PHYSICAL REVIEW E **78**, 050701(R) (2008)

Kerr constant and third-order nonlinear optic susceptibility measurements in a liquid crystal composed of bent-shaped molecules

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(Received 21 August 2008; published 19 November 2008)

We report the determination of the Kerr constant (B) and the real part of the third-order nonlinear optic susceptibility ($\chi^{(3)}$) above the nematic-isotropic phase transition temperature (T_{NI}) of a liquid crystal composed of bent-shaped molecules. The values of B and $\chi^{(3)}$ just above ($\sim 0.3\ °C$) T_{NI} are $\sim 8\times 10^{-12}\ \mathrm{m/V^2}$ and $5\times 10^{-20}\ \mathrm{m^2/V^2}$, respectively. The estimated critical temperature T_C^* is about 1.5 °C below T_{NI} indicating that the nematic-isotropic (NI) transition is weakly first order as in the case of calamitic liquid crystals. The temperature-dependent Kerr constant is found to be in good agreement with the predictions of the Landau–de Gennes theory. The experimental results are compared with those in a calamitic liquid crystal material with negative dielectric anisotropy in the nematic phase.

DOI: 10.1103/PhysRevE.78.050701 PACS number(s): 77.84.Nh, 78.20.Jq, 61.30.Gd, 42.65.Hw

The electro-optical studies on liquid crystals are important both from the technological as well as fundamental points of view. The main objective of such studies is to manipulate the optical properties with the help of an applied electric field or to investigate the correlation between the molecular structure and electric, optical properties. Most of the investigations have been made in the liquid crystalline phase. The effect of short-range order and the fluctuation of orientational order parameter just above the nematic (N) to isotropic (I) transition temperature (T_{NI}) have been theoretically discussed by de Gennes [1]. Since then the interest on the Kerr effect in the isotropic phase of liquid crystalline materials has increased many folds to search for new materials with large Kerr constants and nonlinear optic susceptibility. The number of experimental reports on the electro-optical Kerr effect of calamitic liquid crystals are too large to be cited here in full. In all of these studies the effect of molecular structures, permanent dipole moments, etc., on the short-range order in the isotropic phase has been discussed.

The discovery of electro-optical switching in bent-core liquid crystals has created immense interest in the scientific community [2]. Recently some interesting experimental results are reported on the nematic as well as above the nematic-isotropic phase transition temperature of bent-core liquid crystals. Domenici *et al.* [3] have reported about the alignment of the bent-core molecules under magnetic fields [3]. The critical behavior of the NI transition has been investigated by Wiant *et al.* [4] from magnetic birefringence and light scattering experiments. A nonstandard electroconvection in the nematic phase has been reported by Tanaka *et al.* [5] and Wiant *et al.* [6]. Very recently Wiant *et al.* has also observed a transition between two optically isotropic phases above the clearing point, which is explained by a model for tetrahedratic orientational order in bent-core liquid crystal [7]. All of these reports show that there are some unconventional aspects of NI transition of bent-core liquid crystals than calamitic liquid crystals though the transitions are similar from the symmetry point of view. These studies inspired us to carry out the Kerr measurements on bent-core liquid crystal exhibiting NI transition. There are also various types of interesting electro-optical studies in the mesophases exhibited by such compounds owing to the shape, polarity, and chirality [8,9]. However, there is no report on the measurement of Kerr constant and nonlinear static susceptibility above T_{NI} in liquid crystals composed of bent-core or bent-shaped molecules exhibiting the direct nematic to isotropic transition. The Kerr effect measurements are important to find the effect of bent-shaped structure on the short-range order and fluctuation of orientational order parameter in the isotropic phase of bent-core liquid crystals that show the direct nematic to isotropic phase transition. In this Rapid Communication we present the measurement of the electro-optical Kerr constant (B) and the third-order nonlinear susceptibility ($\chi^{(3)}$) of a bent-core liquid crystal in the isotropic phase.

The chemical structure of the compound is shown at the top of Fig. 1. The details of the synthetic scheme will be reported elsewhere [10]. The compound exhibits the following phase sequence: Cry-97.0 °C-(Col$_r$-81.5 °C)-N-107.2 °C-I. We prepared sandwiched cells with comb-type interdigited electrodes on one of the substrates. The cell thickness (l) was $\sim 2\ \mu$m. The width of each stripe in the comb was 10 μm and the gap between the two consecutive stripes was 15 μm. For Kerr effect measurements, a He-Ne laser ($\lambda = 632.8$ nm) was used to illuminate the cell. The Kerr cell was kept between crossed polarizers making the direction of an applied field 45° with respect to the polarizer. An

