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PAPER

Structure–property correlation of a hockey stick-shaped compound exhibiting N-SmA-SmC_a phase transitions

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We report the measurement of birefringence, dielectric constant, splay, bend elastic constants and rotational viscosity in the nematic phase (N) of a hockey stick-shaped compound exhibiting smectic-A (SmA) and anticlinic smectic-C (SmC_a) phase transitions at lower temperature. It is found that the physical properties are significantly different than calamitics and partially similar to the bent-core liquid crystals. It exhibits the positive dielectric and the negative elastic anisotropy. The optical and the thermal measurements show that all the transitions are first order. The rotational viscosity is comparatively higher than calamitic liquid crystals and exhibits weak pre-transitional divergence. The temperature dependent static dielectric measurements indicate antiparallel correlation of both the longitudinal and the transverse components of dipole moments in both the smectic phases. The parallel component of the dielectric constant exhibits a single Debye type relaxation in all the phases. The activation energy in the N, SmA and SmC_a phases are comparatively larger than that of the respective phases of calamitic liquid crystals and can partially be attributed to the higher rotational viscosity of the hockey stick-shaped compound.

I. Introduction

The structure-property correlation in conventional liquid crystals made of rod-like molecules has been studied extensively and mostly well established. Efforts have always been made to design new molecules with improved physical properties that can enhance the display performance. In this context liquid crystals made of bent-core molecules have created worldwide interest after the discovery of electrooptical switching in achiral bent-core compounds.¹ Subsequently several groups reported the synthesis of new liquid crystal compounds with various molecular shapes like T, H and W.²⁻⁴ It has been established that molecular shape has a significant role on their phase structures and physical properties.⁵⁻⁷ Commonly bent-core molecules exhibit the so called banana mesophases, B_1-B_8 and occasionally they also exhibit some phases of calamitic liquid crystals like N, SmA and SmC etc. To understand the effect of molecular shape nematic has always been preferred for its simple structure and easy to perform experiments. It has been reported that bent-core nematic liquid crystals exhibit sign inversion of elastic anisotropy,^{8,9} unusual electroconvection,10-12 giant flexoelectricity,13,14 large viscosity,15,16 Kerr coefficient,17 induced18 and spontaneous biaxiality.^{19,20} In the case of compounds with T shaped molecules it was reported that the splay and bend elastic constants are almost

equal (*i.e.*, $K_{11} \simeq K_{33}$) in the entire N phase.²¹ As mentioned these compounds also exhibit occasionally various smectic phases at lower temperature and the structure–property correlation of such unconventional liquid crystals in these phases are meagre. In this paper we report measurement of birefringence, static dielectric constant and dielectric dispersion in the N, SmA and SmC_a phases and in addition splay, bend elastic constants, and rotational viscosity of a hockey stick-shaped compound as a function of temperature. The results are compared with conventional calamitic liquid crystals and interpreted in terms of the molecular structure, shape and dipolar correlation in the mesophase.

II. Experimental

Two indium tin oxide (ITO) coated glass plates were thoroughly cleaned to prepare liquid crystal cells. These plates were spin coated with polyimide (AL-1254) and cured at 180 °C for 1 h and rubbed in an antiparallel manner for planar or homogeneous alignment of the sample. ITO plates were spin coated with JALS-204 and were cured at 200 °C for homeotropic alignment of the sample. The cell thickness was measured by using a fibre optic spectrometer (Ocean Optics, HR-4000). The typical cell thickness used in the experiment was ~5 μ m. The empty cell was heated and filled with the sample in the isotropic phase. The phase transition temperatures and enthalpies of the compound were measured using differential scanning calorimetry (DSC) (Perkin-Elmer, Pyris ID). The textures were observed using a polarising optical miscroscope (Nikon, LV100POL). The perpendicular and parallel components of the static dielectric constant were

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measured in planar and homeotropic cells respectively by using an impedance analyser (Novocontrol, Alpha-A). In the case of the planar cell the measuring voltage was below the Freedericksz threshold voltage.

