

# The elastic constants of nematic liquid crystalline terminally substituted azoxybenzenes

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The elastic constants  $K_{11}$ ,  $K_{22}$ , and  $K_{33}$  of some members of two homologous series of nematic liquid crystals, the  $p,p'$ -di- $n$ -alkyl and  $p,p'$ -di- $n$ -alkoxy azoxybenzenes, are reported. Both  $K_{11}$  and  $K_{33}$  become greater with increasing alkyl chain length, while the ratio  $K_{33}/K_{11}$  decreases along the series. For small alkyl chain length we find  $K_{33} > K_{11}$ , for long chain length  $K_{33} < K_{11}$ , while for intermediate chain length  $K_{33} \approx K_{11}$ . In all cases  $K_{22}$  is the smallest of the three elastic constants, while  $K_{22}/K_{11}$  is independent of temperature. The variation of  $K_{33}/K_{11}$  with alkyl chain length can qualitatively be attributed to changes of correlation lengths parallel and perpendicular to the direction. If the nematic distortion free energy is restricted to terms of the order  $S^2$ , where  $S$  is the order parameter, theory predicts  $K_{33} = K_{11}$ . The experiments indicate that this equality holds approximately in some special cases, but in general higher order terms in  $S$  must be included to obtain a correct expression for the nematic distortion free energy.

## I. INTRODUCTION

In the nematic liquid crystalline phase<sup>1,2</sup> the elongated molecules are, on the average, aligned with their long axis parallel to a preferred direction in space. This direction can be labeled by a unit vector  $\mathbf{n}$ , the director. The molecules translate freely, as in the isotropic phase, and the centers of mass of the molecules are distributed at random. In many practical circumstances constraints are imposed on the orientation of the nematic liquid by the walls of the container, which force  $\mathbf{n}$  to be nonuniform. In the bulk the associated elastic properties of the nematic liquid are determined by three elastic constants (Oseen-Frank constants), corresponding to the restoring forces opposing splays ( $K_{11}$ ), twists ( $K_{22}$ ), and bends ( $K_{33}$ ). The distortion-free energy density is<sup>3,4</sup>

$$F_d = \frac{1}{2} [K_{11}(\nabla \cdot \mathbf{n})^2 + K_{22}(\mathbf{n} \cdot \nabla \times \mathbf{n})^2 + K_{33}(\mathbf{n} \cdot \nabla \mathbf{n})^2]. \quad (1)$$

Much of the interest in liquid crystals is associated with the fact that the orientation of the director can locally be influenced by external stimuli. The elastic constants appear in the description of virtually all these phenomena. So far, however, relatively little attention has been paid to the determination of elastic constants.

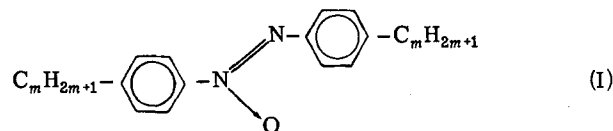
Another reason to measure elastic constants is to investigate eventual relations between these constants, or their ratios, and the molecular structure. Reduced elastic constants have been defined<sup>5</sup>

$$C_{ii} = K_{ii} V^{1/3} / S^2, \quad (2)$$

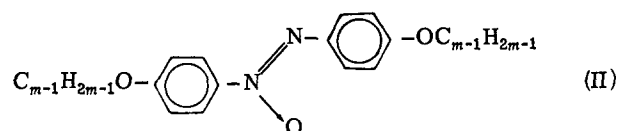
where  $V$  is the molar volume and  $S$  the order parameter that characterizes the orientational order. The  $C_{ii}$  should depend on molecular properties only. Experimental information as to whether this is indeed true is scarce, however. It is well known that the nematic-isotropic (NI) transition temperatures vary regularly with chemical composition. It would be very useful if, for example, a relation between the  $C_{ii}$  and  $T_{NI}$  could be established.

The plan of the paper is as follows. In Sec. II first the theoretical results at present available for the  $C_{ii}$  are summarized. The elastic constants have been mea-

sured by observing the deformation of the director pattern of a uniformly aligned thin nematic slab due to the torque of a variable magnetic field orthogonal to the director (Frederiks transition).<sup>6,7</sup> The theory related to this deformation is summarized in Sec. III, where the experimental methods are also discussed. In Sec. IV we report measurements of the elastic constants, as a function of temperature, of the  $p,p'$ -di- $n$ -alkylazoxybenzenes<sup>8</sup>:



for  $m=3-8$ . This series is compared with the  $p,p'$ -di- $n$ -alkoxyazoxybenzenes<sup>9</sup>:



for  $m=2-9$ . In both series the elastic constants exhibit similar regular trends, which are discussed in Sec. V. It appears that the existing theoretical models for the elastic constants are of limited value for the interpretation of the results. Qualitatively the observed decrease of  $K_{33}/K_{11}$  with alkyl chain length can be attributed to changes in correlation length parallel and perpendicular to the director.

## II. THEORETICAL

First we shall summarize the theoretical situation concerning the dependence of the elastic constants on the order parameter. For simplicity we assume that the molecules composing the nematic liquid crystal are rigid and rodlike in shape. Let  $\mathbf{u}$  be a unit vector along the long molecular axis;  $\mathbf{n}$  is the director. The orientational order in the nematic phase can be described by an order parameter, which is in general a second-rank tensor<sup>1</sup>:

$$S_{\alpha\beta}(\mathbf{r}) = \langle u_\alpha u_\beta - \frac{1}{3} \delta_{\alpha\beta} \rangle \\ = S(n_\alpha n_\beta - \frac{1}{3} \delta_{\alpha\beta}), \quad (3)$$

where the brackets denote a statistical average over the orientations of all molecules in a small but macroscopic volume located at the point  $\mathbf{r}$ . The  $u_\alpha$  are the components of  $\mathbf{u}$  in a laboratory-fixed coordinate system. Choosing  $\mathbf{n}$  along the  $z$  axis only the diagonal elements of  $S_{\alpha\beta}$  are nonzero, with

$$S_{zz} = \frac{2}{3}S, \quad S_{xx} = S_{yy} = -\frac{1}{3}S. \quad (4)$$

The scalar quantity  $S$  is a measure of the degree of alignment of the molecules. If  $f(\theta) \sin\theta d\theta$  is the fraction of molecules whose axes make angles between  $\theta$  and  $\theta + d\theta$  with  $\mathbf{n}$ , we have

$$S = \int_0^\pi (1 - \frac{3}{2} \sin^2\theta) f(\theta) \sin\theta d\theta. \quad (5)$$

In the isotropic phase  $S=0$ , while the other limit  $S=1$  corresponds to the hypothetical case of perfect alignment of all molecules.

