Liquid Crystals
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713926090

On the molecular interpretation of the static dielectric properties of nematic liquid crystals

J. Jadzyn

To cite this Article Jadzyn, J.(1999) 'On the molecular interpretation of the static dielectric properties of nematic liquid crystals', Liquid Crystals, 26: 3, 437 — 442

To link to this Article: DOI: 10.1080/026782999205218

URL: http://dx.doi.org/10.1080/026782999205218

LIQUID CRYSTALS, 1999, VOL. 26, NO. 3, 437–442

On the molecular interpretation of the static dielectric properties of nematic liquid crystals

J. JADŻYN*, S. CZERKAS, G. CZECHOWSKI, A. BURCZYK
Institute of Molecular Physics, Polish Academy of Sciences, Smoluchowskiego 17,
60-179 Poznań, Poland

and R. DĄBROWSKI
Institute of Chemistry, Military Technical Academy, 00-908 Warsaw, Poland

(*Received 10 August 1998; accepted 3 October 1998*)

This paper shows that on the basis of the temperature dependence of the principal static permittivities of nematics $\varepsilon_{\|}(T)$ and $\varepsilon_{\perp}(T)$, using the Maier–Meier equations, the following quantities can be obtained: (*i*) the angle between the dipole moment vector and the long axis of the mesogenic molecules, (*ii*) the square of the apparent molecular dipole moment $\mu_{\mathrm{app}}^2(T)$ and (*iii*) the nematic order parameter $S(T)$.

1. Introduction

The possibility of obtaining a uniform orientation of the molecules in a whole sample by external factors (electric/magnetic field or special surface preparation) is not only the basis of the applications of nematics in many electro-optical devices, but also that which makes them very attractive from the molecular physics point of view. The latter attraction results from the fact that the macroscopic properties of nematics can be measured in directions correlated with the principal molecular axes and this circumstance allows one to determine essential molecular quantities.

The static dielectric properties of nematic liquid crystals have been a subject of interest from the beginning of investigations of these materials [1–3]. In 1961, Maier and Meier published their theory of the static dielectric properties of nematics [4], as an extension of the Onsager theory of isotropic dipolar liquids [5]. The authors showed that the electric permittivities measured respectively parallel ($\varepsilon_{\|}$) and perpendicular ($\varepsilon_{\perp}$) to the molecular alignment (director **n**) are related to the molecular quantities by the following equations:

$$\varepsilon_{\|} = \frac{NhF}{\varepsilon_0}\left\{\alpha + \frac{2}{3}\Delta\alpha\ S + F\ \frac{\mu_{\mathrm{app}}^2}{3kT}[1-(1-\cos^2\beta)S]\right\} \tag{1}$$

$$\varepsilon_{\perp} = \frac{NhF}{\varepsilon_0}\left\{\alpha + \frac{1}{3}\Delta\alpha\ S + F\ \frac{\mu_{\mathrm{app}}^2}{3kT}\left[1+\frac{1}{2}(1-\cos^2\beta)S\right]\right\} \tag{2}$$

where $\varepsilon_0 = 8.85\times10^{-12}\ \mathrm{F\,m^{-1}}$, N is the number of molecules per unit volume, and h and F are the Onsager local field factors:

$$h = \frac{3\varepsilon}{2\varepsilon+1}, \qquad F = \frac{1}{1-\alpha f}, \qquad f = \frac{2(\varepsilon-1)}{2\varepsilon+1}\frac{N}{3\varepsilon_0}. \tag{3}$$

The α and ε are the mean values of the polarizability and the permittivity, respectively:

$$\alpha = \frac{1}{3}(\alpha_l + 2\alpha_t), \qquad \varepsilon = \frac{1}{3}(\varepsilon_{\|} + 2\varepsilon_{\perp}) \tag{4}$$

and

$$\Delta\alpha = \alpha_l - \alpha_t \tag{5}$$

denotes the anisotropy of the polarizability. The α_l and α_t are the components of the polarizability tensor along the long and short molecular axes, respectively (see figure 1). β is the angle between the total dipole moment vector μ of the nematogenic molecule and its long axis. S is the order parameter defined as

$$S = \frac{1}{2}\langle 3\cos^2\Theta - 1\rangle \tag{6}$$

where Θ is the angle between the molecular long axis and the direction of the macroscopic orientation indicated by **n** (see figure 1).

