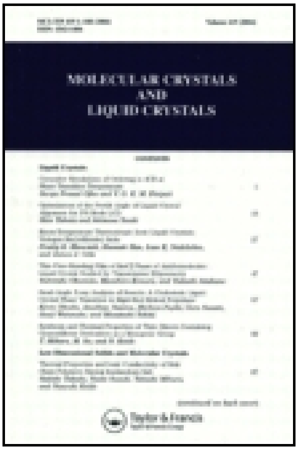

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Temperature Dependence of the Static Relative Permittivity of Octylcyanobiphenyl (8CB)[†]

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Measurements of the relative static permittivity ε of octylcyanobiphenyl (8CB) in the smectic A, the nematic and the isotropic phases between 22°C and 140°C are reported. The resolution of the measurements was better than 0.01% and the temperature stability was better than 0.01°C. Detailed measurements have been carried out near the AN and NI transitions. For the AN transition, no discontinuity in $\varepsilon_\parallel$ or $\varepsilon_\perp$ was observed, which is consistent with the second-order nature of this transition in 8CB. From the dielectric anisotropy in the N-phase, a critical exponent $\beta \simeq 0.25$ was obtained for the temperature dependence of the order parameter. This value of β is in support of the hypothesis of quasi-tricriticality for this transition. In the isotropic phase of 8CB, a pretransitional anomalous maximum in ε was observed near T_{NI}. The same effect was also measured for two other materials with cyano-end groups (undecylcyanobiphenyl and pentylcyanophenylcyclohexane). For two compounds without a cyano-end group (p,p'-di-n-heptylazobenzene and trans-p-methoxy-p'-heptyloxy-α-cyano-stilbene) this pretransitional effect was not observed. An explanation for this effect may be found in local antiparallel orientation of the molecular dipoles of the cyano-compounds. The possible role of nematic fluctuations in the isotropic phase is also discussed.

1. INTRODUCTION

For anisotropic, elongated molecules there exists long-range orientational order in the various liquid crystalline phases. On the average, the molecules are aligned with their long axes parallel to each other and define a macro-

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scopic unique axis characterized by the director. In the nematic (N) phase, the centers of mass are randomly distributed and in the smectic-A (A) phase also a one-dimensional density wave is imposed. The uniaxial symmetry of the N and A phases results in anisotropic behavior for several physical quantities. The polarization (per unit volume) for such an anisotropic material is given by:[1]

$$\mathbf{P} = \varepsilon_0 \, (\varepsilon - I) \cdot \mathbf{E} . \tag{1}$$

ε_0 is the permittivity of free space, **E** is the electric field and ε and I are, respectively, the dielectric and the unit tensor. For polar molecules, the polarization can be written in the following way:[1]

$$\mathbf{P} = N \left(\langle \alpha \cdot \mathbf{E}_i \rangle + \langle \overline{\boldsymbol{\mu}} \rangle \right) \tag{2}$$

combination of Eqs. (1) and (2) results in:

$$(\varepsilon - I) \cdot \mathbf{E} = (N/\varepsilon_0) \left(\langle \alpha \cdot \mathbf{E}_i \rangle + \langle \overline{\boldsymbol{\mu}} \rangle \right) \tag{3}$$

N is the number density, $\mathbf{E}_i$ the internal field acting on a molecule, α the polarizability tensor and $\overline{\boldsymbol{\mu}}$ is the average of the dipole moment in the presence of an electric field. The brackets represent the average over the orientation of the molecules.

By a proper choice of a macroscopic coordinate system with the z-axis parallel to the director, it emerges that for uniaxial symmetry the permittivity differs along the director ($\varepsilon_\parallel$) and perpendicular to it ($\varepsilon_\perp$). From the dielectric anisotropy $\Delta\varepsilon = \varepsilon_\parallel - \varepsilon_\perp$ it is possible to obtain information on the degree of orientational order in the mesogenic phases. In particular, $\Delta\varepsilon$ can be used to investigate the temperature dependence of the nematic order parameter, which is defined microscopically as:[2]

$$S = \frac{1}{2} \langle 3 \cos^2 \theta - 1 \rangle , \tag{4}$$

with θ the angle between the long molecular axis and the director. From Eqs. (2) and (3), it should be clear that for the isotropic phase also, interesting information on the molecular polarizability and on the dipole-moments can be deduced from the permittivity. In particular, dipole correlations might strongly affect the dielectric behavior for polar molecules.

