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, the transition in the bent-core compound is more weakly first-order ($T_{NI} - T^* \approx 0.4°C$), the leading Landau coefficient is ~ 10 times lower, and the viscosity associated with nematic order fluctuations is ~ 50 times higher, than typically observed in calamitic (rod-shaped) liquid crystals. These anomalies can be explained by an unconventional optically isotropic phase composed of complexes of bent-core molecules, such as recently conjectured for the structure of a "tetrahedratic" liquid crystalline phase.

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, of which thermotropic "rod-shaped" (or calamitic) liquid crystals are a classic example. In these materials, optical scattering and birefringence [1,2] experiments demonstrate that the I to N transition is weakly first order, with pretransitional temperature dependence of the order parameter fluctuations describable by a Landau-deGennes (LdG) mean field theory [3] in which the free energy density is expanded in powers of the nematic order parameter. The advent of thermotropic nematics with a bent core [4-6] - i.e., "banana-shaped" liquid crystals, whose smectic phases have already revealed a wealth of new phenomena - provides a qualitatively new system for basic studies of orientational ordering. Moreover, bent-core mesogens are expected 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 "tetrahedratic" phase, a spontaneously chiral nematic phase, and even a macroscopically polar nematic phase. Light scattering studies in the uniaxial nematic phase [9], and recent NMR measurements in the isotropic phase [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 Letter, we report 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, the compound 4-chloro-1,3-phenylenebis[4-(4-n-decenyloxy) benzoyloxy benzoate] [6], shown in Fig. 1 (and abbreviated 10CPBB). This material has a relatively low transition temperature ($T_{NI} \simeq 76.5°C$) 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, Δn = induced refractive index anisotropy) and the relaxation rate (Γ) associated with orientational order parameter fluctuations both show the pretransitional temperature dependence ($T - T^*$), which is predicted by the standard LdG theory and is well established in calamitics. However, the value of $\Delta T = T_{NI} - T^* \approx 0.4°C$ differs significantly from values $\gtrsim 1°C$ typically found in calamitics [1,2]. Here T_{NI} is the actual transition temperature, and T^* is the supercooling limit (or temperature of a "virtual" second order transition). The magnitude of Γ is also substantially lower - approximately two orders of magnitude - in the bent-core material. This result is evidently due to the combined effects of a ~ 50 times higher viscosity associated with order parameter fluctuations in the isotropic phase and a ~ 10 times reduction in the leading Landau coefficient compared to typical values for calamitics. We discuss the significance of our results in light of extended mean field theory and recent theoretical proposals for the structure of isotropic and nematic phases in bent-core liquid crystals.

For the MB study, a rectanguler glass cuvette with a 2mm optical path length was filled with ~ 60 mg of 10CPBB. The cuvette was placed in a two stage oven, which regulated temperature to $< 0.002°C$, and the oven was mounted between the pole faces of a 13.5 kG electromagnet. The field-induced refractive index anisotropy, $\Delta n(H)$, was measured using the standard technique [11] based on photoelastic optical phase modulation and lock-in detection, with a typical sensitivity of $\pm 6 \times 10^{-9}$. For the DLS measurements, 10CPBB was loaded at a temperature $\sim 1°C$ above the $I - N$ transition into an optical cell consisting of

parallel glass substrates treated with rubbed polyimide layers for homogeneous alignment of the nematic optic axis (director). The sample thickness was 10 μm. The filled cell was placed in a temperature regulated oven with optical access. Short term ($\sim$ 1 hr) temperature stability was better than 0.003°C. The sample was illuminated at normal incidence with a 20 mW laser beam from a polarized HeNe laser operating at a wavelength $\lambda = 633$ nm. The incident polarization was vertical (V) to the horizontal (H) scattering plane. Starting at temperatures several degrees into the isotropic phase, 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 toward the nematic phase. Here δQ_{VH} are fluctuations of the uniaxial nematic order parameter tensor corresponding to scattering vector $\vec{q}$ [magnitude $q = (4\pi/\lambda)\sin(\theta/2)$ where θ is the lab scattering angle], which, for sample dimensions large compared to the optical wavelength, is equivalent to the specific wavevector of the fluctuations probed. The dispersion (q dependence) of the relaxation rate Γ of the fluctuations δQ_{VH} was measured over a range, $q = (1-9)\times 10^4$ cm^{-1}, at selected temperatures in the isotropic phase.

