PHYSICAL REVIEW E **68**, 031703 (2003)

Light scattering investigation above the nematic–smectic-*A* phase transition in binary mixtures of calamitic and bent-core mesogens

Mohammad Reza Dodge, Rolfe G. Petschek, and Charles Rosenblatt*
Department of Physics, Case Western Reserve University, Cleveland, Ohio 44106-7079, USA

Mary E. Neubert and Margaret E. Walsh
Liquid Crystal Institute, Kent State University, Kent, Ohio 44242-0001, USA

(Received 8 May 2003; published 11 September 2003)

Quasielastic light scattering measurements were performed in the nematic phase of mixtures consisting of the calamitic mesogen 8OCB doped with small concentrations of the bent-core molecule P-7PIMB. It was found that the regular part of the bend elastic constant decreases strongly with dopant concentration *X*. Close to the nematic–smectic-*A* phase transition temperature, the divergent part of the bend elastic constant, which is proportional to the bare correlation length $\xi_{\|}^{0}$ parallel to the layer normal, also decreases rapidly with *X*. The effect of the dopant on $\xi_{\|}^{0}$ is examined in brief theoretically.

DOI: 10.1103/PhysRevE.68.031703 PACS number(s): 61.30.Gd

On cooling from the nematic (N) to the smectic-*A* (Sm-*A*) phase, orientationally ordered liquid crystalline molecules develop a one-dimensional density modulation parallel to the "director" $\hat{n}$, i.e., parallel to the average molecular orientation. The critical properties associated with this transition have fascinated investigators for more than two dozen years, as the behavior often is found to deviate from the inverted three-dimensional *XY* model [1]. Several factors contribute to these deviations, including the Landau-Peierls instability and coupling between the nematic and smectic order parameters [2]. The addition of a second liquid crystalline species also may give rise to exotic behavior at the N–Sm-*A* transition. The classic example is the existence of a reentrant nematic phase at low temperatures in mixtures of two or more mesogens [3–5], one of which does not have a Sm-*A* phase. More recently Pratibha, *et al.* obtained the temperature-concentration phase diagram for mixtures of bent-core molecules in a calamitic mesogenic solvent [6]. By observing textures in the smectic-*A* phase, they deduced a likely orientation of the bent-core mesogen with respect to the smectic layers and showed that the smectic-*A* phase may be biaxial.

Recently we used the Fréedericksz technique to examine the bend elasticity of a mixture of a small quantity of bent-core ("banana") molecules, 1,3-phenylene bis[4-(4-heptyl phenyliminomethyl benzoate], also known as P-7PIMB, in an ordinary calamitic nematogen 4-butoxybenzylidene-4-octylaniline (4O.8). We found that over much of the nematic phase, but well above the N–Sm-*A* transition temperature T_{NA}, the bend elastic constant K_{33} decreases substantially with increasing bent-core concentration *X* [7]. In fact, for weight fraction $X=10.8\%$ at 8 °C below the nematic-isotropic phase transition temperature T_{NI}, K_{33} was found to be approximately one-half its value for the pure ($X=0$) compound 4O.8. Although our theoretical analysis met with some success, we were unable to explain the full extent of the decrease in bend elasticity. In this paper we turn to a light scattering study of mixtures of bent-core and calamitic mesogens, with special emphasis on the behavior of K_{33} in the vicinity of T_{NA}. As before, we use the bent-core molecule P-7PIMB. However, to avoid complications due to the instability of the Schiff's base in 4O.8, we have chosen to examine mixtures of P-7PIMB in 4′-*n*-octyloxy-4-cyanobiphenyl (8OCB).

Several mixtures were prepared by doping the bent-core compound P-7PIMB in 8OCB (Fig. 1). The compound P-7PIMB was synthesized at the Kent State University, and the compound 8OCB was obtained from Merck. Each concentration of the mixture was prepared by dissolving appropriate quantities of the two components in chloroform and heating the solution to 60–70 °C for several hours to evaporate the solvent. Cells consisted of glass microscope slides that consecutively were washed in detergent, distilled water, acetone, and ethanol. The glass slides then were dried and spin coated with the polyimide RN1266 (Nissan Chemicals) and baked according to the manufacturer's specifications. The polyimide-coated slides were rubbed unidirectionally by

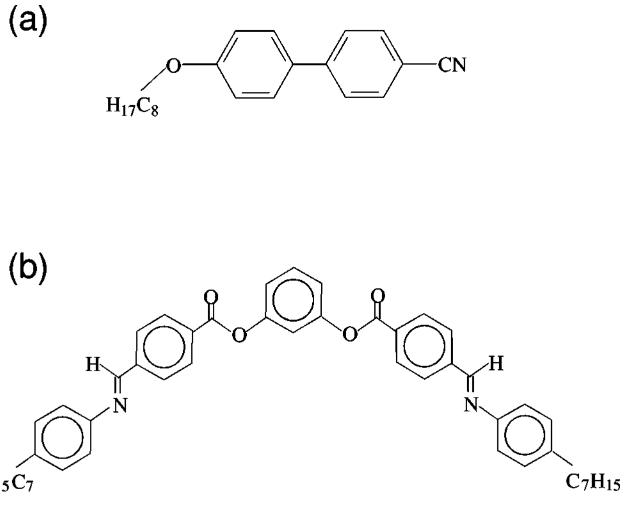

FIG. 1. The chemical structure of (a) the rodlike molecule (8OCB) and (b) the bent-core molecule (P-7PIMB).

