Biaxial model of the surface anchoring of bent-core smectic liquid crystals

Joseph E. Maclennan* and Noel A. Clark

Ferroelectric Liquid Crystal Materials Research Center and Department of Physics, University of Colorado, Boulder, Colorado 80309

David M. Walba

Ferroelectric Liquid Crystal Materials Research Center and Department of Chemistry and Biochemistry, University of Colorado, Boulder, Colorado 80309

In synclinically tilted smectic phases, bent-core liquid crystal molecules aligned with the director in the plane of a cell boundary will, in general, have their molecular (bow) planes parallel to the boundary, normal to it, or at a well-defined intermediate orientation. A model describing the interaction of such bent-core (banana-shaped) molecules with planar surfaces that distinguishes energetically between molecules lying flat on the surface and those oriented edge on is given by a biaxial modification of the uniaxial surface anchoring expression used for chiral smectics of rod-shaped molecules. When combined with a field-induced straightening of the smectic layers, the model provides a mechanism for the transition from an analog to a bistable director response observed electro-optically in the ferroelectric banana-shaped material (R,S)-MHOBOW.

PACS number(s): 61.30.Cz, 61.30.Eb, 61.30.Gd

I. INTRODUCTION

The recent rediscovery of bent-core (banana-shaped) liquid crystals [1] has stimulated a major research effort aimed at understanding their structures and phase behavior. Within smectic layers, the liquid crystal ordering is dominated by steric effects, with the molecules usually packing in a polar fashion. In tilted smectics this results in the formation of chiral (anti)ferroelectric phases which reorient readily in applied electric fields. Indeed, many key insights into the fundamental structures of the banana-shaped phases have been gleaned from the microscopic textures and electro-optic responses of thin cells.

For example, by studying the smectic-C-like $B2$ textures [2] of the prototypical symmetric, achiral alkoxy banana-shaped NOBOW [3] (see Fig. 1), it was recognized that a spontaneous symmetry breaking led to the formation of antiferroelectric domains of arbitrary chirality. The structure of this SmC_SP_A phase was confirmed by electric field experiments on freely suspended films with differing layer numbers. The racemic asymmetric bent-core material (R,S)-MHOBOW (see Fig. 1), on the other hand, was designed to have a ferroelectric ground state, and the SmC_SP_F structure has recently been confirmed with the $B7$ texture [4]. Two different kinds of focal conic domain are observed in virgin MHOBOW cells, both of which appear golden [see Fig. 1(a)] in cells of thickness $d=4$ μm, corresponding to a birefringence $\Delta n \sim 0.07$. They both exhibit a chiral analog response of the optic axis about the layer normal at low fields, although with different electro-optic susceptibilities. Above some applied field threshold ($E_{th} \sim 10$ V/μm), the high susceptibility regions undergo a domain wall-mediated, first order transition to a bistable configuration with a blue birefringence color ($\Delta n \sim 0.14$) and a large apparent optical tilt angle [$\theta=30°$, Fig. 1(b)]. Applying a large field (E

~ 20 V/μm) of one sign to this blue state leads to a small increase in the birefringence (the domains become green, $\Delta n \sim 0.16$) with no observable change in the tilt angle, while applying the other sign of field causes the sample to switch to the other side of the tilt cone. The original, low birefringence, analog domains can be recovered by melting and recooling the liquid crystal.

The "analog gold" to "bistable blue" transition of (R,S)-MHOBOW is thought to be associated with an irreversible straightening of the smectic layers [4]. In this paper we propose a phenomenological model to describe this transformation using a biaxial extension of a uniaxial anchoring energy model previously developed for rod-shaped chiral smectic-C (SmC^*) liquid crystals. In particular, the biaxial model predicts a first order surface orientation transition between an analog state favored when the layers are significantly tilted and bistable states preferred when the layer tilt is small.

The tilted banana phases are in general optically biaxial, with the director **n** (which defines the smectic tilt cone) along the direction of largest refractive index, given approximately by the orientational average of the molecular bow-string unit vectors. The $B2$ and $B7$ phases appear to have C_2 symmetry, with the tilt plane (containing **n** and the layer normal $\hat{z}$) perpendicular to the polarization **P**. The polarization is parallel to **b** and thus resembles an arrow fitted to the molecular bow [Fig. 2(a)]. As usual, the **c** director is the projection of **n** onto the smectic layer plane.

