

Extraordinary Magnetic Field Effect in Bent-Core Liquid Crystals

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A bent-core mesogen that forms a cybotactic nematic phase exhibits a giant magnetic field-induced shift of its nematic-isotropic and smectic-*C*-nematic transition temperatures: $\Delta T(H) = 4$ K for $H = 10$ kOe. In contrast with molecular nematics, in cybotactic nematics the field couples with the anisotropic susceptibility of clusters containing several hundred partially ordered molecules. X-ray diffraction data corroborate a quantitative estimate of inferred cluster size (~ 300 molecules). The results represent an unequivocal demonstration of the cluster picture of the nematic phase of this class of nonlinear liquid crystals.

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The extent of molecular order and the resulting broken symmetry determine the properties and mesophase type of liquid crystals (LCs). Magnetic (H) or electric (E) fields can couple to the inherent anisotropic susceptibilities and reorient the LC director—the phenomenon underlying the ubiquitous LC display. Such fields can also alter LC thermodynamic properties [1], e.g., fields can enhance molecular order [2], shift phase transition temperatures [3–6], generate new symmetries [7,8], and induce a variety of critical phenomena [9–14]. However, these effects are generally subtle and require substantial field strengths to be observed. In this Letter we report an extraordinary H -field-induced perturbation of the nematic (N) phase transition of a bent-core mesogen (BCM). The effect is orders of magnitude larger than previously reported observations [15] and appears to be intimately related to the short-range molecular clustering in this class of LCs [16].

LC phase transitions in H fields have been actively researched since 1970, when Stinson and Lister [9] measured the Cotton-Mouton coefficient near the nematic-isotropic (N - I) phase transition. Subsequently Poggi and Filippini [17] and Malraison *et al.* [18] observed field-induced quenching of long-wavelength director fluctuations, and Keyes and Shane [11] demonstrated that the N - I transition exhibits tricritical exponents. In 1981 Rosenblatt [5] unambiguously verified the theoretically predicted quadratic dependence of the temperature shift, $\Delta T_{N-I}(H) = T_{N-I}(H) - T_{N-I}(0)$, on H and extracted a value of 2.5×10^{-4} mK kOe $^{-2}$ for the slope of the $\Delta T_{N-I}(H)$ vs H^2 plot. The experiment showed that H fields as high as 150 kOe were necessary to produce minute temperature shifts of a few mK. Based on that result the estimated critical field required to reach the N - I critical end point [19] would be well over 10^3 kOe (magnetic induction $B = 100$ T), i.e., fields currently not accessible. Despite this limitation, a significant step towards that goal

was recently reported by Ostapenko *et al.* [15] using both a state-of-the-art high-field resistive magnet and a BCM nematic. They published the first observation of a H -field-induced first-order N - I phase transition, and demonstrated the potential for a H field to substantially alter the N - I transition temperature. A maximum temperature shift of 0.7 K was achieved with $H = 300$ kOe.

Apart from the extreme H field employed by Ostapenko *et al.*, we are convinced that their noteworthy result is integrally related to their choice of a bent-core LC. Thermotropic BCMs represent a new class of LCs exhibiting substantially different physical properties than traditional linear (calamitic) materials [20,21]. These include chiral mesophases composed of achiral BCMs [22], giant flexoelectricity [23,24], biaxial N order [25,26], a ferroelectric response in the N phase [27], and a large flow birefringence [28]. The consensus emerging is that the N phase of BCMs constitutes a new type of mesophase, namely, a cybotactic nematic (N_{cyb}) phase unrelated to pretransition cybotaxis [16,29], in agreement with experimental [16,27,30,31] and theoretical findings [26,32]. This N_{cyb} phase is composed of nanometer-size clusters of bent-core molecules exhibiting a relatively high degree of internal order—orientational as well as translational order (strata) imposed by close packing the BCM nonlinear shape.

