Analysis of the Dielectric Anisotropy of Typical Nematics with the Aid of the Maier-Meier Equations

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Using the experimental data on the dielectric anisotropy, density, polarizability, dipole moment, and order parameter in the nematic phase of seven typical liquid crystalline substances, the applicability of the Maier-Meier theory for the description of the dielectric properties of nematics is checked. Substances with different polarity and different tendency to form associates in the nematic phase were studied. It is found that the Maier-Meier equations describe fairly well the dielectric permittivity components of nematics. The estimated values of the angle β formed by the dipole moment with the long molecular axis are compared with those obtained in other studies.

Key words: Nematic Liquid Crystals; Dielectric Anisotropy; Maier-Meier Equations.

1. Introduction

The dielectric permittivity of nematics is a tensorial quantity with two non-vanishing components $\varepsilon_{\|}$ and $\varepsilon_{\perp}$, corresponding to two geometries, $\mathbf{n} \| \mathbf{E}$ and $\mathbf{n} \perp \mathbf{E}$, see Fig. 1 a, where **E** denotes the external electric field and **n** is the nematic director. They define the dielectric anisotropy $\Delta\varepsilon = \varepsilon_{\|} - \varepsilon_{\perp}$. The value and sign of $\Delta\varepsilon$ are the parameters deciding about a possible application of a substance in liquid crystalline displays. Therefore chemists need basic information on these parameters in order to synthesise substances appropriate for applications. Recently [1–3] quite successful predictions of optical and dielectric anisotropy constants were achieved with the aid of the Maier-Meier (M-M) theory [4]. Therefore it seems worthwhile to analyse the dielectric properties of some typical substances with the aid of the Maier-Meier equations in order to point out the weak and strong sides of the theory.

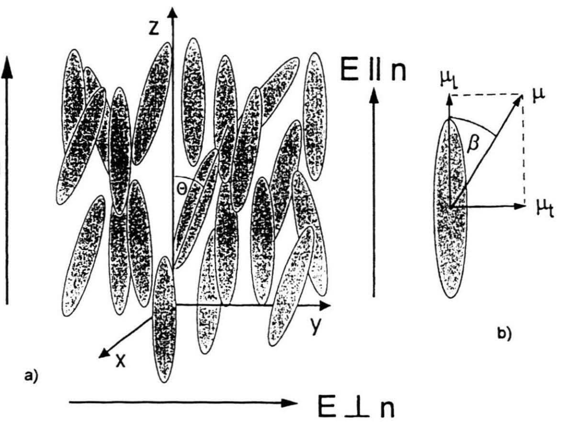

Fig. 1. a) Geometry of dielectric experiments in the nematic phase. **n** is the nematic director, **E** the external electric field, θ the angle between the long axis of a molecule and the director. b) Position of the dipole moment μ with respect to the molecule's long axis.

Maier and Meier have extended the Onsager theory [5] of isotropic fluids to the nematic phase. For simplicity, the molecules were considered as spherical, but their polarizability was supposed to have a longitudinal (α_l) and a transverse (α_t) component. The dipole moment μ in the centre of the molecule forms an angle β with the long molecular axis (Fig. 1 b). The surrounding of the molecules is treated as a continuum which limits the validity of the model to $|\Delta\varepsilon| \ll \bar{\varepsilon}$, where $\bar{\varepsilon} = (\varepsilon_{\|} + 2\,\varepsilon_{\perp})/3$ is the mean permittivity. Moreover, the nematic order is not influenced by the external electric field. On this basis Maier and Meier (M-M) obtained the following equations for the principal permittivity components and the dielectric anisotropy of the nematic phase:

$$(\varepsilon_{\|} - 1) = \varepsilon_0^{-1}\, N \cdot F \cdot h \cdot \left\{ \bar{\alpha} + \frac{2}{3}\Delta\alpha S + F \frac{\mu_{\text{eff}}^2}{3kT}\left[1 - (1 - 3\cos^2\beta)\, S\right] \right\}, \tag{1}$$

$$(\varepsilon_{\perp} - 1) = \varepsilon_0^{-1}\, N \cdot F \cdot h \cdot \left\{ \bar{\alpha} - \frac{1}{3}\Delta\alpha S + F \frac{\mu_{\text{eff}}^2}{3kT}\left[1 + \frac{1}{2}(1 - 3\cos^2\beta)\, S\right] \right\}, \tag{2}$$

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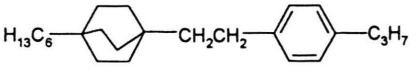
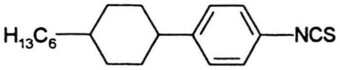
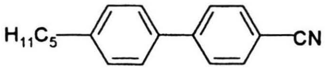
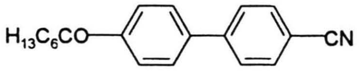
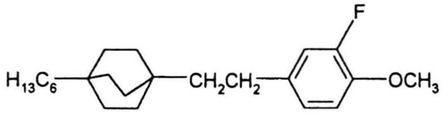
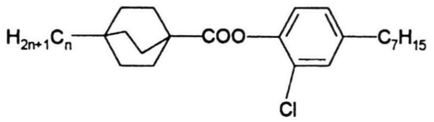
Table 1. Chemical formulae and transition temperatures for substances studied.

