Two-dimensionally periodic phases in mixtures of compounds made of rodlike and bent-core molecules

R. Pratibha, N. V. Madhusudana, and B. K. Sadashiva

Raman Research Institute, C.V. Raman Avenue, Bangalore 560080, India

We report two distinct types of two-dimensionally periodic phases in different concentration regions of a binary system composed of the bent-core (BC) compound 1,3-phenylene bis[4-(3-methylbenzoyloxy)]4′-n-dodecylbiphenyl 4′-carboxylate (BC12) and the rodlike (R) compound 4-n-octyloxy 4′-cyanobiphenyl (8OCB). BC12 exhibits only the lamellar B_2 phase. 8OCB which has a highly polar cyano end group exhibits the smectic-A_d phase with a lamellar structure of partial bilayers made of antiparallel pairs of the polar molecules. The molecular arrangements in the two-dimensionally periodic phases have been deduced based on optical microscopy, polarized infrared and x-ray diffraction studies. The arrangement in the two-dimensionally periodic phase in lower concentration ranges of BC12 (24 to 35 mol%) is dictated by the partial bilayer structure formed by the rods. The BC molecules arrange themselves with their arrow axes parallel to the long axes of the R molecules and the structure conforms to the $c2mm$ space group symmetry. In higher concentration ranges of BC12 (35 to 60 mol%) the structure is dominated by the BC molecules, to form the familiar B_1 phase with the $p2mg$ space group symmetry. The R molecules lie at the interfaces of these domains stabilizing the structure.

I. INTRODUCTION

Currently liquid crystals (LCs) made of bent-core (BC) molecules are being investigated intensively. The B phases exhibited by such compounds are a distinct class of LCs different from the ones exhibited by compounds made of rodlike (R) or disklike molecules. Among the B-type LCs the B_2 phase has a lamellar structure usually with an antiferroelectric interlayer ordering. Within each layer the polar ordering of the molecules combined with a tilting of the molecules about the arrow axes gives rise to layer chirality [1]. The B_1 phase has a two-dimensionally periodic rectangular columnar structure and the B_6 phase has an intercalated layered structure [2]. Usually in a homologous series of compounds made of symmetrically substituted BC molecules, the B_2, B_1, and B_6 phases occur with decreasing chain length [3]. Mixtures of compounds exhibiting LCs have often yielded new phases and phase sequences not present in either of the components. We have carried out extensive studies on mixtures of compounds made of R and BC molecules [4–6]. Different types of molecular arrangements yielding induced phases have been found. Detailed experiments have been reported on the binary system (SI) composed of the compound 1,3-phenylene bis[4-(3-methylbenzoyloxy)] 4′-n-dodecylbiphenyl 4′-carboxylate (BC12) [Fig. 1(a)] made of BC molecules and exhibiting only the B_2 phase and the R compound 4-biphenylyl 4″-n-undecyloxybenzoate (BO11) [7] [Fig. 1(b)] which exhibits the nematic (N) and bilayer smectic-A (A_2) phases. The temperature-concentration phase diagram of SI is shown in Fig. 2. Three phases are induced in this system. In SI the sequence B_2, B_1, and B_6 occurs with increasing concentration of the compound with R molecules. The reasons for the formation of these three phases in both single components made of BC molecules and in mixtures of SI have been discussed in Refs. [6,8,9]. The other interesting feature found in mixtures of SI with low concentrations of

BC12 (4.5–13 mol%) is the induction of the orthogonal biaxial smectic-A phase (SmA_{2b}) [4–6]. A model for the mutual orientations of R and BC molecules in the SmA_{2b} phase was proposed earlier [4,5].
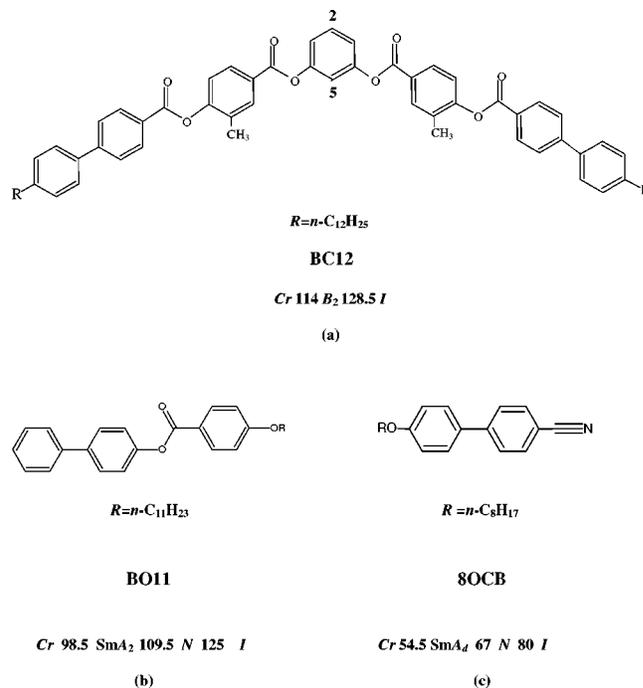

FIG. 1. Molecular structures and phase sequences exhibited by compounds used in the binary mixtures of SI and SII (a) 1,3-phenylene bis[4-(3-methylbenzoyloxy)] 4′-n-dodecylbiphenyl 4′-carboxylate (BC12) made of bent-core molecules and used in both SI and SII (b) 4-biphenylyl 4″-n-undecyloxybenzoate (BO11) made of R molecules and used in SI (c) 4-n-octyloxy 4′-cyanobiphenyl (8OCB) made of R molecules and used in SII.
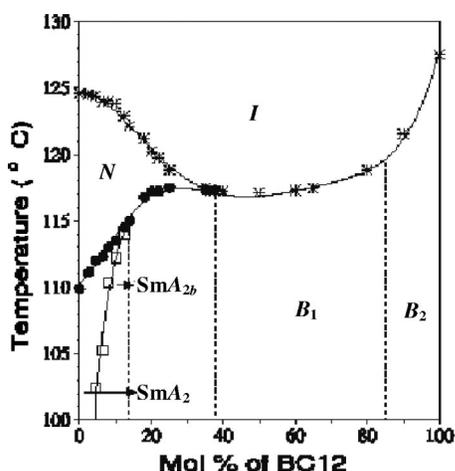
FIG. 2. Temperature-concentration phase diagram of mixtures of SI (reproduced from Ref. [4] with permission from AAAS).

In the present paper, we report detailed experimental studies on a different binary system (SII) with the same compound made of BC molecules, i.e., BC12 used in SI. The compound with R molecules is however the well-known compound 4-n-octyloxy 4$'$-cyanobiphenyl (8OCB) [Fig. 1(c)] which exhibits a partial bilayer smectic-A (SmA_d) phase. This compound has the strongly polar cyano end group and the SmA_d phase forms due to an antiparallel orientation between neighboring polar molecules such that the aromatic cores overlap [10]. The main motivation of choosing 8OCB is to be able to use infrared (IR) dichroism studies on the mutually exclusive nitrile group of 8OCB and the ester groups in BC12 molecules. Such studies enable us to investigate the mutual orientation of the two types of molecules in different liquid crystalline phases. Indeed a preliminary IR study was reported on a mixture with 11 mol% of BC12 in Ref. [6], in which the polar plots of absorbance corresponding to the two chemical groups were presented. A biaxial smectic-A (SmA_{db}) phase is also induced in this system (SII) for concentrations in the range of 10.5 to 24 mol% of BC12. X-ray studies indicate that the R molecules form a partial bilayer structure even in the SmA_{db} phase. The proposed [6] mutual orientation of R and BC molecules in the SmA_{db} phase is shown in Fig. 3. Though both the lengths of the aromatic and the chain moieties of 8OCB are shorter than
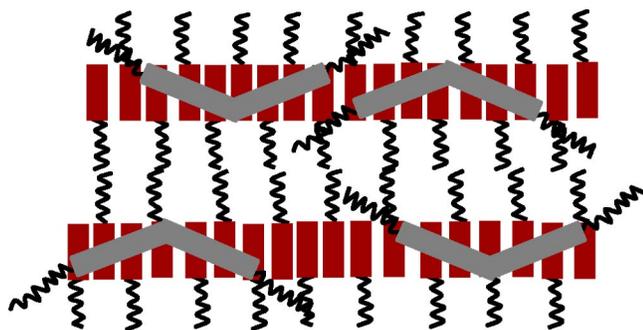

