Splay bend elasticity of a bent-core nematic liquid crystal

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We measured the splay ($K_{11}$) and bend ($K_{33}$) elastic constants in the nematic phase of a bent-core liquid crystal. In the vicinity of the nematic-isotropic transition temperature $K_{11}$ is proportional to the square of the order parameter. In the nematic range $K_{11}$ increases monotonically with decreasing temperature, whereas $K_{33}$ is practically independent of temperature and is smaller than $K_{11}$. $K_{33}$ exhibits a pretransitional slow divergence toward the transition temperature to the smectic phase and becomes slightly larger than $K_{11}$. The small $K_{33}$ is explained on the basis of strong coupling of the bent shape of the molecules with the bend distortion.

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Thermotropic liquid crystals exhibit a variety of phases as functions of temperature. Among the known phases, nematic (N) is the simplest one. It exhibits a long-range orientational order about an axis called director and it is apolar (\(\hat{n}=\hat{d}\)). The electro-optic properties of rodlike N liquid crystals are exploited particularly for flat panel display devices. When the translational symmetry of rodlike molecules is broken it gives rise to smectic liquid crystals. In general N and smectic A (Sm-A) liquid crystals are uniaxial since the molecules, although they are not cylindrical symmetric, freely rotate about the long molecular axis. In the past few years, a new type of molecular shape, namely, bent-core (BC) liquid crystals (with a bent angle of \(\approx 120^\circ\)), has created immense interest in the scientific community because it gives rise to several new liquid-crystalline phases along with some known phases observable in calamitic liquid crystals [1,2]. Many physical properties of bent-core liquid crystals related to the bent structure are not yet understood. The N phase has been chosen for various physical measurements in order to investigate the structure–property relation in bent-core liquid crystals. Recently some interesting experimental results are reported in the N phase of BC liquid crystals, i.e., large flexoelectric coefficient [3,4], unusual electroconvection [5–7], and Kerr effect [8]. There are also some reports on the measurement of splay ($K_{11}$) and bend ($K_{33}$) elastic constants in the mixtures of rod and BC liquid crystals. Dodge et al. showed that dissolving a small concentration of BC molecules into a compound with rodlike molecules can reduce $K_{33}$ by a factor of 2 or more [9,10]. Kundu et al. reported anomalous temperature dependence of $K_{11}$ and $K_{33}$ in the mixtures of rod and BC molecules and explained it on the basis of mutual orientation of rod and BC molecules [11]. On the other hand Olivares et al. [12] conducted a dynamic light scattering measurement in a pure BC compound with oxazole heterocyclic ring in the central core and suggested that the temperature dependence of elastic constants is weak with no signature of pretransitional behavior toward the transition temperature to the smectic (Sm-C) phase. Recently Dozov theoretically showed that a spontaneous symmetry breaking phase transition inside the N phase is possible because of mutual tendency of banana-shaped molecules to induce a local bend director with a negative bend elastic constant [13]. Therefore the knowledge about the elasticity in pure BC liquid crystals is important. However, until now no direct measurement of the temperature-dependent elastic constants for pure BC liquid crystals has been reported. In this Rapid Communication we carry out the temperature-dependent measurements of $K_{11}$ and $K_{33}$ of a pure bent-core liquid crystal and report that the temperature dependence of $K_{11}$ and $K_{33}$ is significantly different from that in rodlike molecules; i.e., $K_{33}$ is much lower compared to $K_{11}$ except very near the Sm-C phase transition.

