

Antagonistic flexoelectric response in liquid crystal mixtures of bent-core and rodlike molecules

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We report the measurements of the temperature variations of the flexoelectric coefficient (e^*/K) of a host calamitic liquid crystal (RO) and its mixture with two guest bent-core (BC-120 and BC-60) liquid crystals. The bent-core (BC) molecules have different core structures and bend angles; namely, $\theta \simeq 120^\circ$ and $\simeq 60^\circ$, respectively. We find that e^*/K is independent of temperature and decreases rapidly with increasing concentration of BC-120 molecules and changes sign from positive to negative. In mixtures with BC-60, e^*/K is always positive and its concentration-dependent variation is not unique. At 7M% it is significantly large (three times) near the nematic-isotropic transition and decreases strongly with reducing temperature. Dielectric measurement suggests antagonistic orientation of the dipole axes (arrow axes) of the two BC molecules in the host liquid crystal, and based on this, the opposite sign of e^*/K is explained.

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I. INTRODUCTION

The average orientational direction of the molecules in liquid crystals is called director and is denoted by \mathbf{n} . In nematic liquid crystals the director is apolar; i.e., \mathbf{n} and $-\mathbf{n}$ are physically equivalent. About 40 years ago, Meyer predicted that the nematic liquid crystals can exhibit microscope polarization due to the distortions in the director field [1]. This is known as flexoelectric effect. It was shown that the distortion-induced polarization is given by

$$\mathbf{P} = e_1(\nabla \cdot \mathbf{n})\mathbf{n} + e_3(\nabla \times \mathbf{n}) \times \mathbf{n}, \quad (1)$$

where e_1 and e_3 are the flexoelectric coefficients connected to the splay and bend distortions, respectively. Since then a large number of experimental investigations have been reported and continuous efforts are being made to enhance and understand this effect in various liquid crystalline systems, such as palladium-containing nematic [2], chiral nematics [3,4], blue phase liquid crystals [5,6], and lipid bilayers [7]. Flexoelectricity can be demonstrated easily in compounds with asymmetric shape, such as seen in bent-core or wedge-shaped molecules. Nematic liquid crystals with wedge-shaped molecules and longitudinal dipole moments can induce flexoelectric polarization when splayed; similarly, bent-core molecules with transverse dipole moments can induce the flexoelectric polarization when it is subjected to a bend deformation. The flexoelectro-optic effect is linear with applied field and exploited to make switchable and bistable device with submillisecond response time [8]. However, their application is limited due to the small flexoelectric polarization in conventional liquid crystals with rod-like molecules. It was theoretically shown by Helfrich [9] that in liquid crystals with bent-core molecules, $e_3 \propto \Theta(b/a)^{2/3}\mu$, where μ is the transverse dipole moment, Θ is the bend angle, and a and b are the length and breadth of the molecule, respectively. Recently, a giant flexoelectricity in pure bent-core liquid crystal was reported by Harden *et al.* [10]. This triggered various flexoelectric studies on pure molecules [11–14] as well as on the binary mixture of rod-like and bent-core molecules

[15–18]. There are also some reports on the flexoelectric studies in bimesogenic liquid crystals [4,19–21] with *cis* form. In most of these studies, a significant enhancement of flexoelectric effect has been observed and it is expected that apart from the bistable device it has the potential to be used in sensors and microelectric power generators.

II. EXPERIMENTAL

We used a hybrid aligned nematic (HAN) cell as proposed by Dosov *et al.* [22] to measure the flexoelectric ratio e^*/K , where K is the average elastic constant of the nematic liquid crystal and $e^* = e_1 - e_3$. The splay-bend distortion, and hence the polarization, is produced by treating the plates with appropriate planar and homeotropic alignment layers (Fig. 1). The inplane electric field was applied by using thin and parallel aluminum strips, which also acts as spacers. The polarization is coupled to the electric field (E) and generates twist distortion along the perpendicular direction of the cell (y axis), which is given by $\phi = -e^*Ed/\pi K$, where d is the cell thickness. In the present experiment, $d = 20 \mu\text{m}$, and the gap between the electrodes is $850 \mu\text{m}$. We used a motorized and computer controlled analyzer to measure ϕ as a function of applied electric field and e^*/K was estimated from the best fit in the linear region. The error in the measurement is about 7%, considering the errors from both the cell thickness measurement and the gradient of ϕ with electric field. It may be mentioned that we did not observe any domain formation in the cell within the range of applied field.

