

## Bend elasticity of mixtures of V-shaped molecules in ordinary nematogens

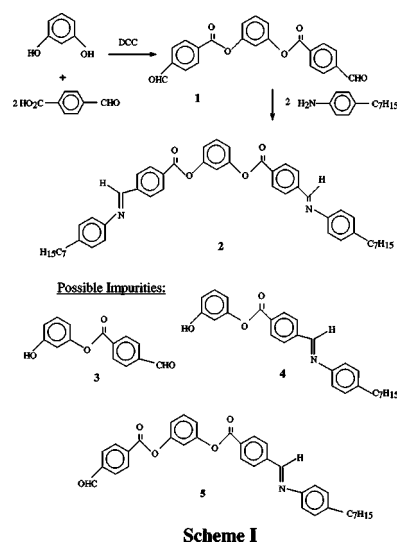
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Freedericksz measurements were performed on mixtures of a nematic mesogen and a V-shaped molecule. The bend elastic constant was found to decrease significantly with increasing concentration of the V-shaped molecule. The results are discussed theoretically, taking into account the detailed structure of the molecules.

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When a uniformly oriented nematic that is composed of rigid rods is subjected to a bend stress, the system relaxes so that  $\hat{n} \times (\vec{\nabla} \times \hat{n}) \neq \vec{0}$ , where  $\hat{n}$  is the nematic director. However, it has been suggested theoretically and demonstrated experimentally in at least two systems [1,2] that if the nematogen has an intrinsically bent shape, the associated bend elastic constant  $K_{33}$  is reduced relative to that expected for a straight mesogen. It is believed that this occurs because the bend stress is relaxed not only by a macroscopic bend distortion in the sample, but also by a rotation of the molecules as well. For a dimer with a bent spacer,  $K_{33}$  is reduced by 20–40% from values typical of nearly linear, low molecular weight liquid crystals [1]. For a bent dendrimer the reduction is far more substantial, with  $K_{33}$  reduced by nearly two orders of magnitude [2]. We believe that the excessive reduction of  $K_{33}$  for the dendrimer is because of hindered internal rotations, locking in the bent conformation of the molecule. For the dimer, rotations in the spacer group are relatively free, and thus the molecule's average shape, particularly in the nematic phase, is only slightly bent. To gain more insight into the phenomenon, we have sought better control of bend. In principle, this can be accomplished either via some external or thermal control of the average shape of the molecules, or by introducing a known concentration of bent mesogens into a nematic that is formed from ordinary, linear molecules. Unfortunately, control of shape is very difficult, and the bent dendrimer is immiscible in a wide variety of low molecular weight liquid crystals. Thus, we instead dissolved small amounts of a bent, V-shaped molecule into an ordinary nematic liquid crystal. Although most of the attention garnered by (achiral) V-shaped molecules is related to their ability to form chiral phases [3–5], appropriate V-shaped molecules provide a dopant with a high degree of expected average bend. When dissolving quantities of up to 11% by weight of the V-shaped molecule 1,3-phenylene bis[4-(4-heptyl phenyliminomethyl) benzoate], (P-7PIMB) **1** (see scheme I) into 4-butoxybenzylidene-4-octylaniline (4O.8),



we observed a systematic and marked decrease of  $K_{33}$  from its value in pure 4O.8. This result indicates that the bend stress may be easily relieved by a rotation of a small number of bent molecules.

Attempts were made to dissolve P-7PIMB into several different classes of low molecular weight linear mesogens. In most cases, the P-7PIMB was found to be immiscible. We were successful, however, in dissolving a small amount (up to about 11% by weight) in 4O.8, which has a negative dielectric anisotropy and a relatively small transverse dipole moment. Our supply of 4O.8 was synthesized a number of years ago by the Harvard group, and used without further purification after cold storage. Four different mixtures were prepared: 0, 4.0, 7.9 and 10.8% by weight P-7PIMB in 4O.8. Mixtures of the two species were found to produce a nematic phase that is only metastable. For low concentrations of P-7PIMB, the nematic phase was often metastable for hours; at higher concentrations (~10%) of the V-shaped mesogen the onset of phase separation occurred on much shorter time

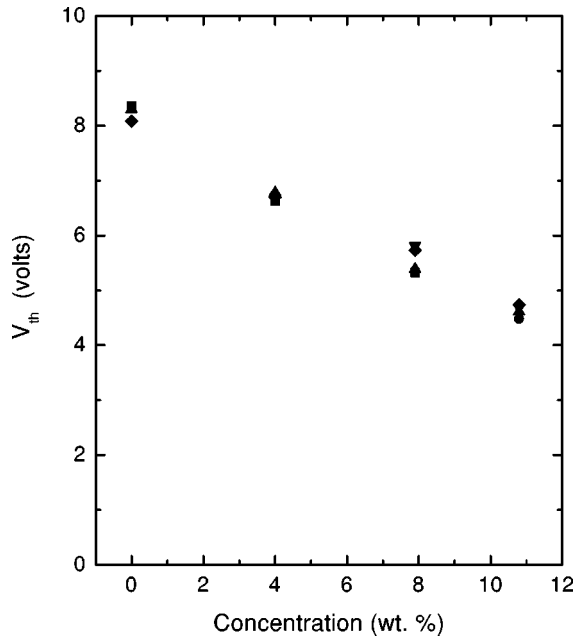


FIG. 1. Freedericksz threshold voltage vs concentration at temperatures  $T_b - T = 2^\circ\text{C}$  (■),  $3^\circ\text{C}$  (●),  $4^\circ\text{C}$  (▲),  $5^\circ\text{C}$  (▼),  $6^\circ\text{C}$  (◆).

scales, typically of order 1 h. For even higher concentrations, of order 13% P-7PIMB, phase separation occurred on such rapid time scales that it was impossible to complete a set of elastic constant measurements. We therefore limited the concentration to 10.8% by weight of P-7PIMB.

