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Spontaneously chiral domains of an achiral bent-core nematic liquid crystal in a planar aligned device

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An achiral fixed bent-core nematic liquid crystal in an antiparallel aligned planar device is observed to form three distinct domains. Regions are observed which are achiral planar, as well as domains displaying both positive and negative chirality that are stable over a significant temperature interval. In such a device the presence of spontaneous positive and negatively twisted domains is highly unusual. By studying the electro-optics of the device relevant director structures are inferred, and it is additionally found that a sufficiently large applied electric field will drive the chiral domains into the achiral state.

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I. INTRODUCTION

Fixed bent-core liquid crystals have been a subject of interest since they were demonstrated by Niori *et al.* to form smectic phases containing a biaxial order within the layers and an associated spontaneous polarization [1]. This was the first example of a ferroelectric phase formed by achiral molecules, and subsequently extensive work followed investigating the various smectic banana phases [2,3]. More recently work has been focused on bent-core molecules in the drive to find a biaxial nematic phase, in the hope that there is a degree of ordering of the bend axis in the nematic phase. As a result a number of bent-core compounds exhibiting thermotropic nematic phases have since been synthesized and have been shown to possess a nonzero biaxial order parameter [4,5].

An interesting feature of the liquid-crystalline phases of bent-core molecules is an ability to form spontaneously chiral structures, despite the achirality of the constituent molecules [6,7]. It has been argued by Walba *et al.* that the origin of the observed chirality in the smectic B2 phase of bent-core compounds is due to a double symmetry breaking in the plane of the smectic layers, resulting in a noncentrosymmetric structure [6,8]. The proposed symmetry breaking in the layers is a tilt of the director from the layer normal combined with a polar ordering of the molecular bend axes in a direction perpendicular to the tilt plane [6]. With regards to nematic phases of bent-core compounds it is suggested that surface interactions may be an important consideration in any observed chirality [8].

Alternatively a recent theoretical study of bent-core compounds in which individual molecular conformations were simulated in the gas phase found that although the net chirality was negligible, a significant number of conformations were highly chiral [9]. It was also suggested that if a bulk chiral phase is induced, then molecular conformations of the same hand as the bulk chirality would be favored. Therefore it has been postulated that a self-assembly process where molecular conformations of one hand pack together forming a helical macrostructure, in turn stabilizing the further packing of molecules in such a manner to form a local cholesteric phase can lower the global free energy [10].

In this paper we report our findings on the nematic phase formed by the symmetric bent-core compound RAR-65 [11], with chemical structure and phase transitions shown in Fig. 1. Small angle x-ray scattering data on the compound indicate the presence of SmC cybotactic groups (a short-range SmC order) within the nematic [11,12]. The material was filled by capillarity between parallel glass plates coated in indium tin oxide. A rubbed polyimide surface treatment (PI2555-Dupont) was applied to each substrate producing homogeneous alignment, with the device assembled such that the rubbing directions were antiparallel. The spacing between the glass plates was fixed to be 3.5 μm using glass microspheres.

II. RESULTS AND DISCUSSION

On cooling the material from the isotropic into the nematic phase, domains of ordered liquid crystal are formed separated by regions of isotropic liquid. The domains are observed to consist of two distinct liquid-crystal states. As the device is rotated between crossed polarizers, the transmission of one of the states is seen to vary uniformly from extinction when the rubbing direction is parallel to one of the polarizers to a maximum when the rubbing direction is at 45° to the polarizers. Therefore this state is manifest optically as a uniform birefringent slab with the optic axis confined to a single plane and from herein will be designated as planar. The transmission of the second state is weakly modulated upon rotation, with maxima and minima for the same device orientation as the planar state, but never reaches extinction. These optical characteristics require some degree of rotation of the liquid-crystal director in the plane of the device and this state will subsequently be referred to as twisted.

