Rotational Viscosity of a Bent-Core Nematic Liquid Crystal

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We report the detailed measurements of the rotational viscosity (γ_1) of a bent-core nematic liquid crystal exhibiting positive dielectric anisotropy by measuring the decay time of the optical phase retardation of the sample. In the nematic phase, $\gamma_1 \simeq 0.25$ Pa s (e.g., at $T/T_{NI} \simeq 0.92$, where T_{NI} is nematic to isotropic phase transition temperature.), which is only slightly larger than the values known for several conventional calamitic nematic liquid crystals. γ_1 starts to increase rapidly below a reduced temperature $T/T_{NI} \simeq 0.9$ showing the effect of short-range smectic fluctuations. The temperature dependence of γ_1 far from the nematic to smectic-C transition temperature is fitted well with the Osipov–Terentjev theory.
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The several physical properties of thermotropic liquid crystals are optimized for practical applications. Among them, rotational viscosity γ_1 is a very important parameter that governs the response time of liquid crystal devices (LCDs). It depends upon the molecular structures, intermolecular interactions, and temperature. There are several experimental and theoretical studies[1–6] on the rotational viscosity of nematic liquid crystals with rod-shaped molecules (calamitic liquid crystals). The interest in studying and understanding the structure-property relation in bent-core liquid crystals has increased recently. Various physical properties, such as flexoelectric coefficient,[7] electroconvection,[8,9] Kerr effect,[10] and elastic constants,[11] have been measured and reported to be significantly different from those of known conventional calamitic liquid crystals. A significant contribution of the bent shape and the intermolecular association is revealed in many of these physical properties. Recently, the rotational viscosity and flow viscosity of a bent-core nematic liquid crystal with negative dielectric anisotropy have been measured by Dorjgotov *et al.*[12] by using pulsed magnetic field and electrorotation, respectively. They reported that the rotational viscosity γ_1 is almost 10 times and the flow viscosity is 100 times larger than those of the conventional calamitic liquid crystals. In this paper, we report the measurement of γ_1 of a bent-core nematic liquid crystal with positive dielectric anisotropy as a function of temperature by using the decay time measurement of the phase retardation of liquid crystal cells. We show that the rotational viscosity for the present compound is only slightly larger than that for the calamitic nematic, and the effect of strong short-range smectic fluctuations arises as the temperature is reduced. The temperature-dependent data can be fitted well with the Osipov–Terentjev[4] theory that gives rise to the activation energy similar to the values of calamitic liquid crystals.

We used phase-decay-time measurement of a parallel-aligned liquid crystal (LC) cell under small excitation voltage. Two indium–tin-oxide-coated glass plates were spin-coated with alignment layer AL-1254 and cured for one hour at 180 °C and rubbed antiparallel to make planar cells. The thickness was measured with a spectrometer by the
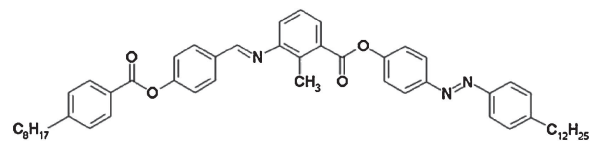
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Fig. 1. Chemical structure of the bent-core molecule used in the experiment.

interferometric method, and the typical cell thickness used in the experiment was 10.3 µm. The cell was filled with the sample in the isotropic phase by using capillary action, and good alignment was observed. The chemical structure of the compound used in the experiment is shown in Fig. 1. It exhibits the following phase transitions: Sm-C 118.5 °C N 176.5 °C I. The Instec (mK1000) temperature controller was used for controlling the temperature of the LC cell with an accuracy of less than 0.1 °C. A He–Ne laser ($\lambda = 632.8$ nm) was used as a light source. The cell was kept between two crossed Glan–Thompson polarizers, and the rubbing direction was made 45° to both the polarizer and analyzer.[5] A signal generator (Tektronix AFG3102) was used to apply a voltage at a frequency 4.111 kHz, and a photomultiplier tube (Hamamatsu H6780-01) was used as a detector to measure the time-dependent transmitted intensity. A small voltage (V_b) corresponding to the first maxima or minima was applied depending on the transmission intensity, such that the total phase retardation of the sample was $n\pi$. At time $t = 0$, the bias voltage (V_b) was removed and the relaxation transmission intensity change of the liquid crystal cell was measured with an oscilloscope (Tektronix TDS 2012B). This procedure was repeated for several temperatures in the entire nematic phase. The time-dependent intensity at a particular temperature is expressed as[3]

$$I(t) = I_0 \sin^2\left[\frac{\Delta_{tot} - \delta(t)}{2}\right], \qquad (1)$$

where I_0 is the maximum intensity change and Δ_{tot} is the total phase difference. The phase difference $\delta(t)$ for small director deformation can be approximated as