The bend elastic constant  $K_{33}$  was determined via the Freedericksz transition technique [6], wherein a uniformly aligned sample undergoes a bend distortion above a threshold voltage  $V_{th} = \sqrt{K_{33}/\Delta\epsilon}$ , where  $\Delta\epsilon$  is the dielectric anisotropy of the liquid crystal. To examine the Freedericksz transition, several pairs of indium-tin-oxide coated glass slides were cleaned and coated with the surfactant hexadecyltrimethylammonium bromide (HTAB) to promote homeotropic orientation. The slides were placed together, separated by Mylar spacers of nominal thickness  $25\ \mu\text{m}$ , and cemented at the edges to create a cell. The actual thickness of each cell was determined using an optical interference scheme [7]. The cells were then filled with a given mixture of P-7PIMB+4O.8 in the isotropic phase and cooled slowly into the nematic phase. Phase separation at the transition was observed, such that the temperature range of the biphasic region was larger for higher concentrations of P-7PIMB. A given cell was placed between crossed polarizers, and light from a 5 mW He-Ne laser passed through the polarizer, the cell, the analyzer, and into a detector. The sample was driven with an ac voltage at frequency 1 kHz, whose amplitude was ramped from just below the Freedericksz threshold  $V_{th}$  to well above  $V_{th}$  in 120 s. The intensity of the light was computer recorded. Measurements were made at several temperatures in the nematic phase for each concentration, although at temperatures near the transition, phase separation precluded us from obtaining useful data. Figure 1 shows the threshold voltage for all four concentrations at several different temperatures below temperature  $T_b$ , where  $T_b$  corresponds to the onset of the biphasic region on cooling from the isotropic

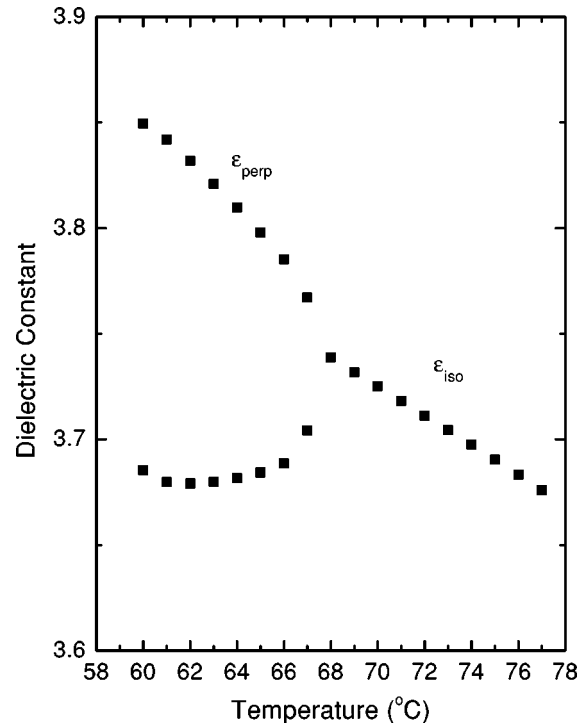


FIG. 2. Dielectric constant measurements vs temperature for 10.7% sample.

phase. As is typical for electric field elasticity measurements, the threshold voltage  $V_{th}$  is only weakly dependent on temperature.

In order to determine  $K_{33}$  from measurements of  $V_{th}$ , we needed to determine the dielectric anisotropy,  $\Delta\epsilon = \epsilon_{\perp} - \epsilon_{\parallel}$ , where  $\epsilon_{\perp}$  and  $\epsilon_{\parallel}$  are the dielectric constants parallel and perpendicular to the director, respectively. For each concentration, we prepared a parallel plate capacitor cell from

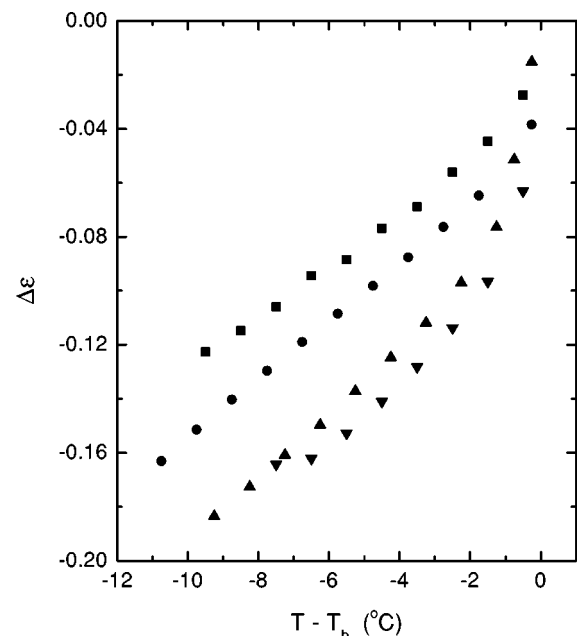


FIG. 3. Dielectric anisotropy  $\Delta\epsilon$  vs  $T - T_b$ . (■) represents the 0% sample, (●) the 4.0% sample, (▲) the 7.9% sample, and (▼) the 10.8% sample.

