Dielectric Constants and Molecular Structure of Nematic Liquid Crystals

I. Terminally Substituted Azobenzenes and Azoxybenzenes

W. H. de Jeu and Th. W. Lathouwers

Philips Research Laboratories, Eindhoven, The Netherlands

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Measurements are presented of the dielectric constants of some p,p′-n-alyl and n-alkoxy substituted azobenzenes and azoxybenzenes in the nematic and in the isotropic phase. Starting from the dipole-less, p,p′,di-n-alkyl-azobenzenes, a systematic interpretation is given of the influence of the molecular structure on the dielectric properties.

1. Introduction

In nematic liquid crystals [1] there exists a long-range orientational ordering. The anisotropic rod-like molecules are, on the average, aligned with their long axis parallel to each other. In this way macroscopically a unique axis (the preferred direction) is defined. The centres of mass of the molecules are distributed at random. The orientational order is given by the order parameter

$$S = \langle \tfrac{1}{2}(3\cos^2\theta - 1) \rangle .$$

The brackets denote a statistical average, while θ is the angle between the long axis of a molecule and the preferred direction. Maier and Saupe [2] have given a molecular-statistical theory of the nematic phase on basis of the anisotropic dispersion forces. Their theory correctly predicts a first-order nematic/isotropic transition, while the transition temperature T_{NI} is proportional to the anisotropy of the molecular polarizability. In their approximation the dependence of the order parameter on the reduced temperature T/T_{NI} is the same for all nematic liquid crystals.

The dielectric constant has a different value along the preferred axis ($\varepsilon_{||}$) from that perpendicular to this axis ($\varepsilon_{\perp}$). The value and sign of the dielectric anisotropy $\Delta\varepsilon = \varepsilon_{||} - \varepsilon_{\perp}$ is of the utmost importance for the behaviour of the nematic in an electric field [3] and therefore for the applicability of the compound for various electro-optic effects. Nevertheless relatively little effort has been put in the study of the dielectric behaviour of mesomorphic materials. The basic work of Maier and Meier in this field [4, 5] is concentrated on the di-alkoxy substituted azo- and azoxybenzenes, which have melting points around or above 100 °C. During the last decade many new low-melting mesomorphic compounds have been synthesized [6]. For these compounds dielectric data have been published only occasionally.

This paper is the first of two in which a systematic discussion will be given of the dielectric constants of nematic compounds in relation to the molecular structure. A suitable starting point for such a comparison is provided by the p,p′-di-n-alkyl-azobenzenes [7a] because they have a zero dipole moment. They are the subject of this paper and will be compared with the alkoxy substituted analogues and the corresponding azoxybenzenes. In part II the influence of the bridging group will be considered for fixed terminal substituents. Smectic liquid crystals will not be included.

Reprint requests to Dr. W. H. de Jeu, Philips Research Laboratories, Eindhoven, the Netherlands.

2. Experimental

The di-alkyl-azobenzenes and di-alkyl-azoxybenzenes were synthesized in the way described in [7]. The quasi-static dielectric constants were measured at a frequency of 1592 Hz using a Wayne-Kerr B 642 autobalance bridge. The dielectric cells consisted of two glass plates with evaporated copper electrodes. The distance was fixed using 80 μm mylar spacers and epoxy resin. Each cell was used only once, and its cell constant was determined at room temperature with chlorobenzene. The calibrated cell with the liquid crystal was placed in a heating stage (similar to the Mettler FP52) built in this laboratory. Alignment was assured by applying a magnetic field of about 13 kOe. The temperature was stabilized within 0.1 °C by a Eurotherm type 017 temperature controller. The set-up was checked by measuring the temperature dependence of the di-

electric constant of *n*-decane. Over the range 20 – 100 °C $d\varepsilon/dt$ could be reproduced within 1%, which is therefore an upper limit for the relative uncertainty. On the other hand the absolute error is estimated to be about 3%, and somewhat larger at temperatures above 100 °C.