The chemical structure of the compound is shown in Fig. 1(a) (inset). It has the following phase transitions: Sm-C, 118.5 °C N, 176.5 °C I. The compound exhibits a large temperature range of the N phase. It is also stable as there was no noticeable change in the transition temperatures after several cycles of heating and cooling. Planarly aligned cells were prepared by using two indium tin oxide coated glass plates. These plates were treated with polyimide and cured at 180 °C for 1 h and rubbed antiparallel to each other. For homeotropic cells, JALS-204 was used as an alignment layer and cured at 200 °C for 1 h. The cell thickness was measured by a spectrometer. The typical cell thickness used for the experiments was \(\approx 5\) μm. The cell was filled with the sample in the isotropic phase and a well-aligned N sample was obtained. The parallel ($\epsilon_\parallel$) and perpendicular ($\epsilon_\perp$) components of dielectric constants were measured in homeotropic and planar cells, respectively, by using a LCR meter (Agilent 4980A). The optical retardation was measured by using a phase modulation technique [14] with the help of a helium-neon laser, a photoelastic modulator (PEM-100), and a lock-in amplifier (SR-830). A sinusoidal voltage with a frequency of 4111 Hz and an amplitude of up to 20 V at steps in the ranges 0.05–0.5 V were used for the measurements by using the same LCR meter. The retardation and also the sample capacitance were measured simultaneously as functions of temperature and voltage. The capacitance value obtained in planar cells at various temperatures far below the Fredericksz threshold voltage also provides the perpendicu-

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lar component ($\epsilon_{\parallel}$) and the extrapolated value at high voltage provides the parallel component ($\epsilon_{\parallel}$) of dielectric constants. The measured value agrees well with the measurements in the independent cells. The splay elastic constant $K_{11}$ was obtained directly from the Freedericksz threshold voltage of the voltage-dependent retardation data by the equation $K_{11} = \epsilon, \Delta \epsilon (V_{th}/\pi)^2$. The voltages above the threshold voltage $V_{th}$ and the retardation $\delta$ are given by the parametric equations

\[
V = \frac{2}{\pi} \sqrt{\frac{1}{1 + \gamma \sin^2(\phi_m)}} \int_0^{\pi/2} \sqrt{\frac{1 + \kappa \sin^2(\phi_m) \sin^2(\psi)}{[1 + \gamma \sin^2(\phi_m) \sin^2(\psi)][1 - \sin^2(\phi_m) \sin^2(\psi)]}} d\psi,
\]

where $d$ is the cell thickness, $\phi_m$ is the tilt angle at the middle of the cell, and the other terms of the reduced quantities are $\gamma = (\epsilon_{\parallel}/\epsilon_{\perp}) - 1, \kappa = (K_{33}/K_{11}) - 1, \nu = (n_2^2/n_1^2) - 1$, and $\sin(\phi) = \sin(\phi_m) \sin(\psi)$. The sample retardation at higher voltage is fitted to the above equations by an iterative procedure to get the bend elastic constant $K_{33}$ [1,16].

We first show the variation of birefringence ($\Delta n$) in the $N$ phase as a function of temperature in Fig. 1(a). It is noticed that birefringence appears abruptly at the $N$-isotropic (NI) phase transition and gradually increases as the temperature decreases in the $N$ phase. A small jump in the birefringence data is also observed near the $N$-Sm-C phase transition at $T - T_{NI} = -64^\circ$. The temperature-dependent birefringence in the $N$ liquid crystals can be approximated by the formula $\Delta n = \Delta n_1 (1 - T/T^*)^\beta$, where $T^*$ and $\beta$ are the adjustable fit parameters and $\Delta n_1$ is the birefringence of the perfectly aligned sample. The equation fits well in the entire nematic range with fit parameters $\Delta n_1 = 0.28$ and $\beta = 0.21$. The order parameter $S$ was estimated using the relation $S = \Delta n/\Delta n_1$. The temperature variation of the calculated order parameter is also shown in Fig. 1(a). The order parameter in the $N$ phase just below the NI phase transition was approximately 0.2 and reached 0.7 with a small jump at the $N$-Sm-C phase transition. The temperature-dependent $S$ was also measured by Weissflog et al. [17] and Dong et al. [18] in the $N$ phase of banana liquid crystals using nuclear magnetic resonance spectroscopy, and similar temperature dependence with slightly smaller values of $S$ was reported.

