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A racemic layer structure in a chiral bent-core ferroelectric liquid crystal

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A fluid smectic phase of a chiral bent-core liquid crystal was found to have a ground state structure that is anticlinic in tilt and ferroelectric in polar order, $SmC_AP_F^*$. The layer chirality of this structure alternates from layer to layer despite their being composed of chiral mesogens. Observations of the optical second harmonic generation signal from well-aligned domains confirm that the ground state of this phase is bistable ferroelectric. In addition to the ground state two types of metastable domains are also observed.

1. Introduction

Molecular chirality in soft condensed matter directly manifests in the macroscopic physical properties. In liquid crystalline phases, the influence of molecular chirality on the macroscopic structure has been an important theme throughout the history of the investigation of liquid crystals (LCs). In the nematic LC phase of rod-like molecules, the molecules are organized with the average direction of their long-axes parallel to the director $\mathbf{n}(x, y, z)$. The introduction of chirality to this system (either through the synthesis of chiral mesogens or addition of a chiral dopant) removes mirror symmetry and thus allows for a spontaneous macroscopic twist in $\mathbf{n}$ producing a helical structure with the helix sign determined by the handedness of the molecules.

Until recently, it was thought to be a general rule that in order to produce chiral or polar structures in fluid phases it is necesary to incorporate chirality at a molecular level. However, in 1996, Niori *et al.* discovered that one of the smectic phases of an achiral bent-core liquid crystal material exhibited electro-optic switching [1]. Observations by Link *et al.* indicated the existence of two distinct antiferroelectric states in this phase, (1) the ground state smectic C_SP_A (SmC_SP_A) (synclinic in tilt and antiferroelectric in polar order), and (2) the smectic C_AP_A (SmC_AP_A) (anticlinic in tilt and antiferroelectric in polar order) [2]; see figure 1 (*b*). This combination of tilt and polar order in the smectic layers results in each layer being inherently chiral, as shown in figure 1 (*a*), with the sign of layer chirality alternating from layer to layer in the SmC_SP_A state (racemic) and remaining uniform in the SmC_AP_A state (homogeneously chiral).

These reports made it clear that chiral macroscopic structures could spontaneously organize in fluids without the introduction of molecular chirality. However, the symmetry rule that the handedness of chiral structures is determined by the molecular chirality, when it is present, remained intact. Even in the case of achiral bent-core materials it was found that the addition of a small amount of a chiral dopant stabilized the homogeneously chiral state of a single handedness [2]. Here, however, we report that in a chiral analogue, 8OPIMB6*, of the achiral bent-core material, 8OPIMB, the ground state (thermodynamically stable state) of the highest temperature phase is anticlinic *ferroelectric*, smectic $C_AP_F^*$, ($SmC_AP_F^*$); see structures in figure 2. This phase has a 'racemic' layer structure despite being composed of chiral molecules, violating the rule that the handedness of chiral structures in fluid phases is determined by the molecular chirality. This same material, however, when used as a chiral dopant in the B_4 phase of a homologue of 8OPIMB, effectively stabilizes one of the two chiral structures [3].

In previous studies of 8OPIMB6* in unaligned cells, we observed a single peak in the polarization reversal current ($\mathbf{P}_s \sim 500\ \mathrm{nC\,cm^{-1}}$), a strong dielectric relaxation mode, and optical second harmonic generation (SHG) in the absence of an electric field, all of which strongly

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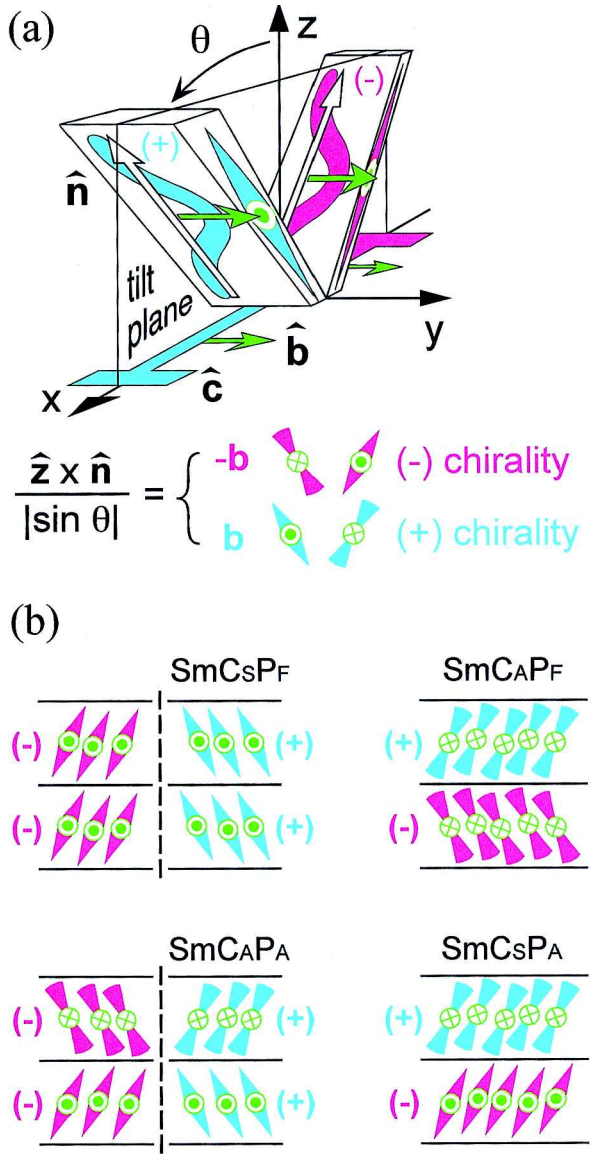

