

Influence of smectic order on the static dielectric permittivity of liquid crystals

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In some *p,p'*-di-*n*-alkyl-azoxybenzenes, an anomalous decrease of ϵ_{\parallel} and increase of ϵ_{\perp} is observed when the nematic phase is cooled to below the nematic/smectic-A transition temperature. This is attributed to dipole-dipole interaction, which becomes especially important for neighboring molecules in the same smectic layer. The Kirkwood-Fröhlich theory for the dielectric properties of anisotropic polar liquids is used in order to account for these interactions.

I. INTRODUCTION

In nematic liquid crystals¹ there is a long-range orientational ordering. The anisotropic molecules are, on average, aligned with their long axes parallel to each other. Macroscopically, a unique axis (the preferred direction) is defined in this way. The centers of mass of the molecules are distributed at random as in an ordinary isotropic fluid. The orientational order is measured by the order parameter $S = \langle \frac{1}{2} (3\cos^2\theta - 1) \rangle$. The brackets denote a statistical average, while θ is the angle between the long axis of a molecule and the preferred direction. The dielectric constant has a different value along the preferred axis (ϵ_{\parallel}) and perpendicular to this axis (ϵ_{\perp}). The contribution of the electronic polarizability to the dielectric anisotropy is always found to be positive ($\Delta n = n_{\parallel} - n_{\perp} > 0$). The dielectric anisotropy ($\Delta\epsilon = \epsilon_{\parallel} - \epsilon_{\perp}$) can have either sign depending on the magnitude μ of the permanent dipole moment and its angle β with the long molecular axis.²

The same long-range orientational ordering occurs in the smectic-A phase as in the nematic phase. In addition, there is a positional ordering in layers. These layers have a thickness of the order of the molecular length and are perpendicular to the preferred direction. The distribution of the centers of mass is again random within the layers. In a first approximation the orientational order can be described by the same order parameter S as in the nematic phase. Although the nematic and the smectic-A phase have the same uni-axial symmetry, the dielectric properties were recently found to be rather different. In *p, p'*-di-*n*-heptyl-azoxybenzene ϵ_{\parallel} decreases and ϵ_{\perp} increases anomalously with decreasing temperature around the nematic/smectic-A transition, leading to a change of sign of $\Delta\epsilon$.³ This behavior has not been observed for the refractive index.

It was suggested in Ref. 3 that the direct dipole-dipole interaction is responsible for the difference in dielectric properties between the nematic phase and the smectic phase. Such interactions are not accounted for in the usual Onsager approach⁴ which has been used by Maier and Meier² to describe the dielectric properties of nematic liquid crystals. This dipole-dipole interaction might be expected to be rather important for dipoles situated

fairly close together in the same smectic layer. The Kirkwood-Fröhlich theory of dielectrics^{4,5} permits account to be taken of these interactions. Recently, the theory has been extended to the case of anisotropy polar liquids.⁶ In the next section this theory will be applied to nematic and smectic-A liquid crystals. Further experimental results are given in Sec. III; a discussion follows in Sec. IV.

II. CALCULATION OF THE DIPOLE CONTRIBUTION TO THE DIELECTRIC CONSTANT

The Kirkwood-Fröhlich equations for the dielectric constants perpendicular to and along the preferred axis, denoted as ϵ_{λ} with $\lambda = x, y, z$, are given by⁶

$$(\epsilon_{\lambda} - \epsilon_{\lambda}^{\infty}) \left\{ \frac{\epsilon_{\lambda} + (\epsilon_{\lambda}^{\infty} - \epsilon_{\lambda}) A_{\lambda}^{\epsilon}}{\epsilon_{\lambda} (\epsilon_{\lambda}^{\infty} - 1)^2} \right\} \left\{ \frac{3(\epsilon^{\infty} - 1)}{\epsilon^{\infty} + 2} \right\}^2 = \frac{4\pi}{kTv} \left\langle \sum_{ij} \mu_{\lambda}^i \mu_{\lambda}^j \right\rangle. \quad (1)$$

