; bent-core molecules

INTRODUCTION

Liquid crystals made of rod-like and disc-like molecules are well known.[1,2] Such molecules do not deviate strongly from a cylindrically symmetric shape and further, the rod-like molecules rotate relatively freely about their long axes in the mesophases. On the other hand, the bent-core (or banana-shaped) molecules [3] are patently biaxial and polar in shape and generate new types of liquid crystalline phases[4], not found in compounds with either rod-like or disc-like molecules. The latter two types of mole-

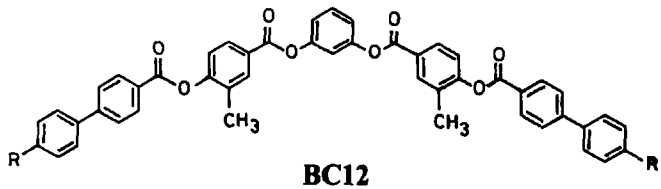
cules do not mix easily: for example, a binary mixture of nematogens with these two types of molecules was found to produce a phase separation between a nematic rich in rods and one rich in discs[5] and not a biaxial nematic as predicted by several theories.[1] In the present paper we report our investigations on binary mixtures of two mesogens, one with bent-core (BC) and the other with rod-like molecules. We have found that by carefully matching the chemical nature and the physical dimensions of the two types of molecules, three liquid crystals not exhibited by either component, are induced as the composition is varied. The compound with rod-like molecules exhibits the bilayer SmA_2 and nematic phases. The compound with BC molecules exhibits the B_2 phase. As the concentration of the rod-like molecules is increased, two mesophases specific to compounds with BC molecules, viz., B_1 and B_6, and a new biaxial smectic $A_2(SmA_{2b})$ phase are induced in the mixtures. A preliminary report of this result has been published by us recently.[6] In the present paper, we give the full details of our experimental results.

EXPERIMENTAL

The structural formulae of the two compounds used in the present study are shown in Figure 1. Both the compounds were synthesized in our laboratory.The details of synthesis are published elsewhere, and here we give only a brief outline of the procedure.

The BC molecules belong to the series 1, 3-phenylene bis [4-(3-methylbenzoyloxy)] 4′ -n-alkylbiphenyl 4′-carboxylates. Homologues with chain length varying from 4 to 12 have been synthesized. It is interesting to note that in this series the 5th to 7th homologues exhibit the B_6 phase, which is characterized by a typical focal conic texture. The 8th to 10th homologues exhibit the B_1 phase which is 2-dimensionally ordered. Homologues higher than the 11th one exhibit the lamellar B_2 phase.[7]

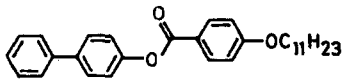
In our studies we have used the 12th homologue, viz. 1,3-phenylene bis [4-(3-methylbenzoyloxy)] 4′-n-dodecylbiphenyl 4′-carboxylate (BC12). This was prepared by condensing 3-methyl 4-benzyloxybenzoic acid with resorcinol in dichloromethane in the presence of N,N-dicyclohexyl carbodiimide (DCC) and N,N-dimethylaminopyridine (DMAP) as catalyst. The resulting product 1,3-phenylene bis [4-(3-methyl 4-benzyloxy)] benzoate was subjected to hydrogenolysis in 1,4-dioxan using 5 % Pd-C as catalyst. The final compound was prepared by reacting the purified 1,3-phenylene bis (3-methyl 4-hydroxy) benzoate with 4-n-dodecylbiphenyl 4′-carboxylic acid using DCC and DMAP. This was purified by column chromatogra-



BC12

$R = C_nH_{2n+1}$, n = 12

Cr 114.0 B_2 126.5 I



BO11

Cr 98.5 Sm A 109.5N 125.0 I

FIGURE 1 Molecular structure of the compounds used in the binary system studied

phy on silica gel and recrystallized several times until constant transition temperatures were obtained. The compound with rod-like molecules, viz., 4-biphenylyl 4″-n-undecyloxybenzoate (B011 for short) was synthesized following a procedure described elsewhere.[8]

Amongst the 'B' (or banana) liquid crystals exhibited by the BC molecules, upto now only the structure of B_2 phase appears to be well understood, especially since the work of Link *et al.*[9] The molecules are packed in layers with their polar (or 'arrow', *a*) axes oriented parallel to one another, giving rise to a transverse polarization *P*. The long (or 'bow-string', *b*) axes are tilted with respect to the layer normal as in the smectic C phase, but because of the transverse polarization along the *a* axis, the layer now becomes chiral, even though the molecules are achiral. Usually successive layers have antiferroelectric ordering in B_2 liquid crystals

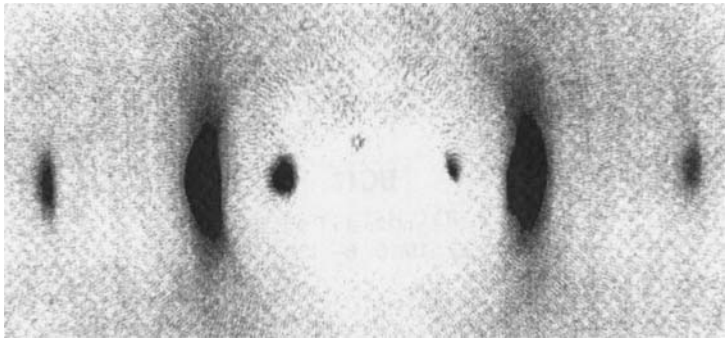


FIGURE 2 X-ray diffraction pattern of an aligned sample of B011 showing that the compound has a bilayer smectic A_2 structure (Reproduced from ref. 20 with permission from AAAS)

though some pure compounds and mixtures exhibiting the ferroelectric ordering have been studied recently [10,11] The structure can be homochiral or racemic depending on the relative orientation of the polarization and tilting directions in successive layers. Both structures coexist in typical samples. The lamellar B_2 phase is easily switchable by an external electric field. The compound with BC molecules used as one of the components in our studies on binary mixtures viz, BC12 exhibits the B_2 phase.

