Two-state model for nematic liquid crystals made of bent-core molecules

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Nematic (N) liquid crystals made of bent-core molecules exhibit unusual physical properties such as an intermediate phase between the N and isotropic (I) phases, a very weak NI transition as inferred from magnetic birefringence measurements in a low field, which is apparently incompatible with a large shift in the NI transition temperature (T_{ni}) measured under a high field. Using our conformational studies on the aromatic cores, we propose that only conformers which are more straightened than those in the ground state (GS) form clusters with a few layers, which persist even in the isotropic phase, as inferred from x-ray and rheological experiments. We present a Landau–de Gennes theory of the medium, including an orientational coupling between the clusters and the GS molecules, which accounts for all the unusual properties. The intermediate phase to isotropic transition is predicted to exhibit critical behavior at a very low magnetic field of <1 kG.

Most nematogenic molecules are rodlike, including those in the ubiquitous liquid crystal displays. Bent-core (BC) molecules exhibit the N phase (BCN) only if the opening angle ψ between the two arms is large enough. A well-studied system has a chlorosubstitution on the central phenyl ring as shown in Fig. 1, with $\psi \simeq 140°$ [1]. Some compounds also exhibit a lower temperature smectic C (SmC) phase, in which the long molecular axes tilt at an angle with respect to the normal to the liquid layers. Both N and SmC phases are nonpolar [2], and BCN has the uniaxial $D_{\infty h}$ symmetry [3]. We summarize below some unusual experimental results, mainly on chlororesorcinol BC compounds (Fig. 1).

(i) Extremely slow dynamics measured in light scattering [4] and nuclear magnetic resonance (NMR) [5] experiments, x-ray scattering on magnetically aligned samples which exhibit a four-spot diffraction pattern [6,7], non-Newtonian flow [8] and very large flow birefringence [9] in the isotropic phase, and cryo-TEM imaging [10] have established that the medium consists of clusters of molecules with SmC-like order, which persist in the isotropic phase. The clusters occupy only a small percentage of the volume [8,9], and their size does not change significantly across T_{ni} [7]. (ii) Magnetic birefringence measurements above T_{ni} show that the leading coefficient of the Landau–de Gennes (LdG) model ["a" in Eq. (1), below] is about 30 times smaller than in nematics made of calamitic molecules, and $T_{ni}-T^*$, where T^* is the temperature corresponding to the lowest supercooling of the isotropic phase is also reduced considerably [11], implying a very weak NI transition. (iii) However, N to field induced paranematic (PN) transition remains first ordered, occurring at $\sim T_{ni} + 0.7$ K for a magnetic field (H) of 31 T [12], the shift from T^* being much larger than $1.5(T_{ni}-T^*)$ predicted by the LdG theory for the critical point. In a BC compound with a five-atom oxadiazole heteroring at the center, the four-spot x-ray pattern was detected at $\sim T_{ni} + 4$ K [13] under $H = 1$ T, and interpreted as a 4 K enhancement in the transition point. (iv) When $H = 0$, heat capacity and other studies [14] on a chlororesorcinol compound show an isotropic to isotropic phase transition at ~ 0.4 K above T_{ni}. The authors suggested

that the intermediate phase may be the theoretically predicted [15] tetrahedratic phase, which is described by a third-rank tensor order parameter allowed by the symmetry of a BC molecule. (v) In cyanoresorcinols [16] the tilt angle *doubles* in SmC phase compared to that in the clusters as the temperature is lowered across T_{cn}, the N-SmC transition point: The molecular interactions generating the tilt are *different* in the clusters and the SmC phase.

In the models proposed in [17,18] clusters fill the entire volume, contrary to the experimental results of [8,9]. Molecular biaxiality has been shown to weaken the NI transition [19], but cannot account for the large field induced shift in the transition temperature. Atomistic simulations on an assembly of 256 oxadiazole BC molecules [20] have shown many conformations and polar domains without SmC-like order in the BCN phase. A Monte Carlo simulation of an assembly of a few thousand (simplified models of) BC molecules [21], each with flexible end groups, and interacting with a soft potential, shows that polar domains with smecticlike order can develop in the nematic phase. It is obviously important to look for specific aspects of conformations of real molecules which can give rise to the clusters.

