

## Critical behavior at the isotropic-to-nematic phase transition in a bent-core liquid crystal

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Magnetic birefringence and dynamic light scattering measurements of orientational order parameter fluctuations at the isotropic-nematic phase transition of a bent-core liquid crystal reveal a pretransitional temperature dependence consistent with the standard Landau-deGennes mean field theory. However, as follows: the transition in the bent-core compound is more weakly first order ( $T_{NI} - T^* \approx 0.4$  °C), the leading Landau coefficient is  $\sim 30$  times lower, the viscosity associated with nematic order fluctuations is  $\sim 10$  times higher, and the density change is  $\sim 10$  times lower, than typically observed in calamitic (rod-shaped) liquid crystals. One consistent explanation for these anomalies is an optically isotropic phase composed of microscopic complexes or “clusters” of bent-core molecules.

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The isotropic to uniaxial nematic ( $I$ - $N$ ) phase transition is characterized by the development of orientational order along one direction in space within a fluid of anisotropically shaped particles. Light scattering and birefringence [1,2] experiments have established that the  $I$ - $N$  transition in calamitic liquid crystals (composed of “rod-shaped” molecules) is weakly first order, with a pretransitional temperature dependence of the order parameter fluctuations describable by a Landau-deGennes (LDG) mean field theory [3]. The advent of a new class of nematics formed by molecules with a bent core [4–6] provides a qualitatively new system for basic studies of orientational ordering. Theoretically, bent-core mesogens are predicted to yield an unusually rich fluid phase behavior—both uniaxial and biaxial phases are anticipated, as well as exotic phases, such as [7,8] an orientationally ordered yet optically isotropic phase, a spontaneously chiral nematic phase, and even a macroscopically polar nematic phase. Light scattering [9], and NMR measurements [10], reveal drastically slower fluctuations in bent-core compounds than observed in typical calamitics, further motivating a comparison of  $I$ - $N$  pretransitional behavior.

In this Rapid Communication, we report, to the best of our knowledge, the first magnetic birefringence (MB) and dynamic light scattering (DLS) measurements of pretransitional fluctuations in nematic order carried out in the isotropic phase of a bent-core LC, 4-chloro-1,3-phenylenebis[4-(4-9-decenyloxy)benzoyloxy benzoate] [6], shown in Fig. 1 (and abbreviated 10CPBB). This material has a relatively low transition temperature ( $T_{NI} \approx 76.5$  °C) and a fairly wide nematic phase ( $\sim 10$  °C), which was previously shown to be uniaxial [9]. We find that the inverse Cotton-Mouton coefficient ( $H^2/\Delta n$ ,  $H$ =applied magnetic field,  $\Delta n$ =induced refractive index anisotropy) and the relaxation rate ( $\Gamma$ ) associated with orientational order parameter fluctuations both show the pretransitional temperature dependence predicted by the standard LDG theory and well established for calamitics—i.e.,  $H^2/\Delta n \sim \Gamma \sim T - T^*$ , for  $T$  close to the supercooling limit  $T^*$ . However, key parameters entering the LDG model and the standard hydrodynamic theory used with it

differ systematically and markedly in magnitude from calamitics. These parameters, whose values are ultimately determined by microscopic details of the isotropic phase, include the temperature independent part of the leading Landau coefficient  $a$  (which is  $\sim 30$  times lower than known values in calamitics), the value of  $T_{NI} - T^*$  (which is  $\approx 0.4$  °C versus values  $\geq 1$  °C in typical calamitics), the viscosity  $\nu$  for order parameter fluctuations ( $\geq 10$  times higher than available data for calamitics), and the density change  $\Delta\rho$  that enters extended LDG treatments of the transition ( $\sim 10$  times lower for the bent-core compound). All of these results can be explained by an unconventional isotropic phase composed of microscopic clusters or complexes of bent-core molecules.