---

*Corresponding author. Email address: rosenblatt@case.edu

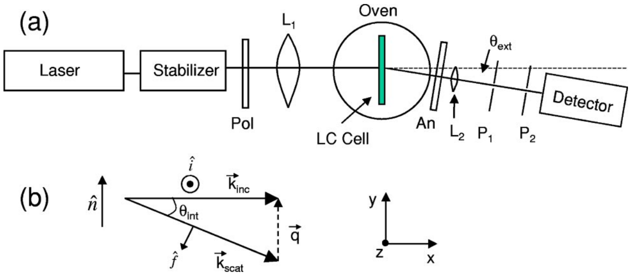

FIG. 2. The light scattering setup.

a velvet cloth, dipped in isopropol alcohol, and then sonicated to remove any particulate matter that may have arisen from the rubbing process. Cells were constructed by placing two slides together, separated by Mylar spacers of nominal thickness 12.5 μm, and cemented. The actual thickness of cells ranged between 16 and 20 μm. Each cell was filled in the isotropic phase of the mixture and cooled slowly to the nematic phase in a chamber designed for light scattering experiments; the chamber was temperature controlled to approximately 10 mK.

Figure 2(a) shows the experimental setup. Light from an argon-ion laser (wavelength $\lambda = 5145$ Å) passed through an intensity stabilizer, a polarizer, a focusing lens ($f = 197$ mm) L_1, and the cell; the diameter of the laser spot was approximately 300 μm at the cell. The light scattered at external angle θ_{ext} passed through an analyzer and a second lens L_2, which was used to form a real image of the scattering region at pinhole P_1. Pinhole P_2 was used to limit the scattered light to a single coherence area, which was detected by a photomultiplier tube. The output from the photomultiplier tube was fed into a pulse amplifier and discriminator, and then into a Brookhaven Instruments BI-9000 digital autocorrelator. Further details are given in Ref. [8]. Figure 2(b) shows the internal scattering geometry. The incoming light $\hat{i}$ was polarized along the z axis and the scattered light $\hat{f}$ was polarized in the xy plane. Because the undisturbed director $\hat{n}$ was oriented in the scattering plane along the y axis, only twist or bend fluctuations $\vec{\delta} n$ of the director were sampled. The average intensity $\overline{I}$ of the scattered light is

$$\overline{I} \propto (\Delta\epsilon)^2 \Gamma(\theta_{int}) k_B T \left(\frac{\cos^2\theta_{int}}{K_{33} q_\parallel^2 + K_{22} q_\perp^2} \right), \tag{1}$$

where $\Delta\epsilon$ is the dielectric anisotropy, k_B is Boltzmann's constant, θ_{int} is the internal scattering angle, K_{22} is the twist elastic constant, and $\vec{q}_\parallel$ and $\vec{q}_\perp$, respectively, are the components of the scattering wave vector $\vec{q}$ parallel and perpendicular to $\hat{n}$. The quantity $\Gamma(\theta_{int})$ is a geometric factor for our apparatus. As $\Gamma(\theta_{int})$ is nearly constant over the range of scattering angles used in the experiment [8], we may take $\Gamma = 1$ for all θ_{ext}. The components of $\vec{q}$ depend on the refractive indices of the sample, viz., $q_\parallel = 2\pi n_e^{eff} \sin\theta_{int}/\lambda$ and $q_\perp = 2\pi(n_e^{eff}\cos\theta_{int} - n_0)/\lambda$, where n_o is the ordinary refractive index and n_e^{eff} is the *effective* extraordinary refractive index. n_e^{eff} is given by $n_e^{eff} = n_o n_e (n_e^2 \sin^2\theta_{int} + n_o^2 \cos^2\theta_{int})^{-1/2}$, where n_e is the extraordinary refractive index. Note that $\Delta\varepsilon = n_e^2 - n_o^2$ and that θ_{int} can be related to the external scattering angle θ_{ext} via Snell's law. For each measurement the scattering angle θ_{int} (and thus θ_{ext}) was adjusted so that $q_\perp = 0$; this allowed us to probe pure bend distortions. To accomplish this we needed to know the dependence of the refractive indices n_o and n_e on temperature and concentration. Measurements for n_o and n_e were made using an Abbe refractometer for the pure ($X=0$) 8OCB and for the $X=6$ wt% mixture, as shown in Fig. 3; the refractive indices for other concentrations were obtained by interpolation.