For the isotropic phase ($\varepsilon_{\|} = \varepsilon_{\perp} = \varepsilon$, $S = 0$), equations (1) and (2) transform into the Onsager equation [6]:

$$\frac{(\varepsilon-n^2)(2\varepsilon+n^2)}{\varepsilon(n^2+2)^2} = \frac{N}{3\varepsilon_0}\frac{\mu_{\mathrm{app}}^2}{3kT} \tag{7}$$

---

*Author for correspondence.

Journal of Liquid Crystals ISSN 0267-8292 print/ISSN 1366-5855 online ©1999 Taylor & Francis Ltd
http://www.tandf.co.uk/JNLS/lct.htm
http://www.taylorandfrancis.com/JNLS/lct.htm

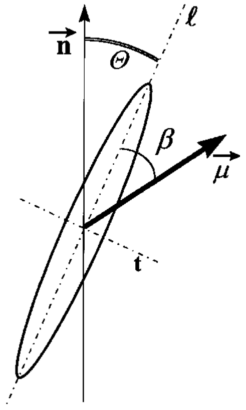


Figure 1. Meaning of some geometrical quantities concerning a dipolar nematogenic molecule (μ) situated inside the oriented nematic phase. The vector **n** denotes the direction of macroscopic nematic orientation. The symbols *l* and *t* denote the molecular long and short axes, respectively.

where the refractive index n and the polarizability α are connected by the Lorenz equation:

$$\frac{n^2-1}{n^2+2}=\frac{N}{3\varepsilon_0}\alpha \tag{8}$$

Because the Onsager local field model does not take into account the intermolecular (dipolar) correlation, the apparent dipole moment (μ_{app}) is introduced in equations (1), (2) and (7) [6, 7]. The relation between μ_{app} and the dipole moment value of the isolated molecule (μ_o) is most often expressed by the Kirkwood correlation factor g:

$$g=\mu_{app}^2/\mu_o^2. \tag{9}$$

The value of g indicates directly the predominant type of intermolecular interaction in the system investigated: for $g > 1$, there are the parallel dipolar correlations; for $g < 1$, the antiparallel correlations.

The Maier–Meier equations (1) and (2) are constantly the basis of molecular interpretations of the static dielectric properties of nematics. Often the so-called ‘effective dipole moments’:

$$\mu_{\parallel eff}^2=\mu_{app}^2[1-(1-\cos^2\beta)S] \tag{10}$$

and

$$\mu_{\perp eff}^2=\mu_{app}^2\left[1+\frac{1}{2}(1-3\cos^2\beta)S\right] \tag{11}$$

are calculated from equations (1) and (2), respectively. Next, the values of $\mu_{\parallel eff}^2$ and $\mu_{\perp eff}^2$ are compared with the values of $\mu_{\parallel}^2$ and $\mu_{\perp}^2$ calculated from the assumed (or resulting from the quantum-mechanics computer programs) geometry of the nematogenic molecule (the β angle). The temperature dependence of the order parameter $S(T)$, appearing in equations (10) and (11), is taken from independent experiments, mainly from measurements of the refractive indices. The ratios $g_{\parallel}=\mu_{\parallel eff}^2/\mu_{\parallel}^2$ and $g_{\perp}=\mu_{\perp eff}^2/\mu_{\perp}^2$ are considered to be the Kirkwood factors for the dipolar correlation in two principal directions of the oriented nematic. It is not easy to understand the physical meaning of $g_{\parallel}$ and $g_{\perp}$, i.e. the anisotropy in dipole–dipole interaction.