The temperature dependent optical retardation in the planar cell was measured by using a phase modulation technique²² with the help of a Helium–Neon laser (HT PS-Ec-1, Thor Labs), photoelastic modulator (PEM-100, Hinds Instruments) and a lock-in amplifier (Ametek, SR-7265). A sinusoidal voltage of frequency 4.111 kHz and amplitude 0.5 V was used for the temperature dependent dielectric measurement. The dielectric dispersion was measured at various temperatures in the frequency range of 100 Hz to 10 MHz. The splay elastic constant (K_{11}) is obtained from the Freedericksz threshold voltage (V_{th}) and is given by $K_{11} = \varepsilon_o \Delta \varepsilon (V_{th}/\pi)^2$, where $\Delta \varepsilon = \varepsilon_{\parallel} - \varepsilon_{\perp}$ is the dielectric anisotropy. At strong surface anchoring condition, the voltages above the threshold voltage V_{th} , the retardation ($\Delta \phi$) is given by the parametric equations:²³

$$\frac{V}{V_{\rm th}} = \frac{2}{\pi} \sqrt{1 + \gamma \sin^2(\phi_{\rm m})} \int_{\psi=0}^{\psi=\frac{\pi}{2}} \times \sqrt{\frac{1 + \kappa \sin^2(\phi_{\rm m})\sin^2(\psi)}{(1 + \gamma \sin^2(\phi_{\rm m})\sin^2(\psi))(1 - \sin^2(\phi_{\rm m})\sin^2(\psi))}} d\psi \quad (1)$$

The rotational viscosity (γ_1) was measured in a planar cell by using a phase-decay time dependant measurement technique. An arbitrary signal generator (Tektronix, AFG3102) was used to apply sinusoidal voltage at a frequency of 4.111 kHz and a photomultiplier tube (Hamamatsu, H6780-01) was used to measure the time dependent transmitted intensity. A small voltage (V_b) corresponding to the first maxima or minima was applied depending on transmission intensity such that the total phase retardation of sample was $n\pi$, where *n* is an integer. At time t = 0, the bias voltage (V_b) was switched off and the relaxation transmission intensity change of the liquid crystal cell was measured with an oscilloscope (Tektronix, TDS 2012B). This procedure was repeated at various temperatures in the entire nematic phase.

The time dependent transmittance at a particular temperature in a planar cell is given by $^{28}\,$

$$I(t) = I_o \sin^2 \{ [\Delta_{\text{tot}} - \delta(t)]/2 \}$$
(3)

where I_o is the maximum intensity change and Δ_{tot} is the total phase difference. The optical phase difference δ (*t*), for small director distortion can be approximated as δ (*t*) = $\delta_o \exp(-2t/\tau_o)$, where δ_o is the total phase difference of a liquid crystal under bias voltage (V_b) that is not far from the Freedericksz threshold

$$\Delta\phi = 2\pi \frac{n_e d}{\lambda} \left(\frac{\int_{\psi=0}^{\psi=\frac{\pi}{2}} \sqrt{\frac{(1+\gamma\sin^2(\phi_{\rm m})\sin^2(\psi))(1+\kappa\sin^2(\phi_{\rm m})\sin^2(\psi))}{(1-\sin^2(\phi_{\rm m})\sin^2(\psi))(1+\nu\sin^2(\phi_{\rm m})\sin^2(\psi))}}}{\int_{\psi=0}^{\psi=\frac{\pi}{2}} \sqrt{\frac{(1+\gamma\sin^2(\phi_{\rm m})\sin^2(\psi))(1+\kappa\sin^2(\phi_{\rm m})\sin^2(\psi))}{(1-\sin^2(\phi_{\rm m})\sin^2(\psi))}}} d\psi - \frac{n_e}{n_e} \right)$$
(2)