FIG. 3. Schematic representation of the molecular arrangement in the SmA_{db} liquid crystal occurring in some mixtures of SII (adapted from Ref. [6]).

those of BO11 used in SI, as seen in Fig. 3, the aromatic core and the chains of BC12 can fit into the partial bilayer structure of 8OCB. Experimental studies with polarized infrared radiation on a mixture with 11 mol% of BC12 have shown that the angular dependence of the peak absorbance is consistent with the proposed model [6]. In this paper we describe the detailed temperature-concentration phase diagram of SII which has been constructed based on textural observations, x-ray diffraction and polarized infrared studies. The molecular arrangements in two different types of two-dimensionally periodic phases induced in this system are also described. One of them corresponds to the B_1 phase formed in pure compounds made of BC molecules which has a domain structure with the arrow axes of the BC molecules lying in the plane of the 2D lattice. One of the lattice parameters ($=b$) corresponds to the width of six to eight molecules. Often there is no tilt of the molecules and the other lattice parameter "a" is equal to the length of the molecule along the bow axis. The medium is nonswitchable. Variants of the B_1 phase showing additional reflections in the x-ray patterns have been observed (B_{1x}) [11] in some mesogens made of BC molecules. More recently switchable variants of the B_1 phase have also been obtained (B_{1rev}) [12]. The 2D periodicity in this case occurs in a plane orthogonal to the arrow axes.

In order to elucidate the 2D structures formed in SII, we have carried out studies with polarized infrared radiation on mixtures having 24 and 35.3 mol% of BC12. Detailed x-ray diffraction studies have also been performed on mixtures with 24 to 55 mol% of BC12. These studies show evidence for two different types of molecular arrangements forming rectangular columnar structures in two concentration ranges. In the lower concentration range of BC12 (24 to 35 mol%) the structure is dominated by the partial bilayer structure formed by the rods. The BC molecules which are oriented with their arrow axes *along* the layer normal of the partial bilayer structure (see Fig. 3), arrange themselves in the layers to generate an additional periodicity along the bow axes. As the microscopic texture of this LC is somewhat similar to that of the B_1 phase we refer to this phase as B_1'. As the concentration of BC12 is increased (35 to 60 mol%), the orientation of the BC molecules with respect to the R molecules changes. The BC molecules form the type of domain structure seen in the usual B_1 phase. The rods, which are now fewer in number, stabilize the structure by lying at the interfaces between the domains as in SI.

II. EXPERIMENTAL RESULTS

In further discussions all concentrations mentioned (X) refer to that of BC12 in mol% in SII and specific mixtures are denoted as MX. The BC compound BC12 has been synthesized in our laboratory [3] and the R compound 8OCB was procured from Hoffmann–La Roche, Switzerland.

A. Optical microscopy

When the sample M24 taken between glass plates treated for homeotropic alignment is cooled from the SmA_{db} phase
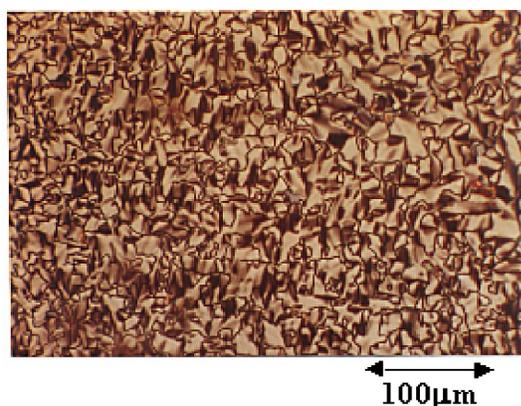
FIG. 4. (Color online) Optical texture exhibited by the lower temperature phase obtained by cooling from the SmA_{db} phase in mixture M24. The brushes present in the schlieren texture exhibited by the SmA_{db} phase now appear as sharp lines (crossed polarizers).

exhibiting a schlieren texture, below a certain temperature there is a slow transformation of the texture indicating a phase transition. This change takes place over 4° implying that there is a coexistence of the SmA_{db} and the lower temperature phase. Though the basic features of the schlieren texture remain, the dark brushes become sharper (Fig. 4) and the fluctuations of the director are no longer visible. We have carried out optical birefringence ($\Delta\mu$) measurements for light propagating along the layer normal as a function of temperature on an aligned sample of M24. In addition to having ODSE coated glass plates to obtain a homeotropic alignment of the rods, a transverse electric field (~ 4 V/μm, 10 kHz) was applied across the region in which the measurements were carried out. This technique enables alignment of all the three directors in the SmA_{db} phase. As shown in Fig. 5 a slope change is seen in the temperature variation of the birefringence across the phase transition temperature. However the change in birefringence is only gradual and no clear jump is seen. This is possibly because of the coexistence of the two phases as seen in the gradual change of texture in a sample observed without the application of a transverse electric field.
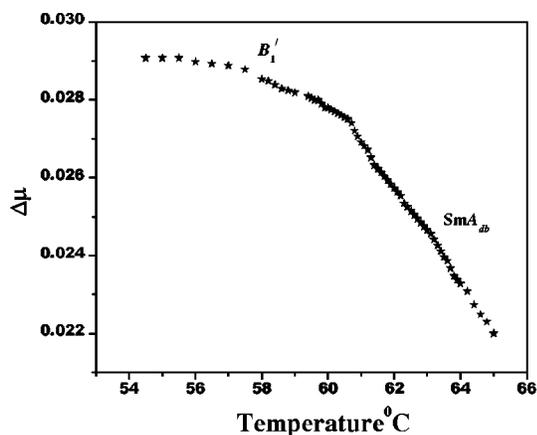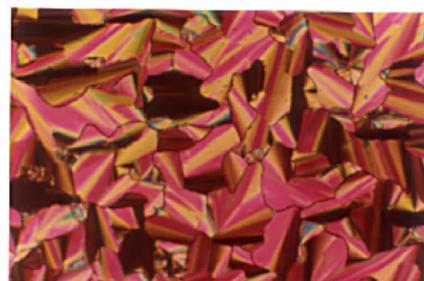

FIG. 5. Optical birefringence ($\Delta\mu$) for light propagating along the layer normal as a function of temperature in the SmA_{db} and the lower temperature phase in the mixture M24.

FIG. 6. (Color online) (a) Optical textures exhibited in the lower temperature phase obtained by cooling from the N phase in M30 (a) and M43 (b) and from the I phase in M50 (c), (crossed polarizers). These textures are usually characteristic of two-dimensionally periodic phases in compounds made of BC molecules.

When the concentration of BC12 is greater than 24 mol% and less than 35 mol%, a texture characterized by broad and smooth domains is obtained at the transition temperature on cooling from the nematic (N) phase in unaligned samples [Fig. 6(a)]. In mixtures with concentrations in the range of 35 to 50 mol%, the domains obtained on cooling from the N phase are very long and a central line is also visible [Fig. 6(b)]. The texture obtained on cooling from the isotropic phase in mixtures having more than 50 mol% of BC12 is very similar to the texture of the B_1 phase and has the central line [Fig. 6(c)]. These textures are characteristic of two-dimensionally periodic phases in compounds made of BC molecules.