The compound with rod-like molecules, viz., B011 has a biphilic nature: it has a strongly aromatic moeity, but with an alkoxy chain only at one end, and exhibits the nematic and smectic A phases as it is cooled from the isotropic phase. Earlier x-ray studies using a photographic film had shown only a spacing corresponding to the molecular length. [12] We have recently conducted a more careful study on a magnetically aligned sample taken in a Lindemann capillary tube using a rotating anode x-ray generator and an image plate. The diffraction pattern (Figure. 2) clearly shows an inner sharp Bragg spot corresponding to a scattering vector q $= \pi/d$, i.e, a bilayer spacing. Such a smectic A_2 structure is known to occur in compounds with highly polar cyano or nitro end groups and other dipoles in the aromatic core which are oriented in an opposite direction to that of the end group.[1] B011 appears to be the first example of a

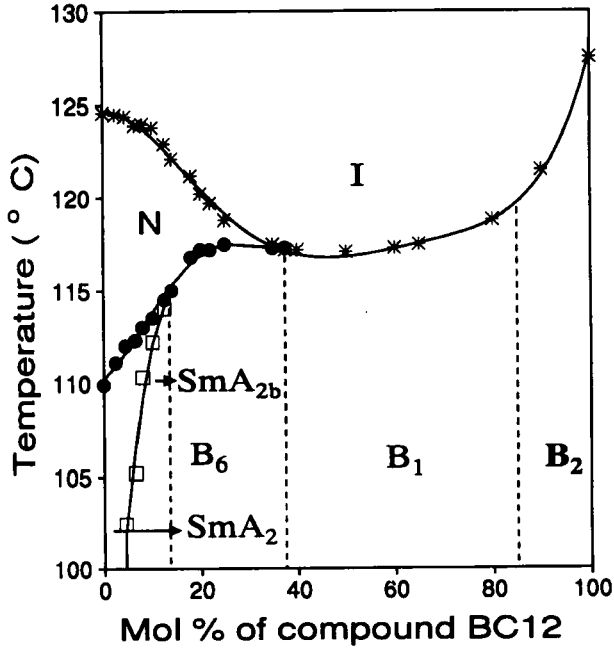


FIGURE 3 Phase diagram of mixtures of compounds BC12 and B011 (Reproduced from ref.6 with permission from AAAS)

compound without the highly polar end group to exhibit the SmA_2 phase implying that the attractive interaction of the aromatic ends of successive layers is rather strong.

The temperature versus concentration phase diagram of the binary mixture of B011 with BC12 is shown in Figure 3. The B_2 liquid crystal of both BC12 and its mixtures with less than 15 mol % of B011 exhibits typical textures with circular domains. As the concentration of B011 is increased the B_2 to isotropic phase transition temperature decreases fairly strongly, and beyond about 15 mol % of B011, the texture of the liquid crystalline phase changes drastically. A dendritic growth (Figure 4) is now seen as the sample is cooled across the isotropic to mesomorphic phase

FIGURE 4 Dendritic growth of the B_1 phase in a mixture with 50 mol % of BC12 at 117.1°C, crossed polarizers, (× 300)
See Color Plate XLII at the back of this issue.

transition temperature, and the field of view is covered with a mosaic texture at lower temperatures. The texture is typical of the B_1 phase. An aligned sample was prepared by placing a drop of the material on a horizontal glass plate pretreated with octadecyl triethoxysilane (ODSE) which gives a homeotropic alignment. The sample was slowly cooled to the required temperature in an appropriate oven and the x-ray diffraction pattern was recorded (Figure 5). It clearly reveals the 2-dimensionally periodic structure characteristic of the B_1 phase. A contact preparation between 1,3-phenylene bis [4-(3-chlorobenzoyloxy)] 4′-n-undecylbiphenyl 4-carboxylate (which shows the phase sequence Cr 128°C B_1 153°C I[7] and the mixture with ~ 40 mol % of B011 shows complete miscibility confirming that the mesophase formed by the mixture is indeed the B_1 phase.

As the concentration of B011 is increased beyond ~63 mol %, the texture again changes. The isotropic phase first goes over to the uniaxial nematic phase from which batonnets form at a lower transition point.

