

Flexoelectric studies on mixtures of compounds made of rodlike and bent-core molecules

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We report measurements of the temperature variations of the flexoelastic ratio $(e_1 - e_3)/K$ of octadecyl cyanobiphenyl and a mixture of this compound with another one with bent-core (BC) molecules, using hybrid aligned nematic cells. Addition of 5 mol % of the BC compound doubles the flexoelastic ratio, implying that the BC compound has ~ 20 times larger value compared to that of the compound with calamitic molecules. Mixtures with >11 mol % of the BC compound exhibit only a homeotropic alignment. We develop a simple model to account for this result which arises because of a large positive self-energy due to flexoelectric polarization. © 2009 American Institute of Physics. [DOI: 10.1063/1.3213544]

The nematic is characterized by an *apolar director* \mathbf{n} , about which the symmetry axes of anisotropic molecules are aligned. The second rank tensor order¹ sustains a nonzero density of quadrupole moments. Divergence of quadrupole density gives rise to polarization.² The flexoelectric polarization \mathbf{P} is associated with gradients in the director field.³ In Meyer's notation,³ $\mathbf{P} = e_1(\nabla \cdot \mathbf{n})\mathbf{n} + e_3(\nabla \times \mathbf{n}) \times \mathbf{n}$, where e_1 and e_3 are the flexoelectric coefficients corresponding to splay and bend distortions of \mathbf{n} , respectively, with the dimension of electric potential and of arbitrary sign. Meyer envisaged that only nematics whose molecules combine *shape polarity* with a relevant electric dipole moment exhibit flexoelectric polarization. The flexoelectro-optic effect in cholesteric liquid crystals⁴ and flexoelectric switching of the zenithal bistable display (ZBD) (Ref. 5) are two device applications which exploit the flexoelectric effect.

Liquid crystals with bent-core (BC) molecules are being studied extensively since 1996,⁶ and the dipolar contribution to flexoelectricity in such compounds is of intrinsic interest. Helfrich⁷ and Osipov⁸ both pointed out that the dipolar contribution to e_3 is proportional to the transverse dipole moment (μ) and the "kink" angle (Θ) of the molecule defined as the angle of deviation from linearity. Helfrich's model⁷ shows that, $e_3 = \mu_{\perp} \Theta K_{33}(b/a)^{2/3} N^{1/3} / (2k_B T)$, where a and b are the length and breadth of the molecule, respectively, K_{33} the bend elastic constant and the number density $N = \rho N_A / M$, where ρ is the density, N_A is the Avogadro number, and M is the molecular weight. a , Θ , and M of typical BC molecules are ~ 2 , 100, and 4 times larger than those of typical rodlike (R) molecules. We can then estimate $(e_3)_{BC} \approx 40(e_3)_R$.

A few techniques have been developed for measuring the flexoelectric coefficients. $(e_1 - e_3) = e^*$ arises only because of dipolar contribution.⁸ Dozov *et al.*⁹ developed a simple technique to measure e^* using a hybrid aligned nematic (HAN) liquid crystal cell of thickness L , with the bottom plate with planar alignment along X axis and the top plate with homeotropic alignment along Z axis. The director field in such a cell has a permanent *splay-bend distortion* (Fig. 1), which generates flexoelectric polarization \mathbf{P} . If a uniform dc electric

field \mathbf{E} is applied along the Y axis, a twist distortion $\phi(z)$ is produced in the medium due to the action of \mathbf{E} on \mathbf{P} . If the birefringence of liquid crystal is large enough, the plane of polarization of an incident light beam follows the twist of the director. Measuring the largest value $\phi(L)$ close to the upper plate ($z=L$) we get the flexoelastic coefficient⁹ $e^*/K = \pi\phi(L)/(LE)$, where K is the average elastic constant of the nematic liquid crystal (LC). As we shall see in our experiment, the angle θ_p at the bottom plate can be less than $\pi/2$. It can be shown that for $\theta_p \leq 1$ radian, $e^*/K \approx 6\phi(L)/(\theta_p LE)$.

