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Electro-optic technique to study biaxiality of liquid crystals with positive dielectric anisotropy: The case of a bent-core material

Khoa Van Le,[1] Manoj Mathews,[2] Martin Chambers,[2,3] John Harden,[2] Quan Li,[2] Hideo Takezoe,[1,*] and Antal Jákli[2]
[1]*Department of Organic and Polymeric Materials, Tokyo Institute of Technology, O-okayama, Meguro-ku, Tokyo 152-8552, Japan*
[2]*Liquid Crystal Institute and Chemical Physics Interdisciplinary Program, Kent State University, Kent, Ohio 44242, USA*
[3]*Department of Physics, Kent State University, Kent, Ohio 44242, USA*

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We propose that, for materials having positive dielectric anisotropy, the biaxiality can be clearly verified or excluded by measuring the transmitted light intensity as a function of electric field. If the material is biaxial and is observed in homeotropically aligned cells, the schlieren texture should not disappear (transmitted intensity is not zero) even at very high fields, since the field does not affect the distribution of the second director normal to the main director. On the other hand, if the material is uniaxial the transmitted intensity should decrease with increasing field and a perfect homeotropic texture can be achieved at high fields. We have studied a bent-core compound in which a uniaxial-biaxial nematic (N_u-N_b) transition has been reported. This material has a positive dielectric anisotropy at low frequencies, so we could apply the technique described above. Our studies indicate that the material is uniaxial in the entire nematic range.

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Most liquid crystals (LCs) have a uniaxial nematic (N_u) phase that is characterized by a director **n**. Meanwhile, the biaxial nematic (N_b) phase of LCs has also attracted much attention since Freiser's theoretical prediction of its existence in 1970 [1]. A decade later, Yu and Saupe experimentally showed evidence of the N_b phase in a lyotropic ternary system [2]. Subsequently, there have also been several attempts to find it in thermotropic LCs as well [3,4]. For practical applications, new types of electro-optic devices with fast response are expected from this phase, due to the fact that the switching of the secondary director **m**, which is perpendicular to principal director **n**, might be much faster than that of **n** [5,6]. However, such devices require homeotropic alignment with in-plane switching, and need large biaxiality or film thickness to achieve gray scale.

On the other hand, LCs composed of bent-core molecules have been studied extensively in recent years since the discovery of polar switching in achiral bent-core mesogens in 1996, particularly from the viewpoint of polarity and chirality [7,8]. Since then, a great number of bent-core compounds have been synthesized and at least eight different phases have been identified and chronologically designated as $B1-B8$ [8]. In addition to these phases, a growing number of bent-core compounds exhibiting the traditional nematic (N) phase have also been reported in the past several years [9]. One of the most remarkable aspects of these nematogens is the possibility of giving rise to biaxial order including N_b phases due to their bent shape. Following this, some bent-core LCs with an oxadiazole core have been reported to exhibit the N_b phase, based on ^{2}H NMR and small-angle x-ray diffraction techniques [10,11].

The study of biaxiality of LCs is a very challenging task, because it is difficult to exclude the effect of surfaces. For example, the formation of a grayish schlieren texture in samples with homeotropic anchoring conditions might be an indication of biaxiality, but it also can be due to a surface pretilt with respect to the substrate normal. In addition, for instance, an anchoring transition [12] may appear to be the N_u-N_b phase transition. We argue that, for materials having positive dielectric anisotropy, the biaxiality can be clearly verified or excluded by measuring the transmitted light intensity as a function of electric field. If the material is biaxial, the schlieren texture should not disappear (transmitted intensity is not zero) even at very high fields, since the field does not affect the distribution of the second director **m** normal to the main director **n**. On the other hand, if the material is uniaxial the transmitted intensity should decrease at increasing fields, and a perfect homeotropic texture can be achieved at high fields. To verify this one simply needs to measure the transmitted light intensity between crossed polarizers with increasing voltage and plot the results versus the inverse square of the applied voltage. As conoscopy is known to be a simple technique for identifying biaxial phases such as N_b, biaxial smectic-A (SmA_b), and smetic-C (SmC) [10,13,14], the light intensity measurements can be corroborated with conoscopic observations at different applied electric fields.

