

## Optical Activity Produced by Layer Chirality in Bent-Core Liquid Crystals

Loren E. Hough,<sup>1</sup> Chenhui Zhu,<sup>1</sup> Michi Nakata,<sup>1</sup> Nattaporn Chattham,<sup>2</sup> Gert Dantlgraber,<sup>3</sup>  
Carsten Tschierske,<sup>3</sup> and Noel A. Clark<sup>1</sup>

<sup>1</sup>LCMRC, Department of Physics, University of Colorado, Boulder

<sup>2</sup>Department of Physics, Faculty of Science, Kasetsart University, Bangkok 10900 Thailand

<sup>3</sup>Institute of Organic Chemistry, Martin-Luther Universität Halle-Wittenburg

(Received 31 August 2006; published 19 January 2007)

Large optical activity has recently been observed in chiral smectic liquid crystalline phases formed from achiral bent-core molecules. The origin of the optical activity remains unclear and has been attributed to both a helical superstructure and the layer chirality produced by simultaneous tilt and polar ordering of bent-core mesogens in the  $B_2$  phase. Here, we directly demonstrate that layer chirality produces optical activity in the well ordered  $\text{SmC}_A P_A$  subphase.

DOI: [10.1103/PhysRevLett.98.037802](https://doi.org/10.1103/PhysRevLett.98.037802)

PACS numbers: 61.30.-v, 42.70.Df, 78.20.Ek

Liquid crystalline phases formed from chiral molecules exhibit a wide variety of chiral optical effects, including Bragg reflection, optical activity and circular dichroism. Spectacular Bragg reflection is produced by macroscopically helical chiral nematic and smectic  $C^*$  phases when the wavelength is commensurate with the helical pitch [1,2]. Lasing has been observed in these systems when doped with an appropriate dye [3]. Optical activity is the difference in index of refraction for left and right hand circularly polarized light, which leads to the rotation of linearly polarized light in isotropic materials. In contrast, circular dichroism is the difference in absorption of left and right hand polarized light. Optical activity and circular dichroism are important probes of structural chirality in liquid crystalline systems. For example, in an isotropic fluid near the isotropic-cholesteric transition, large divergent pretransitional optical activity is produced by helical molecular orientation within cholesteric-like correlation volumes [4,5] and optical activity has been used in the determination of the structure of the blue phases [6].

Chiral optical effects in liquid crystalline systems are typically a result of helical superstructure and produced from chiral mesogens and until recently were not thought to be a dominant effect in chiral phases formed from achiral bent-core mesogens. In these systems, tilt and polar ordering of achiral molecules produces a chiral layer structure (often referred to as tilt chirality), that generally lacks any supermolecular helix [7]. The four bilayer stackings of chiral layers, with syn- or anti-clinic tilt ordering ( $\text{SmC}_S$  or  $\text{SmC}_A$ ) and ferro- or antiferro-electric polar ordering ( $\text{SmCP}_S$  or  $\text{SmCP}_A$ ), form the  $B_2$  phase. The  $\text{SmC}_S P_A$  and  $\text{SmC}_A P_S$  are macroscopically racemic, while the  $\text{SmC}_A P_A$  and  $\text{SmC}_S P_S$  are macroscopically chiral, that is they have the same chirality in every layer. Supermolecular helixing has been proposed in the more highly ordered bent-core  $B_4$  phase, where helixing is accompanied by significant optical activity [8].

Surprisingly, chiral optical effects have been observed even in several bent-core systems not known to have any

helical superstructure. However, the relationship between the layer chirality and the observed optical chirality has remained unclear. Olson *et al.* observed chiral effects in null-transmission ellipsometry of a single-layer freely suspended  $B_2$  film [9], where a helical supermolecular structure was not present. The handedness of the chiral effect in this case was consistent with the layer chirality resulting from simultaneous tilt and polar order. A conglomerate texture of chiral and strongly optically active, yet optically isotropic, domains formed from some bent-core mesogens has been widely observed [10]. This texture is formed by the dark conglomerate phase, which has very short layer correlation length making determination of the local layer structure difficult. We have observed that the optical rotation in the dark conglomerate increases linearly with cell thickness, indicating that it is a bulk effect. Schröder *et al.* and Pyc *et al.* both reported observations of optical activity in the  $\text{SmC}_A P_A$  formed on removal of a sufficiently large applied electric field used to align the layers [11,12], supporting the idea that the chiral layer structure of the  $\text{SmC}_A P_A$  produces significant optical activity. However, they did not directly compare optically chiral domains with domains of tilt chirality. Finally, Jákli and coworkers observed optically active domains in a birefringent sample that were much larger than the local tilt domains [13]. They proposed that this optical activity was caused by twist of the optic axis through the cell; a very different mechanism for producing optical activity than the one described here.

