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Elastic constants of nematic liquid crystalline Schiff's bases

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The three elastic constants of a number of structurally related nematic liquid crystalline Schiff's bases have been measured as a function of temperature. The results are new in the sense that they exhibit a clear distinction in behavior between compounds with a rigid molecular structure and compounds with a molecular structure consisting of a rigid core and a flexible alkyl chain. In particular, it has been found that the ratio of the bend and splay elastic constants K_3/K_1 increases for compounds with a rigid molecular structure with increasing length to width ratio. This trend is the reverse of that observed within homologous series, for which K_3/K_1 has been found to decrease with increasing length of the alkyl chain. New is the experimental finding that the twist elastic constant K_2 of the homologs studied is independent of the length of the alkyl chain. Finally, the experiments show that the average elastic constant $\bar{K} = (K_1 + K_2 + K_3)/3$ is proportional to the smectic-isotropic transition temperature. The results can only be partly understood within the framework of existing theoretical models.

I. INTRODUCTION

Nematic liquid crystalline phases are characterized by a certain degree of long range orientational order. The long axes of the constituent elongated molecules tend to align along a common preferred direction, the director, specified by a unit vector $\mathbf{n}$. The molecular centers of mass, on the other hand, exhibit almost no ordering, i.e., the positional ordering is comparable to that in conventional isotropic fluids.

In a nematic single crystal $\mathbf{n}$ is uniform throughout the sample. More generally, the director pattern is not uniform in space, but *curved*. These curvatures are brought about by external stimuli, like magnetic or electric fields for instance. If $\mathbf{n}(\mathbf{r})$ changes noticeably only over distances large compared with the molecular dimensions, these curvatures can be described in terms of a continuum theory, which disregards the details of the structure on a molecular scale. Based upon this point of view Zocher¹ and Oseen² initiated a phenomenological theory, which was developed further by Frank.³ The theory is in fact an analog of the continuum theory of elasticity of solids. A solid undergoes elastic strains under the influence of small stresses. For small deformations Hooke's law applies, i.e., the strain is proportional to the stress and the distortion free energy is a quadratic function of the components of the strain tensor. In nematic liquid crystals permanent forces opposing changes of distance between molecules are absent. Here the curvature of the director pattern is opposed by restoring *torques* and the distortion free energy density f_d associated with the long wavelength curvatures of the director pattern can be written as a quadratic function of the curvature strains, i.e.,

$$f_d = \frac{1}{2} [K_1 (\nabla \cdot \mathbf{n})^2 + K_2 (\mathbf{n} \cdot \nabla \times \mathbf{n})^2 + K_3 (\mathbf{n} \times \nabla \times \mathbf{n})^2] . \quad (1)$$

The coefficients K_1 , K_2 , and K_3 in this expression, the so-called elastic constants, are associated with the three basic types of distortion, viz., splay, twist, and bend.

During the past few years systematic experimental

studies of curvature elasticity of nematic liquid crystals have been carried out by Karat and Madhusudana⁴ on the alkylcyanobiphenyls, by de Jeu and Claassen⁵ on the dialkoxy- and dialkylazoxybenzenes, by Schad, Baur, and Meier⁶ on the alkylcyanophenylcyclohexanes, and by Schadt and Müller⁷ on a number of commercially available mixtures. These studies deal almost exclusively with homologous series. A common finding in these measurements is that the ratio K_3/K_1 decreases with increasing length of the alkyl chain. This result contrasts with the outcome of theoretical calculations for rigid rods, which predict that K_3/K_1 should increase if the molecular length to width ratio increases. For the twist elastic constant, so far only few reliable data have been reported.

In this paper we present the results of measurements of the elastic constants as a function of temperature for a number of Schiff's bases. In order to test the predictions of existing theoretical models and to investigate which molecular properties determine the elasticity, the effect of small variations in the molecular structure on the elastic behavior has been studied. The molecular structure of the materials investigated is shown in Fig. 1. Besides the compound APAPA itself, we have also investigated a number of homologs of this material; these are denoted by APAPAm, where m stands for the number of carbon atoms of the alkyl chain of the ester group $\text{OCOC}_m\text{H}_{2m+1}$. The melting and clearing points are listed in Table I. We emphasize that the compounds studied only show a nematic liquid crystalline phase, i.e., no nematic-smectic phase transition. It is well known that smectic short range order in the nematic phase near the nematic-smectic transition would strongly influence the elastic behavior.

Various new results have been found. Probably most important is the observation that for the compounds studied with a rigid molecular structure K_3/K_1 indeed increases with increasing molecular length to width ratio, as required by theoretical calculations. In agreement with the results of the measurements on the homologous series reported in the literature cited

FIG. 1. Molecular structures of the compounds studied.

earlier, we observed a decrease of K_3/K_1 with increasing chain length for the homologous series APAPAm. With regard to the measurements of the twist elastic constant K_2 we may mention that by a slight modification of the conoscopic method, we have been able to obtain quite reliable data for this quantity.

The plan of the paper is as follows: In Sec. II we briefly review some theoretical considerations. Section III deals with the experimental methods and the analysis of the experimental data. The results of the measurements are presented in Sec. IV and discussed in Sec. V.