Substance		
Acronym	Chemical formula	Phase transition/K
6BAP3		Cr 326.7 (S_B 319.2) N 333.5 Iso
6CHBT		Cr_I 281 Cr 285.4 N 315.7 Iso
5CB		Cr 289.3 N 308 Iso
6OCB		Cr 332.7 N 350 Iso
6BAP(F)		Cr 331.1 N 341.7 Iso
7CP*n*BOC		
$n=5$		Cr 291.4 N 316.7 Iso
$n=7$		Cr 287.3 N 321.7 Iso

$$\Delta\varepsilon = (\varepsilon_{\|} - \varepsilon_{\perp}) = \varepsilon_0^{-1}\, N \cdot F \cdot h \cdot \left[\Delta\alpha - F \frac{\mu_{\text{eff}}^2}{2\,kT} (1 - 3\cos^2\beta) \right] S, \tag{3}$$

where $N = N_A\, \varrho / M$ (N_A = Avogadro's number, ϱ = density, M = molar mass), ε_0 is the permittivity of free space, $\Delta\alpha = \alpha_l - \alpha_t$ and $\bar{\alpha} = (\alpha_l + 2\,\alpha_t)/3$. The local field parameters F and h are expressed by the mean polarizability $\bar{\alpha}$ and mean permittivity $\bar{\varepsilon}$: $F = 1/(1 - f\,\bar{\alpha})$ with $f = (N/3\;\varepsilon_0)\,[(2\,\bar{\varepsilon}_s - 2)/(2\,\bar{\varepsilon}_s + 1)]$, and $h = 3\,\bar{\varepsilon}_s/(2\,\bar{\varepsilon}_s + 1)$. $S = \langle 3\cos^2\theta - 1 \rangle / 2$ is the order parameter. In order to account for intermolecular associations, the dipole moment μ^2 has to be replaced by μ_{eff}^2, which defines the Kirkwood dipole-dipole correlation factor $g_K = \mu_{\text{eff}}^2 / \mu^2$.

The applicability of the M-M equations to the real nematics was discussed by many authors (e.g. [1–3, 6–10]). However, only quite recently Jadżyn et al. [9, 10] have analysed (1) and (2) taking into account the experimental data on the permittivity and polarizability components of several nematics. These authors fitted the theoretical permittivity components to the experimental ones with β, $\mu_{\text{eff}}^2(T)$ and $S(T)$ as adjustable parameters. In order to achieve consistent fits, they demanded that the $\mu_{\text{eff}}^2(T)$ values obtained from both equations must be the same.

In the present approach we start from (3) and known μ, ϱ, $\Delta\varepsilon$ and S data with the aim to get information about the angle β and the $g_K(T)$-factor. Then, taking the above quantities, the $\varepsilon_{\|}(T)$ and $\varepsilon_{\perp}(T)$ components will be re-established according to (1) and (2) and compared with the experimental data. In two cases the results obtained under high pressure at T = constant will also be analysed. We take into consideration own results obtained for several substances with different dielectric anisotropy and different tendency to form the associates in the nematic phase. It should be mentioned, however, that the number of LC substances for which all quantities occuring in the M-M equations are available, is rather limited.

2. Experimental

The chemical formulae and transition temperatures of the substances studied are listed in Table 1. All of them were synthesised in the Institute of Chemistry, Military University of Technology, Warsaw.

The dielectric permittivity components, $\varepsilon_{\|}$ and $\varepsilon_{\perp}$, were measured with the aid of an HP 4192 A impedance analyser in the range of 10 kHz – 10 MHz. The static permittivity ε_s was taken to be the average of the values of $\varepsilon'(f)$, measured in the region of the plateau of the spectra (usually in the range of 10 – 150 kHz). The parallel-plate capacitor with ca. 0.2 mm distance between electrodes was calibrated with standard liquids. The nematic samples were oriented by a magnetic field of ca. 0.8 T (in the case of substances with the –CN and –NCS terminal groups the parallel orientation was achieved by a DC electric field of ca. 300 V/cm). The temperature was stabilised within ±0.1 K. The refractive indices of 6BAP3 given in Fig. 2b were measured with the aid of an Abbe refractometer. The densities of 6BAP3 and 6BAP(F) were determined with a vibrating-tube densimeter.

