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Bend elastic modulus of a bent and straight dimeric liquid crystal

Gregory A. DiLisi (¹), Charles Rosenblatt (¹,* ) and Anselm C. Griffin (²)

(¹) Department of Physics, Case Western Reserve University, Cleveland, Ohio 44106-7079, U.S.A.
(²) Melville Laboratory for Polymer Synthesis, University of Cambridge, Cambridge CB2 3RA, G.B.

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Résumé. — Des expériences de diffusion de la lumière dans la phase nématique de deux dimères d’unité monomérique 4,4’-dipent Oxynaphal benzoate sont présentées. Un des dimères possède un nombre pair de groupes méthyléniques dans l’espaceur ce qui le rend approximativement linéaire dans une conformation toute trans. L’autre dimère a un groupe méthylénique de moins, ce qui impose une courbure de la molécule. Nous montrons que le rapport du module d’élasticité de torsion sur le module d’élasticité en éventail est presque le même pour les deux dimères, tandis que le rapport du module de courbure sur le module en éventail est considérablement plus petit dans le cas du dimère courbé.

Abstract. — Light scattering measurements in the nematic phase are reported for two dimers based upon the monomer 4,4’-dipentoxyphenylbenzoate. One dimer has an even number of methylene units in the spacer and, in consequence, is approximately straight in the all-trans conformation. The other dimer has one less ethylene unit in the spacer and is, therefore, bent at the spacer group. We find that the ratio of the twist to splay elastic modulus is nearly the same for both species, but that the ratio of the bend to splay modulus is considerably smaller in the bent dimer.

In recent years oligomeric liquid crystals have come under intense scrutiny for the insight they provide about the crossover behavior from monomer to polymer. For example, the magnetic susceptibility, and thus the nematic order parameter, has been reported for the monomer 4,4’-dipent oxyphenylbenzoate « 5005 » [C₃H₁₀OC₆H₄COOC₆H₄OC₃H₁₁], its dimer (composed of ten methylene units in the spacer), and its polymer [1]. Several recent works on the monomer and dimer have yielded the Landau coefficients in the nematic free energy expansion [2, 3], and have provided insight into the relative biaxiality of the nematic phase near the isotropic transition. Even the anchoring strength coefficient of the two species

(*) Also department of Macromolecular Science.
at a rubbed polyimide-coated glass surface was found to differ by an order of magnitude for the two species [4].

Given our current understanding of liquid crystalline elasticity, a study of oligomers might also reveal important structural information about the elastic moduli. To that end the Brandeis group performed a number of elegant experiments on lyotropic polyelectrolytes, such as tobacco mosaic virus and poly penzyl glutamate [5-9]. They demonstrated several important results, such as the relative growth of the bend elastic constant $K_{33}$ with molecular length, as well as the importance of molecular flexibility on the elastic constants. In a more recent work we examined the viscoelastic properties of 5005 and its dimer [10]. Unlike the polyelectrolytes used by the Brandeis group, these systems are dense liquids in which long range attractive interactions are expected to be important, attributes characteristic of thermotropic liquid crystals. Although a naive application of several elastic theories would suggest a dependence of all three elastic moduli on the molecular aspect ratio $L/d$ [1-15], where $L$ is the length and $d$ is the diameter, we found the splay modulus $K_{11}$ and the twist modulus $K_{22}$ vs. reduced temperature to be nearly identical for both monomer and dimer. Only $K_{33}$ differed substantially between the two species, growing appreciably at lower temperatures in the dimer.

During the past year a dimer containing an odd number (nine) of methylene units in the spacer group has become available. Unlike the straight ten methylene dimer discussed above, odd members of the series are inherently kinked in the all-trans conformation, with some characteristic angle between the two mesogenic units. For an isolated molecule, one might expect this angle $\theta_o$ to be approximately 70°, characteristic of tetrahedral bonding. Interactions between the mesogens, however, might diminish this angle somewhat, although it is still expected to be several tens of degrees. One consequence of this bent molecular shape is a substantial biaxial character associated with the nematic phase, as observed near the nematic-isotropic phase transition [3]. In that work we measured, among other things, the quantity $T_c - T^*$ for both the odd and even dimers. Here $T_c$ is the first order NI transition temperature and $T^*$ is the supercooling limit of the isotropic phase. It was found that $T_c - T^*$ is substantially smaller for the odd dimer, consistent with biaxiality.