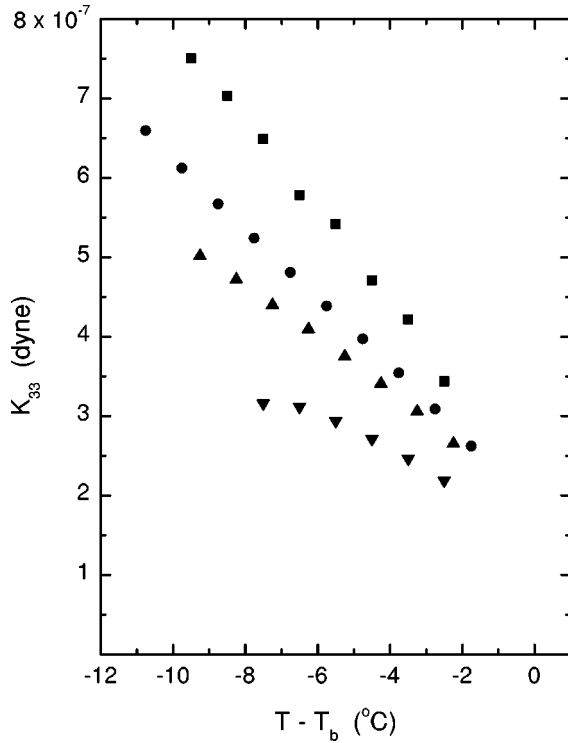


FIG. 4.  $K_{33}$  vs  $T - T_b$ . (■) represents the 0% sample, (●) the 4.0% sample, (▲) the 7.9% sample, and (▼) the 10.8% sample.

indium-tin-oxide coated glass coated with the surfactant hexadecyltrimethylammonium bromide. The overlap area of the electrodes was approximately  $7 \text{ mm} \times 7 \text{ mm}$ , and the nominal cell thickness was 25 mm. The capacitance of the empty cell was measured as a function of temperature with a high precision capacitance bridge, Andeen-Hagerling model 2500, using a 125 mV ac at 1 kHz. The cell was filled with the liquid crystal mixture and the capacitance of the cell was again measured, such that the temperature-dependent dielectric constant was taken to be the ratio of the filled to empty cell capacitance at that temperature. In the isotropic phase, this ratio corresponds to  $\epsilon_{\text{iso}}$ , the isotropic dielectric constant. In the nematic phase, this ratio is  $\epsilon_{\parallel}$ . Figure 2 shows an example of the results, in this case for a concentration of 10.8%. The temperature-dependent dielectric anisotropy  $\Delta\epsilon$  was extracted by extrapolating  $\epsilon_{\text{iso}}$  into the nematic phase and using the relationship  $\Delta\epsilon = \frac{3}{2}(\epsilon_{\parallel} - \epsilon_{\text{iso}})$ . Note that  $\epsilon_{\perp}$  was not determined explicitly owing to our inability to achieve good planar alignment at higher concentrations of P-7PIMB. Figure 3 shows  $\Delta\epsilon$  vs  $T - T_b$  for all four mixtures.

Having obtained the Freedericksz threshold voltages and dielectric anisotropies, we calculated  $K_{33}$  vs concentration and temperature, which is shown in Fig. 4. From these results it is clear the elasticity decreases very substantially with increasing concentration, even at small concentrations of P-7PIMB. In order to make a more meaningful comparison among concentrations, it is preferable to normalize the results to the temperature-dependent nematic order parameter  $S$  by taking the ratio  $K_{33}/S^2$ . Ordinarily, we would take  $S \propto \Delta\epsilon$ . However, for these mixtures this is an inappropriate procedure because of the small negative dielectric anisotropy of 4O.8. As P-7PIMB is significantly more polar than 4O.8, small changes in P-7PIMB concentration result in large frac-

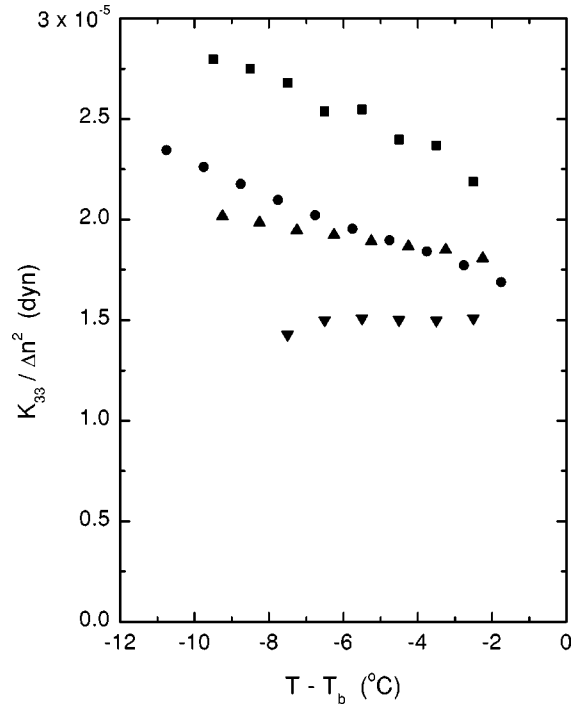


FIG. 5.  $K_{33}/\Delta n^2$  vs  $T - T_b$ . (■) represents the 0% sample, (●) the 4.0% sample, (▲) the 7.9% sample, and (▼) the 10.8% sample.