The densities of the di-alkyl-azoxybenzenes were measured with an accuracy of 0.03% using the digital density meter DMA 10 (Anton Paar, Graz, Austria).

3. Results

The results for the nematic dipole-less di-n-alkyl-azobenzenes are given in Table 1 and the left column of Figure 1. The dielectric anisotropies $\Delta\varepsilon$ are positive and alternate with increasing length *n* of the alkyl chain. When comparing with the alkoxy substituted compounds we assume that an oxygen atom is conformationally equivalent to a methylene

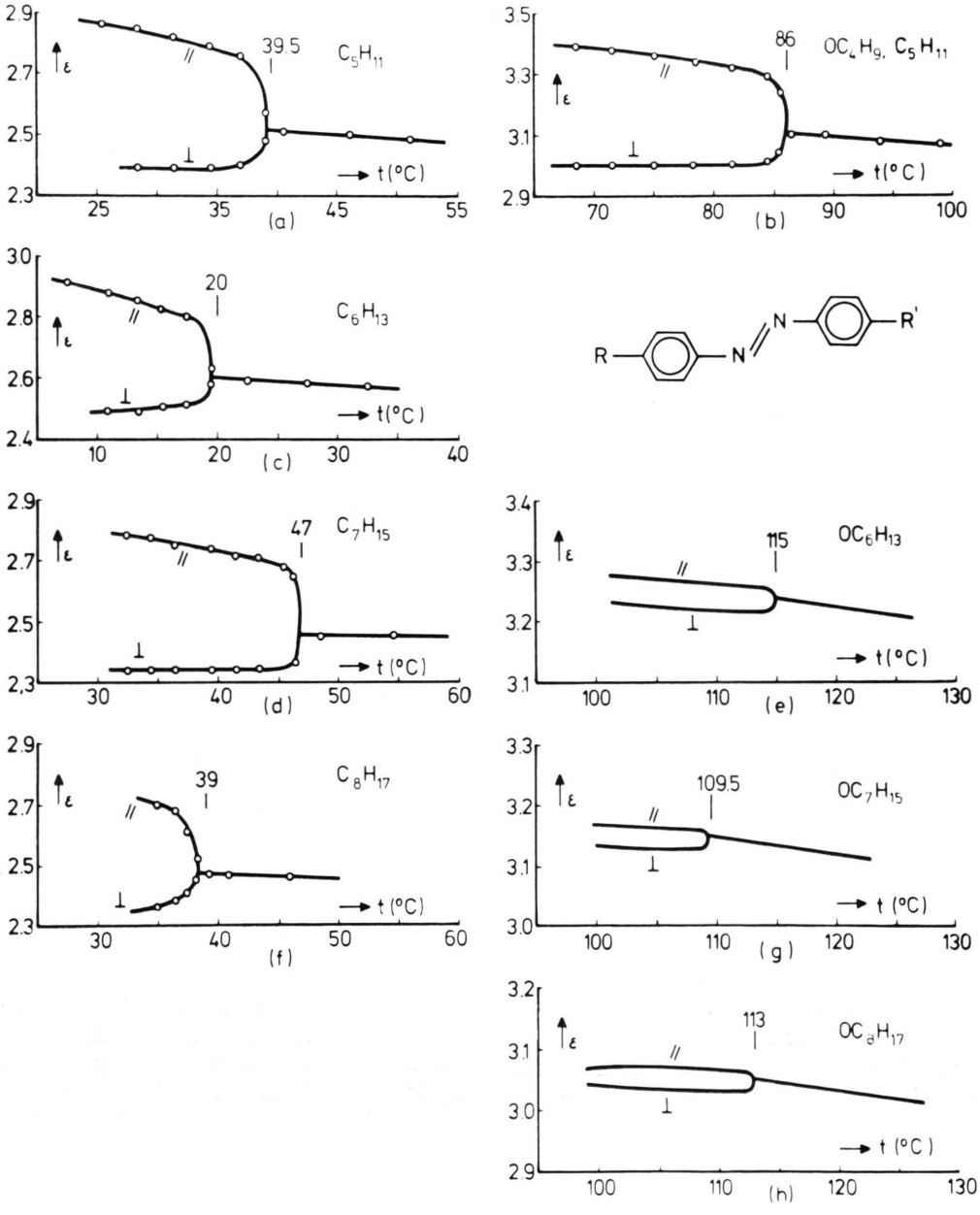

Fig. 1. Static dielectric constants of some p,p′ substituted azobenzenes; (e), (g) and (h) from Reference [5].

Table 1. Dielectric constants of some p,p′-di-n-alkyl-azobenzenes with different length n of the alkyl chain C_nH_{2n+1}.

$n = 5$			$n = 6$			$n = 7$			$n = 8$		
t (°C)	$\varepsilon_{\parallel}$	$\Delta\varepsilon$	t (°C)	$\varepsilon_{\parallel}$	$\Delta\varepsilon$	t (°C)	$\varepsilon_{\parallel}$	$\Delta\varepsilon$	t (°C)	$\varepsilon_{\parallel}$	$\Delta\varepsilon$
51	2.49		32.5	2.57		61	2.44		46	2.46	
46	2.50		27.5	2.58		54.5	2.44		41	2.46	
40.5	2.51		23.5	2.59		48.5	2.45		39.5	2.47	
39	2.57	0.090	19.5	2.63	0.052	46.5	2.65	0.297	38.5	2.52	0.067
37	2.76	0.361	17.5	2.80	0.293	45.5	2.68	0.328	37.5	2.61	0.198
34.5	2.79	0.397	15.5	2.83	0.339	43.5	2.71	0.368	36.5	2.68	0.302
31.5	2.82	0.429	13.5	2.76	0.373	41.5	2.72	0.389	35	2.70	0.326
28.5	2.85	0.459	11	2.88	0.394	39.5	2.74	0.404			
25.5	2.86		7.5	2.91		36.5	2.75	0.417			
						34.5	2.77	0.431			
						32.5	2.78	0.443			

Table 2. Dielectric constants of p-butoxy-p′-pentyl-azobenzene.