This paper shows that the description of the experimental dependences of the parallel $\varepsilon_{\parallel}(T)$ and the perpendicular $\varepsilon_{\perp}(T)$ permittivities of nematics by the Maier–Meier equations (1) and (2) has a physical significance only for very precisely measured values of β and $S(T)$. The lack of the physical meaning arises from the fact that for the improper values of β and/or $S(T)$, one obtains different $\mu_{app}^2(T)$ dependences corresponding to $\varepsilon_{\parallel}(T)$ and $\varepsilon_{\perp}(T)$, which can be interpreted as the anisotropy in the dipolar interactions.

2. Experimental

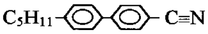
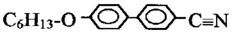
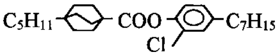
2.1. *Materials*

The nematic liquid crystals studied are presented in the table. They were synthesized in the Institute of Chemistry, Military Technical Academy, Warsaw. The compound 7CP-5BOC (2-chloro-4-pentylphenyl 4-heptylbicyclo-[2,2,2]octan-1-carboxylate) is a new low temperature nematic of a negative dielectric anisotropy. Its synthesis and basic physical properties have been described elsewhere [8].

2.2. *Apparatus*

The static electric permittivity was measured with a Wayne Kerr 6425 Precision Analyser at 10 kHz. The samples were placed in a plane copper capacitor with gold-covered electrodes. The thickness of the liquid crystal layer was 0.5 mm. To orient the nematics, a magnetic field of **B** = 0.8 T was used. The permittivity components $\varepsilon_{\parallel}$ and $\varepsilon_{\perp}$ of the ordered liquid crystal were measured with the electric field **E** parallel and perpendicular to **B**, respectively. The accuracy of the permittivity measurements was 0.01%.

Table. Structures and temperatures of the nematic–isotropic phase transitions of the compounds studied.

Acronym	Molecular structure	T_{NI}/°C
5CB		35.3
6OCB		75.9
7CP-5BOC		43.6

The temperature was controlled with an accuracy of ±0.01°C. The density was measured with an Anton Paar DMA 60/602 densimeter with an accuracy of 0.01%.

3. Results and discussion

The molecular interpretation of the static dielectric properties of nematics is mainly determined, as we will see later, by the temperature dependence of the order parameter $S(T)$. In principle, the $S(T)$ dependence can be derived from measurements of any anisotropic properties of the nematic [9]. Unfortunately, there are no ways of verifying the $S(T)$ dependences obtained by different methods. Only 'reasonable values' of S, i.e. values between about 0.3 (close to the nematic to isotropic transition) and about 0.6 (far from the transition) are criteria for the correctness of the results. Differences of about 10% in the S value determined by different methods are usually ignored.

The general conviction is that the most reliable values of the nematic order parameter are those which are determined from magnetic anisotropy measurements. We will verify this opinion for the case of 5CB for which the order parameter data, obtained by different methods, are exceptionally numerous.

Figure 2 shows the temperature dependence of $\varepsilon_{\|}$ and $\varepsilon_{\perp}$ in the nematic phase and ε in the isotropic phase of 5CB. The results obtained for the nematic phase will be discussed in the frame of the Maier–Meier equations (1) and (2). For the beginning, the dependence $S(T)$, crucial to us, was taken from the paper by Buka and de Jeu [10], where the method of magnetic anisotropy measurements was used. In the same paper the authors proposed an empirical formula for the temperature dependence of the nematic order parameter

$$S(T)=\left(1-A\frac{T}{T_{\mathrm{NI}}}\right)^{z} \qquad (12)$$

where T_{NI} denotes the nematic to isotropic phase transition temperature (in K), and A is a constant. Numerous data presented in the paper [10] show that for all studied nematics, $A \approx 1$ with an accuracy better than 0.1%. In this paper we assumed that $A = 1$. The equation (12) is a very useful form of presentation of the $S(T)$ dependence, since for different nematics (different T_{NI}) the $S(T)$ function is determined by one parameter (z) only. For example, the $S(T)$ dependence obtained by Buka and de Jeu for 5CB has a form:

$$S(T)=\left(1-\frac{T}{T_{\mathrm{NI}}}\right)^{0.14}. \qquad (13)$$

We used this function ($z = 0.14$) in the molecular interpretation of the experimental dependences $\varepsilon_{\|}(T)$ and $\varepsilon_{\perp}(T)$ of 5CB.