In this paper, we report the measurement of e^*/K as a function of temperature of a calamitic liquid crystal RO and its mixture with two bent-core liquid crystals (BC-120 and BC-60) having different molecular structures and bend angles. We found that e^*/K is almost temperature independent and, moreover, it decreases rapidly and changes sign with increasing concentration of BC-120 molecules. In mixtures with BC-60 molecules, it is positive and increases with concentration, except at lower concentration. We present a physical model on the orientation of the arrow axes of the two bent-core molecules that explains the experimental results.

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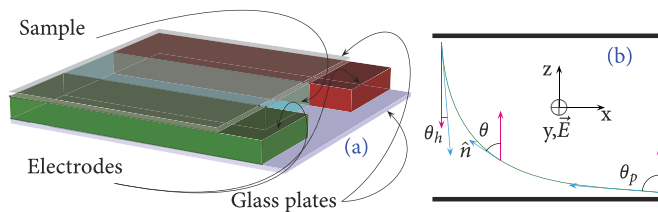


FIG. 1. (Color online) (a) Geometry of the HAN cell used in the measurement of e^*/K . (b) Twist deformation produced by an inplane dc electric field along the y axis. The top plate is coated with a homeotropic alignment layer ($\theta_h \simeq 0^\circ$) and the bottom plate is coated with a planar alignment layer ($\theta_p \simeq 90^\circ$).

III. RESULTS AND DISCUSSION

We prepared two mixtures with different concentrations, namely 4.5M% and 7M% of bent-core compounds with the calamitic compound, RO (Fig. 2). The phase diagram of the binary mixture of BC-120 with RO has already been reported [23]. The core of BC-120 is a resorcinol derivative substituted at the 1,3 position and the bent angle is about 120° . There are some reports on the measurements of various physical properties of these mixtures [24,25]. The compound BC-60 has a naphthalene core in which Schiff's based side wings are substitutes on 1,2 positions. The synthesis and characterization of this compound was reported by Lee *et al.* [26]. It exhibits only the liquid crystalline SmA phase and it was suggested from the x-ray studies that the arrow axis of the molecule is aligned *perpendicular* to the SmA layer. We found that the binary mixture of BC-60 and RO exhibits nematic phase in the low concentration range ($<10M\%$).

We measured the azimuthal twist angle (ϕ) as a function of applied field for all the mixtures and the host compound. A representative variation of ϕ with the applied dc electric field in the mixtures with BC-120 molecule is shown in Fig. 3. It is noticed that the slope decreases and changes sign from positive to negative with increasing concentration

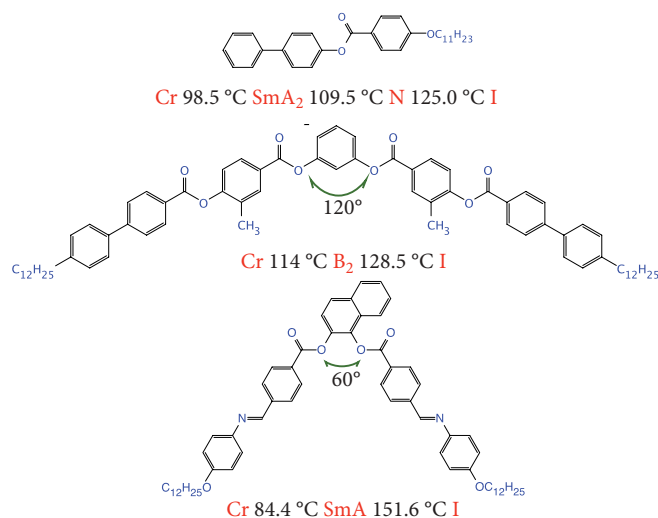


FIG. 2. (Color online) Chemical structures and phase transition temperatures of the compounds. The first, second, and third compounds are designated as RO, BC-120, and BC-60, respectively. The phase transition temperatures are indicated below each compound.