t (°C)	$\varepsilon_{\parallel}$	$\Delta\varepsilon$
99	3.07	
94	3.08	
89	3.10	
86.5	310	
85.5	3.24	0.200
84.5	3.29	0.281
82	3.32	0.314
79	3.34	0.339
76	3.36	0.358
72	3.38	0.373
69	3.39	0.383
66	3.40	0.394

group. In Table 2 and Fig. 1 b the alkyl-substituted analogue of Fig. 1 a is given. This substitution leads to a small decrease in $\Delta\varepsilon$. In Fig. 1 e, 1 g and 1 h the data for di-alkoxy-azobenzenes from [5] are reproduced. The introduction of a second alkoxy group leads to a further shift of $\Delta\varepsilon$ in negative direction.

The results for the di-alkyl-azoxybenzenes are given in Table 3 and the left part of Figure 2. The dielectric anisotropy now is positive and slightly smaller than that of the corresponding azobenzenes. For the hexyl compound $\Delta\varepsilon$ behaves rather anomalously, becoming smaller when the nematic/smectic-A transition is approached. Dielectric data for the di-alkoxy-azoxybenzenes are given in the right-hand part of Figure 2. As in the case of the azobenzenes, this substitution leads to a much stronger increase of $\varepsilon_{\perp}$ than of $\varepsilon_{\parallel}$, giving a negative $\Delta\varepsilon$. For the methoxy, propoxy and butoxy compound the data of Maier and Meier are used [4, 10]; for the ethoxy compound the result of Jezewski [8]. The literature data for the pentoxy compound [9] indicate for the radio-frequencies used a dispersion of $\varepsilon_{\parallel}$ at low temperatures. We therefore repeated the measurements at 1592 Hz. Apart from the dispersion, our data (Table 4) agree with Ref. [9] within 1%.