In the Landau theory of the nematic phase<sup>1</sup> the free energy density  $F(P, T, S_{\alpha\beta})$  is assumed to be an analytical function of the order parameter tensor  $S_{\alpha\beta}$ . To the extent that  $S_{\alpha\beta}$  is small we can expand the free energy in the various orders of  $S_{\alpha\beta}$ . When the order parameter tensor varies slowly from point to point also terms in the gradients of  $S_{\alpha\beta}$  occur in this expansion. The total free energy density up to the second order in  $S_{\alpha\beta}$  then can be written as<sup>10</sup>

$$F = F_i + \frac{1}{2} A S_{\alpha\beta} S_{\alpha\beta} + \frac{1}{2} L_1 (\nabla_\alpha S_{\beta\gamma}) (\nabla_\alpha S_{\beta\gamma}) + \frac{1}{2} L_2 (\nabla_\alpha S_{\alpha\gamma}) (\nabla_\beta S_{\beta\gamma}), \quad (6)$$

where repeated indices are to be summed and  $F_i$  is the free energy density of the isotropic phase. Only two elastic constants occur, denoted by  $L_1$  and  $L_2$ . In order to relate  $L_1$  and  $L_2$  to the Oseen-Frank elastic constants we can substitute Eq. (3) in Eq. (6). Assuming that the variations of  $S_{\alpha\beta}$  are due to variations of  $\mathbf{n}$  only and that  $S$  is spatially constant, the part of the free energy due to the distortion reduces after some manipulations to<sup>11</sup>

$$F_d = S^2 [(L_1 + \frac{1}{2} L_2) (\nabla \cdot \mathbf{n})^2 \\ + L_1 (\nabla \cdot \nabla \times \mathbf{n})^2 + (L_1 + \frac{1}{2} L_2) (\mathbf{n} \cdot \nabla \mathbf{n})^2]. \quad (7)$$

Comparison with Eq. (1) gives

$$K_{11} = K_{33} = 2S^2 (L_1 + \frac{1}{2} L_2), \\ K_{22} = 2S^2 L_1. \quad (8)$$

Thus, to order  $S^2$ ,  $K_{11} = K_{33}$  and all three elastic constants vary with temperature as  $S^2$ . Priest<sup>12</sup> also arrived at this result but in a rather different way by using an expansion of the intermolecular potential in spherical harmonics. For the special case of London-van der Waals or dispersion forces Nehring and Saupe derived (up to the order  $S^2$ )<sup>13</sup>

$$K_{11} : K_{22} : K_{33} = 5 : 11 : 5, \quad (9)$$

in agreement with the general result  $K_{33} = K_{11}$ . Apart from the temperature dependence of the elastic constants via  $S$ , there is also a dependence on the density. If the intermolecular potential varies with  $R^{-6}$  (as in the case

of dispersion forces), according to Saupe<sup>5</sup> the volume dependence of the distortion energy is given by  $R^{-4} = V^{-4/3}$ , and that of the distortion energy per unit volume by  $V^{-7/3}$ . For that reason the reduced elastic constants were defined as in Eq. (2). If the nematic phase cannot be described by an interaction varying as  $R^{-6}$ , a different density dependence of the  $C_{ii}$  will be required.

According to Priest, deviations from the equality  $K_{11} = K_{33}$  are related in a simple way to the ratio  $\bar{P}_4/\bar{P}_2$ , where  $\bar{P}_2 \equiv S$  and  $\bar{P}_4$  represents the average value of the fourth Legendre polynomial:

$$\bar{P}_4 = \frac{1}{8} \langle 35 \cos^4\theta - 30 \cos^2\theta + 3 \rangle. \quad (10)$$

In fact, if  $\bar{K} = \frac{1}{3}(K_{11} + K_{22} + K_{33})$  his result is<sup>12</sup>

$$K_{11}/\bar{K} = 1 + \Delta - 3\Delta' (\bar{P}_4/\bar{P}_2), \\ K_{22}/\bar{K} = 1 - 2\Delta - \Delta' (\bar{P}_4/\bar{P}_2), \\ K_{33}/\bar{K} = 1 + \Delta + 4\Delta' (\bar{P}_4/\bar{P}_2). \quad (11)$$

The quantities  $\Delta$  and  $\Delta'$  are constants depending on molecular properties. Attempts have been made to calculate  $\Delta$  and  $\Delta'$  using a model of rodlike molecules interacting via a hard-core repulsion.<sup>12,14</sup> Experimental tests on Eq. (11) have not yet been reported.

Various authors have tried to obtain expressions for  $K_{33}/K_{11}$  in a semiempirical way.<sup>15-17</sup> Let us assume that the orientation-dependent part of the interaction energy between two molecules 1 and 2 is given by

$$V(r_{12}) P_2(\Omega_1, \Omega_2), \quad (12)$$

where  $\Omega_1$  stands for the set of Euler angles describing the orientation of molecule 1. Then the reduced elastic constants can be written as<sup>17</sup>

$$C_{ii} = -\frac{3}{2} V^4/3 \int g(\mathbf{r}) V(\mathbf{r}) r_i^2 d\tau, \\ r_i = x, y, z \quad \text{for } i=1, 2, 3. \quad (13)$$

Here  $g(r)$  represents the two-particle correlation function. Usually it is assumed that there is cylindrical symmetry around the  $z$  axis. If furthermore the structure of the integrand in Eq. (13) is such that the factor  $r_i^2$  can be taken apart, we obtain

$$C_{33}/C_{11} = K_{33}/K_{11} = Z^2/X^2. \quad (14)$$

$Z$  and  $X=Y$  are two characteristic distances that have been related to the molecular dimensions or to a short-range lattice. The assumption of cylindrical symmetry blurs the distinction between  $x$  and  $y$ , which has been interpreted as  $K_{22}$  being equal to  $K_{11}$  in this approximation. However, in order to make predictions about  $K_{22}$  a unique axis perpendicular to the director has first to be defined along which the twist distortion is to be found. As such an axis cannot be defined without specifying the factor  $g(\mathbf{r})V(\mathbf{r})$ , it seems more appropriate to state that this type of model is not capable of predicting  $K_{22}$ , and only the ratio  $K_{33}/K_{11}$  can be obtained.

