

Anomalous Temperature Dependence of Elastic Constants in the Nematic Phase of Binary Mixtures Made of Rodlike and Bent-Core Molecules

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We report on two anomalous trends in the temperature dependences of the splay (K_{11}) and bend (K_{33}) elastic constants in the nematic (N) phase of mixtures of compounds with rodlike (R) and bent-core (BC) molecules: As the sample is cooled from the isotropic to N transition point, (i) K_{33} increases, attains a maximum value and then *decreases*, and (ii) close to the N to smectic A (SmA) transition point, K_{11} *decreases* sharply. At higher temperatures the *bow axes* of BC molecules are aligned along the director \hat{n} , strongly favoring a bend distortion of \hat{n} as the orientational order parameter is increased. Close to the N - SmA transition point the smecticlike short-range order builds up, and the *arrow axes* of BC molecules are aligned along \hat{n} , facilitating a splay distortion of \hat{n} . A simple model calculation brings out the anomalous trend in K_{33} .

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Liquid crystals combine anisotropic properties with the ability to flow [1,2]. The simplest liquid crystal (LC) is the uniaxial nematic (N) which is characterized by an orientational order of organic molecules with shape anisotropy. The most studied compounds have rodlike (R) molecules, while nematogens with dislike and bent-core (BC) molecules have also been synthesized. The nematic is characterized by an apolar unit vector \hat{n} , called the *director* about which the symmetry axes of rods or discs and the bow-axes of BC molecules are aligned. The orientational order is responsible for the physical properties like refractive indices and dielectric constants to become anisotropic. Further, it leads to curvature elasticity of the medium [1,2]. The order parameter $S = S_{\zeta\zeta} = \langle 3\zeta_z^2 - 1 \rangle / 2$, where ζ is along the long axis of a rodlike molecule and ζ_z the projection of the ζ axis along z , which is itself assumed to be along the director \hat{n} .

In the mean field approximation, the curvature elastic constants K_{ii} ($i = 1, 2, 3$ for splay, twist, and bend, respectively) are proportional to S^2 , increasing as the temperature is lowered. If the compound exhibits a second-order nematic to smectic A (SmA) transition, K_{22} and K_{33} (which involve curl \hat{n} type of distortions) diverge as the N - SmA transition point (T_{AN}) is approached [1,2]. Dodge *et al.* [3,4] have recently shown that adding ~ 3 mol% of BC molecules can reduce K_{33} of a nematic LC made of R molecules by a factor of 2. They also proposed a simple theoretical estimate, which showed that all the three elastic constants are reduced by the addition of BC molecules, though by much smaller amounts compared to the experimental results on K_{33} .

We have recently studied the phase diagrams of some binary mixtures, with one compound made of R molecules while the other is made of BC molecules [5,6]. In the present paper, we present results on mixtures made of two compounds whose structural formulae are shown in Fig. 1. 8OCB exhibits the N and SmA_d phases. The partial

bilayer SmA_d structure arises from antiparallel pair formation of the strongly polar molecules. BC12 exhibits the B_2 phase which also has a lamellar structure with tilted molecules with a polar packing, giving rise to layer polarization. In a range of compositions, with more than 10.5 mol % of BC molecules, the mixtures exhibit a *biaxial* SmA_d (SmA_{db}) phase. Mixtures with 10.5 to 15 mol % of BC molecules have the phase sequence isotropic- N - SmA_d - SmA_{db} as the temperature is lowered, while mixtures with 15 to 24 mol % have a direct transition from the N to SmA_{db} phase [6]. In all these cases, the N phase was found to be uniaxial. Detailed studies have shown that the arrow axes of the BC molecules are aligned along the layer normal in the SmA_d structure made of 8OCB molecules (Fig. 2). This particular arrangement is favored by the layering order of the smectic phase and the favorable interaction between the aromatic and aliphatic moieties of the two types of molecules. The mixtures in the above concentration range exhibit fairly wide ranges of the N phase. It is of obvious interest to find the mutual alignment of the two types of molecules in the N phase, by investigating various physical properties.

