Dielectric Constants and Molecular Structure of Nematic Liquid Crystals
II. Variation of the Bridging Group*

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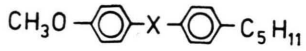
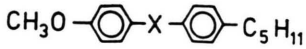
Measurements are presented of the dielectric constants of some nematic compounds with the structure



The following bridging groups X are considered: C≡C, CH=CH, CCl=CH, N=N, CH=N, N=CH, CO–O and O–CO. Starting from the compounds with non-polar bridging groups the influence of the group X on the dielectric properties is systematically evaluated.

1. Introduction

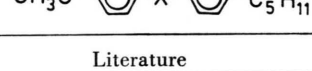
In a nematic liquid crystal the anisotropic molecules exhibit long-range orientational order, while the centres of mass are distributed at random. The dielectric constant has a value along the preferred direction ($\varepsilon_{\parallel}$) that differs from the one perpendicular to this axis ($\varepsilon_{\perp}$). The dielectric anisotropy is defined as $\Delta\varepsilon = \varepsilon_{\parallel} - \varepsilon_{\perp}$. In part I the dielectric properties of terminally alkyl and alkoxy substituted azobenzenes and azoxybenzenes were investigated [1]. In this paper we consider the effect of variation of the bridging group X of compounds of the structure



The choice of the terminal substituents is a compromise. In fact the di-alkyl substituted compounds would be more suitable for studying the effect of the bridging groups, because in their case any dipole contribution to the dielectric constant would be due to X only. However, only a few compounds of this type are known to display nematic behaviour, whereas nematic compounds with the above structure were readily available. The following bridging groups will be considered: C≡C, CH=CH, CCl=CH, N=N, CH=N, N=CH, CO–O and O–CO. In the case of an asymmetric bridge there are two isomers. Asymmetrically substituted azoxybenzenes have been discussed elsewhere [2]. Starting from the non-polar groups C≡C, CH=CH and N=N we will evaluate the influence of the bridging group on the dielectric constants.

2. Experimental

The experimental set-up for the dielectric measurements is as described in part I. The compounds synthesized are listed in Table I. The melting points and nematic-isotropic transition temperatures T_c were determined with a Reichert Thermopan polarizing microscope and a Mettler FP 52 heating stage.

Table I. Melting and clearing points of the compounds 

No.	X	m p (°C)	T_c (°C)	Literature		
				m p (°C)	T_c (°C)	Ref.
1	N=N	38.4 – 39.4	65.4	39	65	[3]
2	CH=N	39.3 – 40.3	62.9	39.7	62.8	[4]
3	N=CH	47.9 – 48.6	63.7	47.5	64.2	[5]
4	CO–O	28.7 – 28.9	41.5 – 41.6	29	42	[6]
5	CH=CH	117.3 – 118.0 †	124.5 – 124.7	–	–	–
6	CCl=CH	35.5 – 35.9	51.4 – 51.5	–	–	–

† Monotropic nematic-smectic B transition at 109.5 – 1.09.8 °C

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Compounds **1** – **4** have been reported before. Compounds **5** and **6** are new, and have NMR spectra in accordance with the assumed structure. The monotropic smectic phase of compound **5** was identified as smectic B from the mosaic texture and its miscibility with the smectic B phase of ethyl *p*-(*p*-ethoxybenzylidine) aminocinnamate [7]. Compound **5** was prepared using methods summarized in Reference [6]. Compound **6** was prepared by Nagano's method [8].

