actant contamination, $\Delta n = 0.0022$. Clearly, as the relative dimer-tetramer equilibrium is changed, Δn changes. We estimate from these observations that $\alpha_d/\alpha_t = 1.4$ to 1.7. Moreover, we observe a substantial change in the attenuation coefficient χ of the laser light when the salt concentration is changed from $0.154N$ to $1.5N$ NaCl, $C = 1\%$: χ increases from $0.22C^{-1}$ to $0.30C^{-1}$ cm^{-1}.

We also checked for the possibility that the dissociation may have been enhanced by the laser light. No changes of the decay constant were observed for a number of concentrations and angles as the laser power was varied over a range from 5 to 20 mW. Convective currents were measured and found to be negligible.

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Dielectric Properties of Di-*n*-Heptyl Azoxybenzene in the Nematic and in the Smectic-*A* Phases

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We report the dielectric constants of *p*,*p*'-di-*n*-heptyl azoxybenzene in the nematic and in the smectic-*A* phase. Around the nematic-smectic transition $\epsilon_\parallel$ decreases with decreasing temperature while $\epsilon_\perp$ increases anomalously. This is explained by an increased dipolar correlation between the molecules due to the formation of the smectic planes.

In a nematic liquid crystal there is long-range orientational order of the anisotropic molecules, while the centers of mass are distributed at random. Consequently, the dielectric constant has different values along the preferred axis ($\epsilon_\parallel$) and perpendicular to this axis ($\epsilon_\perp$). The dielectric anisotropy $\Delta\epsilon = \epsilon_\parallel - \epsilon_\perp$ can be either positive or negative depending on the magnitude μ of the permanent dipole moment and its angle β with the long molecular axis.[1] The temperature dependence of $\Delta\epsilon$ is mainly governed by that of the order parameter S. In the smectic phase the same orientational order exists as in the nematic phase, while in addition the molecules are arranged in layers. In the smectic-*A* phase the long molecular axes are, on the average, normal to the layer. Experimental results for the dielectric constants in a smectic phase are rather scarce[2,3] and are often given without precise information about the orientation of the molecular axis. In this Letter we present results for the dielectric constants in the nematic and in the smectic-*A* phase of *p*,*p*'-di-*n*-heptyl azoxybenzene (HEPTAB). Around the smectic-nematic (SN) transition the temperature dependence of both $\epsilon_\parallel$ and $\epsilon_\perp$ is anomalous, leading to a change of sign of $\Delta\epsilon$.

HEPTAB was synthesized in our laboratory by J. van der Veen[4,5] (melting point: 34°C, T_{SAN}: 54.5°C, T_c: 71°C). The smetic-*A*–nematic transition is only weakly first order, as indicated by the small heat of transition of 160 J/mole.[5,6] The

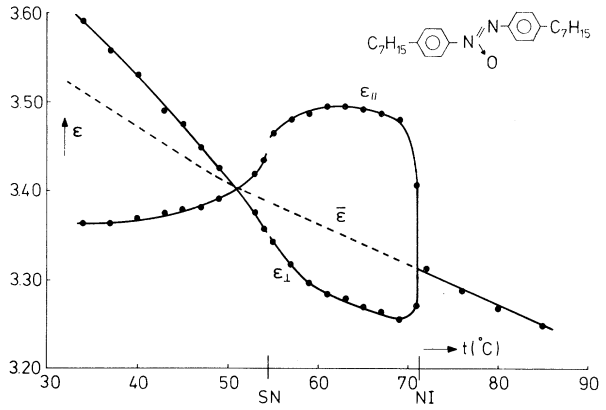

FIG. 1. Static dielectric constants of HEPTAB. Inset: structure of the HEPTAB molecule.