### III. EXPERIMENTAL

The elastic constants have been measured by observing the deformation of the director pattern of a uniformly aligned thin nematic slab under the torque of a vari-

able orthogonal magnetic field. For fixed boundary conditions of  $\mathbf{n}$  the deformation starts at a critical field  $H_c$  determined by<sup>7,18</sup>:

$$\Delta\chi H_c^2 d^2 = K_{ii} \pi^2, \quad i=1, 2, 3, \quad (15)$$

where  $\Delta\chi$  is the anisotropy of the magnetic susceptibility and  $d$  the sample thickness. If the boundary conditions of  $\mathbf{n}$  and the direction of  $\mathbf{H}$  are properly chosen,  $K_{ii}$  can be either the splay, the twist or the bend elastic constant. In the splay configuration the deformation above  $H_c$  is determined by both  $K_{11}$  and  $K_{33}/K_{11}$ , in the bend configuration by  $K_{33}$  and  $K_{33}/K_{11}$ .

Saupe has shown that in the splay and bend configurations the deformation of the director pattern can conveniently be measured by the change in retardation  $\delta$  of components of polarized light propagating normal to the nematic layer.<sup>7</sup> Consider the case of a magnetic field perpendicular to a uniform planar layer (splay configuration). The deformation is described by  $\sin\psi \approx \sin\phi/\sin\phi_0$ ,  $\phi$  being the angle between the director and the substrate and  $\phi_0$  ( $0 \leq \phi_0 \leq \pi/2$ ) its maximum value at  $d/2$ . Then the interrelation between the deformation, the magnetic field, the change in retardation and material parameters can be expressed as<sup>7</sup>

$$H/H_c = (2/\pi) \Pi(\alpha^2, k)/(1 + \kappa \sin^2\phi_0)^{1/2}, \quad (16)$$

$$\delta = n_e d \left[ 1 - \frac{2}{\pi} \frac{H_c}{H} \times \int_0^{\pi/2} \left( \frac{1 + \kappa \sin^2\phi_0 \sin^2\psi}{(1 - \sin^2\phi_0 \sin^2\psi)(1 + \nu \sin^2\phi_0 \sin^2\psi)} \right)^{1/2} d\psi \right]. \quad (17)$$

In these equations  $\kappa \equiv (K_{33} - K_{11})/K_{11}$ ,  $\alpha^2 \equiv \kappa \sin^2\phi_0/(1 + \kappa \sin^2\phi_0)$ ,  $k^2 \equiv (1 + \kappa) \sin^2\phi_0/(1 + \kappa \sin^2\phi_0)$ ,  $\nu \equiv (n_e^2 - n_o^2)/n_o^2$ ,  $n_o$  and  $n_e$  represent the ordinary and the extraordinary refractive index, and  $\Pi(\alpha^2, k)$  is the complete elliptic integral of the third kind. With the known values of  $n_o$  and  $n_e$ <sup>19</sup> a nonlinear least-squares procedure has been used to fit the experimental curve for  $\delta$  vs  $H$  to the theory,<sup>20</sup> resulting in values for the two parameters  $H_c$  and  $K_{33}/K_{11}$ . Since the thickness of the sample and  $\Delta\chi$  are known,<sup>21</sup>  $H_c$  is determined by  $K_{11}$ . Hence both  $K_{33}$  and  $K_{11}$  can be obtained in this way. In the next section we shall compare the results for  $K_{33}$  with those obtained directly from  $H_c$  in the bend configuration (magnetic field perpendicular to the director in homeotropic samples).

In the configuration used to determine  $K_{22}$  the deformation of the director has no influence on the retardation of light propagating normal to the layer. In order to detect the deformation one has to use light incident at a relatively large angle with the normal.<sup>22</sup> In practice this is fairly complicated if the sample is to be thermostated. Therefore we used an over  $\pi/2$  twisted planar layer in combination with a field perpendicular to the layer, for which the threshold is given by<sup>23</sup>

$$\Delta\chi H_c^2 d^2 = (K_{11} + \frac{1}{4}K_{33} - \frac{1}{2}K_{22})\pi^2. \quad (18)$$

As  $K_{11}$  and  $K_{33}$  are known it is thus possible to calculate  $K_{22}$ .

The experimental setup is described in detail in Ref. 24, where it has been shown that the application of Eqs.

(15) and (18) leads in practice to various complications. It will suffice here to recall that the accuracy with which  $\mathbf{H}$  is orthogonal to  $\mathbf{n}$  is very important to prevent a rounding off of the curve of  $\delta$  vs  $H$  near  $H_c$  (compare Refs. 25 and 26). The main uncertainty, however, lies in the surface treatment needed to obtain a sample with a uniform director pattern. The theory is only valid for strong anchoring of the director, which is difficult to realize in practice. To obtain uniform planar samples we used the classical rubbing technique, and also added the surfactant  $\text{CH}_3(\text{CH}_2)_n(\text{OCH}_2\text{CH}_2)_m\text{OH}$  ( $n \approx 15$ ,  $m \approx 20$ , cremophor O, BASF). Alternatively, the substrates were coated with a polymer film of  $(-\text{CH}_2-\text{Ph}-\text{CH}_2)_n$ , poly-*p*-xylylene, before rubbing gently. For the compounds of Series I both techniques were found to give the same threshold field, and we can be fairly confident that strong anchoring of the director does in fact occur.<sup>24</sup> For Series II only the second method was used because at the relatively high temperatures of the nematic phases of this series the cremophor O evidently did not stick to the substrates. It should be emphasized that both errors ( $\mathbf{H}$  not orthogonal to  $\mathbf{n}$ , weak anchoring) lead to apparent values of  $H_c$  that are lower than the real threshold. Hence if  $K_{ii}$  is directly proportional to  $H_c$  [Eq. (15)] a high value of a specific elastic constant is more trustworthy than a lower one.

The transmission of a uniform planar layer between crossed polarizers shows as a function of the magnetic field a series of maxima and minima, starting at the threshold field. From the positions of the maxima and minima a curve for  $\delta$  vs  $H$  can be derived. Examples of these curves can be found in Ref. 24. In fitting the experimental curve to the theory we used only about six maxima and minima, say up to  $1.1 H_c$ , because we could not be sure that the anchoring would still be strong at fields appreciably above  $H_c$ . Hence one cannot assume that the experimental curve necessarily follows the theory. Restricting the number of points has the further advantage of avoiding the strongly curved part of the curve of  $\delta$  vs  $H$ , which depends sensitively on the accuracy with which  $\Delta n = n_e - n_o$  is known.