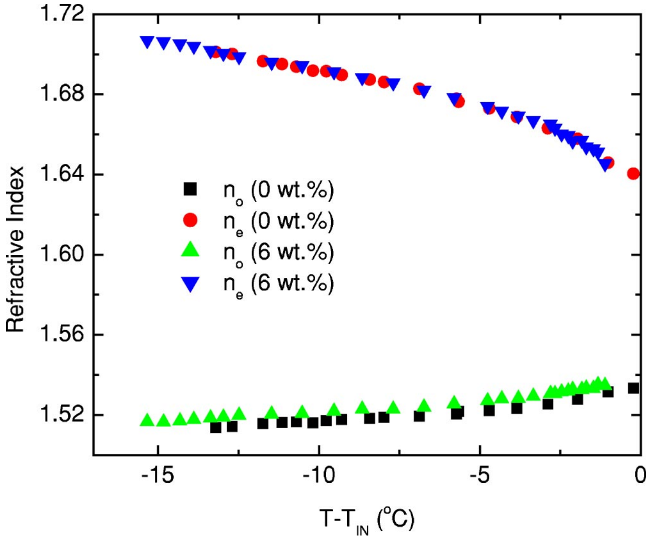

FIG. 3. Extraordinary (n_e) and ordinary ($n_{o)}$ refractive indices for the $X=0$ and $X=6$ wt% mixtures at wavelength $\lambda = 6328$ Å.

For each concentration we measured the temporal autocorrelation function $G(t) = \langle I(t')I(t'+t)\rangle_{t'}$ and the average intensity $\overline{I} = \langle I(t')\rangle_{t'}$ of the scattered light as functions of temperature, where $\langle\ \rangle_{t'}$ corresponds to an average over time. In all cases $G(t)$ was found to exhibit a single exponential decay, indicating that the experiment was operating in the homodyne regime. Examining the intensity data first, we note from Eq. (1) with $q_\perp = 0$ that the bend elastic constant

$$K_{33}(X,T) = \beta(X)[n_e^2 - n_o^2]^2 k_B T \frac{\cos^2\theta_{int}}{\overline{I} q_\parallel^2}, \tag{2}$$

where $\beta(X)$ is a concentration-dependent proportionality constant. To obtain absolute values for K_{33} we determined the proportionality constant $\beta(X)$ in Eq. (2) by scaling the intensity data for pure 8OCB ($X=0$) with values reported in the literature [9] at identical values of $T - T_{NI}$. Figure 4 shows our results for K_{33} vs T at $X=0$. From Fig. 4 it is clear that the temperature dependence of our data is in excellent agreement (to within the scaling factor) with that of Ref. [9] over the entire temperature range that is common to both sets of data. Later we shall determine K_{33} for $X \neq 0$.

Let us now turn to the dynamic data. The relaxation time τ for bend fluctuations was obtained as a function of temperature for each concentration by fitting the homodyne au-

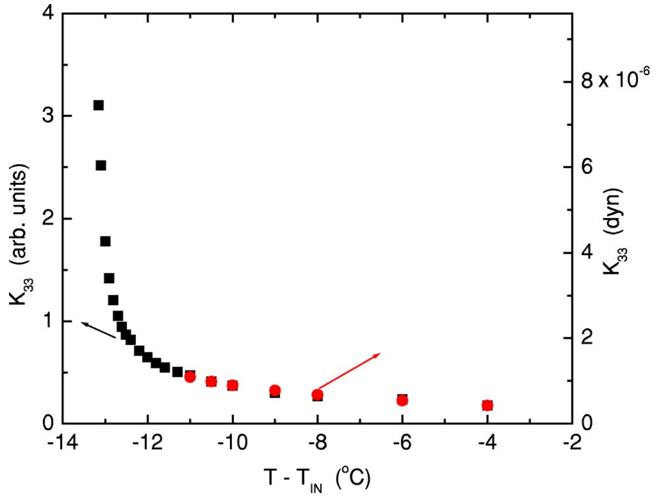

FIG. 4. K_{33} vs $T-T_{NI}$ at $X=0$. Left hand data (■) correspond to our data in arbitrary unit obtained from intensity measurements. Right hand data (●) correspond to data from Ref. [9].