The layering order in thermotropic liquid crystals mainly arises from the biphilicity of the molecules [2], the strength of the London dispersion energy between the aromatic cores with high polarizability being much larger than that between sufficiently long alkyl chains at the two ends. We used the SPARTAN-4 (molecular mechanics) package to look at all the conformations of only the *aromatic core* of chlororesorcinol. The ester group is relatively flexible, and in a vast majority of more than 50 conformations, the lowest moment of inertia (I_{min}, around the long axis of the conformer) is above 19 000 atomic units [Fig. 1(a)]. However, a few conformers which have higher energies, and together account for $\sim 15\%$ in the Boltzmann distribution at 300 K, have $I_{min} < 15\,000$ units [Fig. 1(b)]. The latter, more straightened conformers can approach each other at a closer distance. The dispersion energy, which is $\propto r^{-6}$, is about twice that of the more numerous conformers, *increasing* the thermal stability of the layers.

If n excited-state (ES) conformers, each with an effective area $a,$ form a layer of radius R, the peripheral molecules occupy an area $\pi[R^2-(R-a^{0.5})^2]$, and their number
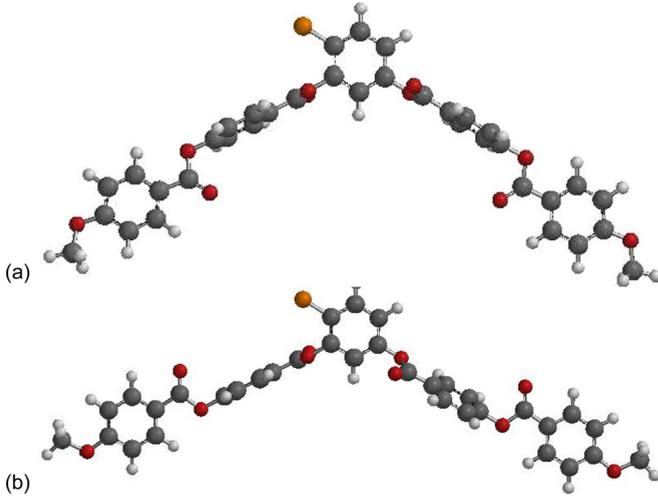
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FIG. 1. Two conformations of the aromatic core of chlororesorcinol BC molecule. With ten carbon-atom chains replacing the methyl groups at both ends, the compound exhibits N phase, which has been extensively studied. Most of the conformations as in (a) have relatively large moments of inertia I_{min} about the long axes, with 15% in excited-state conformations as in (b), with lower I_{min}.

$n_p \approx \pi[2(n/\pi)^{0.5} - 1]$. If E_{ex} is the excitation energy of the conformer, and $-E_{int}$ the energy gained by an ES conformer when it is surrounded by other ES conformers, the total energy of the layer $E_{tot} = nE_{ex} - E_{int}[n - n_p(1-p)]/2$, where p is the fraction defining the number of neighbors of a peripheral molecule compared to that of a molecule in the interior, and the division by 2 takes care of double counting. If $p \approx 0.6$ and $E_{int}/E_{ex} = 2.8$, E_{tot} becomes negative for $n \geqslant 16$, and layers with a larger number of ES conformers can have a relatively long life.

Layers can form randomly when many ES conformers come close together by a favorable concentration fluctuation [22]. A few of these layers can stack up, mainly by the depletion interaction, the surrounding ground-state (GS) molecules (or more realistically, short range ordered groups of such conformers) acting as the depletants [23]. The resulting clusters have a dynamic nature, as molecules at the edges can escape, or a new ES conformer can be absorbed. If the end chains are very long, some additional diffraction spots are seen in the "Cyb$C$" phase, which appears before the transition to the SmC phase [16]. Short range SmC-type order of the *GS conformers*, whose correlation length diverges as T_{cn} is approached [2], can generate the additional diffraction spots. A variety of experimental results on SmC liquid crystals made of rodlike molecules can be understood on the basis of a molecular theory that we had proposed some time ago [24,25]. In this model, *off-axis dipolar groups* in the molecules which rotate freely about their long axes give rise to a strong repulsive intermolecular interaction in a SmA layer, which is reduced by a tilting of the molecules. A competing entropic contribution from the excluded volume effect which increases with the length to width ratio of the molecule opposes tilting, to determine the equilibrium tilt angle. The structure of the BC molecules (Fig. 1) is particularly suitable for tilting in the layers. Indeed the observed reduction of the tilt angle in the clusters as the chain length is increased, and also as

temperature is lowered in a homologue [16], can be understood on the basis of the increased contribution of the excluded volume effect [24].