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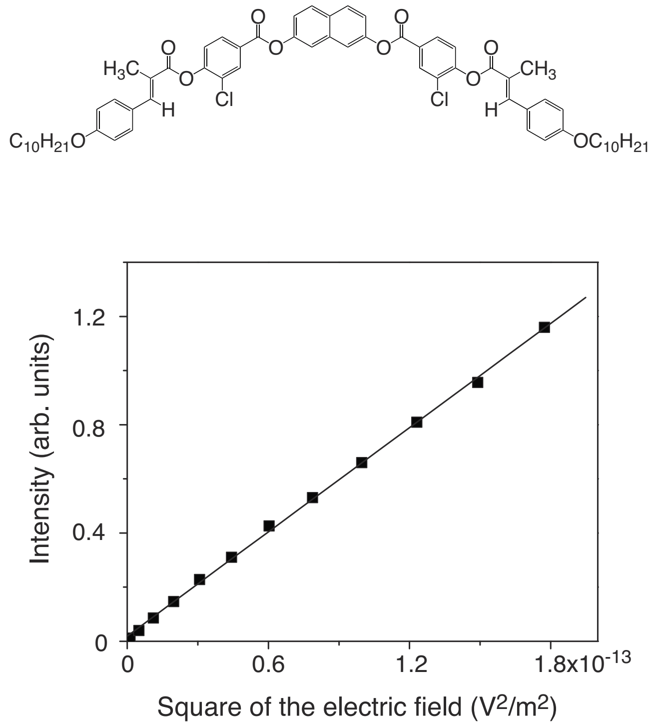

FIG. 1. Transmitted intensity of the modulated signal (I_{ac}) as a function of square of the applied field measured at a frequency 2 kHz. The solid line is the best fit obtained from a least-mean-squares method. The sample used is also shown at the top of the figure.

ac high field of a frequency $f=1$ kHz was applied to the cell. The introduction of a $\lambda/4$ plate between the analyzer and the cell enables us a linear detection of the modulated ac component of the transmittance (I_{ac}) due to the electric-field-induced birefringence (Δn) in the sample. The second-harmonic component ($2f=2$ kHz) of the transmitted intensity was amplified by a lock-in amplifier. The dc component was measured with a digital multimeter. The induced optical phase difference δ was estimated by using the relation [11]

$$\delta = \frac{2\pi l \Delta n}{\lambda} = \frac{I_{\mathrm{ac}}}{I_{\mathrm{dc}}}. \tag{1}$$

According to the Kerr law, Δn is given by

$$\Delta n = B\lambda E^2, \tag{2}$$

where B is the Kerr constant. Since nonvanishing elements of a static third-order nonlinear susceptibility tensor $\chi^{(3)}$ in the present system are $\chi^{(3)}_{1111}$, $\chi^{(3)}_{1122}$, $\chi^{(3)}_{1212}$, and $\chi^{(3)}_{1221}$, where $\chi^{(3)}_{1111}=\chi^{(3)}_{1122}+\chi^{(3)}_{1212}+\chi^{(3)}_{1221}$, Δn at a static field $E(0)$ is given by [12]

$$\Delta n = (24\pi/n)[\chi^{(3)}_{1212}(\omega_1,-\omega_1,0,0) + \chi^{(3)}_{1221}(\omega_1,-\omega_1,0,0)]E^2(0), \tag{3}$$

where n is the refractive index of the sample. Using Eqs. (2) and (3) the Kerr constant can be written as

$$B = (24\pi/n\lambda)[\chi^{(3)}_{1212}(\omega_1,-\omega_1,0,0) + \chi^{(3)}_{1221}(\omega_1,-\omega_1,0,0)]. \tag{4}$$

By applying the Kleinman symmetry [13] due to the experimental far resonance condition in the isotropic medium we can write

$$\chi^{(3)}_{1212} = \chi^{(3)}_{1221} \equiv \chi^{(3)}. \tag{5}$$

Thus the nonlinear susceptibility can be estimated by

$$B = (48\pi/n\lambda)\chi^{(3)}. \tag{6}$$

The refractive index of the compound in the isotropic phase was measured as a function of temperature by using interference fringes of the reflected light from empty and filled cells. Using the experimental values of B and n we calculated $\chi^{(3)}$ at various temperatures above T_{NI}.

In order to confirm the appropriateness of using 2-μm-thick cells, first we measured the modulated ac transmitted intensity from different cell thicknesses of a standard compound 5CB. It was found that at a fixed temperature the intensity scarcely depended on the cell thickness despite that the linear dependence is expected by Eq. (1), indicating that the in-plane field in comb-type cell is confined within a thin layer. The Kerr constant was also measured using a 2-μm-thick cell as a function of temperature and a good agreement was found with the previously reported measurements at all temperatures [14,15]. Therefore, we used thickness of ~ 2 μm for all of the measurements.