The second essential quantity appearing in the Maier–Meier equations is the molecular quantity—the angle β (see figure 1). In common practice for n-alkylcyanobiphenyls, especially for the homologues of a low n-number, one assumes that the dipole moment vector (C≡N) and the molecular long axis lie in the same direction, i.e. $\beta = 0°$ [11].

The values of $\alpha = 33.2 \times 10^{-24}\,\mathrm{cm}^3$ and $\Delta\alpha = 22.1 \times 10^{-24}\,\mathrm{cm}^3$ have been taken from the paper by Karat and Madhusudana [12].

For the constant values $\beta = 0°$ and $z = 0.14$, one obtains a good fitting of the Maier–Meier equations to the experimental dependences $\varepsilon_{\|}(T)$ and $\varepsilon_{\perp}(T)$ (solid lines in figure 2), however, for the different $\mu^2_{\mathrm{app}}(T)$ dependences, as shown in figure 3(*a*). Although there is a strong temptation to interpret this picture as an anisotropy in dipolar interactions ($g_{\|} \approx 0.45$, $g_{\perp} \approx 0.65$), these results have no physical meaning. The $\mu^2_{\mathrm{app}}(T)$ dependence in both Maier–Meier equations (1) and (2) is by definition the same function.

One can suppose that the $S(T)$ dependence with $z = 0.14$ is correct, but the value $\beta \approx 0°$ is a poor approximation. If β is taken as a parameter, then for $z = 0.14$ one obtains a good fitting of the Maier–Meier equations to the experimental $\varepsilon_{\|}(T)$ and $\varepsilon_{\perp}(T)$ dependences (as in figure 2), for $\beta = 21°$. Putting aside that this β value seems to be too high, in this case the fitting also requires different $\mu^2_{\mathrm{app}}(T)$ dependences for $\varepsilon_{\|}$ and $\varepsilon_{\perp}$, as shown in figure 3(*b*). The differences in the $\mu^2_{\mathrm{app}}(T)$ are here not so drastic as for $\beta = 0°$, but this result also has no physical meaning.

If both β and z are the parameters which can change in the course of the fitting procedure and if we add the conditions that the $\mu^2_{\mathrm{app}}(T)$ dependences have to be the same for both components of the permittivity, the Maier–Meier equations reproduce the experimental $\varepsilon_{\|}(T)$ and $\varepsilon_{\perp}(T)$ values (as in figure 2) for $\beta = 13°$ and $z = 0.18$,

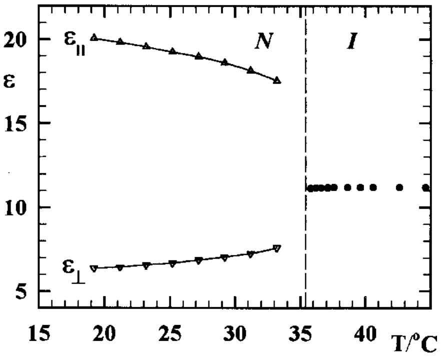


Figure 2. Temperature dependence of the static electric permittivities of 5CB in the nematic (N) and isotropic (I) phases. The solid lines represent the Maier–Meier theoretical predictions, equations (1) and (2).