We propose an LdG theory for the *BCN* phase using the following simplifying assumptions: (i) The medium consists of molecules in only *two* states, viz., the GS, and ES with energy E_{ex}. (ii) The excited molecules form clusters with SmC-type layering, whose effective transition temperature to the isotropic phase is several degrees ($\sim$10 K, say) above T_{ni} of the GS conformers. (iii) The number of excited molecules N_c in the clusters is fixed, and temperature independent as the LdG theory is valid only in the vicinity of T_{ni}. (iv) As $N_c \sim 100$, the clusters have nanometric dimensions, and interact with the surrounding "sea" of GS conformers, and with any external magnetic field, only by appropriate *orientational* couplings. (v) As *BCN* has uniaxial symmetry [3], scalar order parameters are adequate for the analysis [2].

We write the LdG free energy *density* of the medium as

$$F = (1-x)\left\{ \frac{a_g}{2}(T - T^*)S_g^2 - \frac{B_g}{3}S_g^3 + \frac{C_g}{4}S_g^4 - E_h S_g \right\}$$
$$+ \frac{x}{N_c}\left\{ -(1-x)\gamma S_g S_c + \frac{\alpha_c}{2}S_c^2 + \frac{\beta_c}{4}S_c^4 \right\} - xJE_h S_c,$$

(1)

where the subscripts g and c signify GS molecules and clusters of ES conformers, respectively. The mole fraction of the ES molecules is $x = x(T) = \exp(-E_{ex}/k_B T)/[1 + \exp(-E_{ex}/k_B T)]$, increasing with T, where k_B is the Boltzmann constant. The orientational order parameters (OOPs) are given by $S_g = \langle \frac{1}{2}(3\cos^2\theta_g - 1)\rangle$; $S_c = S_{cd}S_e$ with $S_{cd} = \langle \frac{1}{2}(3\cos^2\theta_{cd} - 1)\rangle$ and $S_e = \langle \frac{1}{2}(3\cos^2\theta_e - 1)\rangle$, where θ_g and θ_{cd} are the polar angles made by the long axis of a GS conformer and the local director of a cluster with the director of the medium, θ_e the angle made by the long axis of an ES conformer with the local director of a given cluster, and the angular brackets denote appropriate statistical averages. The GS conformers exhibit a first order nematic to isotropic transition, described by the LdG parameters a_g, T^*, B_g, and C_g. The clusters have a low concentration and in the field-free case their orientational order arises only due to the coupling with the GS molecules, γ being the coupling constant. Saturation terms with coefficients α_c and β_c ensure that $S_c < 1$. The terms in the second pair of curly braces in Eq. (1) are divided by N_c to get the free energy *density*. A magnetic field H acts on the positive anisotropy of (volume) diamagnetic susceptibility of both types of conformers. $E_h = \Delta\chi_g H^2/3$, $\Delta\chi_g$ being the anisotropy when $S_g = 1$. The ES molecules have a larger anisotropy; i.e., $J > 1$.