Tilted layering has been postulated in several bent-core systems. For example, Jákli *et al.* have reported that mechanical shearing gives uniform textures in some $B2$ cells, but with the layers uniformly tilted at an angle δ relative to the cell normal [5,6]. With tilted layers, the ferroelectric coupling with an applied field E is minimized when the polarization (which is confined to the layer plane) reorients to align as well as possible with the field [toward $\phi=0$, where ϕ is the azimuth shown in Fig. 2(b)]. By analogy with well-

---

*Electronic address: jem@colorado.edu
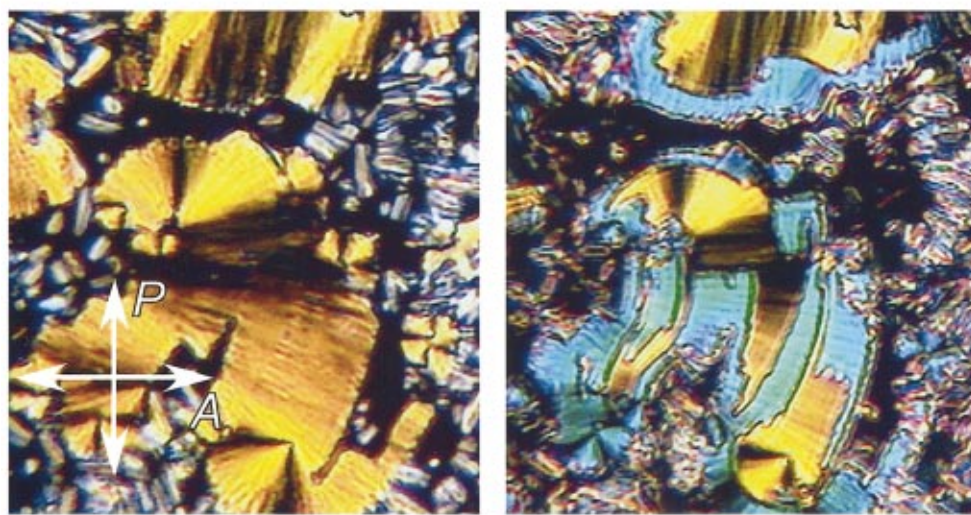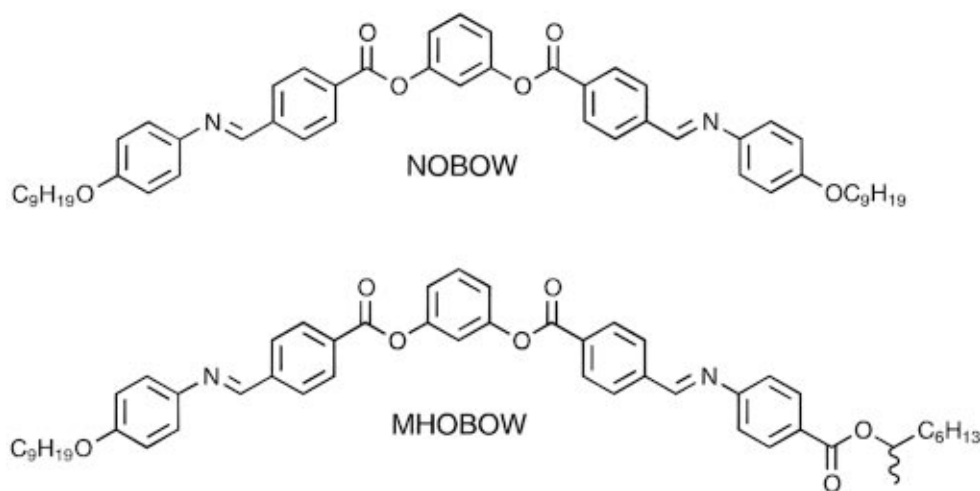
FIG. 1. (Color) Structures of the bent-core liquid crystals NOBOW and MHOBOW and polarized light microscope textures in a 4 μm cell of (R,S)-MHOBOW. (a) Golden focal conic texture before application of a field. (b) Bistable blue domains growing from gold upon application of a field $E > E_{th}$ ~ 10 V/μm. The horizontal dimension of each image is about 80 μm.

studied chevron SmC* structures [7], it has been proposed that when sufficiently large electric fields are applied to cells of smectic banana-shaped molecules (including MHOBOW), the layers tend to stand up [4,6] in order to lower the ferroelectric energy even more.