Figure 1. Geometry for smectic layers and layer stacking in liquid crystalline phases of bent-core mesogens. (*a*) In a smectic layer with layer normal along the *z*-axis composed of bent-core molecules with polar order along **b** parallel to the *y*-axis, two possible *chiral* layer structures are defined by the director **n** tilting by θ either along the positive (cyan) or negative *x*-axis (magenta). The two-dimensional *c*-director (nail) is defined by the projection of **n** onto a surface with the head of the nail indicating which end of the molecule is closest to the top of the surface. (*b*) These layers can organize into four possible states that are distinguished by the relative tilt sense and the polar order between adjacent layers. The notation C_S and C_A refers, respectively, to synclinic and anticlinic tilt while P_F and P_A refer, respectively, to ferroelectric and antiferroelectric polar order in adjacent layers.

indicate the presence of ferroelectric polar order in this phase [4]. In the present paper we report electro-optic and SHG studies of well aligned domains of the ground

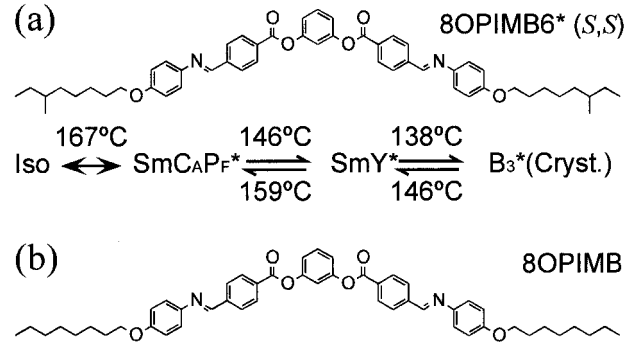

Figure 2. Chemical structures of 8OPIMB6* and 8OPIMB. Transition temperatures of 8OPIMB6* are also shown.

state structure as well as electro-optic observation of two additional states in this phase. These most recent studies allow for the determination of the structures in these three states as being $SmC_AP_F^*$, $SmC_SP_F^*$ and $SmC_SP_A^*$.

2. Experimental procedure

The phase sequence and transition temperature of 8OPIMB6* used in this study are shown in figure 2(*a*). Three phases, $SmC_AP_F^*$, SmY* and crystalline B_3^*, were identified. The $SmC_AP_F^*$ and SmY* phases are ferroelectric phases. Although these phases are not easily distinguished by texture observation, dielectric response indicates a change at the phase transition [4]. The B_3^* phase is crystalline as indicated by sharp diffraction peaks in the wide-angle X-ray observations. This phase shows no electro-optic response. In the present study, we focus only on the highest temperature smectic phase with the $SmC_AP_F^*$ ground state structure.

The sample material was introduced into thin transparent capacitor-type cells from 1 to 20 μm in thickness. Three types of cell were used: normal cells with electrodes in both substrate surfaces (type A), cells with electrodes at one substrate surface to apply an electric field along the surface (type B) and cells with electrodes for field applications parallel and perpendicular to the substrates (type C). Type A cells were used for electro-optic studies of unaligned metastable domains. The three techniques of using polymer alignment layers, shear and application of an electric field across the cells all failed to produce well aligned planar domains. To circumvent these alignment difficulties, cells of type B and C were used to apply an electric field in the plane of the cells resulting in alignment. Type B cells were used for the SHG experiments as they do not have electrodes in the beam path, while type C cells were used for the electro-optic observations of aligned domains. These type C cells, as shown in figure 3, consist of a sandwich of liquid crystal between two glass cover slips (80 μm thick) with patterned indium tin oxide (ITO) electrodes and a third

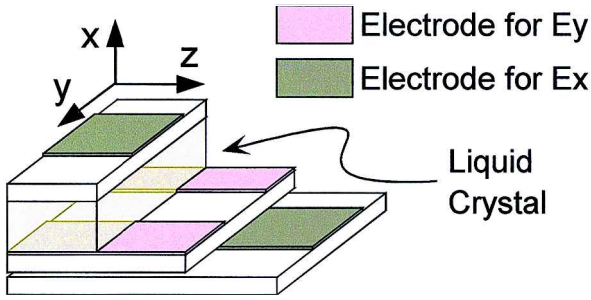

Figure 3. (a) The cell structure for applying electric fields along both the x (perpendicular to the substrates) and y (in the plane of the cell) directions.

glass slip with an additional ITO electrode, so that the cell has two pairs of electrodes along the x (perpendicular to the substrates) and y (in the plane of the cell) directions. Vertical and in-plane electric fields were applied across c. 180 μm and 250 μm gaps, respectively.