tional changes in  $\Delta\epsilon$ , making comparisons at different concentrations difficult. Instead, because the optical polarizability anisotropy of 4O.8 is similar to that of one of the arms of P-7PIMB, and the birefringence  $\Delta n$  scales approximately as  $S$  for small  $S$ , we measured the ordinary and extraordinary refractive indices  $n_o$  and  $n_e$  of the mixtures as a function of temperature using an Abbe refractometer at wavelength 5896 Å. We show the ratio  $K_{33}/\Delta n^2$  in Fig. 5. Note that  $K_{33}/\Delta n^2$  for the two middle concentrations are apparently about the same, although we believe that this is an artifact. Nevertheless, it is clear that there's a substantial decrease of  $K_{33}$ , of order 40%, as the P-7PIMB concentration increases from 0 to 10.8%. This change is real, and is much larger than would reasonably be expected.

It should be remarked that in simple models that predict  $K_{33} \propto S^2$  (independent of concentration), both the birefringence and the dielectric constant should be proportional to  $S$ , and hence to each other at each concentration. We see from Fig. 5 that such simple models cannot be completely correct. Nevertheless, the ratio  $K_{33}/\Delta n^2$  varies appreciably more slowly with temperature than  $K_{33}$  itself and, in any case, the data has also been plotted as a function of  $T - T_b$ . (Note that because of error compounding we are not completely certain that the sign of the slopes of  $K_{33}/\Delta n^2$  vs  $T - T_b$  are correct.) We believe that accounting in this way for the change in transition temperature should explain much of the variation in the bend elastic constant due to the change in the order-parameter environment. Thus, our experimental data clearly demonstrate that the bent mesogens significantly affect the bend elastic constant of the nematic mixture.

Before examining theoretically the possible effects of bend in these molecules, we first discuss the effects that the chemical structure, impurities, and conformers may have on the shape of the molecule. The material was synthesized using the procedures shown in scheme I. Great care was taken

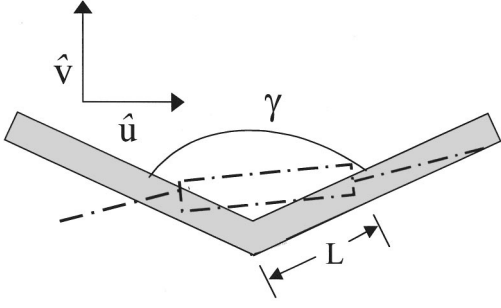


FIG. 6. Schematic representation of molecular configuration.  $\hat{u}$  and  $\hat{v}$  are unit vectors,  $L$  is the distance from the point of intersection to the center of the rod, and  $\gamma$  is the bend angle of the V-shaped mesogen. Dotted mesogen illustrates a host mesogen in the mesogen in a position, the interactions of which are overcounted by the independent rod approximation.

to ensure purity, and we estimate total impurities of less than 0.3 wt%. A discussion of the synthesis and physical properties of the pure material will be given elsewhere [8]. Additionally, all likely contaminants, e.g., 3–5 in scheme I, are less bent than the desired product: Primarily, they result from incomplete esterification or anil formation reactions, so that at least one of the “arms” is shortened, thereby making the molecule (within the context of the discussion below) appreciably less bent. We do not believe that the specific interactions of the functional groups at the ends of these mesogens are likely to be sufficiently strong to form molecular complexes or other interacting molecular associations that are effectively more bent. Thus, insofar as there may be contaminants, we do not believe that they can explain the difference between our experimental and theoretical results, to be described below.

We shall consider the conformation in which there is an approximately  $120^\circ$  bend at the center of the P7-PIMB molecule—at the meta substituted phenyl that is derived from metaresorcinol (meta dihydroxyphenyl.) For reasons discussed below, we suppose that the rigid part of the molecule that is attached to the meta position is essentially straight, and that the alkyl chain attached thereto can be ignored. The alkyl chains of all mesogens are expected to be bent relative to the rigid segments to which they are attached. However, this bend is ubiquitous in liquid crystals, and therefore is not expected to explain the significant changes in bend elastic constant observed on doping 4O.8 with P7-PIMB. Some effects might be expected from this bend if there were a relationship between the direction of this bend and the direction of the bend in the center of P7-PIMB, e.g., if they were always perpendicular. However, there are a large number of semiflexible bonds that make it unlikely that any such correlation is important.

Both the ester (OOC) and anil (CHN) linkages in the rigid part of the molecule have some flexibility. Specifically the phenyl-oxygen “single” bond can have highly bent conformers. However a detailed analysis, presented elsewhere [8], suggests that this is not the case.