In this paper we address the behavior of the bend elastic constant of both odd and even members of the series. Building on Meyer’s flexoelectric work [16] which accounts for a generalized orienting field associated with molecular shape, Gruler [17] and Helfrich [18] independently suggested that a kinked molecule might exhibit a reduced bend elastic modulus, since the elastic strain can be partially relieved by a change in the distribution of molecular orientations; in a sense, the banana-shaped molecules can partially align in "bunches". For a kinked dimer, the shape-dependence of $K_{11}$ and $K_{22}$ would be of higher order, and therefore unimportant. This idea was examined experimentally by Gramsbergen and de Jeu [19], who investigated a number of bent and straight rigid monomers. Contrary to these predictions, their results indicate that a reduction in the aspect ratio, rather than a bend of the molecule, is responsible for a reduction in $K_{33}/K_{11}$. Comparing a straight molecule containing three aromatic groups with a double aromatic molecule having a kink $\theta_o \sim 18°$, they found virtually no difference in $K_{33}/K_{11}$; moreover, these molecules have approximately the same aspect ratio. In conjunction with measurements on straight molecules having different lengths, these results were deemed consistent with the picture of Leenhouts and Dekker [20] in which $K_{33}/K_{11}$ scales with the aspect ratio for rigid molecules, rather than with some intrinsic bend parameter. Despite the care taken by Gramsbergen and de Jeu, it was nevertheless necessary at the time for comparisons to be made among very different sorts of molecules. With the synthesis of our dimers, however, we now have a far less pathological system with which to test the ideas of Gruler and Helfrich: not only are the compositions of
the odd and even molecules virtually identical but $\theta_0$ for the odd species is considerably larger than 18°. Thus, the nine-methylene bent dimer and the adjacent ten-methylene straight dimer provide a nearly ideal system with which one can investigate the behavior of $K_{33}$ vs. molecular shape. To that end we performed a series of temperature-dependent light scattering experiments on the two species so as to determine the ratios $K_{33}/K_{11}$ and $K_{22}/K_{11}$. Our central result is that although the ratio $K_{33}/K_{11}$ for both the odd and even dimers is comparable, $K_{33}/K_{11}$ for the bent (odd) dimer is substantially smaller than it is for its straight (even) counterpart.

The molecules were synthesized according to procedures described elsewhere [21-23]. The even dimer is simply two monomers attached end-to-end, minus a pair of terminal hydrogen atoms; thus, the even dimer contains ten methylene units in the spacer and, in consequence, is approximately straight in the all-trans conformation. In the odd dimer an additional methylene group has been removed, and it thus contains nine methylene units in the spacer. As a result the odd species is bent in the all-trans conformation.

Before performing the light scattering experiments, it was necessary to determine the refractive indice vs. temperature of the two materials. As described in detail elsewhere [10], the extraordinary and ordinary indices $n_e$ and $n_o$ were obtained at 514.5 nm from the average index in the isotropic phase, $n_{iso}$, and from the birefringence $\Delta n$, where it can then be shown that

$$n_e = \frac{2}{3} \Delta n + \left( n_{iso}^2 - 2 \Delta n^2/9 \right)^{\frac{1}{2}}$$

For the odd dimer it was found that $n_{iso} = 1.536 \pm 0.02$, and for the even dimer, $n_{iso} = 1.534 \pm 0.01$. The birefringences vs. temperature are shown in figure 1.

Light scattered by angular fluctuations of the director is composed of two modes corresponding to bend-splay (mode-1) and bent-twist (mode-2) deformations [24, 25]. For the undistorted director $n_0$ parallel to the $z$-axis, the differential scattering cross-section per unit volume is given by

$$\frac{d\sigma}{d\Omega} = \frac{\pi \Delta \epsilon^2}{\lambda^2} k_B T \sum_{\nu = 1, 2} \frac{(i_\nu f_{i\nu} + i_1 f_{e\nu})^2}{K_{33} q^2 + K_{\nu\nu} q^2_{\perp}}$$

(1)

![Fig. 1. — Birefringence vs. reduced temperature for the two species. (Solid line, odd dimer; dashed line, even dimer).](image)
where $k_B$ is Boltzmann’s constant, $T$ is temperature, $\lambda$ is the wavelength of light, and $\Delta \epsilon$ the anisotropy in the optical dielectric tensor. In addition, $\mathbf{q}$ corresponds to the difference between the incident and scattered wavevectors, and has components $q_i$ parallel to $\mathbf{n}_o$ and $q_{\perp}$ in the plane perpendicular to $\mathbf{n}_o$. $i$, $_\nu$, and $f$, are the components of the initial and final polarizations along the $\delta \mathbf{n} = \mathbf{n} - \mathbf{n}_o$ directions for the two modes, formally defined as

$$i_{\nu} = e_{\nu} \ i ; \quad f_{\nu} = e_{\nu} \ f,$$

where

$$e_2 = \mathbf{n}_o \times \mathbf{q} / |\mathbf{n}_o \times \mathbf{q}| ; \quad e_1 = e_2 \times \mathbf{n}_\nu / |e_2 \times \mathbf{n}_\nu| .$$