For an ordinary isotropic LC, 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:

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

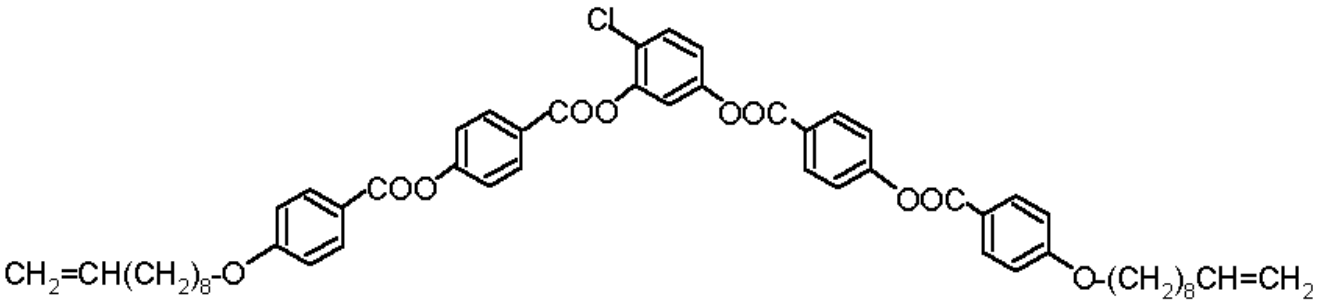
where a, b, c are material-dependent coefficients assumed to be independent of T, $\vec{H}$ is an applied magnetic field, and the anisotropic part of the diamagnetic susceptibility tensor $\chi_{\alpha\beta}$ is proportional to $Q_{\alpha\beta}$. Minimization of F with respect to the diagonalized form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

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

[As discussed below, no effect of gradient terms in δF 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 anistropies in the ordered (nematic) phase (the former at optical frequency), and $\bar{\epsilon}$ is the isotropic part of the dielectric constant tensor. As the linear fit to the data shows, this prediction is well borne out, and we find $a\sqrt{\bar{\epsilon}}/\Delta\epsilon\Delta\chi = 6.38\times 10^{12}$ erg-cm^{-3}°C^{-1} and $T_{NI} - T^* = 0.38 \pm 0.02$°C. ($T_{NI}$ was determined as the point corresponding to an abrupt increase in the sample turbidity.) We obtained the values of the optical parameters from refractive index measurements in the isotropic phase and across the $\sim$ 10 degree nematic range, utilizing a combination of Abbe refractometry and Fabry-Perot interferometry. We find $\sqrt{\bar{\epsilon}} = 1.56$ and estimate $\Delta\epsilon = 0.4$ at saturation. From independent electric and magnetic Freedericksz transition measurements [12], we estimate $\Delta\chi = 3\times 10^{-8}$ (cgs units) at saturation. We then calculate $a = 4.9\times 10^4$ erg cm^{-3}°C^{-1} for 10CPBB, a value that is $\sim$ 10 times *lower* than typical calamitics [1,2]. The value of $T_{NI} - T^* = 0.38$°C is also significantly lower than published values for a variety of calamitics - including cyanobiphenyls, alkylcyclohexylbenzonitriles, as well as the extensively studied compound MBBA - where ΔT ranges from 1 to 7°C [13-16].

We now turn to our light scattering results. Figure 2 displays typical correlation functions obtained from depolarized scattering during a temperature scan through the $I-N$ transition in our 10 μm thick sample. Count rates for these data ranged from $\sim$ 700 at the highest temperature to several thousand per second just above the transition. Therefore, fairly long (45 min) integration times were used in the correlation. We first fit the correlation data to a single exponential decay, using two fitting parameters, an amplitude and decay constant (or relaxation rate of the fluctuations, Γ). However, improved fits (bolder lines in the main figure) could be obtained by using a slightly stretched exponential decay. This systematically reduced the fitted parameter Γ by about 5% relative to the values obtained with a pure exponential, but improved chi-squared by about 30%. The typical value of Γ above the transition is $\sim$ 10 kHz, approximately two orders of magnitude lower than values characteristic of calamitic compounds of comparable molecular size and for similar temperatures relative to the transition. A similarly large difference in relaxation rate was reported in a recent NMR study of molecular reorientation in the isotropic phase of a different bent-core compound [10]. At a single temperature, contributions from both isotropic and nematic (director) fluctuations were observed



