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Unusual temperature dependence of elastic constants of an ambient-temperature discotic nematic liquid crystal†

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We report the first experimental studies on the temperature dependence of viscoelastic properties of a room temperature discotic nematic liquid crystal. The splay elastic constant is greater than the bend elastic constant and both show unusual temperature and order parameter dependence. The rotational viscosity is remarkably larger than conventional calamitic liquid crystals. We provide a simple physical explanation based on the columnar short-range order to account for the the unusual temperature dependence of the elastic constants.

I. Introduction

Discotic liquid crystals (DLCs) consist of disc-like molecules in which the cores are surrounded by flexible alkyl side chains.[1,2] Discotic nematic LCs are very useful for wide and symmetrical viewing angles of LCDs[3] and optical compensating films.[4] They mostly exhibit columnar and nematic phases and relatively a few are known to exhibit the lamellar phase.[5–7] The physical studies on discotic nematic LCs are meagre compared to the number of compounds synthesized. So far physical properties of a few discotic nematic liquid crystals have been reported. For example, Heppke *et al.* have measured the dielectric and elastic properties of hexakis((4-alkylphenyl)ethynyl)benzene.[8,9] Raghunathan *et al.* and Warmardam *et al.* measured the elastic properties of truxene ester compounds.[10,11] Mourey *et al.* have reported various physical measurements on the triphenylene hexa(alkoxybenzoate) nematic discotic compounds.[12] In all these compounds the nematic phase appears much above the ambient temperature. In 2000, Kumar *et al.* reported the first synthesis of room temperature discotic nematic LCs.[13,14] The range of the nematic phase is very wide and the nematic to glass transition occurs much below the ambient temperature. However, so far there has been no report on the viscoelastic properties of these compounds. In this paper we report the first

studies on the birefringence, dielectric and viscoelastic properties of a room temperature discotic nematic LC. We show that the compound exhibits unusual viscoelastic properties, pointing to the existence of a temperature dependent short-range columnar order in the nematic phase.

II. Experimental

The liquid crystal cells were made of two indium-tin-oxide (ITO) coated glass plates with patterned electrodes. These plates were spin coated with polyimide AL-1254 and cured at 180 °C for 1 hour and rubbed in an antiparallel way. It gives the homeotropic alignment of the discotic nematic liquid crystal. It may be mentioned that AL-1254 is usually used for the planar alignment of rod-like molecules. A typical cell thickness used in the experiment was about 8 μm and measured within ±1% accuracy. The empty cell was heated and the sample was filled in the isotropic phase. The alignment of the sample was observed using a polarising optical microscope (Olympus BX51) and a temperature controller (Mettler FP 90). The birefringence was obtained by measuring the transmitted intensity with the help of two crossed Glan–Thompson polarizers, a He-Ne laser source and a photodetector. The dielectric constant was measured using a LCR meter (Agilent, E4980A). The parallel component of the dielectric constant (parallel to the director, *i.e.*, perpendicular to the plane of disc-molecules) was measured at an applied voltage of 0.5 V (below the Freedericksz threshold voltage). The homogeneous alignment of the director in the cells could not be obtained by using standard alignment layers. Hence, to measure the perpendicular component of the dielectric constant (*i.e.*, parallel to the disc-molecules), we have taken the homeotropic cell and used a lock-in-amplifier (LIA) together with a