$\epsilon_{\lambda}^{\infty}$ is the high-frequency dielectric constant determined by the electronic polarizability; $\epsilon^{\infty} = (\epsilon_x^{\infty} + \epsilon_y^{\infty} + \epsilon_z^{\infty})/3$; A_{λ}^{ϵ} is a numerical factor dependent on the anisotropy of the dielectric constant, that arises from the definition of the cavity and reaction field factors.⁵ In general $0 \leq A_{\lambda}^{\epsilon} \leq 1$; when all ϵ_{λ} are equal $A_{\lambda}^{\epsilon} = \frac{1}{3}$. We take the z -axis as the preferred direction; $\epsilon_{\parallel} = \epsilon_z$ and $\epsilon_{\perp} = (\epsilon_x + \epsilon_y)/2$. The components μ_{λ}^i of the permanent dipole moment of molecule i along the λ -axis can then be written as

$$\begin{aligned} \mu_z^i &= \mu_l \cos\theta_i + \mu_q \sin\theta_i \sin\phi_i, \\ \mu_x^i &= \mu_l \sin\theta_i \sin\chi_i + \mu_q (\cos\phi_i \cos\chi_i - \sin\phi_i \sin\chi_i \cos\theta_i), \\ \mu_y^i &= \mu_l \sin\theta_i \cos\chi_i + \mu_q (\cos\phi_i \sin\chi_i + \sin\phi_i \cos\chi_i \cos\theta_i). \end{aligned} \quad (2)$$

θ_i , ϕ_i , and χ_i are the Eulerian angles that describe the orientation of molecule i with respect to the macroscopic coordinate system. θ_i is the angle between the long molecular axis and the preferred direction; μ_l is the component of the permanent dipole moment along the long molecular axis and μ_q the component perpendicular to this axis. The magnitude μ of the total dipole moment is given by $\mu^2 = \mu_l^2 + \mu_q^2$. The summations in the right-hand side of Eq. (1) must be performed over all n molecules in a sphere of macroscopic dimensions with volume $v = 4\pi R^3/3$. The particle density N is defined as $N = n/v$.

The brackets in the right-hand side of Eq. (1) denote the statistical-mechanical average, i. e.,

$$\langle f \rangle = \frac{\int dX f \exp(-U/kT)}{\int dX \exp(-U/kT)}, \quad (3)$$

where $\int dX$ denotes an integration over all possible positions and orientations of the n molecules within the sphere. The potential energy can be written as

$$U = \sum_i W_i + \frac{1}{2} \sum_{\substack{ij \\ i \neq j}} V_{ij}. \quad (4)$$

The first term is the potential energy that gives rise to the orientational ordering in the nematic and smectic phase¹:

$$W_i \propto \frac{1}{2} (3 \cos^2 \theta_i - 1) S. \quad (5)$$

Using Eq. (3) the order parameter is defined self-consistently by $S = \langle \frac{1}{2} (3 \cos^2 \theta - 1) \rangle$. The second term is due to the direct dipole-dipole interaction⁴:

$$V_{ij} = \mu^i \mathbf{T}^{ij} \mu^j; \quad (6)$$

the dipole field tensor \mathbf{T} is given by

$$\mathbf{T} = \left(\frac{1}{r^3} - 3 \frac{\mathbf{r}\mathbf{r}}{r^5} \right), \quad (7)$$

where r is the distance between the two dipoles.

In order to calculate the right-hand-side of Eq. (1) we expand the potential energy as follows:

$$\exp\left(-\frac{U}{kT}\right) = \left(1 - \frac{1}{2kT} \sum_{\substack{ij \\ i \neq j}} V_{ij} + \dots\right) \exp\left(-\sum_i W_i/kT\right). \quad (8)$$

In this approximation the right-hand side of Eq. (1) can be written as

$$\frac{4\pi}{kTv} \left\langle \sum_{ij} \mu_\lambda^i \mu_\lambda^j \left(1 - \frac{1}{2kT} \sum_{\substack{kl \\ k \neq l}} \mu^k \mathbf{T}^{kl} \mu^l\right) \right\rangle, \quad (9)$$

where the averaging now has to be performed with $\exp(-\sum_i W_i/kT)$ only. From the definition of W_i and μ_λ^i in terms of the Eulerian angles it follows that the first term in expression (9) can be written as

$$\frac{4\pi}{kTv} \sum_i \langle (\mu_\lambda^i)^2 \rangle = \frac{4\pi N}{kT} \langle \mu_\lambda^2 \rangle,$$

where $N = n/v$ and $\langle \mu_\lambda^2 \rangle$ ($\lambda = x, y, z$) is given by²