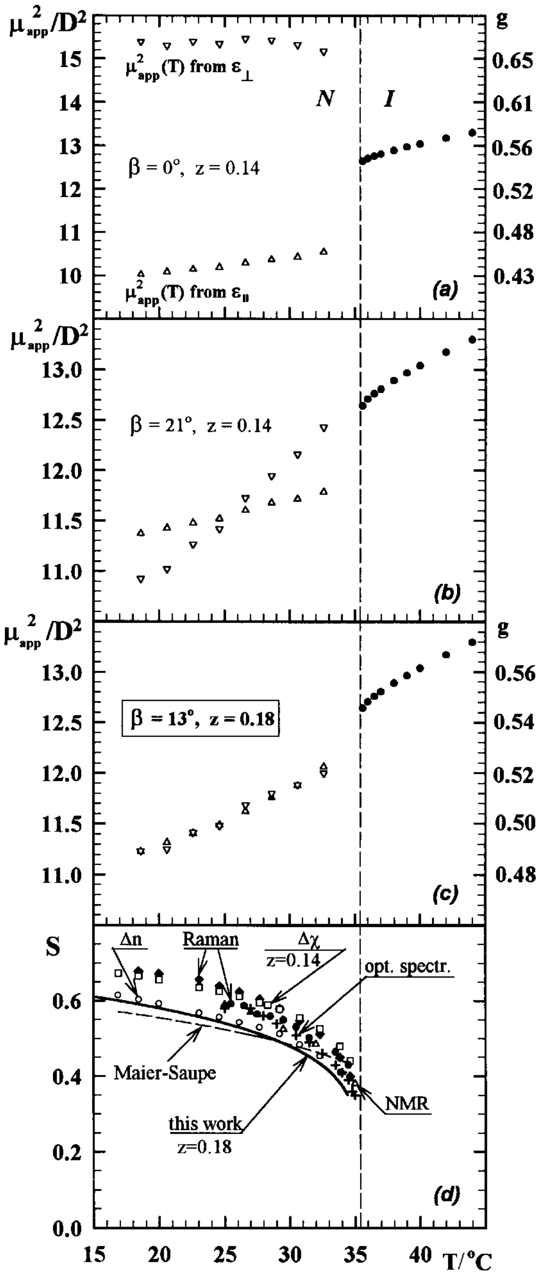


Figure 3. For nematic 5CB a good reproduction of the experimental dependences $\varepsilon_\parallel(T)$ and $\varepsilon_\perp(T)$ by the Maier–Meier equations (1) and (2) (solid lines in figure 2) can be achieved for different sets of β and z values (a, b, c). Only for the values $\beta = 13°$ and $z = 0.18$ do the dependences $\mu^2_{\mathrm{app}}(T)$ resulting from $\varepsilon_\parallel(T)$ and $\varepsilon_\perp(T)$ coincide (c). Part (d) presents the $S(T)$ dependences resulting from measurements based on magnetic anisotropy $\Delta\chi$ [9], Raman scattering (◆ [7], ● [14]), NMR [15], optical spectroscopy [16], and optical anisotropy Δn [17], and those obtained from the Maier–Saupe theory [18] and in the course of this work. g is the Kirkwood correlation factor calculated (equation 9) for $\mu_0 = 4.8$ D [19, 20].

[figure 3 (c)]. The β value is quite reasonable [13] and the $S(T)$ dependence for $z = 0.18$ is presented in figure 3 (d) as a solid line. This line nearly exactly covers the experimental $S(T)$ dependence obtained by Horn from optical anisotropy measurements [17].

For $\beta = 13°$ and $z = 0.18$ the anisotropy in dipolar interactions of 5CB molecules disappears!

The value of the Kirkwood correlation factor g for 5CB is about 0.5 [figure 3 (c)] and its evolution with temperature change, in particular close to the isotropic–nematic phase transition, corresponds to our expectation concerning the dipole–dipole correlation. With temperature decrease, the degree of antiparallel dipolar association rises (g decreases) and the transition from the isotropic phase to the nematic phase manifests itself by an essential intensification of this process.