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voltage amplifier.[15,16] At sufficiently high voltage the director was completely reorientated to the homogeneous state. The bend elastic constant (K_{33}) was obtained from the electric field induced Freedericksz transition and is given by $K_{33} = \varepsilon_0|\Delta\varepsilon|(V_{th}/\pi)^2$, where $\Delta\varepsilon = \varepsilon_\parallel - \varepsilon_\perp$ is the dielectric anisotropy and V_{th} is the threshold voltage. The splay elastic constant (K_{11}) was estimated from the numerical fitting of the voltage dependent dielectric constant with the theoretical variation.[17,18] The rotational viscosity (γ_1) was measured using the phase-decay-time measurement technique.[19] The LCR meter was used to apply voltage at a frequency of 1000 Hz and a photodetector was used to measure the time dependent transmitted intensity. A small voltage (V_b) corresponding to the first maxima was applied depending on the transmission intensity such that the total change of the phase retardation of the sample was $n\pi$, where n is an integer. At time $t = 0$, the bias voltage (V_b) was removed and the transmission intensity change of the liquid crystal cell was measured using an oscilloscope (Tektronix, TDS 2012B). The time dependent intensity at a particular temperature is given by:[19] $I(t) = I_0 \sin^2[\Delta_{tot} - \delta(t)]/2$, where I_0 is the maximum intensity change and Δ_{tot} is the total phase difference. The time dependent optical phase difference $\delta(t)$ for small director distortion can be approximated as $\delta(t) = \delta_0 \exp(-2t/\tau_0)$, where δ_0 is the total phase difference of the liquid crystal under bias voltage (V_b) that is not far from the Freedericksz threshold voltage (V_{th}). The slope of the plot $\ln[\delta_0/\delta(t)]$ with time (t) gives the relaxation time (τ_0). The rotational viscosity (γ_1) is given by $\gamma_1 = \dfrac{\tau_0 K_{33} \pi^2}{d^2}$, where d is the thickness of the sample. This procedure was repeated in the entire nematic range at different temperatures.

III. Results and discussion

The chemical structure and the phase transition temperatures of the compound are shown in Fig. 1. It is a pentaalkynylbenzene derivative having a combination of branched alkoxy chains and a wide nematic range. The compound was synthesized as per the reported procedure.[13,14]
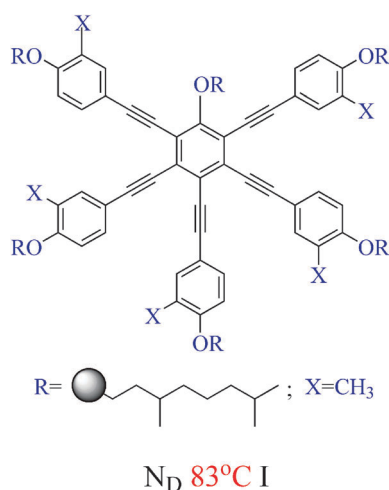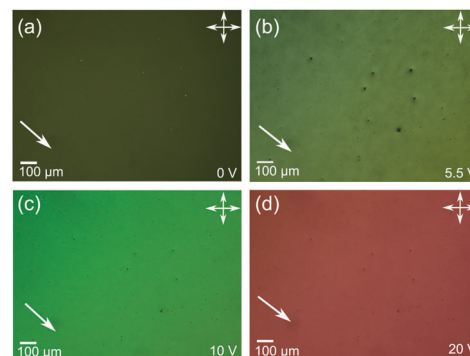
Fig. 2 Photomicrographs obtained in the homeotropic cell at various voltages under a polarising optical microscope. White arrows indicate the rubbing direction.

The alignment of the sample was checked using a polarising optical microscope at various applied voltages and temperatures. Fig. 2(a) shows a dark texture where the short axes of the discs are aligned perpendicular to the plane of the substrate (homeotropic alignment). When the applied voltage is greater than Freedericksz threshold voltage, the field of view becomes brighter and the color change indicates increasing retardation with applied voltage (Fig. 2(a)–(d)). This suggests that the director is continuously tilting from homeotropic to the planar state with increasing voltage. It may be mentioned that no electroconvection was observed in the applied voltage and frequency range.