II. THEORETICAL SURVEY

In the following the assumption is made that the molecules are axially symmetric around the long molecular axis. The orientation of this axis can be specified by the polar coordinate angles θ and ϕ , where θ is the angle between the long molecular axis and the director n , which is chosen parallel to the z axis of a coordinate frame (x, y, z) .

The curvature elasticity is of course directly related to the nature and the strength of the intermolecular forces. This implies that the results of theoretical calculations of the elastic constants depend directly on the underlying microscopic interaction model. Thus far relatively little attention has been paid to the curvature elasticity from a theoretical point of view. The existing calculations are based either solely on the Maier-Saupe theory⁸ or the Onsager model⁹ or combine elements of both. Before discussing the existing theoretical calculations, we first briefly pay attention to the Maier-Saupe and Onsager models.

These models represent two different points of view

with regard to the origin of the long range orientational order in nematic liquid crystals. According to Maier and Saupe nematic order results from attractive dispersion forces between the anisotropically polarizable molecules. Steric repulsions, which are anisotropic due to the elongated molecular shape, are disregarded or assumed to be isotropic, i.e., in a sense the molecules are assumed to be spherically symmetric. However, as pointed out by Cotter,¹⁰ the nematic structure can also be explained on the basis of the Onsager model, where the steric repulsions, i.e., the excluded volume effects, are held responsible for the orientational order. Extensions of the Maier-Saupe and Onsager model have been developed, respectively, by Ypma and Vertogen¹¹ and by Cotter.¹² These theories, which incorporate both attractive forces and anisotropic steric repulsions, have in common that the free energy F can be written as

$$F = U - T\Sigma_o - T\Sigma_p, \quad (2)$$

where U , Σ_o , and Σ_p are the internal energy, the orientational entropy, and the packing entropy, respectively, and T is the temperature. The orientational entropy Σ_o is determined by the degree of orientational order, and the packing entropy Σ_p takes account of the excluded volume effects associated with the steric repulsions of the elongated molecules. Denoting the orientational distribution of the long molecular axes by $f(\Omega)$, where Ω stands for the angles θ and ϕ , and the distribution of the molecular centers of mass by $g(\mathbf{r}_{ij}, \Omega_i, \Omega_j)$, the mean field approximation yields^{11,12}

$$U = \frac{1}{2} N\rho \int d\Omega_i d\Omega_j f(\Omega_i) f(\Omega_j) \times \int d\mathbf{r}_{ij} w_{ij}^{(a)}(\mathbf{r}_{ij}, \Omega_i, \Omega_j) g(\mathbf{r}_{ij}, \Omega_i, \Omega_j), \quad (3)$$

$$\Sigma_o = -Nk_B \int d\Omega f(\Omega) \ln[4\pi f(\Omega)], \quad (4)$$

$$\Sigma_p = -\frac{1}{2} \mu \rho N k_B \int d\Omega_i d\Omega_j f(\Omega_i) f(\Omega_j) V(\Omega_i, \Omega_j). \quad (5)$$

Here N is the number of particles, ρ the number density, and k_B the Boltzmann constant; $w_{ij}^{(a)}(\mathbf{r}_{ij}, \Omega_i, \Omega_j)$ is the attractive part of intermolecular interaction and $V(\Omega_i, \Omega_j)$ is just the volume excluded to the center of a molecule with orientation Ω_i due to the presence of a molecule with orientation Ω_j (Fig. 2). The factor μ equals 1 in the Onsager model⁹ and in the model of Ypma and Vertogen,¹¹ and depends on the packing fraction and the molecular length to width ratio in Cotter's model.¹²

TABLE I. List of nematic liquid crystals studied. T_m and T_c are the transition temperatures crystal-nematic and nematic-isotropic, respectively.

	T_m (°C)	T_c (°C)		T_m (°C)	T_c (°C)
MBBA	18	46.2	APAPA2	72	110.6
OHMBBA	44	64.6	APAPA3	53	112.8
MBCA	106	118.0	APAPA4	61	100.0
MBAPB	119	177.7	APAPA5	83	103.2
APAPA	82	111.0	APAPA9	76	96.5

FIG. 2. The region enclosed by the broken line represents the excluded volume $V(\Omega_i, \Omega_j)$.

Expressions (3)–(5) refer to the undistorted state. In this state the orientation of $\mathbf{n}$ does not vary in space. The corresponding expressions in the distorted state can be obtained readily by changing the orientation of $\mathbf{n}_j$, the director at molecule j , slightly with respect to the orientation of $\mathbf{n}_i$.^{13,14} Since the curvatures of $\mathbf{n}$ are small on a molecular scale, the function $f(\Omega)$ is to a first approximation, not affected by the distortion. This implies that Σ_o does not change and that the distortion free energy can be written as

$$\Delta F = \Delta U - T\Delta\Sigma_p, \quad (6)$$

where ΔU and $\Delta\Sigma_p$ represent the difference in internal energy and packing entropy between the distorted and undistorted state, respectively. By relating ΔF to f_d , given by Eq. (1), according to

$$\Delta F = \int_{\text{sample}} d\mathbf{r} f_d, \quad (7)$$

the macroscopic elastic constants can in principle be calculated for any molecular interaction model.

