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Investigation of the viscoelastic properties of 4-propoxy-biphenyl-4-carbonitrile

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ABSTRACT

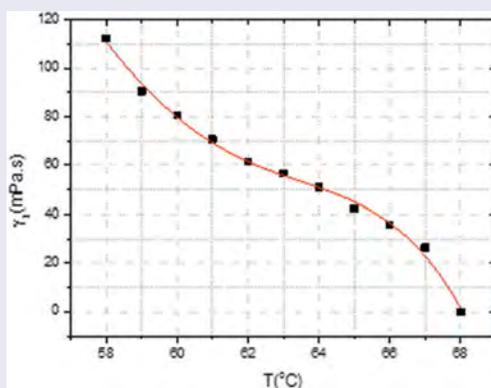
We report on the temperature-dependent measurements of dielectric permittivity, birefringence, elastic constants and rotational viscosity for 4-propoxy-biphenyl-4-carbonitrile in the nematic region. The temperature dependence of the three elastic constants was determined from studies of the Freédericksz transition. The thermal dependence of elastic constants shows features similar to the literature (bend > splay > twist). Elastic constants are proportional to the square of the order parameter. Temperature-dependent dielectric characterisation was carried out at a frequency of 10 kHz. The compound shows positive dielectric anisotropy in the nematic phase. The rotational viscosity is found to be relatively low. Temperature dependence of order parameter is estimated using Haller's method. The figure of merit was also calculated as a function of temperature.

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Liquid crystal; dielectric permittivity; birefringence; elastic constant; rotational viscosity; figure of merit



1. Introduction

Liquid crystals are of great interest for material science as well as for applied aspects [1–5]. Liquid crystals constitute molecules that organise into an intermediate state of matter between the liquid and the solid crystal during their phase transitions. Liquid crystal compounds show different mesophases, which are classified on the basis of the degree of molecular ordering. The simplest one is the nematic phase. On average, the orientation of individual molecules is parallel (or anti-parallel) to a preferred direction (\vec{n}). Nematic liquid crystals are characterised by long-range orientational order and the combination of their fluidity, optical anisotropy and sensitive to electric and/or magnetic fields [1–5]. The nematic liquid crystal materials are applied in various types of optical devices relying upon several properties for instance the elastic constants,

optical birefringence, rotational viscosity, dielectric constant, orientational order parameter etc. [1–3].

The homolog series of 4-alkoxy-4-cyanobiphenyl liquid crystal (*m*OCB) are particularly interesting and useful family of liquid crystal mesogens, where *m* refers to the number of methylenes in the substituent. 4-Alkoxy-4-cyanobiphenyl has a cyanobiphenyl part and an alkoxy chain. The presence of these alkoxy chains is very important in determining the physical properties of the liquid crystal phase [6–10]. The first four members of the series exhibit only a monotropic nematic phase, in which each case can be observed in a super-cooled state, whereas higher ones form enantiotropic nematic and/or smectic phases, since smectic phases are dominant over nematic phase for longer change members [10–16]. Several of them are utilised as components in commercially available liquid crystal mixtures. Since their molecular configurations are rather

simple and asymmetric, they are significant for practical use due to their durability over a large temperature region. Therefore, the most stable phases are found in commercially available powder samples stabilised by preserving at room temperature for a while. These chemical compounds are colourless and stable and have the highly polar nitrile group at one end of the molecule [6–13].

To our knowledge, there has not been a detailed and systematic study on the physical behaviour of 4-propoxy-biphenyl-4-carbonitrile with a strongly polar end group despite many structure behaviours being reported previously [6–34]. Recently, certain dimeric molecules, which comprise two mesogenic units joined by a flexible spacer, exhibit a phase transition from the standard nematic phase to a new type of nematic ground state, often referred to as the twist-bend nematic phase [35–39]. The organisation of the director in this novel phase has a helicoidal structure even though the constituent molecules themselves are effectively achiral. The director is tilted with respect to the helix axis and the spontaneous pitch length is typically around 10 nm. CB6OCB is an example of such liquid crystal dimer [40]. The aromatic and aliphatic parts of 4-propoxy-biphenyl-4-carbonitrile are nearly matched with one half of that. From the viewpoint of the above properties, it is much required to carry out the basic material parameters. Therefore, the aim of this work is to study the temperature dependence of the dielectric permittivity, optical birefringence, elastic constants, order parameter and rotational viscosity of 4-propoxy-biphenyl-4-carbonitrile.

2. Experimental section

2.1. Nematic material

The nematic material was obtained from BDH Ltd. and used without further purification. The phase transition

temperatures and textures were determined by placing the optical cell containing the material under a variable temperature control unit (Linkam hot stage) and a polarising microscope (Olympus BX51P). It exhibited the presence of monotropic nematic phase during cooling between approximately 68.1 and 56.9°C. The alkyl chain can readily rotate around the C–O bond and form an angle with cyano-biphenyl group in the nematic phase [6]. On heating, the material is converted into the isotropic liquid phase at 74.2°C. The chemical structure and microphotograph of 4-propoxy-biphenyl-4-carbonitrile were presented in Figure 1. The nematic phase exhibits a typical schlieren texture formed in cells with no alignment treatment at 65°C, having two- and four-brush defects.