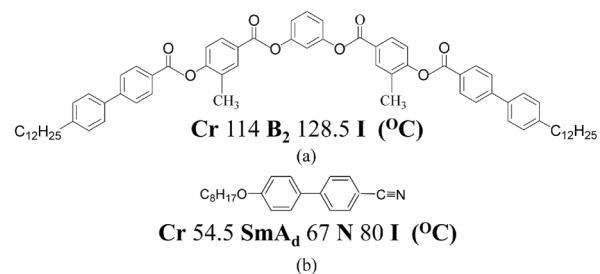


FIG. 1. Molecular structures and phase sequences exhibited by (a) 1,3-phenylene bis[4-(3-methylbenzoyloxy)]4'-*n*-dodecylbiphenyl 4'-carboxylate (BC12) and (b) 4-*n*-octyloxy 4'-cyanobiphenyl (8OCB).

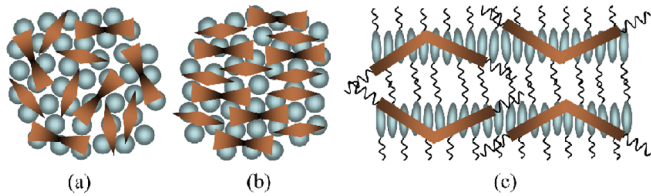


FIG. 2 (color online). Schematic representation of the molecular arrangement in the smectic liquid crystals of the mixtures. Top view of a layer of (a) uniaxial smectic (SmA_d), (b) biaxial smectic (SmA_{db}) and side view of (c) SmA_{db} liquid crystal.

In the present Letter we report our measurements on (i) the optical and dielectric anisotropies (Fig. 3) and (ii) the splay and bend elastic constants (Fig. 4) in the N phase of different mixtures. We argue that the bow axes of the BC molecules align along the director \hat{n} defined by the long axes of the rods in the N phase at higher temperatures. K_{11} decreases sharply as the N - SmA_d (or N - SmA_{db}) transition point is approached [Fig. 4(a)], the anomalous temperature dependence signaling a change in the mutual alignment of the R and BC molecules as the smecticlike short-range order (SRO) builds up. More interestingly, in compositions with more than 14 mol % BC molecules, K_{33} initially increases as expected with decrease of temperature, but starts to *decrease* before eventually increasing

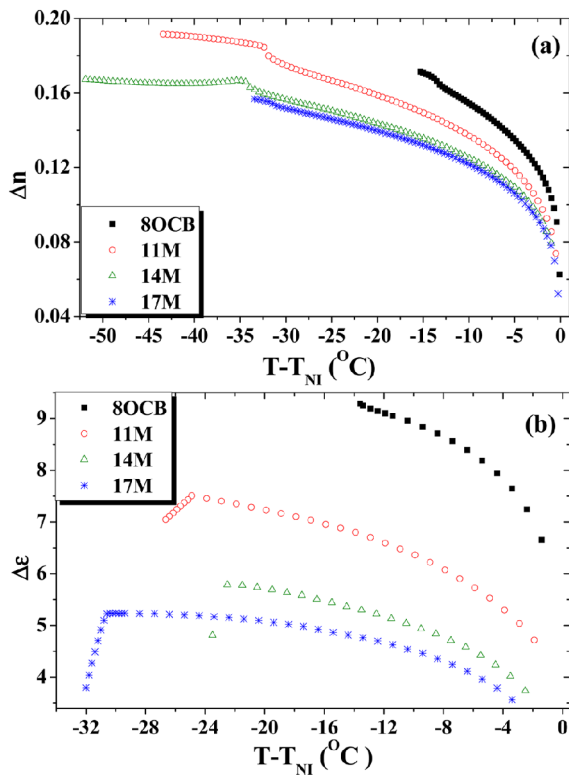


FIG. 3 (color online). Dependence of (a) birefringence and (b) dielectric anisotropy of pure 8OCB and three mixtures on the relative temperatures.

again close to T_{AN} [Fig. 4(b)]. Systems exhibiting the reentrant N phase also show such an anomaly [7] due to smecticlike SRO. We argue that both the anomalies found by us owe their origin to the *bent-shape* of the BC molecules.