The transmission as a function of device rotation between crossed polarizers for the two states is shown in Fig. 2. The measurements were made for normally incident light with a peak wavelength of 560 nm. The data were taken simultaneously for crossed and parallel polarizers to aid normalization. Due to the small nature of the liquid-crystal domains, the intensities were extracted via image analysis of a video of the device rotation.

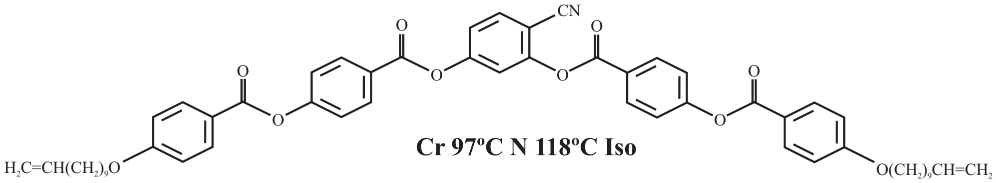

FIG. 1. The molecular structure and phase sequence of RAR-65, the bent-core compound under investigation.

As the temperature is reduced from the isotropic phase the two states appear in roughly equal proportion and both are stable over an interval of ~10 °C. However if the two states are coexistent in one of the domains, the planar state grows at the expense of the twisted state, indicating it to have a slightly lower energy. Additionally a further reduction in temperature causes an increase in the fraction of the device aligned in the planar state.

It may be possible to explain the initial observations in terms of conventional nematic behavior. In fact there is a current bistable technology which relies on the fact that there are stable planar and twisted states in a single device [13]. In such a case the liquid-crystal material is carefully doped to have a pitch exactly four times the device thickness such that both the planar and π twist state have the same energy. The material RAR-65 is comprised of achiral molecules which should eliminate such an effect, but it is conceivable that sample contamination could induce an intrinsic pitch. However if the device is observed between uncrossed polarizers, via a 10° rotation of the analyzer, a proportion of the twisted state increases in intensity while the remainder decreases. On the opposite rotation of the analyzer, the converse is true, as can be seen in Fig. 3. This shows that the twisted state is comprised of regions in which the rotation of the liquid-crystal director is in opposite directions. These regions of opposite chirality are observed in roughly equal measure in the twisted state. Such observations are incompatible with an explanation of sample contamination, as then domains with twist in only one direction would be stable.

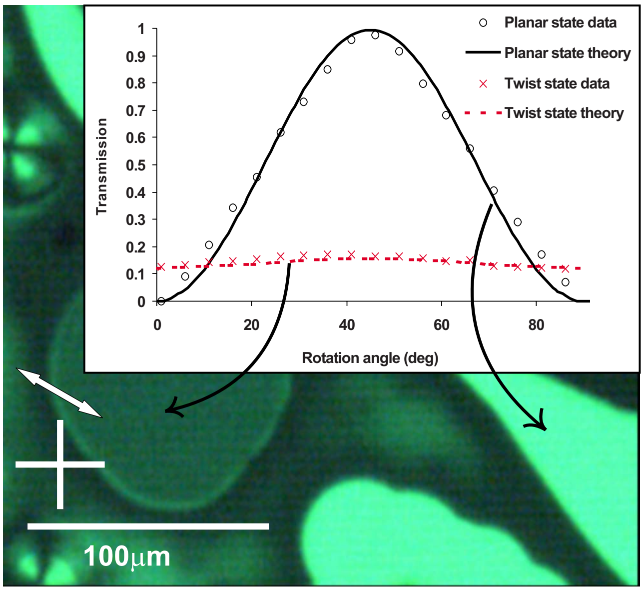

FIG. 2. (Color online) The transmission for the planar and twisted states as a function of rotation between crossed polarizers for normally incident light with a peak wavelength of 560 nm. The theoretical curves are shown for uniform planar and $\pm\pi$ twisted states with a birefringence of $\Delta n = 0.0805$. The + sign and double-headed arrow in the image correspond to the polarizer orientations and the substrate alignment directions, respectively.