3. Results

The results of measurements of the dielectric permittivity components are presented in the lower parts of Figs. 2 – 6 (full symbols) as functions of the shifted temperature $\Delta T = T_{\rm NI} - T$. The anisotropy values are shown in the upper parts of the figures (points). The way of their analysis is as follows. In the first step the function

$$\Delta\varepsilon^{\rm MM}(x) = \varepsilon_0^{-1} \cdot N(x) \cdot h(x) \cdot F(x) \cdot \{\Delta\alpha - F(x) \cdot A(T_{\rm NI} - x) \cdot [g_0 - g_{\rm t}(x)] \cdot B\} \cdot S(x) \quad (4)$$

was fitted to the experimental points, where $A = \mu^2/2\,k_B T$, $x = \Delta T = T_{\rm NI} - T$, $g_{\rm K} = g_0 - g_{\rm t} \cdot \Delta T$, and $B = 1 - 3\cos^2\beta$. The fitting parameters were g_0, $g_{\rm t}$ and B. The data on ϱ, $\Delta\alpha$, $\bar{\alpha}$ and μ were taken from the literature, or come from our own studies (see Table 2). The order parameters $S(T)$ were taken from independent experiments (usually from the optical anisotropy using the equations proposed by Vuks (for discussion of different models see [11]). The fitting procedure becomes easier if $S(T)$ and $S(p)$ are approximated by the Haller-type equations (see [12] and references cited therein)

$$S(\Delta T) = S_0(T_{\rm NI} - T)^{\gamma}, \quad S(\Delta p) = S_0(p - p_{\rm NI})^{\gamma}, \quad (5)$$

with S_0 and γ shown in Table 2. As is seen in upper parts of Figs. 2 – 6 the fits are very good with the parameters gathered in Table 2. Then, using the established quantities, the permittivity components $\varepsilon_{\|}$ and $\varepsilon_{\perp}$ were calculated according to (1) and (2) – open symbols in the figures. The relative deviations from the experimental data $\delta\varepsilon/\varepsilon$, are shown in Table 2.

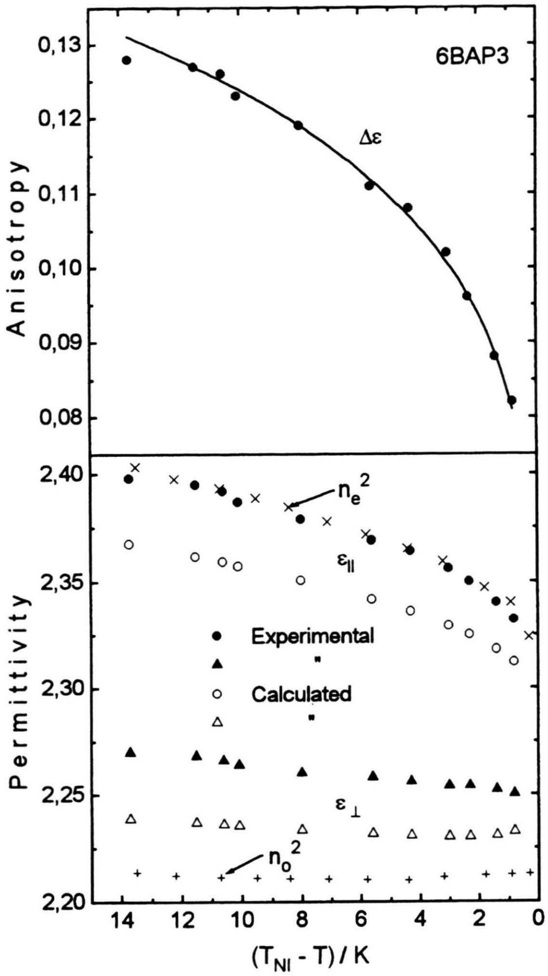


Fig. 2. a) Dielectric anisotropy in the nematic phase of non-polar 6BAP3 versus shifted temperature. The line corresponds to (3) with $\mu = 0$. b) Comparison of the principal permittivity components: experimental (full symbols) and calculated with (1) and (2) (open symbols). n_e and n_o are, respectively, the extraordinary and ordinary refractive indices measured at the D-line of Na.