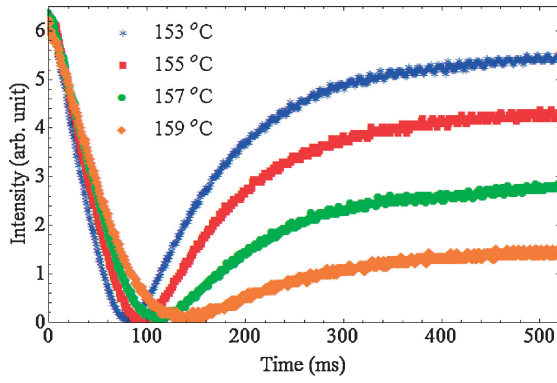$$\delta(t) = \delta_0 \exp\left(-\frac{2t}{\tau_0}\right), \qquad (2)$$

Fig. 2. Time dependent transmission intensity after the removal of the bias voltage V_b at some temperatures.
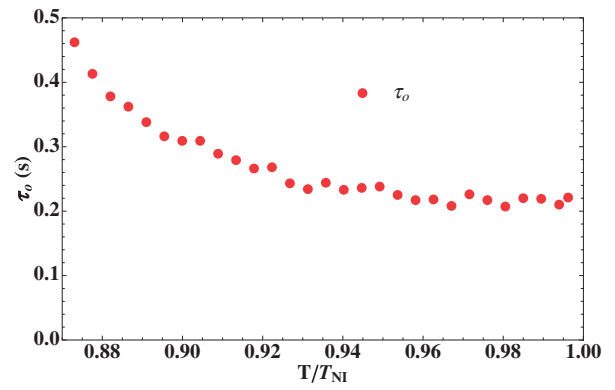

Fig. 4. Variation of the measured relaxation time τ_0 (squares) as a functions of temperature.
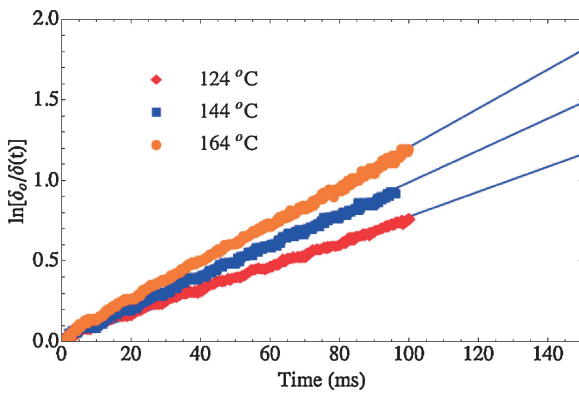

Fig. 3. Linear variation of $\ln[\delta_0/\delta(t)]$ with time (t) at various temperatures. Solid lines are theoretical fits to the experimental data.
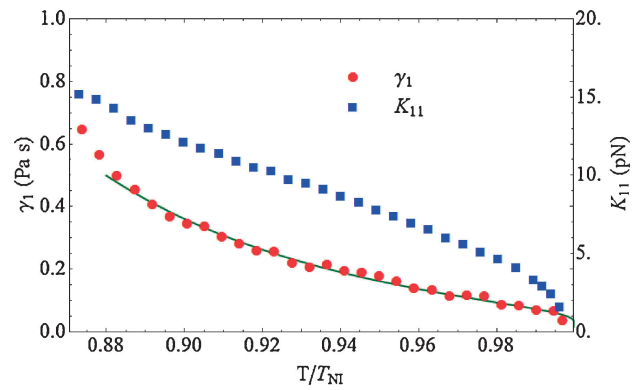

Fig. 5. Variation of measured rotational viscosity (circles) and splay elastic constant K_{11} (squares) obtained from ref. 11 as a function of temperature. Solid line is a fit to the theoretical eq. (5).