In the case of homeotropic textures it is much more difficult to obtain strong anchoring. Moreover, the situation will vary from compound to compound because in general different end chains are involved in the interaction at the substrate. In our situation various methods were applied:

(A) Substrates were coated with 1-dodecanol by heating them in 1-dodecanol at  $200^\circ\text{C}$  for 30 min and degreasing them afterwards. For *p*-azoxyanisole (PAA, Series II,  $m=2$ ) high thresholds were obtained with this method, probably corresponding to a situation close to strong anchoring.<sup>24</sup>

(B) As (A), but with the addition of 0.1% (by weight) cetyltrimethylammoniumbromide (CTAB) to the liquid crystal.<sup>26</sup>

(C) Substrates were coated with CTAB by dipping them in a 400 ppm solution of CTAB in water.<sup>27</sup>

(D) Substrates were coated with a perfluorosilane,

TABLE I. Splay and bend elastic constants of the members of Series I.

$m=3$			$m=4$			$m=5$			$m=6$			$m=7$			$m=8$		
$t$ (°C)	$K_{11}/\Delta\chi$ (dyne)	$K_{33}/K_{11}$	$t$ (°C)	$K_{11}/\Delta\chi$ (dyne)	$K_{33}/K_{11}$	$t$ (°C)	$K_{11}/\Delta\chi$ (dyne)	$K_{33}/K_{11}$	$t$ (°C)	$K_{11}/\Delta\chi$ (dyne)	$K_{33}/K_{11}$	$t$ (°C)	$K_{11}/\Delta\chi$ (dyne)	$K_{33}/K_{11}$	$t$ (°C)	$K_{11}/\Delta\chi$ (dyne)	$K_{33}/K_{11}$
39.6	7.62	1.37	17.0	5.54	0.98	25.1	15.5	0.75	21.1	18.6	0.61	53.9	24.6	2.13	64.5	14.5	0.59
44.7	7.15	1.35	18.0	5.43	0.98	30.2	14.5	0.82	23.2	16.8	0.57	54.1	24.4	1.68	64.7	13.5	0.55
49.7	6.54	1.32	21.0	5.09	0.98	35.2	13.6	0.83	25.7	15.8	0.55	54.7	22.4	0.85	64.9	12.9	0.56
53.7	6.02	1.28	23.9	4.79	0.98	40.3	12.6	0.84	30.3	14.0	0.55	55.7	20.3	0.72	65.1	12.3	0.53
56.8	5.44	1.25	25.1	4.65	0.98	45.3	11.6	0.85	35.4	12.1	0.65	56.7	19.1	0.65	65.3	11.5	0.58
57.8	5.00	1.29	27.1	4.37	0.98	50.4	10.5	0.91	39.5	10.8	0.69	58.8	17.0	0.69	65.5	11.0	0.55
58.8	4.83	1.22	29.3	3.89	0.98	54.4	9.77	0.90	43.5	9.55	0.74	60.8	15.1	0.71	65.9	10.0	0.56
59.8	4.39	1.14	30.6	3.49	0.97	57.5	8.97	0.87	46.6	8.61	0.77	62.8	13.5	0.72	66.2	9.28	0.54
60.1	4.10	...	31.2	3.10	1.00	60.5	8.13	0.91	49.6	7.52	0.82	64.8	11.8	0.75	66.5	8.24	...
60.4	NI		31.9	NI		62.5	7.56	0.96	51.6	6.52	0.86	66.9	10.5	0.74	66.7	NI	
						64.5	6.75	0.95	52.6	5.78	0.91	67.9	9.52	0.80			
						66.6	5.43	0.98	53.6	5.03	0.94	68.9	8.75	0.76			
						67.5	NI		54.2	NI		69.9	7.17	0.82			
												70.6	NI				

Si(OH)<sub>3</sub>(CH<sub>2</sub>)<sub>3</sub>(NH)(CO)C<sub>8</sub>F<sub>17</sub>, by dipping them in a 400 ppm solution in dichloroethane, drying, and polymerizing.

Unfortunately, each of these treatments worked only for a few compounds. In fact we did not succeed at all in obtaining homeotropic samples for the compounds of Series II for  $m > 2$ . The results are discussed in the next section.

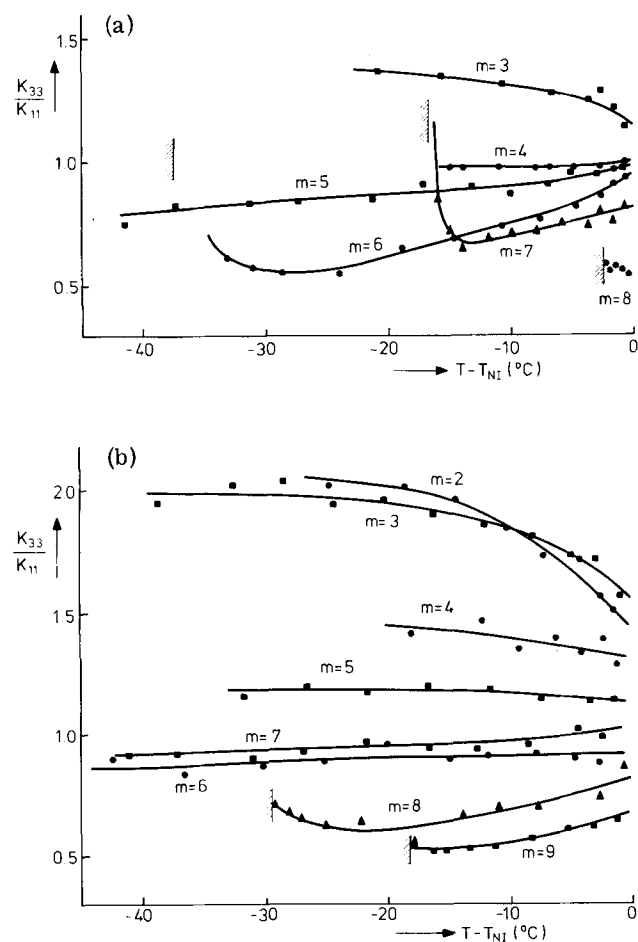


FIG. 1. Ratio of bend and splay elastic constant for the nematic phase of compounds of Series I (a) and Series II (b). The shaded regions indicate a smectic phase.