Thus, given the crudeness of most models for liquid crystalline elastic constants, we feel that it is reasonable to model our dopant as two rigid segments of a molecule attached to each other through a bend of  $\gamma = 120^\circ$ . We shall describe the orientation of such a molecule by using the two orthogonal

unit vectors  $\hat{u}$  and  $\hat{v}$ , shown in Fig. 6. The effective interactions of this molecule with the liquid crystal medium will be modeled via an orientation-dependent interaction potential between the rigid segments of the bent molecule and the surrounding liquid crystal. This interaction will be taken to be the sum of the interactions of the two separate segments. We first consider these interactions integrated over all positions and averaged over the orientations of the surrounding liquid crystal. For simplicity, we shall take this to be of the Maier-Saupe form, viz.,

$$\begin{aligned}
 U_{hd}^{mfu} &= J_{hd} \left\{ \left[ \hat{n} \cdot \left( \hat{u} \sin \frac{\gamma}{2} + \hat{v} \cos \frac{\gamma}{2} \right) \right]^2 \right. \\
 &\quad \left. + \left[ \hat{n} \cdot \left( \hat{u} \sin \frac{\gamma}{2} - \hat{v} \cos \frac{\gamma}{2} \right) \right]^2 \right\} \\
 &= 2J_{rh} S \left[ (\hat{n} \cdot \hat{u})^2 \sin^2 \frac{\gamma}{2} + (\hat{n} \cdot \hat{v})^2 \cos^2 \frac{\gamma}{2} \right]. \quad (1)
 \end{aligned}$$

Here the two terms on the right-hand side are the interactions of the two separate rods in the bent mesogen,  $J_{rh}$  is a characteristic interaction strength between one of the rods of a dopant (P-7PIMB) molecules and a host molecule and  $\hat{n}$  is the liquid crystal director. The approximation that the rods act independently likely overstates the effective bend of the molecule. Specifically, if we consider the strong hard-core interactions between the molecules, e.g., by modeling portions of the molecule as hard cylinders, it is easy to see that configurations in which a host molecule that is oriented approximately parallel to  $\hat{u}$  and located in the middle of the “V” of the dopant molecule will result in two intersections between the host molecule and the dopant. This configuration cannot actually occur, and should be excluded from the allowed configurations. However, the assumption of independently interacting rigid rods excludes it not once (as is appropriate), but twice. Thus, a two-rod interaction that favors alignment of the host molecules parallel to  $\hat{u}$ , i.e., that adds this configuration back in once, should be added to the independent rod interaction.

We shall first find the order parameters associated with  $\hat{u}\hat{u}$  and  $\hat{v}\hat{v}$ , as the combination  $\hat{u}\hat{v}$  clearly has zero average. As integration of the related Boltzmann factor and calculation of the relevant order parameters is quite difficult, we shall simply expand the Boltzmann factor to first order in its argument and calculate the order parameter assuming that this expansion is correct. The integral to be performed, along with its prefactors, is then identical to that which must be performed in order to calculate with identical assumptions the order parameter in the pure host. We shall therefore assume that this integral is the order parameter of the host. With these assumptions these integrals yield

$$\begin{aligned}
 S_{\hat{u}} &= \left\langle \frac{3}{2} (u_z u_z) - \frac{1}{2} \right\rangle = -2 \left\langle \frac{3}{2} (u_x u_x) - \frac{1}{2} \right\rangle \\
 &= -2 \left\langle \frac{3}{2} (u_y u_y) - \frac{1}{2} \right\rangle = \frac{T_1}{T_{NI}} S \left( \frac{1}{2} + \frac{3}{2} \cos \gamma \right), \quad (2)
 \end{aligned}$$



$$\begin{aligned}
S_{\hat{v}} &= \left\langle \frac{3}{2}(v_z v_z) - \frac{1}{2} \right\rangle = -2 \left\langle \frac{3}{2}(v_x v_x) - \frac{1}{2} \right\rangle \\
&= -2 \left\langle \frac{3}{2}(v_y v_y) - \frac{1}{2} \right\rangle = \frac{T_1}{T_{NI}} S \left( \frac{1}{2} - \frac{3}{2} \cos \gamma \right). \quad (3)
\end{aligned}$$

Here  $T_1 = T_{NI} J_{rh} / J_{hh}$ , where  $T_{NI}$  is the nematic-isotropic transition temperature of the pure host and  $J_{hh}$  is the Maier-Saupe interaction parameter between host molecules. While more exact answers could be obtained by numerical integration, or by expanding the exponential to higher order, we believe that the simple analytic approach gives understandable, semiquantitative results that are of accuracy comparable to the model from which they were obtained. The  $S_{\hat{u}}$  order parameter describes the extent of alignment of the molecule with the  $\hat{u}$  axis along  $\hat{n}$ , and so increases the probability of orientations that decrease the bend elastic constant. On the other hand,  $S_{\hat{v}}$  describes the extent to which the molecule aligns with its apex ( $\hat{v}$ ) along the director, and therefore the extent to which the molecule should be considered a wedge, i.e., it describes the extent to which the molecule is expected to decrease the splay elastic constant. All other averages of traceless symmetric tensors that are bilinear in  $\hat{u}$  and  $\hat{v}$  are zero. Note that insofar  $S_{\hat{u}}$  as is large, this molecule is oriented in such a way as to promote bend distortions, while insofar as  $S_{\hat{v}}$  is large, this molecule is oriented in such a way as to promote splay distortions of the system. We expect that the independent rod approximation will underestimate  $S_{\hat{u}}$  and overestimate  $S_{\hat{v}}$ . Also note that, to lowest order, these order parameters have the same temperature dependence, which would predict that the temperature dependence of various anisotropic tensors in the mixture should be the same. This is not observed experimentally for the dielectric anisotropy and birefringence measurements, nor would it be predicted theoretically on the basis of a higher order calculation.