2.2. Preparation for sample cell

For all electrical and electro-optic measurements, the transparent In-SnO₂ (ITO)-coated glass plates were used as electrodes. The effective area of planar and homeotropic cells was 25 mm², which have resistance less than 25 Ω. To promote an unidirectional high-quality planar orientation of the molecules, ITO plates were treated with polyimide PI2555 (HD Microsystems), baked at 90°C for 1 min and then baked at 275°C for 1 h. The uniform planar alignment was achieved by rubbing the substrates with a clean velvet cloth prior to cell construction and assembled one over another in an antiparallel fashion to form a capacitor. The pretilt angle in the planar substrate measured using the crystal rotation method was about 2°. Whereas to achieve homeotropic cells, ITO plates were treated with polyimide SE211 (HD Microsystems), baked at 90°C for 1 min and then additionally cured at 200°C for 1 h. Two plates of the cell were made with a UV-curable Norland adhesive NOA-65 containing glass beads as spacers, ensuring

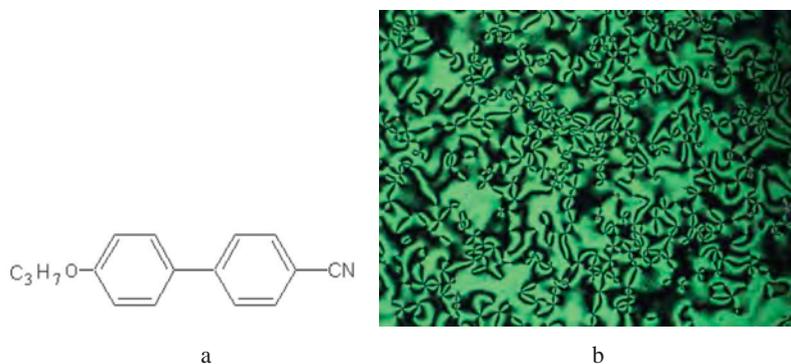


Figure 1. (Colour online) (a) The chemical structure of 4-propoxy-biphenyl-4-carbonitrile and (b) the photomicrograph ($\times 100$) of the schlieren texture in nematic phase at 65°C.

that the effective electrode area overlaps. The cell thickness of each cell was measured by an interferometric technique (Ocean Optic Inc.) with an accuracy of $\pm 1\%$ prior to filling the cell with a suspension. Typical cell thickness used for the experiments was approximately $8 \mu\text{m}$. The capacitance of the empty cell was measured before filling the sample as a standard reference. The empty cells were heated at a temperature of about at 10°C above the clearing point for 0.5 h and then were filled with the sample by means of the principle of capillary action. Excellent monodomain alignments were checked by use of polarising microscopy. The temperature was controlled by a Linkam hot stage LTS350 and a controller TMS94 to ensure a desired temperature of the measurements. The temperature was stable to within $\pm 0.1^\circ\text{C}$.

2.3. Dielectric measurements

Measurements of the dielectric permittivity were taken at a constant frequency of 10 kHz with the aid of a Solartron Schlumberger Impedance Analyzer SI1260 in combination with a Chelsea interface that measures complex values of impedance ($Z = \text{Re}(Z) + i\text{Im}(Z)$). i is the imaginary unit. The effective dielectric permittivity was calculated as $\varepsilon = 1/(C\omega\text{Im}(Z))$, where C_e and ω are the capacitance of the empty cell and the angular frequency of the applied electric field, respectively ($\omega = 2\pi f$). The operating frequency was lower than the relaxation of any dielectric mode for 4-propoxy-biphenyl-4-carbonitrile. The measuring voltage was 0.2 V, which was low enough to avoid non-linear effect as well as the molecular reorientation. The dielectric measurements were investigated with planar and homeotropic alignments of nematic molecules. All measurements were carried out step by step on decreasing the temperature without entering the crystalline phase, which enabled us to supercool the sample.

2.4. Elastic constant measurements

The Oseen–Frank elastic constants are key physical parameters in nematic liquid crystals and their values influence both the response times and threshold voltage of nematic liquid crystal devices [1–6]. The splay and bend elastic constants were determined from the variation of the material capacitance through the electric-field-induced Freédericksz transition technique [41,42]. Under equilibrium conditions, the molecules are oriented parallel to the substrate surface in a uniform planar configuration. Application of an external electric field for the planar liquid crystal cell, above a certain critical threshold voltage (V_{th}), induces a

reorientation of the nematic molecules, and the molecules are completely reoriented normal to the glass surface at high enough field. Therefore, V_{th} depends on the splay elastic constant K_{11} and dielectric anisotropy ($\Delta\varepsilon = \varepsilon_{//} - \varepsilon_{\perp}$) of liquid crystal

$$K_{11} = \frac{\varepsilon_0 \Delta\varepsilon V_{th}^2}{\pi^2} \quad (1)$$

ε_0 is the vacuum permittivity.

