Magnetic-Field Induced Isotropic to Nematic Liquid Crystal Phase Transition

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We report on measurements of magnetic-field induced nematic order in the bent-core liquid crystal 4-chlororesorcinol bis[4-(4-*n*-dodecyloxybenzoyloxy) benzoate]. Using the 31 T solenoid at the National High Magnetic Field Laboratory, we have observed, at temperatures less than 1° above the clearing point, a first-order transition to the nematic phase. The critical magnetic field at which this occurs increases with temperature. We discuss these results within the context of both Maier-Saupe and Landau–de Gennes mean-field models for the nematic-isotropic transition. The implications of possible tetrahedratic order are also discussed. To our knowledge, this is the first observation of such a magnetic-field induced transition in a thermotropic liquid crystal; the reasons for which this behavior is now attainable are discussed.

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Introduction.—Orientational order in liquid crystals couples strongly to applied external fields, particularly electric or magnetic fields [1]. When a liquid crystalline material is in its nematic phase, the scalar order parameter, which characterizes the degree to which molecular orientations are correlated, is only weakly affected by external fields, but rotations of the axis of average molecular orientation (the director) can be caused by relatively small fields. Indeed, the basic mechanism of practically every liquid crystal display is the rotation of the director axis due to an external electric field. In contrast, in the isotropic phase of a liquid crystal material, it is well established that an external field is capable of inducing nematic orientational order from a zero-field state where it does not exist [2]. This is a powerful tool for not only studying orientation fluctuations but also probing the stability limit of the isotropic phase [3].

In addition to the effects noted above, it has long been known that the possibility exists for (a) an external field to substantially alter the nematic-isotropic transition temperature [2,4] and (b) a nematic-isotropic critical end point [5] at a specific temperature and applied field. However, neither effect has ever been produced via a magnetic-field in thermotropic nematics [6]. The principal reason for this situation is that the field strengths required (critical fields estimated well over 100 T for traditional liquid crystal materials) are not accessible. In this work, using both a new class of liquid crystal molecules and a state-of-the-art high-field resistive magnet, we have confirmed the former effect which points towards what is necessary to observe the latter.

Molecules having a bent core (i.e., banana shape) have revolutionized liquid crystal science and technology over the past 10 years [7,8], exhibiting effects as diverse as they are exciting, including chiral mesophases composed of achiral molecules [9], thermotropic biaxial nematic order [10–12], giant flexoelectricity [13,14] and flow birefringence, and indications of possible tetrahedratic order [15]. In addition, and of particular relevance, are our earlier measurements which indicated that the nematic clearing point in two closely related bent-core compounds is only very weakly first order, in fact notably weaker than typical low-molecular weight thermotropics [16].

Background.—The two basic mean-field theories of the nematic-isotropic transition are the Landau–de Gennes (LdG) and Maier-Saupe models. While the Maier-Saupe model is based on an approximate, orientationally dependent intermolecular interaction, the Landau–de Gennes model is a phenomenological Landau-type expansion of the free energy including all symmetry-allowed scalar invariants which can be created from the second-rank tensor nematic order parameter $Q_{\alpha\beta}$. Both predict the existence of a first-order phase transition, and both are easily expanded to include the effects of externally applied fields [17].

The Landau–de Gennes free energy is

$$F = \frac{3}{4}a_0(T - T^*)Q^2 - \frac{1}{4}BQ^3 + \frac{9}{16}CQ^4 - \frac{1}{2}\Delta\chi_0 QH^2, \tag{1}$$

where a_0 is the leading Landau coefficient, B is the cubic Landau coefficient, and T^* is the temperature below which the isotropic phase ($Q = 0$) is unstable. $\Delta\chi_0$ is the saturated diamagnetic anisotropy and H is the applied magnetic field. Q measures the amplitude of uniaxial nematic order, and is related to the principal-axis components of the tensor: $Q_{\alpha\beta}$ by $Q_{xx} = Q_{yy} = -Q/2$, $Q_{zz} = Q$. The standard analytic approach is to find the value of Q which minimizes the free energy in Eq. (1). The model then predicts (at $H = 0$) a first-order phase transition at the clearing point temperature $T_{cp} = T^* + B^2/27a_0C$. When $H \neq 0$, three measurable effects are predicted:

(i) induction of a ''paranematic'' phase for $T > T_{cp}$, (ii) a shift in the first-order phase transition temperature, and (iii) the critical end point referred to earlier. The paranematic phase is well established [3]; it is manifested by observing the Cotton-Mouton effect, i.e., optical birefringence (or refractive index anisotropy Δn) proportional to H^2 and induced at temperatures above the clearing point. Specifically,

$$\Delta n = \frac{\Delta\epsilon_0 \Delta\chi_0 H^2}{9a_0(T - T^*)\sqrt{\bar{\epsilon}}}, \tag{2}$$

where $\Delta\epsilon_0$ is the saturated dielectric anisotropy and $\bar{\epsilon}$ is the isotropic part of the dielectric tensor (at optical frequency).