The equilibrium conditions are $\partial F/\partial S_g = \partial F/\partial S_c = 0$, stability requiring that the Hessian $(\partial^2 F/\partial S_g^2)(\partial^2 F/\partial S_c^2) - (\partial^2 F/\partial S_g \partial S_c)^2 \geqslant 0$, the equality holding *only* at the critical point. The entropy density $\Sigma = -dF/dT$, and the specific heat at constant volume $C_v = -Td^2F/dT^2$ can be calculated by taking into account the explicit dependence of x on T. $F \sim k_B T/$(molecular volume), and usually the numerical values of the coefficients are expressed in 10^7 cgs units. As the molecular weight of a typical BC molecule is 3 to 4 times larger than that of a rodlike molecule, the LdG
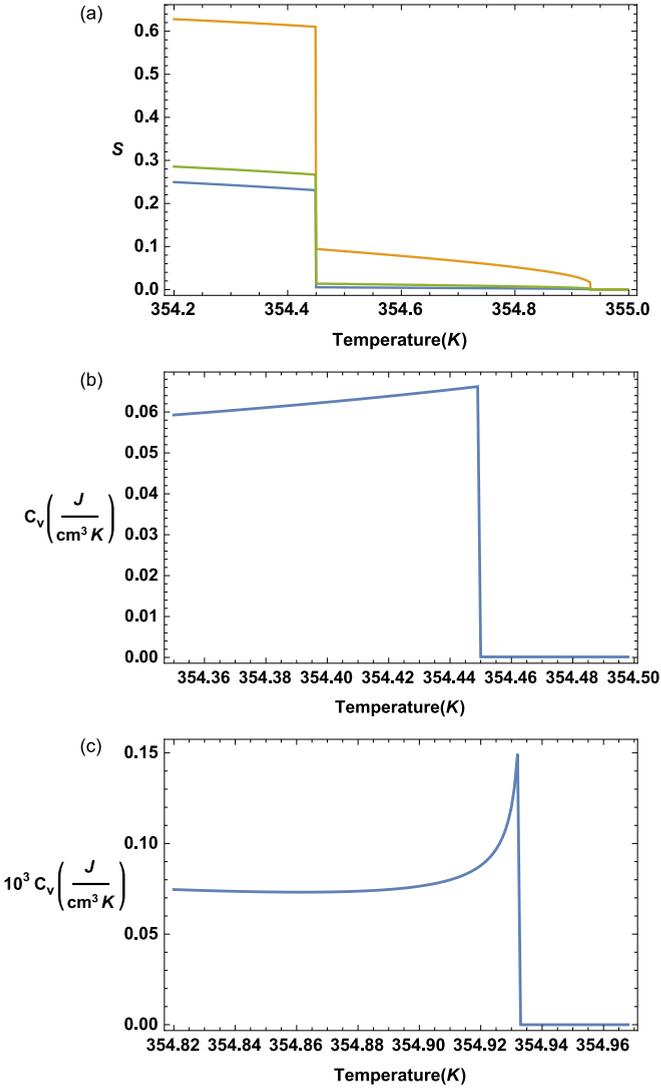
FIG. 2. (a) Temperature variations of the order parameters. S_c (top), S_m (middle), and S_g (bottom) show jumps at the nematic to coupling induced paranematic phase transition at $T_{npn} \simeq 354.45$ K and also at the very weak paranematic to isotropic transition at $T_{pni} \simeq$ 354.93 K. Temperature variations of the specific heat C_v around (b) T_{npn} and (c) T_{pni}. Note the large difference in the C_v scales between (b) and (c).

coefficients of even the GS conformers can be expected to be smaller. We use the following parameters in $10^7/4$ cgs units: $a_g = 0.04$, $B_g = 1.7$, $C_g = 4.5$, $\gamma = 5.0$, $\alpha_c = 0.22$, and $\beta_c = 4.0$. Further, $E_{ex} = 1.1 \times 10^{-13}$ ergs, $T^* = 350$ K, $N_c = 50$, and $J = 1.2$. Properties like optical birefringence sense the *average* OOP [26] which is given by $S_m = (1-x)S_g + xS_c$. We use *Mathematica-10* to look for real solutions S_g and S_c. Far away from any first order phase transition, there is only one real solution, with either $S_g = S_c = 0$ corresponding to the isotropic phase with $F = 0$, or both the OOPs have some fractional positive values in an orientationally ordered phase, with $F < 0$. Note that in the isotropic phase, the order parameter S_e of the ES molecules within a cluster is expected to remain finite, while S_{cd} goes to zero. On approaching a first order phase transition point, there are three solutions,

two minima being separated by a maximum in F, the stable phase having the lower minimum. The concentration x is ~ 0.09, varying only by $\sim 1\%$ in the temperature range of interest.