Figure 4 (a) presents the results of the measurements of the static permittivities for 6OCB. The values of $\alpha = 35.20 \times 10^{-24}$ cm^3 and $\Delta\alpha = 23.25 \times 10^{-24}$ cm^3 have been taken from the paper by Mitra [21]. For $\beta = 17°$ and $z = 0.21$, the Maier–Meier equations perfectly reproduce the experimental results [solid lines in figure 4 (a)] and simultaneously the $\mu^2_{\mathrm{app}}(T)$ dependence is the same for both permittivity components, figure 4 (b). The β value is a little higher than for 5CB, which can be expected because the resulting dipole moment μ of 6OCB is composed of two contributions—from the C≡N and C–O polar groups—which have not exactly the same direction. The $S(T)$ function corresponding to $z = 0.21$ is presented in figure 4 (c) as a solid line. The order parameter values for 6OCB resulting from our studies are somewhat smaller than the value obtained from Δn measurements [21]. The g-factor values for 6OCB are distinctly higher than that for 5CB showing the smaller degree of antiparallel association of 6OCB dipoles as compared with 5CB.

Figure 5 (a) presents the static permittivities for 7CP-5BOC. This compound gives a nematic phase of negative dielectric anisotropy ($\Delta\varepsilon = \varepsilon_\parallel - \varepsilon_\perp < 0$). The values of $\alpha = 50.2 \times 10^{-24}$ cm^3 and $\Delta\alpha = 11.0 \times 10^{-24}$ cm^3 have been taken from the paper by Dąbrowski *et al.* [8]. The solid lines in figure 5 (a) represent the best fitting of the Maier–Meier equations to the experimental values of $\varepsilon_\parallel(T)$ and $\varepsilon_\perp(T)$ for $\beta = 84°$ and $z = 0.17$ [figure 5 (b)]. The β value obtained in our studies is expected if one takes into account the structure of the 7CP-5BOC molecule with a dipolar substituent (–Cl) in a lateral position. The solid line in figure 5 (c) presents the $S(T)$ dependence corresponding to $z = 0.17$. The order parameter values obtained for 7CP-5BOC in dielectric studies are very close to the values obtained from optical anisotropy measurements [8].

4. Conclusions

The Maier–Meier equations describe fairly well the static dielectric properties of homogeneously oriented nematics