Calculating the critical end point is straightforward: after including the magnetic term above, one finds there is only one value of T and H where there is a single root of the minimization condition. This occurs at $T_c = T^* + B^2/18a_0C$ and $H_c = \sqrt{B^3/162\Delta\chi_0 C^2}$. For $H < H_c$, there are multiple roots, and there is an exchange of stability between different roots at the field-induced isotropic-nematic transition, which is the second effect noted above. This occurs at a temperature $T_{NI}(H)$ which increases linearly with H^2, i.e.,

$$\frac{T_{NI}(H) - T^*}{T_{cp} - T^*} = \frac{1}{2}\left(\frac{H^2}{H_c^2} + 2\right). \tag{3}$$

The Maier-Saupe model is a complementary approach which predicts the same three effects noted above, although the quantitative predictions cannot be evaluated analytically. Numerical minimizations of the Maier-Saupe model free energy show equivalent behavior to Eq. (3): an increase in the transition temperature which is quadratic in the applied field, ending at a critical end point [17].

Experiments.—Our observations were made in the course of measuring the magnetic-field induced birefringence above T_{cp}. The liquid crystal material was 4-chlororesorcinol bis[4-(4-*n*-dodecyloxybenzoyloxy) benzoate]; we shall refer to this compound as ClPbis10bbs. ClPbis10bbs is structurally identical to 4-chloro-1,3-phenylene bis 4-[4-(9-decenyloxy) benzoyloxyl] benzoate [18] (ClPbis10BB), except ClPbis10bbs has saturated pendant hydrocarbon chains. ClPbis10bbs exhibits a stable nematic phase between 69.7 °C and 90.1 °C. The phase transition temperatures have been identified and confirmed using polarizing microscopy, differential scanning calorimetry, and, for the present experiment, the onset of turbidity (described below).

We load ClPbis10BBs into a 2 mm × 4 mm rectangular glass capillary, which is subsequently sealed. The inner surfaces of the cell are bare (they were not treated in any way for surface alignment of the liquid crystal). The capillary is then inserted into a brass temperature-controlled oven containing 4 mm holes for optical access (the optical path length through the LC is 2 mm); temperature stability is approximately ±0.05 K. The oven is inserted into the bore of a 31 T resistive solenoid (cell 5) at the National High Magnetic Field Laboratory. The oven (and LC sample within) are oriented so that the optical path is perpendicular to the field. We use the standard optical arrangement for the measurement of birefringence using a photoelastic modulator and lock-in detection [19], with the addition of four mirrors to steer the beam from the optical breadboard into the magnet bore, through the LC, and then back to the breadboard. The details of the optics and the measurement scheme are described in Ref. [20].

There are two, complementary, measurement protocols. First, with the temperature held constant, the magnetic field is slowly ramped up from 0 to 31 T and then back down. At various values of field, we measure (using a digital signal processing lock-in amplifier and digital multimeter) three components of the modulated optical signal (dc, ω, and 2ω), where ω is the angular frequency of the photoelastic modulator. With these three components, we can extract both the phase difference between the ordinary and extraordinary rays through the liquid crystal (which is proportional to the induced nematic order parameter) as well as the overall transmittance. We repeated these measurements at various temperatures beginning about 1 K above the zero-field nematic clearing temperature, and decreasing in 0.1 K steps down until the nematic phase was observed at zero field. The onset of the nematic phase was unambiguously determined, as a function of H for fixed T above T_{cp} (as well as for $T = T_{cp}$ and $H = 0$), through an enormous increase in turbidity, which decreased the sample transmissivity to undetectable levels. The second protocol is to hold the field constant, and then slowly increase the temperature from below T_{cp}, simultaneously measuring all the Fourier components as above. The onset of the paranematic phase is clearly seen when the optical signal becomes immeasurably small.

An example of the data, following the second protocol, is shown in Fig. 1. By taking the ratio of either the ω or the 2ω components to the dc component, we extract the absolute value of either the sine or the cosine of the optical phase difference ϕ between the ordinary and extraordinary rays. As we approach the transition temperature from above, ϕ changes relatively slowly with T as the order parameter in the paranematic phase increases. At the transition, the sample becomes fully turbid and ϕ is not measurable; as the nematic phase coarsens, we recover the signal and observe an extremely rapid change in ϕ reflecting the large birefringence of the nematic. The envelope of the sine and cosine functions is seen to be less than unity; this is caused by dramatic increase in depolarized scattering from fluctuations in the vicinity of the transition temperature.