The molecular structure and transition map of ODBP-Ph-OC₁₂H₂₅ (**1**), a BCM based on the nonlinear 2,5-bis(*p*-hydroxyphenyl)-1,3,4-oxadiazole moiety, is shown in Fig. 1(a). The x-ray diffraction (XRD) measurements were carried out on the BM16-CRG beam line at the ESRF (Grenoble). The energy of the incident beam was 12.65 keV and the resolution was better than $\Delta q = 3 \times 10^{-3}$ Å $^{-1}$. The sample was loaded into a thin planar cell positioned with its surface orthogonal to the incident x-ray beam. The cell (20 μm thick) was prepared using two thin

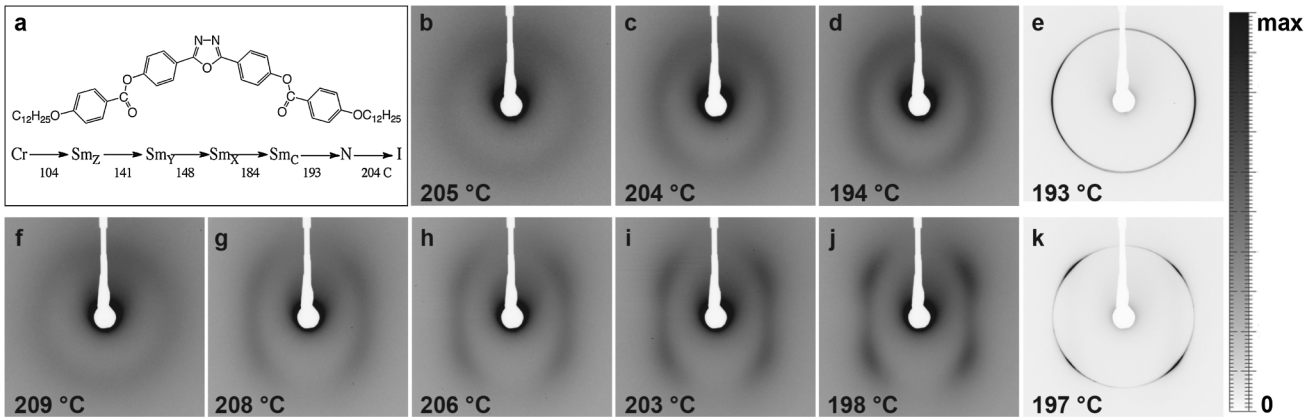


FIG. 1. (a) Molecular structure and transition map of **1**. The transition map was obtained from DSC. (b)–(e) Representative selection of small angle XRD patterns at various temperatures on cooling from the isotropic phase. (f)–(k) Representative small angle XRD patterns at various temperatures on cooling from the isotropic phase in a (horizontal) magnetic field $H = 10$ kOe. The maximum intensity value in the gray scale is (b) 450, (c),(d),(f) 900, (g),(h) 1000, (i),(j) 1100, (e) 1660, (k) 6500.

indium tin oxide-coated glass plates; antiparallel rubbed polyimide layers on the internal cell surfaces provided planar alignment. The cell was mounted on a temperature-controlled hot stage, allowing a static magnetic field $H = 10$ kOe ($B = 1$ T in air) to be applied perpendicular to the incident x-ray beam and parallel to the rubbing direction. A digital temperature controller using a Pt100 thermal probe enabled precision better than ± 0.1 °C over the whole temperature range (20–230 °C) with an accuracy better than ± 0.5 °C confirmed by melting points of standard compounds. The phase transitions were determined from the evolution of the XRD pattern on slowly changing temperature (in steps of 1 K), after allowing the sample to equilibrate at each set point. Under these conditions the system should be in thermodynamic equilibrium, thus obviating any supercooling artifact. Further experimental details are in previous papers [16,27].

Figures 1(b)–1(e) show representative XRD patterns of **1** acquired without a magnetic field ($H = 0$) in a cooling cycle from the isotropic melt, 1 °C at a time. The observed transitions are consistent with the Fig. 1(a) values [from differential scanning calorimetry (DSC) data and microscopy]. The diffuse ring of Fig. 1(b) corresponds to the isotropic phase. Below 204 °C the XRD patterns change to the four-spot patterns of Figs. 1(c) and 1(d) indicative of the skewed cybotactic nematic (N_{cybC}) phase with short-range smectic-C-like local order extensively discussed previously [16,27,30]. The nearly uniform azimuthal intensity distribution reflects relatively poor alignment of the director \mathbf{n} (i.e., the mean direction of the BCM long molecular axes) by the rubbed polyimide at the high operating temperatures. On further cooling, at $T = 193$ °C, the pattern changes to the sharp ring pattern of the smectic C (SmC) phase [Fig. 1(e)] exhibiting only marginal preferential orientation of \mathbf{n} (i.e., alignment of the SmC microdomains) along the rubbing direction.