Optical observations on cells treated for planar alignment show that the mixtures with 24 to 35 mol% of BC12 are well aligned while those with 50–60 mol% of BC12 are not aligned. Mixtures with intermediate concentrations exhibit an overall but poor alignment.
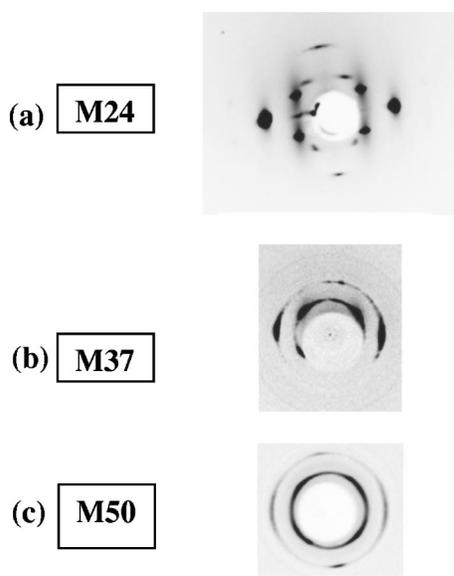
FIG. 7. X-ray diffraction patterns obtained from monodomain samples of M24 at 60 °C, M37 and M50 at 70 °C. The diffraction pattern for M37 is not fully visible because of a partial blockage by the wall of the heater in which the sample is mounted.

B. X-ray diffraction studies

X-ray diffraction studies were carried out using Cu K_{α} radiation from a rotating anode generator (Rigaku Ultrax 18) and an image plate (Marresearch). The sample is mounted as an open drop on a glass plate treated for homeotropic alignment and the x-ray beam is incident at a grazing angle to the glass plate. A magnetic field (1 K Gauss) is applied in a direction orthogonal to the plane of incidence of the x-ray beam on the glass plate. X-ray studies have been carried out on a few mixtures with 24 to 55 mol% of BC12. These mixtures have a tendency to crystallize if the temperature is maintained for more than about half an hour in the temperature range of 60–65 °C. In M24 both the SmA_{db} and the two-dimensionally periodic phases occur around this temperature range and hence it was difficult to obtain good x-ray diffraction patterns in both these phases on the same sample in a single cooling run. However a quick run with an exposure time of about 10 min in the SmA_{db} phase shows that the partial bilayer structure formed by the 8OCB molecules is still intact. The observed spacing gives a value of 28 Å for the partial bilayer thickness. When the sample is cooled into the lower temperature phase additional diffraction spots showing evidence for a 2D lattice are obtained. In order to confirm the presence of the 2D lattice in M24, an independent sample of the same mixture was cooled very fast to about 5° below the temperature at which the SmA_{db} phase transforms to the two-dimensionally periodic phase. The diffraction pattern obtained with an exposure time of about half an hour is shown in Fig. 7(a). The same procedure was followed to obtain the diffraction patterns for the other mixtures. The samples were usually cooled to about 12–13° below the relevant transition temperatures and the diffraction patterns were recorded. There was no significant temperature dependence of the observed spacings. The observed spacings
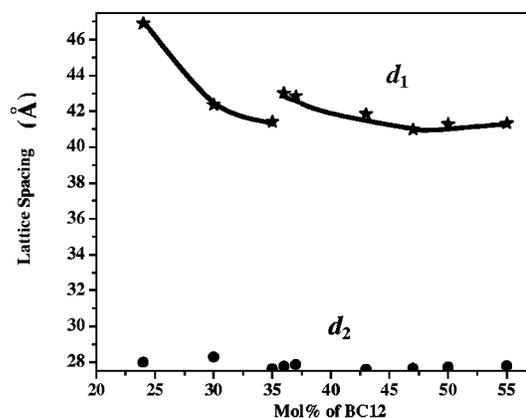

FIG. 8. The lattice spacings d_1 and d_2 obtained from x-ray measurements as functions of the concentration of BC12. Note the sudden increase in the spacing d_1 for a concentration around 35 mol% of BC12.

from the diffraction patterns could be indexed as reflections from a two-dimensional rectangular lattice in all the cases. One of the lattice spacings (d_1) corresponding to the (11) reflection shows a dependence on the concentration of BC12 (Fig. 8). There is a rapid decrease as the concentration is varied from 24 to ∼34.3 mol% of BC12. There is a sudden jump in this spacing for a concentration around 35 mol% of BC12 followed by a broad minimum around ∼50 mol%. The discontinuity in the value of d_1, for mixtures with concentrations around 35 mol% of BC12 indicates that there is some structural change in this concentration region. On the other hand the other lattice spacing (d_2) does not show any significant variation with concentration (Fig. 8).

C. Studies with polarized infrared radiation

Information about the orientation of molecules can be obtained by studying the angular dependence of polarized infrared peak absorbance related with different chemical bonds present in the molecule. In molecules forming liquid crystals it is convenient to specify one principal molecular axis say ζ whose average orientation is related with the orientational order in the medium, and two other transverse axes ξ and η which are mutually orthogonal. Usually in the R molecule ζ is taken to be along the long axis of the molecule. Depending on the orientation of the BC molecules ζ is along the bow axis (line joining the extreme carbon atoms of the aromatic core) or along the arrow axis [orthogonal to the bow axis and passing through carbon atoms at the 2 and 5 positions of the central ring (Fig. 1)]. If x,y,z refer to a laboratory fixed coordinate system, then the orientation of the molecule can be completely specified by the three Euler angles θ, ψ, and ϕ. Here θ is the angle between the z-axis and the ζ axis, ψ is the angle between the ξ axis and the normal to the z-ζ plane describing a rotation of the molecule around its long axis. ϕ is the angle between the x-axis and the normal to the z-ζ plane describing a rotation of the whole molecule around the director. In the uniaxial phase ϕ can take all values with equal probability. As the molecules are not exactly cylindrically symmetric the two transverse axes are distinguishable

and the orientational order must be described by two order parameters $S=(1/2)\langle 3\cos^2\theta-1\rangle$ and $D=(3/2)\times\langle\sin^2\theta\cos 2\psi\rangle$ [13]. D is called the *molecular* biaxiality order parameter. The BC molecules are highly biaxial in shape and an exact determination of the order parameters would require a knowledge of the geometry of the molecule. Also to measure the order parameter D two independent vibrational modes from the *same* molecule which can give rise to isolated bands in the infrared spectrum are required. In the binary system used in our study only the $C\equiv N$ bond (present in the R molecule) and the $C=O$ bond (present in the BC molecule) give rise to vibrational modes which are mutually exclusive to the two types of molecules. Other modes associated with the C–O and phenyl ring stretching are present in both the R and BC molecules and cannot be distinguished. As we have not been able to obtain D we have not measured the order parameters. However, as our main interest is to study the mutual orientation of the R and BC molecules, we have used the polarized IR bands corresponding to the $C\equiv N$ bond of 8OCB and the $C=O$ bond of BC12 (there are four such bonds in each BC molecule). These bonds which are unique to the two compounds yield information about the average orientations of the 8OCB and BC12 molecules independently.

A simplified form for the absorbance for a uniaxial medium involving only the order parameter S is given by

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

where α is the angle made by the chemical bond with the molecular axis which orients along the director and ω is the angle between the polarization direction of the incident radiation and the direction of the axis of symmetry (director) [14]. k is a coefficient related with the magnitude of the transition moment and the thickness of the sample.

The true integrated absorption intensity of a band [15] is proportional to $\ln(I_0/I)_{\nu_{max}}\Delta\nu^t_{1/2}$ where I_0 and I are the incident and transmitted intensities and $\Delta\nu^t_{1/2}$ is the half intensity width. In our experiment we found that there is no significant variation of $\Delta\nu^t_{1/2}$ for different settings of the polarizer. The band intensity is proportional to the peak absorbance $A_{peak}=\log(I_0/I)$ where the log is taken to the base ten and the proportionality constant is equal to $\log_e 10.\Delta\nu^t_{1/2}$. We have used the peak absorbance A_{peak} to get an idea of the mutual orientation of the molecules. I_0 and I are taken to be the experimentally obtained transmittances at the base line and at the peak maximum, respectively.

