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Electric field induced biaxiality and the electro-optic effect in a bent-core nematic liquid crystal

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We report the observation of a biaxial nematic phase in a bent-core molecular system using polarizing microscopy, electro-optics, and dielectric spectroscopy, where we find that the biaxiality exists on a microscopic scale. An application of electric field induces a macroscopic biaxiality and in consequence gives rise to electro-optic switching. This electro-optic effect shows significant potential in applications for displays due to its fast high-contrast response. The observed electro-optic switching is explained in terms of the interaction of the ferroelectric clusters with the electric field. © 2010 American Institute of Physics. [doi:10.1063/1.3280817]

Based on the generalized Maier–Saupé theory, Freiser1 predicted that a reduction in the molecular symmetry could lead to the formation of a biaxial nematic (Ñb) phase in liquid crystals (LCs) in addition to the observed uniaxial nematic phase. The biaxial nematic phase has a secondary director n perpendicular to the primary director m; the latter is always prevalent in the nematic phase. From a practical point of view, the switching of the secondary director is at least a factor of 100 faster than the primary one. Therefore such biaxial nematics with improved response offer significant advantages over the conventional nematics in applications for fast displays and photonic devices. The potential for faster devices has led to a significantly increased interest in theoretical, experimental, and computational studies on the biaxial nematic phase. The experimental proof for the existence of the Ñb phase in a lyotropic LC system was reported in 1980.2 The thermotropic biaxial nematic phase was discovered in 2004 in liquid crystalline polymers,3 organosiloxane tetrapodes,4,5 and in low molar mass bent-core systems.6–8 The possibility for the existence of a biaxial nematic phase in biaxial parallelepiped (or bricklike) shaped molecules9–11 and in bent-core systems12–14 has been supported by numerous theoretical studies.

Experimental studies on a part of the temperature range of nematic phase of the bent-core LCs suggest the appearance of “cybotactic” (smecticlike) clusters.15–21 In such molecules, two rodlike mesogenic groups linked together through a central unit exhibit a near-C₅₅ symmetry. The presence of biaxial clusters was considered a long time ago by De Vries.22 In bent-core systems, a deviation from the calamitic shape and an existence of a large transverse dipole moment gives rise to unusually strong intermolecular interactions that lead to the formation of ferroelectric domains or clusters. On applying the electric field, the collective alignment of domains leads to a macroscopically biaxial ordering.18 On removal of the field the domains are destabilized, with a corresponding drop in the biaxial order parameter. It is still not clear whether such a nematic LC consists of distinguishable clusters of a lower symmetry phase, or correlated regions with a short-range order.

In spite of the obvious progress made in both experimental and theoretical studies, a number of problems remain to be solved23 and therefore the subject of biaxial nematics continues to be a highly debated and challenging in the field of LCs. Despite numerous claims for the existence of biaxial nematic phase in different systems, electro-optic effect has so far not been demonstrated unambiguously. In this letter, we report results of the experimental study of electro-optic effect in a homeotropically aligned biaxial nematic compound. The observed electro-optic switching is explained in terms of the interaction of the ferroelectric clusters with the electric field. The bent-core LC sample under study, C₆-BAN, is synthesized in Halle, Germany. The molecular structure of the studied material is given in Fig. 1. For the optical and electro-optical studies the compound was filled in homeotropically aligned cells of different thicknesses, varying from 4 to 50 μm. The foil stripes of different thicknesses were used as electrodes in order to apply the external electric field parallel to the plane of the glass plates. The gap between the electrodes was fixed to be of the order of ~200 μm. AL60702 (JSR Japan) was used to achieve the homeotropic alignment.

The optical textures for three different thicknesses (50, 25, and 4 μm) of the sample are presented in Figs. 1(a)–1(c). On cooling from the isotropic to nematic phase in a thicker (50 μm) cell, the nematic phase is found to consist of distinguishable clusters of a lower symmetry phase, or correlated regions with a short-range order.

FIG. 1. (Color online) Microphotographs of the textures near T₅₀: The cell thicknesses are d=50 μm for (a) and (d); d=25 μm for (b) and (e); and d=4 μm for (c) and (f). Textures (d), (e), and (f) are recorded after a period of 1 h from those of (a), (b), and (c).

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only two-brush Schlieren texture [Fig. 1(a)] which indicates
the presence of biaxial nematic phase. Nevertheless this bi-
axial nematic texture is not stable with time and during a
period of one hour it transforms to a rather uniform dark
texture [Fig. 1(d)], which nevertheless consists of very small
domains of the approximate size of the wavelength of visible
light. These considerably reduce the overall extinction of
the texture compared with that for the isotropic phase. We assign
these domains to cybotactic clusters, which are observed in
this sample by x-ray diffraction.24 It has been found that the
transition from cybotactic nematic to smectic phases occurs
on elongation of the chains and the clusters in this compound
are observed with three to four molecules correlated in the
transverse direction, and about two molecules correlated par-
allel to the director.24 Textures in these samples are found to
be strongly affected by surfaces. Thus a thin (4 \(\mu\)m) LC cell
finally produces a perfect high-extinction homeotropic align-
ment [Fig. 1(f)]. The textures produced by the cell of inter-
mediate thickness [Figs. 1(b) and 1(e)] are somehow between
those for the two previous cells.