II. MODEL

If we ignore any variations of the director field across the thickness of the cell, the molecular orientation and hence the electro-optic response are largely determined by the surface conditions. Banana-shaped molecules have polar biaxial symmetry and, as we will see, when initially tilted layers stand up an anchoring model that includes biaxial anisotropy gives a discontinuous surface transition from an analog state (with the director reorienting about the bottom of the tilt cone) to a bistable configuration (with the director stabilized at either side of the cone).

Each banana-shaped molecule might be considered as comprising two rodlike halves, rigidly joined together, with each interacting separately with the surface. Since each half is polar (because of the different chemical environments of its ends) this interaction has an instrinsic polar component. In this picture, the effective anchoring depends on the tilts of each half relative to the substrate. These can in turn be related to the molecular orientation, which is described in general by two rotations, about axes along and perpendicular to the director.

It is more convenient to imagine effectively lathelike molecules imbued with a polarity arising from their true molecular bow shape. We assume that the director is confined to the tilt cone, and consider both nonpolar (nematic) [8] and polar (chiral) [9] contributions to the anchoring energy of a banana
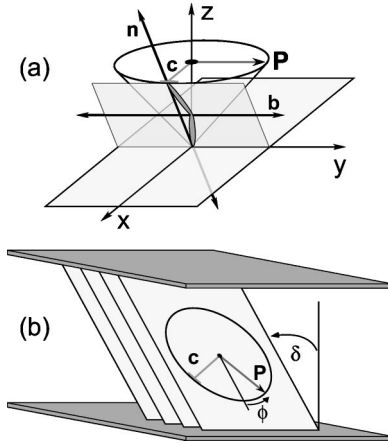
FIG. 2. (a) Geometry of tilted polar smectic phases of bow-shaped molecules. The director **n** is represented by the line joining the ends of the molecule, and the projection of **n** onto the smectic layer plane defines the **c** director (—|). The spontaneous polarization **P** is along the C_2 symmetry axis **b** perpendicular to the tilt plane. (b) Cell with tilted layers. The polarization azimuth is given by ϕ and the layer tilt by δ.

phase with uniform synclinic tilt ($\mathrm{Sm}C_S P$). At the bottom surface of the cell, for example, a biaxial liquid crystal material has an areal energy density

$$f_s = -\gamma_1(\cos^2 \psi) - \gamma_2 \cos \delta \cos \phi$$
$$- \gamma_4 \cos \delta \cos \psi (\cos 4\phi + b \cos 2\phi), \qquad (1)$$

where γ_1 and γ_2 are, respectively, the nonpolar and polar surface energy anisotropies, ψ is the angle between the director **n** and the surface, and γ_4 is the biaxial potential. $\gamma_1 > 0$ favors director orientation parallel to the bounding plates (planar alignment), while $\gamma_1 < 0$ favors the director perpendicular to the plates (homeotropic alignment). A positive (negative) value of γ_2 favors **P** pointing out of (into) the liquid crystal sample at the cell surfaces [10]. A positive γ_4 favors equally the director orientations at the top, bottom, and sides of the tilt cone ($\phi = n\pi/2$, where $n \in \mathcal{Z}$), while a positive biaxial bias b lowers the energy of the two "bistable" states. The geometric prefactors ensure that the biaxial term vanishes if either the layer normal or the director is perpendicular to the cell surfaces. The elevation angle ψ is given implicitly [11] by

$$\cos^2 \psi = \cos^2 \delta \cos^2 \theta + \sin^2 \theta - \cos^2 \delta \sin^2 \theta \sin^2 \phi$$