The relationship between the cell capacitance (C) and applied voltage (V) across the cell is introduced by Uchida [41],

$$\frac{V}{V_{th}} = \frac{2}{\pi} (1 + \chi \sin^2 \varphi_m)^{1/2} \int_0^{\varphi_m} \left[\frac{(1 + \kappa \sin^2 \varphi)}{(1 + \chi \sin^2 \varphi)(\sin^2 \varphi_m - \sin^2 \varphi)} \right]^{1/2} d\varphi \quad (2)$$

and

$$\frac{C}{C_{\perp}} = \frac{\int_0^{\varphi_m} \left[\frac{(1 + \kappa \sin^2 \varphi)(1 + \chi \sin^2 \varphi)}{(\sin^2 \varphi_m - \sin^2 \varphi)} \right]^{1/2} d\varphi}{\int_0^{\varphi_m} \left[\frac{(1 + \kappa \sin^2 \varphi)}{(1 + \chi \sin^2 \varphi)(\sin^2 \varphi_m - \sin^2 \varphi)} \right]^{1/2} d\varphi} \quad (3)$$

where $\kappa = (K_{33}/K_{11}) - 1$, $\chi = (\varepsilon_{//}/\varepsilon_{\perp}) - 1$, φ is the angle between the walls of the substrate and the director and φ_m is the director angle at the middle of the liquid crystal layer. C_{\perp} is the cell capacitance for $V < V_{th}$. When the applied voltage is much higher than V_{th} , the director at the centre of the cell becomes normal to the substrate plane. Then, the above equation reduces to

$$\frac{C(V) - C_{\perp}}{C_{//} - C_{\perp}} = C_R = 1 - \frac{2}{\pi} (1 + x)^{1/2} \int_0^1 \left[\frac{(1 + \kappa x^2)}{(1 + \chi x^2)} \right]^{1/2} dx \quad (4)$$

C_R is the reduced capacitance and $C_{//}$ is the capacitance of the cell by extrapolating to $V^{-1} \rightarrow 0$. Therefore, the variation of the voltage-dependent capacitance tends to saturate at high voltages. For strong surface anchoring for voltages V above V_{th} , K_{33} is fitted to the above equations by an iterative procedure using a computer-fitting program.

The sample capacitance was used by the use of an impedance gain analyser (Hewlett Packard, HP4284A) with an AC electric field of 10 kHz to determine K_{11} and K_{33} . The applied voltage was ramped from 0.01 to 2 V in 0.01 V steps (a delay time of 500 ms) and from 2 to 20 V in 0.1 V increment (a delay time of about 1 min). The delay time was 2 s for each applied voltage to enable the distortions to stabilise before any reading was taken. Any possible contribution owing to flexoelectricity in

the nematic sample was not taken into consideration. This procedure was repeated at various temperatures.

Twist deformation may be induced by an electric field in an in-plane switching (IPS) cell. K_{22} is directly related to the V_{th} by [43]

$$K_{22} = \frac{\epsilon_0 \Delta \epsilon d^2 V_{th}^2}{\pi^2 l^2} \quad (5)$$

Herein l is the electrode gap and d is the thickness of the cell in the in-plane device.

A homogeneously planar aligned IPS device was utilised to determine K_{22} . The IPS cell was treated with mechanically a rubbing direction perpendicular to the electrodes. The cell thickness was 8 μm . The electrode separation and width were 15 and 10 μm , respectively. The IPS cell was placed in a pair of crossed (linear) polarisers with the bottom polariser's transmission axis parallel to the liquid crystal rubbing direction. A He-Ne (laser wavelength, $\lambda = 632 \text{ nm}$) was used as the light source. The photo detector was Model 2031 (New Focus, USA). A signal generator (Tektronix, Model AFG3021C) was employed to apply voltage at a frequency of 10 kHz. A Babinet-Soleil compensator was utilised to control an additional optical phase retardation. The Fréedericksz transition was determined from the transmitted light intensity (at intervals of 10 s) as a function of applied voltage. The approximately linear portion of the transmittance-voltage curve was extrapolated to find the value of the V_{th} . The relative accuracy was much better than 20%.

2.5. Rotational viscosity measurements

The rotational viscosity depends upon the molecular moment of inertia, activation energy, intermolecular interactions, molecular structures and temperature. The switching times are proportional to the coefficient of rotational viscosity, which plays the important role in liquid crystal dynamic behaviour [1-6,44,45]. The phase-decay-time measurement method was used to determine the rotational viscosity by driving the planar liquid crystal cell with small excitation voltage. The sandwich cell was placed between two crossed polarisers oriented at an angle of 45° with respect to their extinction directions in order to get maximum light sensitivity. A linearly polarised He-Ne laser beam ($\lambda = 632 \text{ nm}$) was passed through the planar aligned ITO cell. The Babinet-Soleil compensator was employed to induce the desired optical phase change. A signal generator (Keithley, Model 3390) was utilised to apply voltage at 10 kHz. The photo detector (New Focus, Model 2031) was used to measure the transmitted light intensity and recorded digitally by a data

acquisition system (DAQ, PCI 6110) using LabVIEW. Under small angle approximation, a small voltage (V_b) corresponding to the first minima or maxima was applied depending on the transmission intensity such that the total phase retardation of sample was $n\pi$, where n is an integer number. At $t = 0 \text{ s}$, V_b was removed instantaneously from the liquid crystal cell and the relaxation transmission intensity change of the liquid crystal cell was measured with an oscilloscope (Tektronix, TDS-2014). The time-dependent transmittance at a particular temperature is given by [44]

$$I = I_0 \sin^2 \left(\frac{\delta_{tot} - \delta(t)}{2} \right) \quad (6)$$

where I_0 is the maximum intensity and δ_{tot} is the total phase change. The optical phase difference $\delta(t)$ for small director distortion can be approximated as $\delta(t) = \delta_0 \exp(-2t/\tau_o)$, where δ_0 (at $t = 0 \text{ s}$) is the total phase difference of a nematic liquid crystal under V_b not being far from V_{th} . By plotting $\ln[\delta_0/\delta(t)]$ against time (t), a straight line is expected. The slope of this straight line is equal to $2/\tau_o$ and τ_o is the free relaxation time of the liquid crystal layer. The rotational viscosity of nematic liquid crystal is calculated by $\gamma_1 = \tau_o K_{11} \pi^2 / d^2$. This procedure was conducted in the entire nematic range.