4. Discussion

Some molecular parameters of LC substances are not well known. This especially concerns the angle β. The value of β is measured with respect to the "long molecular axis" treated as the lowest inertia moment axis and thus it is sensitive to the intramolecular motions of molecular fragments. Therefore β can be dependent on the temperature and on an actual phase. For the isotropic phase β might be estimated via a separation of the dielectric increments, $\varepsilon_s - \varepsilon_\infty$, responsible for the

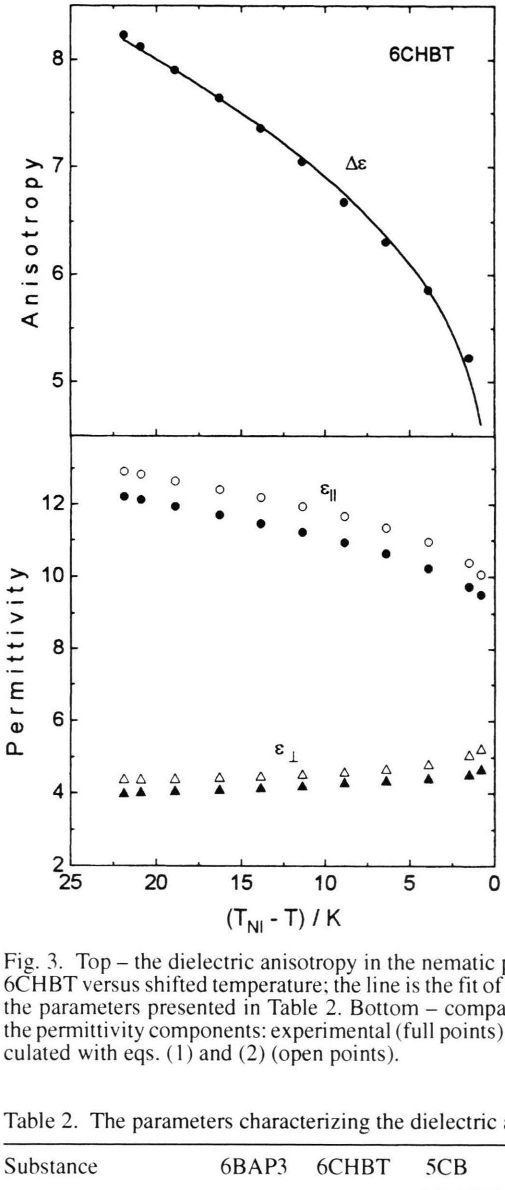


Fig. 3. Top – the dielectric anisotropy in the nematic phase of 6CHBT versus shifted temperature; the line is the fit of (4) with the parameters presented in Table 2. Bottom – comparison of the permittivity components: experimental (full points) and calculated with eqs. (1) and (2) (open points).

molecular rotations around the long and short axes [13–15, 28].

The dielectric permittivities of four of the studied substances (5CB, 6OCB, 7CP5BOC, and 7CP7BOC) were recently analysed by Jadżyn et al. [9, 10] with the aid of (1) and (2). The authors fitted the theoretical permittivity components to the experimental ones with β, $\mu^2_{\mathrm{eff}}(T)$ and $S(T)$ as the adjustable parameters. In order to achieve consistent fits they demanded that the $\mu^2_{\mathrm{eff}}(T)$ values obtained from both equations are equal. The present approach starts from the experimental dielectric anisotropy $\Delta\varepsilon$ and known order parameter, and then the permittivity components $\varepsilon_{\|}$ and $\varepsilon_{\perp}$ are recovered. That means that we consider one Kirkwood correlation factor in the nematic phase. Moreover, it is assumed that g_K depends linearly on the temperature or pressure.

Let us shortly comment the obtained results:

Non-polar substance. 6BAP3 does not contain polar groups, so its permittivity components are comparable with the respective n^2-values, see Fig. 2 (bottom). The dielectric anisotropy is positive and can nicely be described by (3) without the dipolar part, Fig. 2 (top). The calculated permittivity components (open symbols at the bottom) are lower by ca. 2% than the experimental ones (full points).

Substances with positive anisotropies. 6CHBT has a dipole moment created mainly by the –NCS group which is a little smaller than that of the –CN group (Table 2). The substance exhibits a moderate tendency to form antiparallel dimers in the nematic phase [16–18]. The fit shown in Fig. 3 corresponds to β=24.5° and g_K=0.70 (that weakly changes with T), in good agreement with other observations [14, 16]. The permittivity compo-

Table 2. The parameters characterizing the dielectric anisotropy of the nematic phase in particular substances.