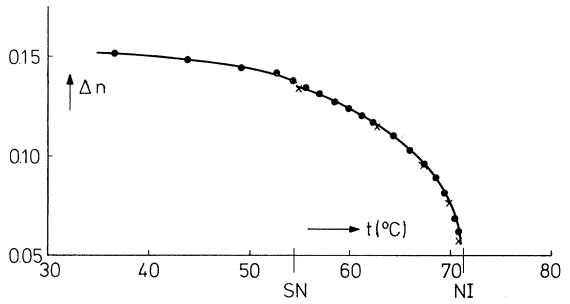

FIG. 2. Anisotropy of the refractive index of HEPTAB at 632.8 nm (crosses and circles refer to samples of different thicknesses).

molecular structure of HEPTAB is shown in Fig. 1. 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 with either copper or indium-oxide electrodes, separated by 50–100-μm Mylar spacers. The cells were calibrated with chlorobenzene at room temperature. In the nematic phase the molecules were easily aligned using a magnetic field of about 13 kOe. When the sample was slowly cooled down to below T_{SN} in the magnetic field, this alignment was preserved in the smectic phase. Furthermore, by use of appropriate surfactants other samples were prepared that were found to be optically almost perfectly homeotropic or planar. Both textures were easily preserved after cooling to below T_{SN}. The homeotropic samples gave a conoscopic cross that remained symmetrical when the temperature was varied over the whole mesomorphic range. $\epsilon_{\parallel}$ and $\epsilon_{\perp}$ from measurements on these uniform samples were consistent within 1% with the results from samples aligned by the magnetic field (the isotropic dielectric constants being matched). The absolute accuracy is estimated to be about 3%.

The results for $\epsilon_{\parallel}$ and $\epsilon_{\perp}$ are given in Fig. 1. Just below T_c, $\Delta\epsilon$ increases with decreasing temperature, as usual. However, the trend is then reversed, leading to a change of sign of $\Delta\epsilon$ at 51°C. On the other hand $\bar{\epsilon} = (\epsilon_{\parallel} + 2\epsilon_{\perp})/3$ does not show anomalous behavior, although there is a slight increase in the slope at 51°C (see Fig. 1). The results did not change when the frequency was varied in the audio range, which excludes any influence of relaxation effects. The behavior of $\Delta\epsilon$ prompted us also to make investigations at optical frequencies, where the contribution of the dipole moment can be neglected. These results for the anisotropy of the refractive index Δn are given in Fig. 2; experimental details are discussed in Ref. 6. In the temperature region where $\Delta\epsilon$ varies strongly Δn does not change much.

In the nematic phase of di-*n*-hexyl and di-*n*-octyl azoxybenzene a similar trend in $\Delta\epsilon$ was observed as given in Fig. 1. Unfortunately, no measurements below the SN transition were possible for the hexyl compound because this transition is monotropic and for the octyl compound because of difficulties in maintaining a well-defined texture. As $\Delta\epsilon$ in the lower members of the di-*n*-alkyl azoxybenzenes shows a "normal" behavior, the decrease of $\Delta\epsilon$ in HEPTAB must be related to the occurrence of the smectic phase. In this phase the interaction of a dipole moment with the dipoles of the surrounding molecules will be influenced by the nonisotropic distribution of the centers of mass of the molecules. As the distance between the molecules in the smectic planes is much smaller than the distance between different planes, an increased antiparallel correlation between the components of the dipole moments along the molecular axis can be expected. Consequently, the effective dipole moment in this direction is reduced, which leads to a decrease of $\epsilon_{\parallel}$. In the following we shall discuss this idea in more detail.

Maier and Meier have put forward a molecular theory of the dielectric properties of nematics.[1] Their theory is essentially an extension to anisotropic media of the Onsager theory for isotropic liquids.[7] A molecule is considered in a cavity of

molecular dimensions surrounded by a continuum with the macroscopic properties of the medium. In this type of theory short-range correlations are neglected. It is possible to include such interactions in the Kirkwood-Fröhlich theory of dielectrics.[7] An extension of this type of theory to anisotropic media will be given elsewhere.[8] For the present discussion it suffices to calculate the difference in dipolar correlation between the nematic and the smectic phases. We restrict ourselves to the permanent part of the dipole moment, which seems to be justified by the relative constancy of Δn around the SN transition where $\Delta\epsilon$ varies strongly.