The experimental cell was made of two ITO coated glass plates. In order to get planar alignment of the sample, SiO was vacuum coated on both the plates at 32° grazing angle of incidence. Cells were made by placing the two plates together, ensuring that the active areas overlap. The separation was controlled by glass-bead spacers with diameter of $\sim 8 \mu\text{m}$, which were mixed with an epoxy glue. The thickness of the empty cell was measured with $\pm 1\%$ accuracy by an interferometric technique using an Ocean Optics Spectrometer. The empty capacitance of the cell was measured before filling the sample by capillary suction in the isotropic phase. As the experimental runs extended for 3–4 weeks, a gradual concentration change was noticed in the cells exposed at two sides. To overcome this problem, the cell was placed in a totally enclosed glass pill box, which was placed inside an Instek mk1 heater to control the temperature to 5 mK accuracy. The hot-stage was in turn placed on the stage of a polarizing microscope (ORTHOLUX, II POL-BK).

A He-Ne laser beam is sent through the sample placed between crossed polarizers oriented at 45° to the director. The transmitted and reference intensities are measured using a dual frequency chopper along with a dual-channel

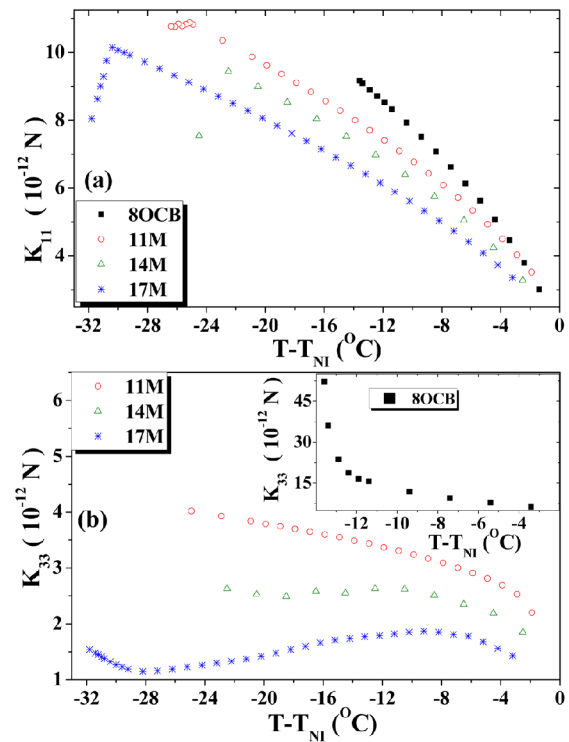


FIG. 4 (color online). Dependence of (a) splay and (b) bend elastic constants of pure 8OCB and three mixtures on the relative temperatures. In (b), the data for 8OCB is shown in the inset.

lock-in amplifier (Perkin Elmer model No. 7265A) using a single photo diode. The transmitted optical intensity is an oscillatory function of the optical phase difference $\delta\Phi$. At a fixed temperature (in the nematic phase), at high applied voltages, $\delta\Phi$ tends to zero. The electric field is then slowly decreased and the absolute phase difference is obtained by counting the number of maxima and minima. The birefringence is obtained from the absolute $\delta\Phi$ for different mixtures.

Another lock-in amplifier (Stanford Research System, model No. SR830) is used for the impedance analysis of the cell which is connected in series with a fixed capacitance ($C_m = 1 \mu\text{F}$) for the purpose. An ac signal of frequency 5641 Hz from the SR830 is applied to the cell and the amplitude and phase of the voltage developed across C_m is measured using the same lock-in amplifier. The dielectric constant of the liquid crystal sample is the ratio of the capacitance of filled cell to that of the empty cell. If a voltage well below the Fréedericksz threshold voltage is applied to the planar liquid crystal cell, the director remains perpendicular to the electric field. This measurement gives the perpendicular dielectric constant (ϵ_{\perp}). The maximum output of SR830 is 5 V. An external amplifier with a gain of 6 is used to attain higher voltages. The applied voltage is varied from 0.2 V to 30 V and the effective dielectric constant is measured as a function of the voltage. The experimental curve tends to saturate at high voltages. The linear part of dielectric constant is plotted against $1/V$ and fitted to a straight line. The dielectric constant corresponds to ϵ_{\parallel} by extrapolating to $1/V = 0$.

The optical phase difference $\delta\Phi$ is also simultaneously measured as a function of applied voltage. A sudden change of $\delta\Phi$ is seen at the Fréedericksz threshold voltage, and using this, the splay elastic constant K_{11} is obtained [8]. The optical phase differences at higher voltages are fitted to an appropriate theory by an iterative procedure to get the bend elastic constant K_{33} [8].