It is possible to obtain twisted domains of both left and right hands in nematic planar devices by appropriate engineering of the surface alignment. For example, if the planar alignment direction differs by 90° between top and bottom substrate, as is the case in a conventional twisted nematic (TN) configuration, states comprising a rotation of the director in either sense would be expected for achiral materials. Alternatively parallel planar alignment conditions promoting a large pretilt in the director can lead to the formation of states with a $\pm\pi$ rotation in the director between the surfaces, the elasticity of such a twist distortion being lower than that for a uniform splay in the director between the substrates. However in the low pretilt antiparallel alignment device architecture considered here such behavior is highly unusual in achiral nematics since the ground state is predicted to exclude any distortion in the director. Therefore the results seem to lead to an explanation that the twisted states are spontaneously chiral in nature.

Previously, spontaneously chiral domains have been observed in the nematic phase formed by the achiral trans-4-alkylcyclohexancarboxylic acids [14]. Analogous to the observations here, cooling from the isotropic phase in a planar aligned device led to the formation of domains with either a uniform planar alignment or alternatively a right- or left-handed twist in the director. The explanation for such effects depends on the ability of these substances to form intermolecular hydrogen bonds, transforming the nonmesogenic monomeric molecules into dimers that have a rigid enough core to stabilize various liquid-crystal phases. Dimers are formed with either two (closed) or one (open) hydrogen bonds, and the latter can combine with further monomers or open dimers by hydrogen bonding to create oligomers. The oligomers provide a microscopic chirality, with the pitch of the chiral structure decreasing with increasing number of monomeric constituents. The probability of formation of left- or right-handed structures is identical and a racemic mixture develops although it is argued that in some domains fluctuations from the equilibrium might occur leading to one chiral species taking abundance and leading to a bulk chirality [14]. Alternatively, depending on the confining surfaces, monomers, or open dimers hydrogen bonded with the substrate can act as centers for oligomerization, resulting in a surface-induced chirality [15].

The hydrogen bonding of monomers to create chiral oligomers is not expected for the bent-core molecules consid-