The cooling cycle was repeated with $H = 10$ kOe after annealing at $T = 215$ °C. The corresponding XRD patterns [Figs. 1(f)–1(k)] show the same mesophase sequence observed without the field, i.e., I - N_{cybC} -SmC, but with clear evidence of an unexpectedly large temperature shift of both the I - N_{cybC} and N_{cybC} -SmC phase transitions. The stronger azimuthal intensity variation in both the N_{cybC} [Figs. 1(g)–1(j)] and the SmC [Fig. 1(k)] patterns demonstrates enhanced preferential orientation of the SmC-like cybotactic clusters and SmC microdomains, respectively, with \mathbf{n} parallel to \mathbf{H} , as anticipated for positive diamagnetic anisotropy. With the H field present, the two phase transitions occur at $T_{N-I} = 208 \pm 0.5$ °C and $T_{\text{SmC}-N} = 197 \pm 0.5$ °C, i.e., four degrees above the corresponding transition temperatures measured without a field. This result is surprising if one considers that a shift of such magnitude, never observed before, is obtained with an H field of only 10 kOe. This finding reveals a strongly enhanced susceptibility of the BCM nematic relative to conventional nematics, and is undoubtedly related to the peculiar nature of the microscopic structure in cybotactic nematics—smecticlike order within clusters as opposed to positionally independent molecules. Remarkably, the temperature shift is the same for both the I - N_{cybC} and N_{cybC} -SmC transitions, leaving unchanged the N range (11 °C) under the applied field.

The H -induced temperature shift was unambiguously confirmed by a second experiment suggested by the preliminary two-dimensional (H, T) phase diagram of Fig. 2. Namely, the ABC path in Fig. 2 is expected to display an H -field-induced N_{cybC} -SmC transition (AB) followed by a T -induced SmC- N_{cybC} transition (BC). To that end, starting from the isotropic phase with $H = 0$, the sample was first slowly cooled just below the N_{cybC} -SmC transition to $T = 193$ °C. The corresponding pattern of the SmC phase is shown in Fig. 2(a). The temperature was then increased by

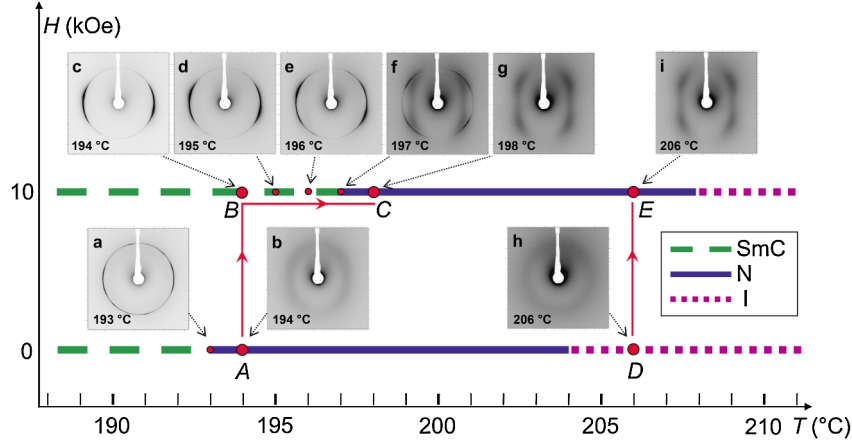


FIG. 2 (color online). Sketch of the phase diagram of **1** in the two-dimensional (T, H) space. The insets show the XRD patterns measured at selected points in the paths across the phase boundaries.