The $C\equiv N$ bond is along the long axis of the 8OCB molecule, which is along the axis of symmetry, i.e., $\alpha=0°$. As mentioned before, depending on the orientation of the BC molecule the arrow or bow axes can be along the axis of symmetry and α with respect to the appropriate axis should be considered. The SPARTAN 04 molecular mechanics (MMFF94) package has been used to obtain the conformation of the aromatic core of the BC12 molecule which is shown in Fig. 9. The angles (α) made by the four $C=O$ bonds indicated by 1,2,3,4 in Fig. 9 are $20°,87°,63°$, and $60°$ yielding $\sin^2\alpha=0.66$ with respect to the arrow axis. The
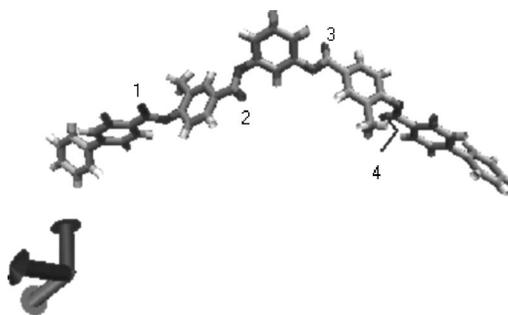

FIG. 9. Conformation of the central core of the BC12 molecule computed using the SPARTAN 04 molecular mechanics package from Wavefunction Inc.

angles are $90°,55°,83°$, and $46°$ with respect to the bow axis giving $\sin^2\alpha=0.79$. The BC molecule is therefore not symmetric as suggested by the structural formula and has a conformation that is chiral in nature. However, both left-handed and right-handed versions are equally possible. We found that each of the angles can vary slightly for different minimization runs such that $\sin^2\alpha$ can change by $\sim 1.5\%$. Further in the liquid crystalline phases the angles can be expected to be influenced by the environment, which depends on the relative concentration of R and BC molecules and the kind of packing in different phases.

Planar aligned samples were obtained using CaF_2 plates coated by oblique deposition of SiO in a vacuum chamber. The cell with a thickness of ~ 15 μm was taken in a suitable heater and the alignment of the sample checked in the nematic phase using a polarizing microscope. A wire grid polarizer (IGP 227, Moleotron Detector Inc.) was used to obtain polarized infrared radiation. The polarized spectra were recorded for different settings of the polarizer angle using the Shimadzu FTIR 8400 spectrophotometer.

The studies have been carried out on M11, M24, and M35.3. Mixtures with still higher concentration of BC12 could not be studied, as it was not possible to get good planar alignment. As we had noted previously [6] in the mixture M11, A_{peak} corresponding to the $C\equiv N$ bond shows a maximum when $\omega\approx 0$ and $180°$ in the nematic (N), SmA_d and SmA_{db} phases. However there is no notable angular dependence of A_{peak} corresponding to the $C=O$ bonds (Fig. 10). The R molecules orient such that the long axes are along the symmetry axis in the uniaxial N and SmA_d phases, and as $\alpha=0°$ for the $C\equiv N$ bond, the maximum in A_{peak} occurs for $\omega\approx 0$ and $180°$ [see Eq. (1)] as expected. Defining the dichroic ratio as $R_d=(A_{peak(\omega=0)})/(A_{peak(\omega=90°)})$, for $\sin^2\alpha=2/3$, $R_d=1$ and there would be no angular dependence of A_{peak}. The absence of angular dependence of A_{peak} in M11 suggests that $\sin^2\alpha$ is close to $2/3$, i.e., the arrow axes are aligned along the director. Also as the concentration of BC12 is small in M11 the order parameter of the arrow axes of the BC molecules can be expected to be relatively low contributing to the absence of dichroism of the $C=O$ band. If the bow axes had oriented along the axis of symmetry $\sin^2\alpha$ would be greater than $2/3$ and the maximum in A_{peak} would have occurred for $\omega\approx 90$ and $270°$.

The plots of A_{peak} as functions of ω for M24 in the N, SmA_{db} and the two-dimensional periodic phases are shown
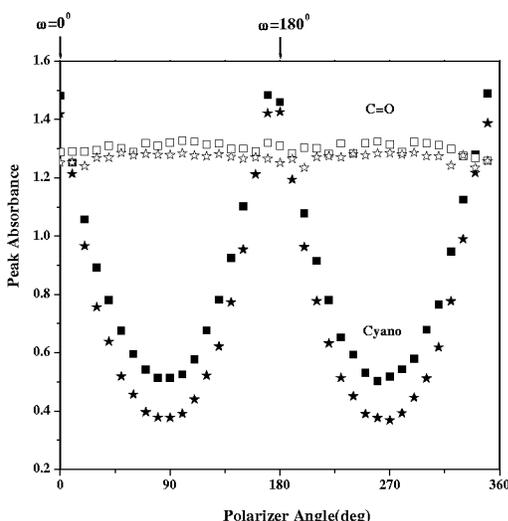
FIG. 10. Variation of the peak IR absorbance as a function of polarizer setting for a planar aligned sample of M11: ■; (Cyano) and □ (C=O) correspond to the N phase; ★ (Cyano) and ☆ (C=O) correspond to the SmA_{db} phase.

in Fig. 11. In all the three phases the maxima in the peak absorption for *both* the C≡N and C=O bonds are in phase and occur for $\omega \approx 0$ and 180°. Because of the higher concentration of BC molecules in this mixture the order parameter of the arrow axis can be larger than in M11. The angular dependence is clearly visible with a maximum in A_{peak} for $\omega \approx 0$ and 180° implying that $\sin^2 \alpha < 2/3$ indicating that α is measured with respect to the arrow axes. So even in M24 it is the arrow axes of the BC molecules which orient along the director which is parallel to the long axes of the R molecules in the nematic phase. The mutual alignment of R and BC molecules remains unaltered in the two-dimensionally periodic phase in M24. As mentioned earlier optical observations also show that the schlieren texture of the SmA_{db} phase persists even in the two-dimensionally periodic phase implying that the alteration in structure is quite small. There is a progressive decrease in the peak absorbances related with both the C≡N and C=O bonds on cooling the sample

FIG. 11. Variation of the peak IR absorbance as a function of polarizer setting for a planar aligned sample of M24: ■ (Cyano) and □ (C=O) correspond to the N phase; ★ (Cyano) and ☆ (C=O) correspond to the SmA_{db} phase; ▲ (Cyano) and △ (C=O) correspond to the two-dimensionally periodic phase.
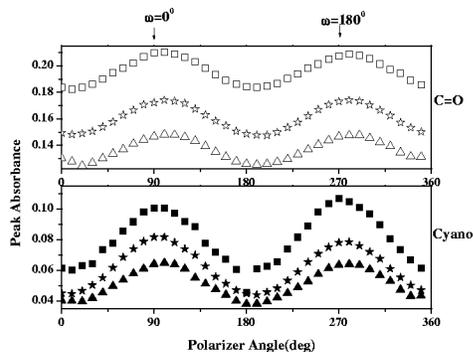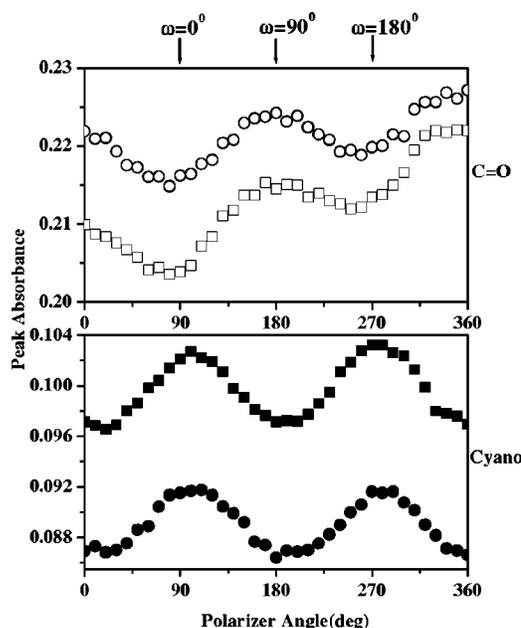

FIG. 12. Variation of the peak IR absorbance as a function of polarizer setting for a planar aligned sample of M35.3: ■ (Cyano) and □ (C=O) correspond to the N phase; ● (Cyano) and ○ (C=O) correspond to the two-dimensionally periodic phase.

from the N into the SmA_{db} and the two-dimensionally periodic phases. This is due to a deterioration of the alignment, which has been seen using a microscope.