3. Results

The experimental results for the dielectric constants of the compounds listed in Table I are assembled in Table II. Together with literature data for the dielectric constants of the corresponding

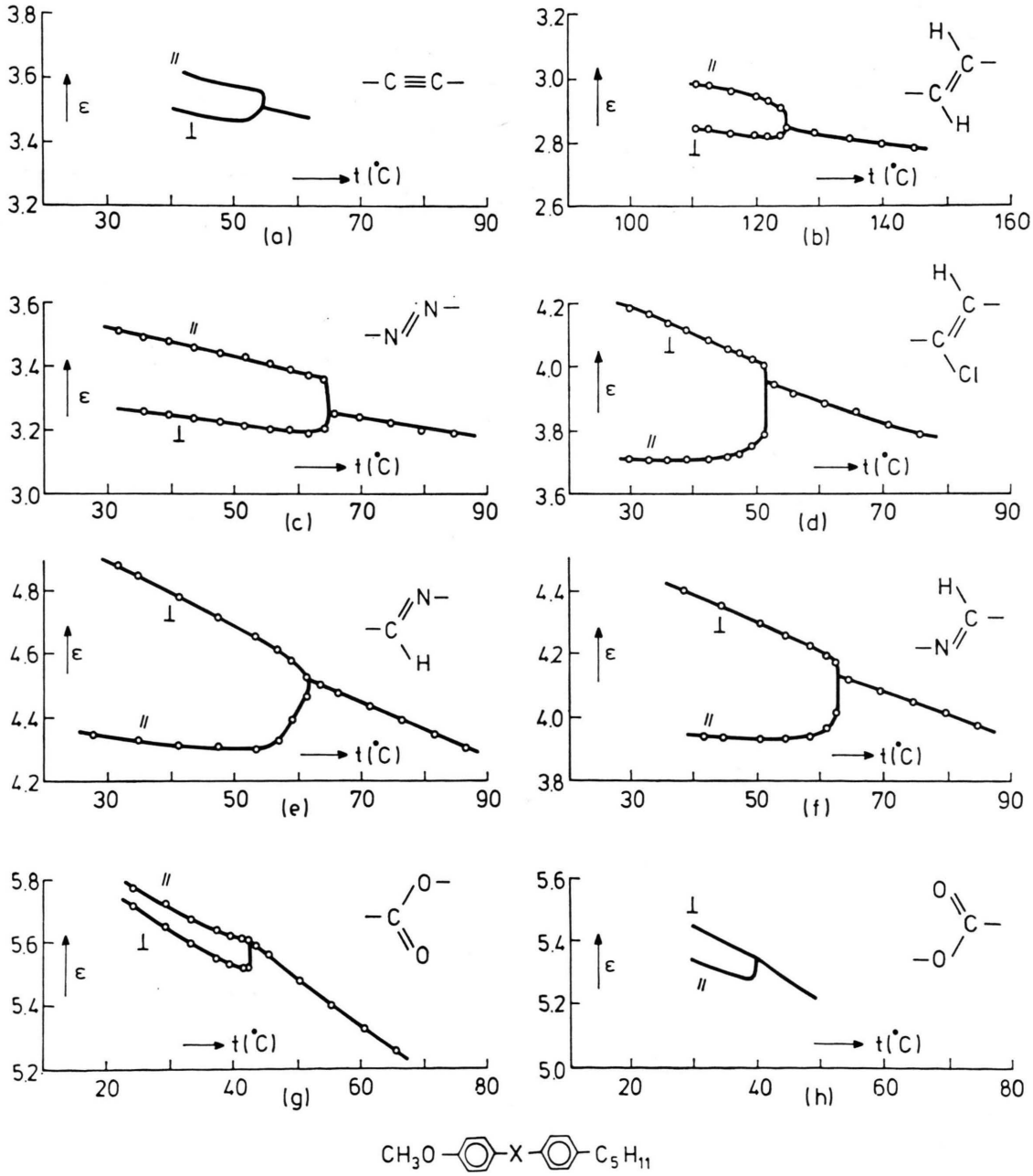

Fig. 1. Dielectric constants of some nematic liquid crystals with different bridging groups (a from Ref. [9]; h from Ref. [10]).

Table II. Dielectric constants of the compounds in Table I; heading the columns the bridging group X is given.