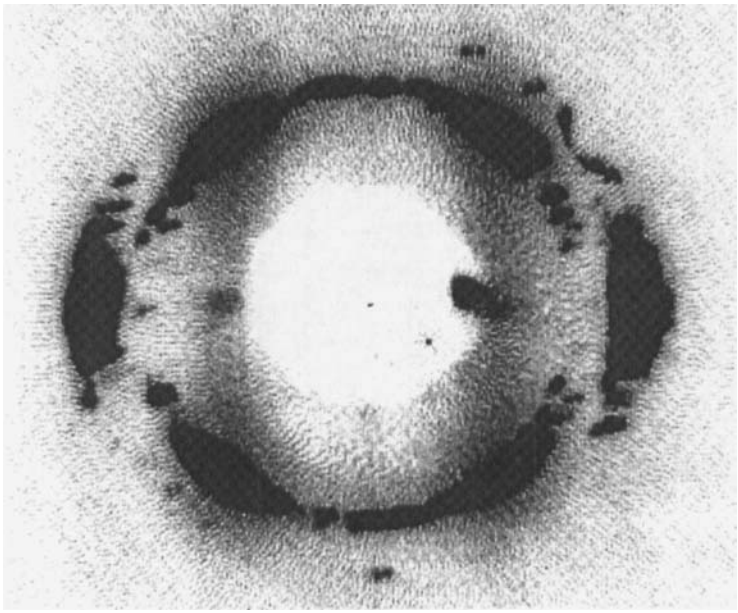


FIGURE 5 X-ray diffraction pattern of a mixture with 60 mol % of BC12 in the B_1 phase at 112°C (Reproduced from ref.20 with permission from AAAS)

The batonnets join together to form a focal conic texture as the temperature is lowered further (Figure 6) clearly showing that the medium has a layered structure. As the temperature is lowered even further, defect walls parallel to the layers are seen to develop. Observations using a polarizer show that they are twist walls. The texture is moderately switchable under a low frequency ($\sim$ 10Hz) external electric field applied between two ITO coated plates. X-ray diffraction studies on a magnetically aligned sample taken in a capillary tube indicate that there is a small tilt angle ($\sim 10^o$) between the director and the layer normal. A contact preparation between the compound 1,3-phenylene bis [4-(3-methyl benzoyloxy)] 4′-n-heptylbiphenyl 4′-carboxylate which has the phase sequence Cr 146°C

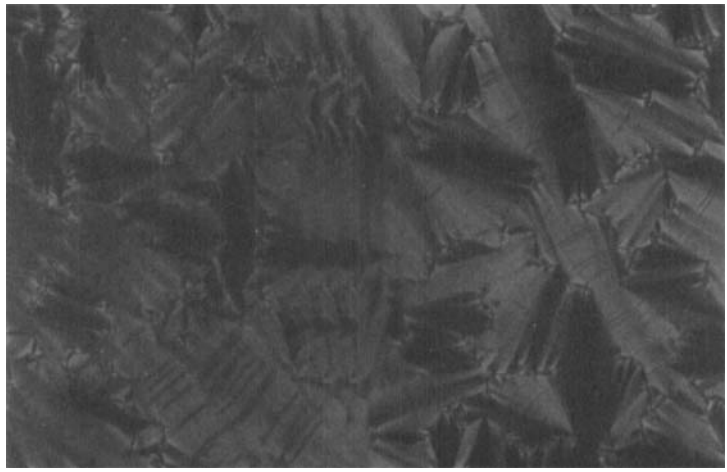


FIGURE 6 Focal conic texture of the B_6 phase in a mixture with 25 mol % of BC12 at 115°C, crossed polarizers, (× 240)
See Color Plate XLIII at the back of this issue.

B_6 147.5°CI[7] and the mixture with ~ 80 mol % B011 shows a complete miscibility of the liquid crystals. Thus the low temperature mesophase exhibited by the mixture is the B_6 phase.

As the concentration of B011 is increased beyond ~ 87 mol %, the nematic goes over to a homeotropically aligned SmA phase as the temperature is lowered in cells whose glass plates are pre-treated with *ODSE*. If the concentration of B011 is below ~ 95.5 mol %, the mixture undergoes an additional phase transition as it is cooled, giving rise to a schlieren texture at lower temperatures (Figure 7). The most important feature of the schlieren texture is that there are a large number of two brush defects, ie., disclinations of strength 1/2. These observations show that the medium develops a vector field in planes parallel to the layers, which is *apolar* in nature. We shall argue in the next section that it is a biaxial smectic A phase in which the BC molecules have changed their orientation, compared to that in the other B phases occuring at lower concentrations of B011.

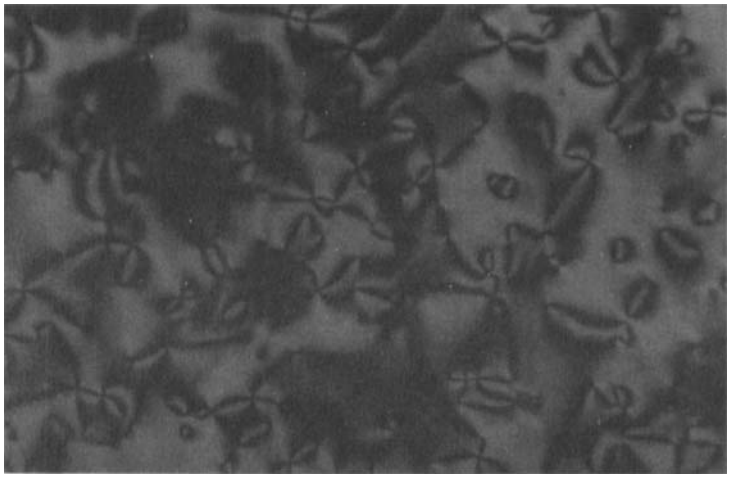


FIGURE 7 Schlieren texture of the SmA_{2b} phase exhibited by the binary mixture with 8 mol % BC12, taken between ODSE coated glass plates at 111.3^oC, crossed polarizers, (× 300). Note the large number of defects with strength 1/2 (Reproduced from ref.6 with permission from AAAS)
See Color Plate XLIV at the back of this issue.