Recently, Prasad *et al.* reported the mesogenic properties of the bent-core compound $A131$ [Fig. 1(a)] as

$$\text{Iso} \underset{176.5\ ^\circ\text{C}}{\leftrightarrow} [N_u] \underset{149\ ^\circ\text{C}}{\leftrightarrow} [N_b] \underset{118.5\ ^\circ\text{C}}{\leftrightarrow} \text{Sm}C$$

phase transitions, along with other unidentified higher-order smectic phases at lower temperatures based on textural observations and x-ray diffraction experiments [15]. A ^{13}C NMR study on the same compound also supported this sequence [16]. In this study, we synthesized the target molecule $A131$, since this material was thought to have positive dielectric anisotropy due to its asymmetric nature not only in the central core and arms but also in the hydrocarbon chains at their terminals. The molecular structure and purity were fully characterized by ^{1}H and ^{13}C NMR spectroscopy, high-resolution mass spectroscopy, and elemental analysis. Differ-

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[*] Corresponding author. takezoe.h.aa@m.titech.ac.jp

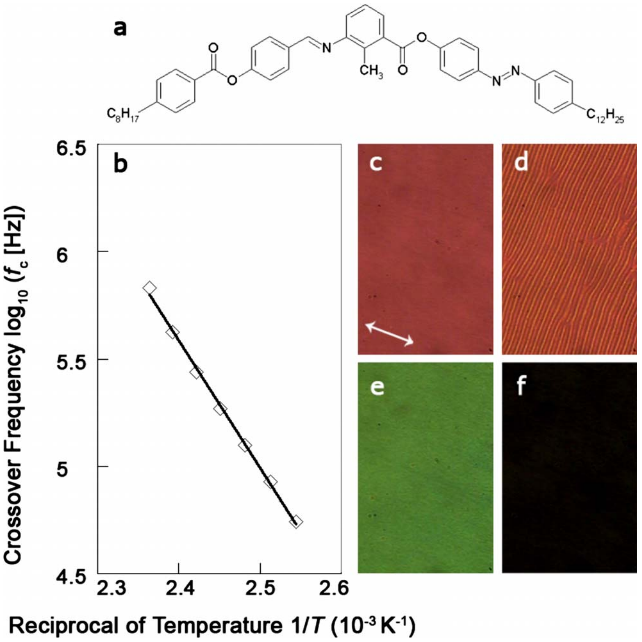

FIG. 1. (Color online) (a) Molecular structure of material *A*131; (b) exponential crossover frequency f_c as a function of inverse temperature; (c) texture of a planar cell in the ground state (without field); (d) a typical prewavy pattern of electroconvection under a rectangular field at high frequency (125 kHz, 7 V); (e) normal switching at low frequency (10 kHz, 2.2 V); and (f) dark view at high field (10 kHz, 15 V). All the pictures are taken at 130 °C under crossed polarizers. The arrow indicates the rubbing direction and is 100 μm long.

ential scanning calorimetry (DSC) revealed signatures for all the phase transitions as reported except for the N_u-N_b transition; i.e., in agreement with the previous report, no DSC signal was observed between the suggested N_u and N_b phases. As expected, when a 5-μm-thick cell with planar alignment coating was filled with the sample, we observed a switching toward homeotropic alignment above a threshold ac voltage at low frequencies (for instance, lower than 125 kHz at 130 °C), indicating positive dielectric anisotropy.

Studying the frequency dependence of the switching, we actually found that there is a temperature-dependent crossover frequency f_c, where the dielectric anisotropy changes sign. To our best knowledge this is the first report of dielectric sign inversion for bent-core LCs. The data from 150 down to 120 °C are shown in Fig. 1(b) for a 5-μm-thick planar cell with antiparallel rubbing direction. Note that, when the frequency of the vertical field exceeds f_c, one observes electroconvection (for $\Delta\epsilon < 0$) rather than the Fréedericksz transition (for $\Delta\epsilon > 0$) with increasing field [see Figs. 1(c)–1(e)]. The temperature dependence of the crossover frequency was best fitted to an Arrhenius relation, namely, $f_c \propto \exp(-E_c/k_B T)$ where E_c is the activation energy, k_B the Boltzmann constant, and T the temperature in kelvin. We found $E_c \approx 1.18$ eV, which is about a factor of 2 larger than reported values in calamitic LCs [17,18].

This enabled us to study the biaxiality of *A*131 by applying electric fields below the crossover frequency based on the technique described above. For this we put *A*131 into a 5-μm-thick cell coated with a polyimide layer (SE-5300, Nissan) which gives homeotropic alignment to calamitic LC molecules. The textures of the nematic phase were observed under a polarizing microscope (BX60, Olympus) on cooling at a rate of 2 °C/min. As shown in Fig. 2(b), unlike in rodlike nematics, here uniform darkness was not achieved; instead there was a highly birefringent schlieren texture with a large number of four-brush defects. On cooling further, excluding the color, the main features of the texture remained unchanged until 138 °C, where a purple domain came out from the yellow background and then abruptly changed to a considerably smaller birefringent texture [see Fig. 2(d)]. The fact that the position of the defects did not change during this transition indicates that a smaller pretilt relative to the substrate normal still exists even in the low-temperature range. Importantly, this transition happens quite far from 149 °C where the N_u-N_b transition was proposed earlier [15], and we did not see any significant change in the textures near this temperature. This confirms that the textural changes found on SE-5300 surfaces are due only to the surface anchoring transition. We suspect that the transition reported in [15] at 149 °C is also related to surface anchoring changes.