CH=CH			CCl=CH		
t (°C)	$\varepsilon_{\parallel}$	$\Delta\varepsilon$	t (°C)	$\varepsilon_{\perp}$	$-\Delta\varepsilon$
140	2.79		66	3.85	
135	2.81		61	3.88	
129.5	2.82		56	3.91	
125	2.84		52.5	3.94	
124	2.90	0.085	51	4.00	0.216
122	2.93	0.111	49.5	4.02	0.280
120	2.94	0.122	45.5	4.05	0.340
116	2.96	0.133	42.5	4.08	0.380
112	2.97	0.139	39	4.11	0.412
110	2.98	0.141	36	4.13	0.432
			30	4.18	0.484

N=N			CH=N		
t (°C)	$\varepsilon_{\parallel}$	$\Delta\varepsilon$	t (°C)	$\varepsilon_{\perp}$	$-\Delta\varepsilon$
80	3.20		77	4.39	
75	3.22		72	4.43	
70	3.24		67	4.48	
66	3.25		63	4.51	
64	3.36	0.061	62	4.53	0.161
62	3.37	0.181	59	4.57	0.182
59	3.39	0.198	55	4.64	0.330
56	3.41	0.207	51	4.68	0.376
48	3.44	0.222	44	4.74	0.434
40	3.48	0.229	38	4.81	0.487
32	3.51	0.230	32	4.88	0.536

N=CH			CO−O		
t (°C)	$\varepsilon_{\perp}$	$-\Delta\varepsilon$	t (°C)	$\varepsilon_{\parallel}$	$\Delta\varepsilon$
80	4.00		60	5.33	
75	4.04		50	5.48	
70	4.07		45	5.56	
65	4.11		42	5.59	
63	4.16	0.160	41	5.61	0.096
61	4.20	0.257	39	5.62	0.088
59	4.21	0.279	35	5.65	0.080
57	4.23	0.305	31	5.69	0.071
53	4.27	0.346	27	5.74	0.063
48	4.31	0.389	24	5.77	0.059
42	4.37	0.439			

compounds with bridges C≡C and O − CO they are summarized in Figure 1. For the non-polar bridging groups (Figs. 1 a, 1 b and 1 c) the dielectric anisotropy is small and positive (0.1 to 0.2). Substitution of chlorine in the α-position of the stilbene derivative leads to a negative dielectric anisotropy of the same order of magnitude as obtained for the Schiff bases (~ -0.5). In the latter case reversal of the *para* substituents does not have much influence on the dielectric anisotropy. For the phenylbenzoates (Fig. 1 g and 1 h) there is a change of sign of the dielectric anisotropy, while the absolute values of $\Delta\varepsilon$ are rather small. In these cases $\bar{\varepsilon} = (\varepsilon_{\parallel} + 2\,\varepsilon_{\perp})/3$ and ε_{is} differ at T_c, similar as discussed in part I for some substituted azoxybenzenes.

4. Discussion

As discussed in part I the dielectric properties of nematic liquid crystals can be understood, at least qualitatively, from Maier and Meier's extension [11] of Onsager's theory. This leads to expressions for $\varepsilon_{\parallel}$ and $\varepsilon_{\perp}$ or alternatively for $\bar{\varepsilon}$ and $\Delta\varepsilon$:

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

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

The symbols are defined as in part I. $\Delta\alpha$ being positive the sign of $\Delta\varepsilon$ is determined by the magnitude μ of the total dipole moment and its angle β with the long molecular axis. Approximately μ and β can be obtained by addition of the group moments of the various polar groups in a molecule. In our case the alkyl group has a dipole moment of about 0.4 D (directed along the $C - C_{ar}$ bond) [12], and the methoxy group a dipole moment of 1.3 D (directed mainly perpendicular to the long molecular axis) [2, 12]. Eventually a third dipole is associated with the bridging group.