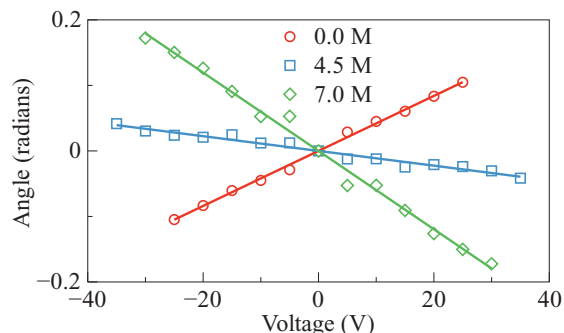


FIG. 3. (Color online) Variation of field-induced azimuthal twist angle as a function of voltage in binary mixture of RO and BC-120 molecules. Solid lines represent the best fit to the equation $\phi = -e^*Ed/\pi K$.

of BC-120 molecules. The temperature variation of e^*/K is shown in Fig. 4. It is noticed that e^*/K decreases and changes sign with increasing concentration of BC-120 molecules [Fig. 4(a)]. For example, in the host compound (RO), at a shifted temperature $T - T_{NI} = -5^\circ\text{C}$, $e^*/K \simeq 1.7 \text{ Cm}^{-1}\text{N}^{-1}$, and it reduces to $\simeq -0.48 \text{ Cm}^{-1}\text{N}^{-1}$ when the concentration of BC-120 molecules is 4.5M%. It further reduces to about $-1.9 \text{ Cm}^{-1}\text{N}^{-1}$ when the concentration is increased to 7M%. Assuming a linear variation, e^*/K of pure BC-120 liquid crystal is expected to be 30 times larger (negative) than the host compound. The temperature variation of e^*/K in the binary mixture of BC-120 and 8OCB (octyloxy cyanobiphenyl) was reported by Kundu *et al.* [17]. They found that e^*/K is negative and the magnitude increases significantly with increasing concentration of BC-120 molecules. They suggested that e^*/K in pure BC-120 compound could be 20 times larger than that of 8OCB. Thus, in the present mixture the enhancement is significantly more than they reported. The compound RO has relatively larger transverse component of

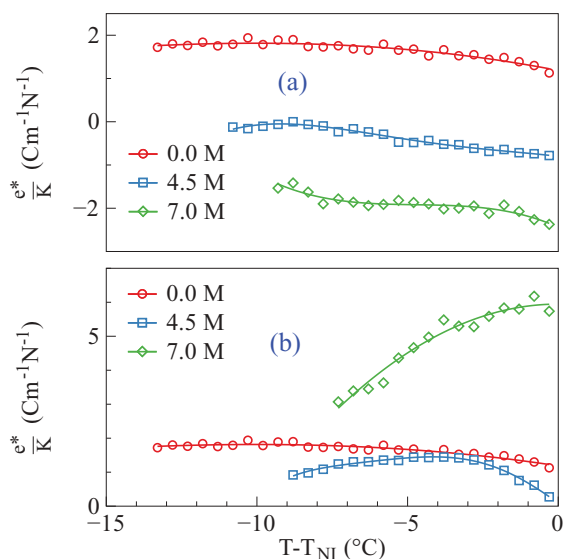


FIG. 4. (Color online) Temperature variation of flexoelectric ratio e^*/K for (a) mixtures with BC-120 and (b) mixtures with BC-60 molecules for three different concentrations, 0, 4.5, and 7M%. Continuous lines are drawn as guides to the eye.