A_{peak} as functions of ω in the N and the two-dimensionally periodic phases are shown in Fig. 12 for the mixture M35.3. As in the case of M11 and M24 the maximum in A_{peak} in the case of the C≡N bond is obtained when $\omega \approx 0$ and 180° and the absorbances are symmetric around the maxima and minima. There are two noteworthy features related with the absorbances associated with the C=O bonds. (a) The maximum absorbance is obtained for $\omega \approx 90°$ and 270°. As discussed above this indicates that $\sin^2 \alpha > 2/3$ which is possible only if the average angle between the bow axes of the BC molecules and the long axes of the rods is relatively small. (b) There is a progressive *increase* in the absorbance corresponding to the C=O bond with time as the spectra are recorded for different angles indicating that there is a slow reorganization of the BC molecules. The measurements taken in the nematic phase was started about half an hour after mounting the sample in the isotropic phase. The entire scan from $\omega = 0$ to 360° in each phase takes about two and a half hours. Using the geometry of the minimized structure we find that the projection of the C=O bonds is larger in a direction perpendicular to the molecular plane which is the plane containing the arrow and the bow axes. The observed time dependence indicates that the BC molecules tend to reorient such that the arrow axes prefer to align perpendicular to the CaF_2 plates. In order to investigate the angular dependence in the two-dimensionally periodic phase the sample had to be cooled by $\sim 15°$ from the N phase and the temperature stabilized. This takes about an hour and the absorbance continues to increase in the two-dimensionally periodic phase as the angular scans are taken. The rate of in-

crease is now slower than that observed in the N phase (Fig. 12). Also the overall absorbance is higher in the two-dimensionally periodic phase as compared to that in the N phase. This trend is contrary to what is observed for the C$\equiv$N bond in M35.3 and for both the C$\equiv$N and C$=$O bonds in M24. The reverse trend is a consequence of the time-dependent reorientation of the BC molecules in M35.3.

The polarized infrared studies indicate that the angle made by the bow axes of the BC molecules with the long axes of the R molecules reduces from 90° in mixtures with less than 35 mol% of BC12 to a small angle in mixtures with more than 35 mol% of BC12. This change in mutual orientation of the R and BC molecules around 35 mol% of BC12 also corresponds to the concentration of BC12 at which x-ray diffraction shows a jump in the lattice spacing d_1. We designate the two-dimensionally periodic phase occurring for mixtures with less than ~35 mol% of BC12 as B_1' and the one occurring in the higher concentration range of BC12 as B_1.

D. Absorption spectra in the UV-visible region

Charge-transfer (CT) interactions are known to occur in binary mixtures of compounds made of R molecules when one of the components has a cyano end group, while the other is not highly polar. Molecular complexing has been found to give rise to an additional CT band or a broadening of the spectrum in the UV-visible region [16]. We studied the spectra in the case of pure 8OCB, BC12 and in the mixtures M24 and M55 in the isotropic (I) and homogeneously aligned LC phases using an Ocean Optics spectrophotometer (S2000). We did not find any evidence for additional bands in the spectra obtained for the mixtures which indicates either the absence of CT interactions or if present the interactions may be too weak.

III. DISCUSSION

The formation of some types of B phases has been discussed in Refs. [6,8,9]. In a pure compound made of BC molecules when the chain length is sufficiently long the molecules have strong biphilicity and there is segregation of the aromatic cores and aliphatic chains. When the chain length is longer than the arm length of the aromatic core this can usually result in a layering order as in the B_2 phase [17]. Because of the bent shape, the molecules cannot rotate freely and within each layer they pack with an in-layer polar ordering. 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 to reduce electrostatic repulsion energy. 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 [18]. Another contributory factor could be a larger molecular cross-section of chains compared to the cores, which can also produce tilt [19]. Though the individual molecules have no chiral centers, as a result of the polar ordering of the molecules and the tilt, the layer becomes chiral [1]. The B_2 phase usually has an antiferroelectric interlayer structure and the medium has no

net polarization. However, in each layer the polarization generates a depolarizing electric field giving rise to a positive self-energy. But unlike in ferroelectric crystals this field cannot be usually reduced by formation of domains within the layers. This would require the arrow axes of BC molecules to reverse sign, which would be unfavored entropically and the layers remain uniformly polarized in the B_2 phase. (However, in the B_7 phase such an in-layer domain formation has been found [20].) If the chain length is shorter than the arm-length the B_1 phase with a rectangular columnar structure is obtained. In this phase there is domain formation without any net polarization of the medium [21]. In the structure, there is some overlap between the aromatic parts of the molecules at the interfaces of neighboring domains which contributes to stabilizing the B_1 phase. However there is also some overlap between the aromatic part of a molecule at the edge of one domain and the aliphatic part of the molecule at the edge of the neighboring domain. This is an unfavorable interaction which would reduce such interfaces, thus determining the size of the 2D lattice in the B_1 phase. If the chain length is still shorter the unfavorable interaction is decreased and molecules can move across the domains gaining entropy and the 2D lattice gets destroyed giving rise to the B_6 phase with an intercalated structure.

In the induced B_1 phase formed in mixtures occurring in SI (with the rodlike compound BO11), the aromatic parts of the R molecules are attracted to the aromatic parts of the BC molecules. The rods lie at the interfaces between neighboring domains (Fig. 13), increasing the attraction between the domains and thus bonding them. With further addition of rods they are no longer confined to the interfaces between the domains and the 2D structure can be disrupted giving rise to the B_6 phase of SI. The B_1 phase is also induced in SII (with rodlike 8OCB molecules). But interestingly in SII with increase in concentration of rods, instead of the B_6 phase a two-dimensionally periodic phase with the molecular arrangement different from the one occurring in the induced B_1 phase described above is obtained.

In SII the polarized infrared studies show that the nature of the angular dependence of A_{peak} related with the C$\equiv$N and C$=$O bonds depends on the concentration of BC12. In M11 and M24 the angular dependence of A_{peak} suggests that the arrow axes of the BC molecules orient along the long axes of the R molecules (see Sec. II C) in the N, SmA_d and SmA_{db} phases in M11 and N, SmA_{db} and B_1' phases in M24.

In the concentration range with less than 35 mol% of BC12 the structure is dominated by the partial bilayer structure formed by the antiparallel pairs of 8OCB molecules. The dimensions of the 8OCB and BC12 molecules are such that, the length of the arrow axis of the BC molecule (~10.3 Å) matches with the length of the aromatic core of the R molecule (~11 Å). Therefore the BC12 molecules can easily fit into the partial bilayer structure formed by the 8OCB molecules if the arrow axes are along the long axes of the 8OCB molecules [Fig. 14(a)]. As the length of the aromatic part of the bow axis of the BC12 molecule is ~29.2 Å this axis cannot fit along the long axis of the rods of the partial bilayer [Fig. 14(b)]. The IR results are consistent with this expectation. The layer spacing of the partial bilayer structure which is 32 Å in the SmA_d phase of pure 8OCB reduces to 30.2 Å