Our scattering apparatus is described in detail elsewhere [10]. In order to determine the ratio $K_{22}/K_{11}$, we utilized a geometry in which $\mathbf{n}_o$ was oriented perpendicular to the scattering plane, the incident laser polarization $i$ was parallel to $\mathbf{n}_o$, and the scattered polarization $f$ was in the scattering plane; this is a VH geometry. Note that in this geometry the component of $\mathbf{q}$ parallel to the director $q_i = 0$. Thus, according to equation (1), bend distortions make no contribution to the scattered intensity $I \propto d\sigma/d\Omega$. In consequence, $I$ is simply the sum of two modes, pure splay and pure twist, weighted by their angular-dependent optical polarization factors. Thus,

$$I \propto \frac{n_\phi^2 \sin^2 \phi}{K_{11} q_{\perp}^2} + \frac{(n_{\text{ord}} - n_\phi \cos \phi)^2}{K_{22} q_{\perp}^2}$$

where $\phi$ is the scattering angle inside the liquid crystal.

Measurements were made at two scattering angles $\theta$ (defined in the laboratory frame) for each material at each temperature: $\theta = 10^\circ$ and $\theta = \theta_{\text{splay}}$ (Note that $\theta$ was determined from the internal angle $\phi$ by means of Snell’s law.) At $10^\circ$ the polarization factors for both the bend and twist modes are comparable; at the special angle $\theta_{\text{splay}}$, typically $30^\circ$-$35^\circ$, the polarization factor for the twist mode vanishes, and $I$ depends solely on $K_{11}$. $\theta_{\text{splay}}$ is, of course, a function of the refractive indices and thus temperature, and is determined by the condition that the scattered wavevector $\mathbf{q} = q_{\perp}$ is parallel to the polarization of the scattered light. At each of the two scattering angles the intensity was determined by counting photons for several minutes. The intensities $I(\theta)$ were taken as the total number of counts divided by the corresponding collection times, multiplied by an angular-dependent scaling factor calibrated for our scattering apparatus [10]. Since $I(\theta = 10^\circ)$ involves both splay and twist and $I(\theta_{\text{splay}})$ involves splay exclusively, the ratio $K_{22}/K_{11}$ could be extracted from the intensity ratios [cf. Eq. (2)]. These results are shown in figure 2.

In order to determine $K_{33}/K_{11}$ we utilized a geometry in which $\mathbf{n}_o$ lies in the scattering plane, $i$ is perpendicular to this plane, and $f$ lies in the scattering plane. This geometry measures a pure mode corresponding to a mixture of bend and twist, where the intensity is given by

$$I \propto \frac{\cos^2 \phi}{K_{33} q_i^2 + K_{22} q_{\perp}^2} .$$

Thus, an experimental determination of the ratio $K_{33}/K_{22}$, multiplied by $K_{22}/K_{11}$ obtained above, will give us the desired ratio $K_{33}/K_{11}$.

Again, temperature-dependent intensity measurements were made at angles (in the laboratory frame) $\theta = 10^\circ$ and the special angle $\theta = \theta_{\text{bend}}$. Since this geometry involves only one mode, the polarization factor in equation (1) does not distinguish twist from bend; rather, the wavevector $\mathbf{q}$ associated with scattering at $10^\circ$ decomposes into $q_i$ associated with
bend and $q_\perp$ associated with twist [cf. Eq. (3)]. Moreover, the angle $\theta_{\text{bend}}$ is defined such that $q_\perp = 0$, and thus the scattered light at this angle involves only bend distortions. At a given temperature and for a given species, the ratio $K_{33}/K_{22}$ was extracted from the ratio $I(\theta = 10^\circ)/I(\theta_{\text{bend}})$ using equation (3). This value must then be multiplied by $K_{22}/K_{11}$ at the same temperature. Since the reduced temperatures of the two scattering experiments do not coincide, we performed a linear fit of the data in figure 2 for each of the two species. This procedure is quite reasonable, especially given the absence of any obvious temperature dependence in figure 2, as well as the small degree of relative scatter. We then multiplied these measured values of $K_{33}/K_{22}$ by the fitted values of $K_{22}/K_{11}$ in order to extract the ratio $K_{33}/K_{11}$, which is shown in figure 3. Note that the error bars in figure 3 represent the total error, involving both sets of measurements.