where δ_0 is the total phase difference of the liquid crystal under bias voltage (V_b), which is not far from the Freedericksz threshold voltage (V_{th}). In case δ_0 is close to $n\pi$, $\delta(t)$ becomes

$$\delta(t) = \delta_0 \exp\left(-\frac{4t}{\tau_0}\right). \quad (3)$$

The slope of the plot $\ln[\delta_0/\delta(t)]$ with time (t) yields the relaxation time (τ_0). The rotational viscosity (γ_1) of the liquid crystal is obtained as

$$\gamma_1 = \frac{\tau_0 K_{11} \pi^2}{d^2}, \quad (4)$$

where d is the thickness of the liquid crystal sample and K_{11} is the splay elastic constant. K_{11} is obtained from the Freedericksz transition given by $K_{11} = \epsilon_0 \Delta\epsilon (V_{th}/\pi)^2$, where V_{th} is threshold voltage and $\Delta\epsilon$ is the dielectric anisotropy.

The time-dependent transmission intensity at various temperatures is shown in Fig. 2. The phase difference $\delta(t)$ is estimated by using eq. (1). Some representative variations of $\ln[\delta_0/\delta(t)]$ with time (t) at various temperatures are shown in Fig. 3. The variation is linear as predicted using eq. (2). The slope ($2/\tau_0$) is obtained as a fit parameter. The relaxation time τ_0 is measured in the entire nematic phase at various temperature. The variation of relaxation time τ_0 as a function of temperature is shown in Fig. 4. It is observed that near the NI transition, the relaxation time τ_0 is $\simeq 0.22$ s

and gradually increases with decreasing temperature, and tends to diverge as the smectic-C (Sm-C) phase is approached. The temperature-dependent splay elastic constant (K_{11}) data were collected from our previous measurements ref. 11 to estimate the rotational viscosity (γ_1) at various temperatures. It may be pointed out that we also measured the pretilt angle (θ_p) in the nematic phase at a few temperatures by crystal rotational method (CRM).[13] The pretilt angle is very small for example; $\theta_p \simeq 1°$ at $T_{NI} - T = 10°$. Similar values were also reported by Le *et al.* on other bent-core nematic liquid crystals.[14] This suggests that the surface anchoring is sufficiently strong and the present rotational viscosity measurements are not affected by the pretilt angle.

The temperature-dependent variation of γ_1 is shown in Fig. 5. It is noted that the value of γ_1 is about 0.1 Pa s or less near the NI transition and increases superlinearly to 0.35 Pa s with decreasing temperature until the reduced temperature $T/T_{NI} \sim 0.9$, and then tends to diverge before the N-to-Sm-C transition occurs. The measurement of γ_1 of a bent-core nematic liquid crystal with negative dielectric anisotropy by pulsed magnetic field was reported by Dorjgotov *et al.*[12] According to their report, the rotational viscosity is almost 10 times larger than those of calamitic liquid crystals. Such larger rotational viscosity was attributed to the formation of temporary clusters owing to the bent shape of the molecules in the sense that the bent shape and transverse

dipole moment of the molecules together facilitate the formation of clusters. On the other hand, the present compound exhibits positive dielectric anisotropy, and the value of γ_1 is slightly larger by a factor of two or three (far from the NI transition) compared with that in many calamitic liquid crystals, suggesting that the formation of temporary clusters is not significant in the present bent-core compound.

Furthermore, the close proximity in the values and temperature dependencies of γ_1 data of the present bent-core compound with those of the calamitic materials urges us to consider and compare the experimental results with the known theories. For example, in the case of rod like molecules in the uniaxial nematic phase according to Osipov and Terentjev,[4] the rotational viscosity is given by

$$\gamma_1 = g_0 \left(\frac{T}{T_c}\right)^4 \left(\frac{E_1}{K_B T_c}\right)^{-3} \left(\frac{J_0 S}{k_B T_c}\right)^{1/2} \exp\left(\frac{E_1 + J_0 S}{k_B T}\right), \quad (5)$$

where g_0 is a constant, $J_0 = B k_B T_c$, E_1 is the activation energy, and S is the order parameter. The temperature-dependent γ_1 can be well fitted to the above equation up to $T/T_{NI} = 0.88$ with the fit parameters $g_0 = 1.9 \times 10^{-4}$ Pa s, $J_0 = 48.5$ meV, and $E_1 = 0.525$ eV. The fitting of the experimental data with the above equation is shown in Fig. 5, showing a very good fit. The fit parameters are comparable to the values known for many calamitic liquid crystals.[5]