Although the bridging groups C≡C, CH=CH, and N=N are in principle non-polar, this is no longer true of the asymmetrically substituted compounds in Figs. 1 a, 1 b and 1 c. Even in the case of symmetrical substitution, however, there are some differences. Stilbene is non-polar because of the uniformity of the charge distribution, all the carbon atoms being sp^2-hybridized. Tolane and azobenzene are non-polar because of the symmetry, but the electron-density is highest at the bridging group. Consequently the C≡C and N=N bridges are expected to be more sensitive to asymmetric substitution. This is reflected in the average dielectric constant, which for the substituted tolane, stilbene, and azobenzene amounts to 3.3, 2.9 [5] and 3.2, respectively (extrapolated to 90 °C from Figures 1a − 1c). As it seems unlikely that the total polarizabilities are very different, this indicates that the stilbene derivative has a somewhat smaller total dipole moment. Of course, this influences also the dielectric anisotropy.

At a reduced temperature of $0.96\,T_c$ the respective values of $\Delta\varepsilon$ for the tolane, stilbene and azobenzene derivative are 0.13, 0.14 and 0.20. With respect to these differences it should be noted that the tolane derivative forms a *linear* molecule, while the stilbene and azobenzene exist approximately in the *trans* configuration. This gives a difference in the definition of the long molecular axis, and consequently in the angle β. Furthermore the stilbene derivative has a relatively high value of T_c. As discussed in part I this indicates a high value of $\Delta\alpha$. The combination of these factors must be responsible for the observed small differences in $\Delta\varepsilon$ of these three compounds. For a more quantitative discussion it would be necessary to have data on the corresponding di-alkyl substituted compounds.

Chlorine substitution in the α-position of the stilbene derivative introduces an extra dipole moment that contributes much more to $\varepsilon_\perp$ than to $\varepsilon_\parallel$, leading to a negative value of $\Delta\varepsilon$ (Figure 1 d). This effect is even stronger when a CN-group is introduced instead of a Cl-atom. In that case anisotropies of the order of -5 can be reached [13].

The CH=N bridge has a dipole moment of 1.16 D [12]. From the addition of the bond dipoles of the C=N, the $C_{ar}-N$ and the C–H bond a value of 1.57 D is found [14]. As the longitudinal component of the C–H dipole and the $C_{ar}-N$ dipole counteract each other, the resultant bridge dipole contributes mainly to $\varepsilon_\perp$ [14]. This explains why $\varepsilon_\perp > \varepsilon_\parallel$, as is observed experimentally (see Figure 1 e). The negative value of $\Delta\varepsilon$ is about the same for the isomer (Fig. 1 f), while the total dipole moment of the molecule is smaller, as indicated by the lower value of both $\varepsilon_\parallel$ and $\varepsilon_\perp$. Clearly reversal of the terminal substituents influences both the relative and the absolute contribution of each of the three bond dipoles to the bridge dipole. This is not surprising as the CH=N plane is about coplanar with the aldehyde ring (and consequently strongly conjugated), while it makes an appreciable angle with the other aromatic ring [15].

The substituted phenylbenzoates (Figs. 1 g and 1 h) finally form a fairly complicated system. The dipole moment of phenylbenzoate itself is 1.90 D [16]. Available dielectric data on p,p′-alkyl di-substituted phenylbenzoates [10, 17] suggest that the total bridge dipole (built from the $C_{ar}-O$ and the C=O dipole) contributes only slightly more to $\varepsilon_\perp$ than to $\varepsilon_\parallel$. The mainly perpendicular contribution of the dipole of the p-methoxy group then leads to values of $\Delta\varepsilon$ close to zero. It is difficult to comment on the small difference between the two isomers. At the most one could say that when the two ether oxygens are attached to the same aromatic ring the total system is likely to be somewhat less polar.

We conclude from the data given in part I and II that Maier and Meier's simple extension of Onsager's theory to nematic liquid crystals gives a qualitatively correct picture of the dielectric properties. It is difficult to test the model quantitatively because of the lack of independent information on the values of the molecular polarizabilities and the dipole moments and their angle with the long molecular axis.

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