where d is the cell thickness, $\phi_{\rm m}$ is the tilt angle at the middle of the cell and the other terms of the reduced quantities are: $\gamma = (\varepsilon_{\parallel})$ ε_{\perp}) - 1, $\kappa = (K_{33}/K_{11}) - 1$, $\nu = (n_e^2/n_o^2) - 1$. ϕ is the z-dependent tilt angle and ϕ_m is the maximum tilt angle at the middle of the cell (z = d/2) and substituted with $\sin(\phi) = \sin(\phi_m) \sin(\psi)$. The sample retardation at higher voltages were fitted to the above equations by an iterative procedure to get the bend elastic constant K_{33} .^{24,25} To verify the anchoring condition we estimated the pretilt angle (α) in the planar cell by putting the lower limit of the integration $\psi = \alpha$ instead of zero in eqn (1) and (2) as a fit parameter. It was found that $\alpha \leq 1^{\circ}$ at all temperatures indicating the strong anchoring at the surface, hence α was assumed to be zero in the present analysis. It has been reported that the pretilt angle of bent-core nematic liquid crystals (BCN) on a planar alignment layer is very low ($\leq 1^{\circ}$) due to the presence of flexible alkyl chains on both sides.²⁶ Recently we have found that a wide temperature BCN provides a very low pretilt angle on the present alignment layer (AL-1254).¹⁶ Further it may be mentioned that the flexoelectric effect in unconventional liquid crystals could be significant and can affect K_{33} measurements. From voltage dependent dielectric measurements it was shown by Brown et al.27 that it can slightly underestimate K_{33} when the flexoelectric effect is neglected. In our experiment we measured retardation over a small region $(<1 \times 10^{-6} \text{ m}^2)$ using a He–Ne laser and expected that such an effect is minimum and hence not included in the present analysis.

voltage (V_{th}). In case δ_o is close to $n\pi$, $\delta(t)$ becomes $\delta(t) = \delta_o \exp(-4t/\tau_o)$. The slope of the variation $\ln[\delta_o/\delta(t)]$ with time (t) yields the relaxation time (τ_o). The rotational viscosity (γ_1) of the liquid crystal is given by $\gamma_1 = \tau_o K_{11}\pi^2/d^2$, where d is the thickness of the liquid crystal sample.

III. Results and discussion

A. Optical and static dielectric measurements

The hockey stick-shaped compound we studied is 4-*n*-butyloxyphenyl[4-(4-*n*-heptyloxybenzoyloxy4-benzoyloxy)]biphenyl-3carboxylate and exhibits metastable liquid crystalline phase transitions. The chemical structure and the phase transition temperatures of the compound is shown in Fig. 1(a). The synthesis and some preliminary characterisation was reported recently.²⁹

The molecule is achiral, asymmetric, hockey stick-shaped and has several strong dipolar groups. The texture obtained in between two glass plates without any surface treatment is shown in Fig. 1(b). In the nematic phase a typical schlieren texture with four brush defects is observed (Fig. 1(b) (i)). SmA is spontaneously aligned homeotropically below the N–SmA transition temperature (Fig. 1(b) (iii)) and again the dark region of the texture is transformed into schlieren texture as the temperature is reduced to SmC_a phase. SmC_a exhibits two and four brush defects with dynamic fluctuations (Fig. 1(b) (iv)), suggesting it to



Fig. 1 (a) Chemical structure of the compound and the phase transition temperatures (heating). (b) Photomicrographs obtained in an untreated cell under cooling at different temperatures (i) N phase (ii) at N-SmA transition (iii) SmA (iv) SmC_a .

be an anticlinic SmC (SmC_a) phase. Recently it has been reported that the bent-core liquid crystals with $\Delta \varepsilon > 0$ can be aligned homeotropically on conventional alignment layers whereas compounds with $\Delta \varepsilon < 0$ in general do not align homeotropically.³⁰ The results were explained due to the stronger dipolar interaction of resultant dipole moment with the surfaces. The present compound exhibits $\Delta \varepsilon > 0$ (see later) and provides good homeotropic alignment both in the N and SmA phases and supports in favour of the explanation *i.e.*, the strong dipolar interaction between the substrate surface and the molecule of materials with $\Delta \varepsilon > 0$ stabilise homeotropic alignment. The textures obtained in planar and homeotropic cells under a polarising optical microscope are shown in Fig. 2. It is noticed that all the phases can be aligned well in planar cells. In the homeotropic cell both N and SmA phases are well aligned. In case of SmC_a phase the overall texture is dark in the homeotropic cell except that some comparatively brighter and smaller regions are seen due to the tilting of the molecules with respect to the layer normal.