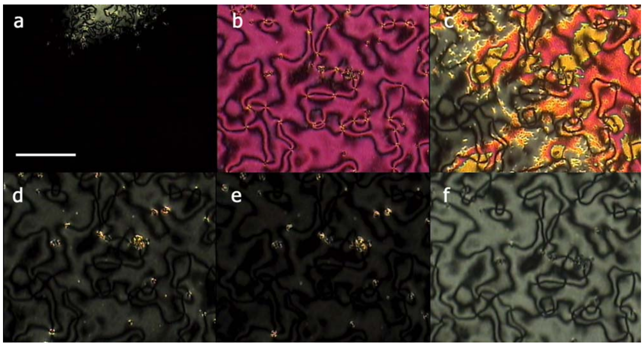

FIG. 2. (Color online) Textures of *A*131 under homeotropic anchoring conditions. (a) Iso-*N* transition at 175.5 °C, (b) schlieren texture at 170 °C, (c) a purple domain grows out of yellow schlieren texture and abruptly diminishes at 138 °C, (d) grayish texture at 138 °C, (e) the birefringence is reduced even with a small field of 500 mV (rectangular, 10 kHz), and (f) texture at 120 °C. Length scale represents 400 μm in (a) and 100 μm in other pictures. The polarizers are along the edges of the pictures.

To study the electric field response, a red solid state laser ($\lambda = 640$ nm) was used to illuminate the homeotropic cell placed between crossed polarizers, and the transmittance with increasing field (rectangular, 10 kHz) was detected by a photodetector. Because of negligible absorption above $\lambda = 600$ nm [19], the laser used here enables us to avoid any light-induced *trans-cis* isomerization of the azo unit incorporated in the molecule. The results with voltages up to 5 V are shown in Figs. 3(a) and 3(b).

The plots apparently show that in the high-temperature region, e.g., 170 °C, the director is quasiplanar and reorients at a threshold voltage of $V_{\mathrm{th}} \approx 0.8$ V. In contrast, there was no threshold voltage at low temperature (130 °C), implying a rather tilted orientation. This is in accordance with the textural observations shown in Fig. 2. The most important feature of the voltage-dependent transmitted light intensity measurements is that the texture monotonically darkens and

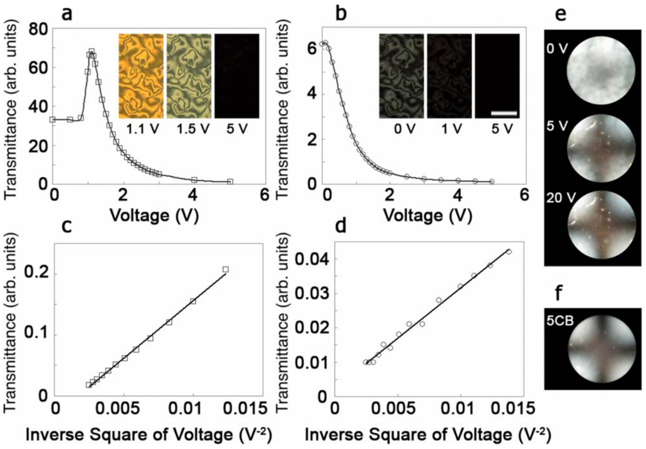

FIG. 3. (Color online) Transmittance vs voltage (I-V) and inverse square of voltage (I-$1/V^2$) in a 5-μm-thick homeotropic cell (a),(c) at 170 °C and (b),(d) at 130 °C. Note that the voltage ranges in (a) and (b) (low voltage) and that in (c) and (d) (high voltage) are different. The insets show the textures under fields (orange at 1.1 V), with the length scale being 100 μm. (e) Change of conoscopic image at 130 °C with applied field; (f) conoscopic image of 4′-n-pentyl-4-cyanobiphenyl (5CB) in a similar 5-μm-thick homeotropic cell for reference.

becomes quasi-isotropic at fields above a few V/μm. The retardation is proportional to the inverse of the applied voltage at high fields [20]. Hence the transmitted light intensity is plotted as a function of the inverse square of the applied voltages in Figs. 3(c) and 3(d). The dependence can be fitted by straight lines that intersect the y axis at practically zero or negative values. This shows that the birefringence becomes zero either already at a finite field (for weak anchoring), or at infinite fields (for strong anchoring). We note that at 130 °C the best fit approaches $I(V=\infty)=0.002$ [see Fig. 3(d)], which may come from even tiny defects or dust and is within experimental error.