The effect of electric field on the textures is studied in a
4 \(\mu\)m cell with foil spacers as electrodes. A square-wave
field 100 Hz is applied across the electrodes in the plane of a
glass plate. The cell was placed between the crossed polar-
izers with an angle of 45° between the electric field direction
and polarizer axis. Initially for a rather small electric field
(<0.3 V/\(\mu\)m), no significant effect is observed and the LC
remains optically uniaxial. On the application of a stronger
electric field, the cell exhibits electro-optical switching from
dark to bright state and reverse when the field is removed
(Fig. 2). The electro-optic response shows dynamics with
different speeds; slow and fast. These suggest coexistence of
the two different processes. This suggestion is supported by
observations under a polarizing microscope (Fig. 3). Figure
3(a) shows the texture for an applied electric field of
0.5 V/\(\mu\)m. On the removal of the field, the cell relaxes to an
apparently initial macroscopically uniaxial state [Fig. 3(c)].

The texture of the cell consists of two following distinct
regions: (i) two bright stripes near the electrodes with slow
dynamics (~10 s) and (ii) a uniform dark region between
the two bright strips with fast dynamics (~1 ms) [see Fig.
3(a) and 3(b)]. A sharp border between the two regions is
clearly seen. At this stage, we surmise that (i) the high-

toherent stripe region is the field induced planar
(or tilt)
alignment and (ii) the second region with a distinctive do-
main boundary is due to the field-induced biaxiality arising
from the alignment of the short axes of the clusters. The fast
electro-optic effect can be exploited in displays due to a fast
high-contrast (Figs. 2 and 3) response. The parasitic slow
response reduces the contrast ratio and the switching speed
and can be overcome using molecules with a strong negative
dielectric anisotropy.

The magnitude of induced biaxiality was measured using
a tilting optical compensator inserted in the polarizing micro-
scope. This allows one to measure rather small values of the
optical retardation for a specific region of the cell, which in
our case is the center between the electrodes of the foil (Fig.
3). Figure 4(a) shows the dependence of the induced biaxi-
ality (\(\Delta n\)) as a function of electric field for different tem-
peratures using a homeotropically aligned cell of thickness
4 \(\mu\)m. Initially (after a threshold field of ~0.3 V/\(\mu\)m
is applied), the induced biaxiality increases gradually with
electric field and then saturates to a constant value.

The magnitude of the induced biaxiality decreases with a
reduction in temperature, which shows that this phase dis-
appears at temperatures below 97 °C. Figure 4(b) presents
the dependence of the induced biaxiality (\(\Delta n\)) as a function
of frequency for an electric field of 0.7 V/\(\mu\)m. On cooling
from 106 to 97 °C, the cut-off frequency of the electro-optic

![FIG. 2. The EO response in a 4 \(\mu\)m homeotropic cell for square-wave
electric field \(E=1\ \text{V/\(\mu\)m}, 100\ \text{Hz, } T=106\ °C\). (a), (b), and (c) on the
electro-optic response refer to three states; the corresponding textures are
shown in Figs. 3(a), 3(b), and 3(c), respectively.](image_url)

![FIG. 3. (Color online) Dynamics of the induced biaxiality (a) at \(E =0.5\ \text{V/\(\mu\)m}\). (b) and (c) are obtained after 1 s and 30 s on the removal of
the field for \(T=106\ °C\). A, P, and E denote the directions of analyzer,
polarizer, and electric field.](image_url)

![FIG. 4. (Color online) (a) Induced biaxiality (\(\Delta n\)) vs electric field at
a frequency of 100 Hz. (b) \(\Delta n\) vs frequency for \(E=0.7\ \text{V/\(\mu\)m}\).](image_url)
The dielectric study was performed on a planar cell of 9 μm thickness using a broadband high resolution dielectric spectrometer (Novocontrol GmbH, Germany). Experiments are performed on cooling the sample from 115 to 60 °C. Figure 5 shows the dielectric loss spectra in the frequency of 10 Hz–10 MHz where the EO response disappears. Dielectric loss spectra (ε″) were fitted to the two relaxation processes. Both spectra show a relaxation process (P1) corresponding to the molecular relaxation around the short molecular axes (flip-flop mode) similar to other uniaxial nematics. The spectra at a temperature of 96 °C can well be fitted by a single relaxation process.

The second spectra for a temperature of 100 °C show an additional process (P2), Fig. 5. This process is observed in the same temperature range (97–106 °C), where the fast EO response is present. Therefore we can relate this definitely to the polar dielectrically active process observed in the EO switching. The two switched-ON states of the opposite polarity (+/−) are optically indistinguishable for the reason that the switching mechanism involves the polar reorientations of the microscopic biaxial domains in the direction of the applied electric field irrespective of its direction. Therefore the EO effect (Fig. 4) is observed between the field induced biaxial (ON) state and the uniaxial (OFF) state.

For temperatures below 97 °C, the sample exhibits neither the dielectric process (P2) nor the fast electro-optic response. This indicates the absence of the polar clusters. Nevertheless neither texture nor the DSC shows any phase transition at 97 °C. The cybotactic clusters have also been found to exist in the temperature range below 97 °C.24 The question arises as what is the phase assignment for temperatures below 97 °C. The plausible explanation is a gradual formation of cybotactic clusters with antiferroelectric order-

In summary, results on nematic phase for a bent-core LC system show that the nematic phase containing biaxial clusters is macroscopically uniaxial but the biaxiality is shown to be induced by the electric field. The electro-optic switching is shown to occur via the short axes. Such LCs, in their intermediate induced biaxial phase can be exploited for applications due to fast field-induced (−1 ms) switching between the uniaxial and biaxial states thus leading to a new concept for the devices.

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