We have studied 8OCB and its mixtures with 11, 14, and 17 mol % of BC12. In all further discussions these mixtures are denoted as 11M, 14M, and 17M, respectively. All the experimental runs are started from the isotropic phase and the sample is cooled to the required temperature in the nematic range. The transmitted intensity and the impedance of the cell are measured after equilibrating for about a minute each at various applied voltages. The birefringence (Δn) of pure 8OCB and all the mixtures increases with decreasing temperature, with a perceptible enhancement near T_{AN} [Fig. 3(a)]. At any given relative temperature, Δn decreases with increasing concentration of the BC compound, reflecting the lower polarizability anisotropy of the BC molecule compared to that of 8OCB. In the mixtures, the orientational order parameter of the two types of molecules should be different in the uniaxial nematic phase. The birefringence reflects an average orientational order of the medium.

The dielectric anisotropy ($\Delta\epsilon = \epsilon_{\parallel} - \epsilon_{\perp}$) which is strongly positive for pure 8OCB decreases as the concentration of BC molecules is increased [Fig. 3(b)]. The BC molecule is not strongly polar, and the net dipole moment of the molecule is along the arrow axis. $\Delta\epsilon$ of pure 8OCB and all the mixtures increase with decreasing temperature in most of the nematic range. The main difference in the temperature variation of $\Delta\epsilon$ of 8OCB and of the mixtures is seen on approaching the N - $\text{Sm}A_d$ transition temperature. In 8OCB, $\Delta\epsilon$ is *enhanced* as the smecticlike SRO builds up reflecting the enhancement in the orientational order parameter [Fig. 3(b)]. However, in all the mixtures, $\Delta\epsilon$ exhibits a sharp *decrease* as T_{AN} is approached. The temperature at which this drop starts corresponds to that at which the smecticlike SRO starts building up. The sharp fall in $\Delta\epsilon$ is associated with that of ϵ_{\parallel} , which we have confirmed by an independent measurement using a small voltage (0.5 V) on a homeotropically aligned sample. In that case, the low value of ϵ_{\parallel} was found to continue in the $\text{Sm}A_d$ phase. The lowered value should arise because the mutual alignment between R and BC molecules is as shown in Fig. 2. It means that the dipole moments of BC molecules no longer contribute to ϵ_{\parallel} , as the molecules cannot reorient about the bow axes. As the temperature is raised in the nematic phase the smecticlike SRO is weakened and the temperature dependence of $\Delta\epsilon$ is reversed, reflecting that of the orientational order (Fig. 3) at higher temperatures. This also means that the mutual alignment between the R and BC molecules has changed, and can be expected to be as shown in Fig. 5(a), with the bow axes of BC molecules aligned *along* the long axes of the R molecules for entropic reasons. The arrow axes of the BC molecules have no preferred orientation in the plane orthogonal to \hat{n} , leading to the *uniaxial* symmetry of the N phase.

Figure 4(a) shows the variations of K_{11} as functions of temperature for 8OCB and the three mixtures. At any given relative temperature, K_{11} decreases as the concentration of BC molecules is increased. For example, in the 17M mixture the decrease is by about 35% from that corresponding to pure 8OCB. The *bent-shape* of the BC molecules which are aligned with the rods as shown in Fig. 5(a) in the N phase, lower the splay elastic constant [3]. In the higher temperature nematic range $K_{11} \sim \Delta n^x$, where $x \approx 2.5$ in all the four samples. In the case of 8OCB, K_{11} continues to increase up to T_{AN} . But in the mixtures the trend is very different close to T_{AN} , and K_{11} starts to *decrease sharply*. As in the case of $\Delta\epsilon$, the rapid fall in K_{11} arises when the smecticlike SRO builds up and the mutual orientation of the two types of molecules is as shown in Fig. 2. The bent shape of BC molecule can in turn distort the local smecticlike (short-range) layering to produce a splay distortion of the director [Fig. 5(b)]. As a result the splay elastic constant can drop and show the anomalous temperature dependence close to T_{AN} . In the