#### IV. RESULTS

We start with the results obtained from uniform planar layers. Tables I and II give the values of  $K_{11}/\Delta\chi$  for Series I and II, respectively, as derived from  $H_c$  [Eq. (15)]. In addition, the values for  $K_{33}/K_{11}$  are included, obtained from a fitting of the  $\delta$  vs  $H$  curve to the theory, using the values of the refractive indices given in Ref. 19. These ratios are shown in Fig. 1. The accuracy of  $K_{11}/\Delta\chi$  and  $K_{33}/K_{11}$  is estimated to be of the order of 3% and 5%, respectively. The results for Series II are at variance with those for the same compounds by Gruler,<sup>25</sup> who has in general lower values of  $K_{11}/\Delta\chi$  and higher values of the ratio  $K_{33}/K_{11}$ . This is exactly what one would expect in the case of weak anchoring. With increasing  $m$  the variation of  $K_{33}/K_{11}$  remains essentially the same.

Homeotropic samples presented considerable problems. In Fig. 2 the results for  $K_{33}/\Delta\chi$  for DIBAB (Series I,  $m=4$ ) as obtained from  $H_c$  are compared for various surface treatments. In this particular favorable

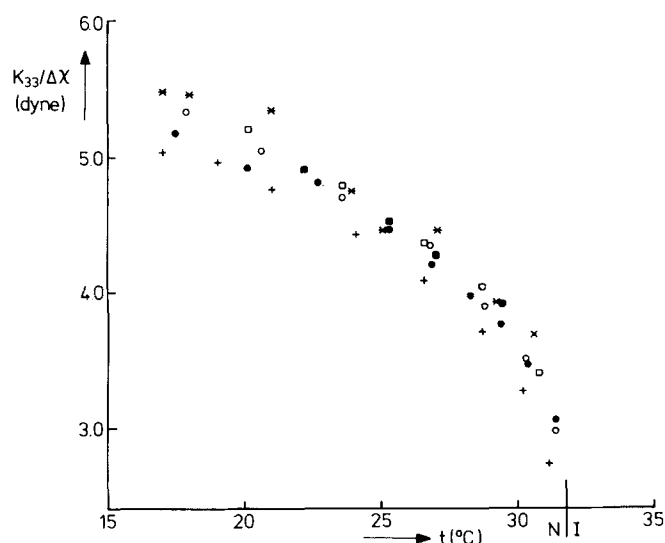


FIG. 2. Bend elastic constants of DIBAB (Series I,  $m=4$ ) from the threshold field of homeotropic samples with different surface treatments:  $\bullet$ , treatment (A) (see text);  $+$ , treatment (B);  $\square$ , treatment (C);  $\circ$ , treatment (D);  $*$ , from ratio  $K_{33}/K_{11}$  and value of  $K_{11}/\Delta\chi$  as obtained from uniform planar samples.

case all four methods induced homeotropic textures and the differences between the thresholds are not large. Method (B) evidently gives a weaker anchoring and thus lower values for  $K_{33}/\Delta\chi$  than the other methods, while Method (A) gives at low temperatures somewhat lower values. Furthermore, for compound (I,  $m=6$ ) treatment (C) led to considerably lower values for  $K_{33}/\Delta\chi$  than (D), in contrast with the situation in Fig. 2. This leaves only (D) as a possible reliable method. However, this treatment induced homeotropic textures only for two compounds (I,  $m=4$  and  $m=6$ ). In all cases where a comparison with other results was possible, the values for  $K_{33}/\Delta\chi$  obtained via the ratio  $K_{33}/K_{11}$  from uniform planar samples are among the highest and are thus the "best" values. Therefore we decided to confine ourselves to these latter data in all the cases where treatment (D) did not work, in spite of their somewhat greater scatter compared with the other results.

In order to calculate the reduced elastic constants we assume that in the nematic phase the molecules can be considered to be effectively axially symmetric, and use<sup>28</sup>

$$S = \frac{\chi_{||}^M - \chi_{\perp}^M}{\chi_{||}^M + \chi_{\perp}^M} = \frac{\Delta\chi^M}{\chi_a^M} \quad (19)$$

In this equation  $\chi^M$  is the molar susceptibility, related to the volume susceptibility  $\chi$  by  $\chi^M = \chi V$  (in  $\text{cm}^3/\text{mol}$ ). Furthermore,  $\chi_{||}^M$  and  $\chi_{\perp}^M$  are the longitudinal and transverse molar susceptibility of a perfectly ordered nematic sample ( $S=1$ ). In principle, information about  $\chi_a^M$  can be obtained from measurements of the susceptibilities of a solid single crystal. The quantity that is usually determined experimentally is the mass susceptibility  $\chi^e$ , given by  $\chi^e = \chi/\rho = \chi^M/M$  (in  $\text{cm}^3/\text{g}$ ), where  $\rho = M/V$  is the density and  $M$  the mass number. Equation (2) then can be rewritten in the form

$$C_{ii} = \frac{K_{ii}}{\Delta\chi} \frac{V^{4/3}}{M} \frac{(\chi_a^M)^2}{\Delta\chi^e} \quad (20)$$

Values for  $K_{ii}/\Delta\chi$  are taken from Tables I and II,  $\Delta\chi^e$  and  $V$  from Ref. 21. For  $\chi_a^M$  we use the same value for all the members of a particular series. For Series I we take the value calculated from the contribution of the two benzene rings only ( $59.7 \times 10^{-6} \text{ cm}^3/\text{mol}$ ) and for Series II the experimental value of PAA ( $62.4 \times 10^{-6} \text{ cm}^3/\text{mol}$ ),<sup>29</sup> which is somewhat larger. Neglecting any contribution from the paraffinic chains to  $\chi_a^M$  probably leads to an underestimation of  $\chi_a^M$  for the higher members of the series. However, the associated error is not expected to be more than a few percent.<sup>30</sup> The results for  $C_{11}$  of Series I and II are given in Fig. 3, and for  $C_{33}$  in Fig. 4.

Finally, we used twisted planar nematic layers to determine  $K_{22}/\Delta\chi = (K_{11} + \frac{1}{2}K_{33} - \frac{1}{2}K_{22})/\Delta\chi$  [see Eq. (18)]. In Table III these values are given for the compounds of Series I, together with the calculated values of  $K_{22}/\Delta\chi$ . The resulting values of  $C_{22}$  are displayed in Fig. 5. Because of the relatively large errors (15%–20%) associated with this indirect method of obtaining  $K_{22}$ , the experiments were not extended to Series II.