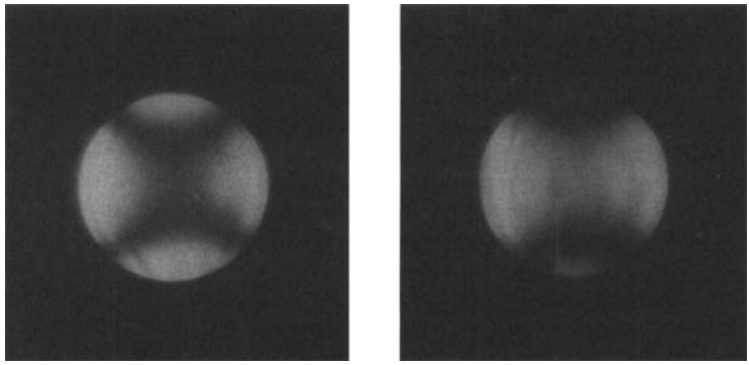
The complete phase diagram is shown in Figure 3. Starting from pure B011, as the concentration of BC12 is increased, the N-I transition point comes down, but the smectic A_2 to N transition point goes up so that the temperature range of stability of the N phase decreases rapidly. It shrinks to zero at a concentration at which the B_1 phase appears, so that four first order lines corresponding to N-I, I-B_1, B_1-B_6 and B_6-N transitions meet at a point. The biaxial smectic phase SmA_{2b} appears when the concentration of BC12 exceeds about 4.5 mol %, and the SmA_{2b} to SmA_2 transition temperature increases rather rapidly as the concentration of BC12 is increased, and thus the temperature range of the uniaxial SmA_2 phase also decreases rapidly. There is a second point at which four first order lines, corresponding to N-B_6, B_6-SmA_{2b}, SmA_{2b} - SmA_2 and SmA_2-N transitions appear to meet.

Starting from the composition with pure BC12, the B_2 to isotropic phase transition point decreases by $\sim 10^o$ as the concentration of B011 molecules is increased to $\sim$ 15 mol %. On the other hand, the B_1 to isotropic phase transition point decreases gradually, only by $\sim 2^o$ as the concentration of B011 is increased. From the phase diagram (Figure 3), it is clear that increasing the concentration of the rod-like B011 molecules induces three liquid crystalline phases in the binary mixtures. The 2-D ordered B_1 phase occurs over the widest composition range, viz., $\sim$ 18 to 63 mol % of B011. The B_6 phase occuring in the range with 63 to 87 mol % of B011 undergoes a transition to the nematic phase at higher temperatures. In the homologous series belonging to the BC molecules used in this study, the B_1 phase occurs in compounds with intermediate chain lengths (n = 8 to 10), while the B_6 phase occurs for relatively short chain lengths, ie., when n = 5 to 7. Thus, increasing the concentration of the rod-like molecules is equivalent to shortening the chain length of the BC molecules.

The most novel feature of the phase diagram is the induction of a new liquid crystalline phase, viz., the biaxial smectic A_{2b} phase, which will be discussed in the next section.

BIAXIAL SMECTIC A PHASE

The widely studied nematic and smectic A liquid crystals made of rod-like molecules are both uniaxial in nature, i.e, there is a cylindrical symmetry in the molecular distribution about the director $\hat{n}$. If the constituent molecules are themselves biaxial, it is in principle possible that the N and SmA liquid crystals themselves can have biaxial symmetry, and the medium has to be then characterized by three directors. The biaxial nematic phase was discovered in a lyotropic system by Yu and Saupe long ago.[13] More recently a polymeric system has been found to exhibit both the biaxial nematic (N_b) and biaxial SmA (Sm A_b) phases.[14] It would be very useful to obtain these liquid crystalline phases in low molecular weight compounds so that physical studies become relatively easier. Over the past couple of decades, there has been a large effort to look for the N_b phase in low molecular weight compounds and though there have been occasional claims of success, there is as yet no unambiguous evidence for a biaxial nematic liquid crystal.[15] Theoretical studies[1] also suggest that binary mixtures of rod-like and disc-like nematogens could give rise to the N_b phase, but as mentioned earlier, an experiment[5] has shown only a coexistence of two uniaxial N liquid crystals in agreement with a model in which the chemical potential of the mixture has been properly evalua-



(a) (b)

FIGURE 8 Photomicrographs of the conoscopic patterns in the SmA_{2b} phase from a free standing film of a mixture with 8 mol% of BC12 (a) The photograph was taken at 102°C and shows the splitting of the pattern (b) The photograph was taken at 95°C and shows the widening of the biaxial angle
See Color Plate XLV at the back of this issue.

ted.[16] Thus it is noteworthy that in the binary mixture studied by us the two types of molecules with very different shapes do indeed mix quite well to induce several liquid crystalline phases not exhibited by either component. This is facilitated by the fact that the aromatic part of the rod-like molecule and one wing of the BC molecule have very similar dimensions as well as chemical structure. The aliphatic chain lengths of the two types of molecules are also similar.