dipole moment than 8OCB and appears to be a good host for BC-120 molecules for large flexoelastic response, perhaps due to its partial structural similarity; i.e., the aromatic and aliphatic parts of the rod are matched with one arm of the BC-120 molecule. Further, it is observed that e^*/K is almost independent of temperature [Fig. 4(a)]. It is expected, as both e^* and K are proportional to the square of the order parameter (S^2). e^* in the host compound RO is positive; i.e., $e_1 > e_3$. Since the dopant molecule (BC-120) has a large dipole moment along the arrow axis (i.e., transverse dipole), the bend distortion of the medium gives rise to a large e_3 with increasing concentration of BC-120 molecules, and as a result e^*/K changes sign beyond a particular concentration. In Fig. 4(b), we show the temperature variation of e^*/K for the mixtures with BC-60 molecules. It remains positive but reduces slightly in the mixture (4.5M%) compared to the host compound (RO) and also exhibits weak temperature dependence. Interestingly, it increases significantly in the mixture with 7M%. For example, at a shifted temperature $T - T_{NI} = -2^\circ\text{C}$, $e^*/K \simeq 1.5 \text{ Cm}^{-1}\text{N}^{-1}$ in host compound RO, and in the mixture it is $\simeq 5.8 \text{ Cm}^{-1}\text{N}^{-1}$, i.e., about four times larger, and decreases rapidly with reducing temperature. Thus, in the mixture (with BC-60), the sign of e^*/K is antagonistic in the sense that e^*/K is largely positive compared to the largely negative value at the same concentration with BC-120 molecules. Hence, it is possible to tune significantly the magnitude and sign of flexoelastic coefficient by adding appropriate bent-core molecules.

To get an idea about the orientation of BC-60 and BC-120 molecules in the mixture, we measured the dielectric anisotropy ($\Delta\epsilon = \epsilon_{\parallel} - \epsilon_{\perp}$) as a function of temperature at a frequency of 4111 Hz. The perpendicular component of dielectric constant (ϵ_{\perp}) was measured by using a LCR meter (Agilent 4980A) below the Fredericksz threshold voltage as a function of temperature. To estimate the parallel component (ϵ_{\parallel}), we measured dielectric constant in the same cell as a function of voltage. Since the dielectric anisotropy is positive, it increases with voltage and saturates at higher voltages. The linear part is plotted against $1/V$ and fitted to a straight line. The extrapolated value of dielectric constant at $1/V = 0$ provides ϵ_{\parallel} . The temperature variation of $\Delta\epsilon$ of all the samples is shown in Fig. 5. Measurement of viscoelastic properties and $\Delta\epsilon$ of the mixtures with BC-120 was reported earlier [24]. It is observed that $\Delta\epsilon$ is small and positive [Fig. 5(a)]. At any shifted temperature it decreases with increasing concentration of BC-120 molecules. This indicates that the arrow axes are orientated perpendicular to the director as shown schematically in Fig. 5(a). With increasing concentration, two or more BC-120 molecules can form pairs or clusters; as a result, quadrupolar contribution to the flexoelastic properties can also be significant. The temperature variation of $\Delta\epsilon$ of mixtures with BC-60 is not unique, in the sense that it decreases at 4.5M% and then tends to increase at 7M% [Fig. 5(b)]. The increase of $\Delta\epsilon$ at 7M% suggests that the effective dipole moment along the director is increased; i.e., the arrow axis of the molecule is orientated parallel to the director as the direction of large dipole moment of the molecule is along the arrow axis. On the other hand, the decrease of $\Delta\epsilon$ at 4M% cannot be understood based on this model. However, it may be noted that the terminal units of BC-60 molecules

