Surface Alignment, Anchoring Transitions, Optical Properties, and Topological Defects in the Nematic Phase of Thermotropic Bent-Core Liquid Crystal A131

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Surface alignment, anchoring transitions, optical properties, and topological defects in the nematic phase of thermotropic bent-core liquid crystal A131

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We study optical, structural, and surface anchoring properties of thermotropic nematic bent-core material A131. The focus is on the features associated with orientational order as the material has been reported to exhibit not only the usual uniaxial nematic but also the biaxial nematic phase. We demonstrate that A131 experiences a surface anchoring transition from a perpendicular to tilted alignment when the temperature decreases. The features of the tilted state are consistent with surface-induced birefringence associated with smectic layering near the surface and a molecular tilt that changes along the normal to the substrates. The surface-induced birefringence is reduced to zero by a modest electric field that establishes a uniform uniaxial nematic state. Both refractive and absorptive optical properties of A131 are consistent with the uniaxial order. We found no evidence of the “polycrystalline” biaxial behavior in the cells placed in crossed electric and magnetic fields. We observe stable topological point defects (boojums and hedgehogs) and nonsingular “escaped” disclinations pertinent only to the uniaxial order. Finally, freely suspended films of A131 show uniaxial nematic and smectic textures; a decrease in the film thickness expands the temperature range of stability of smectic textures, supporting the idea of surface-induced smectic layering. Our conclusion is that A131 features only a uniaxial nematic phase and that the apparent biaxiality is caused by subtle surface effects rather than by the bulk biaxial phase.

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1. INTRODUCTION

A uniaxial nematic (N_u) is an optically uniaxial liquid crystal (LC) showing anisotropy of physical properties with two principal directions along the director \( \hat{n} \) and normal to it \( \hat{m} \). Freiser [2] considered theoretically the biaxial nematic (N_b) phase with orthorhombic symmetry in which physical properties are different along three principal directions defined by directors \( \hat{n} = -\hat{n} \), \( \hat{m} = -\hat{m} \), and \( \hat{I} = -\hat{I} \). In 1980, Yu and Saupe [3] discovered the N_u phase in a lyotropic LC, in which the building units are micelles formed by surfactant molecules. The shape of micelles depends on temperature and composition and in a certain range can become anisometric with three different principal axes. There is a report on the N_b phase in another lyotropic system, a water solution of goethite particles [4]. However, it is the search for the N_b phase in the thermotropic solvent-free materials that has attracted the most attention [5–35] fueled by a hope to achieve a much faster switching time for director reorientation as compared to the uniaxial N_u phase [5,6]. Early reports on the thermotropic N_u phase based on optical studies and textural observations [7–11] were challenged on the basis of NMR and x-ray examination [6,12,13]. Although the two phases, N_u and N_b, have a drastically different set of symmetry-allowed topological defects that can be used for phase identification [14–19,36], textural features of regular samples, such as flat cells, might be similar in the two phases, as shown by Chiccoli et al. [18]. Within the past decade, a new class of materials, with bent-core shape of molecules, emerged as seemingly the best candidate for the N_b order [20–22]. However, identification of the N_b phase in bent-core materials [23–31] is not universally accepted, and alternative nonbiaxial mechanisms are proposed for the observed features [33–35,37,38].

The original bent-core materials reported to be biaxial form the nematic phase at very high temperatures, above 200 °C [20,21]. In 2005, Prasad et al. [22] synthesized and characterized a material A131 with a reportedly much lower temperature range of the N_b phase. However, subsequent electro-optic studies of A131 suggested that the material is uniaxial [35]. A recent study on a similar bent-core nematic by Vaupotič et al. [37] has shown that the x-ray features attributed to N_b can be caused by pretransitional smectic C (SmC) fluctuations (“cybotactic clusters”) that develop in N_u phase over an extended temperature range.

In this work, we address the controversial status of A131 by exploring the material aspects that are directly linked to the type of nematic order but were not considered in prior studies. Namely, we study surface alignment and demonstrate that it depends on temperature resulting in the so-called anchoring transition. We explore birefringence and light absorption of the material in flat sandwich-type cells and topological defects in samples with curved interfaces and show that the observed features are consistent with the uniaxial N_u order; however, near the bounding plates, the material might develop a surface-assisted birefringence associated with smectic layering and a molecular tilt that changes along the normal to the substrates.

2. MATERIALS AND TECHNIQUES

The chemical name of A131 is 4-[4-(dodecylphenyl) diazenyl] phenyl 2-methyl-3-[4-(4-octylbenzoyloxy) benzylede- neamino] benzoate [22] (Fig. 1). The material was synthesized following Ref. [22]. The material was purified by...
column chromatography on silica gel and recrystallized three times from ethanol-CH$_2$Cl$_2$ solvent mixture to obtain as needle-shaped crystals. The molecular structure and purity were determined by $^1$H and $^{13}$C NMR spectroscopy, high-pressure liquid chromatography and mass spectroscopy (HPLC-MS), thin layer chromatography (TLC), and elemental analysis (see Appendix A). Yoon et al. [39] suggested that the difference in the identification of A131 order is related to solvent impurities and/or absorbed gases in the samples and recommended a process of “degassing” as an additional measure of purification. We thus studied two types of A131 samples, pure samples “A” obtained as described above and samples “B” obtained by keeping A-samples of A131 in a vacuum oven at 190 °C for 2 h, as recommended by Yoon et al. [39]. Thin layer chromatography showed no difference between samples A and B (see Appendix A). The difference between A and B samples was in a different value of the surface anchoring transition temperature, as discussed in detail later. We present most of our results for the A samples and add a description of the B samples when their behavior is different from the A samples.

The main features of phase diagram are the same for both A and B samples. In terms of the reduced temperature $t = T - T_N$, where $T$ is the actual temperature and $T_N$=176.5 °C is the temperature of the isotropic (Iso) to $N_s$ phase transition on cooling, we find the “coarse” phase diagram as

$$-93.7 °C \to -58 °C \to 0 °C$$

where Sm denotes one or more smectic phases with a tilted orientation of molecules within the smectic layers, similar to Ref. [22]. Prasad et al. [22] suggested that the nematic ($N$) range is, in fact, comprised of $N_{ub}$ and $N_b$ phases, with the transition point at $t' = -27.5 °C$; $N_{ub}$ is stable at high temperatures $t' < t < 0 °C$, while $N_b$ is stable at low temperatures, $t_N < t < t'$, where $t_N = -58 °C$ is the temperature of the nematic-to-smectic transition.