Conventional microscopic observation were made using cells of types A and C. The birefringence of domains was determined under the microscope by compensating the phase retardation due to the anisotropic domains using a compensator at various wavelengths obtained by passing the illumination light through interference filters. SHG experiments were made using a fundamental beam ($\lambda = 1064$ nm) from a Nd : YAG laser. SHG interferograms from single domains were obtained by a conventional method. As shown in figure 4, the relative phase of the SHG signal from the quartz crystal ($E_{2\omega Q}$) was shifted with respect to the fundamental signal (E_{ω}) by rotating a glass plate inserted in the optical path. This signal then interferes with the SHG signal from the liquid crystal sample ($E_{2\omega S}$) to produce an interferogram.

3. Experimental results

3.1. *Three possible domains*

On cooling from the isotropic to the highest temperature smectic phase, three types of focal-conic domains were observed to coexist in the cells (figure 5). The majority of these domains are in the ground state $SmC_A P_F^*$ (anticlinic in tilt and ferroelectric in polar order), and have an extinction direction parallel to the layer normal, figure 5 (*a*). In addition, domains of two distinct

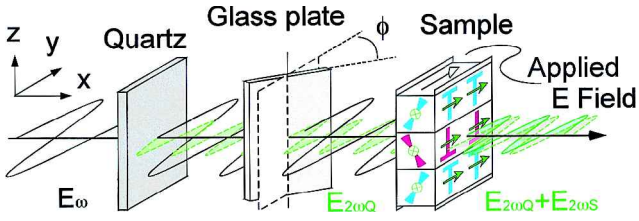

Figure 4. Experimental set-up for SHG interferometry.

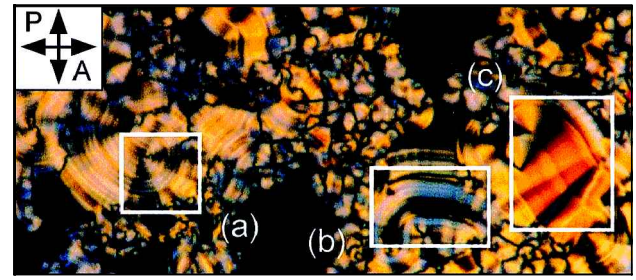

Figure 5. Polarized photomicrograph of the focal-conic domains in the highest temperature smectic phase in a 4 μm thick cell. Three types of domain are observed under the same conditions before applying an electric field: (*a*) domain of the $SmC_A P_F^*$ state; (*b*) domain of the $SmC_S P_F^*$ state; (*c*) domain of the $SmC_S P_A^*$ state.

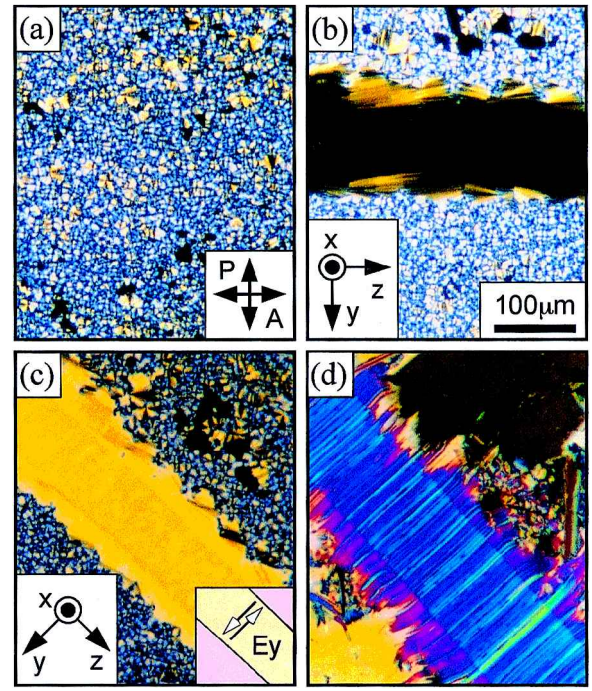

Figure 6. Photomicrographs in a 4 μm thick cell showing the effect of an in-plane electric field. (*a*) Focal-conic domains obtained on cooling from the isotropic to the $SmC_A P_F^*$ phase. (*b*) Development of a uniform domain under the application of a square wave along the y direction. (*c*) A uniform birefringence colour on rotation through 45°. (*d*) Alignment held on cooling into the crystalline B_3^* phase.