FIG. 14. Orientation of a BC12 molecule with respect to the layer normal of the partial bilayer structure formed by the 8OCB molecules in SII. (a) With the arrow axis along the layer normal; (b) with the bow axis along the layer normal.
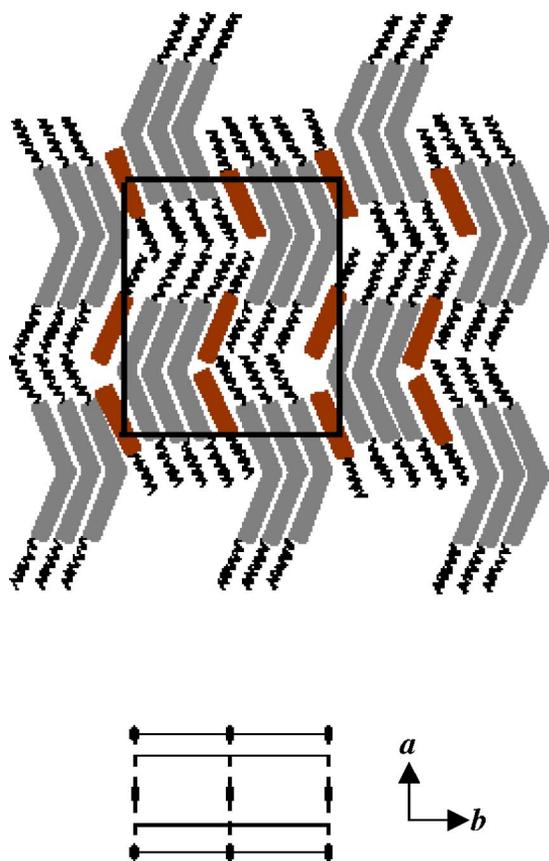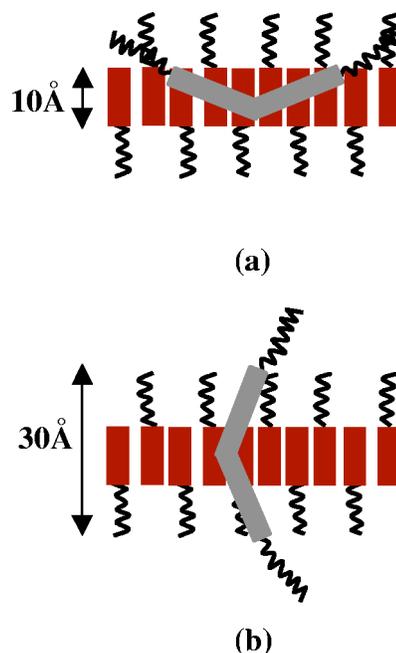

FIG. 13. Schematic representation of the molecular arrangement in the induced B_1 phase exhibited by some mixtures of SI (adapted from Ref. [6]).

and 28 Å in the SmA_{db} phase of M11 and M24, respectively. In the layers (see Fig. 15) the parts containing the aliphatic chains are less densely packed in the mixtures than in pure 8OCB. As such, the chains can bend around with some gauche conformation to fill space thus reducing the layer spacing. Such a folding of the alkyl chains by two gauche kinks to ensure dense packing has been observed at the surface of freestanding films of binary mixtures of two homologues of smectogenic R compounds [22].

In the SmA_{db} phase there is no correlation in positions of the BC molecules within a partial bilayer. On cooling an aligned sample of M24 into the B_1' phase, x-ray diffraction shows evidence for a 2D lattice. Two of the measured spacings are equal to 46.9 Å and 28 Å. From the evolution of the x-ray diffraction pattern it is clear that the 28 Å spacing matches with that of layer spacing of the partial bilayer structure obtained in the SmA_{db} phase. This indicates that the partial bilayer structure remains intact in the B_1' phase also, defining one of the periodicities of the 2D lattice. The diffraction spots corresponding to 46.9 Å occur at an angle to those corresponding to 28 Å (see Fig. 7). The former can be identified with the (11) reflection of the 2D lattice. Infrared experiments show that the arrow axes of the BC molecules are parallel to the long axes of the rods even in the two-dimensionally periodic B_1' phase. The second periodicity is then related with the organization of the bow axes of the BC molecules in the layer plane. In principle the wave vector of

this periodicity can be along any direction in the plane of the partial bilayer. The large spacing (46.9 Å) obtained from x-ray diffraction suggests that the second periodicity is along the length of the bow axes. One possible arrangement is such that within the partial bilayer, the BC molecules can orient with their arrow axes pointing in opposite directions in adjacent domains similar to the arrangement shown in Fig. 3. This leads to a columnar structure which has liquid-like correlations in a direction orthogonal to the plane containing the bow and arrow axes. Across the layers there can then be two possible ways in which the BC molecules can arrange themselves. The schematic representations of these two structures for M24 are shown in Figs. 15(a) and 15(b). They have been constructed taking into account the partial bilayer thickness obtained from x-ray diffraction, the mutual orientation of R and BC molecules as deduced from infrared measurements, the relative concentration of 8OCB and BC12 and the molecular dimensions.

(a) The BC molecules across the layers can line up one below the other with the arrow axes pointing in the same direction. The structure can be described by the 2D space group $p2mg$ [Fig. 15(a)]. The lattice parameter along the layer normal should be equal to the thickness of a partial bilayer. The measured spacing 28 Å then corresponds to (01) reflection. But the spacing corresponding to (11) should be smaller than 46.9 Å. Hence this is not a likely structure.

(b) The second possible structure is such that the BC molecules across the layers can point in opposite directions in an antiferroelectric configuration [Fig. 15(b)]. This structure can be described by the space group $c2mm$. As shown in Fig. 15(b) the lattice parameter along the layer normal (=56 Å) is now twice the thickness of the partial bilayer. The
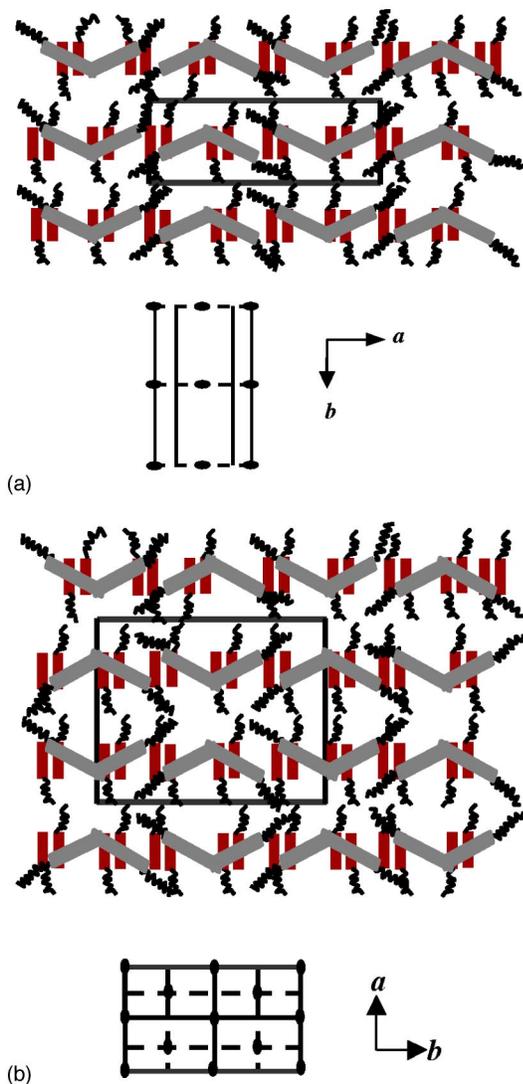
(a)

(b)

FIG. 15. (a) Schematic representation of a possible molecular arrangement in the induced B_1' phase exhibited by M24 conforming to the $p2mg$ space group symmetry. This structure cannot account for the observed (11) spacing. (b) Schematic representation of the proposed structure in the induced B_1' phase exhibited by M24 conforming to the $c2mm$ space group symmetry ($a=56$ Å and $b=86$ Å).

FIG. 16. Schematic representation of the molecular arrangement in the B_1' phase of M30 ($a=56.5$ Å and $b=64$ Å).

28 Å spacing corresponds to the (20) reflection. The measured spacing of 46.9 Å can then be accounted for by the (11) reflection. Even weaker reflections corresponding to (40) and (31) could be observed.