The experimental cells for optical and electro-optical studies were assembled from parallel glass plates with transparent indium tin oxide (ITO) electrodes. For tangential alignment, the ITO layers were spin coated with polyimide PI2555 (HD MicroSystem). The tangential alignment with $\hat{n}$ at unrubbed PI2555 was established by observing half-integer disclinations in the Schlieren textures [36]. For planar (undirectional) alignment, the polyimide was rubbed three to five times with pressure of 800–850 Pa and the cells were assembled in an “antiparallel” fashion. The procedure resulted in a small pretilt angle ($\sim 1°$) between the substrate and the director $\hat{n}$ measured by a crystal rotation method [40].

For homeotropic alignment, we used an inorganic passivation layer NHC AT720-A (Nissan Chemical Industries, Ltd.) as well as clean ITO-coated glass plates. Note that the concepts of “homeotropic” and “planar” alignment in the sense of normal and undirectional planar alignment of the main director $\hat{n}$ are fully applicable only in the upper part of the nematic range $t > -5 °C$, which is universally characterized as occupied by the $N_u$ phase [22,35]; at lower temperatures, the situation is more complex, as described later in this work.

The temperature was controlled with the Linkam controller TMS94 and hot stage LTS120 (Linkam Scientific Instruments) with precision 0.01 °C. An ac or dc voltage was applied to the cells using the function generator DS345 (Krohn-Hite). To address the possible dielectric heating effects, we measured $T_{IN}$ in the presence of the electric field ($\sim 2 V/\mu m$) and without it, the difference was less than 1 °C. Magnetic field (up to 1.4 T) was applied using electromagnet V-3601 (Varian Associates). We used impedance analyzer SI1260 (Schlumberger) for the dielectric spectroscopy measurements.

A polarizing microscope OptiPhot2-Pol (Nikon Instruments, Inc.) was used for conoscopic observations. Conoscopic studies were performed with a Bertrand lens and high power objectives Nikon MPlan 20 $\times$ /NA=0.4 ELWD, MPlan 40 $\times$ /NA=0.5 ELWD, and MPlan 60 $\times$ /NA=0.7 ELWD, where ELWD stands for extra large working distance and NA is numerical aperture. Note that A131 molecules contain an azobenzene moiety and are thus light sensitive with a potential trans-cis-isomerization. To reduce the probability of cis isomerization, we used high-quality interferometric green and red filters. To increase the quality of conoscopic observations, we also used “frosted” glass placed before the sample [42,43]. We used single-wave ($\lambda$) and quarter-wave ($\lambda/4$) plates with $\lambda=530$ nm to determine the sign of birefringence and to characterize small variations of optical retardation [42,44]. The direction of “slow axis” was determined with a Berek compensator, while birefringence was measured with a Sénarmont compensator (Nikon Instruments, Inc.) at $\lambda=656$ nm. The spectral properties of A131 were studied with a microscope-mounted Photometry System P100S (Nikon Instruments, Inc.); the transmitted signal was measured from a circular area with diameter of 40 µm.
In the studies of topological defects, we used cylindrical glass capillaries with inner diameters of 10 and 50 μm (VitroCom) and freely suspended films of A131, prepared with aluminum and copper frames. Aluminum frames had round openings with diameter of ≈1 mm and copper frames had square openings with side length of ≈430 μm. The thin films were studied under the polarizing microscope and with the Abrio-Polscope setup [45] (CRI, Inc.) built on the microscope Eclipse E600Pol (Nikon Instruments, Inc.), which allows one to measure small variations of retardation. The Abrio-Polscope measurements were performed at λ = 546 nm at low intensity of light irradiation, which did not affect the textures.

III. RESULTS AND DISCUSSION

A. Homeotropic alignment and its temperature dependence

Homeotropic alignment in flat sandwich-type cells offers a straightforward approach to discriminate between \( N_u \) and \( N_b \) in optical observations. In the homeotropic \( N_u \) state, the director \( \hat{n} \), which is also the optic axis, is normal to the bounding plates. Orthoscopic transmission of linearly polarized light through such a cell (with wave vector \( \vec{k} \)) should not depend on the direction of polarization \( \hat{e} \); the refractive index \( n_{\perp} \) measured in this geometry is the ordinary index \( n_o \). Structural biaxiality should lift the degeneracy of optical properties so that the refractive index for the linearly polarized light with \( \vec{k} \parallel \hat{n} \) should depend on the direction of \( \hat{e} \) in the plane of \( N_b \) cell. The difference between the principal values of the refractive indices in such a biaxial cell, \( \Delta n_{xy} = n_r - n_{\perp} \), is proportional to the degree of biaxial order. Therefore, if A131 experiences a \( N_u \text{--} N_b \) transition at \( T \), one should observe \( \Delta n_{xy} = 0 \) at \( T > T^* \) and \( \Delta n_{xy} \neq 0 \) at \( T < T^* \). Experiments show a much more complicated behavior, associated with the surface anchoring transition and molecular tilt at the boundaries.

The strictly homeotropic uniaxial alignment of A131 with \( \Delta n_{xy} = 0 \) is observed only near the clearing point \( T_{c} \approx 6 \) [Figs. 2(a) and 2(b)], where \( T_{c} \) is the temperature range of \( (3 \pm 5) ^{\circ}C \), changing from sample to sample, but never approaching the value of \( T^* = 27.5 ^{\circ}C \). Note the difference in the aligning action of NHC AT720-A used in our work and SE-5300 (both Nissan) used by Le et al. [35]. In our case, the nematic does show a homeotropic texture in a limited range of temperatures, while in the case of SE-5300, the surface alignment is always tilted and the normal orientation can be achieved only in sufficiently high electric fields.

Cooling down below \( T_{c} \) causes \( \Delta n_{xy} \neq 0 \) that persists at all temperatures [Fig. 2(c)]. The nonzero \( \Delta n_{xy} \) can be explained by either a transformation \( N_u \rightarrow N_b \) or, if the phase remains uniaxial, by a tilt of \( \hat{n} \). To discriminate between the two, we used the orienting action of an electric field.