tocorrelation function $G(t)$ to a single exponential decay, viz., $G(\tau)=G_0+b\exp(-2t/\tau)$, where G_0, b, and τ are fitting parameters. For $X=0$ we obtain the viscosity of the bend mode, η_{bend}, as a function of temperature from Ref. [2]:

$$\eta_{bend}(T)=K_{33}(T)q_{\|}^2\tau(T). \tag{3}$$

Figure 5 shows η_{bend} at $X=0$. Even though the bend viscosity, like the bend elastic constant, diverges as the temperature approaches nematic–smectic-*A* transition [10], its divergence is not as rapid as that of K_{33}, at least over the measured temperature region. Considering that our most concentrated mixture is $X=6$ wt % (equivalent to less than 0.03 mole fraction) we make the assumption that the temperature-dependent viscosity varies negligibly with X at temperatures well above T_{NA}. Therefore, in the region $4\leqslant T_{NI}-T\leqslant 8$ °C we use the deduced values of $\eta_{bend}(T)$ at $X=0$, the measured relaxation times $\tau(X,T)$, and Eq. (3) to obtain $K_{33}(X,T)$ at temperatures well above T_{NA}. We now return to Eq. (2) in order to obtain $K_{33}(X,T)$ over the *entire* temperature range, including the divergent part near T_{NA}. Since the elastic constant $K_{33}(X,T)$, the refractive indices, the temperature, the scattering angle $\theta_{int}(X,T)$, the wave vector $q_{\|}(X,T)$, and the average intensity $\overline{I}(X,T)$ all are known *well above* T_{NA}, we can obtain the proportionality constant $\beta(X)$ for each concentration X in Eq. (2). Moreover, because Eq. (2) does not depend on the viscosity, once we have obtained the proportionality constants we can determine $K_{33}(X,T)$ over the entire temperature range for all concentrations. Results are shown in Fig. 6.

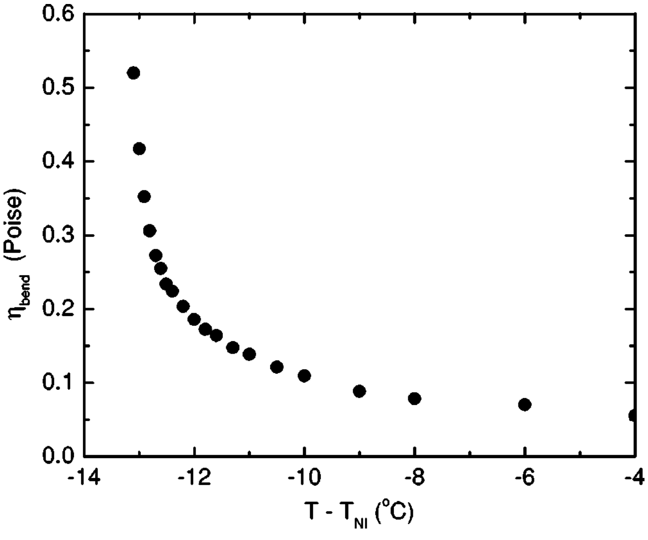

FIG. 5. η_{bend} vs $T-T_{NI}$ at $X=0$.

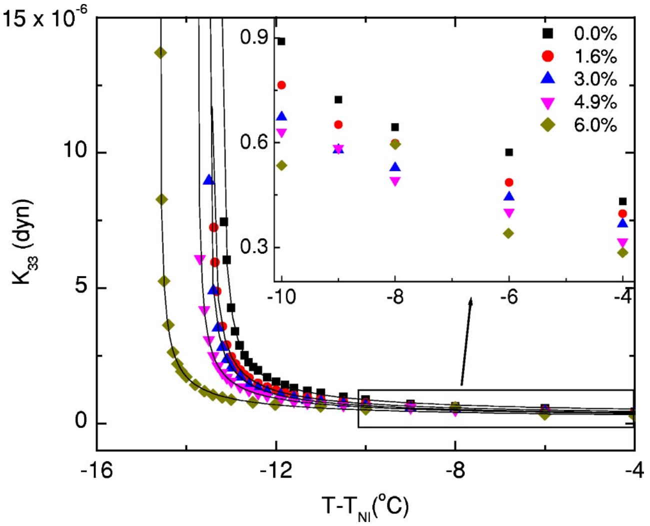

FIG. 6. Deduced bend elastic constant vs $T-T_{NI}$ for all mixtures. Key is shown at the upper right. Details for dashed box are shown in the inset. Solid curves represent fits to Eq. (4).

In a previous paper we had examined the effect of the bent molecule P-7PIMB on the bend elastic constant well above T_{NA} when mixed in small quantities with 4O.8 [7]. It was found that K_{33} was reduced by about one-half for $X=10.8$ wt %, an effect that mirrors the behavior of the much larger bend elastic constant (by about ~30%) for a straight dimeric liquid crystal vs a bent dimeric liquid crystal [11]. (The only difference between the bent and straight dimer is one methylene unit in the alkyl chain spacer). The question we address here is: What is the effect on the elasticity of incipient smectic order in the nematic phase when the Sm-*A* phase is approached from above? For each concentration we performed a three-parameter fit of K_{33} vs temperature, using the form

$$K_{33}(T)=K_{33}^0+\kappa\left(\frac{T-T_{NA}}{T_{NA}}\right)^{-\nu_{||}}, \tag{4}$$

where the fitting parameters are the "bare elastic constant" K_{33}^0 deep inside the nematic phase, a constant κ that is proportional to the bare smectic correlation length $\xi_{||}^0$ parallel to the smectic layer normal, and T_{NA}. The exponent $\nu_{||}$ corresponds to the correlation length exponent, as the divergent part of the bend elasticity is proportional to the smectic cor-