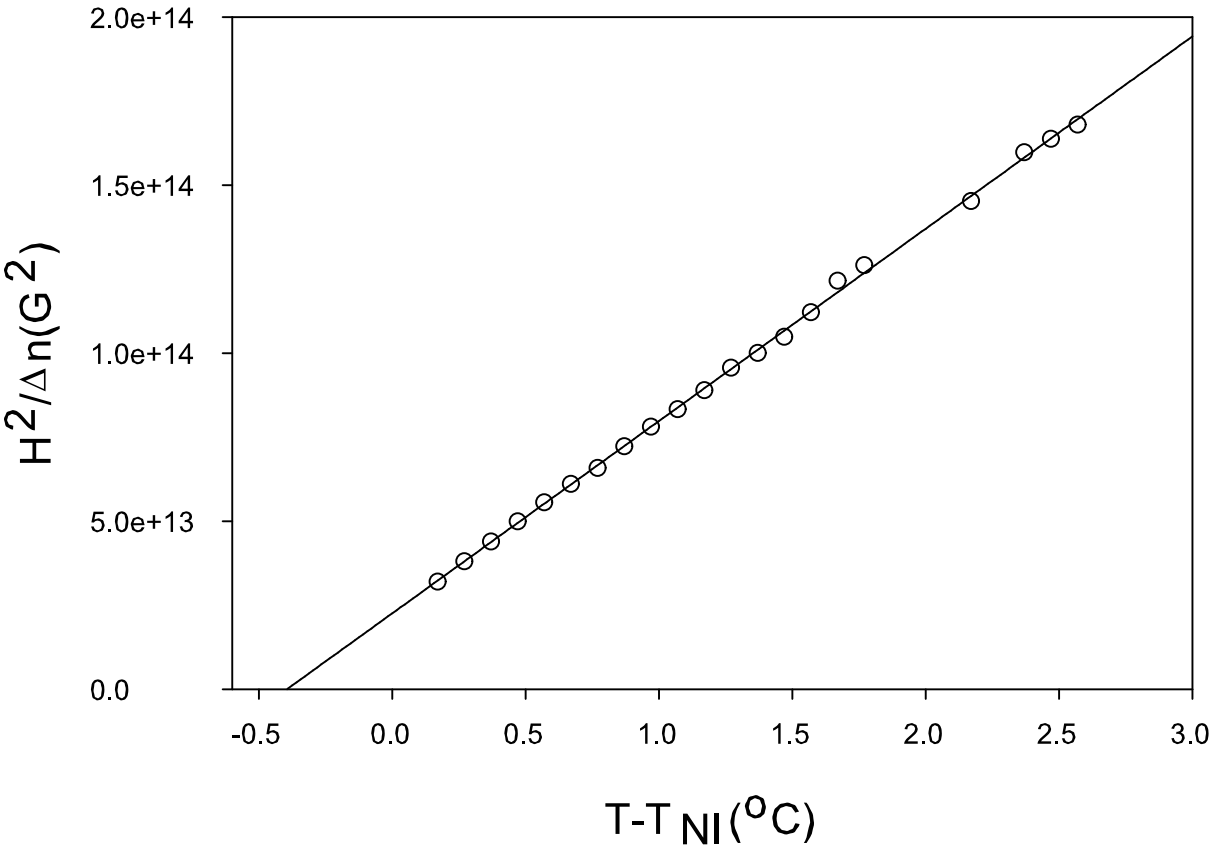


FIG. 1: Temperature dependence of the inverse Cotton Mouton coefficient measured at the $I-N$ transition in 10CPBB. The solid line is a linear fit. The structure of 10CPBB is shown above the main figure.

in the correlation data (see inset to Fig. 2). This point, which apparently corresponds to isotropic-nematic coexistence, was used to fix T_{NI},within ± 0.05°C (the resolution of our scan).