$$+ \frac{1}{2} \sin 2\theta \sin 2\delta \sin \phi,$$

where θ is the usual smectic-C tilt angle and δ the layer tilt. The external field is applied normal to the plates ($\mathbf{E} = E\hat{s}$), with the component parallel to the layers being $E\cos\delta\,\hat{x}$. The azimuthal orientation of **c** on the tilt cone [see Fig. 2(b)] is determined by ϕ, the angle between **P** and $\hat{x}$. The electrostatic energy density of the cell (ignoring dielectric and polarization self-field contributions) is
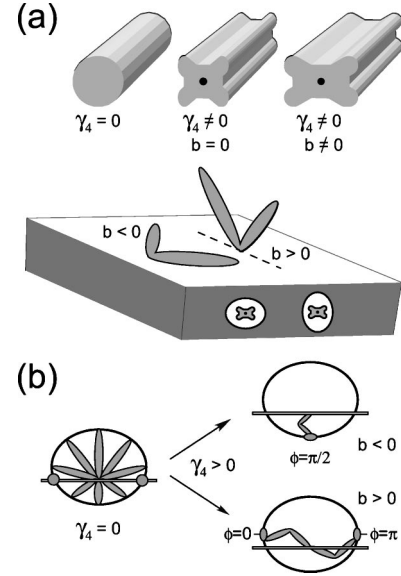

FIG. 3. Biaxial director anchoring. (a) Mechanical analogy of liquid crystal anchoring using rods of different cross sections resting on a planar surface. For uniaxial molecules ($\gamma_4 = 0$, left) rotations about the molecular long axis are degenerate, whereas biaxial molecules have four stable orientations separated by potential barriers ($\gamma_4 \neq 0$, middle), of which two minima may be energetically favored ($b \neq 0$, right). Planar-aligned banana-shaped nematic molecules preferentially orient either flat on the cell substrate ($b < 0$) or edge on ($b > 0$), both states having the director **n** parallel to the substrate. The molecules' effective biaxial shapes are drawn superimposed on their steric cross sections for each case. (b) Anchoring in tilted smectics. In a cell with arbitrarily tilted layers, the uniaxial molecules shown at left prefer the planar state (the gray circles represent the tips of the anchored molecules). In the case of bent-core molecules, the biaxial anchoring biases the director orientation away from being parallel to the glass, in principle favoring the monostable (analog) configuration when $b < 0$ and the bistable configuration if $b > 0$, although the relative stability of these two states also depends on the layer tilt and applied field. The view is along the plane of the glass surface (horizontal bar) toward the apexes of the tilt cones.

$$f_e = -\int_0^d \mathbf{P} \cdot \mathbf{E} = -PEd \cos \phi \cos \delta. \qquad (2)$$

We note that the component of the polarization **P** normal to the bounding plates ($P \cos \delta$) appears both here and, implicitly, in the polar anchoring term in Eq. (1). In the absence of layer tilt ($\delta = 0$), Eq. (1) reduces to

$$f_s = -\gamma_1[C \cos 2\phi + (1 - C)] - \gamma_2 \cos \phi$$
$$- \gamma_4 \cos \psi (\cos 4\phi + b \cos 2\phi),$$

where $C = (\sin^2 \theta)/2$. If we ignore the constant term and set the biaxiality $\gamma_4 = 0$, this expression reduces to the familiar uniaxial free energy density found in the literature [9,11,13].