Recently Harden *et al.*¹⁰ have measured the flexoelectric coefficient e_3 of a nematic LC made of BC molecules. They could not align the compound in a HAN configuration and obtained only a planar alignment. They developed a mechanical technique to measure e_3 , which was found to be three orders of magnitude larger than in calamitics and can result in applications in novel sensors and micro electric power generators.¹⁰

However, most compounds with BC molecules *do not* exhibit the nematic phase. Wild *et al.*¹¹ have made measurements on e^*/K by dissolving a few symmetric thiophene compounds with BC molecules in a commercial multicomponent nematic mixture with R molecules. e^*/K was en-

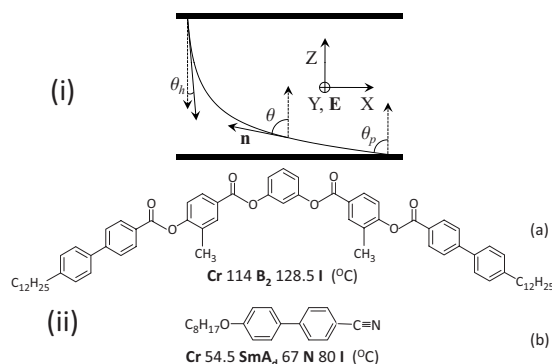


FIG. 1. (i) The geometry of the HAN cell used to measure e^*/K . A dc electric field \mathbf{E} applied along the Y axis produces a twist distortion. Usually $\theta_p = \pi/2$ and $\theta_h = 0$. (ii) Molecular structures and phase sequences exhibited by (a) 1,3-phenylene bis[4-(3-methylbenzoyloxy)] 4'-*n*-dodecylbiphenyl 4'-carboxylate (BC12) and (b) 4-*n*-octyloxy 4'-cyanobiphenyl (8OCB). Temperatures are in °C.

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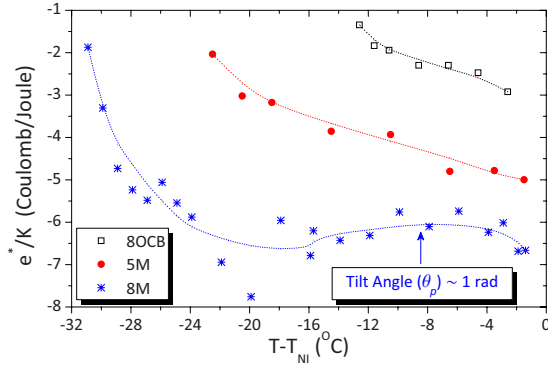


FIG. 2. (Color online) Variations of flexo-elastic ratio $(e_1 - e_3)/K$ of pure 8OCB, 5 M and 8M mixtures with shifted temperature. In 8M the tilt angle θ_p is estimated to be ~ 1 rad. The N-SmA_d transition occurs at $T - T_{NI} = -13$, ~ -22 and ~ -31 °C for 8OCB, 5M and 8M, respectively.

hanced by approximately three to four times by adding 10 wt % of the dopants, though there was no correlation with the dipole moment of the BC molecules. Further, their results on other dopants indicates an inverse correlation with the kink angle Θ . A similar study¹² with other nonsymmetric BC dopants showed no clear increase in e^*/K . These measurements were made at only one relative temperature.

In this letter, we present results on binary mixtures of 8OCB with *R* molecules and BC12 with BC molecules (Fig. 1). The *R* rich mixtures exhibit large nematic ranges¹³ with the smectic phase occurring at lower temperatures. We have reported earlier several physical studies on these binary mixtures.¹⁴ In this letter, we report e^*/K of pure 8OCB, 5M, and 8M mixtures, where *x*M has *x* mol % of BC12. We estimate that e^*/K of BC12 is ~ 20 times larger than that of pure 8OCB. Mixtures with more than 11 mol % of BC12 exhibit only homeotropic alignment. We develop a simple theory to explain the latter result.

The hybrid aligned cell is constructed by using a bottom plate which is vacuum coated with SiO at an oblique angle to generate planar alignment of the nematic director. The top plate is coated with octadecyl triethoxy silane to get homeotropic alignment. Two electrodes which are 25 μm thick flat stainless steel wires are placed ~ 1 mm apart on the bottom plate, such that the wires are parallel to the director on this plate. The liquid crystal sample is filled in the isotropic phase by capillary flow and a hot-stage is used to control the sample temperature. The whole system is placed on the stage of a polarizing microscope (ORTHOLUX, II POL-BK). The polarizer is set parallel to the director plane. In a HAN cell, there are domains with opposite tilts. We choose a region with a large single domain and make measurements by applying an in plane field. As a dc field \mathbf{E} is used, ionic impurities in the sample can shield the field. To reduce this problem, the sign of \mathbf{E} is reversed a few times before each measurement. The rotation angle $\phi(L)$ is measured directly by rotating the analyzer to restore a dark field of view for the given \mathbf{E} .

In both 8OCB and in the mixtures, e^*/K is negative (Fig. 2). Our data on e^*/K of pure 8OCB are $\sim 35\%$ – 50% lower than those of Dozov *et al.*¹⁵ The latter authors used rubbed polyvinyl alcohol (PVA) coating to get planar alignment. The azimuthal anchoring energy (W_a) of an SiO coated surface is higher than that of a polymer coated one.¹⁶ As a result, in the Dozov experiment, the director develops a field dependent

azimuthal angle at the lower plate, increasing the measured values of $\phi(L)$. This in turn leads to an overestimation of e^*/K . Comparing with our 8OCB data we can estimate W_a of PVA to be $\sim 2 \times 10^{-6}$ J/m².