We recently proposed that the optical activity observed in chiral bent-core systems with no macroscopic helix is a result of the chiral layer structure (termed layer optical chirality (LOC)) [14]. The LOC model is based on tilt and polar ordering of the molecules within a layer. Our model is similar in nature to that developed by Olson *et al.* [9] for a single freely suspended film, and by Ortega *et al.* [15] for the  $\text{SmC}_A P_A$ ; the models are based on modulations of the dielectric tensor on the length scale of individual layers. In our previous work, we considered the achiral stacking of chiral layers, as shown in Fig. 1. The chiral layer structure

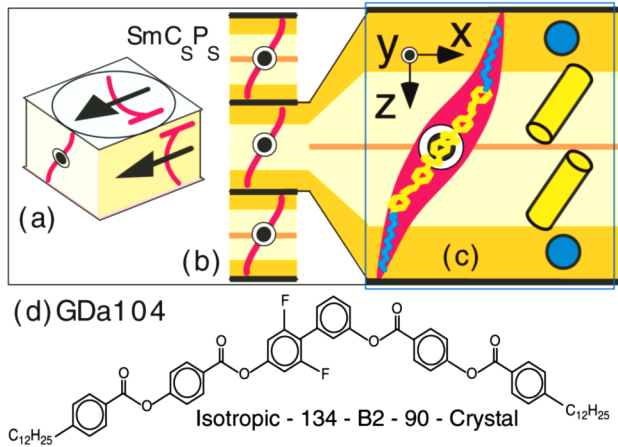


FIG. 1 (color online). A sketch of the LOC model for the  $\text{SmC}_S P_S$ . Significant optical activity results from the achiral stacking (b) of chiral layers (a,c). This model incorporates tilt and polar ordering of the bent-core molecules, where the polar direction is represented by the black arrow (bull's eye), and the tilt direction by the dark (magenta)  $T$  on the surfaces of the cube (a), which in this case is curved to represent the chirality of the layer. The orientation of a typical bent-core molecule within a layer is shown in (c): the dark (magenta) envelope around the molecular structure represents the projection of the molecule out of the plane of the paper: it is thickest for portions of the molecule projecting toward the reader. Each layer is divided into four achiral sublayers, representing the four structural segments of a bent-core molecule: two uniaxial slabs with optic axes parallel to the arms of the bent-core molecule form the core (light cylinders) and two isotropic sublayers represent the aliphatic tails of the molecule (dark circles). (d) The molecular structure and phase sequence on cooling (deg C) of GDa104.

is comprised of four sublayers: two uniaxial sublayers with optic axes along each arm of a bent-core molecule and two isotropic sublayers modeling the aliphatic tails. Guided by the work of Bensimon *et al.* [16], we calculated the optical activity of such a structure. The LOC model predicts that the chiral  $B2$  subphases have significant optical activity and characterizes their wavelength and tilt-angle dependence. There has so far been no direct confirmation of optical activity resulting from tilt chirality in the  $B2$  phase.

In this Letter, we directly demonstrate that tilt chirality produces optical activity in the  $\text{SmC}_A P_A$  phase of GDa104 (Fig. 1). This work supports the idea that optical activity is an intrinsic property of the chiral  $B2$  subphases. Typically, in the  $B2$  phase, significant birefringence dominates the optical texture, masking any chiral optical effects. The  $\text{SmC}_A P_A$  phase of GDa104 has a tilt angle near 45 degrees (nearly orthoconic), and so has very low birefringence allowing for direct observation of the optical activity.