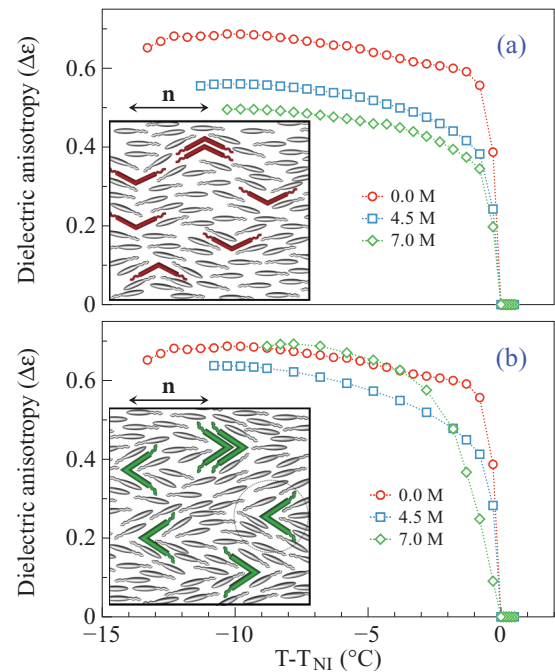


FIG. 5. (Color online) Variation of dielectric anisotropy ($\Delta\epsilon$) with temperature for (a) mixtures with compound BC-120 and (b) mixtures with compound BC-60. Cell thickness $\simeq 8 \mu\text{m}$. The orientations of the bent-core molecules in the respective mixtures and a local domain (dotted circle) are shown schematically in the inset. Dotted lines are drawn as guides to the eye.

are alkoxy chains, which have conformational freedom. As a result, at low concentration of BC-60 molecules, the transverse component of the dipole moment can increase, and hence $\Delta\epsilon$ is reduced. Further, BC-60 can be considered wedge-shaped molecules that can generate substantial splay distortion in the host calamitic sample, reducing the steric interaction, and form local domains in which a bent-core molecule is surrounded by a few rod-like molecules [Fig. 5(b)], as indicated in the recent x-ray studies of Lee *et al.* [18]. In addition, these domains will have asymmetric charge distributions as a result quadrupolar moment contributes significantly to the flexoelectric coefficients. We conjecture that with increasing concentration, the conformational freedom of individual B-60 molecules in the domain is reduced and the longitudinal components of dipole moments can also get weakly correlated; as a result, $\Delta\epsilon$ can again increase. Presence of such local domains in the medium is expected to increase e_1 more significantly than e_3 , as a result, e^*/K is large and positive [Fig. 4(b)]. The effect of conformational freedom on the flexoelastic coefficient in 8OCB liquid crystal was experimentally studied by Dosov *et al.* [27]. They reported that e^*/K decreases with reducing temperature. Using the Landau-de Gennes theory, Osipov [28] showed theoretically that it can be understood based on the average conformational degrees of freedom of alkoxy chains. The anomalous temperature dependence of e^*/K in the present mixture is expected to originate from similar conformational degrees of freedom of terminal alkoxy chains. We also measured the splay elastic constant (K_{11}) in these mixtures (with BC-60), and the details will be reported elsewhere. Interestingly, we found that in the mixture, K_{11}

decreases with increasing concentration of BC-60 molecules. For example, at a shifted temperature $T - T_{NI} = -2^\circ\text{C}$, in the host compound RO, $K_{11} \simeq 4.2$ pN and in 7M% mixture $K_{11} \simeq 2.4$ pN, respectively. Thus, K_{11} is reduced in the mixture due to spontaneous splay deformation caused by the BC-60 molecules as shown schematically in Fig. 5(b).

IV. CONCLUSIONS

In conclusion, we have measured the flexoelastic coefficient of a binary mixture with bent-core molecules having two different bend angles. We showed that both the magnitude and sign can be tuned over a large range by adding small concentration of bent-core molecules with different bend angles.

The arrow axes of the BC-120 molecules in the mixture are aligned perpendicular to the director, whereas they are aligned parallel to the director in the case of BC-60 molecules. We showed that the appropriate selection of bent-core molecules in the binary mixture could provide a viable route to greatly enhance and tune the sign of the flexoelectric properties.

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