Substance	6BAP3	6CHBT	5CB		6OCB		6BAP(F)	7CP5BOC	7CP7BOC
			p = 1 atm	T = 313 K	p = 1 atm	T = 323 K			
μ/D	0	3.48^{b}	4.71^{e}		4.60^{h}		2.31^{m}	1.92^{n}	1.86^{a}
$\bar{\alpha}\times10^{24}$/cm^3	43.82^{a}	34.04^{c}	33.7^{e}		35.2^{i}		40.9^{a}	50.2^{n}	53.8^{o}
$\Delta\bar{\alpha}\times10^{24}$/cm^3	7.65^{a}	16.8^{c}	17.6^{e}		23.25^{i}		11.6^{a}	11.0^{n}	10.1^{o}
β/deg	–	24.5	21.6	21.0	26.3	21.3	66.3	85.5	82.6
S_0	0.365^{a}	0.447^{d}	0.446^{f}	0.283^{g}	0.355^{j}	0.22^{k}	0.413^{a}	0.38^{n}	0.423^{o}
γ	0.163^{a}	0.142^{d}	0.141^{f}	0.17^{g}	0.19^{j}	0.189^{k}	0.134^{a}	0.17^{n}	0.14^{o}
g_0	1	0.70	0.53	0.53	0.79	0.79	1.0	1.0	1.0
$g_t\times10^3$/K^{-1} or MPa^{-1}	0	0.1	0.4	0.45	2.75	0.5	3.0	2.9	2.6
density	^{a}	ref. [16]	ref. [25]	ref. [25]	ref. [27]	^{l}	^{a}	ref. [22]	ref. [10]
$\delta\varepsilon/\varepsilon$% $\|$	–2	+6	–1.5	+3	+1.5	+13	–2	–1.5	–2.5
$\delta\varepsilon/\varepsilon$% $\perp$	–2	+6	–2	+14	+4	+5	–3	+2	–2

[a] this study, [b] [17], [c] [16], [d] according to [16], [e] [7], [f] [12], [g] [26], [h] [28], [i] [23], [j] [24], [k] [21], [l] unknown; we assumed the same compressibility value as was obtained for the N phase of 6CB [25], [m] [13], [n] [22], [o] [10].

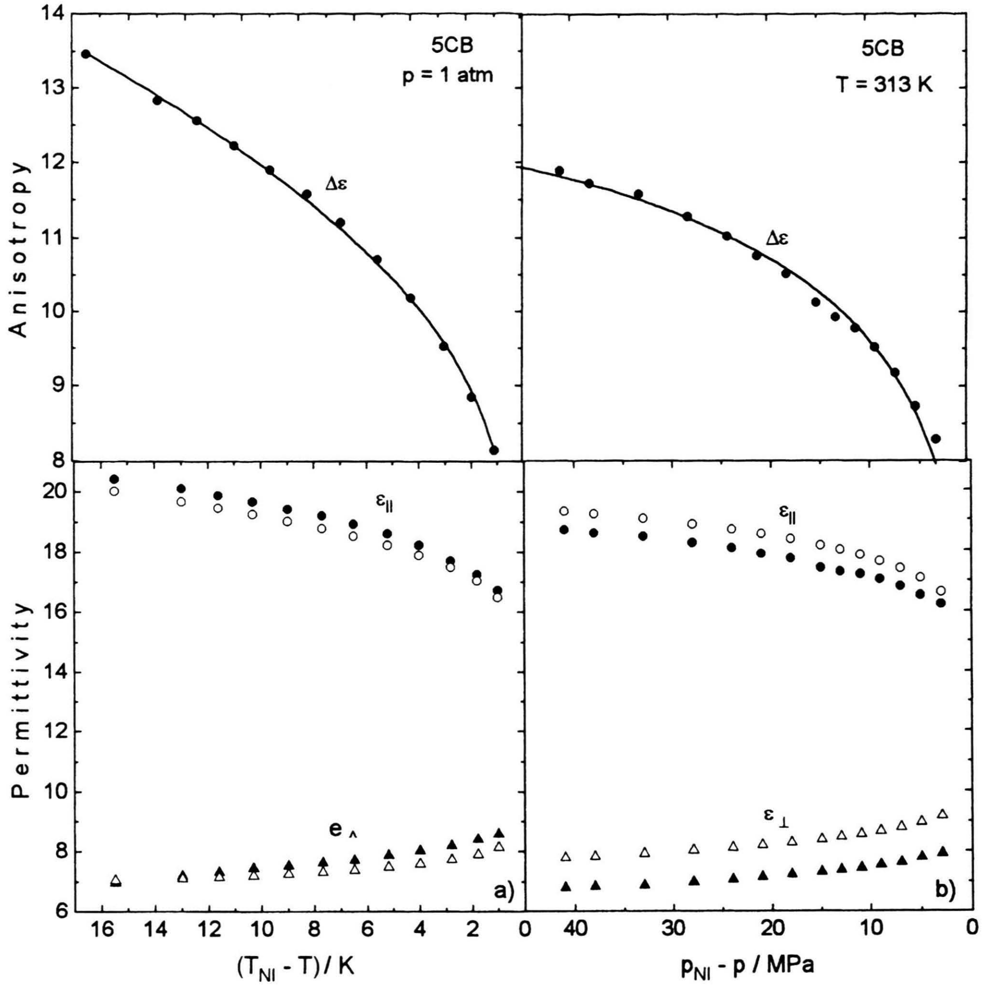


Fig. 4. Dielectric parameters obtained for the nematic phase of 5CB at isobaric (a) and isothermal (b) conditions. The symbols as in Figure 3.