The dielectric properties of A131 are frequency dependent. The dielectric anisotropy \( \Delta e = \varepsilon_0 \varepsilon_r - \varepsilon_0 \varepsilon_1 \), where \( \varepsilon_0 \) and \( \varepsilon_1 \) are the permittivities measured parallel and perpendicular to \( \hat{n} \), respectively, is positive in the frequency range of \( \approx 2 \sim 90 \) kHz and in the entire temperature range \( -58 \sim 0 \) °C \( \leq T \leq 0 \) °C of the \( N \) phase. When \( \Delta e > 0 \), the electric field applied to the ITO electrodes at the glass plates reinforces the homeotropic alignment of \( \hat{n} \). If the phase at \( T < T_{c} \) is \( N_u \) with a tilted \( \hat{n} \), the field should reduce \( \Delta n_{xy} \) to zero. If the phase is \( N_b \), the nonzero \( \Delta n_{xy} \) should persist regardless of the magnitude of the field; the idea behind this experiment is the same as in the work of Le et al. [35].

The orientation of optical axes in both \( N_u \) and \( N_b \) can be established in conoscopic observations [44]. The conoscopic images were taken from the area of \( \approx 1 \) mm in diameter, which is much larger than the size of the typical domains of nonuniform birefringent texture, so that the measurement involved area-averaged data.

Zero electric field. Below \( T_{c} \), with no applied field, one observes a conoscopic pattern with isogyres being slightly split by a distance \( 2a \) and shifted from the center of the field of view by a distance \( r \) [Figs. 3(a) and 3(b)]. The shift represents either the (average) tilt \( \bar{\theta} \) of \( \hat{n} \) with respect to the normal to the cell (if the phase is \( N_u \)) or the (average) tilt \( \bar{\theta} \) of the bisectrix between the two optic axes in the \( N_b \) phase, again with respect to the Z axis [44,46],

\[
\bar{\theta} = \sin^{-1} \left( \frac{r}{R} \frac{NA}{n} \right),
\]

where \( R \) is the radius of the field of view [Fig. 3(a)] and \( n = \sqrt{(n_x^2 + 2n_y^2)}/3 \) is the average refractive index. For \( \bar{n} \), we used the refractive index value of 1.635 measured in the Iso phase. The measured tilt \( \bar{\theta} \) is significant and changes with \( T \) nonmonotonically [Fig. 3(d)].

The separation \( 2a \) of isogyres is related to in-plane (xy) birefringence \( \Delta n_{xy} \). Let us estimate the possible biaxial optical anisotropy of the material by assuming for a moment that the nonzero \( 2a \) is caused by biaxiality. For a uniformly aligned \( N_b \) slab with small \( \theta \), the separation \( 2a = (2 - \bar{n} \cdot R/NA) (n_x/n_y) [(n_x^2 - n_y^2)/(n_x^2 - n_z^2)]^{1/2} \) is related to the three refractive indices \( n_1 < n_2 < n_3 \) [44,47]; in our geometry, \( \Delta n_{xy} = n_2 - n_1 \). For the purpose of estimate, we associate the largest refractive index \( n_3 \) with the extraordinary index \( n_z \) measured in a planar cell of A131 for \( \hat{e} \parallel \hat{n} \) and \( n_1 \) with the
ordinary index $n_r$ measured for $\hat{e} \perp \hat{n}$. We determined $n_r - n_n$ for planar cells ($d=2.5 \mu m$) in the entire range $-58 \degree C \leq t \leq 0 \degree C$, using Sénarmont compensator, at $\lambda = 656$ nm. Note that the temperature dependence of $n_r - n_n$ is similar to the one reported in Ref. [48]. Namely, $n_r - n_n$ varies smoothly with temperature, showing no abrupt changes at $t^*$. The values of $n_r$ and $n_n$ were determined using the measured $n_r - n_n$ and $\vec{n}$ as $n_r = \vec{n} + (n_r - n_n)/3$ and $n_n = \vec{n} - (n_r - n_n)/3$. With $N_A = 0.4$, $n_r = 1.79$, and $n_n = 1.56$ at $t = -46.5 \degree C$ and $a/R = 0.22$ determined with zero voltage [Fig. 3(e)], we estimate $\Delta n_{xy} = 6 \times 10^{-4}$, which is very small compared to $n_r - n_n = 0.23$ at $t = -46.5 \degree C$. The small value of $\Delta n_{xy}$ associated with a possible biaxiality is not, however, the major flaw of the simple biaxial model. A more serious problem is that the splitting of isogyres disappears in the applied electric field, as discussed below.

**Nonzero electric field.** Both the shift $r$ of the conoscopic pattern and the splitting of isogyres $2a$ are strongly influenced by the applied electric field (Fig. 3). At moderate fields, 1 V/\mu m, the shift $r$ is reduced to 0 [Figs. 3(b) and 3(g)]. The separation $2a$ follows the trend, approaching 0 at fields $\approx 7$ V/\mu m [Figs. 3(e) and 3(h)]. The latter feature can be associated only with the $N_h$ order because in $N_a$ the separation $2a$ represents the angle between the two optic axes. The decrease of $2a$ to zero is observed in the entire range $-58 \degree C \leq t \leq 0 \degree C$ of the nematic phase, including the temperatures well below $t^*$. The strong dependence of splitting $2a$ on the applied field suggests that either the biaxial order is weak and is easily reduced to the uniaxial order by a modest electric field (on the order of $\sim 10$ V/\mu m) or that the splitting is caused by mechanisms other than biaxiality. The prime candidate is the nonuniformity of director tilt $\theta$ along the normal (axis Z) to the bounding plates. As we will demonstrate below, such a nonuniformity can produce a nonzero $2a$ and explain its strong dependency on the applied field. This allows us to suggest that the splitting of isogyres in A131 cells below $t_{tilt}$ is caused by formation of surface layers with residual birefringence [Fig. 2(d)]

There are two possible mechanisms. First, the nematic phases in contact with a solid substrate are known to develop a density modulation along the normal to the cell, i.e., a layered smectic ordering [49]. In A131, this smectic ordering is expected to be of the tilted smectic type, as the bulk smectic phases with molecular tilt form at $t < -58 \degree C$ [22]. We measured the in-plane birefringence of freely suspended films of A131 in the smectic state and found it to be $\approx 0.05$ at $t = -60 \degree C$. Since the phase retardation of the A131 nematic cells below $t_{tilt}$ is in the range $100 – 1000$ nm, we conclude that the two surface layers with smectic order and tilted molecules might be of thickness $d_s = 0.1 – 1 \mu m$ each. The possibility of smectic ordering is supported also by the presence of smectic-like modulated structures in the freely suspended films of A131 above $t_{tilt}$ (see Sec. III D 3). The second mechanism is related to the bent shape of A131 molecule and an ambiguity in the alignment of its two arms. In the $N_u$ phase, vertical orientation of $\hat{n}$ implies that each arm of A131 [Figs. 1 and 2(d)] should make a nonzero angle $\phi/2 = 18\degree – 32\degree$ with the normal to the substrate [Fig. 2(d)]. Here, $\phi = \pi - \psi$ and $\psi = 116\degree – 143\degree$ is the apex angle of the bent core [24,25,35]. However, if the surface sets a vertical alignment on the arm that is closest to it, the second arm would have a tilt $\phi$ rather than $\phi/2$. The bulk of the sample and the surface layers might thus have a different tilt not only in a homeotropic cell but also in a cell with tilted $\hat{n}$. Note that the $\phi$-tilted arms are free to rotate and thus can align with respect to each other over large areas, which is consistent with the coherent tilt of the conoscopic patterns taken from a millimeter-size area at zero voltage [see Figs. 3(a), 3(d), and 3(f) and the inset in Fig. 2(c)].