In this paper we report high precision measurements of the static permittivity for the liquid crystalline compound octylcyanobiphenyl (8CB) in its smectic-A (A), nematic (N) and isotropic (I) phases in the temperature range between 22°C (the melting point) and 140°C (100°C above the NI transition). Detailed measurements were carried out near the smectic-A to nematic (AN) and the nematic to isotropic (NI) transition points. Some aspects of the dielectric behavior observed for 8CB are discussed further and have been compared with results from measurements now reported on some other liquid crystals.

2. EXPERIMENTAL

The compound 8CB was obtained from BDH Chemicals Ltd. (Poole, Dorset, U.K.) and was used without further purification. The dielectric measurements have been carried out in the frequency range between 10 Hz and 100 kHz by means of General Radio 1615A and 1616A ratio transformer capacitance bridges. The static ε data reported in Section 3 were measured at 1 kHz (for this frequency the accuracy of the capacitance bridges is highest). However, no dispersion was observed up to 100 kHz.

For convenience two different types of dielectric cells have been used in our experiments. The capacitors in both cells are constructed as three-terminal capacitors; this allows for accurate cancellation of the lead capacitances by the ratio transformer bridges. The first measuring cell (Figure 1), which is only suitable for measurements in the isotropic phase, has a cylindrically symmetric capacitor which gives high stability and reproducibility of C_0, the vacuum capacitance. The reproducibility of C_0 after several temperature cycles is better than 0.02%. The distance between the inner and the outer electrodes is about 0.5 mm. The height of the sample between the electrodes is 10 mm. The capacitance of the empty cell is about 4.75 pF. The cell is vacuum-tight and can be evacuated or filled with an inert gas. The whole measuring cell is immersed in a thermostated water or oil bath. The temperature stability is better than 0.01°C. The temperature is measured by means of an HP2850 Quartz thermometer probe.

In Figure 2 a schematic diagram of our second measuring setup is given. The central part is a three-terminal parallel plate capacitor. The electrodes E_1 and E_2 are two disks (with a diameter of about 15 mm) at a separation of 0.5 mm. The small sample cell consisting of the shielding block S, which holds the two electrodes and the insulating spacers, can be separated from the rest of the apparatus and filled with the liquid crystal. The reproducibility of the vacuum capacitance C_0 (of about 0.75 pF) for this parallel plate capacitor is better than 0.1%. The sample cell is in good thermal contact with and completely surrounded by a first temperature controlling stage with heater H and thermistors R_1 and R_2. One of the two calibrated thermistors is used as a thermometer and the other one serves as a sensor in a temperature controlling system, consisting of a Wheatstone bridge (containing the thermistor R_2 in one arm), a sensitive null detector