nents are by ca. 6% larger, however, than the experimental values (Fig. 3, bottom). The cyano-biphenyl compounds (5CB and 6OCB) are known to show antiparallel associates in the nematic phase characterised by g_K-factors of ca. 0.5 [9, 19–21]. Moreover, these substances have large positive dielectric anisotropies which make the applicability of the M-M equations additionally doubtful. Astonishingly, a nice consistency of the calculated anisotropies with the experimental data was achieved (Figs. 4 and 5). In the case of 5CB and 6OCB the analysis can be done for varying temperature at ambient pressure, as well for varying pressure at $T =$ const [20, 21]. As can be seen in Figs. 4 and 5 (top) the anisotropy measured at isobaric and isothermal conditions can be fitted very well by (4) with similar parameters (Table 2). It should be mentioned, however, that the angle $\beta \approx 21°$ obtained for 5CB is close to that estimated for the isotropic phase (26°) [15], but is markedly larger than that estimated by Jadżyn et al. [9] (13°) and obtained from the ab initio and semi-empirical calculations by Demus and Inukai [3] (ca. 9°). In the case of 6OCB, the present values (26° and 21°) lie between that estimated for the isotropic phase (31°) [15] and from the analysis of the permittivity components (17°) [9]. It

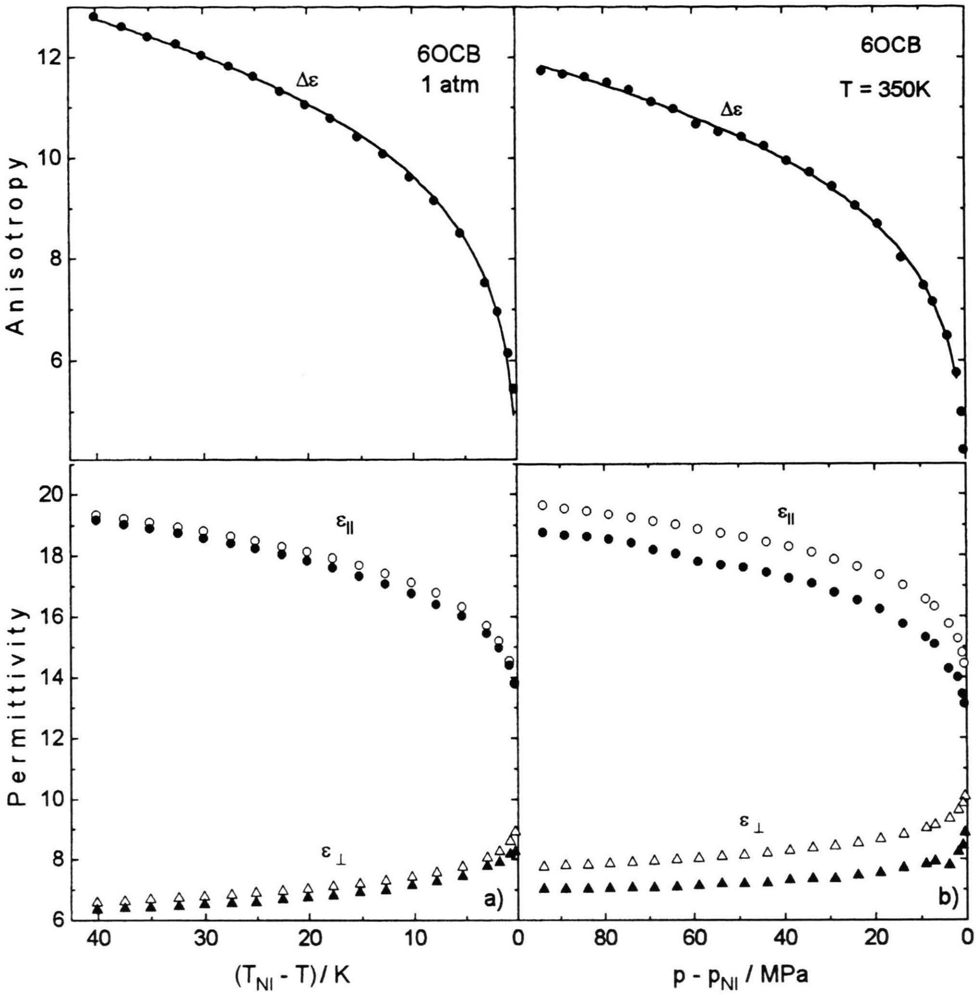


Fig. 5. Dielectric parameters obtained for the nematic phase of 6OCB at isobaric (a) and isothermal (b) conditions. The symbols as in Figure 3.

is characteristic that for both substances the permittivity components obtained in the temperature studies are reproduced markedly better than those coming from the pressure studies (compare Figs. 4 and 5, bottom).