Both mechanisms, the smectic layering and tilt, imply that below the temperature $t_{tilt}$ of the surface anchoring transition, the uniaxial nematic develops a surface-induced in-plane birefringence that can be confused with the occurrence of the bulk biaxial order. The difference between this surface order and the truly biaxial bulk phase is evidenced by the fact that the separation $2a$ of isogyres disappears in the applied electric field [Figs. 3(d) and 3(e)]. Consider a conoscopic pattern of a uniaxial $N_h$ cell in which $\hat{n}$ varies along the axis Z either because of the difference in tilt at the two bounding plates (“hybrid aligned cell”) or because of the smectic layering near the substrates. If the director tilt is $z$ dependent, the split of isogyres is nonzero: $2a = \frac{2a}{N_h} = (\frac{1}{2}\int_0^\theta |\vec{n} - \hat{z} \cdot (\vec{n} \cdot \hat{z})| dz)\hat{z}$, where $\vec{n} = \frac{1}{2}\int_0^\theta |\vec{n} \cdot \hat{z}| dz$. When the electric field is applied parallel to the Z axis, $\hat{n}$ realigns parallel to the field, thus causing both $r$ and $2a$ decrease to 0, as observed in the experiment [Figs. 3(e) and 3(d)]. In Appendix B, we illustrate the effect of isogyre splitting experiment-
The samples undergo a surface anchoring transition at a temperature of $-36.5^\circ C$. These features might be related to the observed homeotropic orientation at $-46.5^\circ C$ before application of electric field. The difference in the properties of interior and surface anchoring transitions and temperature dependency of the scalar order parameter are temperature dependent [25]. Recent studies of A131 by Pan et al. [50] in the studies of a uniaxial to biaxial smectic A transition. Optical ellipsometry of the free-standing smectic films revealed that the surface regions acquire a biaxial smectic order at temperatures much higher (tens of degrees) than the interior regions. In our system, the difference between the surface and interior regions can be further enhanced by the existence of multiple conformers of A131. Recently, Dong and Marini [25] performed detailed conformational study of the five-ring molecular structure of A131 and concluded that the molecule can have different conformers falling into two distinct groups, namely, the banana-shaped and the hockey-stick-shaped forms. The conformers might segregate near the surface, thus contributing to the difference in the bulk and surface layers. The details of the conformers geometry and their effective scalar order parameters are temperature dependent [25] and one can also expect that the relative stability of conformers changes with temperature. These features might be related to the observed temperature dependencies such as the one shown in Fig. 3(d). Note also that the link between the surface anchoring transitions and temperature dependency of the scalar order parameter has been already documented for the uniaxial nematics formed by simple rod-like centrosymmetric molecules [51].

**B samples**. The B samples were studied in the monochromatic green light ($\lambda=546$ nm) to avoid conformational changes [39]. The homeotropic orientation of $\hat{n}$ in the B samples was stable in the wider temperature region $-43.5^\circ C < t < 0^\circ C$ as compared to the A samples [Fig. 4(a)].

Note that the lower boundary $t_{ihn}=-43.5^\circ C$ of the homeotropic $N_h$ state is significantly lower (by 16°C) than $t^\ast$. The samples undergo a surface anchoring transition at $t_{ihn}=-43.5^\circ C$, as evidenced by the appearance of weakly birefringent domains [Fig. 4(b)]. The transition is accompanied by blurring of the conoscopic texture without well defined shift and without a clear splitting of isogyres [Fig. 4(c)], which can be explained by the random azimuthal orientation of the small tilted domains [see Fig. 4(d)]. By applying the vertical electric field, one reorients the tilted state into the homeotropic one [Figs. 4(e) and 4(d)] with a conoscopic pattern characteristic of $N_h$ phase. Note that if one switches the applied field off, the homeotropic structure relaxes back to the tilted state (if the temperature is kept below $t_{ihn}$) with the same microscopic features as before the field was applied [compare Figs. 4(c) and 4(d) with Figs. 4(g) and 4(h)]. The latter demonstrates that the transition from the homeotropic to the tilted state is indeed associated with the surface effects.

**B. Anisotropic absorption and birefringence**

The $N_a$ and $N_h$ phases can be distinguished in anisotropic light absorption and birefringence [44,52]. To characterize the anisotropic optical properties of A131, we used planar and homeotropic cells. The homeotropic orientation of $\hat{n}$ was stabilized by the electric field ($U>60$ V) as described above. A131 strongly absorbs light at wavelength below $\lambda_a=550$ nm in the entire $N$ range, $-58^\circ C \leq t \leq 0^\circ C$. The intensity of light transmitted through an absorbing sample of thickness $d$ is described by Bouguer’s law [52]

$$I = I_0 \exp(-4\pi d/\lambda),$$  

where $I_0$ is the incident intensity and $\pi$ is an extinction coefficient, which depends on the symmetry of the phase and properties of the propagating wave. Let us define $\kappa_\parallel$ as the extinction coefficient measured with light polarization $\hat{e} \parallel \hat{n}$ and $\kappa_\perp$ measured with $\hat{e} \perp \hat{n}$ in a planar cell for normally incident beam, $\hat{k} \perp \hat{n}$. Let $\kappa_{H}$ be the extinction coefficient measured for $\hat{e} \perp \hat{n}$ in a homeotropic cell, $\hat{k} \parallel \hat{n}$. If the phase is $N_a$, $\kappa_{H}$ is independent of $\hat{e}$ direction in the plane of the cell and equal $\kappa_{\parallel}$. In the $N_h$ phase, $\kappa_{H}$ should depend on $\hat{e}$.