1°C and, as anticipated, we observed the $\text{SmC}-N_{\text{cybC}}$ transition [Fig. 2(b)]. Further cycling the temperature down and up by 1°C reversibly reproduced the $\text{SmC}-N_{\text{cybC}}-\text{SmC}$ phase sequence. This result is important as it implies that possible supercooling effects are limited to $<1^\circ\text{C}$, thus excluding the possibility that the transition temperature shift observed on heating may be connected to hysteresis effects. Holding the sample at $T = 194^\circ\text{C}$ (A), we applied the H field and correspondingly observed the expected field-induced $N_{\text{cybC}}-\text{SmC}$ transition, as clearly shown in the sequence of diffraction patterns in Figs. 2(b) and 2(c) along the AB line. Then, at constant $H = 10$ kOe, the temperature was slowly raised by steps of 1°C [Figs. 2(d)–2(f)] until the XRD pattern changed to that of the N_{cybC} phase [Figs. 2(f) and 2(g)], thus confirming the occurrence of the $N_{\text{cybC}}-\text{SmC}$ transition at $T = 197^\circ\text{C}$, i.e., 4°C above that at $H = 0$. We also confirmed the reversibility of the above transitions along the inverse CBA path. Noticeably, the XRD patterns of Figs. 2(c)–2(f) show that the abrupt switching on of H is followed by a slow evolution of the orientation distribution of the SmC microdomains to the preferential equilibrium alignment with \mathbf{n} parallel to \mathbf{H} [Fig. 2(f)]. This stems from the high viscosity of the SmC phase and is different from the response in the N phase on cooling the isotropic phase in the field [Figs. 1(f)–1(k)].

The phase diagram of Fig. 2 also predicts an H -field-induced $I-N_{\text{cybC}}$ phase transition (e.g., along DE) that was confirmed along the $T = 206^\circ\text{C}$ isotherm for $H = 0$ and $H = 10$ kOe [Figs. 2(h) and 2(i), respectively]. We also observed analogous extraordinary field-induced effects with BCM **1** using a low frequency (500 Hz) E field, but the induced shifts $\Delta T(E) = T(E) - T(0)$ were negative for both the $\text{SmC}-N_{\text{cybC}}$ and $N_{\text{cybC}}-I$ transitions, in agreement with negative dielectric anisotropy of **1**.

Within the Landau–de Gennes (LdG) theory of the $N-I$ transition for conventional (linear) uniaxial nematics (N_U)

[33], the applied H field enters the expansion of the free energy F in the last term

$$F = \frac{3}{4}aS^2 - \frac{1}{4}bS^3 + \frac{9}{16}cS^4 - \frac{1}{2}\Delta\chi_0SH^2, \quad (1)$$

where S is the scalar order parameter, $a = a_0(T - T^*)$ with a_0 a positive temperature-independent constant, T^* is the temperature below which the isotropic phase ($S = 0$) is unstable, $\Delta\chi_0$ is the saturated diamagnetic anisotropy, and the coefficients b and c are assumed temperature independent near the phase transition. The model then predicts, at $H = 0$, a first-order phase transition ($N-I$) at the clearing point temperature $T_{\text{cp}} = T(0) = T^* + b^2/27a_0c$ and, for $H \neq 0$, a shift in this phase transition temperature given by

$$\begin{aligned} \Delta T(H) &= T(H) - T(0) = \frac{1}{2}(T_{\text{cp}} - T^*)\frac{H^2}{H_c^2} \\ &= 3\frac{c}{a_0b}\Delta\chi_0H^2, \end{aligned} \quad (2)$$

where $H_c = \sqrt{b^3/162\Delta\chi_0c^2}$ is the critical H field corresponding to the critical point (T_c, H_c) and $T_c = T^* + b^2/18a_0c$ is the critical temperature. Introducing the latent heat (per unit volume) of the transition, $Q = -a_0b^2T_{\text{cp}}/27c^2$, Eq. (2) can be rewritten as

$$\Delta T(H) = \frac{1}{3}T_{\text{cp}}\frac{S_{\text{cp}}\Delta\chi_0}{|Q|}H^2, \quad (3)$$

where $S_{\text{cp}} = b/3c$ is the order parameter at $T = T_{\text{cp}}$. Inserting typical values of the parameters for conventional (molecular) nematics, the above equations predict a critical field of the order of 10^3 kOe [6,34] and a shift of a few mK for H of the order of 100 kOe. The much larger shift (≈ 1 K) obtained by Ostapenko *et al.* [15] with a field $H \approx 300$ kOe was speculated to arise from a combination of two factors: (i) a very high field strength, and (ii) “unconventional aspects” connected with the