TABLE II. Splay and bend elastic constants of the members of Series II.

t (°C)	m=2		m=3		m=4		m=5		m=6		m=7		m=8		m=9		
	$K_{11}/\Delta\chi$ (dyne)	$K_{33}/K_{11}$	t (°C)	$K_{11}/\Delta\chi$ (dyne)	$K_{33}/K_{11}$	t (°C)	$K_{11}/\Delta\chi$ (dyne)	$K_{33}/K_{11}$	t (°C)	$K_{11}/\Delta\chi$ (dyne)	$K_{33}/K_{11}$	t (°C)	$K_{11}/\Delta\chi$ (dyne)	$K_{33}/K_{11}$	t (°C)	$K_{11}/\Delta\chi$ (dyne)	$K_{33}/K_{11}$
110.2	5.62	2.02	129.1	13.0	1.95	110.4	8.57	1.46	99.2	17.4	...	81.0	0.90	0.90	81.0	32.5	0.95
116.4	5.40	2.02	135.2	12.1	2.02	113.4	8.13	1.35	104.2	16.4	1.16	87.1	0.84	0.84	87.1	28.4	0.92
120.5	5.19	1.96	139.2	11.6	2.04	116.4	7.52	1.39	109.2	15.2	1.20	91.6	0.87	0.87	92.2	25.0	0.92
124.6	4.99	1.85	143.3	10.9	1.94	118.4	7.07	1.33	114.2	14.2	1.18	96.7	0.89	0.89	97.3	22.7	0.90
127.7	4.74	1.73	147.4	10.3	1.96	120.4	6.50	1.39	119.3	12.9	1.20	101.8	0.96	0.96	102.4	20.0	0.93
130.7	4.50	1.71	151.5	9.68	1.90	121.4	5.87	1.29	124.3	11.7	1.19	106.9	0.90	0.90	107.5	17.7	0.97
132.4	4.09	1.56	155.6	8.99	1.86	122.6	NI	128.4	10.5	1.15	109.9	0.91	0.91	112.6	15.5	0.95	
133.4	3.87	1.51	159.6	8.21	1.81	132.4	9.05	1.14	114.0	9.58	0.92	116.7	0.92	0.92	116.7	13.8	0.96
134.9	NI	1.51	162.7	7.54	1.73	134.4	7.55	1.14	117.1	8.70	0.90	120.8	0.90	0.90	120.8	11.9	0.94
			164.7	7.05	1.72	135.9	NI	119.1	7.66	0.88	124.9	9.32	1.02	116.2	15.2	0.70	
			166.7	6.25	1.57			120.6	6.77	...	127.0	8.84	0.99	121.3	11.2	0.74	
			167.7	NI				121.8	NI	129.3	NI	129.3	NI	123.3	8.7	0.86	
															123.9	NI	

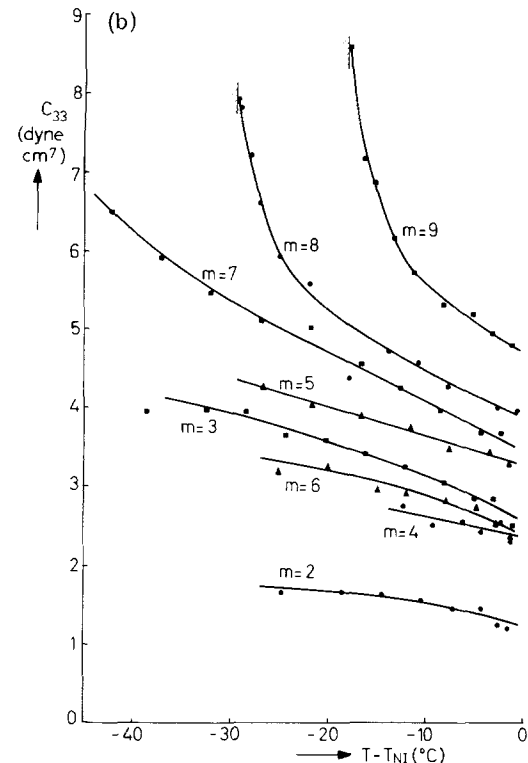
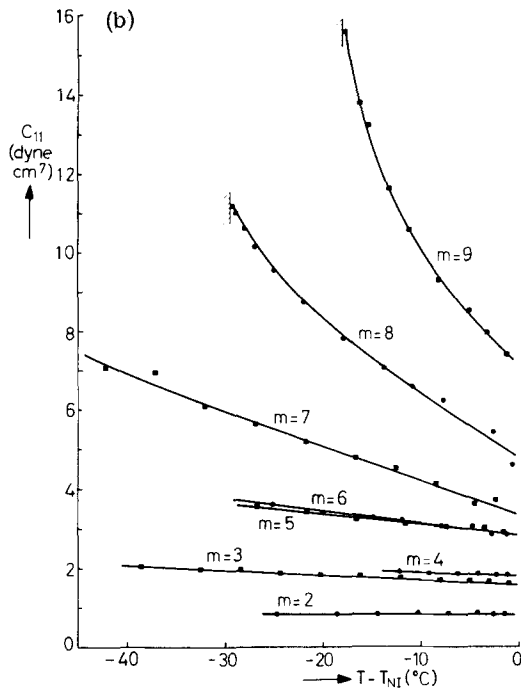
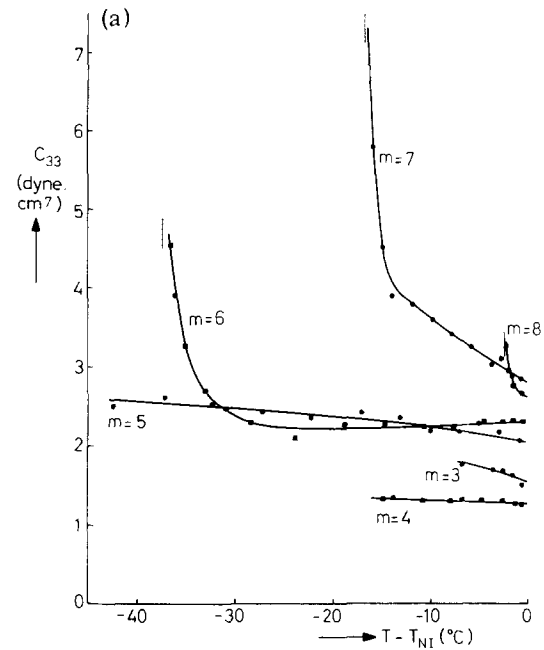
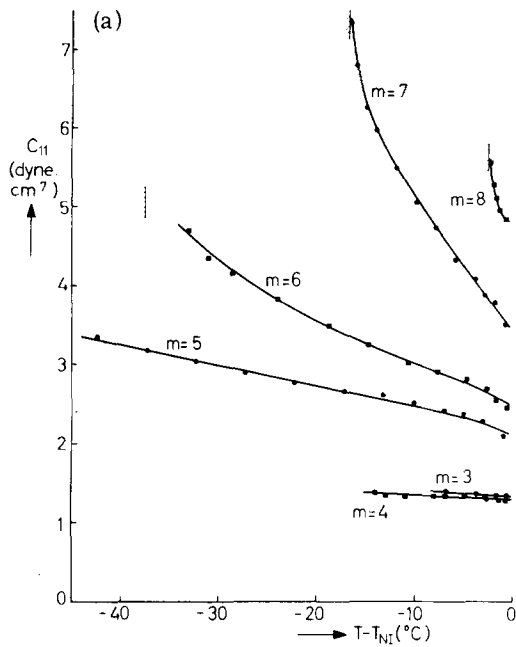