To measure the birefringence (Δn) of the nematic phase (N_D), we first measured the voltage dependent birefringence at room temperature. Beyond the Freedericksz threshold voltage, Δn increases and saturates above 20 V. The saturation of Δn indicates the planar state of the director. We applied 25 V (higher than the saturation voltage) to measure the temperature dependent birefringence. The temperature variation of Δn is shown in Fig. 3. The birefringence is negative i.e., $(n_e - n_0) < 0$ and Δn jumped to $\simeq -0.13$ from zero at the nematic–isotropic

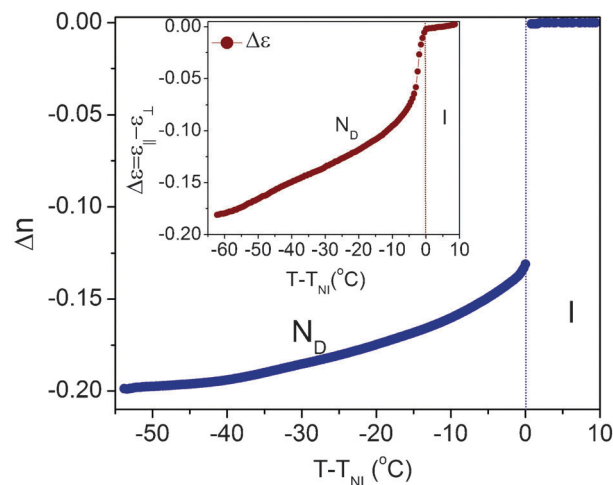Fig. 1 Chemical structure and phase transition temperatures of the discotic compound used in the experiment.

Fig. 3 Variation of birefringence (Δn) as a function of temperature (measured at λ = 632.8 nm). (inset) Variation of dielectric anisotropy ($\Delta\varepsilon$) as a function of temperature. Frequency of measurement: 411 Hz.

(NI) transition and gradually decreased as the temperature is lowered. At room temperature ($T - T_{NI} = -55$ °C) it reaches approximately -0.2. This is comparable to the other discotic nematic compounds having similar molecular structures.[8]

We measured the dielectric dispersion at various temperatures and observed that the parallel component ($\varepsilon_{||}$) does not show any dielectric relaxation whereas the perpendicular component ($\varepsilon_{\perp}$) exhibits dielectric relaxation and the relaxation frequency vary with the temperature in the range of 1 kHz–100 kHz (see the ESI,† ref. 20). The temperature variation of the dielectric anisotropy ($\Delta\varepsilon = \varepsilon_{||} - \varepsilon_{\perp}$) at a fixed frequency (411 Hz) is also shown in Fig. 3. The dielectric anisotropy of the N_D phase, is very small and negative ($\Delta\varepsilon \simeq -0.18$ at $T - T_{NI} = -60$ °C). This is expected as the permanent dipoles are mostly confined in the plane of the disc.

To obtain splay (K_{11}) and bend (K_{33}) elastic constants, we measured the voltage dependent dielectric constant, $\varepsilon_{eff}(V)$ at various temperatures in the N_D phase. The variation of the normalised dielectric constant at a few representative temperatures is shown in Fig. 4. It is clearly observed that the threshold voltage increases with decreasing temperature. The temperature variation of K_{11} and K_{33} is shown in Fig. 5(a). Interestingly we observe $K_{11} > K_{33}$ at all temperatures and they show very different temperature dependence. For example, as the temperature is reduced from the NI transition point, both the elastic constants increase but K_{11} increases more rapidly than K_{33}. Below $T - T_{NI} = -45$ °C, K_{11} saturates whereas K_{33} shows a kind of diverging behavior. The temperature variation of K_{11}/K_{33} is also shown in the inset of Fig. 5(a). It is observed that the ratio increases as the temperature decreases and reaches a maximum around $T - T_{NI} = -40$ °C. Below this temperature it reduces rapidly as the ambient temperature is approached. To gain insight into the relationship between the order parameter and the elastic constants, we plotted the variation of K_{33} and K_{11} with Δn (near NI transition) according
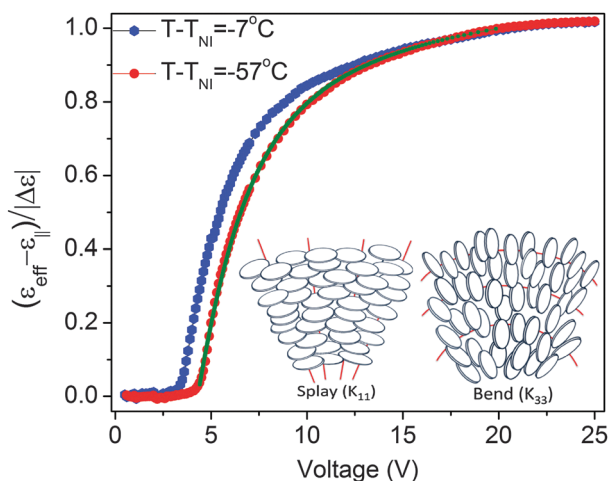