Simple mean-field calculations of the elastic constants have been performed for lyotropic [9] and thermotropic [10] liquid crystalline monomers, as well as polymers, dimers [11] and other structures. These calculations assume that the only correlations between molecules are the result of some underlying and unchanging ‘‘hard sphere’’ correlation function, or are the result of either their direct interactions or of their interaction with the mean field. Gelbart showed [10] that the configurational entropy does not contribute to the elastic constants, and gives the elastic constant as the change in the average energy. Thus, to second order in the gradients of the director, the elastic constants correspond to the change of

$$\Delta F = \frac{1}{2} \sum_{ij} \rho_i \rho_j \langle U_{ij}^{\text{eff}} \rangle. \quad (4)$$

Here  $\rho_i$  is the density of particles of type  $i$  and the average is over both molecular orientations and the separations of the molecular centers and  $U_{ij}^{\text{eff}}$  is the effective interaction between molecules of types  $i$  and  $j$ . We will assume that the *a priori* likelihood of all separations is the same. Prior work we have cited deals with pure compounds, not mixtures. However, all this implies is that it is necessary to average over the type of molecule as well as the orientation of the

molecule. As we discuss below in the situations of interest in this paper the average over the types of molecules is trivial: It simply requires replacing the total density with the density of particles of a given type and summing over the types of molecules. The effective potential is approximately equal to the temperature times the Mayer  $f$  function [10], incorporating both the temperature times a hardcore repulsion and a Van der Waals attraction. Here the averages are assumed to be taken with respect to independent probability distributions for the two separate particles. The probability distribution for each type particle is given by

$$P_i \sim \exp(-U_i^{mf}/k_B T), \quad (5)$$

where

$$U_i^{mf} = \sum_j \rho_j \langle U_{ij}^{\text{eff}} \rangle \quad (6)$$

and in Eq. (6) the average is only over the separation of the molecular centers and the orientation of the particle labeled  $j$ .

It is not our intent to analyze this equation or the elastic constants in their entirety: rather we want to examine these equations heuristically to see if they plausibly contain an explanation for the large change in bend elastic constant that has been observed experimentally. To simplify the calculation we shall assume that there are only two types of molecules: the host and the dopant. We suppose that the dopant concentration is small, and consider only effects to first order in the concentration of the dopant. This is consistent with the experimental situation.

We shall also assume that the interactions of the host molecules are unchanged by a change in sign of the orientation of the host. This is to say that these interactions do not involve steric (or other) dipoles. This is in contrast to the interactions of the bent dopant, which do change upon change of the sign of an orientation ( $\hat{v}$ ) of the molecule. It is known that this implies that the mean-field potential and the probability distribution for the host will not change to first order in the gradients of the director, as a gradient of the director implies a field that is odd under reversal of an orientation. It is also the steric and other dipoles that result in the usual claims that bent/splayed/twisted molecules should have smaller bend/splay/twist elastic constants than ‘‘expected.’’ That is to say, in the presence of a gradient in the director, a molecule with dipolar interactions will orient itself by an amount proportional to the gradient in the field. The resulting change in the free energy is proportional to the square of the degree of reorientation, and is always negative: A bent molecule reorients in such a way as to make additional bend in the direction of an initial bend easier. Alternatively this can be seen as a consequence of second order perturbation theory.

Our goal is to understand approximately the change in the free energy given a spatial variation in the director and these approximations. There are a number of possible contributions to the elastic constants. First, there can be changes in the mean field as a function of temperature. Such changes are difficult to predict—*ab initio* calculations of transition temperatures are very difficult. However we believe that such changes are adequately modeled by rescaling the temperature

and direct measurement of comparison with the order parameter. Hence they will not be considered further. Second, the chemical potential of the particles can change in response to the spatial variation in the director. This would likely result in much larger changes in the densities and, in consequence, in the elastic constant in a mixture than in a pure fluid. However, except in the case of a chiral molecule and a twist elastic deformation, there are no linear couplings between gradients of the director and the density of a molecule. This dopant molecule is nonchiral and, in consequence, there are no such linear couplings. Such changes, moreover, are likely to be small, given that helical twisting powers are typically small. Hence, such changes are irrelevant to this paper and will not be further considered: Equivalently only the orientation dependent changes in  $U^{mf}$  will be considered.

Next, there will be changes in both  $U^{mf}$  and the average of the interaction potential that are proportional to the product of two gradients ( $\partial_i n_j \partial_k n_l$ ) and the second gradient of the director ( $\partial_i \partial_j n_k$ ). At the order to which we are working there are two changes in these terms. First there is a ‘‘dilution’’ term for the host-host interaction: The total density of matter is expected to remain approximately constant so addition of the dopants implies a smaller density of the host and fewer host-host interactions. Second there is a host-dopant interaction. Both terms are difficult to calculate. The dilution term is expected to make a negative contribution which is expected to be canceled (probably more than canceled) by the contribution from the dopant. The dopant should make positive contributions that, because the dopant is physically larger, are likely to be larger (for the same order parameter). Thus these two terms are likely to approximately cancel each other or, if anything, increase the elastic constant. As we are attempting to explain a seemingly large decrease in the elastic constants we will also ignore these terms below. In any case, this difference depends on a number of parameters which are clearly distinct from those on which the terms we will calculate depend, and so this difference can reasonably be considered to be a model parameter.