metastable states, $SmC_S P_F^*$ (synclinic in tilt and ferroelectric in polar order) and $SmC_S P_A^*$ (synclinic in tilt and antiferroelectric in polar order), were observed. In the absence of an electric field the $SmC_S P_F^*$ state domains have no extinction brushes, figure 5 (*b*), while extinction brushes and a high birefringence are observed for the $SmC_S P_A^*$ state domains, figure 5 (*c*). In this report we will demonstrate the structures of these states based on texture observation, SHG interferometry and birefringence.

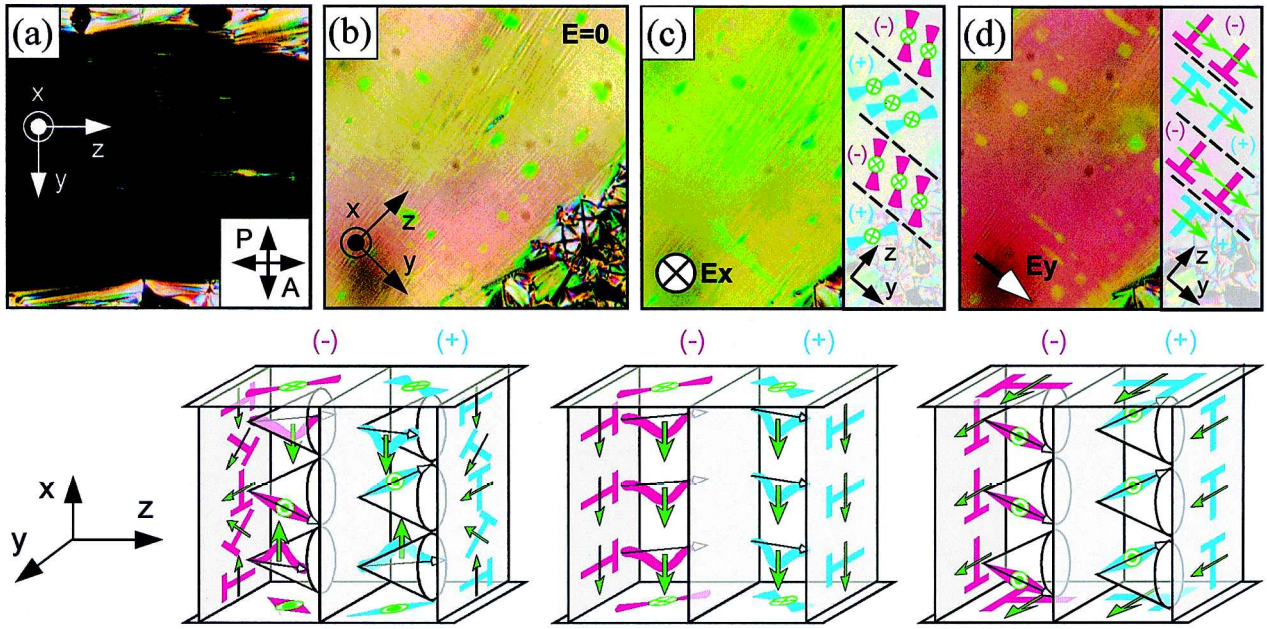

Figure 7. Photomicrographs of a well aligned *c*. 18 μm thick cell of 8OPIMB6*. (*a*) The ground state $SmC_A P_F^*$ with layer normal along one of the polarizers in the absence of a field; (*b*) the same state after rotating the extinction direction of the aligned domain to bisect the polarizers; (*c*) and (*d*) photomicrographs of the same region with a field applied along the cell normal ($E \sim 10$ V μm^{-1}) and with a field applied in the plane of the cell ($E \sim 1.5$ V μm^{-1}). Schematics below the micrographs show the anticlinic ferroelectric structure in each of the three cases; on removing the field, the structures in (*c*) and (*d*) return to that of (*b*). Note that the layer chirality alters from layer to layer to form a racemic layer structure.

3.2. *$SmC_A P_F^*$ state*

Let us first demonstrate how alignment is achieved by applying an in-plane electric field. On direct cooling from the isotropic to the $SmC_A P_F^*$ phase the cell is filled with small focal-conic domains, as shown in figure 6(*a*). These focal conic domains turn to a uniform domain by application of a square wave ($E \sim 1.5$ V μm^{-1} at 10 Hz) along the *y* direction, figure 6(*b*). Clear birefringence colour was observed by rotating the sample 45°, and almost no disclination lines were observed, figure 6(*c*). This alignment was maintained when the sample was cooled into the crystalline SmZ* phase. However disclination lines and several birefringence colours could be seen, as shown in figure 6(*d*).