Finally, we want to briefly comment on the temperature dependence of γ_1. Prasad *et al.*[15] had reported a uniaxial-to-biaxial nematic transition at $T/T_{NI} \sim 0.93$, though later on, Le *et al.*[16] showed that the medium is uniaxial. Again, recently, Yoon *et al.*[17] have claimed the existence of the transition. It is clear, however, that there is no indication of the transition at the temperature $T/T_{NI} \sim 0.93$. Moreover, the temperature dependence of the rotational viscosity was well fitted to the Osipov–Terentjev theory[4] over a wide temperature range, including the suggested transition temperature $T/T_{NI} \sim 0.93$. An upward deviation from the Osipov–Terentjev theory at lower temperature was also observed in calamitic liquid crystals,[5] and was explained by the pretransitional effect when approaching the crystal phase. We can also attribute the deviation below ($T/T_{NI} \sim 0.9$) to the effect of short-range smectic fluctuations. Thus, a rapid increase in τ_0 and, hence, the γ_1 is due to the onset of the smectic short-range fluctuations in the nematic phase.

In conclusion, we showed that the values and temperature dependence of rotational viscosity in a bent-core nematic liquid crystal with positive dielectric anisotropy near the NI transition are comparable to those in calamitic liquid crystals. The temperature dependence of rotational viscosity shows a strong effect of smectic short-range-order fluctuations. The temperature-dependent viscosity data prior to the onset of smectic fluctuations can be fitted well with the Osipov–Terentjev theory. Such bent-core compounds may be useful as a component in the calamitic nematic mixtures to access partially some of the extraordinary physical properties of pure bent-core materials, such as the large flexoelectric coefficient, Kerr coefficient, and negative elastic anisotropy ($K_{33} - K_{11}$), to optimize for practical application.

1) A. C. Diogo and A. F. Martins: Mol. Cryst. Liq. Cryst. **66** (1981) 133.
2) N. Kuzuu and M. Doi: J. Phys. Soc. Jpn. **52** (1983) 3486.
3) S. T. Wu and C. S. Wu: Phys. Rev. A **42** (1990) 2219.
4) M. A. Osipov and E. M. Terentjev: Z. Naturforsch. A **44** (1989) 785.
5) M. L. Dark, M. H. Moore, D. K. Shenoy, and R. Shashidhar: Liq. Cryst. **33** (2006) 67.
6) S. T. Wu: J. Appl. Phys. **60** (1986) 1836.
7) J. Harden, B. Mbanga, N. Eber, K. Fodor-Csorba, S. Sprunt, J. T. Gleeson, and A. Jakli: Phys. Rev. Lett. **97** (2006) 157802.
8) D. Wiant, J. T. Gleeson, N. Eber, K. Fodor-Csorba, A. Jakli, and T. Toth-Katona: Phys. Rev. E **72** (2005) 041712.
9) S. Tanaka, S. Dhara, B. K. Sadashiva, Y. Shimbo, Y. Takanishi, F. Araoka, K. Ishikawa, and H. Takezoe: Phys. Rev. E **77** (2008) 041708.
10) S. Dhara, F. Araoka, M. Lee, K. V. Le, L. Guo, B. K. Sadashiva, K. Song, K. Ishikawa, and H. Takezoe: Phys. Rev. E **78** (2008) 050701(R).
11) P. Sathyanarayana, M. Mathew, Q. Li, V. S. S. Sastry, B. Kundu, K. V. Le, H. Takezoe, and S. Dhara: Phys. Rev. E **81** (2010) 010702(R).
12) E. Dorjgotov, K. Fodor-Csorba, J. T. Gleeson, S. Sprunt, and A. Jákli: Liq. Cryst. **35** (2008) 149.
13) T. J. Scheffer and J. Nehring: J. Appl. Phys. **48** (1977) 1783.
14) K. V. Le, S. Dhara, B. K. Sadashiva, Y. Takanishi, and H. Takezoe: Jpn. J. Appl. Phys. **45** (2006) L1013.
15) V. Prasad, S.-W. Kang, K. A. Suresh, L. Joshi, Q. Wang, and S. Kumar: J. Am. Chem. Soc. **127** (2005) 17224.
16) K. V. Le, M. Mathews, M. Chambers, J. Harden, Q. Li, H. Takezoe, and A. Jakli: Phys. Rev. E **79** (2009) 030701(R).
17) H. G. Yoon, S. W. Kang, R. Y. Dong, A. Marini, K. A. Suresh, M. Srinivasarao, and S. Kumar: Phys. Rev. E **81** (2010) 051706.