Synthesis, current response, and initial electro-optic investigations of GDa104 were reported by Dantlgraber *et al.* [17]; the chemical structure and phase sequence on cooling are given in Fig. 1. The polarization current response of this material shows two peaks, indicating that the material is antiferro-electric and consistent with optical investiga-

tion indicating coexistence of the  $\text{SmC}_A P_A$  and  $\text{SmC}_S P_A$  subphases. A third peak was initially observed and attributed to coexistence of ferroelectric domains; however, this peak is a result of ion flow and can be eliminated by well insulating the material from the electrodes.

We made freely suspended films of GDa104 in order to verify that the optical activity was produced by the  $\text{SmC}_A P_A$  phase rather than a tight pitch helix [7,18]. We observed their behavior under an applied electric field while simultaneously measuring the layer thickness. The  $\text{SmC}_A P_A$  and  $\text{SmC}_S P_A$  coexisted within the films, as evidence by even layered domains showing either longitudinal polarization or no net polarization while the odd layered films showed transverse polarization (Fig. 2). In particular, we saw no even layer films with transverse polarization, which would be evidence of the  $\text{SmC}_S P_S$ : the expected stable structure for a very thin film when a tight pitch helix is present in the bulk.

We focus on the  $\text{SmC}_A P_A$ , which is the predominant  $B2$  subphase present on cooling GDa104 from the isotropic and has a typical texture and electro-optic behavior. In the  $\text{SmC}_A P_A$ , the optic axis is parallel to the layer normal. Because the tilt angle is nearly 45 degrees and so the optic axes in adjacent layers are nearly orthogonal, the  $\text{SmC}_A P_A$  has very low birefringence,  $\Delta n = 0.005$ , and appears dark gray in a  $4.5 \mu\text{m}$  thick capacitor cell (Fig. 3). Orthoconic materials, those with a tilt angle of exactly 45 degrees, have been recognized for their use in display applications [19] and have been observed in bent-core systems [13]. Application of a large electric field ( $20 \text{ V}/\mu\text{m}$ ) switches

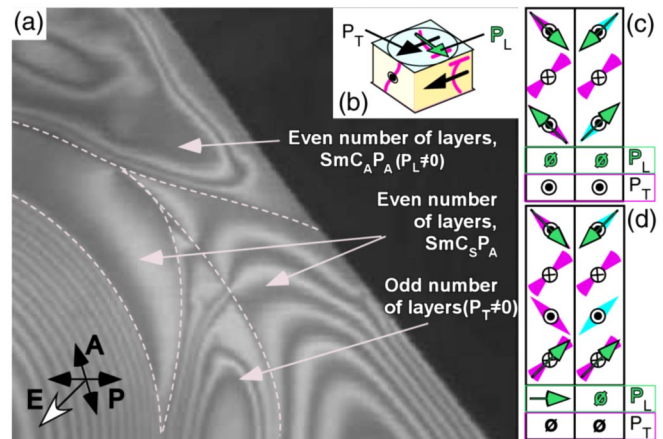


FIG. 2 (color online). (a) A freely suspended film of GDa104 showing coexistence of  $\text{SmC}_A P_A$  and  $\text{SmC}_S P_A$ . (b) Transverse polarization ( $P_T$ ) is perpendicular to the tilt plane of the molecules, while longitudinal polarization ( $P_L$ ) is within the tilt plane. (c,d) The polarization of each layer is diagrammed for the  $\text{SmC}_A P_A$  (left column) and the  $\text{SmC}_S P_A$  (right column). (c) Odd layered films of either the  $\text{SmC}_A P_A$  or  $\text{SmC}_S P_A$  have  $P_T \neq 0$ , in this case out of the plane of the page (bullseye) [7]. (d) Surface polarization along the long axis of the molecules (green/light gray arrows) results in  $P_L \neq 0$  in even layered  $\text{SmC}_A P_A$  films [18].

the sample to a high birefringence  $\text{SmC}_S P_S$  state, and the extinction brushes rotate to nearly 45 degrees from the analyzer or polarizer. The direction of rotation depends on the tilt chirality.

GDa104 is an ideal material to test the LOC model because domains of opposite tilt chirality coexist within a single fan-shaped area. In the  $\text{SmC}_A P_A$ , this allows for the direct observation of the optical activity produced by tilt chirality without the need to correct for changes in optic axis or birefringence. In the  $\text{SmC}_A P_A$  (Figs. 3 and 4), the only difference between two adjacent chiral domains within a single fan-shaped domains is the tilt chirality. The optic axis is parallel to the layer normal which is continuous across the chiral domain boundary.