The temperature dependent variation of Δn and a differential scanning calorimetric (DSC) thermogram are shown in Fig. 3(a). The enthalpies of I to N, N to SmA and SmA to SmC_a transitions are 0.38, 0.98 and 0.23 kJ mol⁻¹ respectively. Δn jumps to ≈ 0.06 from 0 at the nematic–isotropic (NI) transition and gradually increased as the temperature was lowered. At N–SmA transition it shows a significant increase (≈ 0.02) and tends to saturate in the SmA phase. A similar jump (≈ 0.02) in Δn is also seen at SmA–SmC_a transition and it further increases as the temperature is decreased. Since $\Delta n \propto S$, where S is the orientational order parameter, it is anticipated that the orientational order parameter increases with decreasing temperature showing finite jumps across the transitions. Hence, these are first order phase transitions. Further, N–SmA transition (Fig. 3(a)) is comparatively



Fig. 2 Photomicrographs obtained in planar cell (i, iii, v) and in homeotropic cell (ii, iv, vi) at various temperatures under a polarising optical microscope. White arrows indicate the rubbing directions.

less sharp than SmA-SmC_a transition due to the presence of smectic short-range fluctuations in the N phase. Finite enthalpies of these transitions also suggest that the transitions are first



Fig. 3 (a) A DSC thermogram in cooling cycle (rate 5° min⁻¹) and variation of birefringence (Δn). (b) Variation of the real part of the dielectric constant ($\epsilon_{\parallel}, \epsilon_{\perp}$ and $\bar{\epsilon}$) as a function of temperature. Dotted vertical lines are drawn to indicate the transitions. Dashed line denotes the extrapolated value of isotropic dielectric constant.

order. It may be pointed out that usually the measurement of Δn in lower symmetric smectic phases are difficult and rare due to poor alignment. Moreover SmC_a is biaxial because of tilting of the molecules from the layer normal. The narrow lines along the rubbing direction in Fig. 2(v) could be due to the local biaxial order of SmC_a phase. Nevertheless in the present system it was possible to measure Δn because the director in the SmA phase is well aligned (Fig. 2(iii)) and the effective principal axis in the SmC_a phase still remains parallel to the rubbing direction because of opposite tilt of the molecules in the successive layers.

Temperature dependent variation of dielectric constants ε_{\parallel} , ε_{\perp} and average value, $\bar{\epsilon} (=(\epsilon_{\parallel} + 2\epsilon_{\perp})/3)$ are shown in Fig. 3(b). $\bar{\epsilon}$ in the nematic phase is less and further reduces in smectic phases from the extrapolated value of the isotropic dielectric constant. Usually $\bar{\epsilon}$ is expected to increase as the temperature is reduced due to the increase in density and the contribution from the orientational polarisation.³¹ In the present compound the opposite behaviour, especially in the smectic phases, is due to the strong antiparallel correlation of the longitudinal components of dipole moments. The dielectric anisotropy $\Delta\epsilon~(=~\epsilon_{\parallel}~-~\epsilon_{\perp})$ is positive in all the phases. ϵ_{\parallel} increases as the temperature is lowered in the N phase and starts to decrease sharply at the N-SmA transition and decreases rather slowly in the SmC_a phase. The decrease in ε_{\parallel} in conventional and in unconventional compounds with similar molecular structure is also reported and attributed to the increase in antiparallel correlation between the long axis components of dipoles in the SmA layer.8,21 The slow decrease of ε_{\parallel} as the temperature is reduced in the SmC_a phase is due to the tilting of the molecules in addition to the antiparallel correlation. ε_{\perp} decreases in the N phase as the temperature is decreased from the I phase. It is further lower in the SmA phase than both N and SmC_a with slope change at the transitions. The lower value of ε_{\perp} in the SmA phase suggests that there is also an antiparallel correlation between the short axis components of the dipoles in the SmA layer. This result is opposite to the behaviour seen in other unconventional liquid crystals reported recently.8,21 It may be mentioned that since the molecules have anticlinic tilt in successive layers of the SmC_a phase, ε_{\parallel} in this phase refers to the dielectric constant when the electric field is parallel to the layer normal rather than the director. Further, both the planar and homeotropic alignment of the SmCa phase are relatively poorer than the SmA phase due to the reason mentioned above and the absolute accuracy in the measurements of Δn , ε_{\parallel} and ε_{\perp} in this phase is expected to be somewhat less than both in N and SmA phases.