Next the modulated ac signal intensity was measured as a function of square of the field up to $\sim 1.8\times 10^{13}$ $\mathrm{V}^2/\mathrm{m}^2$. In further experiments, however, we restricted our measurements upto $\sim 1.8\times 10^{12}$ $\mathrm{V}^2/\mathrm{m}^2$ which is 10 times smaller to avoid any thermal and chemical degradation under high and prolonged applied field in the isotropic phase. The linear relationship shown in Fig. 1 certifies that the electro-optic response is due to the Kerr effect. The variation of induced birefringence (Δn) as a function of the square of the applied field (E^2) at various temperatures is shown in Fig. 2. It is obvious that Δn increases linearly with E^2 at every temperature. The experimental data at various temperatures were fitted with Eq. (2) by a least-square-fitting procedure to obtain Kerr constant. The variation of the Kerr constant as a function of temperature is shown in Fig. 3. It is seen that the Kerr constant is strongly temperature dependent and follows the Landau–de Gennes theory given by [1]

$$B = K_B/(T - T_C^*), \tag{7}$$

where T_C^* is the critical temperature at which the nematic coherence length (ξ) diverges to infinity and K_B is a constant. To obtain T_C^*, we plot the inverse of the Kerr constant as a function of temperature. T_C^* was found to be 1.5 °C below T_{NI}. Such typical values are also reported in several other calamitic nematogens [16,17].

To calculate $\chi^{(3)}$, we measured refractive index of the medium in the isotropic phase as a function of temperature. The temperature variation of $\chi^{(3)}$ is shown in Fig. 4; $\chi^{(3)}$ is about 6×10^{-20} $\mathrm{m}^2/\mathrm{V}^2$ at 0.3 °C above T_{NI} and is reduced with increasing temperature. To compare with the compound ex-

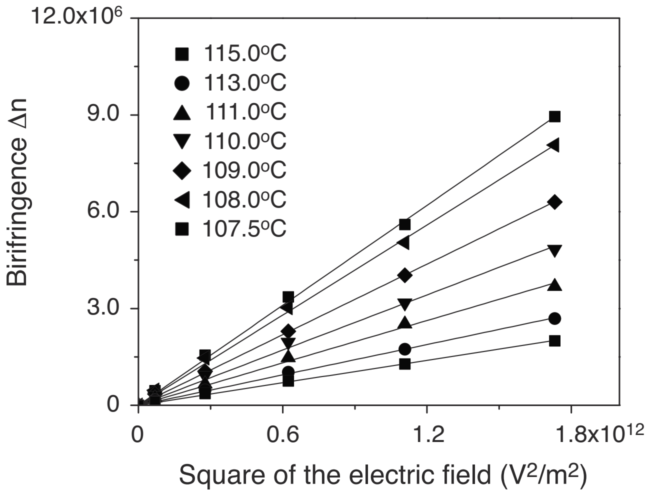

FIG. 2. Induced birefringence Δn as a function of square of the applied field at various temperatures. Solid line is the best fit obtained from a least-mean-squares method.

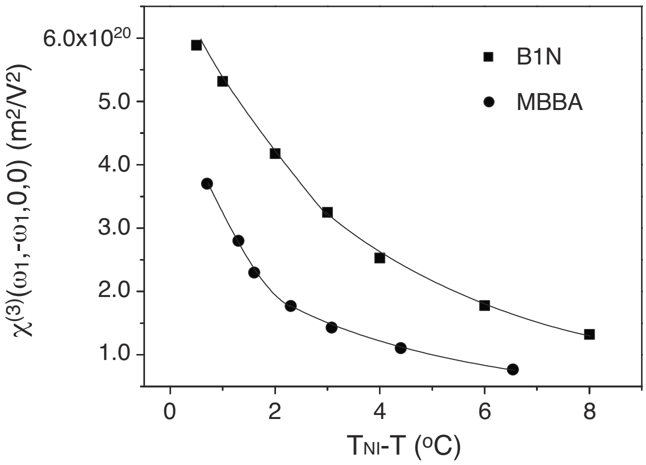

FIG. 4. Variation of nonlinear static susceptibility $[\chi^{(3)}(\omega_1,-\omega_1,0,0)]$ as a function of temperature. Data corresponding to the solid squares are obtained from the present bent-core compound and those of solid circles are from Ref. [18]. Solid lines are drawn as guides to the eye.

hibiting negative dielectric anisotropy, reported $\chi^{(3)}$ values in MBBA [18] are also shown in Fig. 4. It is noticed that the values for the present compound are almost double at all temperatures. The marked difference is that the temperature dependence of the bent-core compound is much slower as the T_{NI} is approached compared to MBBA. Actually, estimated K_B values are 2.3×10^{-11} mK/V^2 and 7.4×10^{-12} mK/V^2 for the present compound and MBBA, respectively.