We measured absorption as a function of an angle $\alpha$ characterizing the azimuthal orientation of $\hat{e}$ in planar and homeotropic cells at $\lambda=488$ nm [Figs. 5(a) and 5(b)]. In planar
cells, the absorption was maximum when ˆε∥n. In homeotropic cells, the absorption was independent of α. When ˆn in the planar cells is reoriented homeotropically by the strong electric field (U = 110 V), the absorption becomes independent of α [Figs. 5(a) and 5(b)].

Figure 6 shows the dispersion of extinction coefficients κ∥, κ⊥, and κH calculated [53] using the transmission spectra measured for A131 in the planar and homeotropic cells at t = −46.5 °C. For the homeotropic cell with an applied field, we find κH = κ⊥. We conclude that the behavior of absorption below and above t* corresponds to the uniaxial phase.

In the part of spectrum where absorption is negligible, λ > λ0, the optical anisotropy of A131 is characterized by birefringence. The intensity of light transmitted through an electrically controlled birefringent cell between crossed polarizers is [36,54]

\[ I = I_0 \sin^2 2\alpha \sin^2 \frac{\pi \Delta n_{eff}(U)d}{\lambda} \]  

(3)

In the $N_a$ planar cell subjected to an applied voltage U, $\Delta n_{eff}(U) = \frac{n_e}{2} \int \left[ n_e^2 \cos^2 \theta(z, U) + n_c^2 \sin^2 \theta(z, U) \right]^{-1/2} - 1 \right] dz$, where θ is a function of U and the vertical coordinate z across the cell and α is the angle between the polarization ˆε and the projection of ˆn on the plane of cell. In the homeotropic $N_h$ cell, $\Delta n_{eff}(U) = 0$ and t = 0. In the homeotropic $N_h$ state, $\Delta n_{eff}(U) = \Delta n_{xy} \neq 0$ and I should depend on α, which in this case characterizes the direction of ˆε with respect to the biaxial directors ˆn and ˆl.

Polar plots in Figs. 5(c) and 5(d) show that the angular dependence of light transmittance in planar and homeotropic cells disappears when the electric field reorients ˆn vertically. The planar and homeotropic cells in strong electric fields show the same ˆε-independent value of I. The behavior is observed at temperatures above and below t*.

Note that the field-dependent increase and decrease of I should not be confused with the director tilt “down” and “up” as I depends on the sine of the effective retardance and $\Delta n_{eff}(U) \cdot d \lambda$ so that a change of $\Delta n_{eff}$ can cause either an increase of I or a decrease of I. Therefore, both absorption and birefringence data demonstrate that A131 is uniaxial in the entire range, 0 °C ≤ t ≤ 65 °C.

C. Homeotropic sample in crossed electric and magnetic fields

A recent model [32] proposes that the biaxiality in nematic materials might be masked by random orientation of microscopic biaxial clusters. To verify whether A131 fits this model, we measured light transmission through the homeotropic cell in crossed electric and magnetic fields (Fig. 7). The cell was kept in a special hot stage between the poles of

FIG. 5. Absorption at $\lambda = 488$ nm (a) and (b) and transmittance between crossed polarizers at $\lambda = 633$ nm (c) and (d) of A131 measured in the cells (d = 10 μm) above and below t*. The applied voltage U has a sinusoidal wave form with frequency f = 70 kHz. Symbols with dashed lines show data measured for the planar cell. Solid line shows data measured for cells with homeotropic alignment of ˆn stabilized by the applied voltage $U = 75$ V.

FIG. 6. Dispersion of extinction coefficients κ∥, κ⊥, and κH as calculated from transmission spectra for A131 at t* = −46.5 °C. The shaded area shows the wavelength range of the absorption band.
In $N_{sb}$, isolated point defects cannot exist: a radial configuration of one director implies that the two other directors are defined at a spherical surface and thus should form additional singularities emanating from the center of the defect, similarly to the famous “Dirac monopole” structure with a radial magnetic field and vector-potential perpendicular to it [36]. The disclinations can be of strength 1/2 and 1. In the case $|s|=1$, the escape of one director does not remove the defect core as two other directors restore the singularity.

At the surface of both $N_u$ and $N_b$ one can observe surface point defects-boojums. The strength $s_b$ of a boojum at a surface of $N_u$ with a tangential $\hat{n}$ is defined by the number of director turns by $2\pi$ when one circumnavigates the defect core along the pathway at the surface; the smallest value is $s_b=1$ as 1/2 would correspond to an end of a disclination [57]. In $N_b$, the smallest value of $s_b$ is 2; a defect with $s_b=1$ represents an end of a singular disclination with $s=1$.

1. Escape of director in a round capillary with $A_{131}$

We studied cylindrical capillaries of diameters 10 and 50 $\mu$m filled with $A_{131}$ in its Iso phase and then slowly cooled down (0.1 °C/min) into the $N$ phase. To eliminate the optical distortions caused by glass capillary we placed it between two flat glass plates and filled the gap with an immersion oil of a refractive index 1.51 [58]. The glass capillary provided homeotropic alignment and thus a radial director configurations near the walls, as established by polarizing microscopy with optical compensators. In the center, $\hat{n}$ realigns along the axis, as expected for the $N_u$ phase [55,56]. Since the two possible directions of the escape are of equal probability, cooling from the Iso phase results in a number of point defects-hedgehogs of radial and hyperbolic type, separating the zone of different directions of escape (Fig. 8). The defects annihilate with each other, but this process slows down as the separation between the points becomes much larger than the diameter of the capillary, and thus interactions between them become weaker.