B. Viscoelastic measurements

To measure K_{11} and K_{33} we measured the voltage dependent optical retardation ($\Delta \phi$) at various temperatures in the nematic phase. The temperature variation of K_{11} and K_{33} is shown in Fig. 4(a). A typical variation of $\Delta \phi$ together with the best fit of eqn (1) and (2) is also shown in the inset of Fig. 4(a). K_{11} is significantly higher than K_{33} in the entire N phase except very close to the NI transition, hence elastic anisotropy ($\Delta K = K_{33} - K_{11}$) is negative. K_{33} increases much slower than K_{11} with decreasing temperature and shows strong pre-transitional divergence as the SmA phase is approached. In case of calamitic liquid crystals with rigid rod-like molecules ΔK is mostly positive



Fig. 4 (a) Variation of splay (K_{11}) and bend (K_{33}) elastic constants in the N phase as a function of temperature. (inset) Retardation ($\Delta\phi$) as a function of applied voltage at T – T_{NI} = -4.5 °C. Continuous line in the inset is a theoretical fit to eqn(1) and (2). (b) Variation of rotational viscosity (γ_1) as a function of temperature. (inset) Variation of $\ln[\delta_o/\delta(t)]$ at two temperatures namely T – T_{NI} = -7.5 °C and -2.5 °C with best fits. Continuous red and green lines are drawn as a guide to the eye.

whereas in pure bent-core compounds and in their mixtures it has been found to be negative.^{8,32,33} It has been shown that the bentshape of the molecules facilitates bend distortion and as a result K_{33} is lower than K_{11} . The hockey stick-shaped molecule also has an asymmetric bent-shape and the present result is the manifestation of the same effect.

We also measured rotational viscosity (γ_1) in the N phase as a function of temperature by using the time dependent phasedecay method. Representative variation of $\ln[\delta_o/\delta(t)]$ with time (t) at two different temperatures together with the best fits are shown in the inset of Fig. 4(b). γ_1 increases as the temperature is lowered in the N phase and a change in curvature is observed at T $-T_{NI} \simeq -5$ °C suggesting a pre-transitional effect of the smectic short-range order in the N phase. γ_1 in this compound is slightly larger than in pure bent-core nematic liquid crystals¹⁶ and significantly higher than that of many known calamitic nematic liquid crystals and their mixtures.^{16,32} The larger rotational viscosity in this hockey stick-shaped compound partially may arise due to the effect of molecular weight compared to the calamitics. However in the case of bent-core compounds it was attributed to the existence of temporarily fluctuating smectic clusters of a few molecules in the N phase that are expected to originate from the restricted free rotation of the bent-core molecules along the long axis.9,15 Existence of such temporary clusters in the nematic phase is also revealed in rheological³⁴ and dynamic light scattering³⁵ studies and more recently in small angle X-ray studies.^{36–39} The hockey stick-shaped molecule can be considered as a highly asymmetric bent-core molecule and hence the enhanced rotational viscosity is believed to originate from the temporarily fluctuating clusters.

C. Dielectric relaxation

The hockey stick-shaped molecule has several dipolar groups which are oriented in different directions. Since $\Delta \varepsilon > 0$, it is anticipated that the molecule has relatively strong longitudinal dipole moment along the long axis and as a result ε_{\parallel} can relax at relatively low frequency. In the case of ε_{\perp} no dipolar relaxation was found up to 10 MHz. Variation of ε_{\parallel} as a function of frequency in the three phases at three different temperatures are shown in Fig. 5(a). It is observed that there are two relaxations, one is temperature dependent (below ~ 1 MHz) and the relaxation frequency decreases with decreasing temperature. The other one is above ~ 1 MHz frequency and temperature independent. The high frequency relaxation is temperature independent and is attributed to the relaxation due to the finite resistance of ITO which is even present in the empty cell. The low frequency relaxation is due to the longitudinal component of the molecular dipole moment of the long axis. Cole-Cole plots of the dielectric constant are shown in Fig. 5(b). They are semicircular with the centers on the x-axis suggesting that the relaxation is Debye type. Similar low frequency relaxations are also seen in other bent-core