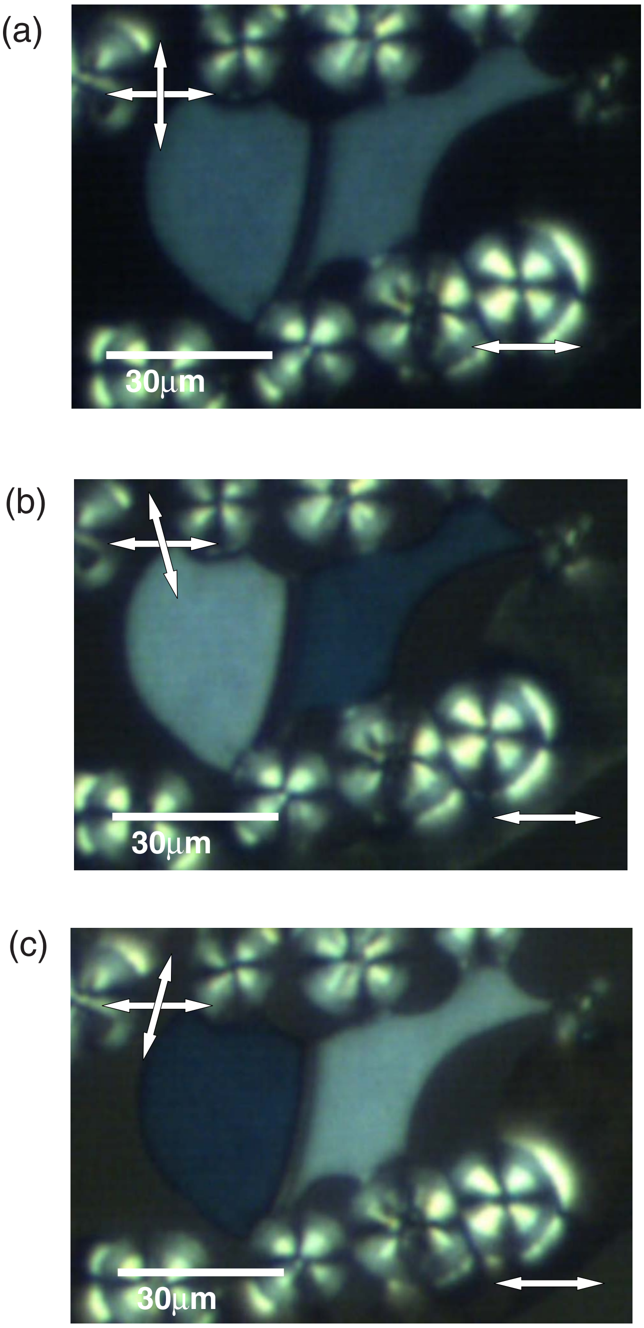

FIG. 3. (Color online) The twisted domains observed between (a) crossed polarizers, (b) with the analyzer rotated 10° anticlockwise, and (c) the analyzer rotated 10° clockwise. The relative change in intensity for the two domains shows them to have opposite twist, indicating that the domains are spontaneously twisted in nature. The single arrow shows the substrate alignment directions, while the twin arrows correspond to the polarizer and analyzer orientations.

ered here, but as noted above numerical simulations have indicated that in general the ground state is a racemic mixture in which some molecular conformations are highly chiral [9]. In analogy with the carboxylic acids, fluctuations might lead to a local abundance in one chiral species. It is then believed that a self-assembly process occurs causing neighboring molecules to adopt conformations of the same hand and spontaneously chiral domains ensue [10]. However, there are alternative explanations for the observation of spontaneously chiral domains in bent-core liquid crystals. Rather than the chirality arising from the bulk it could instead be induced from the surface alignment. Indeed there are both theoretical [16] and experimental [17,18] observations of a chiral surface inducing a twist in the director of an achiral liquid crystal about an axis perpendicular to the surface. Such a situation may occur if the bent-core molecules interacting with the surface preferentially adopt chiral conformations, creating a chirality at the surface that may propagate into the bulk. Alternatively it was noted above that SmC phases formed by bent-core compounds tend to be chiral due to the double symmetry breaking of the tilt axis and the molecular bend axis within the smectic layers [6]. Previously small angle x-ray scattering on the compound RAR-65 has indicated that the nematic phase contains a short-range SmC cybotactic order. Therefore a third possible mechanism arises to explain the formation of the observed spontaneously chiral domains: that interactions between neighboring cybotactic domains transfer an intrinsic cluster chirality into a bulk effect. Such a phenomenon has already been considered in relation to the carboxylic acids, predicting the bulk chirality to depend on the cluster density and the intrinsic cluster chirality [19]. Considering the results so far, it is not clear whether one of these mechanisms dominates in the formation of the chiral domains or whether a combination needs to be taken into account.

Now concentrating on the structure of the observed states, it is possible to draw some conclusions from our initial observations. The boundary conditions imposed by the surface treatment of the substrates force there to be an integer number of π rotations of the liquid-crystal director across the device thickness for standard liquid-crystal materials. All the regions of the twisted state have identical transmission through crossed polarizers confirming that they all have the same pitch. The coexistence of the planar and twisted states implies that they are similar in terms of energy, which combined with the surface limitations renders it likely that the twisted states are comprised of a $\pm\pi$ rotation of the director in the plane of the device.

Theoretical plots for the transmission between crossed polarizers for planar and $\pm\pi$ twist states are also shown in Fig. 2. The transmission for the planar state is given by $T=\sin^2(2\Psi)\sin^2(\Gamma/2)$ while for a $\pm\pi$ twist state $T=(\sin X/X)^2[\pi^2+\sin^2(2\Psi)(\Gamma/2)^2]$, where $X^2=[\pi^2+(\Gamma/2)^2]$ and $\Gamma=2\pi\Delta n d/\lambda$. A good fit to the experimental data is achieved for both states using $\Delta n=0.0805$, a value which seems reasonable from inspection of the molecular structure. Therefore the zero-field transmission characteristics are consistent with an explanation of planar and $\pm\pi$ twist states.