The textural features with the escaped nonsingular core and isolated point defects do not change upon cooling the sample below $t'=−27.5$ °C; Fig. 8(b) shows the typical texture at $t=−46.5$ °C. If there were an $N_b$ phase below $t'$, one would expect the nonsingular escaped configuration [Figs. 8(a) and 8(c)] either to transform into a singular line [Fig. 8(d)] of strength $s=1$ (with a singularity in the secondary directors [18]) or to split into two lines with $s=1/2$ each, as observed in the biaxial smectic A [59]. None of these $N_b$ scenarios was observed [Figs. 8(a) and 8(b)] despite our efforts to enhance the visibility of defects by using optical compensators and by rotating the capillary. The textures of the escape configuration are rotationally invariant and symmetric with respect to the central axis [Fig. 8(e)]. This axial symmetry of the texture eliminates the possibility of other biaxial arrangements in the capillaries, such as a nonsingular defect $s=1$ in $\hat{n}$ associated with disclinations in the secondary director(s) that are located at the boundary of the capillary (rather than along the central axis). The topological features of textures in cylindrical capillaries are thus consistent with the $N_u$ order in the entire range of the nematic phase below and above $t'$.
FIG. 8. (Color online) Nematic A131 in a round capillary (diameter 50 μm): (a) escaped texture at $t=-16.5$ °C; (b) escaped texture at $t=-46.5$ °C; (c) schematic of escaped director configuration in the square outlined area in (a) showing point defects hedgehogs (black filled circles); (d) a hypothetical scheme of directors configuration in $N_p$ with a nonsingular line defect of strength $s=1$ with a singularity in the secondary directors (thick black line); solid lines show $\hat{n}$ and short normal segments show one of the secondary directors; (e) transmitted light intensity profile measured with Abrio-Polyscope along the thin solid line in (f) for the capillary in two configurations that differ from each other by a 12° rotation around the capillary’s axis; (f) Abrio-Polyscope texture of capillary (diameter 10 μm) at $t=-46.5$ °C filled with A131; dashed white circle shows the point defect. $Z^*$ is a slow axis of inserted full or quarter-wave ($\lambda=530$ nm) plates.

Similar uniaxial features of defects in capillaries were observed for B samples, with well-defined nonsingular disclinations and isolated point defects at the temperatures above and below $t^\ast$ [Figs. 9(a) and 9(e) and Figs. 9(b) and 9(f)].

Below $t_{nil}=-41$ °C, the textures of capillary B samples are distorted by the surface anchoring transition [Figs. 9(c) and 9(g)] rather than by transition into the biaxial phase because the escape line and point defect preserve their internal structure and all changes occur near the surface. Distortions of the defects pattern reproduce themselves when the sample is heated above $t^\ast$ and then cooled back below $t_{nil}$, indicating the prime role of the surface interaction [compare Figs. 9(c) and 9(g) with Figs. 9(d) and 9(h)].

FIG. 9. Escaped disclination and point defect (shown by the arrow) in the capillary with B-sample viewed in the monochromatic light ($\lambda=546$ nm) between crossed polarizers (a)–(d) and without analyzer (e)–(h): (a) and (e) $t=-11.5$ °C; (b) and (f) $t=-36.5$ °C; (c) and (g) nonuniformity of escaped disclination at $t=-51.5$ °C on first cooling; (d) and (h) nonuniformity of escaped disclination at $t=-51.5$ °C on second cooling.

2. Point defects at colloidal spheres in A131

We also explored the behavior of surface point defects boojums formed at the surface of spherical inclusions in the $N$ phase. Small (diameter of 10 μm) spherical particles of borosilicate glass were added to A131 [19,60] and studied in planar cells of thickness $d=25$ μm (Fig. 10).

The textures show a quadrupolar symmetry of distortions of $\hat{n}$ with two point defects, boojums, at the poles of the sphere [Figs. 10(a) and 10(c)] along the axis that is parallel to the overall direction of $\hat{n}_b$ set by rubbing. Their existence is dictated by the topological requirement: a director field tangential to the surface of a sphere should contain singularities with the total strength equal to the Euler characteristic of the sphere, which is $2\Sigma s_b=2$ (see, e.g., Ref. [36]). The texture with two isolated boojums at the poles is a natural solution of the boundary conditions in the $N_p$ phase but not for the $N_b$ phase. In the $N_p$ phase, the relationship $\Sigma s_b=2$ is still valid, but the isolated boojums of strength $s_b=1$ cannot exist, as they should represent the ends of disclination lines.
of strength \( s = 1 \) terminating at the surface of the spherical particle. Close examination of the boojums in our samples reveals that their cores remain limited by the vicinity of the sphere and do not extend into two singular lines \( s = 1 \) below \( t^* \) [Fig. 10(d)]. There is also no tendency of the boojums to merge into a single boojum with \( s_b = 2 \) that is allowed in the \( N_b \) phase.

As already indicated, the director pattern around the sphere in the \( N_u \) phase is quadrupolar. When a few such spheres cluster, they attract each other along a line that makes a large angle, \( \gamma \approx 30^\circ \), with \( \hat{n}_b \) \[60,61\]. Such a tilted pattern of clustering is clearly observed [Fig. 10(b)] in our samples. Cooling below \( t^* \) does not perturb these quadrupolar arrangements. If there were disclinations terminating at the boojums, one would expect a rearrangement that would decrease \( \gamma \) aimed at shortening the length of disclinations. The rearrangements of colloids should be detectable even if the core of the disclinations is invisible under the microscope.

The features of topological defects considered above are fully consistent with the features of the uniaxial \( N_u \) phase but not with the expected properties of the \( N_b \) phase.

3. Freely suspended films of A131

We prepared freely suspended thin \(( \leq 500 \text{ nm}) \) films of A131 by pulling the melted material over the opening in the frame. The films were prepared at temperatures below \( t = -31.5^\circ \text{C} \) and examined in the range \(-58^\circ \text{C} \leq t \leq -27.5^\circ \text{C} \). Typically, the films ruptured at \( t > -27.5^\circ \text{C} \). The film thickness \( d \) was determined by the measurements of reflected light intensity \[62\].

The relatively thick film \(( d = 270 \pm 10 \text{ nm}) \) features an distinct central area with a bright birefringent meniscus at the periphery [Fig. 11(a)] in the range \(-56^\circ \text{C} \leq t \leq -27.5^\circ \text{C} \). The retardation of the central area is very small, fluctuating around 1 nm (which corresponds to the in-plane birefringence \( \Delta n_{xy} = 3 \times 10^{-3} \)) [Fig. 11(d)]. Near the bulk nematic-smectic transition temperature \( t_{NS} = -58^\circ \text{C} \), the central part acquires higher retardation and shows well-defined patterns with the distinct feature of almost equidistant stripes [Figs. 11(b) and 11(c)]. The thinner the film, the wider is the temperature range above \( t_{NS} \) where the birefringent patterns are observed. Namely, for the films with \( d = 270 \pm 10 \text{ nm} \), the central area becomes birefringent at \( t = -56^\circ \text{C} \), while...
for the thinner films, \( d = 100 \pm 10 \) nm, the central part becomes birefringent at even higher temperatures, \( T = -42 \) °C.