Using this technique we prepared a large well aligned domain shown in figure 7. The domain has an extinction direction parallel to the layer normal, (*a*) and (*b*), and a low birefringence. (The birefringence as a function of wavelength is shown in figure 8.) The birefringence decreases upon application of an electric field across the cell, figures 7(*c*) and 8, while a slight increase is indicated by the change in birefringence colour when an electric field is applied in the plane of the cell, figure 7(*d*). In all cases the extinction direction remains parallel to the layer normal. Schematics below the photomicrographs of figure 7 indicate how the molecules are organized

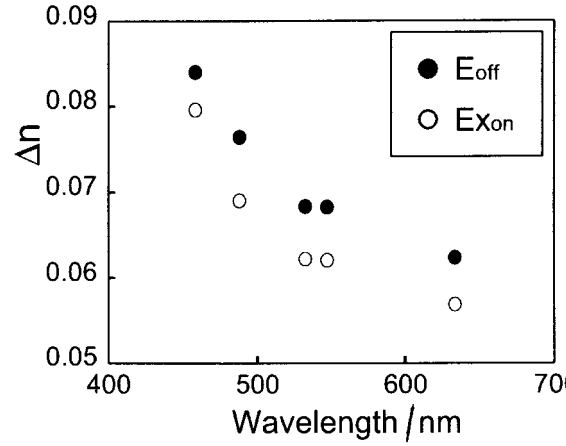

Figure 8. Birefringence of the ground state $SmC_A P_F^*$ as a function of wavelength. Birefringence decreases in all wavelengths on application of an electric field along the *x* direction.

in each state. In the field-on states, assignment of the molecular orientation is rather straight forward, since the polarization orients toward the electric field direction. Based on the polarization and the extinction direction (parallel to the layer normal) directions, ferroelectric nature of the phase and molecular tilt [5], we can conclude that the anticlinic structure is organized with

a uniform polarization parallel to the electric field, $SmC_A P_F^*$. In the zero-field state, we have to take into account the SHG results reported in our previous paper [5]. Namely, maximum SHG intensity is obtained at 0 V even for normal incidence, suggesting the existence of an in-plane non-linear polarization component. The molecular orientation shown in figure 7 (*d*) is a candidate for the model structure, but this state has a slightly higher birefringence than the ground state in the absence of a field, figures 7 (*a*) and 7 (*b*). Hence the ground state is similar to figure 7 (*d*) but should not be the same. Thus, we can speculate the plausible model structure of the ground state, as shown in the illustration below figure 7 (*b*). Namely, the polarization is splayed and the director is twisted from top to bottom of the cell. Hence the optic axis remains uniform parallel to the layer normal throughout the cell in this splayed state allowing for high contrast extinction with crossed polarizers, as experimentally observed. Note that the twist sense of the director is the same from layer to layer, so that macroscopic rotation of linear polarization of light cannot be observed. The most important observation that should be made in these molecular orientation schematics is the racemic layer structure, i.e. the chirality due to the molecular tilt alters from layer to layer in a system with molecular chirality.

Observation of the SHG signal from a well aligned region of a 12 μm thick cell, indicates a large non-linear susceptibility [4, 5] and polar order in the plane of the cell, perpendicular to the layer normal. Studies of the phase of the SHG signal were made by interfering the SHG signal from the sample with that of a quartz plate (see optical path in figure 4). Interferograms of the SHG signal at zero field after the application of positive ($I+$) and negative ($I-$) voltages in the plane of the cell are shown in figure 9 (*a*). The π-difference in phase between $I+$ and $I-$ indicates a reversal in the direction of polar order in the cell and a bistable surface-stabilized ferroelectric state. This SHG behaviour is consistent with the model structure shown in the schematic below figure 7 (*b*). Both bistable states are twisted states as shown in the schematics of figures 9 (*b*) and 9 (*c*), in which surface orientations are identical but the rotational senses of the *c*-director from the top to bottom surface are opposite. A detailed report of the SHG measurements is in preparation [5].