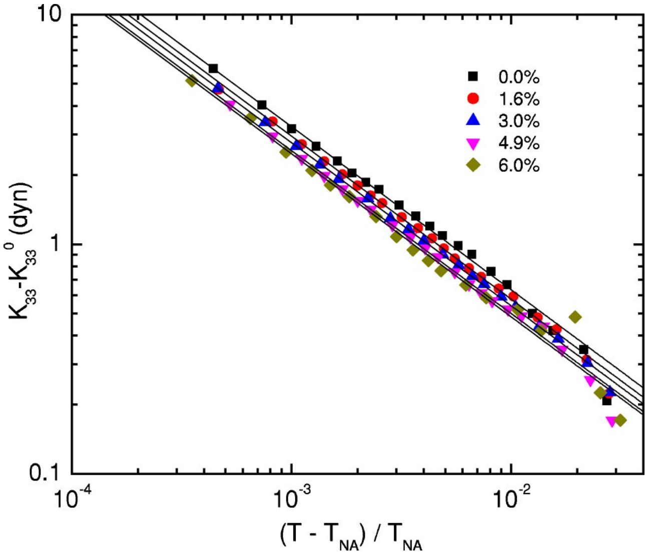

FIG. 7. Divergent part of bend elastic constant vs reduced temperature $(T-T_{NA})/T_{NA}$. Solid lines represent fit to Eq. (4). See Fig. 6 for key.

relation length $\xi_{||}$ parallel to the smectic layer normal. For purposes of the fitting we treat $\nu_{||}=0.71$ [5,10,13] as a constant, the value for pure 8OCB. It is assumed that the exponent is independent of concentration *X*, at least for the small concentrations of bent-core molecules used in the experiment. Had data been collected very close to the transition temperature, corresponding to $q_{||}\xi_{||}\approx 1$, the nonhydrodynamic Jähnig-Brochard form for K_{33}, in which the growth of the elastic constant begins to saturate close to T_{NA}, would have been required [12]. However, because $q_{||}\xi_{||}\ll 1$ for the temperature range investigated, we find that the simplified version [Eq. (4)] yields fits that are virtually identical to the full Jähnig-Brochard form. Thus, for simplicity, fittings were performed using Eq. (4) for the five concentrations. The solid curves in Fig. 6 display the fittings vs $T-T_{IN}$, and Fig. 7 shows the divergent part of the bend elastic constant on a log-log plot vs reduced temperature $(T-T_{NA})/T_{NA}$. Values for K_{33}^{0} and κ vs *X* are shown in Fig. 8. K_{33}^{0}, which corresponds to the bare elastic constant, decreases by about one-half over the concentration range investigated. This is not surprising, as the decrease is comparable to the decrease seen in the P-7PIMB–4O.8 mixtures over much of the nematic temperature range, but far above T_{NA} [7]. What is new is the behavior of κ as a function of bent-core molecule concentration. As seen in Fig. 8, κ decreases with increasing concentration, although only by about one-third over the concentration range investigated.

The quantity $\kappa\propto\xi_{||}^{0}q_{X}$, where q_X is the wave vector of the smectic order parameter, i.e., 2π divided by the smectic layer spacing. The quantity $q_{X=0}=0.193$ Å^{-1} for pure 8OCB [5]. Moreover, for pure 8OCB the quantity $\xi_{||}^{0}q_{X=0}$ is equal to 1.22 ± 0.36 from light scattering measurements and is equal to 1.08 ± 0.16 from x-ray measurements [14]. Thus we can extract the bare correlation lengths $\xi_{||}^{0}=6.3\pm1.8$ and 5.6 ± 0.8 Å from the light and x-ray scattering measurements, respectively, which corresponds well with a value

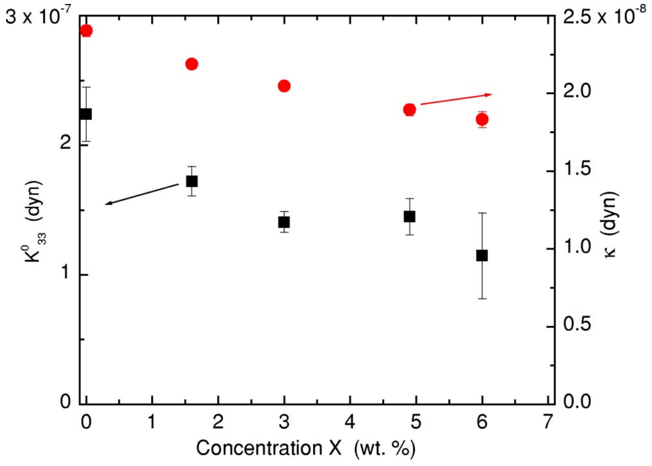

FIG. 8. Bare bend elastic constant K_{33}^{0} (■) and parameter κ (●), proportional to the bare correlation length $\xi_{||}^{0}$) vs *X*.