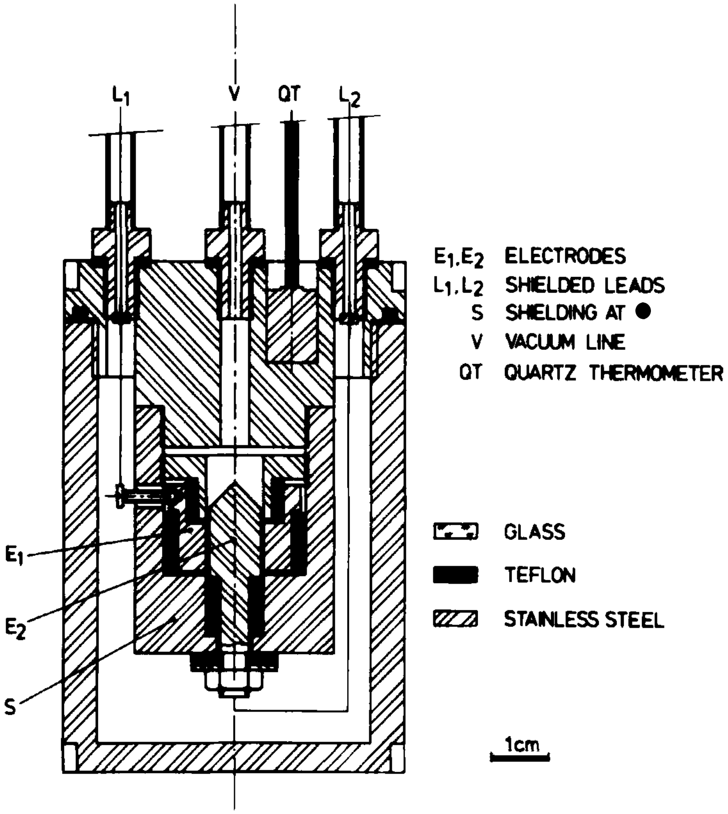

FIGURE 1 Dielectric measuring cell for measurements on the isotropic phase.

and a power amplifier, which delivers the necessary power to the heater H. This first thermal stage is thermally insulated from a second stage around it. The temperature of this shield is kept a few tenths of a degree below the temperature of the central stage and regulated by means of a flow of water at constant temperature through a helicoidal groove machined in the wall. Space between the two thermal stages can be evacuated. With this setup the temperature of the measuring capacitor can be kept constant within a few mK. This apparatus is mainly used for measurements on liquid crystalline phases. The orientation of the sample is obtained by a magnetic field (usually larger than 1 T). For magnetic fields between 0.8 and 1.8 T the measured $\varepsilon_\parallel$ and $\varepsilon_\perp$ values were constant within the quoted accuracy. The part of the apparatus containing the measuring cell fits between the poles of the magnet at a separation of 5 cm. The orientation of the electric field

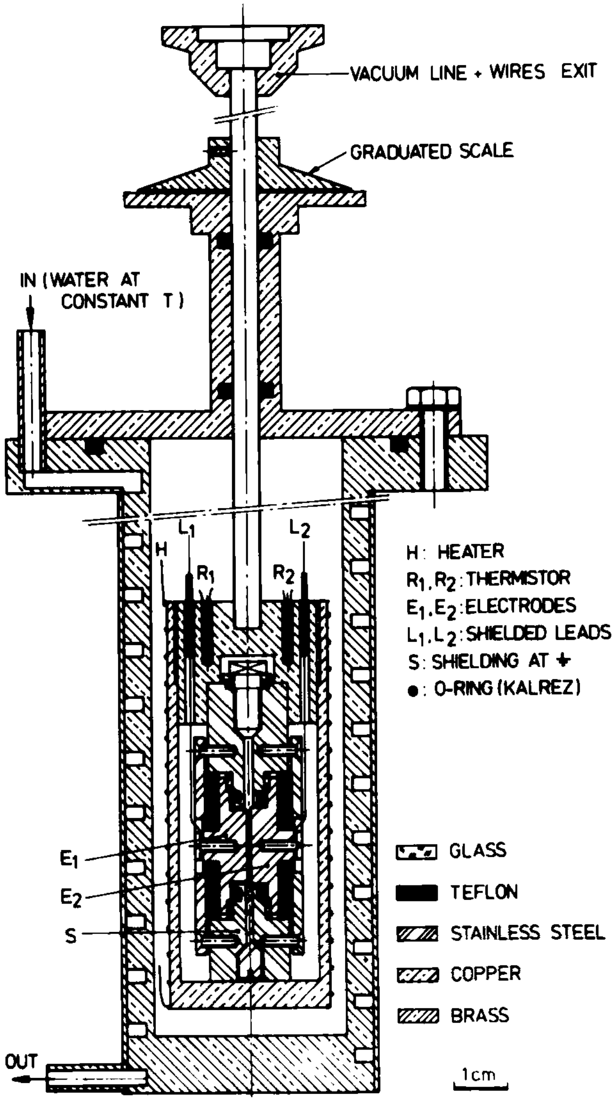

FIGURE 2 Dielectric measuring cell with temperature controlling system for measurements on smectic and nematic phases.