It has been reported that usually the Kerr constant is smaller in materials with negative dielectric anisotropy than those with positive dielectric anisotropy; ($B=1.1\times10^{-10}$ m/V^2) in 5CB [14,15] and ($B=4\times10^{-12}$ m/V^2) in MBBA [18]. The reason is very simple: The director of nematic cybotactic clusters in the isotropic sea gets aligned along the field direction in positive-type materials, since the average dipole is parallel to the director. In contrast, negative-type materials make their director perpendicular to the field, so that we observe the reduced anisotropy by rotational average of the cluster (director) orientation about the field direction. Now let us discuss the different Kerr constants in liquid crystals composed of bent-shaped molecules and calamitic molecules; i.e., B or $\chi^{(3)}$ of the former is about double those of the latter. Δn is given by [19]

$$\Delta n = \Delta n^0 \rho \Delta\epsilon E^2/2\pi a_0(T-T_C^*), \tag{8}$$

where Δn^0 is Δn of a perfectly aligned liquid crystal, ρ density, $\Delta\epsilon$ dielectric anisotropy, and a_0 coefficient of Landau expansion. Since the refractive index anisotropies of the bent-core mesogen and MBBA are both about 0.1 just below T_{NI}, only the difference arises from $\Delta\epsilon$'s. They are −0.8 and −0.4 for bent-core mesogen and MBBA just below T_{NI}, respectively. Thus, the different B or $\chi^{(3)}$ originates from the dielectric anisotropy. This conclusion is consistent with the fact that the present bent-core material seems to show negligible biaxiality, because the formation of cybotactic clusters with a biaxial nematic order and their field-induced orientation would give smaller B or $\chi^{(3)}$ by rotational average about the axis of second largest refractive index parallel to an electric field.

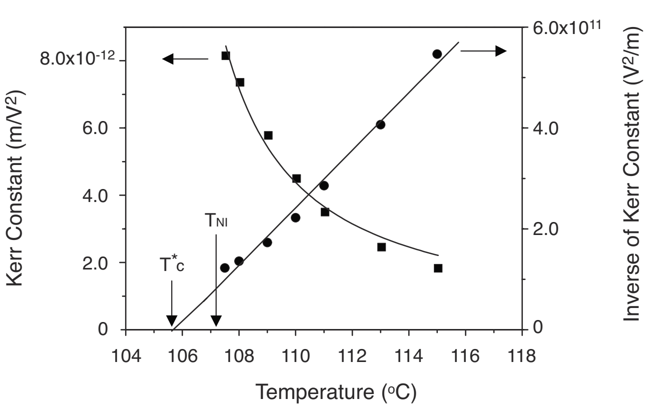

FIG. 3. Solid squares represent the variation of Kerr constant (B) as a function of temperatures. The inverse Kerr constant $1/B$ is also plotted by solid circles to show the Landau–de Gennes-type temperature dependence. Actually $1/B\propto(T-T_C^*)$ is shown by the best fit to the data points from a least-mean-squares method. T_C^* is found to be almost 1.5 °C below T_{NI}.

In conclusion, we performed the Kerr effect measurement and estimated the Kerr constant and the static nonlinear optic susceptibility as a function of temperature above T_{NI} of a liquid crystal composed of bent-shaped molecules. The temperature-dependent Kerr constant follows the behavior predicted by the Landau–de Gennes theory, where T_C^* is about 1.5 °C below T_{NI} indicating that the NI transition is weakly first order as in the case of calamitic liquid crystals. The static susceptibility is larger almost by a factor of 2 compared to that of the negative-type calamitic material MBBA, and is explained by the different dielectric anisotropy. These results are useful for investigating other physical phenomena of bent-core liquid crystals in the vicinity of

NI transition. For example, it is also possible to form a polar cluster owing to the polar packing of the bent-shaped molecules under high electric field and hence a linear coupling of electric field with the order parameter can give rise to an optical second harmonic generation in the isotropic phase. At present we are pursuing some investigation to explore such possibilities. We expect our present results will inspire more electro-optic Kerr measurements on the bent-core liquid crystals to investigate the effect of molecular shape and structures on the short-range cybotactic clusters.

This work is partly supported by Grant-in-Aid for Scientific Research (S) (Grant No. 16105003) from the Ministry of Education, Culture, Science, Sports and Technology of Japan. One of the authors (S. D.) gratefully acknowledges the support from the DST, Government of India for the Contract No. SR/FTP/PS-48/2006 under the SERC Fast Track Scheme.

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