Now we come to a discussion of the results of the existing theoretical calculations. We will specify the orientational order, as customary, by the parameters $\langle P_{2l} \rangle$, the statistical averages of the Legendre polynomials $P_{2l}(\cos\theta)$:

$$\langle P_{2l} \rangle = \int_{-1}^{+1} d(\cos\theta) f(\theta) P_{2l}(\cos\theta) \quad (l=1, 2, 3, \dots). \quad (8)$$

Note that the orientational distribution function f only depends on θ , as dictated by the uniaxial symmetry of the nematic phase around $\mathbf{n}$.

The first calculations of the elastic constants, based on the Maier–Saupe theory, were carried out by Saupe and Nehring;¹⁵ they found

$$K_1 : K_2 : K_3 = 5 : 11 : 5 \quad (9)$$

and

$$K_i = C_i \eta^{7/3} \langle P_2 \rangle^2 \quad (i=1, 2, 3), \quad (10)$$

where η is the packing fraction and C_i is a constant. We recall that in the Maier–Saupe theory the molecules are assumed to be spherical. This implies that also the excluded volume $V(\Omega_i, \Omega_j)$ is spherical and Σ_p does not contribute to the distortion free energy. Moreover, the distribution function g [see Eq. (3)] was assumed to be spherically symmetric and independent of the molecular orientations. Priest¹⁶ extended the

calculations of Nehring and Saupe using an arbitrary intermolecular interaction, i.e., without specifying the nature of the intermolecular forces. He derived to order $\langle P_4 \rangle / \langle P_2 \rangle$,

$$\begin{aligned} K_1/\bar{K} &= 1 + \Delta - 3\Delta' \langle P_4 \rangle / \langle P_2 \rangle, \\ K_2/\bar{K} &= 1 - 2\Delta - \Delta' \langle P_4 \rangle / \langle P_2 \rangle, \\ K_3/\bar{K} &= 1 + \Delta + 4\Delta' \langle P_4 \rangle / \langle P_2 \rangle, \end{aligned} \quad (11)$$

where

$$\bar{K} = (K_1 + K_2 + K_3)/3 \sim \eta^2 \langle P_2 \rangle^2. \quad (12)$$

In order to calculate the quantities Δ and Δ' , a specific choice for the intermolecular interaction and molecular shape has to be made. Priest derived expressions for Δ and Δ' for the special case of spherocylinders interacting via a hard core repulsion, i.e., on the basis of the Onsager model, in which the attractive forces are disregarded ($U=0$). He found to order $\langle P_4 \rangle / \langle P_2 \rangle$,

$$\begin{aligned} \Delta &= (2R^2 - 2)/(7R^2 + 20), \\ \Delta' &= (9/16)(3R^2 - 8)/(7R^2 + 20). \end{aligned} \quad (13)$$

Here $R = (L - W)/W$, where L and W are the overall length and width of the spherocylinders, respectively. Following a somewhat different approach, Straley¹³ obtained approximately the same results. Note that the molecular length to width ratio enters in the expressions for the elastic constants if the curvature elasticity in nematic liquid crystals is attributed primarily to the difference in packing entropy between the distorted and undistorted state. Finally, we mention that the calculations of Priest have been extended to non-axially symmetric molecules by van der Meer and Vertogen.¹⁷

Various authors^{18–20} have derived expressions for the elastic constants using a lattice model, i.e., by making a particular choice for the distribution function $g(\mathbf{r}_{ij}, \Omega_i, \Omega_j)$. The results of these calculations can be summarized by the formulas

$$\begin{aligned} K_3/K_1 &= C(L/B)^2, \\ K_1 &= K_2, \end{aligned} \quad (14)$$

where C is a constant and L and W stand for the molecular length and width, respectively, or the dimensions of the lattice cell chosen.

III. EXPERIMENTAL METHODS

A. Frederiks transitions

The elastic constants have been measured by following optically the Frederiks transition of uniformly aligned layers in a magnetic field; the experimental geometries are shown in Fig. 3. The distortion starts at a critical field given by²¹

$$(H_c)_i = (\pi/d) (K_i/\Delta\chi)^{1/2}, \quad (15)$$

where $i=1, 2$, and 3 for case a , b , and c , respectively; d stands for the thickness of the nematic layer and $\Delta\chi$ is the anisotropy of the diamagnetic volume susceptibility. The thickness was measured interferometrically and $\Delta\chi$ using the Faraday–Curie method. Results of the measurements of $\Delta\chi$ have been published

FIG. 3. Experimental configurations for determining the critical field for splay (a), twist (b), and bend (c).

previously.²² The preparation of the planar and homeotropic layers has been discussed in Refs. 23 and 24.