To calculate the temperature dependence of the relaxation rate Γ, 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 the LdG free energy density with the hydrodynamic equations for an isotropic liquid crystal. The latter contain the fluid velocity, density (ρ), and temperature fluctuations, as well as the primary order parameter $\delta Q_{\alpha\beta}$. However, the theory simplifies considerably in the limit of an incompressible, isothermal fluid (or for sufficiently slow fluctuations such as the order parameter near the phase transition). If, in addition, the viscosity associated with coupling of $\delta Q_{\alpha\beta}$ to velocity gradients is much less than either the fluid shear viscosity or the viscosity ν characterizing the damping of $\delta Q_{\alpha\beta}$, one

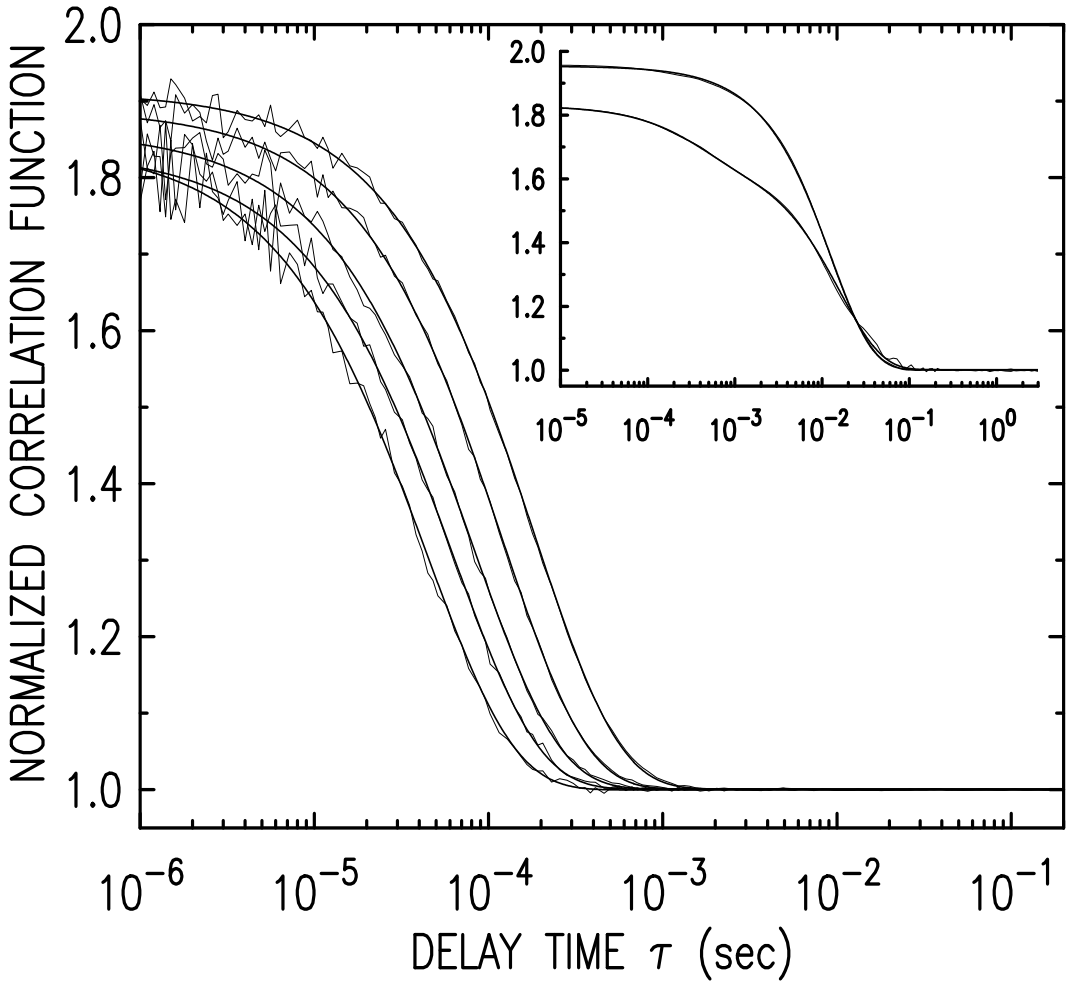


FIG. 2: Typical DLS correlation functions in the isotropic phase of 10CPBB at various temperatures (79.04, 78.54, 78.04, 77.63, 77.33°C, left to right) in the isotropic phase just above the $I-N$ transition. The lighter lines are data; the bolder lines are best fits to a slightly stretched single exponential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

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 $\Gamma = a(T-T^*)/\nu$. Previous frequency domain light scattering measurements in the isotropic phase of the calamitic liquid crystal MBBA demonstrate that the condition on the viscosities is met. The situation is even better in our bent-core compound, since, as we shall see below, ν has a much larger value than typical calamitics.