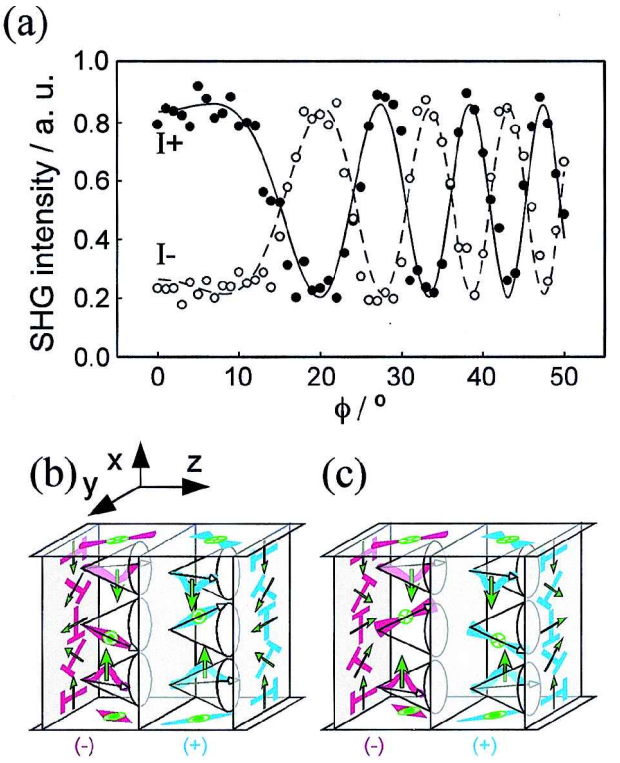

Figure 9. Interferograms in the absence of an external electric field after application of positive ($I+$) and negative ($I-$) in-plane electric fields. (*a*) The π-difference in phase between these signals as observed in the interferograms indicates a reversal of the polar order in the liquid crystal and two bistable ferroelectric states as sketched in (*b*) after applying $+E$, and (*c*) after applying $-E$. The solid lines in (*a*) are fits to an equation describing the phase shift with respect to angle of rotation ϕ of the glass plate from normal.

3.3. *$SmC_S P_F^*$ state*

Now let us consider the first of the metastable states, the homogeneously chiral $SmC_S P_F^*$ state. This state is only observed on rapid cooling from the isotropic phase and occupies the second largest percentage of the total cell area. In the absence of an electric field this state also has a structure with splayed polarization from the top to bottom surface, see figure 10 (*b*). In a synclinic state, however, this splay in polarization results in the extinction direction rotating from $+\theta$ to $-\theta$, where θ is the angle that the director makes with the layer normal, and hence only weak extinction brushes are observed. High contrast extinction can be obtained by uncrossing the polarizers by about 30° for a 4 μm thick cell. With crossed polarizers, application of an electric field along the cell normal results in high contrast extinction brushes rotated by $\pm 34°$ from the layer normal depending on the sign of E and a large birefringence ($\Delta n \sim 0.15$), see figures 10 (*a*) and 10 (*c*). Schematics representing the organization of the molecules in each of the field-on and zero-field states are shown in figure 10 below the photomicrographs. The layer structure of domains in this state is homogeneously chiral, while the ground state shown in figure 7 is racemic. Two types of the $SmC_S P_F^*$ domain exhibiting opposite rotation direction of extinction brushes under application of E have been observed, indicating that these homogeneously chiral domains form having