$$\begin{aligned} \langle \mu_x^2 \rangle &= \mu_1^2 \langle \cos^2 \theta \rangle + \frac{1}{2} \mu_2^2 \langle \sin^2 \theta \rangle = \frac{1}{3} \mu^2 (1 - S) + \mu_1^2 S, \\ \langle \mu_y^2 \rangle &= \frac{1}{2} \mu_1^2 \langle \sin^2 \theta \rangle + \frac{1}{4} \mu_2^2 (1 + \langle \cos^2 \theta \rangle) = \frac{1}{3} \mu^2 (1 - S) + \frac{1}{2} \mu_2^2 S, \\ \langle \mu_z^2 \rangle &= \langle \mu_x^2 \rangle. \end{aligned} \quad (10)$$

The elements of the tensor \mathbf{T}^{kl} depend only on the relative positions of the molecules and not on their orientations. Neglecting the dependence of the relative probability of the positions on the orientation, the averaging over positions and orientations can be done separately. Since the distribution of the positions of the molecules is rotationally symmetric with respect to the preferred axis, the nondiagonal elements of the tensor \mathbf{T} can then be disregarded. Denoting the diagonal elements by T_{xx} ,

T_{yy} and T_{zz} the second part of expression (9) can be written as

$$-\frac{4\pi}{kTv} \frac{1}{2kT} \times \left\langle \sum_{ij} \mu_\lambda^i \mu_\lambda^j \sum_{\substack{kl \\ k \neq l}} (\mu_x^k T_{xx}^{kl} \mu_x^l + \mu_y^k T_{yy}^{kl} \mu_y^l + \mu_z^k T_{zz}^{kl} \mu_z^l) \right\rangle. \quad (11)$$

For given i, j , and λ the only contributions come from terms for which $k=i$ and $l=j$, or $k=j$ and $l=i$ when at the same time x, y or $z = \lambda$. Thus expression (11) reduces to

$$\begin{aligned} &-\frac{4\pi}{(kT)^2 v} \sum_i \left[\langle \mu_\lambda^2 \rangle \left\langle \sum_{j \neq i} \langle (\mu_\lambda^j)^2 \rangle T_{\lambda\lambda}^{ij} \right\rangle \right] \\ &= -\frac{4\pi N}{(kT)^2} \langle \mu_\lambda^2 \rangle \left\langle \sum_{j \neq i} T_{\lambda\lambda}^{ij} \right\rangle. \end{aligned} \quad (12)$$

Again $\langle \mu_\lambda^2 \rangle$ is given by Eq. (10); $\langle \sum_{j \neq i} T_{\lambda\lambda}^{ij} \rangle$ is the value of $\sum_{j \neq i} T_{\lambda\lambda}^{ij}$ averaged over all positions of the molecules j in the macroscopic sphere with respect to an arbitrarily chosen reference molecule i . It is in the calculation of this average over the positions that the difference between the nematic and the smectic phase occurs.

In the *nematic* phase we have around the reference molecule i a uniform density N . The reference molecule i is represented by an ellipsoid with long axis $2a$ and short axis $2b$. We can now write

$$\left\langle \sum_{j \neq i} T_{\lambda\lambda}^{ij} \right\rangle = N \int d\mathbf{r} T_{\lambda\lambda}(\mathbf{r}), \quad (13)$$

where the integration is performed over the whole macroscopic sphere with exclusion of the ellipsoidal volume of molecule i . Assuming that the long axis coincides with the preferred direction this integral can be evaluated using standard results of the electrostatic theory. The electric field E_λ inside a homogeneously polarized ellipsoid resulting from this homogeneous polarization P_λ is given by⁷:

$$E_\lambda = -4\pi A_\lambda^{\text{sh}} P_\lambda \equiv -P_\lambda \int d\mathbf{r} T_{\lambda\lambda}. \quad (14)$$

A_λ^{sh} is a shape factor depending only on the ratio a/b (Ref. 4, p. 141); for a sphere, $A_\lambda^{\text{sh}} = \frac{1}{3}$ (independent of the radius). Hence by combining Eqs. (13) and (14) we find

$$\left\langle \sum_{j \neq i} T_{\lambda\lambda}^{ij} \right\rangle = 4\pi N \left(\frac{1}{3} - A_\lambda^{\text{sh}} \right). \quad (15)$$