We now return to the full anchoring potential for biaxial molecules as embodied in Eq. (1). For the sake of illustration, we first consider a biaxial nematic phase, shown in Fig. 3(a). We can use a mechanical analogy to compare uniaxial
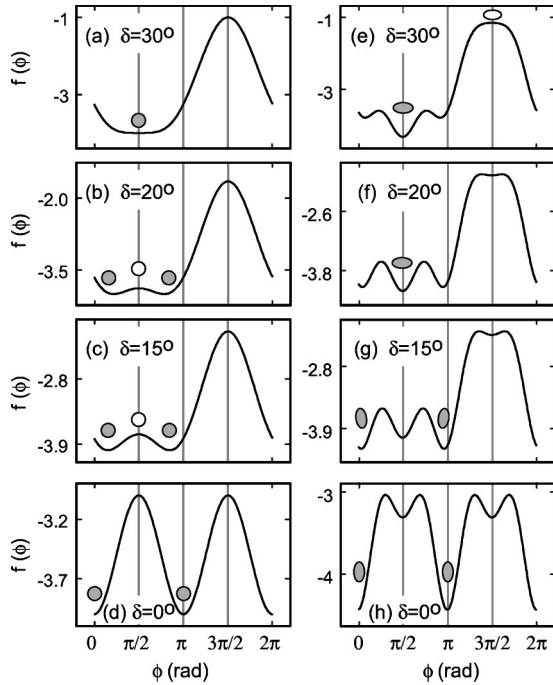
FIG. 4. Free energy density of a smectic-C cell $f(\phi)$ as a function of layer tilt δ for uniaxial (left) and biaxial (right) molecules. Highly tilted layers favor the monostable (analog) state at $\phi=\pi/2$ in both cases. As the tilt is reduced, however, the energy of the bistable states eventually becomes smaller. In uniaxial systems [plots (a) to (d)] this transition is continuous, whereas in biaxial systems [plots (e) to (h)] there is a critical tilt below which the bistable states are favored and the orientational transition is first order. With $\theta=30°$, $\gamma_1=2$, $PE=0$, $\gamma_4=0.2$, and $b=0.1$, the transition is at a layer tilt $\delta\sim16°$. Solid (empty) circles or ovals symbolize stable (unstable) orientations of the molecules.

and biaxial "molecules" resting on a planar surface: round molecules have degenerate anchoring while those with approximately square or rectangular cross sections have distinct orientationally preferred states separated by energy barriers. For nematics with $\gamma_1>0$, where $\mathbf{n}$ orients preferentially parallel to the surface ($\psi=0$), banana-shaped nematic molecules will align either flat or edge on to the glass (depending on the sign of the biaxial bias b).

Similarly, in the SmC phase, where the molecules are geometrically confined to the tilt cone, the biaxiality γ_4 introduces a fourfold anisotropy in the azimuthal anchoring potential that distinguishes energetically, in the simplest case, between planar-aligned molecules with their $\mathbf{c}$-director orientations perpendicular and parallel to the glass.

The general case of anchoring in a SmC cell with tilted layers and favoring planar anchoring of the director ($\gamma_1>0$) is illustrated in Fig. 3(b). In the absence of biaxiality ($\gamma_4=0$) and ignoring the polar anchoring for now ($\gamma_2=0$), the director orients preferentially parallel to the glass ($\psi=0$), the minimum energy states being defined by the intersections of the tilt cone with the surface. Molecular biaxiality, however, in general prefers different azimuthal orientations, with the director either at the top or bottom of the tilt cone, or near the sides (at the same positions favored by the polar surface anisotropy γ_2), as indicated in the figure.
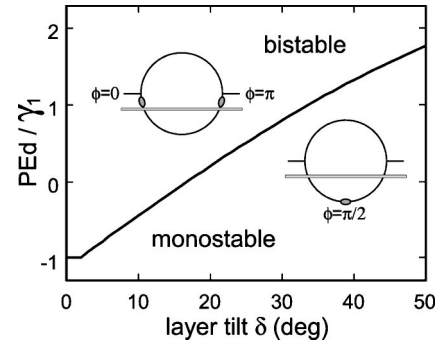

FIG. 5. Stability plot for uniformly aligned biaxial banana molecules in a cell with tilted layers in an applied field. Even in the absence of field, bistability ($\phi=0$ or π) is favored for sufficiently small layer tilt ($\delta\to0$). The parameters used are $\theta=30°$, $\gamma_1=2$, $\gamma_4=0.2$, and $b=0.1$. Solid ovals symbolize stable orientations of the molecules.

The dependence of the total free energy density $f(\phi)$ $=f_e+\Sigma f_s$ on director azimuth in the absence of applied field varies with layer tilt as shown in Fig. 4 for both uniaxial and biaxial systems. With a large layer tilt (i.e., when δ is comparable to the SmC cone angle θ) we see that the most stable state in either system is at $\phi=\pi/2$, where the director is at
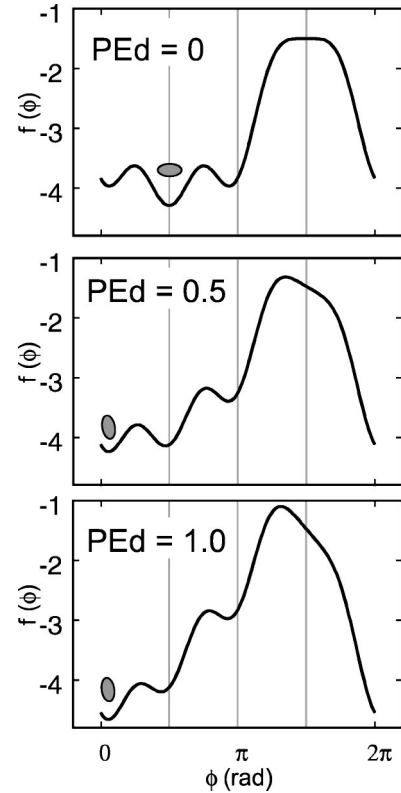