Temperature variations of S_g, S_c, and S_m are shown in Fig. 2(a) for the field-free case. The most important result is that the *nematic phase undergoes a transition to a "paranematic" (PN) phase* with extremely low values of the OOPs at T_{npn}. PN has a weak first order transition to the isotropic phase at a higher temperature T_{pni}. The intermediate phase arises due to the coupling between S_c and S_g, and its width decreases as α_c is increased. Ignoring the cubic and quartic terms in S_g in Eq. (1), $S_c^2 \simeq [\gamma^2 x(1-x)/N_c a_g(T - T^*) - \alpha_c]/\beta_c$. Fixing all other parameters at the values listed above, the nematic has a direct transition to the isotropic phase if $\alpha_c \geqslant 0.244$. $S_c > S_g$ in the ordered phases, and T_{npn} is higher than T_{ni} (=353.57 K) of only the GS molecules (with $x = 0$). The temperature variations of C_v near the two transitions are shown in Figs. 2(b) and 2(c). In the mean field model, fluctuations are ignored, and experimentally it is known [2] that C_v does not jump down to zero at T_{ni}. As the temperature range of the PN phase is just $\sim 0.5°$, in experiments the two specific
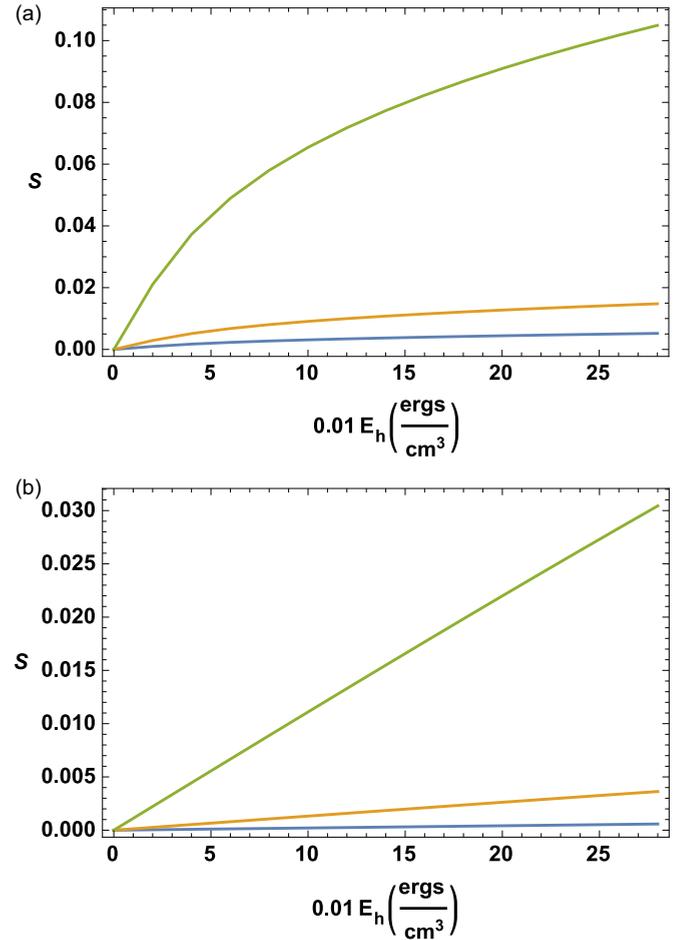