Asymmetric substitution leads for the azoxybenzenes usually to a mixture of two isomers that cannot easily be separated. This situation therefore will not be considered here; for one particular case it has been discussed elsewhere [11].

For the di-alkyl-azobenzenes the curve for $\bar{\varepsilon} = (\varepsilon_{\parallel} + 2\varepsilon_{\perp})/3$ practically coincides at T_{NI} with the curve for ε_{is}. For the other compounds, however, this is not the case. In Fig. 1 b and for the di-alkyl-azoxybenzenes (left column of Fig. 2) there is a small but significant discontinuity of ~ 0.01 at T_{NI}. For the di-alkoxy substituted compounds this decrease at T_{NI} is even larger (~ 0.03).

4. Discussion

Maier and Meier [10] have extended the Onsager theory of the dielectric properties of isotropic liquids [12] to nematics. Essentially they consider a molecule with polarizabilities α_l and α_q and dipole components $\mu_l = \mu\cos\beta$ and $\mu_q = \mu\sin\beta$. μ is the dipole moment making an angle β with the long molecular axis; the indices l und q refer to the directions along and perpendicular to this axis. The molecule is considered to be in a spherical cavity surrounded by a continuum with the macroscopic properties of the dielectric. The results can be summarized in formulae for $\varepsilon_{\parallel}$ and $\varepsilon_{\perp}$ or alternatively for ε_{is} or $\bar{\varepsilon}$ and $\Delta\varepsilon$ [10]:

$$\frac{\bar{\varepsilon}-1}{4\pi} = N h F\left\{\bar{\alpha} + F\,\frac{\mu^2}{3kT}\right\}, \qquad (1)$$

$$\frac{\Delta\varepsilon}{4\pi} = N h F\left\{\Delta\alpha - F\,\frac{\mu^2}{2kT}\,(1-3\cos^2\beta)\right\}S\,; \qquad (2)$$