Results.—At low values of applied magnetic field we observe, above T_{cp}, the well-known field-induced nematic order as predicted by Landau–de Gennes theory, specifi-

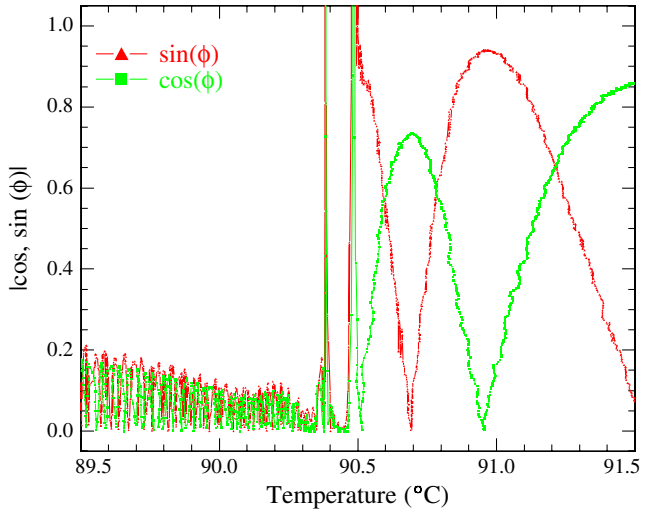

FIG. 1 (color online). Magnitudes of sine and cosine of optical phase difference versus temperature at $H = 20$ T. At 90.48 °C there is a first-order paranematic-nematic transition at which point the material becomes fully turbid and the optical signal is lost. About 0.10 °C below this temperature, the fully nematic phase becomes sufficiently transparent that we can again measure the optical phase difference, but since the birefringence is now large, the sine of the optical phase difference oscillates very rapidly as the temperature changes.

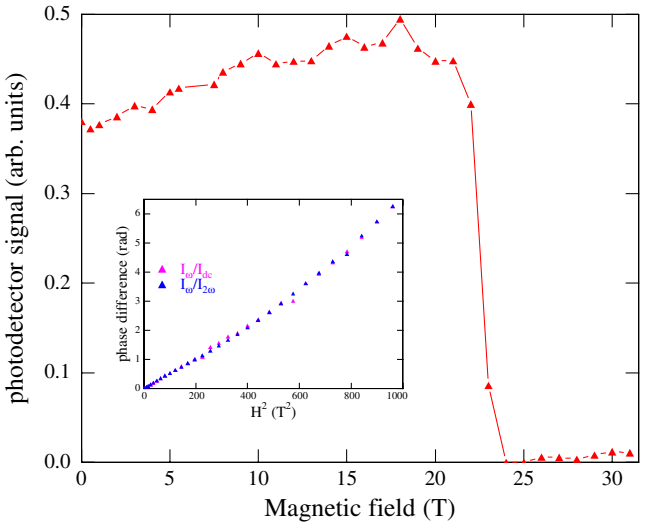

FIG. 2 (color online). Transmittance K of liquid crystal versus applied magnetic field at 0.35 K above the zero-field clearing point. At $H = 23$ T the liquid crystal becomes fully turbid indicating the onset of the nematic phase. Inset: Example of optical phase difference (computed in two different ways) versus square of magnetic field.

cally, $\Delta n \propto H^2$. From these data, and their dependence on temperature, we can determine not only the ratio $\Delta\chi\Delta n_0/a_0$ where Δn_0 is the saturated birefringence, but also T^*. This behavior is documented in Ref. [16]. Furthermore, when the temperature is substantially larger than the clearing point, this effect persists (with some deviation from linearity) for extremely large values of magnetic field, as can be seen in the inset of Fig. 2.

As the temperature approaches the clearing point, at large magnetic fields the sample becomes fully turbid as reflected in the total light transmission. The transmissivity is measured by evaluating the combination $[I_\omega/J_1(A)]^2 + [I_{2\omega}/J_2(A)]^2$, which is independent of the optical phase difference; $J_n(A)$ is Bessel's function and A is the amplitude of photoelastic modulation. An example is shown in Fig. 2, where one sees that 0.35 K above the clearing point, when the magnetic field reaches 23 T, the liquid crystal becomes fully turbid, indicating the onset of the fully nematic phase. This is the first observation of a *magnetic-field induced* first-order isotropic-nematic transition in a thermotropic liquid crystal. Furthermore, theory predicts that the field strength necessary to induce the transition should increase (until the temperature reaches T_c); this is borne out by the measurements shown in Fig. 3. The inset of Fig. 3 shows the data plotted following Eq. (3), using the value of T^* calculated by extrapolating the inverse Cotton-Mouton coefficient in the paranematic phase.