(perpendicular to the capacitor plates) with respect to the magnetic field, is measured by means of a graduated scale attached to the stainless steel tube holding the central temperature controlling stage with the sample cell. The zero adjustment (to better than half a degree) for the angle between the magnetic and the electric field direction, is made optically by reflection of a laser beam on the back of the capacitor plates and a reference direction parallel with the magnetic field. For this purpose the outer thermal shielding and part of the central stage are removed.

3. RESULTS

In Figure 3 a general survey of the ε results obtained for 8CB in the temperature range 22°C to 140°C is given. A more detailed plot for the data for the nematic and the smectic-A phase is given in Figure 4. Dielectric measurements for 8CB have been reported previously in literature. Druon and Wacrenier[3] reported a qualitative characterization (with four or five data points for each phase) of the ε behavior between 22°C and 60°C. The qualitative behavior of $\varepsilon_{\parallel}$, $\varepsilon_{\perp}$ and ε_{is} was also reported for $22°\mathrm{C} < T < 50°\mathrm{C}$ by Bata and Buka.[4] More detailed results for the nematic phase and a few points for the isotropic phase have been reported by Ratna and Shashidhar.[5] Data for the isotropic phase between 40°C and 90°C have recently been reported by Bradshaw and Raynes.[6] As far as the graphical representation in the different publications allows us to assess, there seem to be quite substantial differences in absolute value of the permittivity. This can be verified easily by comparing the ε_{is} values just above T_{NI}. The data of Druon and Wacrenier,[3] Bradshaw and Raynes[6] and our data are in quite good agreement. The results of Ratna and Shashidhar[5] and of Bata and Buka[4] fall, respectively, about 5% and about 10% lower than the ε_{is} data from the above three sources. For the mesophases, about the same discrepancies exist between the data of Refs. 4 and 5 on one side and our data and the data of Druon and Wacrenier[3] on the other.

From Figures 3 and 4, several observations regarding the temperature dependence of $\varepsilon_{\parallel}$, $\varepsilon_{\perp}$ and ε_{is} can be made. In the nematic as well as in the smectic-A phase, a quite large positive dielectric anisotropy ($\Delta\varepsilon \simeq 8$) is present. The temperature dependence of $\varepsilon_{\parallel}$ and $\varepsilon_{\perp}$ in the two phases shows some striking differences. Whereas in the N-phase, the increase in $\Delta\varepsilon$ with decreasing temperature reflects the increasing nematic order (see Section 4), there is a saturation for $\Delta\varepsilon$ and a decrease in $\varepsilon_{\parallel}$ in the smectic-A phase. It should, however, be noted that we did not observe a discontinuity in $\varepsilon_{\parallel}$ or $\varepsilon_{\perp}$ at T_{AN}. This is consistent with the second-order character of the AN transition as observed in adiabatic scanning calorimetric measurements.[7] At the NI transition, there is a discontinuity in the $\varepsilon_{\parallel}$ and $\varepsilon_{\perp}$ behavior. With our temperature resolution of a few mK, it was possible to approach this phase transition very closely from the nematic as well as from