$\xi_{||}^{0}=5.3\pm1.0$ Å obtained from Fréedericksz methods [15]. For purposes of data analysis, we shall assume that q_X is independent of dopant concentration *X*. In our theoretical treatment, however, we will carry through and discuss concentration-dependent corrections to $q_{X=0}$. As our data indicate that $\xi_{||}^{0}q_{X}$ decreases by about 25% from $X=0$ to $X=6$ wt %, this would correspond to a decrease in $\xi_{||}^{0}$ of approximately $1\frac{1}{2}$ Å for $X=6$ wt % P-7PIMB, assuming the results could be attributed solely to a decrease in the bare correlation length $\xi_{||}^{0}$. This is a moderately large change in $\xi_{||}^{0}$ for a rather small concentration of bent-core dopant.

In order to get a better—if only semiquantitative—understanding of this behavior, we consider the effect that a dopant is expected to have on the bare correlation length. There are several potential effects due to the presence of a dopant, which we will discuss qualitatively. We consider the free energy functional

$$F=\int d^{3}x\left\{\frac{1}{2}r|\psi|^{2}+\frac{1}{2}c|(\vec{\nabla}+iq_{X}\delta n)\psi|^{2}+\frac{1}{2}c'|\hat{n}\times\vec{\nabla}\psi|^{2}\right.$$
$$+u|\psi|^{4}+\frac{1}{2}w^{-1}\rho^{2}++g\rho|\psi|^{2}+\frac{1}{2}K_{11}(\vec{\nabla}\cdot\hat{n})^{2}$$
$$\left.+\frac{1}{2}K_{22}(\hat{n}\times\vec{\nabla}\times\hat{n})+\frac{1}{2}K_{33}(\hat{n}\cdot\vec{\nabla}\times\hat{n})^{2}\right\}, \qquad (5)$$

where ψ is the two-component smectic order parameter, ρ is the concentration of the dopant P-7PIMB, and K_{11} is the splay elastic constant. The phenomenological parameters are K_{11}, K_{22}, and K_{33}, the elastic constants; T_{NA}^{*}, the unrenormalized transition-temperature; $r=a(T-T_{NA}^{*})$, the temperature dependent tendency of the material to order; *c*, the tendency of the smectic order parameter to be uniform in space and parallel to the director $\hat{n}$; $c+c'$, the tendency of the smectic order parameter to be uniform in space perpendicular to the director; *w*, the magnitude of the fluctuations in the dopant density—this is (approximately), proportional to the concentration of the dopant; and *g*, the coupling coefficient between the order parameter and the density fluctuations. All the phenomenological parameters are expected to depend on the concentration X of the bent-core dopant. However, except for $w \propto X$, it is generally expected that the dependences of these parameters on X should be relatively weak [16]. The bare correlation length $\xi_{||}^{0}$ parallel to the director, which is of central interest to us, is defined as

$$\xi_{||}^{0} = \lim_{T \to T_{NA}^{+}} \xi_{||} \left(\frac{T - T_{NA}}{T_{NA}} \right)^{+\nu_{||}}, \tag{6}$$

which is given approximately for the model in Eq. (5) as

$$\xi_{||0}^{0} = \left(T_{NA} \frac{d(r/c)}{dT} \right)^{-1/2}. \tag{7}$$

This formula is evaluated for a free energy that includes fluctuations on all length scales longer than q_X^{-1}, and essentially is a mean-field model. However, $\xi_{||0}^{0}$ also is the parameter with dimension of length that most directly determines the bare correlation length. The actual bare correlation length $\xi_{||}^{0}$ differs from $\xi_{||0}^{0}$ by a factor of order unity times a function that gives the corrections to asymptotic scaling. Thus the ratio $\xi(X)_{||}^{0}/\xi(X=0)_{||}^{0} \sim \xi(X)_{||0}^{0}/\xi(X=0)_{||0}^{0}$, which becomes an equality when corrections to scaling do not change with concentration X. These corrections to scaling come from the renormalization of the free energy in Eq. (5), most strikingly in the renormalization for the temperature coefficient a of the leading term in Eq. (5), viz., $a = dr/dT$. The coefficient a is expected to be renormalized differently at different concentrations of dopant, although we shall argue that the X dependence to the renormalization is weak. This is consistent with our assumption that the critical exponent is constant, which also is verified approximately by the good quality of our fits [Eq. (4)]. The most important corrections to scaling come essentially from changes in the Ginzburg length, $k_B T u c^{-2}$, so we shall now examine such effects in Eq. (5). As is well known [2], fluctuations in quantities that substantially affect the transition temperature, such as concentration or nematic order parameter fluctuations, tend to make the transition less strongly first order by decreasing the effective value of u. Fluctuations in the density ρ, for example, cause a reduction in u by an amount $g^2 w$. Similar changes also occur due to fluctuations of the nematic order parameter and/or decreases of the nematic elastic constants. *If* the decrease of u were so large that the range of temperatures over which there are nonclassical critical phenomena shrinks appreciably, such corrections would be important. However, our experiments indicate that nonclassical critical behavior occurs over a wide temperature range above T_{NA}, and thus we believe that these correction terms play a minimal role. Moreover, because T_{NA} changes only slightly (a few degrees) with X, we conclude that g must be relatively small. Similarly, the temperature range of the nematic phase changes only a fraction of a degree in this concentration range. Therefore the change in u resulting from the change in the amplitude of nematic fluctuations is likely to have little impact. Finally, although our data show that the bare elastic constant K_{33}^{0} changes substantially with X, it does not seem plausible that increased fluctuations due to the decrease in K_{33} can, by themselves, cause a significant decrease in the effective bare correlation length. Thus, for our case it would seem that effects due to r and c [Eq. (7)] should cause the bulk of the decrease in $\xi_{||}^{0}$ with X.