B. Splay and bend

The splay elastic constant (Fig. 3; case *a*) has been measured by recording the intensity of a laser beam (HeNe; $\lambda = 633$ nm) traversing the nematic layer, which is subjected to a magnetic field.²¹ The field is swept very slowly (≈ 7 Oe/min) through the Frederiks transition. The sample is placed between crossed polarizers. As soon as the field H exceeds H_c , the intensity changes continuously as a result of the changing phase difference δ between the two normal components of the light beam propagating in the medium. The interrelation between δ , H , and H_c and various material parameters is given by²¹

$$\delta = \frac{2\pi}{\lambda} n_e d \left\{ 1 - (2H_c/\pi H) \int_0^{\pi/2} d\psi \times \left[\frac{1 + \kappa \sin^2 \alpha_m \sin^2 \psi}{(1 - \sin^2 \alpha_m \sin^2 \psi)(1 + \nu \sin^2 \alpha_m \sin^2 \psi)} \right]^{1/2} \right\}, \quad (16)$$

with

$$H/H_c = (2/\pi) \int_0^{\pi/2} d\psi \left(\frac{1 + \kappa \sin^2 \alpha_m \sin^2 \psi}{1 - \sin^2 \alpha_m \sin^2 \psi} \right)^{1/2}. \quad (17)$$

Here $\sin \psi = \sin \alpha / \sin \alpha_m$, where α is the angle between the director and the zero field alignment direction and α_m the value of α in the middle of the sample; $\kappa = (K_3 - K_1)/K_1$ and $\nu = (n_e^2 - n_o^2)/n_o^2$, where n_e and n_o are the extraordinary and ordinary refractive index, respectively. Using Deuling's²⁵ computer program, we have fitted the experimental data to the theory with H_c and K_3/K_1 as parameters (n_e and n_o have been measured independently). Expressions (16) and (17) apply also to configuration *c*, provided n_e and n_o as well as K_1 and K_3 are interchanged. Details of the experimental setup and possible sources of errors have been published previously.²³

C. Twist

Since the optical method employed for the detection of the splay and bend thresholds fails for configuration *b* (Fig. 3), the twist elastic constant has been determined using conoscopy. The conoscopic pattern of a planar oriented nematic layer placed between two polarizers

consists of hyperbolas. Upon inducing a twist deformation by means of a magnetic field, applied perpendicular to the director $n(0)$ of the undistorted sample, the pattern rotates by an amount δ given by²⁶

$$\delta = \frac{1}{2} \arctan \{ 2 \sin \alpha_m / [2E(\pi/2, \alpha_m) - F(\pi/2, \alpha_m)] \}, \quad (18)$$

with

$$\pi H / 2H_c = F(\pi/2, \alpha_m), \quad (19)$$

where F and E are the complete elliptic integrals of the first and second kind, respectively, and α_m is the twist angle in the middle of the sample. Figure 4 shows the angle δ as a function of H/H_c . The crosses represent measured values and the solid curve is a least squares fit using Eqs. (18) and (19) with H_c as parameter.

The conoscopic pattern can rotate either clockwise or counterclockwise, since these two senses of rotation are equally probable if H is oriented exactly perpendicular to $n(0)$. Often, therefore, a pattern is observed originating from two domains rotating in opposite senses. In that case an accurate determination of δ is practically impossible. To avoid this difficulty, the sample is therefore positioned such that $n(0)$ is oriented not exactly normal to H , but at some angle ($90 - \alpha_0$). Denoting the distortion angle by $\alpha - \alpha_0$, it can be shown by minimizing the sum of the distortion and magnetic free energy that in this case the interrelation between H , H_c , α_0 , α_m , and δ is given by

$$(\pi H / 2H_c) = \int_{\psi_0}^{\pi/2} d\psi (1 - \sin^2 \alpha_m \sin^2 \psi)^{-1/2}, \quad (20)$$

$$\delta = \frac{1}{2} \arctan \times \left[\frac{2(\sin^2 \alpha_m - \sin^2 \alpha_0)^{1/2} \cos 2\alpha_0 - H(\psi_0, \alpha_m) \sin 2\alpha_0}{2(\sin^2 \alpha_m - \sin^2 \alpha_0)^{1/2} \sin 2\alpha_0 + H(\psi_0, \alpha_m) \cos 2\alpha_0} \right]. \quad (21)$$

Here, $\sin \psi_0 = \sin \alpha_0 / \sin \alpha_m$ and $H(\psi_0, \alpha_m)$ is given by

FIG. 4. Rotation angle δ as a function of H/H_c . The crosses represent measured values and the solid curve is a least squares fit to Eqs. (18) and (19). The broken curve represents a theoretical calculation according to Eqs. (20) and (21).

$$H(\psi_0, \alpha_m) = 2 \int_{\psi_0}^{\pi/2} d\psi (1 - \sin^2 \alpha_m \sin^2 \psi)^{1/2} - \int_{\psi_0}^{\pi/2} d\psi (1 - \sin^2 \alpha_m \sin^2 \psi)^{-1/2}. \quad (22)$$

The broken curve in Fig. 4 represents the angle δ as a function of H/H_c as calculated from Eqs. (21) and (22) with $\alpha_0 = 3.5^\circ$. Note that the distortion starts at $H=0$, i.e., the deformation is not a true Frederiks transition. In practice, we limited α_0 to values of some degrees. By recording δ as a function of H and fitting the data to the theoretical curves both H_c and α_0 can be obtained. We emphasize that the introduction of a small angle α_0 strongly enhances the experimental usefulness of the conoscopic method. The experimental setup has been discussed extensively previously.²⁴

D. Evidence for strong anchoring

Expressions (16) and (17) and the equations describing the rotation angle of the conoscopic pattern (Sec. III C) apply only in the case of strong anchoring, i.e., if the orientation of the director near the boundaries is not affected by the magnetic field. A convincing argument that the condition of strong anchoring was indeed satisfied for the twist experiments can be derived from Fig. 4. The solid curve fits the experimental data excellently; this would not have been observed if the anchoring had been weak.^{27,28}

The same argument can not be applied to the splay and bend geometries since in these cases the form of the theoretical curves depends on more parameters. For case *a* (Fig. 3) the existence of strong anchoring has been demonstrated by verifying the validity of Eq. (15). Figure 5 shows that the values of $1/H_c$, measured for samples with different thicknesses, lie on a straight line which goes right through the origin. In the case of weak anchoring lower values of H_c would have been found corresponding to effective thicknesses $(d+b)$, where b is a constant.²⁹ Finally, we note that the values of $K_3/\Delta\chi$ calculated using Eq. (15) were not lower than those obtained from the computer fits using Eqs. (16) and (17). Hence, we are confident that the condition of strong anchoring was fulfilled also for the homeotropic samples.