These stripe patterns are associated with the modulation of phase retardation [Figs. 11(e) and 11(f)] and azimuthal direction of the in-plane optic axis. Although the stripe pattern is similar to the “fingerprint” textures of cholesteric liquid crystals [1], it is very unlikely to be associated with the periodic helicoidal twist of the director. First, A131 is nonchiral. Second, we observe that the period of stripes depends on the thickness of the film, becoming larger in thinner films [compare Figs. 11(b) and 11(e)]. The textures are similar to those reported for smectic phases formed by nonchiral bent-core molecules [63]. As explained in Ref. [63], the stripes are caused by the frustrated nature of packing the bent-core molecules into the smectic layers. In our case, thinner films have a larger periodicity of the stripe patterns [63]. The similarity of the birefringent textures in freely suspended films to those reported by Coleman et al. [63] supports the idea of surface-induced smectic layering in A131 above \( T_{NS} = -58 \) °C. Note that the fact of persistence of the smectic layering well into the nematic range [by 10–40 °C above \( T_{NS} \)] is well established experimentally (see, for example, Ref. [64]). The very fact of stability of freely suspended films above \( T_{NS} = -58 \) °C is consistent with the idea of surface-induced smectic order in A131 films.

IV. CONCLUSIONS

We studied the physical properties, namely, birefringence, anisotropic absorption, and topological defects in confined volumes of a thermotropic bent-core material A131 to determine whether the material has a bulk biaxial nematic order in the range 118.5–149 °C (i.e., \(-58 \leq T \leq -27.5 \) °C) [22]. The bulk features of A131 are consistent with those of a uniaxial nematic \( N_u \) in the entire temperature range 118.5–176.5 °C (i.e., \(-58 \leq T \leq 0 \) °C). The absorption coefficients show just two different principal values (“di-chroism”) and not three (“tri-chroism”) as expected for a biaxial material. The birefringence of A131 oriented by a strong electric field along the direction of propagating light is zero, which is inconsistent with the presence of secondary directors of a biaxial material. The birefringence of A131 is caused by the frustrated nature of packing the bent-core molecules into the biaxial nematic order.

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One of the most intriguing features of A131 is its surface alignment. We have achieved a uniaxial homeotropic alignment of A131. However, this alignment is stable only within a certain temperature range between the \( N \)–\( Iso \) phase transition and \( t_{tilt} \) that varies in a broad range depending on the substrate and the prehistory of the material. We found the cases when \( t_{tilt} \) is higher than the temperature \( T^* \) previously associated with the \( N_u \)–\( N_{Is} \) transition [22] and also cases when \( t_{tilt} < T^* \). Below \( t_{tilt} \), the director is tilted, giving rise to a shift of the conoscopic pattern. Moreover, the conoscopic pattern often shows a small splitting of isogyres. Both the tilt and splitting can be removed by an electric field that enforces a homeotropic orientation of \( N \). The isogyres splitting is typically attributed to the biaxial order, but in our case, the splitting is associated with the nonuniform tilt of the director along the normal to the plates. The nonuniformity of molecular orientation along the normal to the bounding plates can be promoted by surface-induced smectic layering and tilt of bent core molecules different from their orientation in the bulk. Finally, observations of smectic textures in freely suspended films above \( t_{NS} \) support the idea of surface-induced smectic order with ensuing in-plane birefringence of the samples.

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APPENDIX A: MOLECULAR STRUCTURAL CHARACTERIZATION DATA FOR A131

1. Nuclear magnetic resonance spectroscopy

The \(^1H\) NMR (Varian Inova, 750 MHz) and \(^{13}C\) NMR (Varian NMRS, 500 MHz) spectra were acquired for samples A and B in the NMR research facilities of the Magnetic Resonance Center (the University of Akron, Akron, OH). High resolution NMR spectroscopy did not indicate any difference between samples A and B and confirmed the structure of A131 in both of them.

**Sample A:** \(^1H\) NMR (750 MHz, CDCl\(_3\)): \( \delta = 8.37 \) (s, 1H, \( -\text{CH}==\text{N}−\)), 8.13–7.84 (m, 9H, ArH), 7.39–7.14 (m, 10H, ArH), 7.27–2.68 (m, 7H, Ar–CH\(_2\)), 2 × Ar–CH\(_3\)), 1.67–1.26 (m, 32H, -CH\(_2\)), and 0.89 (m, 6H, 2 × -CH\(_3\)) ppm; \(^{13}C\) NMR (CDCl\(_3\)): \( \delta = 164.0, 163.12, 157.66, 152.16, 151.26, 151.0, 149.45, 149.0, 148.28, 145.31, 133.47, 132.73, 129.35, 129.15, 128.95, 128.15, 127.79, 127.09, 125.75, 125.5, 123.14, 122.07, 121.58, 121.53, 121.45, 37.27, 37.07, 33.17, 33.11, 32.55, 32.38, 30.95, 30.88, 30.8, 30.73, 30.65, 30.59, 30.57, 30.53, 24.14, 24.11, 16.98, and 15.76 ppm.

**Sample B:** \(^1H\) NMR (750 MHz, CDCl\(_3\)): \( \delta = 8.37 \) (s, 1H, \( -\text{CH}==\text{N}−\)), 8.13–7.84 (m, 9H, ArH), 7.39–7.14 (m, 10H, ArH), 7.27–2.68 (m, 7H, Ar–CH\(_2\)), 2 × Ar–CH\(_3\)), 1.67–1.26 (m, 32H, -CH\(_2\)), and 0.89 (m, 6H, 2 × -CH\(_3\)) ppm; \(^{13}C\) NMR (CDCl\(_3\)): \( \delta = 164.01, 163.12, 157.67, 152.16, \)
2. Analytical methods

The high-pressure liquid chromatography and mass spectrometry (HPLC-MS) analysis of the samples A and B has been carried out in the Chemistry Research Facilities of the University of Akron by using a liquid chromatograph Agilent 1100 (Agilent Technologies, Inc.) coupled with an Esquire ion trap mass spectrometer (Bruker Daltonics, Inc., Billerica). A C18 column was used for liquid chromatography separation and the mobile phase was THF-H2O (tetrahydrofuran-water). HPLC-MS analysis resulted in the same data for both samples A and B and verified the presence of only one chemical component, A131 (C54H65N3O4H): MS m/z calculated for C54H65N3O4H (M+H) 820.5; found in samples A and B 820.7; MS m/z calculated for C54H65N3O4Na (M+Na) 842.5; found in samples A and B 842.6.

Elemental analysis (Robertson Microlit Laboratories, Inc.) for C54H65N3O4: calculated (found): C, 79.08 (78.90); H, 7.99 (8.12); N, 5.12 (5.16).