Discussion.—The possibility of a first-order field-induced isotropic-nematic transition has been apparent since the earliest days of the Maier-Saupe and Landau–de Gennes theories. However, experimental realizations have been out of reach, primarily because sufficiently large fields have been inaccessible. The field strength available using Bitter resistive magnets is the most obvious factor enabling the present observation. However, the unconventional aspects of nematic liquid crystals having a bent molecular core are also important. Previous results on the (structurally almost identical) compound ClPbis10BB revealed that the first-order character of the nematic clearing point is substantially weaker than typically reported for

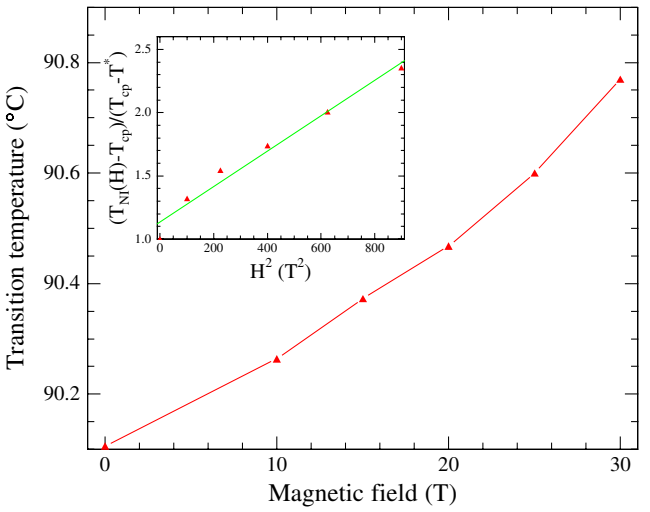

FIG. 3 (color online). Nematic-isotropic transition temperature versus applied magnetic field. Inset: Same data plotted according to Eq. (3); the line represents the best linear fit.

calamitic (rod-shaped) thermotropic liquid crystals. For example, the change in density in ClPbis10BB is approximately 10 times smaller than in methoxy-benzoyl butylaniline. Additionally, the temperature difference between the clearing point and the supercooling limit $T_{cp} - T^* = B^2/27a_0C$ is more than twice as small as for any calamitic for which results have been reported. The presence of the Q^3 term in the LdG free energy forces the N-I transition to be first order; as B becomes smaller, the transition becomes more weakly first order. Crucially, within the framework of LdG theory, the upper critical field H_c is proportional to $B^{3/2}$. This indicates a significantly smaller magnetic field should be required to observe the field-dependent change in the clearing point for bent-core nematics.

Both the Landau–de Gennes and the Maier-Saupe models predict that the clearing point should increase quadratically with magnetic field. Figure 3 shows that in our bent-core liquid crystal, this is only approximately the case. In addition, there is a further quantitative discrepancy with the Landau–de Gennes model: Since T_c is the largest temperature at which an N-I transition can be observed, the largest possible value of $\frac{T_{NI}(H)-T^*}{T_{cp}-T^*}$ is $3/2$ (1.515 in the Maier-Saupe model); this result was confirmed using a calamitic in Ref. [4]. In the inset of Fig. 3 it is seen that this quantity approaches $5/2$, and we have not yet reached the critical point. However, recent results [21] strongly indicate that the optically isotropic phase immediately above T_{cp} may actually be a tetrahedratic phase [22] (making the nematic phase actually nematic-tetrahedratic (N_T) [23]. Intriguingly, including contributions from tetrahedratic order in Eq. (1) (i.e., allowed couplings between the tetrahedratic order parameter, the nematic order parameter, and the magnetic field as in Ref. [21]) alters the predicted value of T_c. This in turn leads to

$$\frac{T_c - T^*}{T_{cp} - T^*} = \frac{3}{2} + \frac{27C}{B^2}\frac{w_{h1}^2 \Delta\chi_0^2 H_c^4}{3c_\tau}, \tag{4}$$

where w_{h1} is the coupling coefficient between Q, H, and the tetrahedratic order parameter τ, and c_τ is the (positive definite) coefficient of the τ^4 term . Since the second term in Eq. (4) must be positive, this is one possible explanation of the larger than expected value of $T_{NI}(H) - T^*$ we measured.

To summarize, the long-predicted magnetic-field dependence of the nematic-isotropic phase transition temperature has been observed. This is owing not only to the availability of enormously powerful electromagnets but also to new bent-core liquid crystalline compounds with substantially different physical properties than traditional (calamitic) materials. While the behavior found is qualitatively well described by familiar theories of the N-I transition, the extent to which the transition temperature changes is greater than predicted. If this discrepancy is indeed caused by the presence of tetrahedratic order (which remains to be confirmed), this is yet another indirect indication that such an optically isotropic ordered fluid exists.

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