FIG. 3. Reduced splay elastic constants for the compounds of Series I (a) and series II (b).

FIG. 4. Reduced bend elastic constants for the compounds of Series I (a) and Series II (b).

## V. DISCUSSION

First we shall consider the results for  $K_{33}/K_{11}$  (see Fig. 1). Disregarding the pretransitional effects near the nematic-smectic phase transitions for a moment, we note that the results are very similar for both series. For small  $m$  we have  $K_{33} > K_{11}$ , while  $K_{33}/K_{11}$  decreases with increasing  $m$ , leading to  $K_{33} < K_{11}$  for large  $m$ . Around  $m = 4$  and  $5$  approximately  $K_{33} \approx K_{11}$  at all temperatures in the nematic phase. In general the ratio  $K_{33}/K_{11}$  is certainly not equal to unity at all temperatures. Hence we conclude that terms in the free energy of higher order than  $S^2$  are necessary for a theoretical descrip-

tion of the elasticity of nematic liquid crystals. With increasing temperature  $S$  decreases, and the errors due to the disregarding of higher order terms become smaller. Indeed, the temperature dependence of  $K_{33}/K_{11}$  is such that with increasing temperature the values of  $K_{33}$  and  $K_{11}$  approach each other.

It would be interesting to test whether the differences between  $K_{33}$  and  $K_{11}$  can be accounted for by Eq. (11). Unfortunately, for the present compounds no information

TABLE III. Twist elastic constants of the members of series I.

m=3			m=4			m=5			m=6			m=7			m=8		
t (°C)	$K_{\text{eff}}/\Delta\lambda$ (dyne)	$K_{22}/\Delta\lambda$ (dyne)	t (°C)	$K_{\text{eff}}/\Delta\lambda$ (dyne)	$K_{22}/\Delta\lambda$ (dyne)	t (°C)	$K_{\text{eff}}/\Delta\lambda$ (dyne)	$K_{22}/\Delta\lambda$ (dyne)	t (°C)	$K_{\text{eff}}/\Delta\lambda$ (dyne)	$K_{22}/\Delta\lambda$ (dyne)	t (°C)	$K_{\text{eff}}/\Delta\lambda$ (dyne)	$K_{22}/\Delta\lambda$ (dyne)	t (°C)	$K_{\text{eff}}/\Delta\lambda$ (dyne)	$K_{22}/\Delta\lambda$ (dyne)
46.7	6.41	5.62	17.0	5.19	3.41	25.1	14.1	8.59	21.1	16.5	2.49	54.0	27.4	17.2	64.5	13.4	6.22
49.7	5.94	5.53	18.0	5.10	3.32	30.2	13.6	8.05	23.2	15.0	2.17	54.3	25.3	13.1	64.7	12.4	5.70
53.7	5.48	4.95	19.5	5.00	3.15	35.2	12.7	7.81	26.2	13.7	2.15	54.6	23.5	9.78	65.0	11.2	6.30
56.8	4.76	4.79	21.0	4.80	3.07	40.3	11.8	7.21	30.3	12.0	2.21	54.8	22.7	8.00	65.2	10.6	5.60
58.8	4.22	4.20	23.7	4.54	2.92	45.3	10.9	6.72	35.4	10.6	1.99	55.3	21.6	6.67	65.4	10.3	5.05
59.8	3.74	3.83	26.9	4.10	2.76	50.4	10.0	5.75	39.5	9.30	2.05	56.4	19.6	6.75	65.6	10.0	4.42
			29.2	3.59	2.56	54.4	9.30	5.38	43.5	8.20	1.97	57.4	18.2	6.56	65.8	9.40	4.62
			30.4	3.23	2.37	57.5	8.44	5.24	46.6	7.44	1.91	59.4	16.2	6.13	66.3	7.64	
			31.2	2.80	2.15	60.5	7.66	4.79	49.6	6.44	1.94	61.4	14.6	5.28			
						62.5	7.13	4.45	51.6	5.61	1.90	63.4	12.9	5.07			
						64.5	6.41	3.93	52.6	4.93	1.90	65.5	11.2	4.62			
						66.5	5.31	2.93	53.6	4.26	1.88	67.5	9.80	4.21			
												69.5	7.60	3.90			
												70.1	6.70	3.21			

on  $\bar{P}_4$  is available. However, Eq. (11) can be tested in the case of *N*-(*p*-methoxybenzylidene)-*p'*-*n*-butylaniline, MBBA. For this compound  $K_{33}/K_{11}$  varies from 1.3 near the melting point to about 1.2 close to  $T_{\text{NI}}$ .<sup>24</sup> However,  $\bar{P}_4/\bar{P}_2$  varies over the same temperature region from about 0.4 to 0.<sup>31</sup> Hence, because of the strong variation of  $P_4$  with temperature, substitution of these values in Eq. (11) cannot lead to constant values for  $\Delta$  and  $\Delta'$ .

Next we come to the individual  $C_{it}$ . From Figs. 3–5 we see that for small  $m$  indeed a reduced elastic constant can be given that is independent of temperature. For larger  $m$  the  $C_{it}$  have a considerable temperature dependence and increase with decreasing temperature. In this situation the concept of a reduced elastic constant as defined in Eq. (2) is not meaningful anymore. In all cases the  $C_{it}$  tend to increase with increasing  $m$  (increasing chain length) while there is some alternation, which is particular strong for  $C_{33}$ . Although this alternation of the  $C_{it}$  parallels the well-known alternation of  $T_{\text{NI}}$ , there is no direct proportionality, as has been suggested in the literature.<sup>16</sup> The decrease of  $K_{33}/K_{11}$  with increasing  $m$  is due to the fact that the increase of  $C_{11}$  with  $m$  is stronger than that of  $C_{33}$ .