Substances with a negative anisotropy. Due to the *ortho*-position of the F or Cl atoms in 6BAP(F) and 7CP*n*BOC, the angle β is large and the substances exhibit a negative dielectric anisotropy in the N phase [9, 10, 13]. The fits of (4) to the experimental points are again quite satisfactory (Figs. 6a, b, c). The estimated β-values are close to those reported previously [9, 10, 13].

It should be added that the value of the Kirkwood g_K-factor strongly depends upon the assumed value of the dipole moment μ corresponding to a free molecule. In the case of the substances studied here, careful measurements in diluted solutions have been done for 5CB [8, 29] and 6CHBT [17] only. For other substances, μ was estimated using the Onsager equation for the isotropic liquid or by group dipole moment calculations. Therefore, we do not discuss the values of the g_K factor.

5. Conclusions

In spite of drastic assumptions (isotropic cavity field, spherical shape of molecules) the Maier-Meier equations

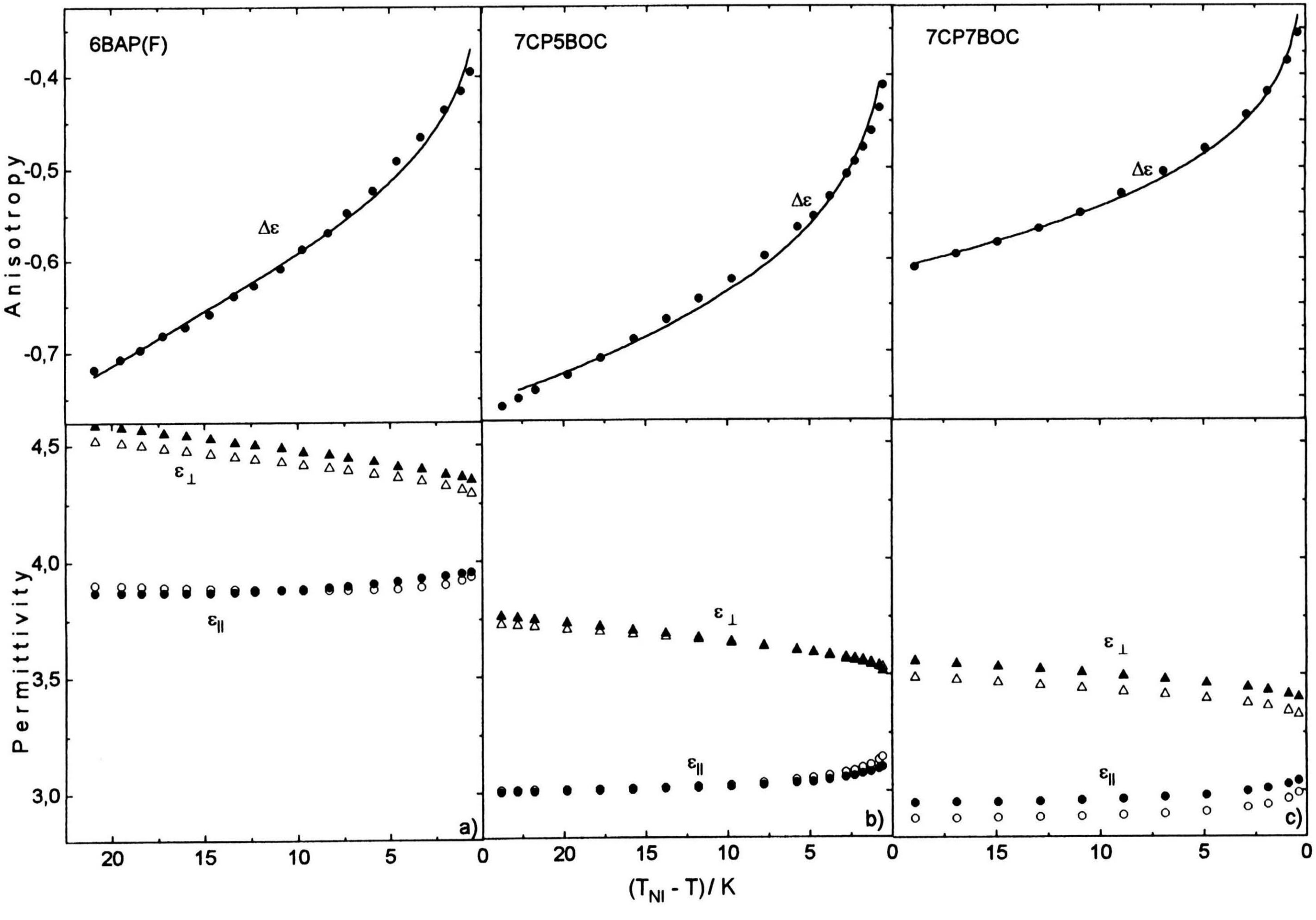


Fig. 6. Dielectric parameters obtained for the nematic phase of three substances with negative anisotropy: (a) 6BAP(F), (b) 7CP5BOC and c) 7CP7BOC. The symbols as in Figure 3.

describe fairly correctly the dielectric permittivity components of nematics. Having the anisotropy $\Delta\varepsilon\ (T)$ and the order parameter $S(T)$, one can obtain information about the angle β and the dipole correlation factor in the N phase. Knowing the parameters of (3), one can determine both components of the permittivity according to (1) and (2) with an accuracy of ca. 6% or better. The above concerns substances with both positive and negative dielectric anisotropies, with strong longitudinal as well as zero dipole moment. Astonishingly, in the case of the isothermal pressure studies the M-M equations do not correlate with the experimental data so well.