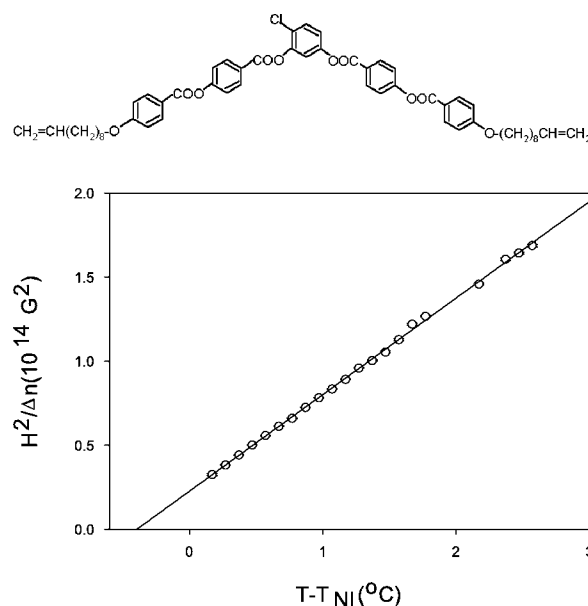


FIG. 1. Temperature dependence of the inverse Cotton Mouton coefficient measured at the  $I$ - $N$  transition in 10CPBB. The temperature was regulated to  $< 0.002$  °C. The solid line is a linear fit. The structure of 10CPBB is shown above the main figure.

For the MB study, a rectangular glass cuvette with a 2 mm optical path length was filled with 10CPBB. The cuvette was placed between the pole faces of a 13.5 kG electromagnet. The field-induced refractive index anisotropy  $\Delta n(H)$  was measured using a standard technique [11] based on a photoelastic optical phase modulation and lock-in detection, with a typical sensitivity of  $\pm 6 \times 10^{-9}$ . For the DLS measurements, a 10  $\mu\text{m}$  thick sample of 10CPBB was confined in an optical cell consisting of parallel glass substrates treated with rubbed polyimide layers for a homogeneous alignment of the nematic optic axis (director). The alignment layers had no effect on the measured pretransitional behavior, as similar results were obtained in a 50  $\mu\text{m}$  cell and also in a cell with no surface treatment. The sample was illuminated with a 20 mW HeNe laser beam (wavelength  $=\lambda=633$  nm). The incident polarization was vertical (V) to the horizontal (H) scattering plane. The time correlation function of the scattered intensity,  $\langle I_{VH}(-\vec{q}, 0)I_{VH}(\vec{q}, \tau) \rangle \propto \langle \delta Q_{VH}(-\vec{q}, 0)\delta Q_{VH}(\vec{q}, \tau) \rangle$ , was recorded in the homodyne regime at discrete temperatures on cooling from the isotropic phase. Here  $\delta Q_{VH}$  are fluctuations of the uniaxial nematic order parameter tensor corresponding to the scattering vector  $\vec{q}$  [magnitude  $q=(4\pi/\lambda)\sin(\theta/2)$  where  $\theta$  is the lab scattering angle], which, for sample dimensions large compared to the optical wavelength, is equivalent to the specific wave vector of the fluctuations probed. The dispersion ( $q$  dependence) of the relaxation rate  $\Gamma$  of the fluctuations  $\delta Q_{VH}$  was measured over a range,  $q=(1-9) \times 10^4$   $\text{cm}^{-1}$  at fixed temperature.

For an ordinary isotropic liquid crystal, the LDG orientational free energy density, expressed in terms of a traceless, symmetric, spatially invariant order parameter tensor  $Q_{\alpha\beta}$  for a uniaxial nematic, reads

$$F = \frac{1}{2}a(T - T^*)Q_{\alpha\beta}Q_{\beta\alpha} - \frac{1}{3}bQ_{\alpha\beta}Q_{\beta\gamma}Q_{\gamma\alpha} + \frac{1}{4}c(Q_{\alpha\beta}Q_{\beta\alpha})^2 - \frac{1}{2}\chi_{\alpha\beta}H_{\alpha}H_{\beta},$$

where  $a, b, c$  are material-dependent coefficients assumed to be independent of  $T$ ,  $\vec{H}$  is an applied magnetic field, and the anisotropic part of the diamagnetic susceptibility tensor  $\chi_{\alpha\beta}$  is proportional to  $Q_{\alpha\beta}$ . Minimization of  $F$  with no applied field gives  $T_{NI} = T^* + b^2/(27ac)$ . In the isotropic phase, the minimum  $F$  with  $H=0$  corresponds to  $Q_{\alpha\beta}=0$ , so one finds the lowest order, thermally fluctuating part of the free energy to be simply

$$\delta F(\vec{q}) = a(T - T^*)\delta Q_{\alpha\beta}(\vec{q})\delta Q_{\beta\alpha}(\vec{q})/2. \quad (1)$$

(As discussed below, no effect of gradient terms in  $\delta F$  was observed in our experiments.)