The variation of parallel ($\epsilon_{\parallel}$) and perpendicular ($\epsilon_{\perp}$) components of dielectric constants as a function of temperature is shown in Fig. 1(b). In the $N$ phase, the dielectric anisotropy is small positive and changes sign in the Sm-C phase. The temperature-dependent dielectric anisotropy can be understood as follows: the molecules have both longitudinal and transverse dipole components mainly due to the ester linkages. In the $N$ phase, molecules freely rotate about their long axis, so that the effect of transverse dipoles is suppressed. But the longitudinal dipoles respond to an electric field electrically. Hence, positive dielectric anisotropy results in the $N$ phase. The change of sign of dielectric anisotropy from the $N$ phase to the Sm-A phase of rodlike molecules was reported by de Jeu et al. [19] and was explained by an increased dipolar correlation between the molecules in the same layer. In addition to such an effect, we should consider the bent shape of the molecules, i.e., local packing of the bent-shaped molecules in the Sm-C layers hinders the free rotation about their molecular long axis, leading to quasimacroscopic transverse dipoles, which respond to the electric

\[
V = \frac{2}{\pi} \sqrt{\frac{1 + \gamma \sin^2(\phi_m)}{1 + \kappa \sin^2(\phi_m)}} \int_0^{\pi/2} \sqrt{\frac{1 + \kappa \sin^2(\phi_m) \sin^2(\psi)}{[1 + \gamma \sin^2(\phi_m) \sin^2(\psi)][1 - \sin^2(\phi_m) \sin^2(\psi)]}} d\psi,
\]

where $\delta = 2\pi \frac{n_d d}{\lambda} \left( \int_0^{\pi/2} \sqrt{\frac{1 + \gamma \sin^2(\phi_m) \sin^2(\psi)}{[1 - \sin^2(\phi_m) \sin^2(\psi)][1 + \nu \sin^2(\phi_m) \sin^2(\psi)]}} d\psi - \frac{n_d}{\epsilon} \right).

\[
\epsilon_{\parallel} = \epsilon_{\perp} = \frac{\epsilon_{\parallel} \epsilon_{\perp}}{\epsilon_{\parallel} + \epsilon_{\perp}} = \frac{\epsilon_{\parallel} \epsilon_{\perp}}{\epsilon_{\parallel} + \epsilon_{\perp}} = \frac{\epsilon_{\parallel} \epsilon_{\perp}}{\epsilon_{\parallel} + \epsilon_{\perp}}.
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\epsilon_{\parallel} = 1.5, \epsilon_{\perp} = 3.5.
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\epsilon_{\parallel} = 1.5, \epsilon_{\perp} = 3.5.
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field, contributing the increase in $\epsilon_{\parallel}$. The increasing $\epsilon_{\parallel}$ with decreasing temperature is caused by larger rotational hindrance. As discussed by de Jeu et al. [19], the decrease in $\epsilon_{\parallel}$ is explained by the increased antiparallel correlation between the dipoles along the molecular long axis. This could be possible even in the local packing condition. In addition, the layer formation suppresses the dielectric response about the molecular short axis, contributing the decrease in $\epsilon_{\parallel}$ in the Sm-$C^*$ phase. The sharp variation of dielectric constants across the $N$-$Sm-C^*$ transition [Fig. 1(b)] in the present bent-core liquid crystal compared to the slow variation in rodlike molecules reported [19] is due to the contribution of rotational hindrance.