In the *smectic* phase the molecules are arranged in layers of thickness $2a$. In the layers we have an isotropic distribution with two-dimensional density $2aN$. Perpendicular to the layers we assume a discrete distribution, i. e., along the z -axis the molecular dipoles are situated at $z = \pm z_n = \pm n(2a)$, $n = 0, 1, 2, \dots$; $n = 0$ denotes the layer of the reference molecule i . Thus we can write

$$\begin{aligned} &\left\langle \sum_{j \neq i} T_{zz}^{ij} \right\rangle \\ &= 2aN \left[\int_{kb}^R \frac{2\pi\rho}{\rho^3} d\rho + 2 \sum_{n=1}^{R/2a} \int_0^{(R^2 - z_n^2)^{1/2}} d\rho 2\pi\rho \left(\frac{\gamma^2 - 3z_n^2}{\gamma^5} \right) \right], \end{aligned} \quad (16)$$

$$\left\langle \sum_{j \neq i} T_{xx}^{ij} \right\rangle = 2aN \left[\int_{\kappa b}^R d\rho 2\pi\rho \left(\frac{2 - \frac{3}{2}\rho^2}{\rho^5} \right) + 2 \sum_{n=1}^{R/2a} \int_0^{(R^2 - z_n^2)^{1/2}} d\rho 2\pi\rho \left(\frac{r^2 - \frac{3}{2}\rho^2}{r^5} \right) \right], \quad (17)$$

$$\left\langle \sum_{j \neq i} T_{yy}^{ij} \right\rangle = \left\langle \sum_{j \neq i} T_{xx}^{ij} \right\rangle, \quad (18)$$

where $r^2 = \rho^2 + z_n^2$ and $\rho^2 = x^2 + y^2$. The lower limit κb in the first integrals excludes the reference molecule from the integration over the reference plane. The numerical factor κ has been introduced because it is not *a priori* clear which value should be taken for the lower limit (b , $2b$, or some value in between). κ will be chosen later such that the average value $\langle \sum_{j \neq i} T_{\lambda\lambda}^{ij} \rangle$ vanishes for $a = b$. Equation (16) can be evaluated as follows:

$$\begin{aligned} \left\langle \sum_{j \neq i} T_{xx}^{ij} \right\rangle &= 4\pi aN \left[-\frac{1}{R} + \frac{1}{\kappa b} + 2 \sum_{n=1}^{R/2a} \int_{z_n}^R dr r \left(\frac{r^2 - 3z_n^2}{r^5} \right) \right] \\ &= 4\pi aN \left[-\frac{1}{R} + \frac{1}{\kappa b} - 2 \sum_{n=1}^{R/2a} \left(\frac{1}{R} - \frac{z_n^2}{R^3} \right) \right] \\ &= 4\pi aN \left[-\frac{1}{R} + \frac{1}{\kappa b} - \left\{ \frac{1}{a} - \left(\frac{1}{3a} + \frac{1}{R} + \frac{4a}{3R^2} \right) \right\} \right] \\ &= 4\pi N \left(-\frac{2}{3} + \frac{a}{\kappa b} + \frac{4a^2}{3R^2} \right), \quad (19) \end{aligned}$$

where both $z_n = n(2a)$ and the identity

$$\sum_{n=1}^{R/2a} n^2 = \frac{1}{3} \left(\frac{R}{2a} \right)^3 + \frac{1}{2} \left(\frac{R}{2a} \right)^2 + \frac{1}{6} \left(\frac{R}{2a} \right)$$

have been used. Since a is of molecular and R of macroscopic dimension the last term in Eq. (19) can be neglected. Thus we find

$$\left\langle \sum_{j \neq i} T_{xx}^{ij} \right\rangle = \frac{8}{3} \pi N \left(\frac{a}{b} - 1 \right), \quad (20)$$

where κ has been put equal to $\frac{3}{2}$ so that Eq. (20) vanishes for $a = b$. In the same way with $\kappa = \frac{3}{2}$ we find:

$$\left\langle \sum_{j \neq i} T_{xx}^{ij} \right\rangle = \left\langle \sum_{j \neq i} T_{yy}^{ij} \right\rangle = -\frac{4}{3} \pi N \left(\frac{a}{b} - 1 \right). \quad (21)$$