FIG. 5. Plot of $1/H_c$ versus the thickness d (OHMBBA).

FIG. 6. K_1 as a function of temperature. Circles, APAPA; triangles, APAPA5; crosses, APAPA9.

IV. EXPERIMENTAL DATA

As illustrative examples of our experimental results, we have displayed in Figs. 6 and 7 the splay and twist elastic constants, respectively, as a function of the reduced temperature T/T_c for some materials. For the sake of clarity not all experimental data for the materials considered have been included in the figures. The solid curves through the points represent least squares fits according to the formula

$$K_i(T/T_c) = K_i^0 (1 - \beta T/T_c)^\gamma \quad (i = 1, 2, 3). \quad (23)$$

Rather than presenting the curves for all compounds studied we have collected the coefficients K_i^0 , β , and γ so obtained for splay, twist, and bend in Tables II, III, and IV, respectively. The data for MBAPB have not been included in the tables since for this material $\Delta\chi$ has not been measured. In Fig. 8 we have shown the quantities $K_i/\Delta\chi$ for MBAPB together with the corresponding data for APAPA and MBAC. Note that MBAPB has been measured only up to $T/T_c = 0.94$, because the epoxy resin used for the construction of the sample cells could not stand higher temperatures. Finally, we note that Eq. (23) can be applied with sufficient reliability only up to $T/T_c \approx 0.995$, since the elastic constants could not be measured with sufficient accuracy above this temperature.

FIG. 7. K_2 as a function of temperature. Circles, MBBA; triangles, OHMBBA.

TABLE II. Coefficients to calculate the splay elastic constant K_1 according to Eq. (23).

	K_1^0 (10^{-7} dyn)	β	γ
MBBA	15.81	0.9973	0.3610
OHMBBA	20.47	0.9972	0.3727
MBCA	18.19	0.9988	0.2874
APAPA	17.98	0.9970	0.3355
APAPA2	16.57	0.9978	0.3352
APAPA3	37.12	0.9840	0.5910
APAPA4	27.30	0.9959	0.4547
APAPA5	32.53	0.9950	0.4641
APAPA9	78.30	0.9840	0.7470

For comparison of the elastic properties of different compounds one often considers ratios of the elastic constants. We have, therefore, listed the values of K_2/K_1 and K_3/K_1 collected at the same reduced temperature $T/T_c = 0.95$ in Table V.

About the accuracy of the experimental values of the elastic constants the following may be said: Taking into account the errors in $\Delta\chi$ and d , the errors in the values of the elastic constants calculated directly from the values of H_c are estimated to be not greater than 4%. It should be mentioned, however, that for the compounds MBBA, APAPA5, and MBAPB no proper homeotropic samples could be obtained. For these materials the bend constant K_3 has therefore been determined from computer fits employing expressions (16) and (17); the errors in these K_3 values are estimated to be not greater than 6%. The errors in the ratios of the elastic constants are small (not greater than 4%) since the ratios are not affected by possible systematic errors in d , H , and $\Delta\chi$.

V. DISCUSSION

The molecules of the nematogenic materials studied have the same rigid core and differ only in their end and side groups. These groups show mutually rather great differences in dipole moment, polarizability, dimensions, and flexibility. No evidence has been found of a noticeable influence of differences in polarizability and dipole moment on the elastic behavior. Rather, it seems that the elastic constants, at least of the com-

TABLE IV. Coefficients to calculate the bend elastic constant K_3 according to Eq. (23).

	K_3^0 (10^{-7} dyn)	β	γ
MBBA	31.08	0.9933	0.4924
OHMBBA	27.23	0.9968	0.4470
MBCA	58.14	0.9975	0.4531
APAPA	51.28	0.9966	0.4322
APAPA2	45.42	0.9978	0.4692
APAPA3	55.07	0.9934	0.5155
APAPA4	60.69	0.9910	0.6522
APAPA5	107.37	0.9858	0.7835
APAPA9	66.58	0.9917	0.6715

pounds with a rigid molecular structure, are related to the molecular dimensions. Before we discuss the differences in elasticity between the various compounds in detail, we shall first pay attention to the average elastic constant $\bar{K} = (K_1 + K_2 + K_3)/3$.