A comparison of figures 2 and 3 reveals the central result of this work, viz., a banana-shaped molecule significantly reduces the bend elasticity relative to splay and twist. Over the entire temperature range, in fact, $K_{33}/K_{11}$ for the odd dimer is only about 60 to 65% of the value of the even dimer, whereas the twist to splay ratios are nearly the same. As noted in the introduction, Gruler [16] and Helfrich [17] suggested just this sort of effect. Gruler, for example, calculated the change in the elasticity as a function of empirical material parameters which describe the inherent bend of the molecule. Using reasonable values for these parameters, he pointed out that the bend modulus for a banana-shaped molecule might be reduced so much that it can even become negative [16]; Helfrich's corrections, on the other hand, were somewhat smaller [17]. In this light our results clearly indicate that the effective material parameters for our odd dimer lie within a reasonable range. More recently, Terentjev and Petschek developed a theory specifically for dimers with a semiflexible spacer [26]. They considered anisotropic mesogens which interact via both an attractive part of the potential (including isotropic and anisotropic contributions), and a hard core repulsive part. In addition, they included both a stiffness parameter $\Omega$ for the spacer and a «bare» angle $\theta_0$ between the two mesogens. For the even dimer in the limit $\Omega \to \infty$ (a rigid spacer) they found that $K_{22}/K_{11} \approx 1/3$; similar results were found for the odd (bent) dimer. For both dimers, and assuming a completely rigid spacer, $K_{33}/K_{11}$ was found to exhibit the same qualitative temperature dependence observed experimentally and shown in figure 3.

Fig. 2. — $K_{22}/K_{11}$ vs. reduced temperature for the even (●) and the odd (▲) dimer. Typical error bar is shown.
behavior arises from the order parameter dependence of $K_{33}$, such that $K_{33}$ diverges as the nematic order parameter $S \to 1$. Terentjev and Petschek also numerically examined finite values of $O$, which would correspond to some degree of spacer flexibility. They found that on introducing flexibility, the qualitative temperature dependence of $K_{33}/K_{11}$ remains, although the divergence at lower temperatures tends to be weaker. Finally, they examined the behaviour of $K_{33}/K_{11}$ as a function of the mesogenic angle $\theta_0$ in conjunction with a physically appropriate stiffness parameter $\Omega$. For $\theta_0 = 20^\circ$ they found a significant reduction in $K_{33}/K_{11}$ relative to the straight dimer ($\theta_0 = 0^\circ$). For $\theta_0 = 40^\circ$ they found an even greater reduction, corresponding approximately to the behavior shown for the odd dimer in figure 3. (It should be noted molecules attempt to straighten in the nematic phase.) This is not to say that $\theta_0$ for our odd dimer is necessarily $40^\circ$, but rather that when a significant angle (tens of degrees) exists between the mesogens, one can expect a significant reduction in $K_{33}$. Moreover, we point out that the qualitative aspects of these results are consistent with the predictions of Gruler and Helfrich, and are precisely what would be expected on intuitive grounds.

Our results, which clearly suggest that the bend elasticity is reduced for a banana shaped molecule, is inconsistent with the interpretation Gramsbergen and de Jeu ascribed to their data [19] for rigid molecules. It should be noted, however, that for some molecules with semiflexible terminal groups, the ratio $K_{33}/K_{11}$ decreases with increasing length of the terminal alkyl group [20, 27]. This behavior has been theoretically attributed [28] to smectic-like correlations in the nematic phase associated with the longer molecules, a result borne out experimentally by Bradshaw, et al. [27]. In our dimer system, however, this is unlikely to be the operative mechanism. For dimers based upon the monomer 5005, only a two methylene spacer yields a smectic phase [29]. For homologous series of dimers based upon similar monomers, however, several molecules with shorter spacer groups in a given series exhibit a smectic A phase [29]. In all cases the clear pattern is that the even (straight) dimers have a much larger propensity to form a smectic A phase than do the odd (kinked) dimers. Yet, for the dimers discussed herein, the even (ten-methylene) spacer has a much larger ratio
$K_{33}/K_{11}$, inconsistent with the notion that smectic correlations tend to diminish this ratio. We thus feel that smectic correlations play at most a minor role in these systems, and the behavior of $K_{33}/K_{11}$ can be ascribed to the bent shape of the odd member of the series.

As noted above, dimers of the sort used in this study were unavailable several years ago. Although the earlier comparisons within a terminal group homologous series, let alone among different classes of molecules, are useful, they must be treated cautiously. As long as the system is thermal and long range interactions are important, one cannot base elasticity ratios solely on hard core aspect ratios. Rather, one requires a system of virtually identical molecules; this would tend to suppress differences in the non-steric (i.e., long range) contribution to the potential associated with the various parts of the molecule. Thus, only systems similar to those used in this investigation might represent a fair test of the theories promulgated by Gruler, Helfrich, and Terentjev and Petschek.

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