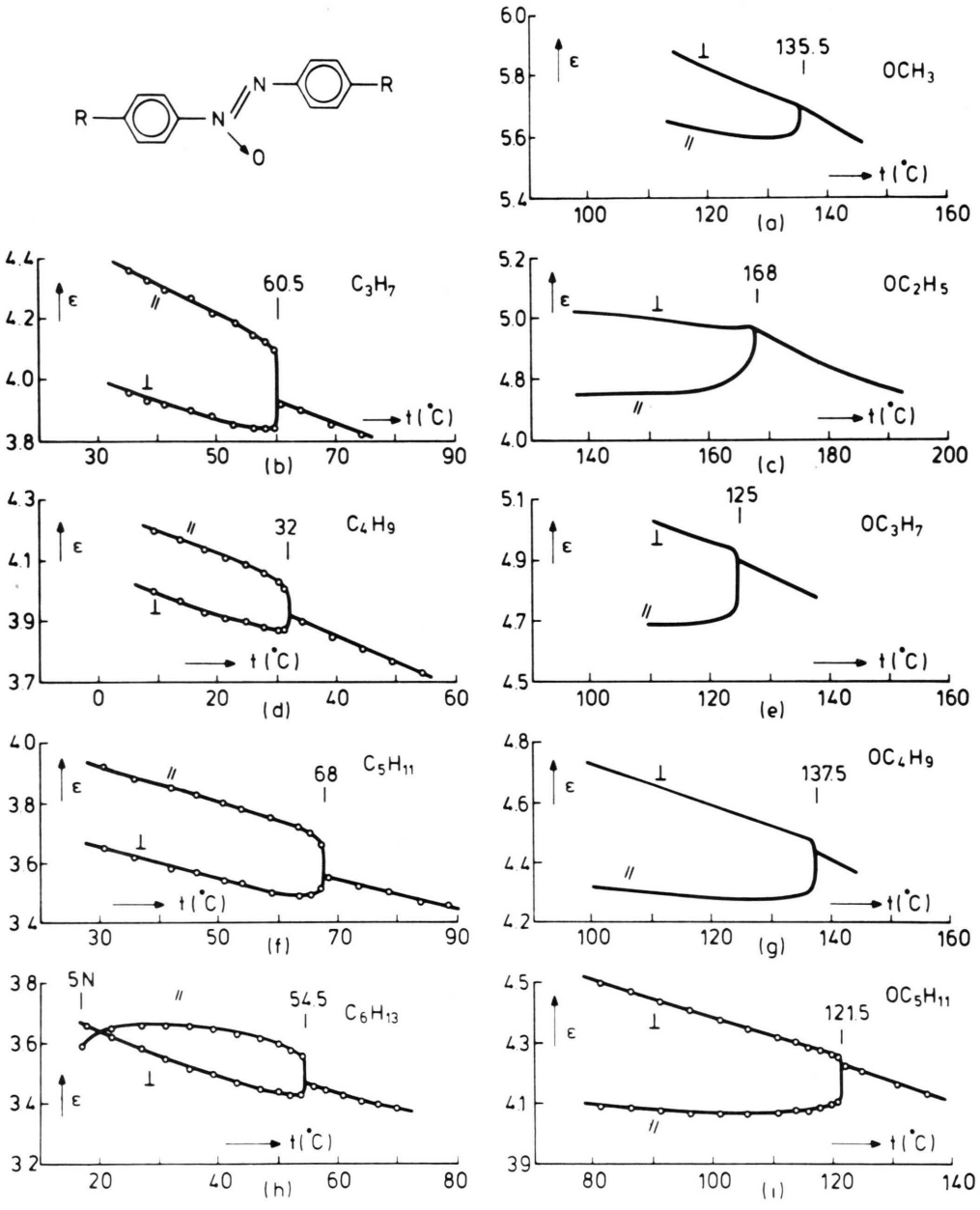

Fig. 2. Static dielectric constants of some symmetrically substituted azoxybenzenes; (a) from Ref. [10]; (c) from Ref. [8]; (e) and (g) from Reference [4].

$N = \varrho N_A/M$ is the particle density, where ϱ is the density, N_A Avogrado's number and M the molecular weight; $\bar{\alpha} = (\alpha_l + 2\alpha_q)/3$ and $\Delta\alpha = \alpha_l - \alpha_q$; h is the cavity field factor for the empty cavity and F the reaction field factor, both calculated using an isotropic continuum.

Derzhanski and Petrov [13] have extended this type of theory taking also the anisotropic shape of the molecules into account by considering an ellipsoidal cavity. Although this does not lead to a functional dependence that is different from Eqs. (1) and (2) it gives some correction factors that can be numeri-

Table 3. Dielectric constants of some p,p-di-n-alkyl-azoxybenzenes with different length n of the alkyl chain C_nH_{2n+1}.