The most novel feature of the phase diagram of the binary system is the induction of the biaxial smectic A phase. When the concentration of the BC12 is in the range of $\sim$ 4.5 to $\sim$ 13 mol %, the nematic goes over to the uniaxial smectic A phase which can be aligned homeotropically between two ODSE coated plates. Such a preparation exhibits a dark field of view between crossed polarizers. As the temperature is lowered a phase transition takes place at a temperature which decreases rapidly as the concentration of BC12 molecules is lowered. Below the transition point, the homeotropically aligned sample exhibits a schlieren texture (Figure 7), with dark brushes emerging from several points. This clearly

indicates that the medium is no longer cylindrically symmetric about the layer normal, and it is biaxial in nature. If the biaxiality is due to a tilting of the molecules as in smectic C or B_2 liquid crystals, only 4-brush defects with strength $\pm$ 1 can be seen in the field of view, as the C-vector is a polar vector. On the other hand in the sample studied by us we see a large number of 2-brush defects with strength $\pm$ 1/2. X-ray studies indicate that in these B011 rich compositions, the medium has a bilayer structure as in pure B011 and the medium can be characterized as SmA_{2b}. The biaxiality of the medium was also confirmed by a conoscopic observation of a 100μm thick free standing film mounted in a 2mm diameter hole in a glass slide. As seen in Figures 8a and 8b, the uniaxial cross splits below the transition point and the biaxial angle increases substantially as the temperature is lowered. These observations indicate three possibilities:

i) The BC molecules are arranged such that the arrow or symmetry axes lie in the layer planes as shown in Figure 9a, such that each BC molecule is accommodated in a bilayer. This is possible since the dimensions of both aromatic and aliphatic parts of the two species match in this configuration. Packing efficiency would favour the BC molecules to lie parallel in the bilayers and thus generate a *polar* vector field. However, it is possible to get defects with two brushes in this case also if neighbouring bilayers have an antiferroelectric orientation of the BC molecules and the 1/2 strength disclination is coupled to a screw dislocation with a Burgers vector whose magnitude is equal to a bilayer spacing. This results in a dispiration as in antiferroelectric liquid crystals.[17] We denote this configuration by the symbol SmA_2 T_{af} which indicates that we have a bilayer of rods and a transverse antiferroelectric configuration of the BC molecules.

ii) The BC molecules can be oriented with their arrows in the layers as in the previous configuration, but within each bilayer the arrow directions can take two opposite orientations with equal probability in view of the low concentration of the BC molecules (Figure 9b). In this case the director in the layer plane is *apolar* in nature and can generate the 1/2 strength disclinations. We denote this structure by the symbol SmA_2 T_{ap} where the suffix *ap* indicates 'apolar'.

iii) The BC molecules can change their orientation such that the arrow directions are *along* the layer normal, as shown in Figure 10a. This is possible in the present case as the dimensions of the aromatic and aliphatic parts of the BC molecules again match with those of rods in one layer. It is also clear from Figure 10a that in this configuration, the BC molecules are oriented such that the arrows necessarily point in opposite directions in the two layers of a bilayer. The transverse (i.e, in-layer) director in this

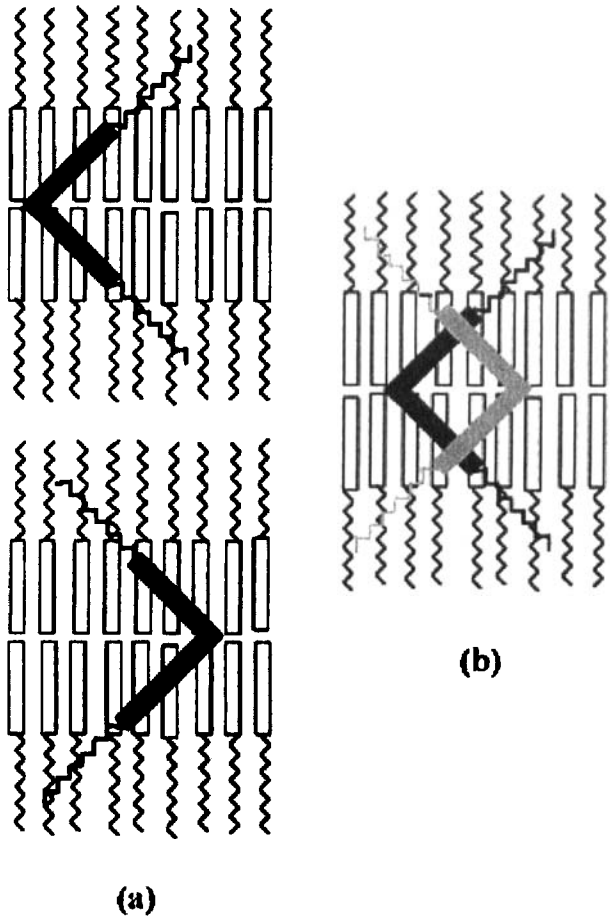


FIGURE 9 Schematic representation of (a) SmA_2 T_{af} structure showing the bilayer of rods and a transverse antiferroelectric configuration of the BC molecules (b) SmA_2 T_{ap} structure showing that the director in the layer plane is apolar in nature. The 2 different shades of the BC molecules indicate that they are in different planes

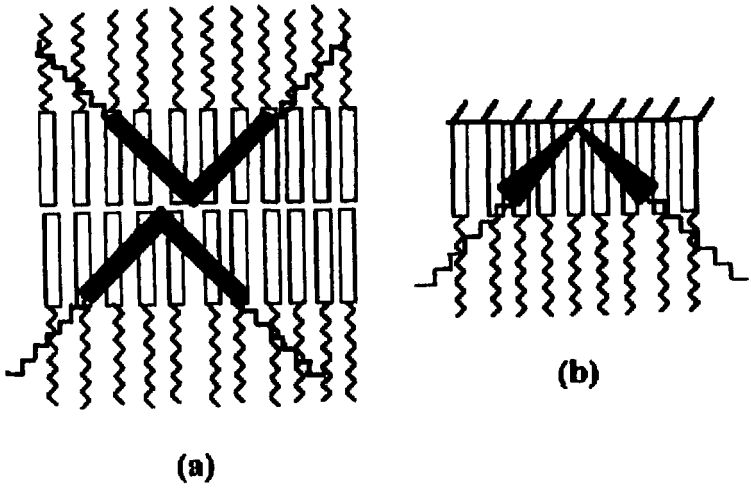


FIGURE 10 Schematic representation of the (a) SmA_2 L_{af} structure indicating longitudinal antiferroelectricity (b) BC molecules in a SmA_{2b} layer adjacent to an untreated glass plate

case is automatically *apolar* in nature and can give rise to defects of strength 1/2. We call this configuration SmA_2 L_{af} which indicates the longitudinally antiferroelectric nature of the structure.