A. Relation between $\bar{K}$ and T_c

As pointed out by De Gennes,²⁹ one should expect that the elastic constants are approximately equal to u/r , where u is the orientation dependent part of the energy per molecule in the field of its neighbors and r is an average intermolecular nearest neighbor distance. In molecular statistical theories it is found quite generally that, to a first approximation, u is proportional to $\langle P_2 \rangle^2$ and $k_B T_c$ (see, for instance, Ref. 8), i.e.,

$$\bar{K}(T/T_c = 1.0) \simeq k_B T_c \langle P_2 \rangle_c^2 / r, \quad (24)$$

where $\langle P_2 \rangle_c$ is the order parameter at T_c . To test the validity of this result we calculated the right hand side of Eq. (24) as follows: The values of $\langle P_2 \rangle_c$ were obtained from the measured values of the anisotropy of the diamagnetic susceptibility. For the value of r we have taken the radius of a sphere with a volume equal to that available per molecule:

$$r = (3M/4\pi N_A \rho_{dc})^{1/3}, \quad (25)$$

where M is the molar mass, N_A Avogadro's number,

TABLE III. Coefficients to calculate the twist elastic constant K_2 according to Eq. (23).

	K_2^0 (10^{-7} dyn)	β	γ
MBBA	10.25	0.9973	0.3696
OHMBBA	14.56	0.9962	0.4249
MBCA	11.62	0.9959	0.2925
APAPA	11.99	0.9947	0.3182
APAPA2	11.58	0.9992	0.3166
APAPA3	16.13	0.9911	0.4300
APAPA4	17.81	0.9906	0.4855
APAPA5	19.48	0.9913	0.4821
APAPA9	19.25	0.9955	0.4679

FIG. 8. $K_i/\Delta\chi$ as a function of temperature ($K_3 > K_1 > K_2$). Crosses, MBBA; circles, APAPA; triangles, MBAPB.

TABLE V. K_2/K_1 and K_3/K_1 at $T/T_c = 0.95$.

	K_2/K_1	K_3/K_1		K_2/K_1	K_3/K_1
MBBA	0.63	1.38	APAPA2	0.73	1.84
OHMBBA	0.61	1.07	APAPA3	0.64	1.69
MBCA	0.64	1.97	APAPA4	0.62	1.29
APAPA	0.71	2.15	APAPA5	0.59	1.47
MBAPB	0.73	2.56	APAPA9	0.48	0.96

and ρ_{dc} the density at T_c . Data of $\langle P_2 \rangle_c$ and ρ_{dc} have been published previously.²²

In Fig. 9 we have plotted experimental values of $\bar{K}(1.0)$ versus those calculated from Eq. (24). The trend predicted by this formula is indeed confirmed. Moreover, the calculated values are nearly quantitatively correct, which is gratifying in view of the crudeness of the model used. Since Eq. (23) can be applied only up to $T/T_c \approx 0.995$, the experimental values of $\bar{K}(1.0)$ in Fig. 9 were obtained by extrapolation, based on the experimental finding that $\bar{K}$ is proportional to $\eta^2 \langle P_2 \rangle^2$, as will be shown in Sec. IV C.

B. Rigid molecules

The ratio K_3/K_1 of the compounds with a *rigid* molecular structure, i.e., the materials MBBA, APAPA, and MBAPB, is directly related to the molecular length to width ratio.³⁰ This is illustrated in Fig. 10, where K_3/K_1 ($T/T_c = 0.95$) has been plotted versus the parameter $R = (L - W)/W$, where L and W represent the molecular length and width, respectively. From the values of L and the molecular volumes, which were calculated

FIG. 9. Measured values of the average elastic constant $\bar{K}$ versus those calculated from Eq. (24).

FIG. 10. K_3/K_1 ($T/T_c = 0.95$) versus R , where $R+1$ is the spherocylindrical length to width ratio.

using tabulated bond lengths and "intermolecular" radii,^{22,31} the widths could be calculated readily by assuming that the molecules can be represented by spherocylinders. Also included in Fig. 10 are the data for *p*-azoxyanisole (PAA) measured by De Jeu *et al.*³² Although PAA belongs to a totally different group of compounds, it fits the observed trend quite well.

Obviously, the results obtained for the materials MBBA, APAPA, and MBAPB can not be understood in terms of the calculations of Saupe and Nehring¹⁵ [see Eqs. (9) and (10)]. Instead, the experimental results indicate that we have to rely on models that take account of the characteristic elongated molecular shape. In Sec. II it has been pointed out that, only for the special case of spherocylinders interacting via hard core repulsions (Onsager model), equations have been derived which relate the elastic constants to the molecular dimensions. The results will now be discussed in terms of this specific model, i.e., on the basis of Eqs. (11) and (13).

In Table VI we have collected the experimental data of the reduced elastic constants $K_i/\bar{K}$ as well as the theoretical values derived from formulas (11) and (12), where we used the values of R employed previously in Fig. 10. For the compounds under consideration no values of the parameter $\langle P_4 \rangle$ are known. We have taken $\langle P_4 \rangle / \langle P_2 \rangle$ equal to 0.5; this value is comparable with earlier reported values of this quantity for structurally related materials.³³ Table VI shows that the experimentally observed trends in $K_3/\bar{K}$ and $K_1/\bar{K}$ agree qualitatively with the trends predicted by the theory. The quantitative agreement, however, is poor. This is not surprising, since it is well known that the values of various microscopic properties, predicted by the On-

TABLE VI. Experimental and theoretical values of the quantities $K_i/\bar{K}$ at $T/T_c = 0.95$. The theoretical values were calculated using Eqs. (11) and (13) with $\langle P_4 \rangle / \langle P_2 \rangle = 0.5$.