As both e^* and K are proportional to S^2 in the mean field approximation,⁹ e^*/K can be expected to be independent of temperature. The decrease in the magnitude of e^*/K as the temperature is lowered in all cases arises because K_{33} diverges, as the N-SmA_d transition point is approached.¹ At higher temperatures, the magnitude of e^*/K of 5M mixture is ~ 2 times larger than that of pure 8OCB (Fig. 2). In the 8M mixture the director develops a *large tilt angle* at the bottom plate treated for planar alignment. This effectively reduces the flexoelectric polarization, and hence the measured $\phi(L)$. Assuming for simplicity, a linear relationship of e^*/K with the concentration *x*, from the measured e^*/K of 5M and 8OCB we get, $(e^*/K)_{BC} \approx 20(e^*/K)_{8OCB}$. From the value of $(e^*/K)_{BC}$ we have estimated the tilt angle $\theta_p \approx 1$ radian for the 8M mixture. In the case of mixtures with even higher concentrations of BC molecules like 11M, θ_p reduces to zero and the sample is homeotropically aligned. We develop a simple model to account for this result.

Let W_p and W_h be the *polar* anchoring energies and θ_p , θ_h be the tilt angles of the director on the plates treated for planar and homeotropic alignments, respectively. For simplicity, we assume that the nematic liquid crystal is a perfect insulator. Thus in the absence of an applied field the *z* component of dielectric displacement $D_z = 0$. Taking into account the self energy of the flexoelectric polarization, the dielectric energy, the distortion energy of the director and the anchoring energies at the surfaces, we get a dimensionless energy of the cell as¹⁷

$$W_T = \int_0^1 F[\theta] \left(\frac{d\theta}{d\rho} \right)^2 d\rho + \frac{L}{2\lambda_p} \cos^2 \theta_p + \frac{L}{2\lambda_h} \sin^2 \theta_h, \quad (1)$$

where $\rho = z/L$, $F[\theta] = \frac{1}{4}[(\kappa + 1) + (\kappa - 1)\cos 2\theta + (e_f^2 \sin^2 2\theta)/(2\epsilon_0 \epsilon_{zz} K_{11})]$, $\kappa = K_{33}/K_{11}$, $e_f = (e_1 + e_3)$, and $\epsilon_{zz} = (\epsilon_{\perp} + \Delta\epsilon \cos^2 \theta)$, $\Delta\epsilon$ the dielectric anisotropy. $\lambda_p = K_{11}/W_p$ and $\lambda_h = K_{11}/W_h$ are the extrapolation lengths at the surfaces treated for planar and homeotropic alignments, respectively. The Euler-Lagrange equation leads to the condition that the energy density is constant ($=C$) across the cell. C has to satisfy the condition $\int_{\theta_h}^{\theta_p} \sqrt{F[\theta]}/C d\theta = 1$. The tilt angles θ_p and θ_h also satisfy the torque balance conditions at the two surfaces. We show the calculated θ_p and θ_h as functions of e_f in Fig. 3, assuming other physical parameters to be those of 11M mixture¹⁴ at the temperature $T_{NI} = 8^\circ$. As the mixture also exhibits SmA_d phase, W_h can be expected to be larger than W_p . The polar angle θ_p at planar surface is largest ($\sim 87^\circ$) for $e_f = 0$, and monotonically decreases as e_f increases. The rate of decrease is very sharp between $e_f = 100$ to 500 pC/m. Beyond 500 pC/m, θ_p asymptotically approaches 0. θ_h starts from $\sim 1.7^\circ$, increases to $\sim 4.8^\circ$ at $e_f \sim 150$ pC/m and then decreases continuously with increase of e_f . The bulk energy which is positive is lowered by decreasing $d\theta/d\rho$. This is achieved for lower values of e_f by decreasing θ_p and increasing θ_h . For $e_f > 100$ pC/m, the reduction in θ_p is very steep and θ_h then tends to decrease to zero, favoured by the stronger anchoring at that surface. $(\theta_p - \theta_h)$ monotonically decreases with e_f (Fig. 3). e_3 of BC