Optical activity can be clearly observed in the  $\text{SmC}_A P_A$  when the analyzer is decrossed relative to the polarizer. Between perfectly crossed polarizer and analyzer, the two chiral domains are identical and no domain boundary is visible. A very slight difference can be seen in Fig. 3(b) due to the difficulty in perfectly crossing the analyzer and polarizer. Decrossing the analyzer relative to the polarizer reveals a distinct contrast between the two domains; one becomes brighter and the other darker [Figs. 3(c), 3(d), and 4(b)]; this contrast is inverted when the direction of decrossing is reversed. This is a clear indication of optical activity; decrossing the analyzer relative to the polarizer clockwise or counterclockwise yields identical results in an optically achiral phase. If there were no birefringence, the linearly polarized light would be rotated, but would remain linearly polarized as it propagated through the sample. However, with birefringence, as for GDa104, light leaves the sample elliptically polarized. As discussed below, the magnitude of the optical rotation can be found from the contrast difference between right- and left-handed domains.

We confirmed that the chiral domains identified by their optical activity are domains of tilt chirality, showing a typical chiral response under application of an electric field. With a strong applied field, the domains switch to

the  $\text{SmC}_S P_S$  while maintaining their layer chirality. Strong pretransitional effects, where the tilt angle and birefringence increase simultaneously with increasing field, allow for the direct observation of the rotation of the optic axes, which go in opposite directions for the two chiral domains. In the final switched state, the extinction brushes appear to be nearly continuous across the domain boundaries; the optic axes are nearly orthogonal in the two domains and so when the optic axis in one domain is parallel to the analyzer, the optic axis in the other domain is nearly parallel to the polarizer, and is also dark. However, as seen in Fig. 3(a), a small discontinuity in the brush direction across the chiral domain boundary is visible. Finally, the domain boundaries appear to have very low birefringence due to the averaging of the optic axes of the two domains (as in the  $\text{SmC}_A P_A$ ). The domain boundaries appear to be darker than the  $\text{SmC}_A P_A$  only because the exposure time is much longer for the  $\text{SmC}_A P_A$  images than for the  $\text{SmC}_S P_S$  image.

To quantify the optical activity, we measured the gray scale intensity of the images taken with the analyzer decrossed by 5 degrees relative to the polarizer. We define the contrast as the ratio of the difference in the intensity of the two domains to the average intensity. The contrast depends somewhat (roughly a factor of 3) on the orientation of the optic axis relative to the analyzer and polarizer, and so we measured the contrast when the optic axis was  $\sim 45$  degrees to the analyzer. In this case, the contrast is  $\sim 10\%$  in the  $\text{SmC}_A P_A$ .

The optical activity that would result in this contrast was found by modeling the sample as a uniaxial medium where the optical activity is produced by complex off-diagonal terms,  $\pm i\gamma$ , in the dielectric tensor,

$$\epsilon = \begin{pmatrix} \epsilon_{\parallel} & i\gamma \\ -i\gamma & \epsilon_{\perp} \end{pmatrix} \quad (1)$$

where  $\Delta\epsilon = \epsilon_{\parallel} - \epsilon_{\perp}$ . The optical rotation per unit length,  $\phi$ , of linearly polarized light as it passes through a sample