Finally, there can be orientation-dependent changes to  $U^{mf}$  proportional to the gradient of the director provided the potential itself is not changes when one of the orientations of the molecule (dopant) changes sign. Because the gradient of the director is odd under inversion, unless the interaction potential is also odd the average of Eq. (6) cannot depend on the gradient. Given our assumption that the interactions of the host molecules are centrosymmetric, we then see that there will be no change in  $U^{mf}$  for the host. There are in principle two changes in  $U^{mf}$  for the dopant, one due to host-dopant and the other due to dopant-dopant interactions. The latter is small for small concentration of dopant, and will be ignored. We will concentrate our efforts on calculating the change in the elastic constants related to these changes associated with the changes in the orientational distribution of the dopant, e.g., related to this term in the free energy.

In order to model the change in the elastic constants, it is necessary to model the position-dependent interactions of the molecules. If we are considering effects that are linear in the concentration of the dopant, it is adequate to consider the interactions of the host with the dopant, and not necessary to consider interactions between dopant molecules. We shall suppose that the interactions of the bent molecule can be

taken as the sum of the interactions of the two mesogens the centers of which are separated by a distance  $2 \sin(\gamma/2)L$  along the direction  $\hat{u}$ . We then assume that the interaction energy of a dopant molecule with the remainder of the system is given by a sum of two effective interaction potentials, each due to one of the rods,

$$U_{hd}^{\text{eff}} = U_{\text{rod}}^{\text{eff}} \left\{ \left[ \hat{n}(\vec{r}) \cdot \left( \hat{u} \cos \frac{\gamma}{2} + \hat{v} \sin \frac{\gamma}{2} \right) \right]^2; \vec{r} - L\hat{u} \sin \frac{\gamma}{2} \right\} + U_{\text{rod}}^{\text{eff}} \left\{ \left[ \hat{n}(\vec{r}) \cdot \left( \hat{u} \cos \frac{\gamma}{2} - \hat{v} \sin \frac{\gamma}{2} \right) \right]^2; \vec{r} + L\hat{u} \sin \frac{\gamma}{2} \right\}. \quad (7)$$

Here  $\hat{n}(\vec{r})$  is the director a vector distance  $\vec{r}$  from the center of the V shaped molecule. The interaction  $U_{\text{rod}}^{\text{eff}}$  has been taken to be a function of the square of the cosine of the angle between the rigid rod segments of the molecules. It is also a function of the separation between the centers of the rods in the V-shaped molecule, located at  $\vec{r}_r = \pm \hat{u}L \sin(\gamma/2)$ , and the centers of the molecules with which it interacts, which are at  $\vec{r}$ . It is also convenient to assume that the effective interaction  $U_{\text{rod}}^{\text{eff}}$  is proportional to the interaction potential between host molecules, and is independent of the sign of its argument: that is that the only steric dipole in the interaction between the host and the dopant is the V shape of the molecule. This is a ‘‘harmless’’ assumption: if the rod has this symmetry and/or a steric dipole, a small change in the definition of the center of the rod will obviate the steric dipole.

With all these assumptions it is easy to calculate  $U^{mf}$  for the dopant to first order in the gradient of the director. In particular the constant term is simply that given in Eq. (1). The term proportional to the gradient of the director is easily calculated by considering the averages over the two separate rods forming the dopant separately. These integrals do not contain steric or other dipoles so that they are independent of the gradients of the order parameter, provided that the order parameter is taken to be at the center of each rod. Hence, these integrals, to linear order in the gradients, can be taken to depend on the gradients only indirectly through the director at the center of the rod. Then expanding the director at the center of each rod in terms of the director at the center of the dopant and the gradient at the center of the dopant yields

$$U_d^{mf} \rho_h \langle U_{hd}^{\text{eff}} \rangle = U_{hd}^{mfu} + \Delta U_{hd}^l, \quad (8)$$

where

$$U_{hd}^l = J_{hd} S L \sin \frac{\gamma}{2} \left\{ \left[ \hat{n} \cdot \left( \hat{u} \sin \frac{\gamma}{2} + \hat{v} \cos \frac{\gamma}{2} \right) \right] \times \hat{u} \cdot \nabla \hat{n} \cdot \left( \hat{u} \sin \frac{\gamma}{2} + \hat{v} \cos \frac{\gamma}{2} \right) \right] - \left[ \hat{n} \cdot \left( \hat{u} \sin \frac{\gamma}{2} - \hat{v} \cos \frac{\gamma}{2} \right) \right] \times \hat{u} \cdot \nabla \hat{n} \cdot \left( \hat{u} \sin \frac{\gamma}{2} - \hat{v} \cos \frac{\gamma}{2} \right) \right\}$$

$$= J_{hd} S L \sin \frac{\gamma}{2} \sin \gamma (\hat{n} \cdot \hat{v} \hat{u} \cdot \vec{\nabla} \hat{n} \cdot \hat{u} + \hat{n} \cdot \hat{u} \hat{u} \cdot \vec{\nabla} \hat{n} \cdot \hat{v}). \quad (9)$$