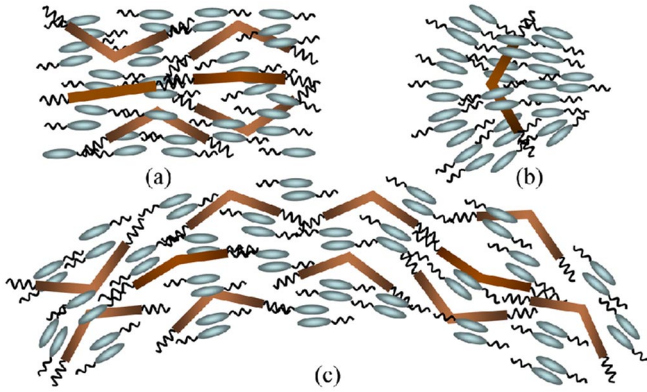


FIG. 5 (color online). (a) Mutual alignment of R and BC molecules in the nematic phase. (b) When smecticlike short-range order builds up, the BC molecules reorient and facilitate splay distortion of the director. (c) In the nematic phase BC molecules facilitate the bend distortion of the director.

$\text{Sm}A_d$ phase itself, the layers can be expected to become flat as in Fig. 2.

At any relative temperature the bend elastic constant K_{33} also decreases with the concentration of BC molecules, though the decrease is much more drastic than that in the case of K_{11} . In the 17M mixture K_{33} decreases by 7 times from that corresponding to 8OCB at 10 °C below the isotropic-nematic transition point. This sharp reduction has to be attributed to the shape of the molecule which is now oriented as in Fig. 5(c) in the medium with a bend distortion. In 8OCB as T_{AN} is approached K_{33} diverges because the smecticlike SRO builds up [Fig. 4(b) inset] [1,2]. In the case of 11M mixture, K_{33} increases with decrease of temperature in the N range and we do not have data close to T_{AN} . As the concentration of BC molecules is increased to 14M, K_{33} shows a maximum followed by a small reduction as the temperature is lowered, and again increases close to T_{AN} . The anomalous decrease of K_{33} with decrease of temperature becomes very prominent in the case of 17M mixture. The maximum and minimum values of K_{33} are 1.8×10^{-12} N and 1.2×10^{-12} N respectively, i.e., the decrease is by about 40% from the maximum value. In 8OCB, at all temperatures, $K_{33} > K_{11}$. In all the mixtures, $K_{33} < K_{11}$ and at $T_{NI} - T = 28$ °C, the 17M mixture has $K_{33} \sim 0.1K_{11}$. The order parameter itself increases monotonically as reflected in the variation of Δn with decrease in temperature. However, with the enhanced orientational order of the BC molecules, their bent shape can couple better to the bend distortion of the director, thus decreasing K_{33} . Only near T_{AN} , the build up of smecticlike SRO again gives rise to an increase in K_{33} . However, in view of the mutual alignment of the two types of molecules being as shown

in Fig. 5(b), the enhancement of K_{33} due to the short-range smectic order is not as pronounced as in pure 8OCB.

In the mean field model, far above T_{AN} , $K_{ii} = K_i^0 S^2$ ($i = 1, 3$). For pure 8OCB, we set $K_i^0 = K_i^r$. In the mixture with a small mole fraction C_b of BC molecules, we can write $K_i^0 = (K_i^r - \alpha_i C_b)$, giving rise to a reduction of both K_{11} and K_{33} as C_b is increased. As the coupling between the bent-shape of BC molecule and bend distortion is enhanced with the order parameter S , we can further assume that $\alpha_3 = \beta_3 S$. Using this, we can deduce that K_{33} exhibits a maximum at the order parameter $S_m = 2K_3^r / (3\beta_3 C_b)$. The maximum occurs at a lower value of S_m , i.e., at a higher temperature, as C_b is increased, reflecting the experimental trend [Fig. 4(b)]. From our experimental data we estimate that $\alpha_1 / K_1^r \approx 2$ and $\beta_3 / K_3^r \approx 6$. Our experiments show that the anomalous temperature dependence of K_{11} close to T_{AN} and that of K_{33} at higher temperatures arise from different mutual alignments of the two types of molecules. Further, the anomaly in K_{33} shows that the coupling between the bent shape of the molecule with the bend distortion of $\hat{\mathbf{n}}$ is stronger when the orientational ordering is higher. The anisotropy of elastic properties of the 17M mixture increases to an extremely large value as the temperature is lowered in the N phase, before decreasing again after smecticlike SRO develops in the medium. The unusual sign and large magnitude of the elastic anisotropy in a low-molecular-weight system should be of interest for a variety of physical studies which involve director distortions.

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