Fig. 5 (a) Variation of splay (K_{11}) and bend (K_{33}) elastic constants as a function of temperature. (inset) Variation of the ratio of K_{11}/K_{33} with temperature. (b) Variation of K_{11} and K_{33} with Δn. Corresponding temperature range is also shown in the upper abscissa (green colour). Continuous lines are best fits to the equation, $K_{ii} \propto \Delta n^x$.

to the mean-field, $K_{ii} \propto S^2 \propto \Delta n^2$, where S is the order parameter.[21] Interestingly we observed that $K_{33} \propto \Delta n^{1.1}$ and $K_{11} \propto \Delta n^{4.1}$ respectively (Fig. 5(b)). Thus both K_{33} and K_{11} exhibit significant deviations from the mean-field behavior.

There are a very few reports on the temperature dependence of splay and bend elastic constants of the N_D phase. Sokalski et al. theoretically predicted that for discotic nematic with a long-range orientational order, $K_{11}/K_{33} > 1$.[22] This has been experimentally verified by a couple of experiments. For example, Heppke et al., measured both the splay and bend elastic constants of a homologous series of non-polar nematic discotic compounds showing I to N_D transition.[8,9] They reported that in most of the compounds, $K_{11}/K_{33} > 1$. Warmardam et al. measured the elastic constants of two discotic compounds with a polar molecule.[11] In addition to the N_D phase these compounds also exhibit two columnar phases. They reported that in the N_D phase, $K_{11}/K_{33} > 1$. Raghunathan et al., measured the elastic properties of truxene compounds and found that $K_{11}/K_{33} < 1$.[10] In their compounds the nematic phase appeared between two discotic columnar phases and it was attributed to