Note that all the three proposed configurations can be described as orthogonal smectic A which is biaxial (SmA_{2b}). We have conducted some experiments to distinguish between the three possibilities:

(a) A homeotropically aligned sample was prepared between two glass plates, one of which had an ITO coating in which a gap of $\sim 100\mu$m was etched out. An AC electric field applied across the gap aligned the in-layer director. If the structure corresponds to SmA_2 T_{af} an external field can induce a ferroelectric structure whose polarization can switch under a reversal of the field. However, when a DC voltage of $\sim$ 200V applied across the sample was reversed, no switching was seen in the sample, in

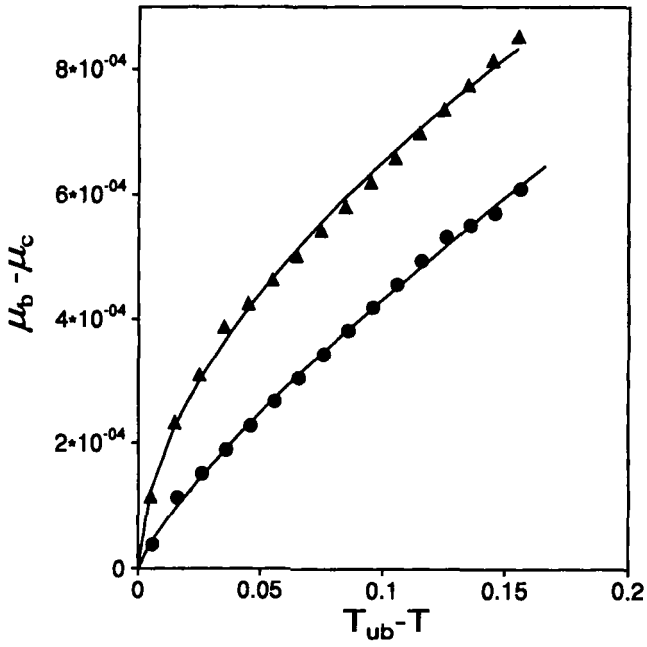


FIGURE 11 Measured birefringence μ_b-μ_c whose nonzero value is a measure of the biaxial order parameter. The symbol ▲ corresponds to a mixture with 8 mol % BC12 and • corresponds to 4.5 mol% of BC12. The lines are theoretical fits to the equation 2 in the text (Reproduced from ref.20 with permission from AAAS)

the mixture with 8 mol % BC12 which can be expected to have a polarization of a few 10s of nC/cm^2 in the structure shown in Figure 8a.

(b) We measured the birefringence of the field aligned sample as a function of temperature using a quarter wave plate (λ5893Å as the compensator. The sample temperature was controlled to $\sim$ 10mK using an INSTEC hot stage. The data for two different compositions are shown in Figure 11. If

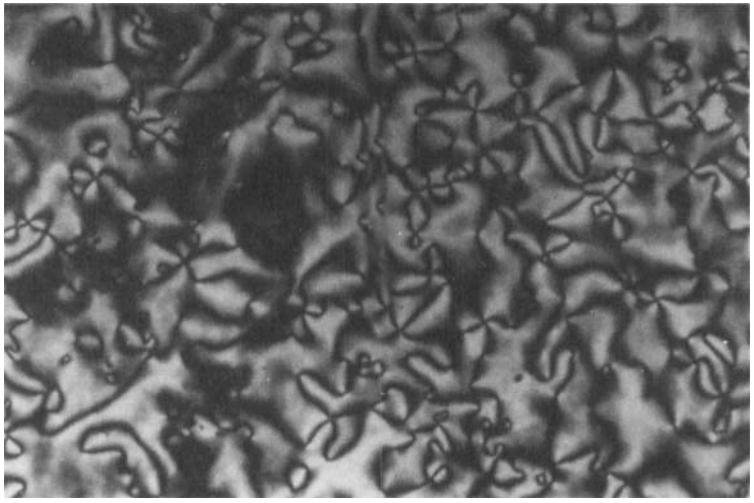


FIGURE 12 (a) Schlieren texture exhibited by the SmA_{2b} phase in a mixture with 8 mol % of BC12. Crossed polarizers, (× 300). Note the presence of defects with strength ± 1 and ± 1/2
See Color Plate XLVI at the back of this issue.

the configurations of the SmA_{2b} phase is either SmA_2 T_{af} or SmA_2 T_{ap}, the birefringence corresponds to μ_a - μ_c where μ_a is the refractive index of the medium for a light beam having a polarization parallel to the arrow ($\hat{a}$) director and μ_c that for the polarization along $\hat{c}$ director, which corresponds to the axis perpendicular to the molecular plane of the BC molecule. On the other hand, for the configuration SmA_2 L_{af}, the birefringence corresponds to μ_b - μ_c where μ_b is the refractive index for a light beam which is polarized along the bow ($\hat{b}$) director. From the known principal polarizabilities of the rods and the BC molecules, and the concentration of the latter, we can estimate the birefringence for the two types of anisotropies if the biaxial order parameter is known. If the orientational order parameter corresponding to the rods in the smectic A_2 background is considered to be practically temperature independent, we