FIG. 6. Free energy density of the cell $f(\phi)$ as a function of applied field E with fixed layers. With moderately tilted layers, the monostable (analog) state at $\phi=\pi/2$ is favored in the absence of applied field. As E is increased, one of the bistable states ($\phi\sim0$), with the director at the side of the tilt cone, becomes more stable. In this example, $\theta=30°$, $\delta=25°$, $\gamma_1=2$, $\gamma_4=0.2$, and $b=0.1$. Solid ovals denote the stable orientations of the molecules.
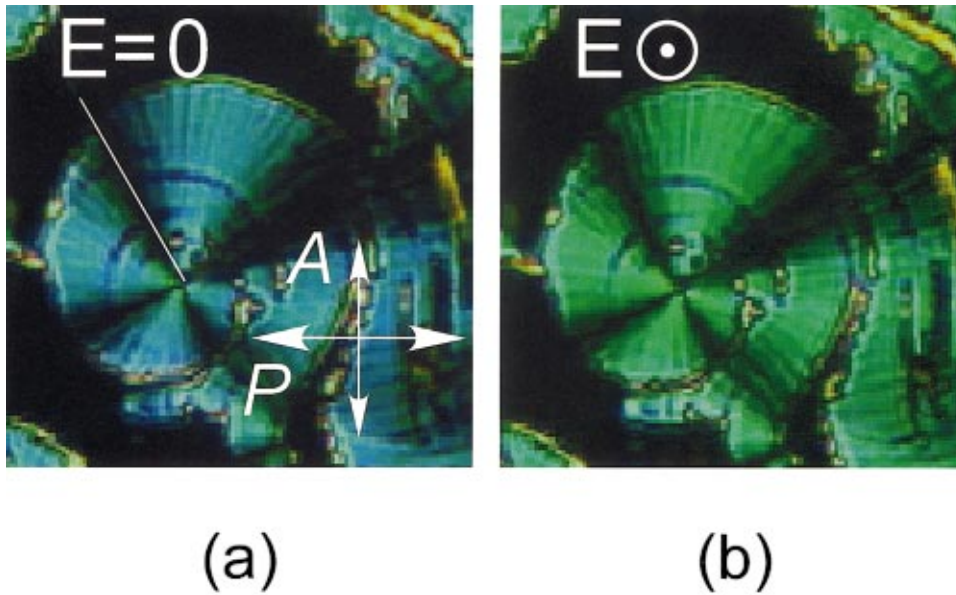
(a)   (b)

FIG. 7. (Color) Reversible birefringence enhancement in bistable blue states of (R,S)-MHOBOW. (a) Ferroelectric domains are blue ($\Delta n \sim 0.14$) when $E = 0$. (b) An applied field ($E = 10$ V/μm) temporarily changes the birefringence color to green ($\Delta n \sim 0.16$), without discernibly affecting the optic axis orientation. The cell thickness is $d = 4$ μm and the polarizer and analyzer are oriented as shown. The horizontal dimension is approximately 50 μm.

the bottom of the tilt cone, corresponding to the analog electro-optic state. In the biaxial case $\phi = 0$ is metastable under these circumstances. As $\delta \to 0$, the favored orientation changes continuously to 0 or π in the uniaxial system (left), whereas in the biaxial case (right) there is a threshold tilt ($\delta \sim 16°$ in this example) below which states on the sides of the tilt cone (corresponding to the usual optically bistable states of surface stabilized ferroelectric liquid crystals [12]) are energetically preferred. A nonzero biaxial bias b seems physically likely in banana phases given the anisotropic cross section of the molecules, although it is not necessary to include this in the theory to obtain a first order orientational transition.