$n=3$			$n=4$			$n=5$			$n=6$		
t (°C)	$\varepsilon_{\parallel}$	$\Delta\varepsilon$	t (°C)	$\varepsilon_{\parallel}$	$\Delta\varepsilon$	t (°C)	$\varepsilon_{\parallel}$	$\Delta\varepsilon$	t (°C)	$\varepsilon_{\parallel}$	$\Delta\varepsilon$
81	3.78		51	3.77		89.5	3.46		67	3.39	
76	3.82		45.5	3.81		85	3.47		64	3.40	
71	3.85		40.5	3.85		79.5	3.50		61	3.41	
65	3.90		35	3.90		74	3.52		58	3.43	
61	3.92		33	3.91		68.5	3.55		56	3.45	
60	4.10	0.264	31.5	4.01	0.137	67.5	3.66	0.132	54	3.56	0.129
58.5	4.13	0.293	30.5	4.03	0.156	65.5	3.70	0.211	52	3.58	0.153
56.5	4.15	0.309	28.5	4.06	0.180	61.5	3.73	0.236	50	3.60	0.160
54	4.19	0.339	27	4.07	0.183	57	3.76	0.249	43	3.63	0.160
50	4.22	0.344	25	4.09	0.192	51	3.80	0.257	35	3.66	0.134
46.5	4.27	0.379	22	4.11	0.197	47	3.83	0.262	31	3.66	0.110
42	4.30	0.384	18.5	4.14	0.204	43	3.85	0.265	27	3.66	0.083
39	4.33	0.398	14	4.17	0.199	40	3.87	0.259	22	3.65	0.034
36	4.36	0.400	9	4.20	0.196	37	3.88	0.262	20	3.64	0.004
						32	3.92	0.263	18	3.61	−0.048

Table 4.
Dielectric constants of p,p′-di-pentoxy-azoxybenzene.

t (°C)	$\varepsilon_{\perp}$	$-\Delta\varepsilon$
132	4.24	
127	4.27	
125	4.28	
122	4.30	
121	4.33	0.147
118	4.35	0.195
112	4.38	0.248
106.5	4.40	0.278
101.5	4.43	0.312
96.5	4.45	0.335
91.5	4.47	0.361
86	4.50	0.391
81	4.52	0.414
76	4.54	0.432

cally important. For example, according to Eq. (2) the dipole contribution to $\Delta\varepsilon$ is positive if $(1-3\cos^2\beta)<0$ or $\beta<55°$. Taking the anisotropy of the molecular shape into account this value becomes smaller. Using the data of Ref. [13] one can calculate for p-azoxyanisole an angle of 45° instead of 55°.

For the di-alkyl-azobenzenes Eqs. (1) and (2) simplify considerably because $\mu=0$. Experimentally it is observed that there is almost no temperature dependence of ε_{is}, while the curves for $\bar{\varepsilon}$ and ε_{is} coincide at T_{NI}. These facts agree nicely with Equation (1). For a more quantitative discussion it would be necessary to consider the molar susceptibility $\sigma=[(\varepsilon-1)/4\pi]M/\varrho$, in which the influence of the density is incorporated. Unfortunately the di-alkyl-azoxybenzenes are not easily accessible to density measurements because the nematic behaviour is mainly monotropic. Finally we remark that $\Delta\varepsilon$ is larger when T_{NI} is higher; in the homologous series $\Delta\varepsilon$ alternates in a similar way as T_{NI}. This is in agreement with the fact that both $\Delta\varepsilon$ and T_{NI} are proportional to the anisotropy of the electronic polarizability. From the known densities of the corresponding azoxybenzenes we conclude that this alternation is not due to the density and is probably even stronger for $\Delta\sigma$ than for $\Delta\varepsilon$.

The azoxybenzenes differ from the azobenzenes with respect to the presence of a dipole moment of 1.7 D in the central part of the molecule [14]. Usually it is assumed that this dipole is approximately directed along the NO-bond. When we compare the di-alkyl-azoxybenzenes with the corresponding azobenzenes we see that this leads to an increase of both $\varepsilon_{\parallel}$ and $\varepsilon_{\perp}$. The dielectric anisotropy has decreased somewhat; for example for the di-pentyl compounds at $0.97\,T_{NI}$, $\Delta\varepsilon=0.44$ for the azobenzene and 0.24 for the azoxybenzene. Results for $\Delta\sigma=(\Delta\varepsilon/4\pi)M/\varrho$ are given in Figure 3 a. $\Delta\sigma$ is rather constant for temperatures not too close to T_{NI}. In this case of a small dielectric anisotropy the positive contribution of the polarizability and the negative dipole contribution are not very different in magnitude [see Equation (2)]. The former varies with S, the latter goes with S/T. Clearly these counteracting effects lead to an almost constant $\Delta\varepsilon$ or $\Delta\sigma$. The strong decrease of $\Delta\sigma$ for the hexyl compound has a completely different origin and is associated with the nematic/smectic-A transition. As discussed extensively elsewhere [15, 16] there is a strong dipole-dipole correlation within the smectic layers for compounds where the dipole moment is