Figure 1 shows the pretransitional temperature dependence of the measured ratio  $H^2/\Delta n$  (inverse Cotton-Mouton coefficient). According to the LDG model for the isotropic to uniaxial nematic transition [1], one expects  $H^2/\Delta n = 9a\sqrt{\bar{\epsilon}}(T - T^*)/\Delta\epsilon\Delta\chi$  close to  $T^*$ , where  $\Delta\epsilon$  and  $\Delta\chi$  are the saturated dielectric and diamagnetic anisotropies in the ordered (nematic) phase (the former at optical frequency), and  $\bar{\epsilon}$  is the isotropic part of the dielectric constant tensor. The linear fit to the data validates this prediction, and we find

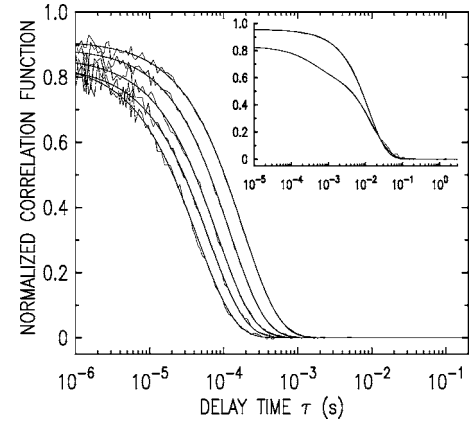


FIG. 2. Typical DLS correlation functions in the isotropic phase of 10CPBB at various temperatures (79.04, 78.54, 78.04, 77.63, and 77.33  $^{\circ}\text{C}$ , left to right) in the isotropic phase just above the  $I$ - $N$  transition. The temperature was regulated to  $<0.003$   $^{\circ}\text{C}$ . The lighter lines are data; the bolder lines are best fits to a slightly stretched single exponential decay. The inset shows a single temperature (77.13  $^{\circ}\text{C}$ , lower plot), where coexisting order parameter and nematic director fluctuations were observed, and also a purely nematic correlation function at 77.03  $^{\circ}\text{C}$  (upper plot).

$a\sqrt{\bar{\epsilon}}/\Delta\epsilon\Delta\chi = (6.3844 \pm 0.0007) \times 10^{12}$   $\text{erg cm}^{-3} \text{ } ^{\circ}\text{C}^{-1}$  and  $T_{NI} - T^* = 0.38 \pm 0.02$   $^{\circ}\text{C}$ . We measured  $\sqrt{\bar{\epsilon}} = 1.56 \pm 0.01$  and estimate  $\Delta\epsilon = 0.40 \pm 0.08$  at saturation. From independent electric and magnetic Freedericksz transition measurements [12], we estimate  $\Delta\chi = (3.0 \pm 0.6) \times 10^{-8}$  (cgs units) at saturation. We then calculate  $a = (5 \pm 1) \times 10^4$   $\text{erg cm}^{-3} \text{ } ^{\circ}\text{C}^{-1}$  for 10CPBB, a value that is  $\sim 30$  times lower than the mean value for six typical calamitics on which we have found published results [1,2,13]. Our measurement of  $T_{NI} - T^* = 0.38$   $^{\circ}\text{C}$  is also significantly below the mean value of 1.7  $^{\circ}\text{C}$  obtained from the low end of available data for 17 different calamitic compounds [14–17], where only one (80CB) has a value (0.65) ever reported to be less than 1  $^{\circ}\text{C}$ .

We now turn to our light scattering results. Figure 2 displays typical normalized correlation functions obtained from depolarized scattering during a temperature scan through the  $I$ - $N$  transition in our 10  $\mu\text{m}$  thick sample. We first fit the correlation data to a single exponential decay, using two fitting parameters, an amplitude and a decay constant (or relaxation rate of the fluctuations,  $\Gamma$ ). However, improved fits could be obtained by using a slightly stretched exponential decay. This systematically reduced the fitted parameter  $\Gamma$  by about 5%, but improved  $\chi^2$  by about 30%. The typical value of  $\Gamma$  above the transition is  $\sim 10$  kHz, of order 100 times lower than values characteristic of calamitic compounds at similar temperatures relative to the transition [1,13]. At a single temperature, contributions from both isotropic and nematic (director) fluctuations were observed in the correlation data (see inset to Fig. 2). This point, which apparently corresponds to an isotropic-nematic coexistence, was used to fix  $T_{NI}$ , within  $\pm 0.05$   $^{\circ}\text{C}$  (the resolution of our scan).