	Experiment			Theory		
	$K_1/\bar{K}$	$K_2/\bar{K}$	$K_3/\bar{K}$	$K_1/\bar{K}$	$K_2/\bar{K}$	$K_3/\bar{K}$
MBCA	0.83	0.53	1.64	1.06	0.75	1.19
APAPA	0.78	0.55	1.67	1.04	0.67	1.29
MBAPB	0.70	0.51	1.79	1.00	0.55	1.45

sager model, do not agree at all with experimental data. Particularly, rather low values of the packing fraction are predicted. The compounds under consideration, however, are rather densely packed; packing fractions of about 0.64 have been calculated.^{22,24} Merely intuitively, one would expect that the molecular packing has a strong influence on the elastic properties of fluids consisting of elongated particles.

Despite the qualitative agreement between the trend in the values calculated on the basis of the Onsager model and that in the experimental values, it is still impossible to determine to what extent the elastic behavior is governed by excluded volume effects, i.e., by the packing entropy [see Eq. (5)]. This is due to the fact that the contribution of the attractive forces [see Eq. (3)] can not be estimated, since the distribution function $g(\mathbf{r}_{ij}, \Omega_i, \Omega_j)$ for the compounds studied is unknown.

We conclude that for rigid molecules the trends in $K_1/\bar{K}$ and $K_3/\bar{K}$ can be understood within the framework of the Onsager model. Moreover, in contrast to the Saupe-Nehring calculations, the calculations of Priest are successful in predicting that K_2 should be the smallest of the three elastic constants.

C. Temperature dependence

In Fig. 11 we have plotted the quantities $K_1/\bar{K}$ and $\bar{K}/(\eta^2 \langle P_2 \rangle^2)$ versus the reduced temperature T/T_c for the compound APAPA. Assuming again that the molecules can be represented as hard spherocylinders, the quantities Δ and Δ' are positive for the calculated value of R . Since $\langle P_4 \rangle / \langle P_2 \rangle$ is found to decrease with increasing temperature,³³ Eqs. (11) and (13) predict, in agreement with the experimentally found trends, that $K_1/\bar{K}$ and $K_2/\bar{K}$ should increase with increasing temperature whereas $K_3/\bar{K}$ should decrease. Expression (12) predicts that $\bar{K}/(\eta^2 \langle P_2 \rangle^2)$ should be independent of temperature, in reasonable agreement with the dashed curve in Fig. 11.

It should be noted that these findings as such give no

FIG. 11. Temperature dependence of the parameters $K_1/\bar{K}$ and the quantity $\bar{K}/(\eta^2 \langle P_2 \rangle^2)$ for APAPA.

FIG. 12. Elastic constants versus the number of carbon atoms of the alkyl chain for the homologs APAPAm. Circles, K_1 ; triangles, K_2 ; crosses, K_3 .

evidence as to the validity of the Onsager model, since Eq. (11) is capable of predicting the observed temperature dependence for positive values of the parameters Δ and Δ' whether these are given by Eq. (13) or not.

For the other compounds we have observed a temperature dependence similar to that found for APAPA, i.e., an increase of $K_1/\bar{K}$ and a decrease of $K_3/\bar{K}$, i.e., a decrease of K_3/K_1 . However, the temperature dependence of K_3/K_1 decreases if the value of the ratio decreases.²³ The same trend has been reported earlier by De Jeu and Claassen,⁵ who measured two homologous series of azoxy compounds.

D. Molecules with alkyl chains

As shown in Sec. IV B, an increase of the length to width ratio for rigid molecules leads to an increase of K_3/K_1 . Similarly, incorporation of a hydroxy group at an *ortho* position of a benzene ring, which broadens the rigid core, leads to a reduction of K_3/K_1 , as is demonstrated by the results for MBBA and OHMBBA (see Table V).

A totally different trend has been found in the homologous series APAPAm, for which the elastic constants are shown in Fig. 12. Here K_3 decreases with increasing chain length and K_1 increases, i.e., K_3/K_1 decreases as the length of the flexible alkyl chain increases. Superposed on the trends mentioned, an odd-even alternation is observed that can be attributed to the alternation in $\langle P_2 \rangle$.²² The decrease of K_3/K_1 with increasing chain length has also been observed for the alkylcyanobiphenyls by Karat and Madhusudana,⁴ for the dialkoxycyanobiphenyls by De Jeu and Claassen,⁵ and for the alkylcyanophenylcyclohexanes by Schadt, Baur, and Meier.⁶

Whereas K_1 and K_3 depend on the length of the alkyl chain, we have found that K_2 remains practically constant (see Fig. 12). A similar behavior of K_2 has not yet been reported before.

First we shall investigate whether the trend in K_3/K_1 can still be understood somehow within the framework of Priest's calculations for hard spherocylinders. One may question whether this particular model is applicable at

all since the chains are not rigid but flexible, i.e., jumpwise transitions occur continuously between various chain conformations. On the other hand, it should be noted that the lifetime of a particular chain conformation is large compared with the time associated with the rotations around the long molecular axis (10^{-11} s).³⁴ So on a short time scale the chains can be considered as rigid.