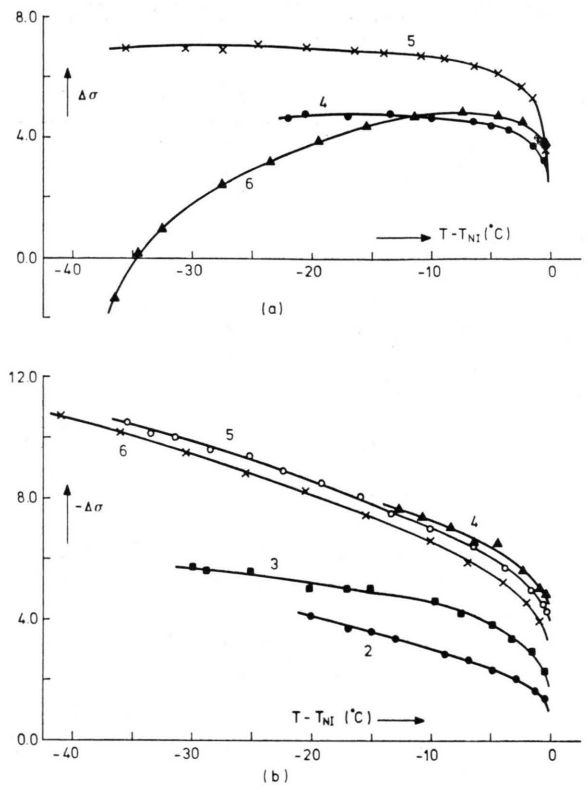

Fig. 3. Anisotropy of the molar susceptibility $\Delta\sigma = \frac{\Delta\varepsilon}{4\pi}\frac{M}{\varrho}$ for the p,p′-di-alkyl- (a) and di-alkoxy-azoxybenzenes (b). The number indicates the number of carbon plus oxygen atoms in the end chains.

located in the central part of the molecule. This leads to a decrease of $\varepsilon_{\parallel}$ and an increase of $\varepsilon_{\perp}$ in the smectic phase. That this effect occurs already in the nematic phase can be attributed to the presence of cybotactic groups with smectic order in the nematic phase.

When a methoxy group is placed in the para-position of an aromatic ring an extra dipole moment of 1.28 D is added [17]. From the dipole moments of para-substituted anisoles an angle of 72° between this dipole and the pp-axis is derived. We assume that this is a typical value for an alkoxy group that rotates freely. The angle between the pp-axis and the long molecular axis will be small ($\sim 10°$). Therefore on replacing an alkyl by an alkoxy group (Fig. 1 a and 1 b) one can expect a large contribution to $\varepsilon_{\perp}$ from the additional dipole moment. However, $\varepsilon_{\parallel}$ is also influenced because the alkyl dipole moment and the parallel component of the alkoxy dipole do not compensate. Furthermore, due to the conjugation between the electrons of the oxygen atom and the aromatic electrons, $\alpha_{\parallel}$ can be expected to increase somewhat (as is also reflected by the higher T_{NI}). These two effects on $\varepsilon_{\parallel}$ add up. For the azobenzenes of Fig. 1 a and 1 b the increase of $\varepsilon_{\perp}$ dominates slightly over that of $\varepsilon_{\parallel}$: at a fixed reduced temperature of 0.97 T_{NI}, $\Delta\varepsilon$ decreases from 0.44 to 0.36. A shift of $\Delta\varepsilon$ towards a negative direction on replacing one alkyl by an alkoxy group has also been observed in some azoxybenzenes [11] and in some phenyl benzoates [18].