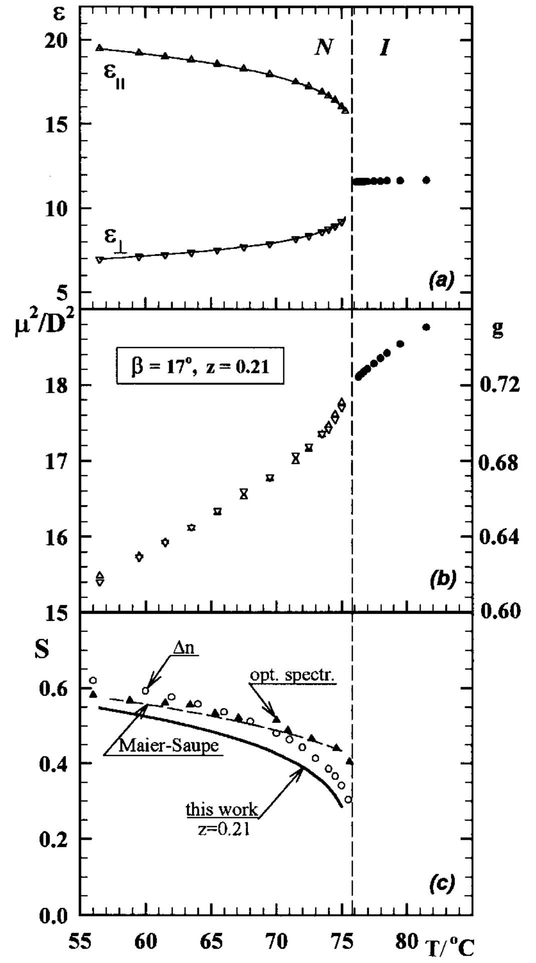


Figure 4. For nematic 6OCB the best fitting of the Maier–Meier equations (1) and (2) to the experimental dependences $\varepsilon_{\|}(T)$ and $\varepsilon_{\perp}(T)$ [solid lines in (*a*)] with the condition of $\mu^2_{\mathrm{app}}(T)$ coincidence (*b*), are obtained for $\beta = 17°$ and $z = 0.21$. The $S(T)$ dependence obtained in this work is compared (*c*) with that obtained from Δn measurements [21], optical spectroscopy [22], and Maier–Saupe predictions [18]. g is the Kirkwood correlation factor calculated (equation 9) for $\mu_0 = 5$ D [23].

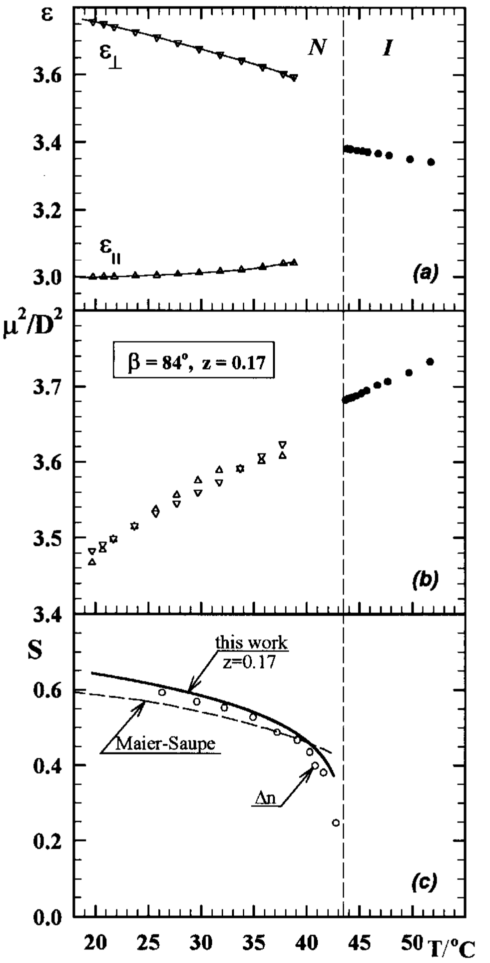


Figure 5. For nematic 7CP-5BOC, the best fitting of the Maier–Meier equations (1) and (2) to the experimental $\varepsilon_{\|}(T)$ and $\varepsilon_{\perp}(T)$ dependences [solid lines in (*a*)] with the condition of coincidence of $\mu^2_{\mathrm{app}}(T)$ (*b*), are obtained for $\beta = 84°$ and $z = 0.17$. In (*c*) the $S(T)$ dependence obtained is compared with that resulting from Δn measurements [8] and Maier–Saupe theory [18].

and allow one to obtain simultaneously important molecular quantities (the β angle and the $\mu^2_{\mathrm{app}}(T)$ dependence) and, no less important, the (macroscopic) nematic order parameter $S(T)$. Resulting from the dielectric studies, the $S(T)$ values are close to those obtained from the optical anisotropy measurements, but the case of 6OCB shows [figure 4 (*c*)] that this does not always happen.

The results presented in this paper show that the analysis of the static dielectric properties of nematics with the use of experimental S values should be made with care. The differences in the $\mu^2_{\mathrm{app}}(T)$ dependences obtained from $\varepsilon_{\|}(T)$ and $\varepsilon_{\perp}(T)$, which can be interpreted as an anisotropy in dipole–dipole interactions, depend strongly on the chosen $S(T)$ function: too high S values can lead to the conclusion that $g_{\|} < g_{\perp}$, as in figure 3 (*a*), and too low S values can lead, for the same system, to the reverse conclusion. Which $S(T)$ dependence is true for the nematic studied? This is a very difficult question and perhaps the results presented in this paper gave some indications relevant to this matter.