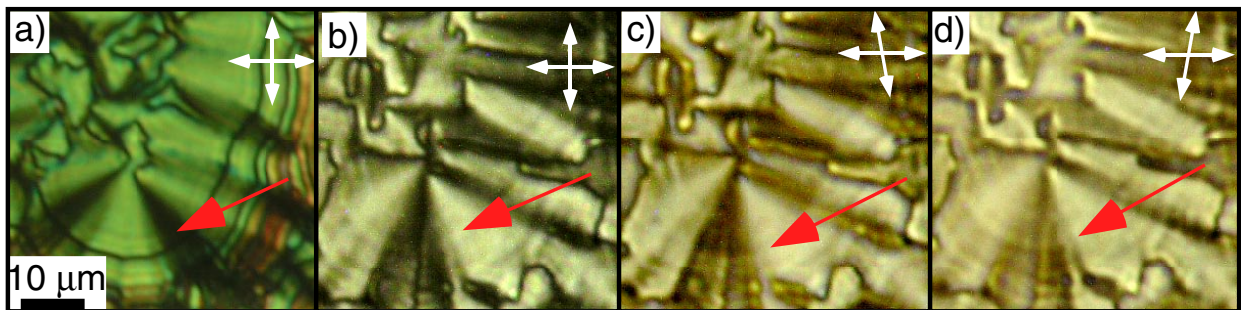


FIG. 3 (color online). Optical activity is visible in chiral domains of GDa104 in the low birefringence ( $\Delta n = 0.003$ )  $\text{SmC}_A P_A$ . (a) The tilt chirality of the domains was confirmed in the field-induced  $\text{SmC}_S P_S$  (crossed polarizers), where domains of opposite chirality within a single fan-shaped region are separated by a dark line (red arrow). The birefringence of the  $\text{SmC}_S P_S$  is  $\Delta n = 0.17$ , and so it appears green in a  $4.5 \mu\text{m}$  display cell. (b) In the  $\text{SmC}_A P_A$ , such domains appear identical under crossed polarizers. (c) Contrast between the domains becomes apparent when the analyzer is decrossed relative to the polarizer, and (d) this contrast inverts when the decrossing direction is reversed. In these images, the decrossing angle is 5 degrees, and the contrast has been enhanced for clarity.

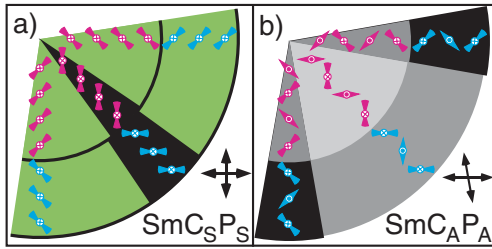


FIG. 4 (color online). Molecular orientation and typical texture within a fan-shaped domain of the (a)  $\text{SmC}_S P_S$  and (b)  $\text{SmC}_A P_A$  with tilt angle near 45 degrees. The layer chirality is indicated by the color of the schematic molecules (cyan or magenta), and portions of the bent-core molecules which project toward the reader are thicker. The polar direction is into (cross) or out of (bullseye) the plane of the paper. The optic axis in the  $\text{SmC}_S P_S$  is nearly 45 degrees from the layer normal, in opposite directions for the two chiralities; as a result, the extinction brushes in the two domains are nearly parallel. The optic axes of the two domains are averaged at the resolution limited domain boundary, making it quite dark. In the  $\text{SmC}_A P_A$ , the optic axis is  $\text{SmA}$ -like (parallel to the layer normal) and thus continuous across the chiral domain boundary. The only difference between the two domains is the layer chirality, and the contrast between the domains visible (dark and light gray) when the analyzer is decrossed relative to the polarizer is due to optical activity.

with the same optical activity but no birefringence is  $\phi = k_o^2 \gamma / (2\epsilon)$  [14]. Although the LOC model and measurements in the dark conglomerate indicate that there is a strong wavelength dependence, we do not consider that here because the wavelength dependence is dominated by the birefringence and we are mainly interested in the average magnitude of the optical rotation. Although analytically difficult, it is straightforward to numerically solve for the transmitted intensity, which depends on the decrossing angle (5 deg), sample thickness (4.5  $\mu\text{m}$ ), and dielectric tensor [Eq. (1)]. The contrast is relatively insensitive to the average dielectric constant, which we took to be 2.4, and  $\Delta\epsilon$  was found from the birefringence. For the  $\text{SmC}_A P_A$ , the measured contrast of 10% would correspond to an optical rotation 0.2 deg/ $\mu\text{m}$  in an isotropic sample, consistent with the OR measured in some dark conglomerate materials (which we have observed to range from 0.1–1 deg/ $\mu\text{m}$  for  $\lambda = 650 \text{ nm}$ ). Note that even though GDa104 has relatively low birefringence,  $\gamma$  is still 20 times smaller than  $\Delta\epsilon$ .