In order to calculate approximately the contributions to Eq. (7), we model the interaction between molecules—this really is the change in the free energy of the system due to the relative motion of two molecules—as an effective pair interaction, roughly the thermal energy times the Mayer f function $U(T)_{eff} \sim k_B T[\exp(v/k_B T) - 1]$. Here v is the interaction potential. We define the smectic order parameter $\psi = \langle \exp(i\hat{n} q_X \vec{x}) \rangle$, where $\langle\ \rangle$ indicates the average over the positions and other descriptors of the particles and $\vec{x}$ is the position of some point that is chosen appropriately on each type of molecule. We include the concentration in this average, as well as the average below, so that, e.g., $\langle \delta(\vec{x}) \rangle = \Sigma_i C_i$, where C_i is the concentration of each kind of molecule. Note that it might be advantageous to weigh this formula for the degree of smectic character associated with each species, and to average over several points for dimers or polymers. This formula is adequate for our present purposes. With these assumptions, we see that the terms in the free energy that are proportional to the square of the smectic order parameter are

$$[r + c(\vec{k} + \delta q \hat{n})^2 + c' |\hat{n} \times \vec{k}|] + O(k^3)$$
$$= k_B T \sum_i C_i + \langle \exp[i(\vec{k} + q_0 \hat{n}) \cdot (\vec{x} - \vec{x}\,') U(T)_{eff}/k_B T] \rangle, \tag{8}$$

where $\vec{x}$ and $\vec{x}\,'$ are the chosen points on two interacting particles, $q_X = q_0 + \delta q$ is the wave vector of the smectic order parameter in the presence of the dopant, and $\vec{k}$ is a (small) wave vector. (Note that we have defined $q_0 \equiv q_{X=0}$.) The first term on the right-hand side of Eq. (8) is the simple ''ideal'' entropic term and the second is an approximation to the interaction term. This implies that

$$r = k_B T \sum_i C_i + \langle \exp[i q_0 \hat{n} \cdot (\vec{x} - \vec{x}\,')] U(T)_{eff} \rangle - c\, \delta q^2, \tag{9}$$

$$c = -\langle [\hat{n} \cdot (\vec{x} - \vec{x}\,')]^2 \exp[i q_0 \hat{n} \cdot (\vec{x} - \vec{x}\,')] U(T)_{eff} \rangle + O(\delta q), \tag{10}$$

and

$$\delta q = \langle i \{ \hat{n} \cdot (\vec{x} - \vec{x}\,') \exp[i q_0 \hat{n} \cdot (\vec{x} - \vec{x}\,')] U(T)_{eff} \} \rangle / c. \tag{11}$$