Consider a fixed molecule of ellipsoidal shape with long axis a and short axis b in a macroscopic sphere. The final results were found to change little if the radius of this sphere is restricted to a, which simplifies the calculation considerably in the smectic case. The average moment of the sphere in the field of the central dipole is given by $\bar{\mu}$.[7] In order to calculate $\bar{\mu}$ approximately we restrict ourselves to the component $\bar{\mu}_{\parallel}$ and assume perfect order ($S=1$). The average moment of a particle at a distance r from the fixed molecule is taken as $\mu_{\parallel}^2 E(r)/kT$, where $E(r)$ is the field of the central dipole. This implies that for these fields at molecular distances saturation effects are still neglected, and only two-particle interactions are included. Then in the nematic case

$$\bar{\mu}_{\parallel}(\mathrm{nem}) = \mu_{\parallel} + \frac{N\mu_{\parallel}^2}{kT} \iiint_{V_{\mathrm{sph}}-V_{\mathrm{ell}}} dV E, \tag{1}$$

where $N = 3/4\pi ab^2$ is the dipole density. By standard methods we obtain

$$\iiint dV E = -4\pi A_{\parallel}^{\mathrm{sh}} \mu_{\parallel}, \tag{2}$$

where the shape factor $A_{\parallel}^{\mathrm{sh}}$ is equal to $\frac{1}{3}$ for a sphere[7]; for an ellipsoid with $a \gg b$ we have $A_{\parallel}^{\mathrm{sh}} \ll \frac{1}{3}$ and part of the integral can be neglected. Then

$$\bar{\mu}_{\parallel}(\mathrm{nem}) \approx \mu_{\parallel}[1 - (\mu_{\parallel}^2/kT)(1/ab^2)]. \tag{3}$$

For the smectic-A phase we assume in addition to $S=1$ that the centers of mass of the molecules are exactly arranged in layers. The integration over the volume of the sphere in Eq. (1) then reduces to integration over a circular surface S:

$$\bar{\mu}_{\parallel}(\mathrm{sm}) = \mu_{\parallel} + (N'\mu_{\parallel}^2/kT) \iint_S dS E, \tag{4}$$

where now $N' = 1/\pi b^2$ is the surface dipole density. Over the surface[7]

$$\iint_S dS E = 2\pi\mu_{\parallel}(1/a - 1/b). \tag{5}$$

Again using $a \gg b$ we find

$$\bar{\mu}_{\parallel}(\mathrm{sm}) \approx \mu_{\parallel}[1 - (\mu_{\parallel}^2/kT)(2/b^3)]. \tag{6}$$

Comparing Eqs. (3) and (6) we see that in the smectic phase the correction to $\mu_{\parallel}$ is a factor of $2a/b \approx 10$ larger than in the nematic phase. The order of magnitude of the corrections can be estimated by noting that the total dipolar contribution to the dielectric constant is of the order $\epsilon_{\parallel} - \epsilon_{\parallel\infty}$, where $\epsilon_{\parallel\infty}$ is the dielectric constant at very high frequencies. This leads in the nematic case to $\bar{\mu}_{\parallel} \approx 0.8\mu_{\parallel}$. With this value the smectic correction is found to be unrealistically high, the expression between the square brackets in Eq. (6) even becoming negative. This is not surprising in the light of the severe approximations used. Nevertheless, the calculation indicates that the dipolar correlation leads to an effective decrease of $\mu_{\parallel}$ and thus of $\epsilon_{\parallel}$. This effect is much stronger in the smectic phase than in the nematic phase, in agreement with the experimental observations (Fig. 1).