2.6. Birefringence measurements

Birefringence plays an important role in understanding the molecular reorientation mechanisms [1-5]. The birefringence was obtained through measuring the phase retardation. At a given temperature, the transmitted light intensity by the voltage-dependent optical phase retardation is given by

$$I(V) = I_0 \sin^2 \left(\frac{\pi d \Delta n}{\lambda} \right) \quad (7)$$

where $\Delta n = n_e - n_o$, n_e and n_o are the birefringence, extraordinary and ordinary refractive indices of the nematic sample, respectively. The intensity of transmitted light was measured as a function of applied voltage, from 0 to 20 V. The interference maxima were calculated and the total phase retardation of the cell was given the value of Δn . This procedure was repeated at various temperatures.

3. Result and discussions

In the molecule of 4-propoxy-biphenyl-4-carbonitrile, two main polar groups, C-O and -CN, can be

discriminated. These two groups give contributions to the resulting the permanent dipole moment and its direction does not correspond to exactly the same direction molecular long axis. The alkoxy chain is likely in an extended configuration in the nematic phase and the long molecular axis would be tilted to the line joining the centres of the two benzene rings [11,27,28]. In nematic phase, the molecular motions mainly involve rotation around the molecular long axis which is associated with the transverse dipole moment, rotation around the molecular short axis which involves the longitudinal dipole and the precession of the long axis around the director which also involves the longitudinal dipole. Thus, at least two dispersion regions related to the longitudinal (μ_l) and transverse components (μ_t) of the dipole moment occur in the dielectric spectrum [1–5]. Principal dielectric constants ($\epsilon_{//}$ and ϵ_{\perp}) of 4-propoxy-biphenyl-4-carbonitrile were measured at 10 kHz and their temperature variation is shown in Figure 2a. $\epsilon_{//}$ and ϵ_{\perp} are the permittivity measured for electric field along the director and perpendicular to the director, respectively. The dielectric permittivities in the isotropic phase are almost the same for planar and homeotropic alignment cells. As the temperature reaches at 67°C, the permittivity splits into different paths. The parallel component is larger than the perpendicular component of dielectric permittivity in the nematic phase, since greater contribution to dielectric permittivity comes from the parallel component as compared to the perpendicular component of dipole moment [1–5]. As the temperature is decreased into the isotropic–nematic transition, there is a discontinuity in $\epsilon_{//}$ and ϵ_{\perp} behaviours, which is consistent with the first-order phase transition. $\epsilon_{//}$

monotonically increases according to the decreasing temperature, as proposed by the Maier–Meier model [46]. However, ϵ_{\perp} decreases inversely (Figure 2(a)). The value of dielectric constant parallel to the molecular axis is about 18 near nematic to crystal transition as compared to the component perpendicular to the molecular axis (about 8). Since the molecules have quite strong axial dipole moment, the average value of the dielectric permittivities [$\epsilon_{av} = (\epsilon_{//} + 2\epsilon_{\perp})/3$] in the nematic phase near the transition is found to be lower than that of its extrapolated isotropic value, which can be ascribed to the antiparallel alignment of the molecules with their strong dipole moments in the nematic phase [46–52]. This is in accordance with the theory and the results reported by the earlier investigators for strongly polar liquid crystal materials [31,32,47]. In contrary, non-polar molecules, di-alkyl azobenzenes, do not exhibit such discontinuity due to the presence of short-range or nearest neighbour antiparallel correlations with a decrease in the long-range nematic ordering [52]. The large dielectric increment results from the large longitudinal dipole moment given by the –CN group [11,21,23,26–28]. The –CN group ($\mu_{CN} = 4.05\text{D}$), phenyl rings and C–O group ($\mu_{CO} = 0.8\text{D}$) give rise to the shift of the electronic cloud from the oxygen atom to the nitrogen one. Thus, the negative charge is settled down the nitrogen atom and the positive charge is located over the oxygen atom. The –CN bond of one molecule is found in the near vicinity of the C–O bond of the neighbour molecules [11,15,27,28]. The alkoxy chain does not stretch significantly further than the nitrogen from the polar –CN group of the neighbour molecules. Each molecule is characterised by an important dipole moment which is directed along the