[1] M. Klasen, M. Bremer, A. Goetz, A. Manabe, S. Naemura, and K. Tarumi, Japan J. Appl. Phys. **37,** L945 (1998).
[2] A. Fujita, M. Ushioda, H. Takeuchi, T. Inukai, and D. Demus, Mol. Cryst. Liq. Cryst. **331,** 2165 (1999).
[3] D. Demus and T. Inukai, Liq. Cryst. **26,** 1257 (1999).
[4] W. Maier and G. Meier, Z. Naturforsch. **16a,** 262, 470 (1961).
[5] L. Onsager, J. Amer. Chem. Soc. **58,** 1486 (1936).
[6] W. H. de Jeu, Physical Properties of Liquid Crystalline Materials, Gordon and Breach 1980, Chapt. 5.
[7] H. Kresse, Adv. Liq. Cryst. **6,** 109 (1983).
[8] D. A. Dunmur, M. R. Manterfield, W. H. Miller, and J. K. Dunleavy, Mol. Cryst. Liq. Cryst. **45,** 127 (1978).
[9] J. Jadżyn, S. Czerkas, G. Czechowski, A. Burczyk, and R. Dąbrowski, Liq. Cryst. **26,** 437 (1999).
[10] R. Dąbrowski, J. Jadżyn, J. Dziaduszek, Z. Stolarz, G. Czechowski, and M. Kasprzyk, Z. Naturforsch. **54a,** 448 (1999).
[11] J. Kędzierski, Z. Raszewski, J. Rutkowska, W. Piecek, P. Perkowski, J. Żmija, R. Dąbrowski, and J. W. Baran, Mol. Cryst. Liq. Cryst. **282,** 205 (1996).
[12] S. Urban, A. Würflinger, and B. Gestblom, Phys. Chem. Chem. Phys. **1,** 2787 (1999).
[13] S. Urban, B. Gestblom, R. Dąbrowski, and H. Kresse, Z. Naturforsch. **53a,** 134 (1998).
[14] S. Urban, B. Gestblom, and R. Dąbrowski, Liq. Cryst. **24,** 681 (1998).
[15] S. Urban, B. Gestblom, and A. Würflinger, Mol. Cryst. Liq. Cryst. **331,** 1973 (1999).
[16] J. W. Baran, Z. Raszewski, R. Dąbrowski, J. R. Kędzierski, and J. Rutkowska, Mol. Cryst. Liq. Cryst. **123,** 237 (1985).
[17] P. Kędziora and J. Jadżyn, Acta Phys. Polon. **A77,** 605 (1990).
[18] P. Kędziora, J. Jadżyn, and P. Bonnet, Ber. Bunsenges. Phys. Chem. **97,** 864 (1993).
[19] D. A. Dunmur and K. Toriyama, Liq. Cryst. **1,** 169 (1986).
[20] S. Urban, Z. Naturforsch. **50a,** 826 (1995).
[21] S. Urban, Z. Naturforsch. **54a,** 365 (1999).
[22] R. Dąbrowski, J. Jadżyn, S. Czerkas, J. Dziaduszek, and A. Walczak, Mol. Cryst. Liq. Cryst. **332,** 2571 (1999).
[23] M. Mitra, Mol. Cryst. Liq. Cryst. **241,** 17 (1994).
[24] R. Y. Dong and G. Ravindranath, Liq. Cryst. **17,** 47 (1994).
[25] M. Sandmann and A. Würflinger, Z. Naturforsch. **53a,** 233 (1998); M. Sandmann, Thesis, Ruhr University of Bochum 1998.
[26] R. G. Horn, J. Physique, **39,** 167 (1978); R. G. Horn and T. E. Faber, Proc. Roy. Soc. A, **368,** 199 (1979).
[27] M. J. Bradshaw, E. P. Reynes, J. D. Bunning, and T. E. Faber, J. Physique **46,** 1513 (1985).
[28] S. Urban, B. Gestblom, H. Kresse, and R. Dąbrowski, Z. Naturforsch. **51a,** 834 (1996).
[29] P. Kędziora and J. Jadżyn, Liq. Cryst. **8,** 445 (1990).