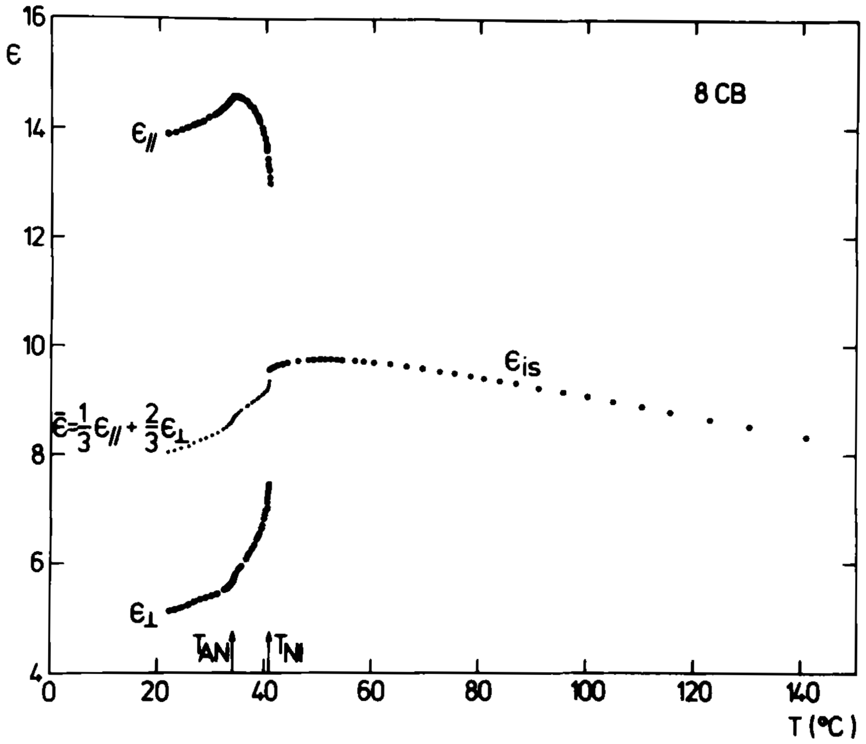

FIGURE 3 Temperature dependence of the permittivity of 8CB over the entire investigated temperature range.

the isotropic side. It was clearly observed that the transition was slightly impurity-broadened over about 90 mK. This is consistent with the first-order nature of the transition. Data obtained in this two-phase region (between 40.69°C and 40.78°C) have not been displayed in Figures 3 and 4. From Figure 4 it can also be seen that at the NI transition, there remains a difference $\delta\varepsilon = 0.25$ (or about 2.5% of ε_{is}) between the extrapolated ε_{is} and $\bar{\varepsilon} = \frac{1}{3}(\varepsilon_{\parallel} + 2\varepsilon_{\perp})$ of the nematic phase, although the temperature dependence of $\bar{\varepsilon}$ and ε_{is} do not differ very much near T_{NI}.

As far as the isotropic phase is concerned, one observes in Figure 3 an increase in ε_{is} with increasing temperature, reaching a maximum at about T_{NI} + 10°C, and followed by a gradual, almost linear decrease for higher temperatures. This is more clearly displayed in Figure 5. This pre-transitional effect in ε_{is} has recently also been observed by Bradshaw and Raynes[6] for 8CB and a series of other compounds with cyano-end groups.

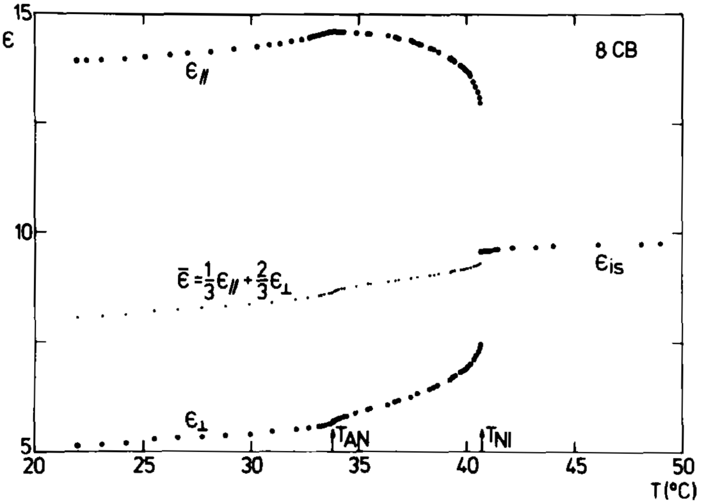

FIGURE 4 Detailed plot of the permittivity of 8CB in the smectic-A phase, the nematic phase and in the isotropic phase near the NI phase transition.