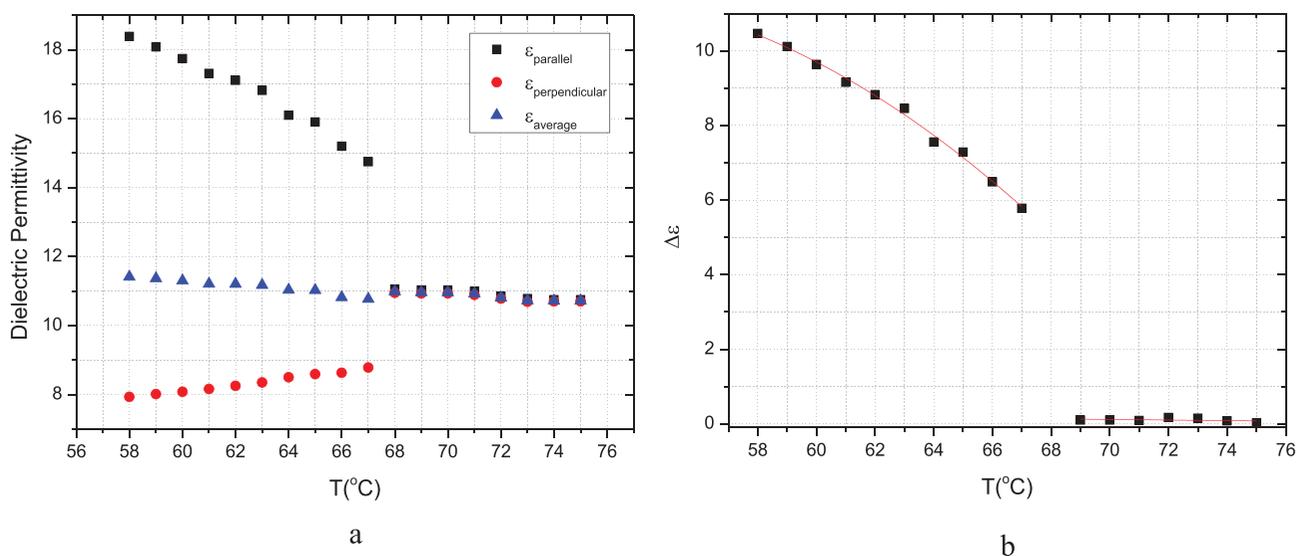


Figure 2. (Colour online) (a) The dielectric permittivity and (b) the dielectric of anisotropy $\Delta\epsilon$ of 4-propoxy-biphenyl-4-carbonitrile at 10 kHz. Solid lines are drawn as guides to the eye.

long axis [7,11,21,27]. X-ray diffraction studies exhibited that the mesophases have inter-digitated structures with overlapping of their core regions owing to the strong dipole moment of the $-\text{CN}$ group [18,31,32]. In addition, the rotations about the $\text{O}-\text{C}$, $\text{C}-\text{O}$ and $\text{C}-\text{C}$ bonds are limited [23,30]. The alkyl chain to the phenylene ring is hindered by a strong steric repulsion between the second methylene group of the chain and the hydrogen atom at the *ortho* position on the ring [15,17].

Dielectric anisotropy stands for the difference between the parallel and perpendicular components of the dielectric constant. The dielectric constant of a liquid crystal molecule is governed by the dipole moment and its relative position concerning the principal molecular axis. Thus, it is a vital parameter that influences the threshold voltage of a liquid crystal material and determines the interaction strength of the liquid crystal with the electric field [1–5]. The dielectric anisotropy of 4-propoxy-biphenyl-4-carbonitrile increases with decreasing temperature due to the increase in the degree of orientation of nematic liquid crystal and the density of substance (Figure 2(b)). Its value is positive across the entire nematic phase regime due to the presence of the strong permanent electric dipole moment of the end $-\text{CN}$ group directed almost parallel to the molecular long axis. It means that the conjugation of the $-\text{CN}$ group with the pentyl-substituted benzene ring allows the withdrawal of π -electrons from the benzene ring and gives rise to a permanent dipole oriented at an angle to the molecular long axis making a contribution to both components of the permanent dipole [28–30].

The curvature elastic constants of nematic material are affected by the orientational order, shape and conformation of molecules [1–6]. The elastic constants of 4-propoxy-biphenyl-4-carbonitrile as a function of temperature are shown in Figure 3(a). They exhibit a monotonic increase upon lowering temperature due to the enhanced ordering of the molecules and indicate the relative order $K_{33} > K_{11} > K_{22}$ in the absence of flexoeffects, analogous to the behaviour of most other rod-shaped molecules (calamitic liquid crystals) [53–62]. $K_{33} > 2K_{22}$ is valid. However, the order of the magnitude of elastic constants is sensitive to the molecular shape. The few bent-core liquid crystals and mixtures of rod-like and bent-core materials exhibit the opposite, i.e. $K_{11} > K_{33}$, which is naturally explained by the bend angle with the bend distortion and the existence of strong short range smectic clusters or cybotactic groups [63–65].