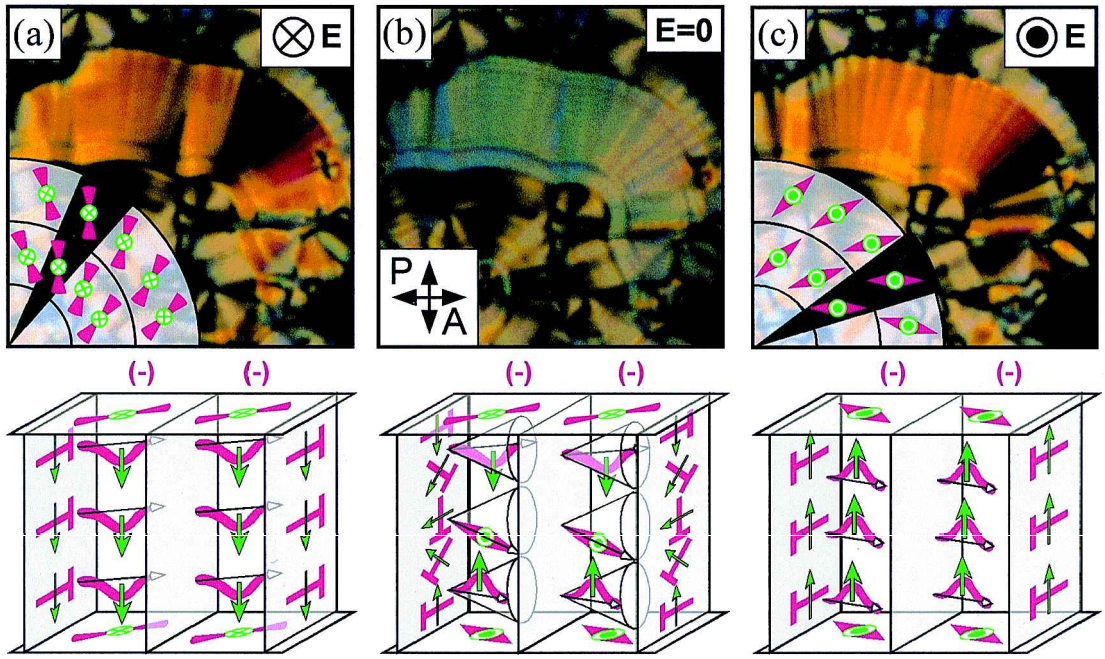

Figure 10. Polarized photomicrographs of the $SmC_SP_F^*$ domains of 8OPIMB6* in a 4 μm thick cell. The $SmC_SP_F^*$ domains (synclinic in tilt and ferroelectric in polar order) are homogeneously chiral and thus in the presence of an electric field ($|E| > E_{th}$) have an extinction direction rotated with respect to the layer normal by $+$ or $-\theta$ depending on the sign of the applied electric field and handedness of the domain as shown in (*a*) and (*c*). In the absence of a field, (*b*), high contrast extinction can only be achieved by uncrossing the polarizer and analyser indicating a twisted structure. The layer structures of the state are sketched below the photomicrographs.

either handedness. During the application of an electric field, the synclinic $SmC_SP_F^*$ domains are slowly converted into the ground state $SmC_AP_F^*$ structure passing through intermediate mixed states that exhibit a reduction in both tilt angle and birefringence.

3.4. *$SmC_SP_A^*$ state*

The third type of domain, shown in figures 11 (*a–c*), occupies the smallest area of the cell on cooling from the isotropic state. Domains in this metastable state have the racemic layer structure $SmC_SP_A^*$, as is consistent with the experimental observations described below. It has an extinction direction that is rotated by 34° with respect to the layer normal in the absence of an electric field and a birefringence of $\Delta n \sim 0.15$ (the same as for the field-on states of $SmC_SP_F^*$). Upon the first application of a $|E| > E_{th}$ this third type of domain is switched into the ground state $SmC_AP_F^*$, figure 11 (*b*), and never returns to the original state ($SmC_SP_A^*$). Rather, upon removal of the field it forms a splayed $SmC_AP_F^*$ domain, figure 11 (*c*). Note that when the domain is driven from the $SmC_SP_A^*$ state to the $SmC_AP_F^*$ state the layer chirality does not change. Both the $SmC_SP_A^*$ and $SmC_SP_F^*$ states are found only to be produced on rapid cooling from the isotropic state in the absence of an electric field.

4. Discussion

All of the electro-optic properties of these three domains are consistently explained by variations in the stacking of tilted-smectic layers where in the ground state the layers form an anticlinic ferroelectric structure. This model explains the low birefringence of the ground state domains having an extinction direction parallel to the layer normal for both field-on and zero-field states and bistable ferroelectric properties as observed by optical SHG. The birefringence ($\Delta n = 0.08$) of the anticlinic structures, as calculated from the synclinic structures with tilt angle 34° ($\Delta n = 0.15$), are in good agreement with experiment. As observed, this model predicts that the two synclinic states, $SmC_SP_A^*$ with no field and $SmC_SP_F^*$ with a field, should have the same birefringence and their extinction directions should be rotated by the same angle θ from the layer normal.

It has long been an accepted fact that in the case of chiral materials, symmetry demands that the sign of the polarization in a given smectic layer be completely determined by the handedness of those molecules. Spontaneous symmetry-breaking in the B_2 phase of achiral bent-core materials results in two layer structures which have opposite layer chirality, see figure 12 (*a*). These (+) or (−) chirality layers are 'enantiomers' of each other, i.e., they are related by mirror symmetry.