The bent-core P-7PIMB dopant is rather large compared to the 8OCB molecule. It is an oddly shaped dopant that does not fit well into the structure of the liquid crystal. It is neither clear theoretically nor well-established experimentally how this molecule should be oriented by the nematic field. Our own work on elastic constants, specifically the large decrease in the bare bend elastic constant relative to the decrease in the splay elastic constant [7], suggests that the molecule more often is aligned with its longest axis—the "bowstring" at the ends of the banana—parallel to the nematic director. However, there are suggestions in the literature [6] that the orientation of the molecule can be different from this, particularly in smectic phases, and that the orientation can depend on the nature of the smectic phase. If the orientation distribution of the bent-core molecule were to change as a consequence of the incipient smectic order, this would be expected to change the "bare" elastic constant K_{33}^0 in ways that are not reflected in Eq. (5). However, this would result in only a simple energylike cusp in the elastic constant, which is unlikely to explain our data. If we assume that the dopant molecule is aligned as we have proposed, with the long (bowstring) axis along the director, then there are large contributions to Eq. (10) from large separations. If the long axis were aligned otherwise, e.g., as suggested by Ref. [6], then the contributions from large separations would be smaller. Hence our results suggest alignment of the bowstring along the nematic director. The value of r also is likely to decrease in the presence of the dopant, but by a smaller amount, as there is less emphasis on large separations in the evaluation of r. The effect of X on the temperature derivative $d(r/c)/dT$ is less obvious, as temperature can affect either the potential $U(T)_{eff}$ or the molecular-scale positions, that is to say the distribution used to average over the locations of the particles. We note that T_{NA} was observed to vary only weakly with X, which empirically would indicate that r varies only weakly with X. In addition to the effects on the entropic term, the temperature derivative of r can come from two different sources: the temperature dependence of the effective interaction and thermal changes in the average/changes in fluctuations. Thermal changes in the effective interaction are likely to be small and similar to changes in the athermal steric or "hard core" interactions; hence this is not expected to result in large changes in $d(dr/dT)/dX$ if dr/dX is small. The changes in the thermal averaging are similar to the changes due to fluctuations, which have been discussed above. Thus, although $d(dr/dT)/dX$ could be large even though dr/dX is small, we do not believe that this is likely; *rather, we believe that the most significant effect due to the addition of the P-7PIMB dopant is a significant decrease in c with increasing X*. Although the P-7PIMB dopant clearly would disrupt local smectic order, the fact that the dopant molecule is incommensurate with the smectic layer spacing $2\pi/q_X$ would cause it to significantly disrupt smectic correlations. The change $\delta q = q_X - q_0$ is less clear, even as to sign. The integral in the numerator of the predicted value of δq [Eq. (11)] also emphasizes large separations and, in fact, is quite similar to the integral for the denominator, although there are substantial differences for very large separations. A decrease in q_X with increasing dopant concentration *could* mimic the apparent decrease in bare correlation length $\xi_{||}^0$. Nevertheless, we do not believe that q_X could change sufficiently at such small dopant concentrations to produce the observed results. To keep the analysis simple, we assume that all of the observed effect is due to a large decrease in $\xi_{||}^0$, an assumption that is reflected in the calculations used to extract the data shown in Fig. 8.

The effects of dopants on the regular part of the nematic elastic constants are well documented experimentally, and partially understood theoretically. In this paper we report on initial investigations of the effects on the *diverging* part of the bend elastic constant close to the N–Sm-*A* phase transition. Clearly, additional experiments with molecules that "fit" in various ways into the smectic layers, e.g., molecules with differing molecular lengths or dimeric [17,18] or fraternal twin molecules [19], would be highly useful in this regard. Further experiments and development of a more robust theory are planned.

This work was supported by the National Science Foundation under Grant No. DMR-9982020.

[1] B.I. Halperin, T.C. Lubensky, and S.K. Ma, Phys. Rev. Lett. **32**, 292 (1974).

[2] P.G. DeGennes and J. Prost, *The Physics of Liquid Crystals* (Clarendon, Oxford, 1994).

[3] P.E. Cladis, Phys. Rev. Lett. **35**, 48 (1975).

[4] D. Guillon, P.E. Cladis, and J. Stamatoff, Phys. Rev. Lett. **41**, 1598 (1978).

[5] A.R. Kortan, H. von Känel, R.J. Birgeneau, and J.D. Litster, J. Phys. (France) **45**, 529 (1984).

[6] R. Pratibha, N.V. Madhusudana, and B.K. Sadashiva, Science **288**, 2184 (2000).

[7] M.R. Dodge, C. Rosenblatt, R.G. Petschek, M.E. Neubert, and M.E. Walsh, Phys. Rev. E **62**, 5056 (2000).

[8] G.A. DiLisi, C. Rosenblatt, A.C. Griffin, and U. Hari, Phys. Rev. A **45**, 5738 (1992).

[9] N.V. Madhusudana and R. Pratibha, Mol. Cryst. Liq. Cryst. **89**, 249 (1982).

[10] A. Madsen, J. Als-Nielsen, and G. Grübel, Phys. Rev. Lett. **90**, 085701 (2003).

[11] G.A. DiLisi, C. Rosenblatt, and A.C. Griffin, J. Phys. II **2**, 1065 (1992).

[12] F. Jähnig and F. Brochard, J. Phys. (France) **34**, 411 (1973).

[13] C.W. Garland and G. Nounesis, Phys. Rev. E **49**, 2964 (1994).

[14] S. Sprunt, L. Solomon, and J.D. Litster, Phys. Rev. Lett. **53**, 1923 (1984).

[15] G.P. Sinha, C. Rosenblatt, and L.V. Mirantsev, Phys. Rev. E **65**, 041718 (2002).

[16] L.D. Landau and E.M. Lifshits, *Statistical Physics* (Addison-Wesley, Reading, MA, 1958).

[17] See, e.g., G.A. DiLisi, C. Rosenblatt, A.C. Griffin, and U. Hari, Phys. Rev. A **45**, 5738 (1992).

[18] E.M. Terentjev, C. Rosenblatt, and R.G. Petschek, J. Phys. II **3**, 41 (1993).

[19] S.S. Keast, M.E. Neubert, and R.G. Petschek, Liq. Cryst. **21**, 695 (1996).