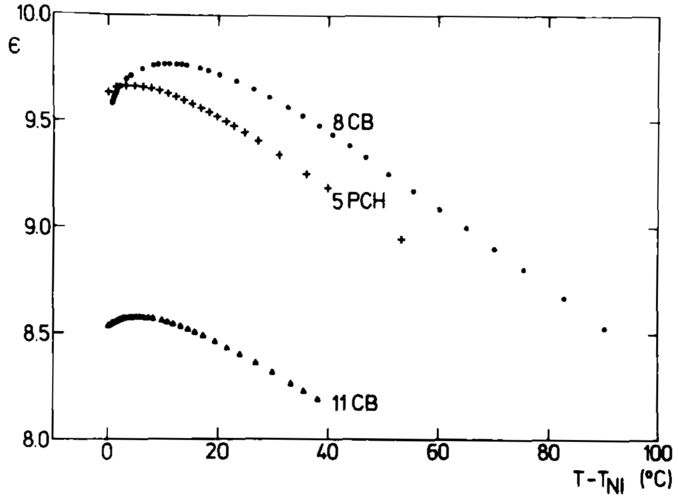

FIGURE 5 The permittivity in the isotropic phase as a function of temperature for three different *para*-cyano-substituted compounds.

They did, however, not observe it for heptylphenyl propylbenzoate, without a cyano-group. In Figure 5 two other compounds, undecylcyanobiphenyl (11CB) and pentylcyanophenylcyclohexane (5PCH), with a cyano-end group also show the same pretransitional effect as 8CB. In order to verify the predominant role of the cyano-end group for the pretransitional effect, we investigated *p,p'* diheptylazobenzene (HAB) without a cyano-end group, and the compound *trans*-*p*-methoxy-*p'*-heptyloxy-α-cyanostilbene (MHCTS) with a cyano-group near the center of the molecule and a large dipole component perpendicular to the long molecular axis resulting in an appreciable negative dielectric anisotropy. The results for the isotropic phase of HAB are given in Figure 6. Data for MHCTS are displayed in Figure 7. For this last material we also obtained some data for the nematic phase. The phase of MHCTS was monotropic with respect to the melting temperature at 66°C. The two-phase region in this sample had a width of about 0.3°C. It is also interesting to note that a very small $\delta\varepsilon = 0.05$ jump between $\bar{\varepsilon}$ and ε_{is} is present at the NI transition. From Figures 6 and 7 is it quite clear that no pretransitional effect for ε_{is} is observed for these two compounds without a cyano-end group.

4. ANALYSIS AND DISCUSSION

In this section we concentrate on the temperature dependence of the dielectric anisotropy $\Delta\varepsilon$ in the nematic phase and on the pretransitional effect in the isotropic phase.

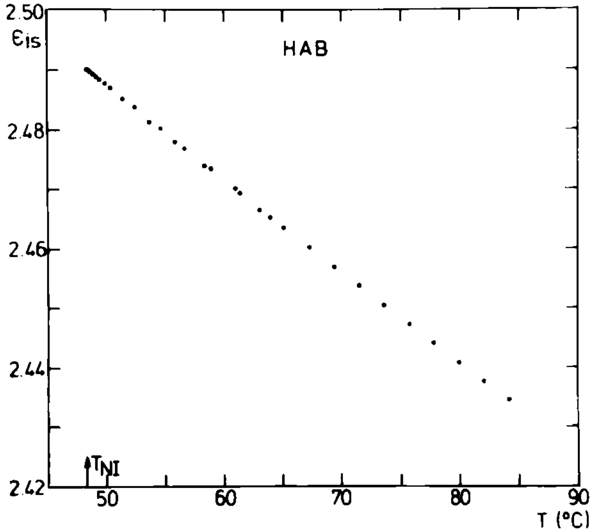

FIGURE 6 Temperature dependence of the permittivity in the isotropic phase of the nonpolar liquid crystal *p,p'*-diheptylazobenzene (HAB).