In the *liquid* columns line densities of dipoles are oriented orthogonal to the column axis as well as to the layers. Electrostatic interactions would stabilize the structure [Fig. 15(b)] within a layer with the *column polarizations* in neighboring columns having opposite directions. But the dipolar interactions cannot stabilize the structure across the layers. However, thermal fluctuations of the layers [23] which result in a splay of the column polarization, can stabilize the structure shown in Fig. 15(b). The resulting charges in the adjacent polarized columns have opposite signs both within the partial bilayer and across the layers. We may point out that a
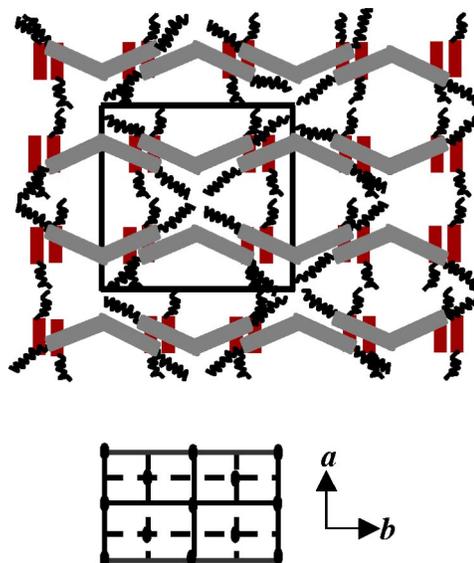
columnar structure with the $c2mm$ space group symmetry has been found in the smectic-A antiphase ($\tilde{A}$) [24] exhibited by binary mixtures of two compounds made of R molecules having strongly polar end groups. In this case the antiparallel dipoles form bilayer domains which are arranged on a centered rectangular lattice.

As the concentration of BC12 is increased the BC molecules are packed closer together and there is some overlap between the arms of the BC molecules in adjacent columns within the layers resulting in a decrease in the lattice parameter "b." A schematic diagram of the molecular arrangement in the B_1' phase in mixtures with 30 mol% of BC12 is shown in Fig. 16.

In the mixture M35.3 the infrared studies show that there is a 90° shift between the angles of the maxima in A_{peak} corresponding to the C≡N and C=O bonds. This shift is present in both the N and the two-dimensionally periodic phases (Fig. 12). This indicates that the R molecules make a small angle with the bow axes of the BC molecules and there is a change in the overall structure. This changeover is also reflected in the x-ray diffraction studies where a sudden increase in the spacing d_1 is observed for concentrations around 35 mol% of BC12. As shown in Figs. 15(b) and 16 with increase in concentration of BC12 there is a decrease in the density of dimers of 8OCB in the partial bilayers. With greater than 35 mol% of BC12 the partial bilayer structure cannot be sustained. The 2D lattice is likely to have the type of domain structure found in the induced B_1 phase of SI (Fig. 13). The 8OCB dimers lie at the interfaces between domains and as explained before the 2D lattice can be stabilized. This structure conforms to the $p2mg$ space group symmetry.

The 8OCB molecules at the interfaces are likely to exist as antiparallel pairs. For a given direction of the long axis of the pair an orthogonal line joining the two molecules can have different orientations with respect to the plane of the 2D lattice. As shown in Figs. 17 and 18 the aromatic cores of both BC and R molecules are oriented at an angle ≈60° with
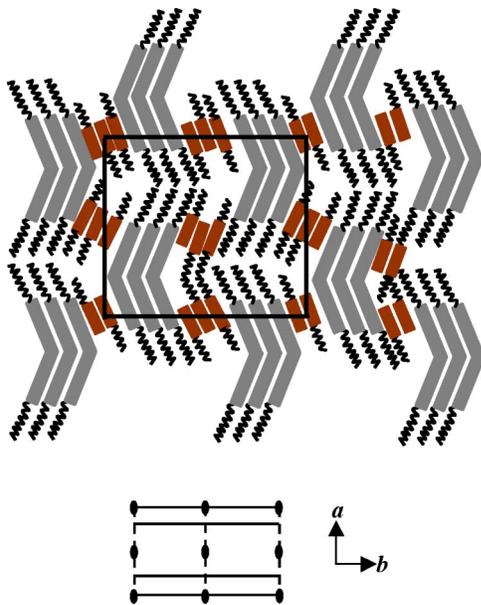
FIG. 17. Schematic representation of the molecular arrangement in the B_1 phase of M37 conforming to the $p2mg$ space group symmetry ($a=55.7$ Å and $b=67$ Å).

respect to the "b" direction and their average projected width along this direction is ~5.75 Å. As shown in Fig. 17 for M37 in each unit cell about six BC12 molecules and ten projected 8OCB molecules can satisfy the concentration ratio and give the observed lattice parameter "b" $=67$ Å. As the concentration of BC12 is increased the number of BC molecules in each domain increases and the number of 8OCB dimers at the interfaces decreases. For example, in M55 as shown in Fig. 18 each unit cell can have on the average about eight BC molecules and about six and a half projected 8OCB molecules to account for the concentration ratio and for the measured value of "b" $=62$ Å. When the chains of the BC molecules are in the fully stretched configuration and
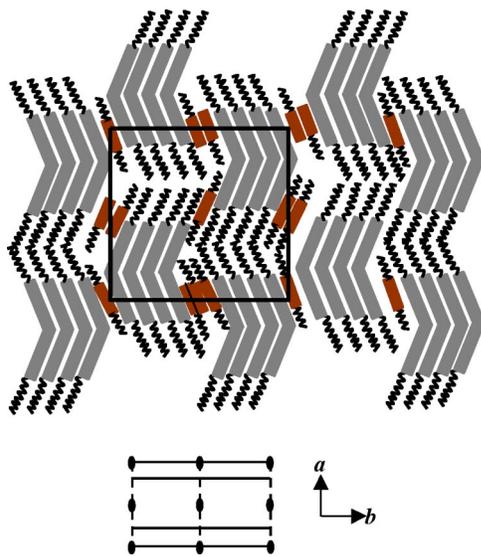

FIG. 18. Schematic representation of the molecular arrangement in the B_1 phase of M55 ($a=55.6$ Å and $b=62$ Å).

lie in the plane of the aromatic core the length of the long axis is ≈ 60 Å. As the core of the BC12 molecule is not symmetric (see Fig. 9) and because of steric effects the chains may be disposed out of the plane of the aromatic core in the LC phases. Further as pointed out earlier, the chains can bend to fill space and lead to a reduction in the length of the BC molecule. From x-ray diffraction studies the spacing corresponding to the allowed (20) reflection is ~28 Å in both M37 and M55. This is roughly half the effective length of the long axis of the BC12 molecule and does not exhibit any significant dependence on concentration. Curiously this length closely matches with the partial bilayer thickness formed by 8OCB molecules in liquid crystalline phases exhibited by mixtures with 24 to 34.3 mol% of BC12 molecules. The jump in the "d_1" spacing however shows that the two-dimensionally periodic structure drastically changes between M34.3 and M36.

In order to look for any structural changes caused by application of an external field in the concentration region where there is a change over from B_1' to B_1 phase we have studied the effect of an ac electric field on M35.3. When this mixture was taken between ITO plates treated for planar alignment the sample was reasonably well aligned in the B_1 phase and the effective path difference (Δl) could be measured. When an electric field (10 kHz) was applied between the plates to such a cell with thickness of ~5 μm a *gradual* increase of Δl was observed with increasing field. Δl increases by about 60% when the applied field is raised to 10 V/μm. This increase implies a reorientation of the structure due to the transverse dielectric anisotropy. The arrow axes of the BC molecules, which may be initially oriented parallel to the plates reorient along the field direction leading to an increase of Δl. However there is no evidence for a sudden increase in Δl at any field, which would have indicated a structural change.

IV. PHASE DIAGRAM

Keeping in view all the above experimental results which are based on textural observations under a polarizing microscope along with x-ray diffraction and polarized infrared studies the detailed temperature-concentration phase diagram in SII has been constructed (Fig. 19).