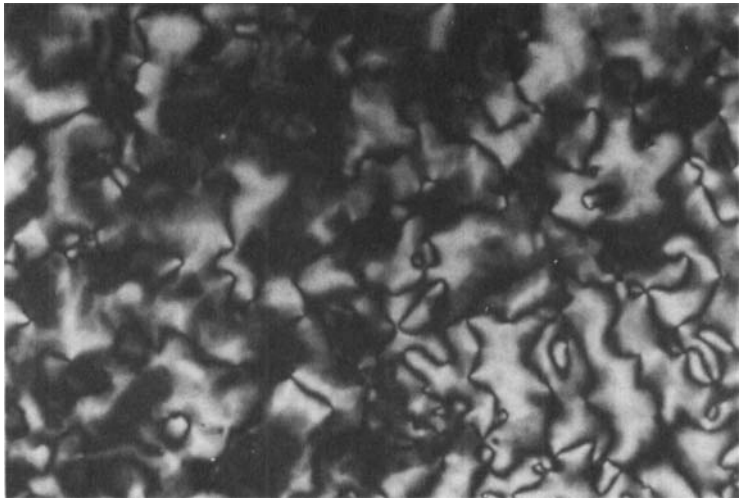


FIGURE 12 (b) Same sample as in Figure 12a. Note that the defects of strength 1 have split into defects of strength 1/2 after the passage of wave-like fluctuations.
See Color Plate XLVII at the back of this issue.

can define the biaxial order parameter as

$$\eta = < \cos 2\phi > \quad (1)$$

where ϕ is the azimuthal angle made by the *'a'* or the *'b'* axes of the BC molecules in the two configurations respectively with the relevant director, and the angular brackets denote a statistical average. If $\eta \simeq 0.3$, for the mixture with 4.5 mol % of BC molecules at T_{bu}-10 °C, the expected value of $\mu_b - \mu_c \simeq .007$, which compares well with the experimental value. On the other hand, $\mu_a - \mu_c$ is about 3 times smaller. This clearly favours the structure SmA_2 L_{af} for the biaxial smectic phase.

(c) An interesting observation on the cells made of ODSE-coated plates is that as the temperature is lowered in the SmA_{2b} phase the schlieren

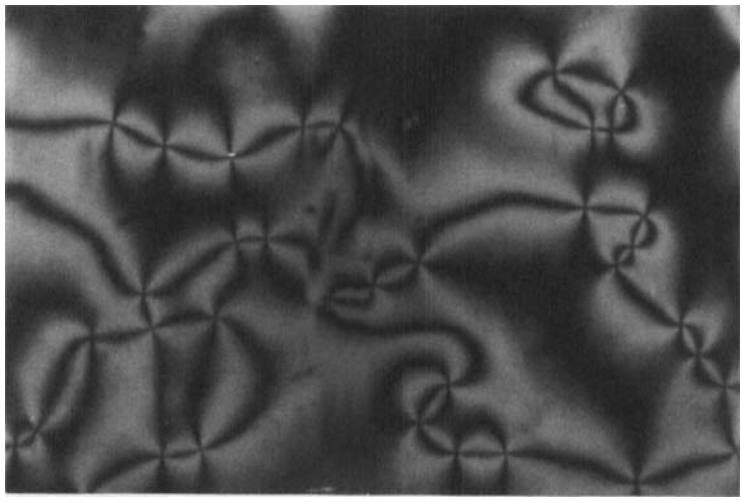


FIGURE 13 Schlieren texture exhibited by the SmA_{2b} phase in a mixture with 8 mol % BC12, taken between untreated clean glass plates, crossed polarizers (× 300). Note the presence of defects with strength ±1 only.

See Color Plate XLVIII at the back of this issue.

texture is not static. Wave-like fluctuations occur in the medium, similar to those seen in ferrielectric liquid crystals. Sometimes this results in a splitting of a strength 1 defect to two strength 1/2 defects (Figures 12a,b). One possible origin of the fluctuations is a reorientation of the in plane director as a consequence of a motion of smectic bilayers in the sample. Indeed when the cell is constructed with cleaned but otherwise untreated glass plates, the texture looks very different from the previous case. There are defects of strength ± 1 only in the field of view (Figure 13), which do not exhibit any wave-like fluctuations when the temperature is varied. Presumably the silicon dioxide surface of the glass attracts the highly aromatic parts of both types of molecules in the mixture resulting in a tilting of the 'arrow' axes of the BC molecules (Figure 10b) near the glass