Experimental results for the temperature dependence and dispersion of Γ for VH scattering from the two samples of 10CPBB studied 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 Γ with the scattering vector q. Figure 3(top) confirms this prediction in the isotropic phase of a bent-core LC, and justifies the omission of gradient terms in the free energy density, Eq. (1). The experimental results for Γ versus temperature, plotted in Fig. 3(b), clearly exhibit the linear pretransitional temperature dependence predicted by the LdG theory; the linear fit yields $a/\nu = (4.31 \pm 0.22) \times 10^3$ sec^{-1}°C^{-1}, a value that is two to three orders of magnitude lower the typical magnitude $\sim 10^6$ sec^{-1}°C^{-1} for calamitics [1]. With the values of T_{NI} obtained from the single correlation functions where coexistence of isotropic and nematic fluctuations was observed, we also find $\Delta T = T_{NI} - T^* = 0.43 \pm 0.05$°C. Thus, our results for $T_{NI} - T^*$ obtained from the MB and DLS measurements agree within experimental uncertainty. [The temperature range of

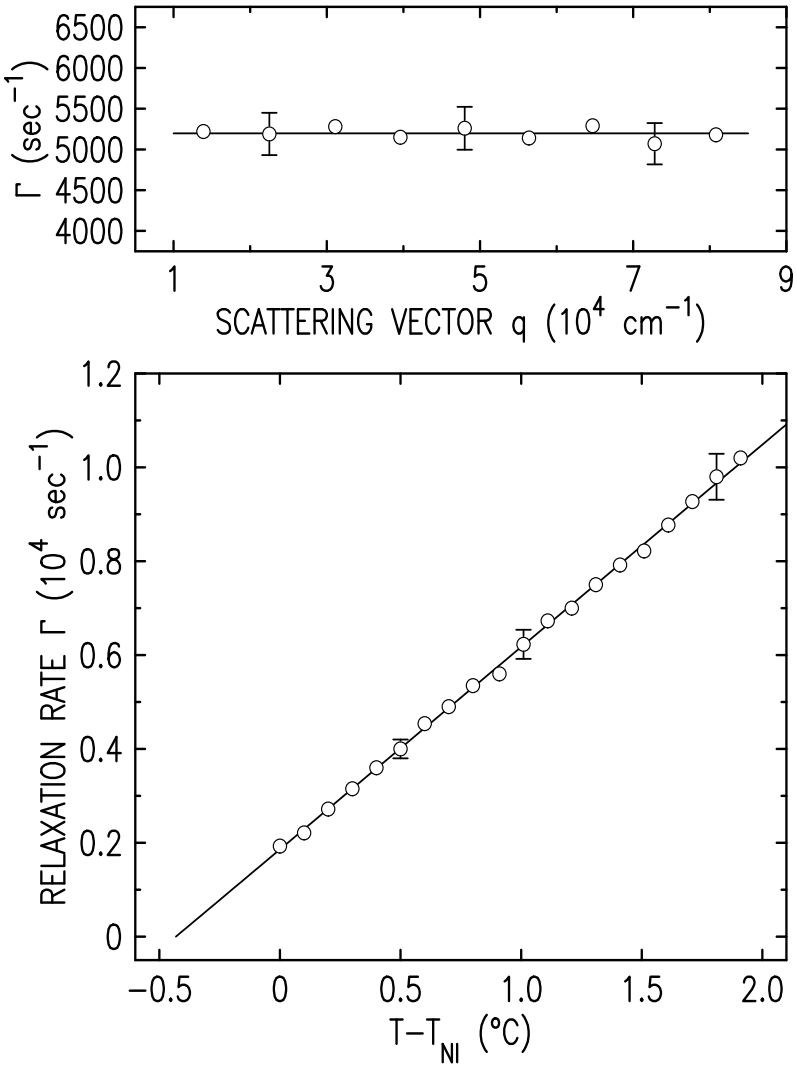


FIG. 3: Top: Nonhydrodynamic q dependence of the relaxation rate for order parameter fluctuations observed at 77.89°C in the isotropic phase of 10CPBB. Bottom: Temperature dependence of the relaxation rate at the $I-N$ transition for a fixed scattering vector $q = 76000$ cm^{-1}. The solid line is a linear fit.