bent-core nature of the nematogens, which should be manifested as a drastic reduction of the b parameter compared to conventional linear nematics. In fact, the presence of the S^3 term in Eq. (1) forces the N - I transition to be first order: as the coefficient b becomes smaller, the transition becomes more weakly first order and $\Delta T(H)$ increases [see Eq. (2)]. Equivalently, the upper critical field $H_c \propto b^{3/2}$ is reduced and smaller H fields are required to observe the field-induced shift of the clearing point. Their speculations, however, fail to provide a quantitative justification of their observed large $\Delta T_{N-I}(H)$. In fact, the limited data in the literature [15] point to b values less than 1 order of magnitude smaller than in conventional nematics. These speculations become even more tenuous in our case where a coefficient b that is 3 orders of magnitude smaller than that in Ostapenko's paper would be required to justify a shift of 4 K using an H field of only 10 kOe. This would imply a negligibly small latent heat, contrary to the measured value $Q = -0, 9$ kJ/mol [35], a value quite comparable to that of conventional nematics. On the other hand, if the LdG theory is extended to allow for nematic biaxial order (N_B), then: (i) the free energy of Eq. (1) is expanded in powers of the tensor order parameter $Q_{\alpha\beta}$ involving two scalar order parameters, and (ii) an extra term proportional to $(Q_{\alpha\beta}Q_{\beta\gamma}Q_{\gamma\alpha})^2$ must be included in the expansion [33]. The theory then predicts (at $H = 0$) a first-order N - I transition except at an isolated bicritical point $a = b = 0$, where the jump of the order parameter vanishes and the transition becomes second order. This is the Landau point [33], where one N_B , two N_U , and the I phase meet on the phase diagram (Fig. 12b of Ref. [33]). When $H \neq 0$ the Landau point splits into the critical and tricritical points (Fig. 22 of Ref. [33]), both having coordinates $b \neq 0$; these points are driven further apart along the b axis of the phase diagram when the field is increased. Accordingly, for b to be vanishingly small (very close to the Landau point), first a very low H intensity is required and second, the N - I transition must be very weakly first order (i.e., almost second order). None of these requirements correspond to our experimental conditions of $H = 10$ kOe and $|Q| = 0.9$ kJ/mol.

Consequently, we believe that the explanation of our extraordinary sensitivity to the H field lies in the peculiar biaxial-cluster picture of the N_{cyb} phase. In a molecular nematic an H field (or equivalently an E field) coupling to the anisotropy of individual molecules has a minute effect on molecular orientational ordering [1]. By contrast, if the field couples to an entire (biaxial) cluster of partially ordered molecules, its influence is magnified by a factor proportional to the average number of molecules per cluster. We estimated the size of the cybotactic clusters from the longitudinal ($\parallel \mathbf{H}$) and transverse ($\perp \mathbf{H}$) correlation lengths deduced from the intensity profiles of the four-spot patterns. Following the procedure outlined in previous papers [27,30,36], we found a longitudinal

cluster size corresponding to about 3 molecular lengths ($L \approx 48$ Å) and an average transverse size corresponding to about 10 intermolecular distances ($D \approx 4.5$ Å). Such a cluster size corresponds to $N \approx 3 \times 10 \times 10 = 300$ molecules per cluster. Accordingly, an enhancement between 2 and 3 orders of magnitude of the sensitivity of the system to the applied H field should be expected due to the cluster nature of the N_{cyb} phase.

This description is consonant with the phenomenological theory developed by Vanakaras and Photinos [26] for the molecular order in the N phase of BCMs. Their Landau expansion involves two order parameters, one associated with the ordering within the clusters and the other associated with the macroscopic order. Their expansion shows analytically the effect of enhanced susceptibility in the cluster phase compared to a conventional molecular phase. The relevant expression for the coupling of the H field would be completely analogous to that derived by Vanakaras and Photinos [26] for the E field (i.e., quadratic in H). In sum, the peculiar short-range structure of the N_{cyb} mesophase of BCMs—evanescent, biaxial clusters of tilted and stratified nonlinear mesogens percolating the nematic fluid—accounts for their unusual properties, e.g., biaxial order [26], ferroelectric response [27], and, as reported here, extraordinary field-induced effects.

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