On application of an electric field to the device the planar state is seen to switch uniformly toward extinction for voltages above a certain threshold ($V_{thP}=2.95$ $\mathrm{V_{RMS}}$ at 1 kHz). The behavior is accordant with a positive $\Delta\epsilon$ material, whereby the director reorients parallel to the field direction provided that the dielectric torque is greater than the elastic constraints of the medium. However, the threshold voltage does display a strong frequency dependence indicating dielectric relaxation to a negative $\Delta\epsilon$ regime for frequencies

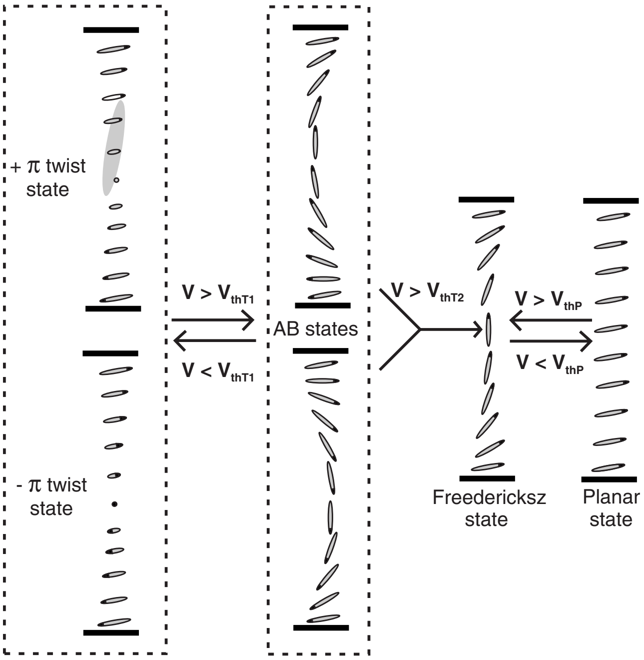

FIG. 4. The transitions with increasing voltage for the planar and $\pm\pi$ twist states. The planar state switches for voltages $V > V_{thP}$ into a single Fréedericksz state. For voltages greater than V_{thT1} the twist states are driven into either possible asymmetric bend (AB) state. At higher voltages the Fréedericksz state is the minimum energy state since it lacks the large splay distortion adjacent to one of the substrates present in both AB states. However the Fréedericksz state is not topologically similar to either AB state so the transition can only occur through a nucleation process at voltages $V > V_{thT2}$. When the voltage is subsequently removed the Fréedericksz state relaxes back to the planar state.

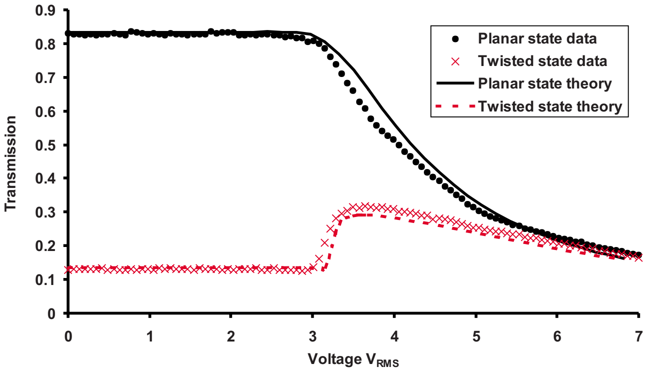

FIG. 5. (Color online) The transmission for both the planar and twisted states as a function of voltage. The applied voltage was a 1 kHz sine wave, and the data were taken at a device rotation of 45° between the rubbing direction and crossed polarizers. The light was normally incident and had peak wavelength of 560 nm. Also shown are theoretical fits to the data for both states using uniaxial continuum theory.