According to Priest, the mean field theory is referred as [66]

$$\frac{K_{11}}{\bar{K}} = 1 + \Delta - 3\Delta' \left(\frac{\bar{P}_4}{\bar{P}_2} \right) \quad (8)$$

$$\frac{K_{22}}{\bar{K}} = 1 - 2\Delta - \Delta' \left(\frac{\bar{P}_4}{\bar{P}_2} \right) \quad (9)$$

$$\frac{K_{33}}{\bar{K}} = 1 + \Delta + 4\Delta' \left(\frac{\bar{P}_4}{\bar{P}_2} \right) \quad (10)$$

where $\bar{P}_2 = S$, \bar{P}_4 represents the average value of the fourth Legendre polynomial and $\bar{K} = (K_{33}$

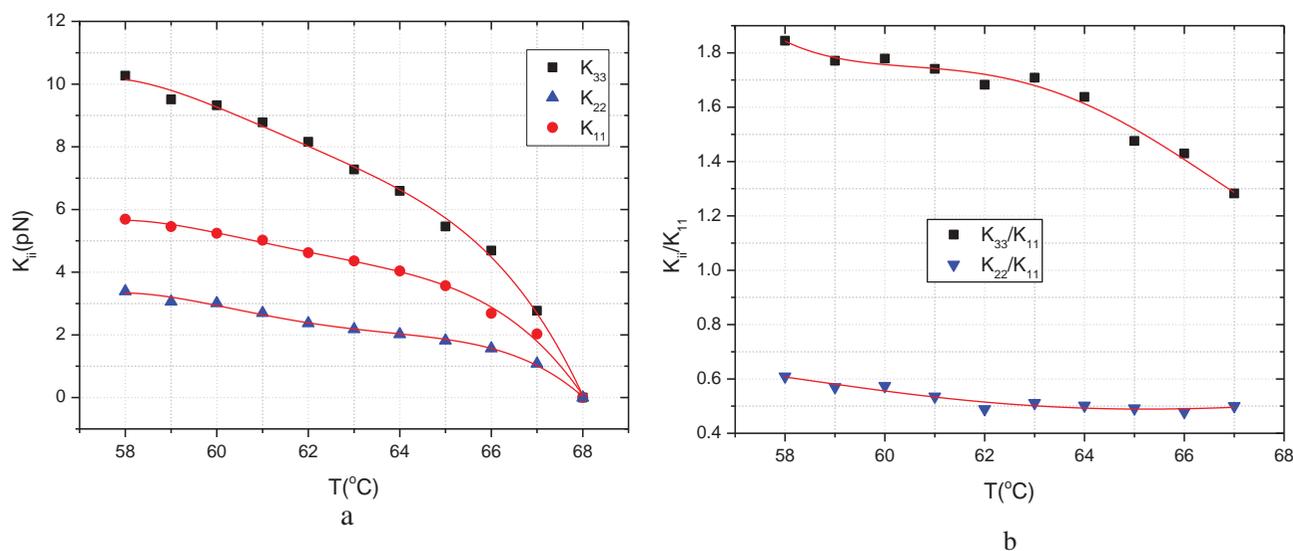


Figure 3. (Colour online) (a) Temperature dependence of elastic constants and (b) temperature variation of the elastic ratio. Solid lines are drawn as guides to the eye.

$+K_{22} + K_{11})/3 \sim \overline{P_2}^2$. The quantities of Δ and Δ' are constants depending on molecular properties.

$$\Delta = (2R^2 - 2)/(7R^2 + 20) \quad (11)$$

$$\Delta' = 27(R^2/6 - 1/6)/(7R^2 + 20) \quad (12)$$

$R = (l - b)/b$, l and b are the overall length and width of the spherocylinders, respectively.

It is found that the ratio of K_{33}/K_{11} is increased upon lowering temperature (Figure 3(b)), since $\overline{P_4}/\overline{P_2}$ decreases with increasing temperature [56]. $K_{33}/K_{11} \propto (L/W)^2$, where L and W are the length and the width of the liquid crystal molecule, respectively. The degree of molecular association is smaller at higher temperatures. Therefore, the L/W values of more single molecules are different than that of the associated molecular pairs. Flexible aliphatic chains probably increase the width more than the length of the molecule [60,61,66]. In addition, the value of L/W is decreased with increasing the degree of overlapping of the rigid molecule cores. It is well known that the two benzene rings of 4-propoxy biphenyl-4-carbonitrile are coplanar and are relatively rigid molecules consisting of a CN group, which influences the molecular interactions and the packing of the molecules [18]. Therefore, the effective length may become larger than the effective width with decreasing temperature and the strong intermolecular correlation exists in the nematic phase.

The ratios of K_{22}/K_{11} are more or less independent of temperature, which indicate that the temperature dependence of both constants is nearly the same. ($K_{22} < K_{11}$) is in satisfactory agreement with Equation 9 under the assumption of axial symmetry of the molecules.

The temperature-dependent variation of γ_1 is shown in Figure 4(a). Rotational viscosity increases with decreasing temperature in the nematic phase as expected due to increasing in the orientational order parameter (S). Its value is relatively low as compared to other nematic liquid crystals with a similar nematic temperature range [44,45,67].

The temperature dependence of γ_1 is fitted with the following Arrhenius-type expression using the values of the orientational order parameter (S) from birefringence measurement [45]

$$\gamma_1 = \gamma_o \text{Sexp} \left(\frac{-E_A}{k_B T} \right) \quad (13)$$

where E_A is the activation energy of the liquid crystalline material, k_B is Boltzmann's constant and T is the

temperature on the absolute scale. The variation of $\ln(\gamma_1)$ with $1/T$ is illustrated in Figure 4(b). From the slope of the curve, the associated activation energy can be evaluated. E_A is found to be about 92.4 ± 3.3 kJ/mol in the order of magnitude for conventional calamitic molecules [44,45,67].