our data is sufficiently narrow that the effect of the expected activated (Arrhenius) temperature dependence in ν, $\nu \simeq \nu_0 \exp[3000/T(K)]$ is not significant.] Combining our average result for a/ν with the value for a, obtained from the MB experiment, we find a viscosity $\nu = 11$ P for orientational order fluctuations in the isotropic phase of 10CPBB. This value is ~ 50 times higher than in a typical calamitic such as MBBA [1], where $\nu \simeq 0.25$ P for a similar range of $T - T_{NI}$. The much slower relaxation rate of isotropic phase fluctuations in the bent-core compound is therefore due to the *combined* effect of a significantly higher viscosity and lower value of the leading Landau coefficient a.

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 $\Delta T = T_{NI} - T^*$ and Landau coefficient a, and significantly higher viscosity for orientational fluctuations - can be understood in a unified framework by envisioning that the basic consituents of the isotropic phase are not single molecules, but molecular complexes or "clusters" instead. As argued over a decade ago [17,18], extending mean field models to include coupling of nematic orientational order to the mass density ρ provides a mechanism for reduced ΔT through a concomitant reduction in the density change $\Delta\rho_{IN}$ at the $I-N$ transition. A smaller $\Delta\rho_{IN}$ 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 [19]) is given by $a = 5k_B n$ (n = particle number density) [20], a lower number density of larger particles (molecular clusters) occupying the sample volume naturally implies the observed reduction in a compared to standard calamitics. It is also interesting to note that the value of $\Delta\chi$ in 10CPBB (3×10^{-8}) is nearly an order of magnitude lower than the typical value (2×10^{-7} [1,3]) in calamitics. This reduction is potentially another effect of bent-core molecular clusters that have a more isotropic shape than single rods. Finally, clusters could have a substantially larger effective surface area, implying the significant enhancement in rotational viscosity that we indeed detect in the bent-core material.

The explanation for reduced ΔT suggested above hinges on a lower value of $\Delta\rho_{IN}$ for bent-core liquid crystals. To check this, we independently measured the reduced volume change, $(\Delta V/V)_{IN} = (\Delta\rho/\rho)_{IN}$, in 10CPBB by observing (at the optical diffraction limit) the linear shift in the meniscus of a small column of sample ($\simeq$ 2.1 cm in length) filled from the sealed end of a 0.1 $\times$ 1.0 mm rectangular glass capillary. Special precautions - including a solid copper support and aluminum jacket surrounding the sample in the hot stage and the use of a small (2.8 mm diameter) C-cut sapphire window - were taken to ensure temperature uniformity across the capillary. We confirmed the accuracy of this set-up by obtaining the literature value $(\Delta V/V)_{IN} = (2.1 \pm 0.2) \times 10^{-3}$ for the calamitic liquid crystal 5CB [21]; this agreement also indicates a negligible effect due to thermal expansion of the capillary itself. For 10CPBB, we find $(\Delta V/V)_{IN} = (1.2 \pm 0.8) \times 10^{-4}$, demonstrating that $\Delta\rho_{IN}$ is indeed at least an order of magnitude lower in the bent-core material than in a typical calamitic.

In summary, our results indicate that the nanostructural organization of the isotropic phase of bent-core liquid crystals is likely based on molecular "clusters" (or some short range structural association of molecules), although the $I - N$ transition has the same symmetry as in standard calamitics. This scenario broadly agrees with recent theoretical studies [8] of the (optically) isotropic to (optically) uniaxial phase transition in bent-core liquid crystals. In addition to the usual $I - N$ transition, the authors of these studies propose an alternative transition from a liquid composed of tetrahedrally coordinated complexes of bent-core molecules ("tetrahedratic" or T phase [7,8]) 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. In the future, it would be interesting to probe measurable quantities [8] that are expected to couple selectively to the tetrahedratic order parameter, in order to expose a possible transition between clustered and neat isotropic phases at higher temperature.

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