Fig. 4 (a) Variation of the normalised dielectric constant ($\varepsilon_{eff} - \varepsilon_{||}$)/$\Delta\varepsilon$ at a few representative temperatures. The continuous line is the best fit with the theoretical variation. Schematic representation of splay and bend distortions of the discotic nematic liquid crystal.
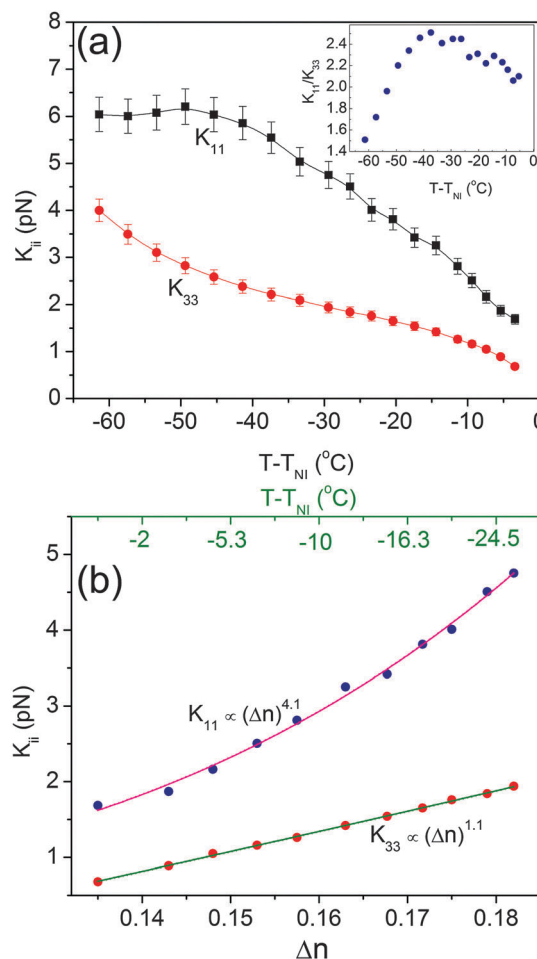
the short-range columnar order. Phillips *et al.*, studied the elastic properties of triphenylene discotic nematic liquid crystals.[23] These compounds exhibit I to N_D phase transition much above the ambient temperature. They found that the ratio, K_{11}/K_{33} is very high ($\simeq 5$) and decreases ($\simeq 3$) as the temperature is decreased.[23] It has been reported that three types of discotic nematic can be envisaged based on the local organization of the disc-like molecules and they are known as N_D, N_{col} and N_L. In the N_{col} and N_L phases there is a short-range columnar order and a short-range 2D lattice respectively.[24] The effect of a short-range columnar order in the discotic nematic has also been studied by computer simulation.[25] It was reported that the onset of growth in the orientational order in the parent phase is found to induce the translational order, arising from short-range columnar structures. We attribute this unusual temperature dependence of elastic constants to the short-range columnar order. We provide a simple physical explanation that accounts for the effect of short-range columnar order on the splay and bend distortion (Fig. 6). A short-range columnar order does not hinder the splay distortion hence the splay elastic constant is not significantly affected. On the other hand the short-range columnar order can increase the bend stress as it is energetically unfavorable to bend the columns. This leads to a rapid increase of K_{33} than K_{11} and possibly a cross-over may take place at a much lower temperature with the growth of orientational order. Thus the elastic properties at a higher temperature are due to the long-range orientational order. The short-range columnar order increases as the temperature is decreased and the elastic constants show unusual temperature dependence.

We further measured the rotational viscosity (γ_1) of the N_D phase as a function of temperature. It may be mentioned that the direct value of γ_1 of discotic nematic has not been reported so far. The normalized transmission intensity at some representative temperatures are shown in Fig. 7(a). It is observed that at lower temperature (*e.g.*, $T - T_{NI} = -57.4$ °C) it (intensity) takes about 200 s to decay to the zero value. Linear variation of $\ln[\delta_o/\delta(t)]$ with time is shown in the inset of Fig. 7(a). The rotational viscosity γ_1 increases very rapidly with decreasing temperature (Fig. 7(b)). For example, near the NI transition $\gamma_1 = 0.1$ Pa s and it increases to $\simeq 200$ Pa s at room temperature. Warmerdam *et al.* directly measured the temperature dependence of $\gamma_1/\Delta\chi$, where $\Delta\chi$ is the diamagnetic susceptibility anisotropy.[26] Assuming a typical value of $\Delta\chi$ they estimated that γ_1 for discotic

Fig. 7 (a) Time dependent normalised transmitted intensity after the removal of bias voltage (V_b) for various temperatures. (inset) Variation of $\ln[\delta_o/\delta(t)]$ with time at $T - T_{NI} = -41.5$ °C. (b) Variation of rotational viscosity (γ_1) as a function of temperature. Continuous line is the best fit. (inset) A linear variation of $\ln(\gamma_1/\Delta n)$ with $1/T$.