The final result for Eq. (1) can be summarized as:

$$\begin{aligned} (\epsilon_\lambda - \epsilon_\lambda^\infty) \left\{ \frac{\epsilon_\lambda + (\epsilon_\lambda^\infty - \epsilon_\lambda) A_\lambda^e}{\epsilon_\lambda (\epsilon_\lambda^\infty - 1)^2} \right\} \left\{ \frac{3(\epsilon^\infty - 1)}{\epsilon^\infty + 2} \right\}^2 \\ = \frac{4\pi N}{kT} \langle \mu_\lambda^2 \rangle \left(1 - \frac{4\pi N}{kT} \langle \mu_\lambda^2 \rangle T_\lambda \right), \quad (22) \end{aligned}$$

where $\langle \mu_\lambda^2 \rangle$ is given by Eq. (10) and the T_λ are given by the following expressions:

Nematic phase

$$T_z = \left(\frac{1}{3} - A_z^{sh} \right), \quad 0 \leq A_z^{sh} \leq \frac{1}{3}; \quad (23)$$

$$T_x = T_y = - \left(A_x^{sh} - \frac{1}{3} \right), \quad \frac{1}{3} \leq A_x^{sh} \leq \frac{2}{3}; \quad (24)$$

Smectic-A phase

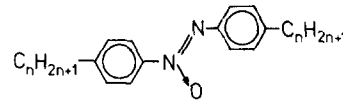
$$T_z = \frac{2}{3} \left(\frac{a}{b} - 1 \right), \quad \frac{a}{b} > 1; \quad (25)$$

$$T_x = T_y = -\frac{1}{3} \left(\frac{a}{b} - 1 \right), \quad \frac{a}{b} > 1. \quad (26)$$

Finally it should be noted that for $a/b = 1$ ($T_\lambda = 0$) the second term at the right-hand-side of Eq. (22) vanishes. Then this equation is essentially equivalent to the results of Maier and Meier.² This is easily seen by substituting the appropriate values for α_λ , h_λ and F_λ in terms of ϵ_λ and ϵ_λ^∞ in the final equations of Ref. 2.

III. EXPERIMENTAL RESULTS

Dielectric measurements were performed on some members of the series of p , p' -di- n -alkyl-azoxybenzenes,^{8,9}



The compounds with $n = 6, 7$, and 8 exhibit both a nematic and a smectic-A phase. For $n = 6$ the (monotropic) smectic-nematic (SN) transition is practically second-order, almost no heat of transition being detectable.¹⁰ For $n = 7$ the SN transition is only weakly first-order (the transition heat is very small); for $n = 8$ the transition is clearly first-order.¹⁰ In these substances the dipole moment is situated in the center of the molecule and approximately directed along the NO bond.

The dielectric constants were measured at 1592 Hz with a Wayne Kerr B642 autobalance bridge. The dielectric cells consisted of two glass plates, partly covered with either copper or indiumoxide electrodes, separated by 50–100 μm mylar spacers. The cells were calibrated at room temperature with chlorobenzene. In the nematic phase the samples could easily be aligned by using a magnetic field of about 13 kOe. For $n = 6$ no measurements in the smectic phase were possible because crystallization occurs at the monotropic SN transition. For $n = 7$ homeotropic or planar aligned smectic textures could be obtained by cooling the sample slowly below T_{SN} in the magnetic field. Furthermore, other nematic samples were prepared by using appropriate surfactants. These were found to be optically almost perfectly homeotropic or planar. For $n = 7$ both textures were easily preserved after cooling below T_{SN} . The homeotropic samples gave a conoscopic cross that remained symmetrical when the temperature was varied over the whole mesomorphic range. From measurements on these uniform samples, $\epsilon_{||}$ and ϵ_{\perp} were found to be consistent to within 1% with the results from samples aligned by the magnetic field (the isotropic dielectric constants being matched). For $n = 8$ no well-aligned smectic samples could be obtained by simply cooling in the magnetic field. We attribute that to the larger density change at T_{SN} which is due to the first-order nature of this transition. However, a planar nematic sample

obtained by using surfactants was found to have an almost perfect smectic planar texture after being slowly cooled to below T_{SN} . Homeotropic samples gave rise to problems. At best, an imperfect homeotropic smectic texture could be obtained with the combination of surfactants and a field. Consequently, the relative uncertainty in the values for $\epsilon_{||}$ in the smectic phase for $n=8$ is somewhat larger. The absolute accuracy of all the dielectric measurements is estimated to be about 3%.