To calculate the temperature dependence of the relaxation rate  $\Gamma$ , which combined with our MB results will allow us to extract the orientational viscosity of the isotropic phase of 10CPBB, we must combine Eq. (1) for the fluctuating part of

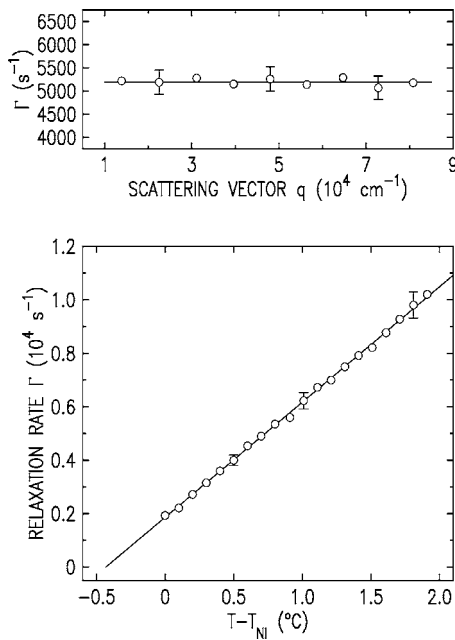


FIG. 3. Top: Nonhydrodynamic  $q$  dependence of the relaxation rate for order parameter fluctuations observed at  $77.89^\circ\text{C}$  in the isotropic phase of 10CPBB. Bottom: Temperature dependence of the relaxation rate at the  $I$ - $N$  transition for a fixed scattering vector  $q=76\,000\text{ cm}^{-1}$ . The solid line is a linear fit.

the LDG free-energy density with the hydrodynamic equations for an isotropic liquid crystal. The theory simplifies in the limit of an incompressible, isothermal fluid (or for slow order parameter fluctuations near the phase transition), and if the viscosity associated with the coupling of  $\delta Q_{\alpha\beta}$  to velocity gradients is much less than either the fluid shear viscosity or the viscosity  $\nu$  characterizing the damping of  $\delta Q_{\alpha\beta}$ , one calculates [1] a simple exponential decay of the order parameter correlation function similar to that observed in Fig. 2,  $\langle \delta Q_{VH}(0)\delta Q_{VH}(\tau) \rangle^2 \propto \exp(-2\Gamma\tau)$ , where  $\Gamma = a(T - T^*)/\nu$ . However, as shown below,  $\nu$  has a much larger value in our bent-core compound than typical calamitics.

Experimental results for the temperature dependence and dispersion of  $\Gamma$  for 10CPBB are shown in Fig. 3. Fluctuations of the nematic order parameter in the isotropic phase are nonhydrodynamic (e.g., the free energy must increase for an infinitesimal, spatially uniform increase in the nematic order parameter), and to lowest order one expects no variation of  $\Gamma$  with the scattering vector  $q$ . Figure 3 (top) confirms this prediction in the isotropic phase of 10CPBB, and justifies the omission of gradient terms in the free-energy density, Eq. (1). The experimental results for  $\Gamma$  versus temperature, plotted in Fig. 3 (bottom), clearly exhibit the linear pretransitional temperature dependence predicted by the LDG theory; the linear fit yields  $a/\nu = (4.3 \pm 0.2) \times 10^3 \text{ sec}^{-1} \text{ }^\circ\text{C}^{-1}$ , a value that is more than 100 times smaller than the typical magnitude  $\sim 10^6 \text{ sec}^{-1} \text{ }^\circ\text{C}^{-1}$  for calamitics [1,13]. With the value of  $T_{NI}$  corresponding to the point where the coexistence of isotropic and nematic fluctuations was observed, we also find  $T_{NI} - T^* = 0.43 \pm 0.05^\circ\text{C}$ . Thus, our results for  $T_{NI} - T^*$  from the MB and DLS measurements agree within experimental uncertainty. Combining our

average result for  $a/\nu$  with the value for  $a$ , obtained from the MB experiment, we find a viscosity  $\nu = 11 \pm 3 \text{ P}$  for orientational order fluctuations in the isotropic phase of 10CPBB. This value is 10–15 times higher than in typical calamitics such as the cyanobiphenyls [13]. The much slower relaxation rate of isotropic phase fluctuations in the bent-core compound is therefore due to the *combined* effect of a higher orientational viscosity and lower magnitude of the leading Landau coefficient  $a$ . We should also note that anomalous values of  $T_{NI} - T^*$  and  $a/\nu$  are apparently not unique to 10CPBB, since preliminary light scattering on a different bent-core compound, 4-chloro-1,3-phenylenebis[4-(4-n-dodecyloxy) benzoxy benzoate], gives  $T_{NI} - T^* = 0.30 \pm 0.07^\circ\text{C}$  and  $a/\nu = (11 \pm 1) \times 10^3 \text{ sec}^{-1} \text{ }^\circ\text{C}^{-1}$  [18].