FIG. 3. Variations of the field induced order parameters with E_h. From top to bottom, S_c, S_m, and S_g. (a) At $T = 355.4$ K, ~ 1 K above T_{npn}, S_c saturates at higher values of E_h inducing similar variations in S_g and S_m. (b) $T = 366.4$ K is ~ 12 K above T_{npn}, and the smaller values of the order parameters exhibit linear variations.
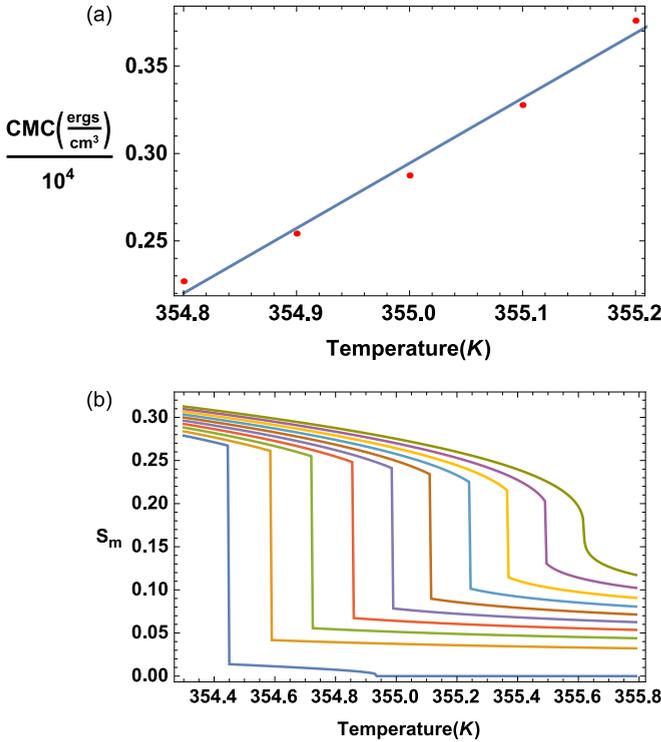
FIG. 4. (a) Effective inverse Cotton-Mouton coefficient CMC $= E_h(1 - x + Jx)/S_m$ as a function of temperature for $E_h = 25 \, \text{ergs/cm}^3$. (b) Temperature variations of S_m for different magnetic fields. The lowest curve is for $E_h = 0$, with an increment in E_h of $1.35 \times 10^3 \, \text{ergs/cm}^3$ (or about $120 \, \text{T}^2$) between successive higher curves. The highest, $E_h = 12.15 \times 10^3 \, \text{ergs/cm}^3$, is close to the critical value, with $T_{\text{crit}} \approx 355.62 \, \text{K}$.
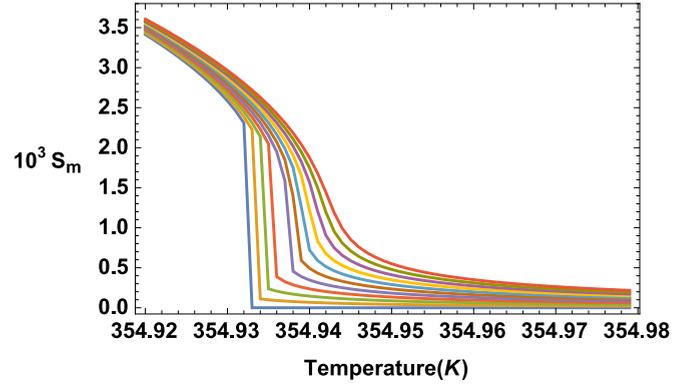

FIG. 5. Temperature variations near T_{pni} of the average orientational order parameter at different magnetic fields. The lowest curve is for $E_h = 0$, with an increment of $0.011 \, \text{ergs/cm}^3$ in E_h between successive curves. The critical field corresponds to $E_h = 0.055 \, \text{ergs/cm}^3$, and the critical temperature $\simeq 354.938 \, \text{K}$.

heat peaks can be expected to ride on a large background. Fluctuations can also make the very weakly ordered PN phase to have a practically "isotropic" appearance, and may account for the second specific heat peak (at constant pressure) found at $T_{ni} + 0.4 \, \text{K}$ in [14]. The viscosities were also found to drastically decrease at $\sim 5 \, \text{K}$ above T_{ni} [14]. It is tempting to attribute this to the *melting of the clusters* around that temperature.

A field H also induces a PN phase above T_{npn}, with weak order parameters. S_c is *much larger than S_g in the field induced phase* [Figs. 3(a) and 3(b)] and has a profound influence on the properties of that phase. Close to T_{npn}, S_c rapidly increases with H, but starts saturating due to the α_c and β_c terms of Eq. (1), giving rise to the nonlinear variations seen in Fig. 3(a). At a much higher temperature, S_c remains small, and the variation is linear [Fig. 3(b)], in agreement with experimental trends [14].