3. Thin layer chromatography

Thin layer chromatography (TLC) analysis for A131 shows retardation factor $R_f = 0.6$ in 20% EtOAc-hexane (ethyl acetate-hexane). The chromatograms developed on TLC plates (Analtech, Inc.) after eluting the “fresh” (right after the dissolving in chloroform) A and B samples are shown in Fig. 12. There is only one spot along the direction of solvent movement corresponding to a single compound in both samples.

A131 molecule contains azobenzene group (Fig. 1), which makes it sensitive to photoisomerization about nitrogen-nitrogen double bond [65]. The significant amount of cis-isomer occurs in the dissolved material with azobenzene group under the irradiation with the ultraviolet (UV) light and can be isolated with the chromatographic analysis [65]. Therefore, to verify the effect of photoisomerization in A131 we performed the TLC analysis on samples A exposed to the ambient light (sample C) and irradiated with the UV light (sample D) for a short period of time, ~2–15 min (Fig. 13). Both samples, C and D, developed additional weak spots on TLC plate (Fig. 13), which indicate the presence of A131 cis-isomers resulting from photoisomerization. It is worth noting here that A131 molecule also has a Schiff base (or azomethine) (Fig. 1), which makes it also possible for the isomerization about the carbon-nitrogen double bond to occur [65].

APPENDIX B: SPLITTING OF ISOGYRES IN UNIAXIAL CELLS

The splitting $2\alpha$ of isogyres in the conoscopic interference image is a feature characteristic of an optically biaxial phase [44]. However, the splitting can also be observed if the material is optically uniaxial, but the optic axis (parallel to the director $\hat{n}$) is distorted along the direction of light propagation, as we demonstrate by two experimental examples below (Fig. 14).

FIG. 12. (Color online) The chromatogram produced from fresh samples A and B of liquid crystal A131.

FIG. 13. (Color online) The chromatogram produced from samples A, C, and D of liquid crystal A131: A is a fresh sample of A131; C is a sample A exposed to the ambient light for ~10–15 min; and D is a sample A irradiated with the UV light (λ < 370 nm) for ~2 min.

FIG. 14. (Color online) Isogyres split in the conoscopic images of uniaxial N_un samples: (a)–(c) composite cell; (d)–(f) planar cell. Arrow shows the rubbing direction in the planar samples.
In the first example, we use a composite cell comprising of a smectic A (octyloxyanobiphenyl) cell of thickness \(d_f=85 \mu m\) with strictly homeotropic \(\hat{n}\) sandwiched between two planar cells with the nematic material (ZLI-2806 or ZLI-3412) of low birefringence \(\Delta n_p\) with optical retardation \(\delta_p=80 \text{ nm}\) each [Fig. 14(a)]. The homeotropic cell alone produces the conoscopic image with crossed isogyres, but adding two planar cells results in the separation of isogyres in the direction normal to the rubbing direction in the planar cells [Fig. 14(b)]. The splitting of isogyres is caused by uncompensated retardation \(2\delta_p=2\Delta n_p' \cdot d_p\) introduced by the two planar cells of thickness \(d_p\) each. The retardation \(2\delta_p\) can be compensated by the retardation \(\delta_{st}=\Delta n_{effst} \cdot d_{st}\) of the birefringent material that fills the homeotropic cell, where \(d_{st}=d_f/\cos \phi\) is the (tilted) pathway of the light ray, \(\phi=\tan^{-1} \alpha'/d_f\) is the angle between the propagation direction of light and the normal to the bounding surfaces. The distance \(2a\) between the two points at which the total retardation is 0, measured at the exit plane of the LC slab, corresponds to the splitting \(2a\) of isogyres in the conoscopic image: \(2a'=d_f/2\alpha/\cos \phi = 2\alpha/NA/(R \cdot \hat{n})\) [44], where \(R\) is the radius of the field of view, NA is a numerical aperture of the objective, and \(\hat{n}\) is an average refractive index of LC. The effective birefringence (along the path \(d_p'\) of the material filling the homeotropic state is \(\Delta n_{effst}=n_{effst}(n_{eff}^2 \cos^2 \phi+n_{eff}^2 \sin^2 \phi)^{-1/2} 1\), where \(n_{effst}\) and \(n_{eff}\) are extraordinary and ordinary indices of refraction, respectively, of this material. As a result, for small \(\phi\), one can find the relation between the uncompensated retardation \(\delta_p\) introduced by the planar cell and splitting of isogyres in the conoscopic image as \(2a=(2-R \cdot \hat{n}/NA-(2\delta_p/\delta_{st})^{1/2}\), where \(\delta_{st}=(n_{effst}-n_{eff}) \cdot d_{st}\).

In the second example, an electric field is applied across the thickness \(d_p\) of a planar \(N_{ph}\) cell (5CB) with \(\Delta \varepsilon>0\) [Fig. 14(d)] to reorient the director \(\hat{n}\) vertically. The reorientation starts in the middle of the cell and propagates toward the plates as the field increases [1]. When the applied voltage \(U\) is much larger than threshold voltage \(U_{th}\) of the Fréedericksz transition, such a cell can be thought as comprised of three regions: a bulk region with the homeotropic \(\hat{n}\) confined between two surface regions of thickness \(\varepsilon_E=(d_p/\pi) \cdot (U_{th}/U)\) [66,67] each with a hybrid alignment of \(\hat{n}\). This nonuniform director orientation across the thickness of the cell [Fig. 14(d)] produces the conoscopic pattern with split isogyres [Fig. 14(f)]. In our experiments, \(\varepsilon_E=0.4–0.2 \mu m\) at \(U=40–100 \text{ V}\). The isogyres are separated along the direction perpendicular to the original planar \(\hat{n}\) [Fig. 14(f)]. The splitting of isogyres is caused by uncompensated retardation \(\delta_p=\Delta n_p \cdot \varepsilon_E\) introduced by surface regions of thickness \(\varepsilon_E\) [Fig. 14(d)]. Therefore, at high voltages, \(2a\) decreases when \(U\) increases, according to the equation \(2a=(2-R \cdot \hat{n}/NA)-(U_{th}/(\pi \cdot U))^{1/2}\). In a similar way, the splitting of isogyres produced in the composite cell by two planar cells [Fig. 14(a)] can be reduced by applying the electric field to these planar cells [Fig. 14(c)].

The two examples demonstrate that the splitting of isogyres in conoscopic patterns can be produced even if the material is a uniaxial nematic \(N_{ph}\) provided that the director orientation is nonuniform across the cell.

SURFACE ALIGNMENT, ANCHORING TRANSITIONS,...