Nonetheless, we estimate the maximum possible biaxiality by assuming that any transmittance at high voltages is due to biaxiality. The transmitted intensity in this limit can be written as

$$I = I_0\langle \sin^2(2\phi)\rangle \sin^2(\pi d\,\delta n/\lambda), \tag{1}$$

where ϕ is the azimuthal angle between the analyzer and the second director $\mathbf{m}$ normal to the director $\mathbf{n}$, $d=5$ μm is the film thickness, and $\delta n = n_2 - n_3$ is the value of the biaxiality. The brackets ⟨ ⟩ indicate averaging over the transversal optical axis. Since the defect structure changes neither with temperature (see Fig. 3) nor under voltage, $I_0\langle \sin^2(2\phi)\rangle$ corresponds to the maximum value of the light intensity (≈ 68 mV signal of the photodiode). This allowed us to estimate that the photodiode signal of 0.002 mV corresponds to $\delta n = 2 \times 10^{-4}$, which is the upper limit of possible biaxiality. This value is two orders of magnitude smaller than that measured in the biaxial smectic phase of bent-core materials [21], and is small even compared with some nematic LCs which have less biaxial molecular shape, namely, bimesogenic twin molecules [13,22].

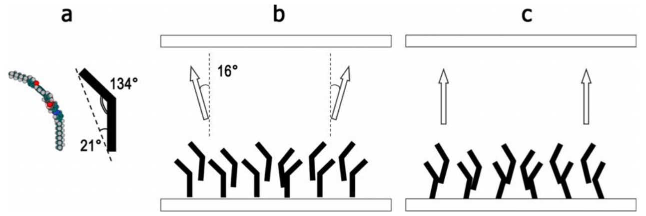

FIG. 4. (Color online) (a) Optimized structure of $A131$ by quantum-chemical calculations (MOPAC method, AM1 Hamiltonian) with a bend angle of 134°, which agrees quite well with the NMR result [16]. (b),(c) Schematic illustration of the orientation of bent-core molecules near the alignment layer's boundary and resulting tilting directors (arrows) of two adjacent domains in the bulk (b) without field and (c) with very high field.

We also employed conoscopic observation to confirm the genuine uniaxiality of $A131$. Figure 3(e) shows how the conoscopic image changes with increasing field at 130 °C. The uniaxiality is evident (clear Maltese cross) at the voltage of 20 V in comparison with the uniaxial 5CB [Fig. 3(f)]. Based on these observations, we conclude that $A131$ is uniaxial in the entire nematic region and there is no N_u-N_b transition at 149 °C, in contrast to the previous report [15].

It should be noted that there are also some reports on schlieren textures or nonalignment of nematic bent-core LCs with homeotropic alignment layers [10,23,24]. We suggest these are due to the tilt of the director with respect to the substrate normal. Concerning the texture observed at 130 °C in our study, it is possible to estimate the average tilt angle θ under zero electric field from Fig. 3(b) by using Eq. (1) with δn being replaced by $\Delta n_{\mathrm{eff}}(\theta)$, which is the effective birefringence due to the tilt in director. Using $\Delta n = 0.198$, which was preliminarily measured in the planar cell, we found $\theta \approx 16°$ with respect to the vertical direction. The interpretation of this result is that the alignment layers align only one of the arms of bent-core molecules in the vicinity of substrate surfaces, and thus a schlieren texture results due to the free orientation of the other arm. This proposed model is illustrated in Fig. 4.

In summary, a nematic bent-core liquid crystal which was reported to be biaxial in the low-temperature range was confirmed to be uniaxial by means of the electro-optic technique. The grayish schlieren texture, which was taken to indicate biaxiality, was shown to be merely due to the nonuniform tilt of the director. The method proposed here cannot be used to study biaxiality of bent-core LCs that are typically symmetric and have negative dielectric anisotropies. Even for such materials, however, the same idea can be applied by using an in-plane electric field. One may also use a strong magnet to align the main director. The method is also expected to be widely applicable for molecular shapes other than bent-core systems. In addition to ^{2}H NMR, which is inherently insensitive to the surface effect, our method provides a simple way to distinguish spontaneous biaxiality from surface effects.

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