We have plotted an effective inverse Cotton-Mouton coefficient (CMC) versus T in Fig. 4(a) for $E_h = 25 \, \text{ergs/cm}^3$ [27–29]. A linear fit up to $\sim T_{npn} + 2 \, \text{K}$ yields $a_m = 0.0015$ and $T_m^* = 354.2 \, \text{K}$, just $\sim 0.25 \, \text{K}$ below T_{npn}, which is significantly smaller than $T_{ni} - T^* \approx 3.6 \, \text{K}$ of only the GS molecules when $x = 0$. Further, a_m, which is the coefficient of the quadratic term of an *effective* LdG model of the medium, is about 25 times smaller than the assumed $a_g = 0.04$. Both these trends agree with the experimental data of [11]. However, the

extrapolated value of T_m^* is *sensitive* to E_h, and decreases as E_h is increased, and may account for $T_{ni} - T^* = 0.8 \, \text{K}$ found in a later experiment [14]. A crude evaluation shows that $d(1/S_c)/dT \simeq 1/S_c(T - T^*)$. For low values of H and high temperatures, S_c is small and the slope is large, which enhances the effective T_m^*. As the transition point is approached, S_c becomes large enough to start to saturate, and the slope actually starts to decrease [Fig. 4(a)]. At higher values of E_h, S_c is large, leading to a smaller slope, which effectively decreases T_m^*. However, a_m depends on the small value of $x\alpha_c/N_c$, and does not vary much with E_h. The theoretical phase diagram [Fig. 4(b)] under H shows a large enhancement of T_{npn} with E_h. Thus both the weakened NI transition as measured at low E_h [11], and the persistence of a *first-order* nematic to field induced PN transition at a large E_h [12] arise due to the strong response of the clusters to the field. From Fig. 3(a), $S_c \simeq 0.03$ at $T = T_{npn} + 1 \, \text{K}$ for $E_h = 20 \, \text{ergs/cm}^3$, which corresponds to $H \simeq 1 \, \text{T}$. However, from Figs. 3(a) and 4(b), the medium is in the PN phase with a low value (<0.005) of S_m. $N_c \approx 300$ in the oxadiazole BC compound used in [13], and the field induced S_c appears to become sufficiently large even at $T_{ni} + 4 \, \text{K}$, for the four-spot x-ray diffraction pattern to show up using an intense synchrotron source, though S_m can be expected to remain small. The medium would be in the field induced PN phase, and the observations do not signify a large shift in T_{npn} itself.

An obvious question of interest is the response of the intermediate, coupling induced PN phase to an external magnetic field. From Fig. 4(b), when H is more than 10 T, the field induced order parameter dominates and the effect of the intermediate phase is practically invisible. The PN to PN transition shows a critical point at $E_h \simeq 0.055 \, \text{ergs/cm}^3$, which corresponds to $H \sim 700 \, \text{G}$, and the critical transition point is only $\sim 0.006 \, \text{K}$ above T_{pni} (Fig. 5). However, the characteristic sigmoid shape of the temperature variation of the order parameter persists up to a few kilogauss, which betrays the underlying weakly ordered phase. Careful low field experiments will be able to test this prediction of our model.

In summary, it is argued that only the ES conformers with reduced moments of inertia about the long axes form clusters

with SmC-type order. Using the LdG theory, the following results which agree with experiments, are found to arise from the substantially larger order parameter of the clusters compared to that of the GS conformers: the occurrence of a coupling induced paranematic phase in a small temperature range above the main transition in a field-free sample; a weakening of the transition as shown by the Cotton-Mouton effect at low fields, in spite of which there is a large shift in the nematic to field induced paranematic transition temperature under a high magnetic field; and nonlinear variations with H^2 of the induced order parameters just above the transition point.

The coupling induced paranematic to isotropic transition itself is predicted to become critical at a low value of magnetic field. The model is obviously highly simplified, as in the real compound there are about 50 conformers, and the dynamic clusters can be expected to have a distribution of sizes. Dielectric and flexoelectric properties of *BCN* also exhibit very unusual trends [1]. However, unlike the magnetic properties, they are sensitive to the polar or apolar nature of the structure of the clusters [1].

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[27] If $E_h = 25\,\text{ergs/cm}^3$ corresponds to $H = 1.5\,\text{T}$, $\Delta\chi \simeq 3\times10^{-7}$ cgs units, which is consistent with the value estimated as $\chi_a(4\pi) \simeq 5.8\times10^{-7}$ cgs at $T_{ni}-2\,\text{K}$ in Ref. [28], and the density functional calculation on a closely similar BC molecule in Ref. [29].

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