(a) Mixtures with up to ~10.5 mol% of BC12 exhibit the N and SmA_d phases as in the case of pure 8OCB. (b) In mixtures with 10.5 to 15 mol% of BC12 the uniaxial SmA_d phase undergoes a transition to the biaxial SmA_{db} phase and in mixtures with 15 to 24 mol% of BC12 the N phase directly transforms to the biaxial SmA_{db} phase without the intervention of the uniaxial SmA_d phase. Experimental observations indicate that the nematic phase itself is uniaxial. (c) In the mixture with ~24 mol% of BC12 there is a transition from the SmA_{db} phase to the B_1' phase. (d) In the range of 24 to 35 mol% of BC12 the nematic phase exhibited by the mixtures transforms directly to the B_1' phase. (e) The B_1 phase forms in mixtures with ~35 mol% to 60 mol% of BC12. (f) In the mixtures with 50 to 60 mol% of BC12 the B_1 phase initially starts forming from the isotropic phase. Before the phase transition is complete the remaining I phase
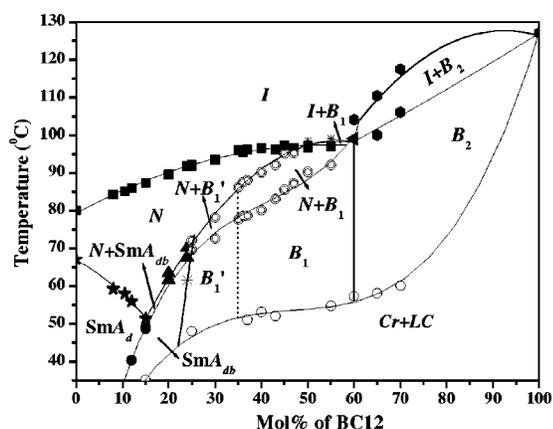
FIG. 19. Temperature-concentration phase diagram of mixtures of SII.

which has a higher concentration of R molecules transforms to the N phase as the temperature is decreased. Eventually the N phase also changes to the B_1 phase. (g) For concentrations of BC12 higher than 60 mol% the mixtures exhibit the B_2 phase.

A notable difference between the phase sequences in SI and SII is the absence of the induced B_6 phase in SII and the occurrence of the two-dimensionally periodic induced B_1' phase instead. A possible reason for this difference is the formation of antiparallel pairs of 8OCB molecules having the strongly polar cyano end group. In the induced B_6 phase of SI, the BO11 molecule, which has an alkyl chain at one end is accommodated between the intercalated BC12 molecules to gain entropically. On the other hand, the 8OCB antiparallel pairs have chains at both ends and they cannot be accommodated between the intercalated BC12 molecules without the chains of the former lying close to the aromatic cores of the latter. The associated enthalpic cost appears to be too high and the B_6 phase is not observed in SII. For concentrations with less than 35 mol% of BC12 these antiparallel pairs which have a length incommensurate with the molecular length form the partial bilayer structure. When the concentration of BC molecules is low the latter arrange themselves in the partial bilayer structure to form the SmA_{db} phase. For slightly higher concentrations of BC12 the BC molecules further order forming the 2D lattice of the B_1' phase. As the concentration of BC12 is increased further, the antiparallel pairs lie at the interfaces between the domains of BC molecules stabilizing the domain structure of the B_1 phase.

V. CONCLUSION

Two different types of two-dimensionally periodic rectangular columnar structures have been found in mixtures of the binary system consisting of 8OCB and BC12 molecules. The two structures have been characterized by x-ray diffraction, polarized infrared studies and polarizing microscopy.

The molecular arrangement in the B_1' phase in the lower concentration region (<35 mol%) of BC12 is dictated by the partial bilayer structure formed by the 8OCB molecules. The BC molecules arrange themselves in a two-dimensionally periodic lattice with their arrow axes along the layer normal. The orientations of adjacent BC molecules within a partial bilayer and across the neighboring layers are such that their arrow axes point in opposite directions. This structure conforms to the $c2mm$ space group symmetry. As the concentration of BC12 is increased there is a change in the mutual orientation of the R and BC molecules. The two-dimensionally periodic phase that is formed in mixtures with greater than 35 mol% of BC12 has a domain structure similar to the B_1 phase and the rods lie in between the domains stabilizing the structure. This structure has the $p2mg$ space group symmetry. The new feature in this study is the occurrence of the B_1' phase in lower concentration regions of BC12 which was absent in similar mixtures of the same BC compound with the R compound BO11 exhibiting the bilayer smectic phase. The stability of the partial bilayer structure of 8OCB in lower concentration regions of BC12 and the favorable dimensions of the aromatic parts of the 8OCB and BC12 molecules are responsible for the occurrence of the B_1' phase in this system.

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

[2] G. Pelzl, S. Diele, and W. Weissflog, Adv. Mater. (Weinheim, Ger.) **11**, 707 (1999).

[3] B. K. Sadashiva, V. A. Raghunathan, and R. Pratibha, Ferroelectrics **243**, 249 (2000).

[4] R. Pratibha, N. V. Madhusudana, and B. K. Sadashiva, Science **288**, 2184 (2000).

[5] R. Pratibha, N. V. Madhusudana, and B. K. Sadashiva, Mol. Cryst. Liq. Cryst. Sci. Technol., Sect. A **365**, 755 (2001).

[6] R. Pratibha, N. V. Madhusudana, and B. K. Sadashiva, Pramana **61**, 405 (2003).

[7] B. K. Sadashiva, Mol. Cryst. Liq. Cryst. **55**, 135 (1979).

[8] N. V. Madhusudana, presented at the Boulder FLC Workshop, Univ. of Colorado, 2002 (http://anni.Colorado.edu/bananas).

[9] D. Shen, A. Pegenau, S. Diele, I. Wirth, and C. Tschierske, J. Am. Chem. Soc. **122**, 1593 (2000).

[10] A. J. Leadbetter, R. M. Richardson, and C. N. Colling, J. Phys. Colloq. **36**, C1-37 (1975).

[11] J. P. Bedel, J. C. Rouillon, J. P. Marcerou, M. Laguerre, H. T. Nguyen, and M. F. Achard, Liq. Cryst. **27**, 1411 (2000).

[12] J. Szydlowska, J. Mieczkowski, J. Matraszek, D. W. Bruce, E. Gorecka, D. Pociecha, and D. Guillon, Phys. Rev. E **67**, 031702 (2003).

[13] R. Keifer and G. Baur, Mol. Cryst. Liq. Cryst. **174**, 101 (1989).

[14] K. H. Kim, K. Ishikawa, H. Takezoe, and A. Fukuda, Phys. Rev. E **51**, 2166 (1995).

[15] D. A. Ramsay, J. Am. Chem. Soc. **74**, 72 (1952).

[16] K. Praefcke and D. Singer, in *Handbook of Liquid Crystals*,

edited by D. Demus, J. W. Goodby, G. W. Gray, H. W. Spiess, and V. Vill (Wiley-VCH, New York, 1998), Vol. 2B, Chap. XVI, p. 945.

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

[18] A. S. Govind and N. V. Madhusudana, Eur. Phys. J. E **9**, 107 (2002).

[19] Y. Lansac, N. A. Clark, and M. A. Glaser, poster presented at the 19th International Liquid Crystal Conference, Edinburgh, U.K., 2002.

[20] D. A. Coleman, J. Fernsler, N. Chattham, M. Nakata, Y. Ta-

kanishi, E. Korblova, D. R. Link, R. F. Shao, W. G. Jang, J. E. Maclennan, O. Mondainn-Monval, C. Boyer, W. Weissflog, G. Pelzl, L. C. Chien, J. Zasadzinski, J. Watanabe, D. M. Walba, H. Takezoe, and N. A. Clark, Science **301**, 1204 (2003).

[21] J. Watanabe, T. Niori, T. Sekine, and H. Takezoe, Jpn. J. Appl. Phys., Part 2 **37**, L139 (1998).

[22] H. R. Keymeulen, W. H. de Jeu, J. T. Slattery, and M. Veum, Eur. Phys. J. E **9**, 443 (2002).

[23] R. Bruinsma and J. Prost, J. Phys. II **4**, 1209 (1994).

[24] A. M. Levelut, J. Phys. (France) Lett. **45**, L603 (1984).