above ~50 kHz. The twist states also exhibit reorientation of the director for an applied voltage above a certain threshold V_{thT1} which is observed to be similar to V_{thP}. Above threshold the twist states undergo a transition into two optically equivalent states. On application of the voltage, the switched states grow from domain walls separating regions of opposite chirality. Upon rotation of the device between crossed polarizers, the transmission of the switched twisted states is very similar to that of the switched planar state. On removal of the electric field, the initial twisted states grow from the domain walls separating regions of the two different switched twist states. If the electric field is increased further to $V_{thT2} \simeq 10\ \mathrm{V_{RMS}}$ (1 kHz) the twisted states are irreversibly converted to the planar state.

The electro-optic observations provide further indication that the twisted states are comprised of a 180° director rotation, with the rotation axis perpendicular to the substrates. The director at the center of a π twisted state in an antiparallel aligned device is parallel to the substrates and hence degenerate with respect to tilt direction when reorienting with an applied electric field. Above the threshold for switching the central director can tilt in either direction, leading to the formation of two possible asymmetric bend (AB) states, shown in Fig. 4. The two AB states are distinguished from each other by the position of the large splay distortion at opposite boundaries but optically would appear identical. In each of the AB states the director is confined to a single plane, and hence there is no longer any optical rotation of an incident polarization state. Therefore this explanation is consistent with the experimental observation that above threshold the twisted states switch into two optically equivalent states, which rotate to extinction when the rubbing direction is parallel to one of the crossed polarizers.

The planar state in an antiparallel aligned device switches into a Fréedericksz state, where the surface conditions dictate that there is no degeneracy in tilt for the central director resulting in a single-switched state. For voltages above threshold the Fréedericksz state is a lower energy than the AB states since it avoids the large splay distortion at the surface. However the Fréedericksz state is not topologically similar to the AB states, and a transition between the two has to take place via a nucleation process. At higher voltages ($V > V_{thT2}$) this is realized and when the voltage is removed the initially twisted states now relax back to the planar state.

Figure 5 shows the transmission for the planar and twist states between crossed polarizers as a function of voltage. Again the measurements are taken for normally incident light with a peak wavelength of 560 nm via image analysis of a video showing the device after application of a slow voltage ramp. Also shown are theoretical fits to the data for the two states, assuming uniaxial continuum theory is applicable for this material. Initially the equilibrium configuration of the director is determined for each applied voltage, which can be achieved by minimizing the free energy of the system:

$$f(\hat{\mathbf{n}}) = \frac{1}{2}K_1[\boldsymbol{\nabla}\cdot\hat{\mathbf{n}}]^2 + \frac{1}{2}K_2[\hat{\mathbf{n}}\cdot(\boldsymbol{\nabla}\times\hat{\mathbf{n}}) + q]^2 + \frac{1}{2}K_3[\hat{\mathbf{n}}\times(\boldsymbol{\nabla}\times\hat{\mathbf{n}})]^2 - \frac{1}{2}\epsilon_0\Delta\epsilon(\hat{\mathbf{n}}\cdot\mathbf{E})^2, \qquad (1)$$

where the first three terms describe the Frank elastic energy for splay, twist and bend director deformations, while the fourth term is related to the coupling of the dielectric polarization with the electric field. The helical wave number q