Our main findings—that the  $I$ - $N$  transition in a bent-core liquid crystal has the same symmetry as in calamitics, but exhibits substantially lower values of  $T_{NI} - T^*$  and Landau coefficient  $a$ , and significantly higher viscosity for orientational fluctuations—can be understood in a unified framework by envisioning that in the isotropic phase the bent-core molecules form or associate into small complexes or “clusters,” which are larger and more isotropic in shape than single molecules. As argued over a decade ago [19,20], extending mean field models to include coupling of nematic orientational order to the mass density  $\rho$  provides a mechanism for reduced  $T_{NI} - T^*$  through a concomitant reduction in the density change  $\Delta\rho$  at the  $I$ - $N$  transition. A smaller  $\Delta\rho$  could result from molecular clusters that, possessing a more spherical shape than single liquid crystal molecules, experience less change in excluded volume as a consequence of nematic orientational order. Moreover, since the connection between the Landau coefficient  $a$  and more fundamental parameters (used in the Maier-Saupe molecular field theory [21]) is given by  $a = 5k_B n$  ( $n$  = particle number density) [22], a lower number density of larger particles (molecular clusters) occupying the same sample volume naturally implies the observed reduction in  $a$  compared to standard calamitics. In fact, one cannot account for the observed  $\sim 30$ -fold reduction in  $a$  from calamitics on the basis of molecular size alone, since the molecular weight of 10CPBB is no more than 4 times those of the cyanobiphenyls. Finally, clusters could have a substantially larger effective surface area, implying the significant enhancement in rotational viscosity that we detect in the bent-core material. The explanation for reduced  $T_{NI} - T^*$  suggested above hinges on a lower value of  $\Delta\rho$  for bent-core liquid crystals. To check this, we determined the reduced volume change  $\Delta V/V = \Delta\rho/\rho$  in 10CPBB by optically measuring the linear shift in the meniscus of a small column of the sample ( $\approx 2.1 \text{ cm}$  long) in a  $0.1 \times 1.0 \text{ mm}$  rectangular glass capillary with one end sealed. Special precautions were taken to ensure temperature uniformity across the capillary. We confirmed the accuracy of this setup by obtaining the literature value  $\Delta V/V = (2.1 \pm 0.2) \times 10^{-3}$  for the calamitic liquid crystal 5CB [23]; this agreement also indicates a negligible effect due to the thermal expansion of the capillary itself. For 10CPBB, we find  $\Delta V/V = (1.2 \pm 0.8) \times 10^{-4}$ , demonstrating that  $\Delta\rho$  is indeed of order 10 times smaller in the bent-core material than in typical calamitics such as the cyanobiphenyls and

4'-methoxybenzylidene-4-n-butylaniline (MBBA) [23–25].

In summary, we have conducted a detailed study of the  $I$ - $N$  transition in a bent-core liquid crystal using sensitive optical methods. Our results indicate that, while the transition has the same symmetry as in standard calamitics, the nanostructural organization of the isotropic phase is rather different, and is likely based on molecular “clusters” (or some short range structural association of the bent-core molecules), as has, in fact, been recently suggested for the nematic phase on the basis of deuterium NMR studies [26]. The only available theory that specifically describes a clustering of bent-core molecules in the  $I$  phase proposes an optically isotropic phase of tetrahedrally coordinated complexes of bent-core molecules (“tetrahedratic” or  $T$  phase) [7,8]. This

theory also predicts a transition to a nematic phase based on a uniaxial distortion of these complexes ( $N_T$  phase). The  $T$ - $N_T$  transition has the same symmetry as the usual  $I$ - $N$ , and so one expects the usual LDG model to apply to the pretransitional behavior. Although the experiments reported in this paper cannot specifically address the question of tetrahedratic order, we hope that our present work will inspire new experiments on bent-core liquid crystals designed to probe directly the short range structure of the isotropic phase.

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