We have calculated the root mean square length L_c of the alkyl chain defined by

$$L_c = (\langle \mathbf{L}_{ac} \cdot \mathbf{L}_{ac} \rangle)^{1/2}, \quad (26)$$

where the brackets denote a statistical average over all chain conformations. The vector $\mathbf{L}_{ac}$ which connects the first and last carbon atom of the alkyl chain can be written as

$$\mathbf{L}_{ac} = \sum_{i=1}^m \mathbf{l}_i, \quad (27)$$

where the vectors $\mathbf{l}_i$ denote the individual carbon-carbon bonds. Using Flory's matrix technique,³⁵ we have calculated L_c .²⁴ The assumption was made that the carbon-carbon bonds of the chain can occur only in the energetically favorable *trans* state and the two *gauche* states, i.e., we have applied the *rotational isomeric state* approximation. The effective energy difference E_{st} between the *trans* and *gauche* states has been taken equal to 600 cal/mol. This value has been calculated from experimental data of the entropy change at the nematic-isotropic transition.^{22,24} Knowing the average length L_c of the chain, we have calculated the molecular length L , the volume v_0 ,³¹ the width W , and the parameter $R = (L - W)/W$ assuming a spherocylindrical shape. The results have been listed in Table VII. Also included in this table are the values of L_c for $E_{st} = \infty$ (rigid chain). It is observed that with increasing number of carbon atoms, a considerable shortening of the effective chain length occurs. The width W exceeds the width of the rigid core (≈ 4.83 Å) if the chain consists of more than five carbon atoms. This indicates that, as a result of the flexibility, the chains tend on average more and more towards a spherical shape if the chain length increases. Nevertheless, a decrease of R is not obtained. We must conclude, therefore, that this type of approach based on effective spherocylinders does not allow an explanation of the experimentally observed trends for molecules with flexible hydrocarbon chains.

For a possible explanation one might start from a

TABLE VII. Lengths L_c of the alkyl chains calculated for $E_{st} = \infty$ (a) and $E_{st} = 600$ cal/mole (b). L , W , and v_0 are the lengths, widths, and volumes of the spherocylinders, respectively; $R = (L - W)/W$.

	$L_c(a)$ (Å)	$L_c(b)$ (Å)	v_0 (Å ³)	L (Å)	W (Å)	R
APAPA	1.53	1.53	258	15.7	4.83	2.25
APAPA2	2.53	2.53	275	16.7	4.82	2.46
APAPA3	3.81	3.52	292	17.7	4.81	2.68
APAPA4	5.07	4.39	309	18.6	4.81	2.87
APAPA5	6.34	5.21	326	19.4	4.83	3.02
APAPA9	11.42	7.86	395	22.0	4.97	3.43

FIG. 13. Schematic representation of a "normal" nematic (a) and a nematic in which the molecular positions are locally correlated (b).

suggestion raised by De Jeu⁵ and Karat,⁴ who attributed the decrease of K_3/K_1 with increasing chain length to an increasing degree of short range positional order in a plane perpendicular to the director $\mathbf{n}$. The physical content of this idea is visualized by Fig. 13. Assuming that case (a) corresponds to a "normal" nematic, case (b) shows schematically some short range smectic-like positional order. The difference can equivalently be described in terms of a difference in the pair distribution function $g(\mathbf{r}_{ij}, \Omega_i, \Omega_j)$ [see Eq. (3)]; in case (b) the function g is strongly peaked at the nearest neighbor distance in the plane perpendicular to $\mathbf{n}$.

van der Meer *et al.*³⁶ have made calculations using a lattice model, which makes it possible to simulate the two situations drawn in Fig. 13. These calculations show that K_3/K_1 decreases as the actual situation shifts from case (a) to (b). If it is assumed that the lengthening of the alkyl chains leads to an increase of the positional correlation, this could provide a basis for understanding the experimental trend for K_3/K_1 within homologous series. We note that an increase of the positional correlation in a plane perpendicular to the director is compatible with the increasing tendency to form smectic phases. On the other hand, it should be noted that the members of the series APAPAm only show nematic liquid crystalline behavior, in contrast with the alkylcyanobiphenyls⁴ and azoxybenzenes.⁵

VI. CONCLUSIONS

The measurements of the elastic constants of the Schiff's bases presented in this paper have shown that for compounds with a rigid molecular structure K_3/K_1 increases with increasing molecular length to width ratio. This finding can be understood qualitatively within the framework of the Onsager model, which stresses excluded volume effects. A fuller explanation, however, can only be given if more information becomes available regarding the distribution of the molecular centers of mass.

A decrease of K_3/K_1 with increasing chain length is observed for the series APAPAm, in agreement with results reported for some other homologous series.

In the series APAPAm, K_2 has been found to be independent of the length of the alkyl chain. A similar behavior has not yet been reported before.

The results found for homologous series can not be interpreted, not even qualitatively, in terms of existing models. Complicated as these models sometimes are already, they apparently simplify the real situation too strongly. Especially, it seems necessary to incorporate the effect of the length and the flexibility of the alkyl chains in forthcoming theories.

The suggestion has been raised that the decrease of K_3/K_1 with increasing chain length within homologous series is due to an increasing short range correlation in a plane perpendicular to the director. However, in the absence of detailed information about the positional distribution, it seems somewhat premature to conclude that the decrease of K_3/K_1 is solely due to this effect.

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