Figure 5 exhibits the temperature variations in birefringence and order parameter of 4-propoxy-biphenyl-4-carbonitrile. On cooling from the isotropic phase, a sharp increment in Δn is observed at the isotropic to nematic phase transition due to the increase in the nematic order. Δn increases monotonically with decreasing temperature as observed for nematic system, reaching a maximum value of 0.2 near the transition to the crystal phase. Polar terminal CN group increases the birefringence by elongating the molecular conjugation and short flexible chain may give rise to large π -electron conjugation along the molecular axis [4].

The order parameter in nematic liquid crystals is one of the most important physical parameters which critically affect its performance in display devices, since the anisotropies of the dielectric, optical and magnetic properties depend on the order parameter in a more or less straight forward way [1–6]. The temperature variation of Δn of a liquid crystal can be expressed as $\Delta n = \Delta n_o (1 - T/T_1)^\beta$ [68], where β is the adjustable parameter, T_1 is the clearing temperature and Δn_o is the birefringence of the perfectly aligned nematic sample (at $T = 0K$). The exponent β depends on molecular structure and β is ~ 0.19 instead of 0.5, which is predicted by mean-field theory. Similar value of β was reported in many other liquid crystals [44,69–71]. The orientational order parameter (S) is the average value of $\frac{3}{2}(\cos^2\theta - 1)$ and θ is the angle between the effective long molecular axis and the director. Therefore, the increment in θ might be due to increase in S . S is estimated via the relation $S(T) \approx \Delta n(T)/\Delta n_o$. On cooling the sample, the value of S was monotonically increased similar to $\Delta \epsilon$ in Figure 2 (b). S is responsible for the decrease in $\Delta \epsilon$. To understand the relationship between the order parameter and the elastic constants, we plotted the variation of elastic constants (K_{ii}) as a function of Δn in Figure 6. K_{ii} was fitted with Δn^x . We obtained $K_{33} \propto \Delta n^{2.77}$, $K_{22} \propto \Delta n^{2.37}$ and $K_{11} \propto \Delta n^{2.27}$, respectively. In the mean field theory, curvature elastic constants are proportional to the square of the orientational order parameter [3,4]. The fitted lines show good overall agreement between the experimental results and theoretical prediction [4].

Figure of merit (FoM) is mostly used to compare the performance of a liquid crystal compound or mixture since it is independent of the cell gap [72].

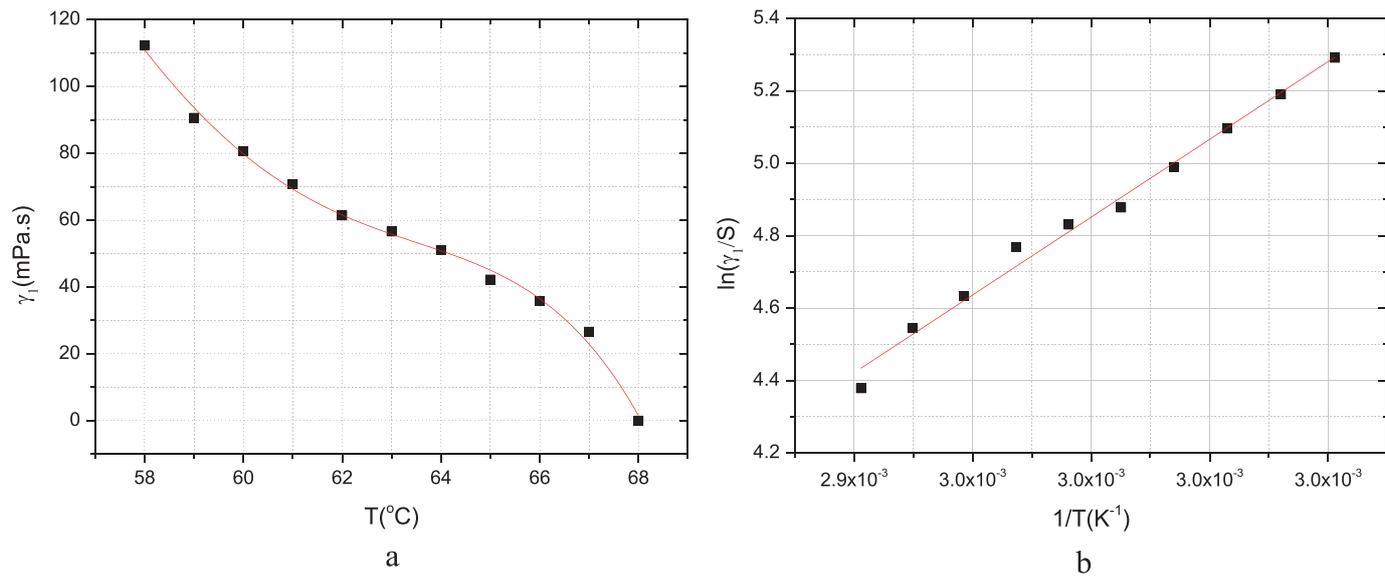


Figure 4. (Colour online) Variation of the rotational viscosity (γ_1) of 4-propoxy-biphenyl-4-carbonitrile as a function of temperature. Solid lines are drawn as guides to the eye.