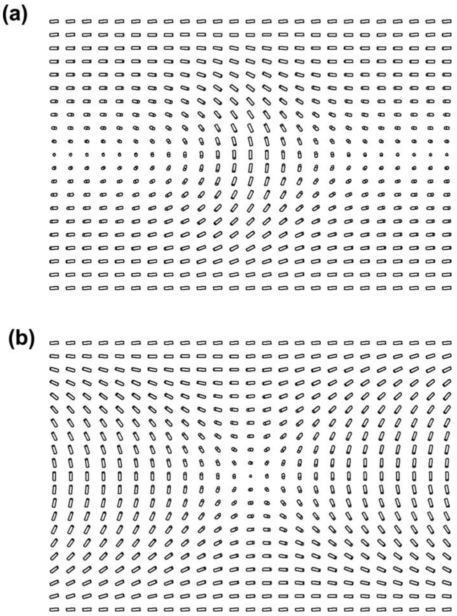

FIG. 6. (a) Director structure of a cross-section through a wall separating domains of opposite π twist with zero applied voltage. The cross section shown lies parallel to the substrate alignment direction, and the director at the center of the wall is aligned in an asymmetric bend state. (b) Director structure of a wall separating opposite asymmetric bend states with a voltage applied above threshold. The cross section shown lies parallel to the substrate alignment direction and the director at the center of the wall undergoes a π twist in the plane of the device.

$=\frac{2\pi}{P}$ allows for an intrinsic twist of the director of pitch P, with a positive q defining a right handed rotation. The transmission at normal incidence is calculated for the resultant director profile using a Jones matrix method. It has been proposed that for a nematic composed of bent-core molecules the bend elastic constant K_3 might be very small or even negative, leading to a spontaneous bending of the medium [20]. It is also interesting to consider the twist elastic energy since a low or negligible value of K_2 in a material may induce the formation of domains possessing some rotation in the director. Such a scenario might occur if the elastic energy of a twist distortion is of the order of the thermal energy fluctuations close to the phase transition. However we find that the best fit to the experimental data for each state is achieved for a parameter set as might be expected for standard nematic materials. The theoretical curves shown in Fig. 5 are calculated with $K_1/\Delta\epsilon\epsilon_0=1.02\ \mathrm{N}^2\,\mathrm{C}^{-2}\,\mathrm{m}^2$, $K_1/K_3=0.9$, $K_2=K_3/2$, $q\approx 0$, and $\Delta n=0.0805$. Interestingly the combination of a typical value of K_2 and negligible q presents difficulties in reconciling the twisted states with a spontaneous bulk chirality in the limits of uniaxial continuum theory. Rather the theoretical fit to the data indicates surface considerations to be important as a driving mechanism for the formation of the chiral domains, with the molecules potentially interacting with the alignment layer in such a manner as to create a chiral surface.

With no applied electric field states of positive and negative π twist are observed adjacent to each other in some regions, as shown in Fig. 3. It is interesting to consider the director structure in the walls separating these domains. A two dimensional numerical method is used to model a cross section through such a wall. The director at either side of the cross section is fixed to be opposite π twist states and the director at the substrates is constrained to remain parallel to the boundary in accordance with strong planar anchoring. The director is then allowed to relax minimizing the free energy given in Eq. (1) as outlined in detail elsewhere [21]. For a continuous variation in the director, it is found that the structure at the center of the wall is in fact one of the asymmetric bend states, as can be seen in Fig. 6(a). Therefore when a field is applied above threshold the asymmetric bend states grow from such domain walls, as observed in experiment.