The relative stability of the monostable and bistable states also depends, in general, on the applied field and the polar anchoring, whose energy terms, as we pointed out earlier, have the same functional dependence on layer orientation and can in some cases be lumped together. By combining Eqs. (1) and (2) and including both cell surfaces (assumed to be identical, so that the polar anchoring terms cancel), we obtain the stability diagram of Fig. 5, from which we see that for a given applied field there is a well-defined maximum layer tilt above which the monostable state is energetically favored. We thus propose that when MHOBOW cells are exposed only to small external fields, the layers remain significantly tilted and the field modulates the director around its monostable orientation at the bottom of the tilt cone. Once the layer tilt has been reduced, however, the bistable states are preferred. The essential effect of the biaxiality is thus to create an energy barrier between the analog and bistable director orientations that is not present in uniaxial chiral smectics (where this transition is continuous).

The variation of the total free energy density $f(\phi)$ with applied field is illustrated for the case of fixed layers in Fig. 6. We see that a sufficiently large field always favors one of the bistable states. However, high electric fields not only drive the director to the sides of the tilt cone: they simultaneously cause the smectic layers to stand up. When the layers have been driven sufficiently vertical, the state with the

director at the bottom of the tilt cone no longer minimizes the free energy and the system finds itself instead in the bistable region (to the left of the diagonal stability line in Fig. 5) for any applied field. During subsequent field reversals the director does not linger at the bottom of the tilt cone but switches completely from one side to the other.

An alternative possible explanation for the observed transition from analog to bistable electro-optic switching behav-
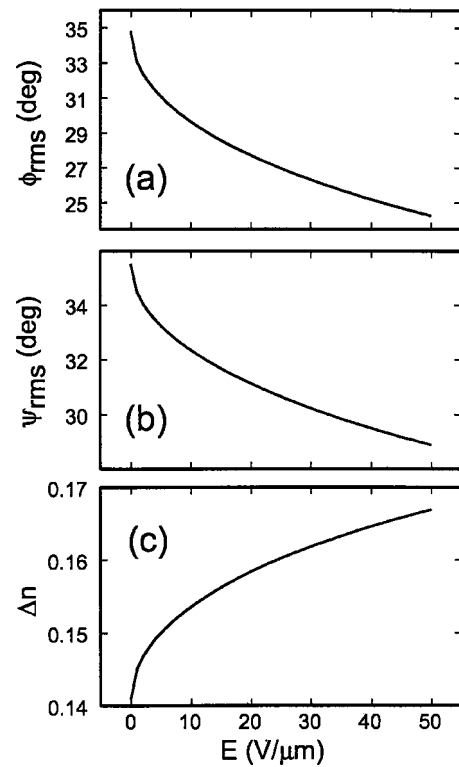

FIG. 8. Birefringence enhancement with field. (a) Thermal fluctuations $\phi_{\rm rms}$ of the director on the tilt cone are partially quenched by an applied electric field. (b) This in turn reduces the average pretilt $\psi_{\rm rms}$ of the optic axis and leads (c) to an increase in the overall birefringence Δn.

ior is that large applied fields $E > E_{th}$ could, in principle without affecting the layers, drive the director all the way to the side of the tilt cone, where it could get trapped in a metastable state upon removal of the field. This seems to be unlikely in our cells, though, because there seems to be no field treatment that allows the bistable blue state ever to revert to analog gold electro-optics. In addition, since the threshold field for switching between the bistable blue states is considerably smaller than E_{th}, it seems probable that the transition from analog gold to bistable blue is accompanied by a significant structural change, with a straightening of the layers being the most likely modification.