nematic is about 10 to 100 times larger compared to the rod-like mesogens. In our compound it is about three orders of magnitude larger than conventional calamitic liquid crystals and this could be attributed to the effect of the short-range columnar order. In addition, such a large rotational viscosity could be due to the effect of glass transition below the room temperature. In this sample the glass transition temperature is reported to be at -35 °C.[13] The rotational viscosity can be written as $\gamma_1 \sim S \exp(W/kT)$, where S is the order parameter and k is the Boltzmann constant.[27] Since $S \propto \Delta n$, we show the variation of $\ln(\gamma_1/\Delta n)$ with $1/T$ in the inset of Fig. 7(b). The estimated activation energy is about 837 meV, which is about double compared to the values known in conventional calamitic liquid crystals.[28] It may be mentioned that theoretically it has been shown that the microscopic friction coefficient of discotic nematic shows an exponential temperature dependence with a large activation energy.[29]

IV. Conclusion

In conclusion, we measured birefringence, dielectric and curvature elastic properties of an ambient-temperature discotic nematic
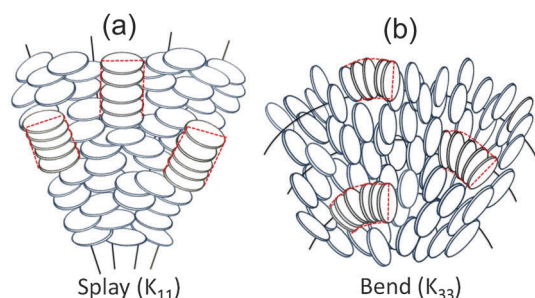

Fig. 6 Schematic representation of (a) splay and (b) bend distortion in a discotic nematic liquid crystal. Columnar short-range order is shown using dotted red lines.
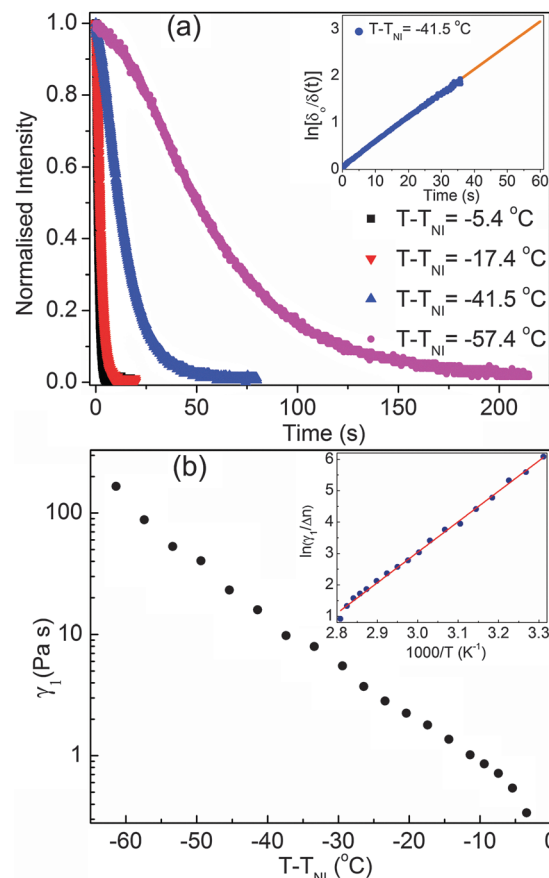
liquid crystal with a wide temperature range. Both the birefringence and the dielectric anisotropy are negative. Near the NI transition, K_{11} and K_{33} exhibit quartic and linear variation with birefringence respectively. This is not in accordance with the prediction of mean-field. As the ambient temperature is approached the elastic constants show unusual temperature dependence. The rotational viscosity is three orders of magnitude high at room temperature and the corresponding activation energy is more than double compared to conventional calamitic mesogens. These results suggest that viscoelastic properties near the ambient temperature are dominated by the effect of the short-range columnar order. Further experiments are underway to quantify the temperature dependent columnar order from the X-ray scattering studies.

Acknowledgements

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