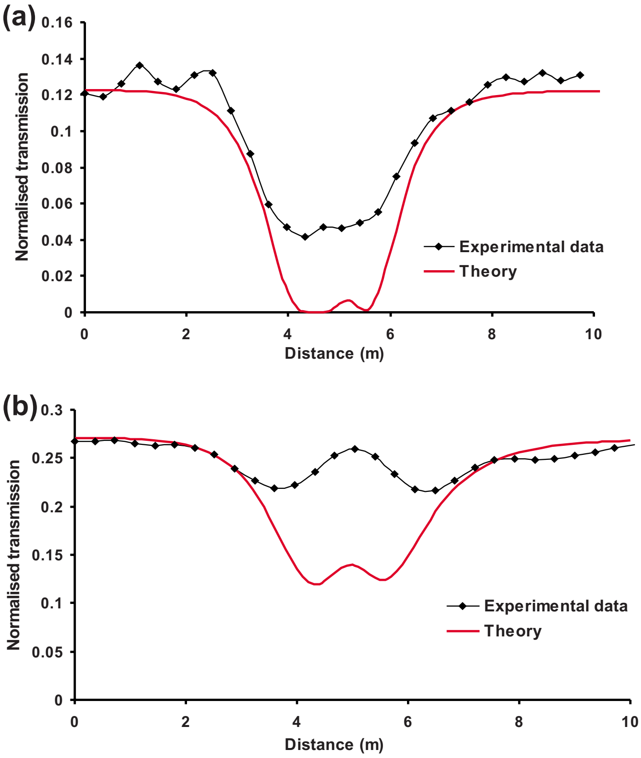

FIG. 7. (Color online) Experimental results and theoretical predictions for the transmitted intensity as a function of distance along a particular direction in the plane of the device. (a) Cross section of a wall separating domains of opposite π twist with zero applied field. The wall lies perpendicular to the substrate alignment direction and parallel to one of the crossed polarizers. (b) Cross section of a wall separating regions of opposite asymmetric bend states with 5 $\mathrm{V}_{\mathrm{RMS}}$ applied. The wall runs parallel with the substrate alignment direction and is at 45° to the crossed polarizers.

In the center of the twist domains, a sudden application of voltage above threshold results in the formation of domains of opposite asymmetric bend states. It is also interesting to consider the structure of the walls separating these switched domains. The director configuration is calculated for a cross section of the wall in a manner analogous to that above but with either side of the wall initially seeded to form opposite asymmetric bend states and allowed to relax under voltage application. For a smooth variation in the director it is found that the structure at the center of the wall is a 180° rotation of the director in the plane of the device, as shown in Fig. 6(b). Therefore on voltage removal π twist states grow from such walls, again as observed in experiment.

Figure 7 shows experimental results and theoretical predictions of the transmitted intensity as a function of distance along a particular direction in the plane of the device, hereafter designated as line scans. Figure 7(a) displays experimental and theoretical line scans across a section of a wall separating opposite π twist states at zero voltage. The section of wall used for the plot runs perpendicular to the substrate alignment direction and parallel to one of the crossed polarizers. The experimental data are extracted from a polarizing microscopy image similar to Fig. 3(a). The theoretical prediction is calculated by determining the equilibrium director configuration for the wall as described above, while employing the material parameter set used in the fitting of the transmission-voltage curves in Fig. 5. The transmission through the resulting structure is subsequently calculated at a series of points along the cross section using a Jones optics routine, for normally incident light averaged over a range of wavelengths spanning the visible spectrum. Figure 7(b) shows experimental and theoretical line scans for a wall separating regions of opposite asymmetric bend states with a voltage of 5 $\mathrm{V_{RMS}}$ applied. The wall now lies parallel to the substrate alignment and at an angle of 45° to the crossed polarizers. There is a good qualitative agreement between the experimental results and theoretical predictions, with the dependence on position for the transmitted intensity through the wall corresponding closely for the two cases, adding extra weight to the given explanation for the structures involved. There is some disparity in absolute magnitudes between the experimental and theoretical results, which is attributed to the fact that the calculations did not take into account the uncollimated nature of the illumination or any scattering from the liquid-crystal structure.

III. CONCLUSION

We have demonstrated that in a homogeneously aligned device filled with a fixed bent-core nematic material, there is coexistence of uniform planar alignment, and positive and negatively twisted states. The observation of positively and negatively twisted states as stable in a low pretilt antiparallel aligned device is indicative of a spontaneous formation of chiral domains. Electro-optic studies of the device confirm that the behavior of the twisted states is consistent with that for $\pm\pi$ twist states, and we find that it is possible under application of moderate electric fields ($\lesssim 3\ \mathrm{V}\,\mu\mathrm{m}^{-1}$) to switch from the twisted to planar states. Analysis of the transmission as a function of voltage for both the planar and twisted states, in the limit of uniaxial continuum theory, suggests that surface interactions play an important role when considering the mechanism driving the formation of the chiral domains.

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