Our experience shows that results for $\varepsilon_{\|}(T)$ and $\varepsilon_{\perp}(T)$ obtained for an imperfectly oriented nematic sample cannot be interpreted in the frame of the Maier–Meier equations, i.e. with the same β, $S(T)$ and $\mu^2_{\mathrm{app}}(T)$ both for $\varepsilon_{\|}(T)$ and $\varepsilon_{\perp}(T)$. This problem often occurs in the temperature range just before the nematic–isotropic phase transition, where the molecular orientation forced by the magnetic field (for example) can be strongly disturbed by nematic–electrode surface interactions.

Such effects can be seen in figures 2 and 5 where the experimental results are described by the Maier–Meier equations only for temperatures several degrees below the isotropic–nematic phase transitions.

References

[1] De Jeu, W. H., 1980, *Physical Properties of Liquid Crystalline Materials* (Gordon and Breach).

[2] Kresse, H., 1983, *Advances in Liquid Crystals*, Vol. 6, edited by G. H. Brown (Academic Press), pp. 109–172.

[3] Urban, S., and Würflinger, A., 1997, *Advances in Chemical Physics*, Vol. 98, edited by I. Prigogine and S. A. Rice (John Wiley & Sons), pp. 143–216.

[4] Maier, W., Meier, G., 1961, *Z. Naturforsch. A*, **16**, 262.

[5] Onsager, L., 1936, *J. Am. chem. Soc.*, **58**, 1486.

[6] Böttcher, C. J. F., and Bordewijk, P., 1978, *Theory of Electric Polarization*, Vol. 2 (Elsevier).

[7] Dalmolen, L. G. P., Picken, S. J., de Jong, A. F., and de Jeu, W. H., 1985, *J. Phys. (Paris)*, **46**, 1443.

[8] Dąbrowski, R., Jadżyn, J., Czerkas, S., Dziaduszek, J., and Walczak, A., *Mol. Cryst. liq. Cryst.* (in the press).

[9] de Gennes, P. G., and Prost, J., 1993, *The Physics of Liquid Crystals*, 2nd Edn (Clarendon).

[10] Buka, A., and de Jeu, W. H., 1982, *J. Phys. (Paris)*, **43**, 361.

[11] See for example Stegemeyer, H., 1994, *Topics in Physical Chemistry*, edited by H. Baumgärtel, E. U. Franck, and W. Grünbein, Vol. 3, *Liquid Crystals* (Springer), p. 72.

[12] Karat, P. P., and Madhusudana, N. V., 1976, *Mol. Cryst. liq. Cryst.*, **36**, 51.

[13] Ferrarini, A., and Nordio, P. L., 1991, *Mol. Cryst. liq. Cryst.*, **198**, 159.

[14] Miyano, K., 1978, *J. chem. Phys.*, **69**, 4807.

[15] Emsley, J. W., Luckhurst, G. R., and Stockley, C. P., 1981, *Mol. Phys.*, **44**, 565.

[16] Bauman, D., 1988, *Mol. Cryst. liq. Cryst.*, **159**, 197.

[17] Horn, R. G., 1978, *J. Phys. (Paris)*, **39**, 167.

[18] Maier, W., and Saupe, A., 1959, *Z. Naturforsch. A*, **14**, 882.

[19] Dunmur, D. A., Manterfield, M. R., Miller, W. H., and Dunleavy, M. K., 1978, *Mol. Cryst. liq. Cryst.*, **45**, 127.

[20] Kędziora, P., and Jadżyn, J., 1990, *Liq. Cryst.*, **8**, 445.

[21] Mitra, M., 1994, *Mol. Cryst. liq. Cryst.*, **241**, 17.

[22] Moryson, H., Kozłowski, K., and Bauman, D., *Mol. Cryst. liq. Cryst.* (in the press).

[23] Druon, C., 1984, PhD thesis, University of Lille, France.