Given this form we now need to calculate the change in  $F$ , given by Eq. (3), that is a calculation of the change in  $\rho_d \rho_h \langle U_{ds}^{\text{eff}} \rangle$ . The average over the orientation of the host molecule is exactly the average performed to find the (gradient dependent) mean field of the dopant yielding  $\rho_d \langle U_d^{mf} \rangle$ . Again, this average is independent of the direction of the director so that we can calculate the change in  $F$  simply by expanding in  $\Delta U$  to obtain the change as

$$- \frac{1}{2} \rho_d \langle (\Delta U_d^{mf})^2 / k_B T \rangle_0. \quad (10)$$

Here the average is taken with respect to the dopant orientation with the mean field potential that it would have in the uniform case. As previously remarked, this will decrease the elastic constants. Substituting Eq. (8) into Eq. (9) we see that it is necessary to calculate the tensor average  $\langle \hat{u} \hat{u} \hat{u} \hat{v} \hat{v} \hat{v} \rangle$ . In so doing we will ignore the Boltzmann factor: this again allows the analytic calculation of qualitative results. The average is then easily calculated. With these assumptions we find for the bend, splay, and twist, elastic constants

$$\begin{aligned} \Delta K_{33} &\sim - \frac{29}{105} \rho_d (J_{rh}^2 / k_B T) S^2 \left( L \sin \frac{\gamma}{2} \sin \gamma \right)^2, \\ \Delta K_{11} &\sim - \frac{8}{35} \rho_d (J_{rh}^2 / k_B T) S^2 \left( L \sin \frac{\gamma}{2} \sin \gamma \right)^2, \\ \Delta K_{22} &\sim - \frac{2}{21} \rho_d (J_{rh}^2 / k_B T) S^2 \left( L \sin \frac{\gamma}{2} \sin \gamma \right)^2. \end{aligned} \quad (11)$$

Many of these terms are intuitive, do not require detailed calculation, and are expected to be more general. Specifically,  $\rho_d$  is the density of dopants, so that the energy of interaction of such dopants with the background is proportional to  $S J_{rh}$ . Similarly the magnitude of the reorientation of the dopants by a spatially varying director is proportional to  $S J_{rh} / k_B T$ . The quantity  $[L \sin(\gamma/2)]^2$  is the square of half the distance between the two centers of force in the bent molecule, which is the important length in determining the steric dipole which results in the changes we have calculated in the elastic constants. The factor  $\sin \gamma$  results from the fact that nematic rods interacting via a potential proportional to the square of the angle between them exert a maximum torque when one is at  $45^\circ$  with respect to the other rod and exert no torque at either  $0^\circ$  or  $90^\circ$ . Thus, when  $\gamma$  is  $90^\circ$  degrees, the applied torque is largest; when  $\gamma$  is  $0^\circ$  or  $180^\circ$  the molecule is straight and does not exert appropriate torques.

This leaves only the numerical factors, which must be calculated, to be explained. As discussed above, this calculation needs either to be a detailed numerical calculation or to involve simplifying assumptions. We chose to make simplifying assumptions and found results that are small compared to unity. However, some general statements can be made. These are averages of sums of various dot products of the unit vectors  $\hat{n}$ ,  $\hat{u}$ , and  $\hat{v}$ . It is clear, therefore, that they cannot exceed the maximum value that these products can assume. This maximum, for the bend elastic constant, is unity and is achieved only when the order parameters are  $S_{\hat{u}} = 1$  and  $S_{\hat{v}} = -\frac{1}{2}$ . In more realistic cases where  $S_{\hat{u}}$  is positive and  $S_{\hat{v}}$  is negative (e.g., the bent molecules are oriented in such a way as to favor bend but are generally not oriented so as to favor splay), we believe that the numerical factor for the bend constant has been somewhat underestimated while those for the splay and twist constants have been somewhat overestimated.

Examination of these formulas suggests that our theoretical results for the change in the bend elastic constant is one to two orders of magnitude smaller than the actual measured change. This is less serious than might appear at first sight, as two of our approximations, viz., the rotational average taken without the appropriate Boltzmann factor and the use of  $2L \sin(\gamma/2)$  as the separation between the centers of force for the interactions with the two mesogens, each might be expected to underestimate the change in the bend elastic constant by as much as a factor of 2 or 3. We have confirmed that the large experimental change cannot be due to a change in the order parameter or other thermodynamic change in the system. It may be that these dopant molecules are sufficiently unusually shaped that they induce appreciable changes in the local ordering of the liquid crystal. Certainly, the change in solubility of the dopant when the system becomes nematic suggests that there is a large change in the allowed configurations of the dopant associated with this phase change. This would be consistent with the V-shaped molecule inducing large, local changes in the ordering of the nematic. Such changes can not easily be reflected in the simple theories that we have advanced above or which have been performed to date.

In summary, our experimental results demonstrate that rigidly bent molecules can very significantly decrease the bend elastic constant in the nematic phase when diluted into an approximately linear, low-molecular-weight mesogen. Moreover, this change is much larger than our theoretical analysis would suggest, indicating both additional experimental work on similar molecules and more detailed theoretical analysis are required, particularly a more exact treatment of local interactions.

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