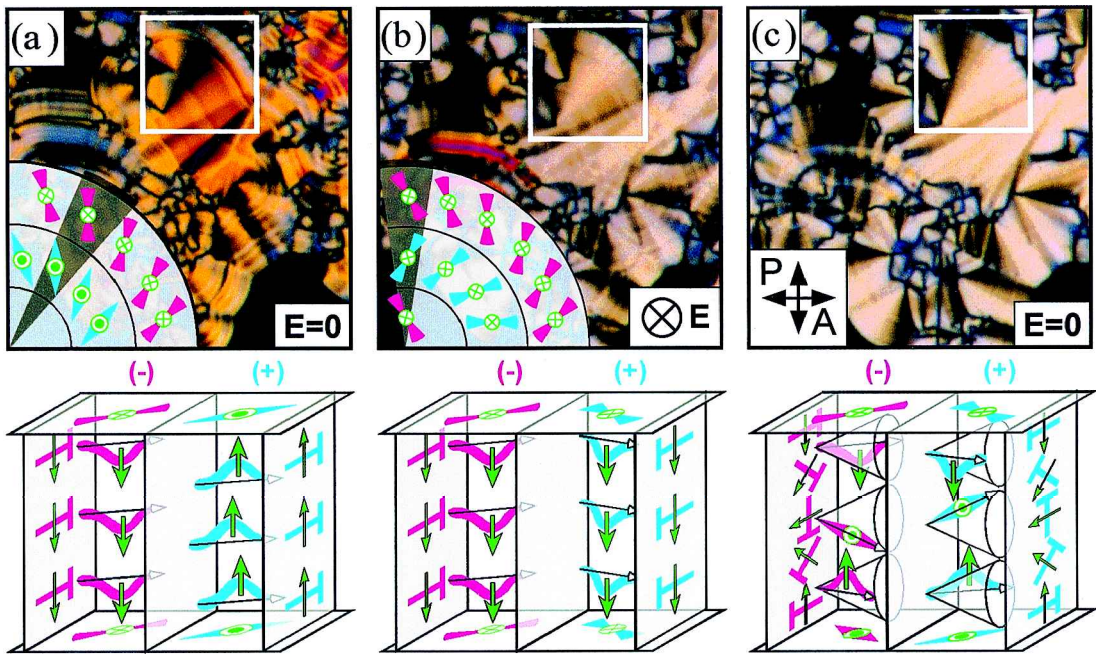

Figure 11. The $SmC_S P_A^*$ domains (synclinic in tilt and antiferroelectric in polar order) are racemic in layer chirality. In the absence of a field, (*a*), the birefringence colour and rotation of the optic axis from the layer normal to this structure are the same as for the $SmC_S P_F^*$ structure in the presence of an applied field. However, the application of an electric field derives the molecules to rotate on the tilt cone into the $SmC_A P_F^*$ ground state structure (*b*), so that after a single application of the field the molecules never return to the $SmC_S P_A^*$ structure (*c*). The layer structures of these states are sketched below the photomicrographs.

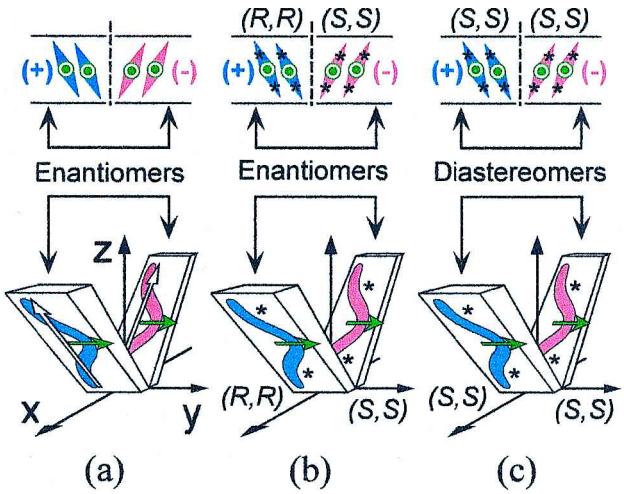

Figure 12. Sketch showing layer chirality. (*a*) If the system consists of achiral molecules, the structures with opposite tilts are mirror images of each other, i.e. enantiomers. (*b*) If (*R*, *R*) and (*S*, *S*) molecules form layers with opposite tilts, the structure is still composed of enantiomers. (*c*) However, if the molecules in both structures are of the same chirality then layers of opposite tilt are diastereomers.

Considering only single layers, these two enantiomeric structures should have the same free energy and occur in equal numbers as is found in the B_2 phase [6], see figure 1 (*b*). However, the situation is different when the two layers are composed of chiral molecules. The addition of molecular chirality to layers of opposite layer-chirality removes the mirror relationship between them, i.e. they now are diastereomers, figure 12 (*c*). As such there must be a free energy difference between them and it is expected that the ground state structure should be homogeneous in layer chirality—either $SmC_S P_F^*$ or $SmC_A P_A^*$ in figure 1 (*b*). Even if the rotation around the molecular long axis is strongly hindered because of the 'bent' molecular shape and this results in slow conversion between (+) and (−) layers, homogeneously chiral structure should be expected for the ground state of a chiral bent-core liquid crystalline phase from symmetry considerations. However, we have clearly shown that 8OPIMB6* organizes into layers having alternating layer-chirality despite molecular chirality. To explain this seemingly unlikely structure, we propose that steric interactions between the tails at the layer interfaces determines the relative tilt (synclinic or anticlinic) and polar order (ferroelectric or antiferroelectric) of the layers and not the chirality of the mesogens themselves. This is consistant with the suggestions of Walba *et al.* in [7].

5. Conclusion

Three molecular orientation states were found to exist in the highest temperature smectic phase of chiral

bent-core mesogens. They were identified to be the $SmC_A P_F^*$, $SmC_S P_F^*$ and $SmC_S P_A^*$ states based on microscope observation, birefringence measurements and SHG interferometry. The most stable structure, the ground state $SmC_A P_F^*$, exhibits surface-stabilized bistability with opposite orientation of polarization in the plane of the cell. This is the first observation of a smectic phase with racemic layer chirality that is composed of chiral molecules.

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