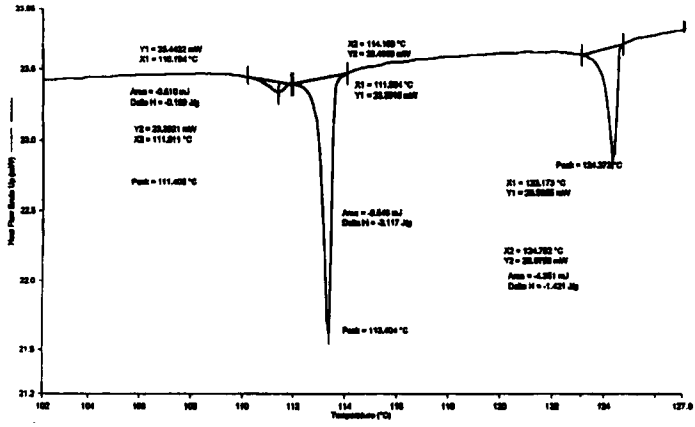


FIGURE 14 (a) Differential scanning thermogram of a mixture with 8 mol % of compound BC12 in the cooling mode. The peaks at $\sim$ 124.4°C, 113.4°C and 111.4°C correspond to I-N, N-SmA_2 and SmA_2-SmA_{2b} transitions respectively (Reproduced from ref.20, with permission from AAAS)

plates to increase the attractive interaction. This tilted orientation of the *'a'* director leads only to $\pm$ 1 defects as in smectic C liquid crystals. The absence of wave-like fluctuations might be due to an effectively stronger anchoring of the biaxial director on the surfaces. This observation also supports the SmA_2 L_{af} structure of the SmA_{2b} phase.

The uniaxial to biaxial SmA_2 transition in the mixture arises from an orientational transition of the BC molecules in the background anisotropic SmA_2 medium made of rod-like molecules. Differential scanning calorimeter runs (using a Perkin-Elmer Pyris 1D) clearly indicate a weak first order transition (Figure 14 a,b). The heat of transition is $\sim$ 200 J/mol for a concentration of $\sim$ 8 mol % of BC12 and reduces to $\sim$ 20 J/mol for the mixture with 4.5 mol % of BC12. It may be worth noting that the only other biaxial smectic A liquid crystal occurs in a polymeric system and is

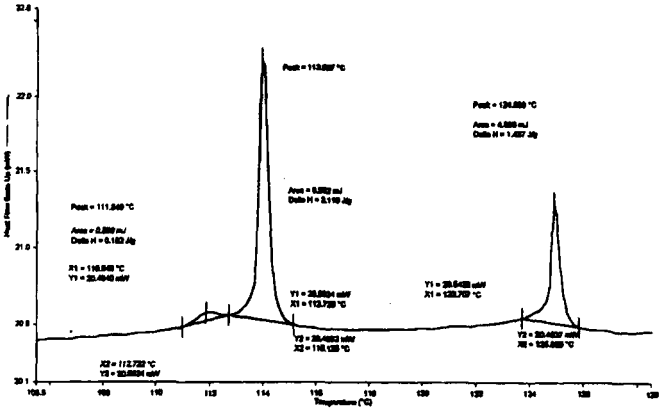


FIGURE 14 (b) Differential scanning thermogram of the same mixture as in Figure 14 (a) in the heating mode, showing that all the three transitions are reversible (Reproduced from ref.20 with permission from AAAS)

obtained on cooling from the N_b phase.[14] Further, when the polymer is mixed with its monomeric species the mixtures exhibit the SmA_b and N_b phases when the concentration of the polymer is higher than some value, and only the uniaxial phases below that value. There is no uniaxial to biaxial transition either in the nematic or smectic phase in this system. The mixture studied by us exhibits a rather different behaviour in which the BC molecules undergo an orientational transition when their concentration is as low as 4.5 mol%.

The uniaxial to biaxial transition can be expected to be described by xy models. The birefringence $(\mu_b - \mu_c)$ is a measure of the order parameter η and we fitted the data for the two concentrations shown in Figure 11 using the equation

$$\mu_b - \mu_c = C(T_{bu} - T)^{\beta} \tag{2}$$

to get the order parameter critical index β. For the xy model, $\beta \simeq 0.35$.[18] We found that for the mixture with 4.5 mol % of BC molecules, $\beta \simeq 0.79$ and for that with 8 mol % of BC molecules, $\beta = 0.56$. As seen in the phase diagram, the biaxial to uniaxial transition line tends to become vertical near 4.5 mol % . In that case β is expected to be doubled due to geometrical reasons as has been found in systems exhibiting the reentrant nematic phase which has a similar sharp curvature in the phase boundary.[19] Even though the curvature of the boundary is lower for mixtures with higher concentrations of the BC12 (Figure 3), it is not small enough to recover the normal xy value of β.

CONCLUSIONS

We have found that three liquid crystalline phases not exhibited by either component are induced in binary mixtures of B011 and BC12,. Two of them, viz., the 2-dimensionally ordered B_1 and the as yet not well understood B_6 phases are known to be exhibited by compounds with BC molecules. Increasing the concentration of rod-like molecules is equivalent to a shortening of the chain length of BC molecules. At sufficiently low concentrations of BC12 a new liquid crystal which has to be described as SmA_{2b} phase is induced as well, and we have argued that it corresponds to a reorientation of the BC molecules such that their arrow directions are along the layer normal, while in the B-liquid crystals they are in the plane of the layers. It is also noteworthy that any given mixture exhibits only one of the liquid crystals and there is no phase transition between B_2 to B_1, B_1 to B_6 or even B_6 to SmA_{2b} liquid crystals, and the relevant transition lines are essentially vertical (Figure 3). It is known that compounds with BC molecules are generally monomesomorphic in nature.

A well studied case of induced phase is that of a smectic A which is obtained in binary mixtures of two nematogens, one with the highly polar cyano or nitro end group and the other without such a group.[2] Charge transfer complex formation between the two species appears to favour the layering order in that case. The detailed structures of B_6 and B_1 liquid crystals which are induced in the mixture studied here are not yet fully established, and the intermolecular interactions responsible for the induced phases remains to be explained.

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