In all cases  $C_{22}$  is the smallest of the three elastic constants, in contrast to the theoretical result of Nehring and Saupe [Eq. (9)]. The ratio  $K_{22}/K_{11}$  is approximately constant for the lower members of Series I that do not have a smectic phase. Using results from Ref. 24 we calculated that for PAA and MBBA, to a good approximation,  $K_{22}/K_{11}$  is independent of temperature too.

Simple rationalizations of the results for the  $C_{it}$  are not available. One could try to correlate  $C_{11}$  and  $C_{33}$  with characteristic distances  $X$  and  $Z$ <sup>15,16</sup> [see Eq. (14)]. In that case it is clear that the ratio  $Z/X$  cannot be related in a simple way to the length/width ratio of the molecules, as this would lead to an increase of  $K_{33}/K_{11}$  with increasing  $m$ , contrary to the experimental results. A better alternative would be to interpret  $X$  and  $Z$  as effective correlation lengths in the directions perpendicular and parallel to the director, respectively. An estimate of the ratio  $Z/X$  in this interpretation can be obtained from measurements of the anisotropy of correlation lengths in the isotropic phase just above  $T_{\text{NI}}$ . Re-

cently this ratio has been measured to be 1.15 for MBBA,<sup>32</sup> while for a similar compound with longer alkyl chains, having a smectic phase that clears directly into the isotropic liquid, a value much smaller than one was found. Both the ratio  $K_{33}/K_{11}$  and the shape of MBBA are very similar to that of the present compounds in case of small  $m$ . Hence it seems plausible to assume that in our cases the ratio  $Z/X$  is also somewhat larger than one for small  $m$  and decreases with increasing chain length. This is mainly due to an increased correlation in the  $x$  direction with increasing  $m$ , related to the tendency to form smectic phases. When Eq. (14) is used this effect can account at least qualitatively for the decreases of  $K_{33}/K_{11}$  with increasing  $m$  as observed.

For series I we find for  $m \geq 6$  a nematic-smectic A phase transition, while for Series II there is a nematic-smectic C phase transition for  $m \geq 7$ . In the smectic phases twist and bend deformations are practically forbidden because they require a variation of the layer thickness.<sup>33</sup> In the smectic C phase a splay deformation is difficult too. Hence pretransitional increases of the elastic constants can be expected if a nematic-smectic phase transition is approached. These effects are particularly pronounced for  $C_{22}$  and  $C_{33}$  of Series I,  $m = 6$

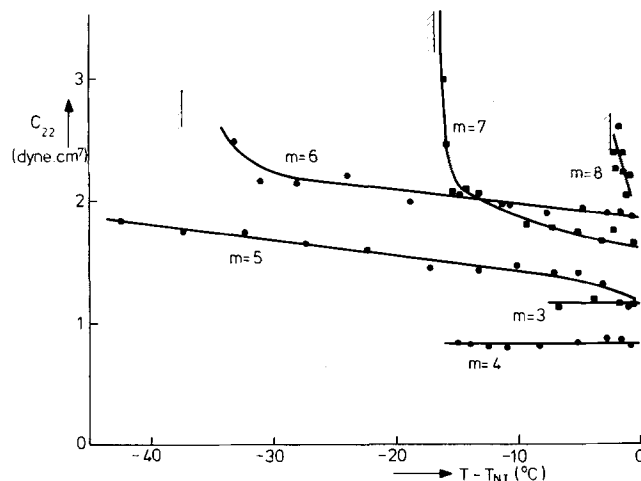


FIG. 5. Reduced twist elastic constants for the compounds of Series I.

and  $m = 7$  (see Figs. 4 and 5). In these cases the transition heat is very small and the transition is practically second order. However, as  $C_{11}$  also shows a pretransitional increase, although less pronounced (see Fig. 12), it seems difficult to obtain from the data reliable values of the critical exponents.

The observed systematic trend in the values of the elastic constants of both homologous series, and especially in the ratio  $K_{33}/K_{11}$ , has some important consequences.

(i) In theoretical models for various effects in nematic liquid crystals the assumption  $K_{11} = K_{33}$  is often made because it may simplify the calculations considerably. In order to compare the results with experiments it is necessary to have model compounds where this condition is fulfilled. Therefore it is of great practical importance that in  $p, p'$ -di- $n$ -butylazoxybenzene (Series I,  $m = 4$ )  $K_{11}$  equals  $K_{33}$  over the whole nematic temperature range. Conveniently, this compound is nematic around room temperature.

(ii) Various electro-optic effects that are used in liquid crystal displays are related to the Frederiks transitions discussed here. The multiplexibility of a particular effect depends on the threshold voltage and the saturation voltage.<sup>34</sup> The latter depends on the voltage dependence of the deformation of the director above the threshold and thus on  $K_{33}/K_{11}$ . From our results we see that compounds with long alkyl chains have a relatively high value of  $K_{11}$  and a low value of  $K_{33}/K_{11}$ . For a uniform planar sample this leads to a high threshold voltage in combination with a small ratio of saturation voltage to threshold voltage, which in principle should extend the possibility of multiplexing.

#### IV. CONCLUSIONS

Thanks to a precise consideration of the technique of the Frederiks transition the elastic constants of some nematic liquid crystals could be determined in relation to the molecular structure. For two homologous series of nematic azoxybenzenes similar regular trends have been observed with increasing alkyl chain length  $m$ :

(i)  $C_{33}/C_{11} = K_{33}/K_{11}$  decreases with increasing  $m$ , while  $K_{33} > K_{11}$  for small values of  $m$  and  $K_{33} < K_{11}$  for large  $m$ .

(ii)  $C_{22}/C_{11} = K_{22}/K_{11}$  is approximately independent of the temperature, while this ratio tends to decrease with increasing  $m$ .

(iii) The  $C_{11}$  increase with decreasing temperature, the temperature dependence and the value at  $T_{NI}$  be-

coming greater with increasing  $m$  (apart from some alternation).

Qualitatively the decrease of the ratio  $K_{33}/K_{11}$  with increasing  $m$  can be attributed to changes in the correlation length parallel and perpendicular to the director, the increase in the latter direction (due to the tendency to form smectic phases) being dominant.

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