The results for $\epsilon_{||}$ and ϵ_{\perp} are given in Fig. 1. Just below the nematic-isotropic transition (T_{NI}) $\Delta\epsilon$ increases with decreasing temperature, as is usual for a positive $\Delta\epsilon$. However, in all cases the trend then is reversed, leading finally to a change of sign of $\Delta\epsilon$. This is once more illustrated in Fig. 2 where the temperature dependence of the density ρ has been incorporated by considering the anisotropy of the molar susceptibility $\Delta\sigma = (\Delta\epsilon/4\pi)M/\rho$ (M is the molecular weight). The densities were measured with an accuracy of about 0.03% using the digital density meter DMA 10 (Anton Paar, Graz, Austria). On the other hand, the temperature dependence of $\bar{\epsilon} = (\epsilon_{||} + 2\epsilon_{\perp})/3$ is fairly normal. The results did not change when the frequency was varied in the audio range, which excludes the possibility of any influence from relaxation effects. Measurements of the anisotropy of the refractive index Δn of these compounds have been given elsewhere.¹⁰ In the temperature region where $\Delta\epsilon$ decreases strongly, Δn either does not change much (for $n=6$ and 7) or it increases as expected (for $n=8$). Consequently, the anomalous behaviour of $\Delta\epsilon$ must be attributed to the dipole contribution to the dielectric constant.

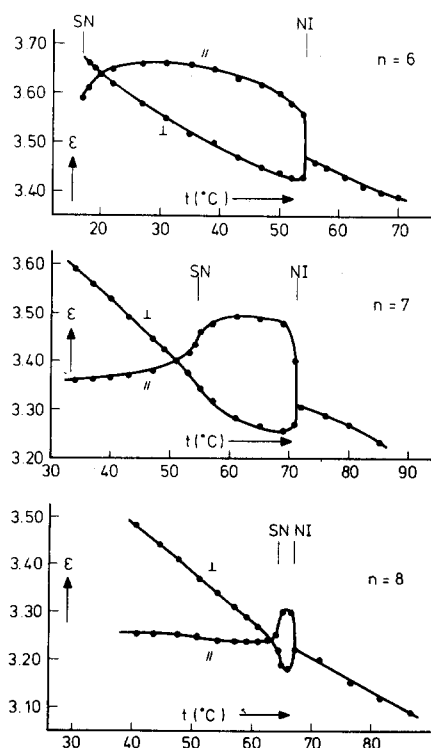


FIG. 1. Dielectric constants of some p,p' -di- n -alkyl-azoxybenzenes for various lengths of the alkyl chain C_nH_{2n+1} .

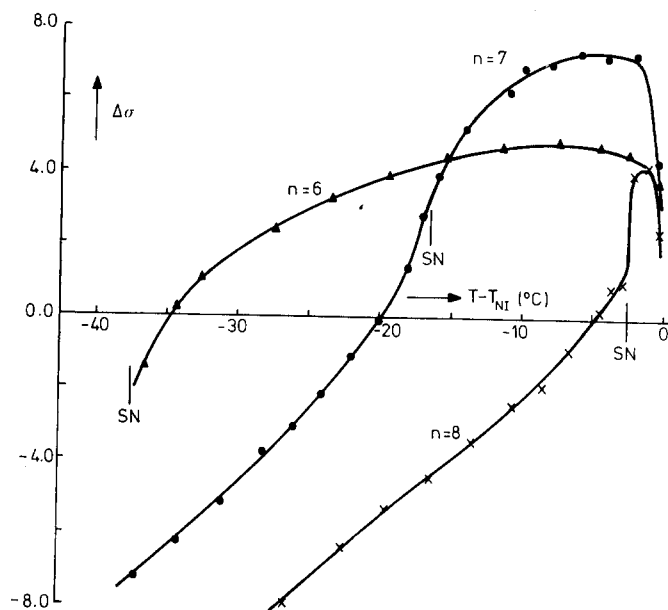


FIG. 2. Anisotropy of the molar susceptibility $\Delta\sigma = (\Delta\epsilon/4\pi)M/\rho$ for the same compounds as in Fig. 1.