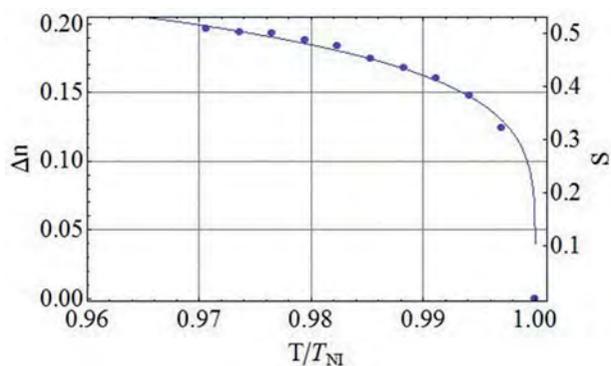


Figure 5. (Colour online) Optical birefringence (Δn) and order parameter (S) as a function of temperature. Solid lines are drawn as guides to the eye.

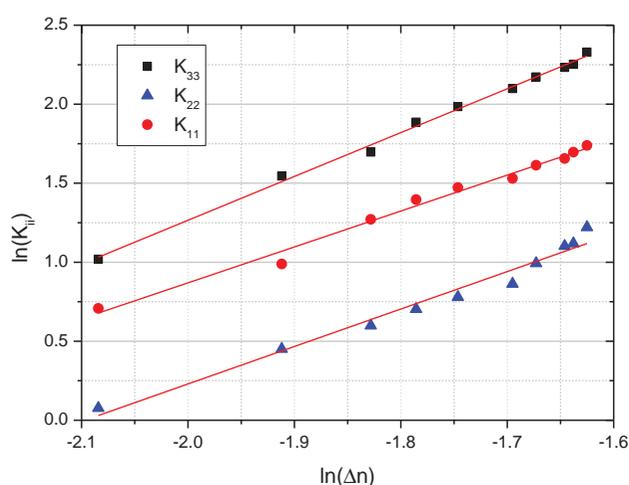


Figure 6. (Colour online) Variation in K_{ij} as a function of Δn . Solid lines are linear fit to the data points.

To characterise the performance of the liquid crystal materials, we estimated FoM by using the following formula: $FoM = K_{33}\Delta n^2/\gamma_1$ as a function of temperature. The FoM values also allow determination of the ideal operating temperature range. Figure 7 exhibits the temperature variation of the FoM. The FoM increases gradually prior to reaching the optimal operation temperature (62°C) and then decreases steeply when the temperature approaches the clearing temperature.

4. Conclusions

We have measured the birefringence, dielectric, rotational viscosity and curvature elastic properties of 4-propoxy-biphenyl-4-carbonitrile as functions of temperature. The material exhibits a relatively large positive dielectric anisotropy due to the contribution of the permanent dipole moment of the $-\text{CN}$ group. On

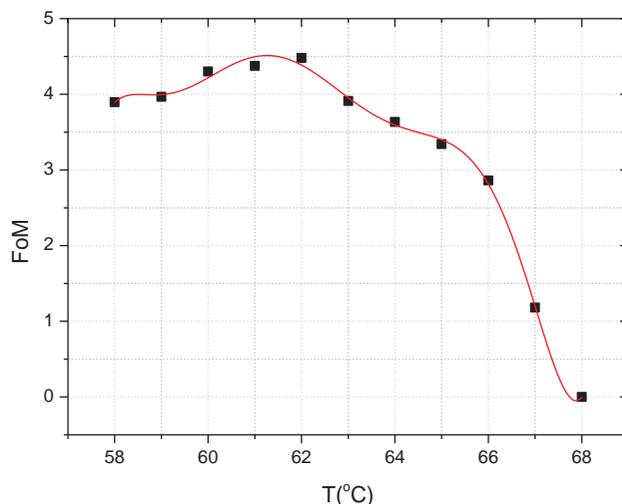


Figure 7. (Colour online) Temperature variation of figure of merit (FoM) at $\lambda = 633$ nm. Solid lines are drawn as guides to the eye.

transition from the isotropic to the nematic phase, the average permittivity is seen to decrease as temperature is reduced on account of the antiparallel association of the dipole moment in the nematic phase of the liquid crystals. As expected, all three elastic constants decrease with increasing temperature and exhibit the relative order $K_{33} > K_{11} > K_{22}$. The ratio K_{33}/K_{11} is greater than 1 and dependent on the temperature. The length of the molecule may become larger than the effective width of that due to the presence of short flexible alkyl chain. However, the ratio K_{22}/K_{11} is almost temperature independent throughout the entire nematic phase. The temperature dependence of the birefringence is well fitted by the Haller model for estimation in the orientation order. The rotational viscosities from the phase-decay-time method gradually increase with decrease in temperature. The values are relatively low in comparison to other nematic liquid crystals within similar nematic temperature range due to the geometrical structure of the molecule and the distribution of electron density [59]. Therefore, this type of compound was helpful for preparing of practical liquid crystal mixtures. Additionally, such experimental results may lead to a better understanding of the physical properties of the cyanobiphenyl-based liquid crystal dimers and help in designing future compounds with desirable material characteristics for practical applications.

Disclosure statement

No potential conflict of interest was reported by the authors.

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