Finally, we address the field-induced increase in the optical birefringence of the bistable blue state illustrated in Fig. 7. The transition from blue to green is continuous and reversible and occurs with no change in the apparent tilt angle. We propose that the applied electric field couples to the spontaneous polarization to partially quench the thermal fluctuations in the molecular orientation, which in turn increases the effective birefringence of the cell. For a field favoring $\phi = 0$, the mean square amplitude of the azimuthal fluctuations of the director on the tilt cone is given by [14]

$$\langle \delta\phi(r)^2 \rangle \approx \frac{k_B T q_c}{4\pi^2 K} \left[1 - \frac{1}{\xi q_c} \tan^{-1} \xi q_c \right]$$

where K is a Frank elastic constant, $k_B T$ the thermal energy, and $\xi = (K/PE)^{1/2}$ the electric field correlation length. Taking the cutoff wave vector $q_c = 2\pi/\ell$, with $\ell = 50$ Å com-

parable to the molecular length, and assuming $K = (5 \times 10^{-7}) \sin^2 \theta$ erg/cm with $\theta = 30°$ gives an rms fluctuation amplitude in the absence of field $\delta\phi_{rms} \approx 35°$ [Fig. 8(a)]. The applied field reduces the magnitude of these fluctuations, which in turn decreases the rms pretilt ψ of the optic axis [Fig. 8(b)]. The effective birefringence then varies approximately as

$$\Delta n(\psi) = n_e(\psi) - n_o$$

$$= \left[\frac{n_e n_o}{\sqrt{n_o^2 \cos^2 \psi + n_e^2 \sin^2 \psi}} - n_o \right].$$

This index anisotropy is a sensitive function of the (saturated) refractive indices, parameters that are essentially unknown for most banana-shaped molecules. Taking $n_e = 1.73$ and $n_o = 1.50$, we find [see Fig. 8(c)] that a field of about 20 V/μm applied to an FLC with the polarization of (R,S)-MHOBOW ($P = 315$ nC/cm^2) increases the effective birefringence by an amount in qualitative agreement with experiment.

[1] T. Niori, T. Sekine, J. Watanabe, T. Furukawa, and H. Takezoe, J. Mater. Chem. **6**, 1231 (1996); T. Sekine, T. Niori, M. Sone, J. Watanabe, S. W. Choi, Y. Takanishi, and H. Takezoe, Jpn. J. Appl. Phys., Part 1 **36**, 6455 (1997). Bent-core molecules were first synthesized by Vorländer's group in the 1920s [D. Vorländer, E. Schroedter, and W. Zeh, Ber. Dtsch. Chem. Ges. **62**, 2831 (1929)], although their unusual electro-optic properties were not appreciated at the time.

[2] S. Diele, G. Pelzl, and W. Weissflog, Liq. Cryst. Today **9**, 8 (1999). This article describes the $B1-B7$ banana phase classifications adopted at the workshop on banana-shaped liquid crystals held at the Technical University of Berlin in December 1997.

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

[4] D. M. Walba, E. Körblova, R. Shao, J. E. Maclennan, D. R. Link, M. A. Glaser, and N. A. Clark, Science **288**, 2181 (2000).

[5] A. Jákli, S. Rauch, D. Lötzsch, and G. Heppke, Phys. Rev. E **57**, 6737 (1998).

[6] A. Jákli, C. Lischka, W. Weissflog, S. Rauch, and G. Heppke, Mol. Cryst. Liq. Cryst. Sci. Technol., Sect. A **328**, 299 (1999).

[7] Y. Sato, T. A. Tanaka, H. Kobayashi, K. Aoki, H. Watanabe, H. Takeshita, Y. Ouchi, H. Takezoe, and A. Fukuda, Jpn. J. Appl. Phys., Part 2 **28**, L483 (1989).

[8] A. Rapini and M. Papoular, J. Phys. (Paris), Colloq. **30**, C4-54 (1969).

[9] M. A. Handschy, N. A. Clark, and S. T. Lagerwall, Phys. Rev. Lett. **51**, 471 (1983).

[10] In cells with uniform director fields, the polar anchoring energy contributions at the top and bottom glass plates cancel identically but the terms are included here for completeness.

[11] J. E. Maclennan, M. A. Handschy, and N. A. Clark, Liq. Cryst. **7**, 787 (1990). The elevation angle ψ is equivalent to the director pretilt (the "polar" angle of nematics).

[12] N. A. Clark and S. T. Lagerwall, Appl. Phys. Lett. **36**, 899 (1980).

[13] M. A. Handschy and N. A. Clark, Ferroelectrics **59**, 69 (1984).

[14] J. E. Maclennan and N. A. Clark, Phys. Rev. A **44**, 2543 (1991).