Let us describe the $K_{11}$ and $K_{33}$ measurements. First, the observed retardation is shown in Fig. 2 as a function of the applied voltage at 157 °C. From the critical voltage (2.85 V) of the Fredericksz transition we estimated $K_{11}$ as 6.5 pN. A typical best fit of the overall data to Eq. (2) with $K_{33}$ as a fitting parameter is shown in Fig. 2, giving $K_{33}=3.7$ pN. The temperature dependence of $K_{33}$ and $K_{11}$ is shown in Fig. 3. $K_{11}$ and $K_{33}$ were also plotted as functions of the birefringence. As shown in the inset, $K_{33}$ is proportional to $\Delta n^2 (=s^2)$ in the vicinity of the $N$ transition as predicted by the simple mean-field theory. The value of $K_{11}$ however monotonically increases as the temperature is lowered and no pretransitional divergence is observed. $K_{11}$ is also fitted with $K_{11}\sim\Delta n^n$ and the value of $n\sim2.9$. Slightly lower value of $n$ ($\sim2.5$) was reported in the rod and bent-core mixtures [11]. However, the value of $K_{33}$ at a given temperature is always lower than $K_{11}$ except when very close to the $N$-$Sm-C^*$ transition. For example, at $T-T_{N3}=1$ °C, i.e., just below the $N$ transition $K_{33}/K_{11}\sim0.7$ and reduces to $\sim0.4$ at about $T-T_{N3}=45$ °C. Then because of pretransitional increase in $K_{33}$ below $T-T_{N3}=50$ °C, $K_{33}/K_{11}$ increases to $\sim1$ with approaching to the $N$-$Sm-C^*$ transition. In the case of rodlike molecules [e.g., octyl cyano biphenyl (8OCB)] it is known that $K_{33}$ is always higher and the ratio is $\sim2$, very close to the $N$ transition and increases to $\sim6$ as the Sm-$A$ phase is approached [9,11]. Interestingly the values of $K_{11}$ in both 8OCB and the present compound are comparable, although the temperature dependence of $K_{11}$ is stronger in the pure bent core than in 8OCB as seen with the larger value of $x$.

The sign inversion of elastic anisotropy ($K_{33}-K_{11}$) and the temperature dependence of these two elastic constants are expected to originate from the bent structure of the molecules. A schematic representation of splay and bend distortion of bent-core molecules is shown in Figs. 4(a) and 4(b). The almost linear increase in $K_{11}$ can be attributed to the increase in the order parameter as seen in the birefringence measurement [Fig. 1(a)]. Here, the bent shape does not facilitate the splay distortion in the medium [Fig. 4(a)]. However, as the temperature is lowered the molecular bent shape coupled to the bend distortion easily facilitating the bend distortion. As a result $K_{33}$ becomes lower in the $N$ phase. In the case the strain in the bend distortion partly relieved by changing the equilibrium distribution of the molecules with one side “up” or “down” as shown in Fig. 4(b). As the temperature is lowered toward the Sm-$C^*$ phase, because of smectic short-range fluctuations, $K_{33}$ starts to change the temperature dependence at $T-T_{N3}=30$ °C. The divergence of elastic constants near the Sm-$C^*$ phase has been theoretically studied by de Gennes [20] and Chen and Lubensky [21]. According to both theories all three elastic constants show pretransitional divergence. In the present compound we find no pretransitional divergence in $K_{11}$ and the exponent of divergence of $K_{33}$ is $\sim0.43$, which is much lower than the predicted value ($\sim0.7$) indicating that the existing theoretical models are insufficient to explain the pretransitional behavior near Sm-$C$ of bent-core liquid crystals. It may be pointed out that there are also some experimental reports on the elastic constant measurements of some binary mixtures by using a
light scattering technique above the $N$ to Sm-$C$ transition [22,23]. They reported that $K_{33}$ obtains a maximum value just above the $N$ to Sm-$C$ transition point and such a behavior is not anticipated by any of the existing models.

Previously the compound was reported to show the uniaxial to biaxial $N$ transition [24] at $T - T_{NI} \approx -30^\circ$C, although recently Van Le et al. [25] showed that the medium is uniaxial. Interestingly the temperature at which $K_{33}$ starts changing the temperature dependence ($T - T_{NI} \approx -30^\circ$C) coincides with the $N_sN_b$ transition temperature reported [24], suggesting the onset smectic short-range fluctuations at that temperature. Thus, the biaxial-like order seen in the x ray as reported in Ref. [24] could be due to the presence of smectic short-range fluctuations, as suggested [26,27].

In conclusion we measured the $K_{11}$ and $K_{33}$ elastic constants as functions of temperature in a pure bent-core liquid crystal. Our measurement shows that $K_{33}$ is much lower than $K_{11}$ except for the temperature regions close to the $N$ to Sm-$C$ transition. The temperature dependence clearly shows a strong coupling of bent shape with the bend distortions in pure compound. Thus, various physical properties and their temperature dependence related to $K_{33}$ are strongly influenced and further the bent shape has to be taken into account in understanding the physical properties in bent-core molecules.

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