Figure 1 strongly suggests that the decrease of $\Delta\epsilon$ is associated with the formation of the smectic phase. Further evidence is provided by the fact that a "normal" behavior of $\Delta\epsilon$ is observed for the lower members of the di- n -alkyl-azoxybenzenes.¹¹ Finally we note that the nature of the SN transition is also reflected in the results (see Fig. 2). For $n=6$ the second-order SN transition causes large pretransitional effects: the variation of $\Delta\sigma$ is fairly smooth and extends far into the nematic phase. For the first-order SN transition in $n=8$ the change in $\Delta\sigma$ at T_{SN} is rather abrupt.

IV. DISCUSSION

Experimentally we have seen that $\epsilon_{||}$ decreases and ϵ_{\perp} increases as a result of the formation of the smectic-A phase. The fact that this effect starts already in the nematic phase can be attributed to pretransitional smectic order. The existence of cybotactic groups of molecules with smectic order in a nematic phase above a smectic one has been established by x-ray diffraction.¹² The extent to which this happens is determined by the first- or second-order nature of the SN transition. Unfortunately, there is a lack of further data on the dielectric properties of smectics. Variations of $\Delta\epsilon$ similar to those shown in Fig. 1 have been described by Klingbiel *et al.*,¹³ but in these cases no information about the type of smectic phase and the precise orientation of the preferred axis is available.

From Eqs. (23) and (25) we see that T_g is always positive. Hence the dipole-dipole interaction does, in fact, tend to decrease the dipole contribution to $\epsilon_{||}$ [see Eq. (22)] as was observed experimentally. This effect is much stronger in the smectic phase than in the nematic phase. For instance when $a/b = \frac{5}{2}$, $T_g \approx 0.2$ for the nematic phase, whereas for the smectic phase $T_g = 1$. On the

other hand T_x is always negative [see Eqs. (24) and (26)]. The dipole-dipole interaction increases the dipole contribution to ϵ_{\perp} . Again this effect is much stronger in the smectic phase. When $a/b = \frac{5}{2}$, $T_x \approx -0.1$ for the nematic phase, whereas for the smectic phase $T_x = -0.5$. In the case of molecules that exhibit a smectic phase, a/b will generally be greater than $\frac{5}{2}$ (say 5). In the nematic phase, T_g and T_x are then approximately equal to their limiting values $1/3$ and $-1/6$, respectively. In the smectic phase they have the values $8/3$ and $-4/3$, respectively. Since $4\pi N \langle \mu_x^2 \rangle / kT$ is of the order $(\epsilon_{\perp} - \epsilon_{\parallel}^{\infty})$ the corrections are now certainly too large. This can be understood from the approximation made in Eq. (8) where we considered only the first term of the expansion. By doing so we have in fact calculated the tendency of $n-1$ polar molecules to align themselves, *independently of each other*, parallel or antiparallel to one chosen molecule. We thus ignore the dipole-dipole interactions between neighbouring molecules which counteract such a situation to some extent. For a better estimate of the total effect of the dipole-dipole interaction higher order terms should be included. This calculation would be rather complicated and will not be attempted at present.

It is interesting to consider the effect of the smectic correction factors on $\bar{\epsilon} = (\epsilon_{\parallel} + 2\epsilon_{\perp})/3$. From Eqs. (22) to (26) we see that since $T_g = -2T_x$, $\bar{\epsilon}$ is not affected if $\mu_g^2 = \mu_x^2$. It is known that in the *p, p'*-di-*n*-alkyl-azoxybenzenes μ_x is slightly larger than μ_g .⁸ Consequently we can expect a slight increase in the slope of $\bar{\epsilon}$ against temperature below T_{SN} , and this is indeed observed in Fig. 1. It would be interesting to investigate this effect in a compound where μ_g and μ_x differ widely.

Finally we note that the calculations make use of the fact that nematic and smectic-A liquid crystals are uniaxial. Accordingly, the theory cannot be applied directly to smectic-C. On the other hand, the results will not be affected when additional ordering occurs within the smectic planes (for example in smectic-B) as long as the long molecular axes are, on average, parallel to the

layer normal. Furthermore, it should be noted that the effect of the dipole-dipole interaction will only be substantial for dipole moments that are more or less situated in the central part of the molecule.

We conclude that the available experimental results can be explained by the theory presented here. The crux of the explanation is that the interaction between the central dipoles of neighboring molecules in the same smectic plane is large as compared with that between these dipoles in different smectic planes. In the nematic phase the dipole-dipole interactions are smeared out as a result of the uniform density of the molecules, and the effect is much less important than in the smectic phase.

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