So far only $\mu_{\parallel}$ has been considered. Similarly, a positive correction to $\mu_{\perp}$ can be calculated, leading to an extra increase of $\epsilon_{\perp}$. This is also observed experimentally. Furthermore, we note that the di-n-alkyl azoxybenzenes have in general a somewhat smaller dielectric anisotropy than the dipole-less di-n-alkyl azobenzenes.[4] If it is assumed that the polarizabilities of both series are not very different, this indicates that μ_1 is slightly larger than $\mu_{\parallel}$. Therefore, the total effect of the corrections in the smectic phase will be to increase $\bar{\epsilon}$ somewhat, which is indeed observed in HEPTAB (see Fig. 1). It would be interesting to investigate this effect on $\bar{\epsilon}$ in a compound where $\mu_{\parallel}$ and $\mu_{\perp}$ differ strongly. The decrease of $\Delta\epsilon$ in the nematic phase can be attributed to pretransitional smectic order. The existence of cybotactic groups of molecules with short-range smectic order in a nematic phase above a smectic one has been established by x-ray diffraction.[9]

In a smectic-A phase the longitudinal dielectric constant $\epsilon_{\parallel}$ shows an anomalous decrease with decreasing temperature. This can be understood from a decrease of the contribution of the orientational polarization to $\epsilon_{\parallel}$ due to an increased dipole correlation in the smectic layers. The opposite effect is found in $\epsilon_{\perp}$.

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Divergence of Cholesteric Pitch near a Smectic-*A* Transition*

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We have measured the detailed temperature dependence of the cholesteric pitch in cholesteryl nonanoate near the smectic-*A* transition. The data show a power-law behavior with an exponent $\nu = 0.675 \pm 0.025$, in agreement with theoretical prediction and with elastic-constant measurements in nematics.

Studies near the nematic or cholesteric to smectic-*A* transitions in liquid crystals have been of intense current interest[1-8] since the McMillan–de Gennes suggestion[9-11] that they may be second-order in nature, and that they are analogous to, but in many respects more tangible than, the superconducting transition. The buildup of short-range smectic order in the nematic or cholesteric phase is characterized by a coherence length ξ which diverges toward an apparent transition temperature T_c in the form

$$\xi = \xi_0 (T - T_c)^{-\nu}, \tag{1}$$

where the critical exponent ν is typically between 0.6 and 0.7 from model calculations and experiments on magnets and fluids.[12] This pretransitional behavior manifests itself in liquid crystals in the anomalous increase of the twist and bend elastic constants K_{22} and K_{33}, and of the cholesteric pitch p. Physically, the presence of short-range smectic order in a nematic makes twist and bend distortions energetically costly, and leads to additional contributions to the respective elastic constants which are expected to be proportional to ξ.[10] A similar situation applies to the elastic constants in a cholesteric. Furthermore, the "rotary" part of the free energy, proportional to K_{22}/p, is believed to depend mainly on the intermolecular interactions and therefore to be unaffected by the smectic transition. Hence K_{22} and p should have similar temperature dependences,[13] and the latter is expected to diverge like

$$p = p_0 + c(T - T_c)^{-\nu}, \tag{2}$$

where p_0 is the pitch in the absence of the smectic ordering. Experimentally, the untwisting of the cholesteric texture in the vicinity of the smectic-*A* transition, with the accompanying dramatic color changes, is well known,[14-16] but has not been studied carefully in the light of recent theoretical advances. In this paper we present the results of a detailed measurement of the temperature dependence of the pitch of cholesteryl nonanoate (CN) near the smectic-*A* phase and the first report of the value of a critical exponent for a cholesteric–smectic-*A* transition.

Our samples of CN were obtained from Vari-Light Corporation. On cooling from the isotropic liquid, CN forms a cholesteric phase at 91°C and a smectic-*A* phase at 74°C. We found using differential scanning calorimetry that the cholesteric–smectic-*A* transition entropy was $0.05R_0$, in agreement with previous measurements.[1,17] The samples were placed between glass slides separated by a 12-μm Mylar spacer. A planar structure with the helical axis perpendicular to the slides was formed by displacing the top slide when the liquid was in the cholesteric phase. Both untreated slides and slides coated with obliquely deposited SiO thin film[18] were used, the latter giving more uniform tex-