When we compare di-alkyl- and di-alkoxy-azobenzenes the parallel components of the end dipoles compensate in both cases. The experimentally observed increase of $\varepsilon_{\parallel}$ can be attributed to a larger value of $\alpha_{\parallel}$, in agreement with the much higher values of T_{NI}. Due to the free rotation of the end groups the perpendicular components of the alkoxy dipole moments contribute both to $\varepsilon_{\perp}$. The increase of $\varepsilon_{\perp}$ appears to be larger than that of $\varepsilon_{\parallel}$, leading to values of $\Delta\varepsilon$ close to zero, though still positive (Fig. 1 e, 1 g and 1 h). That $\Delta\varepsilon$ is rather constant for temperatures not too close to T_{NI} (or even decreases, Fig. 1 h) can again be understood from the opposite sign and different temperature dependence of the contributions from the polarizability and from the dipoles.

The results when going from di-alkyl- to di-alkoxy-azoxybenzenes (Fig. 2) are very similar to those given for the corresponding azobenzenes. Now, however, the total anisotropy becomes negative. Using literature values for the densities of the di-alkoxy-azoxybenzenes [3, 19, 20] the values of $\Delta\sigma$ can be calculated and are given in Fig. 3 b. The temperature dependence of the dipole contribution to $\Delta\sigma$ now dominates over the whole temperature range. Consequently $\Delta\sigma$ decreases with decreasing temperature ($|\Delta\sigma|$ increases). The dielectric constants in the nematic phases of the higher homologues have also been given in the literature [4, 21]. They are very similar to those quoted here. In particular, above the smectic phase (in these cases, smectic-C) no effect of dipole correlation is observed as for the di-alkyl-azoxybenzenes.

As soon as dipole moments are introduced, $\bar{\varepsilon}$ is somewhat lower than ε_{is} at the nematic/isotropic transition. This jump at T_{NI} cannot be explained by the small change in the density and is therefore not in agreement with Equation (1). An explanation has been proposed [22] based on the idea of flexo-

electricity in liquid crystals [23]. Both for $\varepsilon_{\parallel}$ and $\varepsilon_{\perp}$ negative corrections are predicted [22] of the order of 0.01, which is the right order of magnitude. However, flexo-electricity requires a shape polarity of the molecules [23] (wedge-like for a coupling with splay, banana-like for a coupling with bend). Even for asymmetric nematic molecules this is difficult to imagine because of the free rotation of the end groups. For the di-alkoxy-azobenzenes it is even impossible because of the symmetry. Therefore the proposed explanation of the drop in $\bar{\varepsilon}$ at T_{NI} does not seem to be correct. Especially in the first three members of the series of the di-alkoxy-azobenzenes this effect is quite large. When we study the region around T_{NI} more closely we note for p-azoxyphenetole (Fig. 2 c) that with increasing temperature, just before T_{NI}, not only $\varepsilon_{\parallel}$ but also $\varepsilon_{\perp}$ increases somewhat. We have repeated these old measurements of Jezewski [8] and found this effect to be quite real, and even larger in our case. In the last 0.5° before T_{NI} both $\varepsilon_{\parallel}$ and $\varepsilon_{\perp}$ increase substantially. This seems to indicate that $\bar{\varepsilon}$ is in fact continuous at T_{NI} but drops very rapidly to a lower value when the temperature is decreased. We expect such an effect to be influenced strongly by the sharpness of T_{NI} (purity of the sample). Careful dielectric measurements around T_{NI} are necessary to settle this question more definitely.

We conclude that the functional dependence of the dielectric constants can be well understood from Eqs. (1) and (2). A problem remains for the polar compounds where $\bar{\varepsilon}$ is somewhat lower than ε_{is} at T_{NI}.

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