Fig. 5 (a) Frequency dispersion of the real $(\varepsilon_{\parallel})$ (open symbols) and imaginary $(\varepsilon_{\parallel})$ (filled symbols) parts of the dielectric constant at three different temperatures namely 119 °C (N), 112 °C (SmA) and 104 °C (SmC_a). Continuous lines are theoretical fit to eqn (4). (b) Cole–Cole plot for ε_{\parallel} relaxation at the same temperatures. The centers of the semicircles lie on the ε_{\parallel} axis suggesting that the relaxation is Debye type. Dashed lines are theoretical fit to the Cole–Cole equation. The high frequency portion of the semicircles are due to the ITO cell relaxations.

compounds.⁴⁰ Since the relaxation region due to ITO is partially overlapped with dipolar relaxation we fitted complex dielectric constant ($\varepsilon(\omega) = \varepsilon'(\omega) - i\varepsilon''(\omega)$) as a function of frequency to find the exact dipole relaxation frequency. The complex dielectric function is given by

$$\varepsilon(\omega)^* = \varepsilon_2 + \frac{\varepsilon_o - \varepsilon_1}{1 + (i\omega\tau_1)^{1-\alpha_1}} + \frac{\varepsilon_1 - \varepsilon_2}{1 + (i\omega\tau_2)^{1-\alpha_2}}$$
(4)

where ε_o is the static dielectric permittivity, ε_i and τ_i are the frequency limits and relaxation times of the *i*th mode. α_i is the Cole–Cole distribution parameters of the respective modes.

It is found that both α_1 and α_2 are very small (<0.01) at all temperatures and the relaxation time τ_2 is independent of temperature as expected. The temperature variations of dielectric strength ($\varepsilon_0 - \varepsilon_{\infty}$) and relaxation time τ_1 with temperature are shown in Fig. 6. The dielectric strength increases rapidly in the N phase due to the increase in the orientational order and decreases sharply at the N-SmA transition (Fig. 6(a)). The sharp decrease below N-SmA transition is due to strong antiparallel correlation of the longitudinal components of the dipoles in the smectic phases as discussed earlier. τ_1 increases and varies linearly with the inverse of temperature (Fig. 6(b)) and can be fitted well with the Arrhenius equation, $\tau_1 = \tau_0 \exp(U/RT)$. The activation energy U of the N, SmA and SmC_a phases are 158, 117 and 127 kJ mol⁻¹, respectively. These values are comparatively higher than many calamatics in their respective phases.41,42 Similar behaviour was also reported very recently in a binary liquid crystal mixture (rod and bent-core) showing N-SmC_a phase transition.⁴⁰ Since the activation energy represents the energy barrier associated with the flip-over of the long molecular axis it suggests that the



Fig. 6 (a) Variation of dielectric strength $(\varepsilon_0 - \varepsilon_{\infty})$ with temperature. (b) Variation of relaxation time τ_1 as a function of 1/T. Dashed lines are theoretical fit to the equation $\tau_1 = \tau_0 \exp(U/RT)$. Vertical lines indicate the phase transition temperatures.

flip-over motion is relatively less easy in hockey stick or bent-core systems than in calamitic liquid crystals. Presumably this could arise due to the shape and larger rotational viscosity (Fig. 4(b)) of the hockey stick-shaped and bent-core compounds. However further investigations are needed to shine more light on this aspect.

IV. Conclusion

In conclusion, we have measured detailed physical properties of an unconventional liquid crystal with hockey stick-shaped molecules for the first time. All phase transitions are detected to be first order from optical and thermal (DSC) measurements. Dielectric measurements indicate that there exists antiparallel dipolar correlation of both the longitudinal and transverse components of dipole in the SmA and SmC_a phases. The bend elastic constant is significantly lower than splay elastic constant as seen in other bent-core nematic liquid crystals. Rotational viscosity is comparatively larger than calamitics and are influenced by pre-transitional smectic fluctuations. Dielectric relaxation of the longitudinal components of dipole moments is Debye type and the relaxation frequency exhibits Arrhenius behaviour with comparatively higher activation energy. Finally it may be asserted that some of the physical properties of hockey stickshaped compounds are noticeably different than that of calamitic liquid crystals and the shape is an important parameter for tuning the physical properties.

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