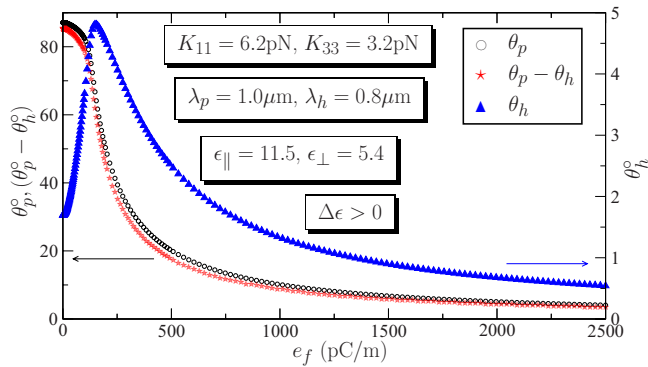


FIG. 3. (Color online) Variations of tilt angles at the two surfaces as functions of $e_f = e_1 + e_3$. The physical parameters used in the calculations are shown in the insets.

molecules can be expected to be much larger than e_1 , and we estimate $e_f \approx 50$ pC/m for 11M from measurements on e^* and using a linear extrapolation. However, as x increases the BC molecules can form polar clusters,^{10,18,19} which can enhance e_f to a much larger value compared to that got by the linear extrapolation. This may be the reason for finding homeotropic alignment for $x > 11$ M. Indeed formation of large polar clusters was suggested to be the reason for the very large value of e_3 found by Harden *et al.*¹⁰ in the pure BC nematic compound. We have extended our calculation using the physical parameters of the pure BC nematogen^{10,20} which has a negative $\Delta\epsilon$, to find that the cell will have only a planar alignment as found in the experiment.¹⁰ The main reason for getting a uniform alignment in both cases is the large positive self energy in the HAN configuration when e_f is high. Materials with very high flexoelectric coefficients are

thus unsuitable for the ZBD device, as one of its bistable states has to be in the HAN configuration.⁵

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- ¹P. G. de Gennes and J. Prost, *The Physics of Liquid Crystals*, 2nd ed. (Clarendon, Oxford, 1993).
- ²J. Prost and J. P. Marcerou, *J. Phys.* **38**, 315 (1977).
- ³R. B. Meyer, *Phys. Rev. Lett.* **22**, 918 (1969).
- ⁴H. J. Coles, M. J. Clarke, S. M. Morris, B. J. Broughton, and A. E. Blatch, *J. Appl. Phys.* **99**, 034104 (2006).
- ⁵C. V. Brown, L. Parry-Jones, S. J. Elston, and S. J. Wilkins, *Mol. Cryst. Liq. Cryst.* **410**, 417 (2004).
- ⁶T. Niori, T. Selkine, J. Watanabe, T. Furukawa, and H. Takezoe, *J. Mater. Chem.* **6**, 1231 (1996).
- ⁷W. Helfrich, *Z. Naturforsch.* **26a**, 833 (1971).
- ⁸M. A. Osipov, *Sov. Phys. JETP* **58**, 1167 (1983).
- ⁹I. Dozov, P. Martinot-Lagarde, and G. Durand, *J. Phys.(France) Lett.* **43**, L365 (1982).
- ¹⁰J. Harden, B. Mbanga, N. Éber, K. Fodor-Csorba, S. Sprunt, J. T. Gleeson, and A. Jáklí, *Phys. Rev. Lett.* **97**, 157802 (2006).
- ¹¹J. H. Wild, K. Bartle, N. T. Kirkman, S. M. Kelly, M. O'Neill, T. Stürner, and R. P. Tuffin, *Chem. Mater.* **17**, 6354 (2005).
- ¹²N. Aziz, S. M. Kelly, W. Duffy, and M. Goulding, *Liq. Cryst.* **35**, 1279 (2008).
- ¹³R. Pratibha, N. V. Madhusudana, and B. K. Sadashiva, *Phys. Rev. E* **71**, 011701 (2005).
- ¹⁴B. Kundu, R. Pratibha, and N. V. Madhusudana, *Phys. Rev. Lett.* **99**, 247802 (2007).
- ¹⁵I. Dozov, P. Martinot-Lagarde, and G. Durand, *J. Phys. (France) Lett.* **44**, L817 (1983).
- ¹⁶A. Sugimura, in *Physical properties of liquid crystals: Nematics*, edited by D. Dunmur, A. Fukuda, and G. Luckhurst (Inspec, London, 2001), p. 493.
- ¹⁷B. Kundu, A. Roy, and N. V. Madhusudana (unpublished).
- ¹⁸S. Stojadinovic, A. Adorjan, S. Sprunt, H. Sawade, and A. Jáklí, *Phys. Rev. E* **66**, 060701 (2002).
- ¹⁹A. G. Vanakaras and D. J. Photinos, *J. Chem. Phys.* **128**, 154512 (2008).
- ²⁰D. Wiant, J. T. Gleeson, N. Éber, K. Fodor-Csorba, A. Jáklí, and T. Tóth-Katona, *Phys. Rev. E* **72**, 041712 (2005).