This calculation highlights the difficulty in measuring the optical rotation in a typical  $B2$  phase. For example, the field-induced  $\text{SmC}_S P_S$  of GDa104 has  $\Delta n = 0.17$ , and so the same optical activity would give a contrast difference of only 0.05%. The LOC model predicts a slightly higher (factor of 2) optical activity in the  $\text{SmC}_S P_S$  than in the  $\text{SmC}_A P_A$ , but still not enough to be experimentally observable by this method given that domains with parallel optic axis are not adjacent in the  $\text{SmC}_S P_S$ . Therefore, the scarcity of optical activity observations in the  $\text{SmC}_S P_S$  could be a result of the difficulty in the measurement, not

necessarily a result of any difference in the magnitude of the optical activity relative to the  $\text{SmC}_A P_A$ . In fact, there are dark conglomerate phases which have a single peak in the current response, indicating that they are ferroelectric (and so presumably locally  $\text{SmC}_S P_S$  since they are chiral) [20].

Thus, we directly observed that domains of tilt chirality in the  $\text{SmC}_A P_A$  phase of GDa104 have significant optical activity. In agreement with the LOC model [14], we propose that the optical activity is an intrinsic quality of the chiral  $B2$  phases, but the optical properties of the phase are typically dominated by the birefringence.

We would like to acknowledge support from NSF MRSEC Grant No. DMR0213918, NSF GRF and NSF No. GAANN P200A030179.

- 
- [1] H. de Vries, *Acta Crystallogr.* **4**, 219 (1951).
  - [2] H. Hoshi, D. Chung, K. Ishikawa, and H. Takezoe, *Phys. Rev. E* **63**, 056610 (2001).
  - [3] V.I. Kopp, H.K.M. Vithang, B. Fan, and A.Z. Genack, *Opt. Lett.* **23**, 1707 (1998).
  - [4] J. Cheng and R.B. Meyer, *Phys. Rev. Lett.* **29**, 1240 (1972).
  - [5] V. Dolganov, S. Krylova, and V. Filev, *Sov. Phys. JETP* **51**, 1177 (1980).
  - [6] P.J. Collings, *Phys. Rev. A* **30**, 1990 (1984).
  - [7] D.R. Link, G. Natale, R. Shao, J.E. MacLennan, N.A. Clark, E. Körblova, and D.M. Walba, *Science* **278**, 1924 (1997).
  - [8] J. Thisayukta, H. Takezoe, and J. Watanabe, *Jpn. J. Appl. Phys.* **40**, 3277 (2001).
  - [9] D.A. Olson, X.F. Han, P.M. Johnson, A. Cady, and C.C. Huang, *Liq. Cryst.* **29**, 1521 (2002).
  - [10] J. Thisayukta, Y. Nakayama, and J. Watanabe, *Liq. Cryst.* **27**, 1129 (2000).
  - [11] M.W. Schroder, S. Diele, G. Pelzl, and W. Weissflog, *Chem. Phys. Chem.* **5**, 99 (2004).
  - [12] P. Pyc, J. Mieczkowski, D. Pocięcha, E. Gorecka, B. Donnio, and D. Guillon, *J. Mater. Chem.* **14**, 2374 (2004).
  - [13] A. Jakli, Y.M. Huang, K. Fodor-Csorba, A. Vaida, G. Galli, S. Diele, and G. Pelzl, *Adv. Mater.* **15**, 1606 (2003).
  - [14] L.E. Hough and N.A. Clark, *Phys. Rev. Lett.* **95**, 107802 (2005).
  - [15] J. Ortega, C.L. Folcia, J. Etxebarria, N. Gimeno, and M.B. Ros, *Phys. Rev. E* **68**, 011707 (2003).
  - [16] D. Bensimon, E. Domany, and S. Shtrikman, *Phys. Rev. A* **28**, 427 (1983).
  - [17] G. Dantlgraber, D. Shen, S. Diele, and C. Tschierske, *Chem. Mater.* **14**, 1149 (2002).
  - [18] D.R. Link, J.E. MacLennan, and N.A. Clark, *Phys. Rev. Lett.* **77**, 2237 (1996).
  - [19] K. D'havé, P. Rudquist, S.T. Lagerwall, H. Pauwels, W. Drzewinski, and R. Dabrowski, *Appl. Phys. Lett.* **76**, 3528 (2000).
  - [20] G. Dantlgraber, A. Eremin, S. Diele, A. Hauser, H. Kresse, G. Pelzl, and C. Tschierske, *Angew. Chem., Int. Ed. Engl.* **41**, 2408 (2002).