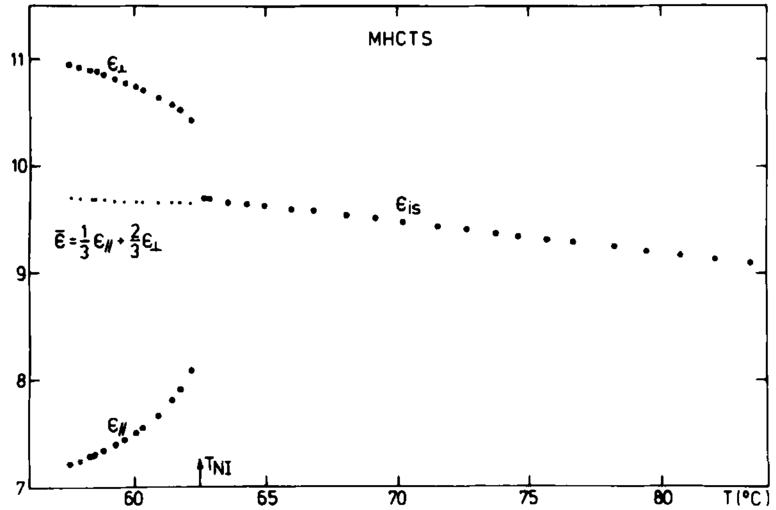

FIGURE 7 The permittivity as a function of temperature for *trans*-*p*-methoxy-*p*′-heptyloxy-α-cyanostilbene (MHCTS).

On the basis of an extension of the Onsager theory to liquid crystals by Maier and Meier[8] the following expression for $\Delta\varepsilon$ is obtained:[1,8]

$$\Delta\varepsilon = \varepsilon_\parallel - \varepsilon_\perp = \frac{NhF}{\varepsilon_0}\left[(\alpha_l - \alpha_t) - \frac{F\mu^2}{2kT}(1 - 3\cos^2\phi)\right]S, \tag{5}$$

with α_l and α_t, respectively, the polarizability parallel and perpendicular to the long molecular axis. ϕ is the angle between the dipole and the long molecular axis. N is the number density and h and F are given by the following expressions:

$$h = 3\bar{\varepsilon}/(2\bar{\varepsilon} + 1), \tag{6}$$

$$F = \left(1 - \frac{\bar{\varepsilon} - 1}{2\bar{\varepsilon} + 1}\frac{2N\bar{\alpha}}{3\varepsilon_0}\right)^{-1} \tag{7}$$

with $\bar{\varepsilon} = ⅓(\varepsilon_\parallel + 2\varepsilon_\perp)$ and $\bar{\alpha} = ⅓(\alpha_\parallel + 2\alpha_\perp)$. Within the nematic phase, the order parameter S in Eq. (5) is expected to follow a power law

$$S = S_0 + S_1\left(\frac{T^{**} - T}{T^{**}}\right)^\beta, \tag{8}$$

with S_0 and S_1 constants, and T^{**} the effective second-order point seen from below T_{NI}. β is a critical exponent, which has a value of ½ in the Landau-de Gennes[9] theory for the NI transition. Combining Eqs. (5) and

(8), and considering only the explicit temperature dependence present in these equations, we arrive at the following fit equation:

$$\Delta\varepsilon = \left(C_0 + \frac{C_1}{T}\right) + \left(C_2 + \frac{C_3}{T}\right)\left(\frac{T^{**} - T}{T^{**}}\right)^{\beta} \tag{9}$$

In this equation, which expresses $\Delta\varepsilon$ in terms of the reduced temperature difference $t \equiv (T^{**} - T)/T^{**}$ and the critical exponent β, we have as possible adjustable parameters T^{**}, β, C_0, C_1, C_2, C_3. We have analyzed our $\Delta\varepsilon$ data for the nematic phase with Eq. (9) by means of a nonlinear least-squares procedure. We have also applied range shrinking in an effort to determine the asymptotic value (at T^{**}) of the critical exponent β or its possible range dependence. In Figure 8, β and also T^{**} are given as a function of $t_m \equiv [(T^{**} - T)/T^{**}]_{\max}$, the largest value of t for the data used in that particular fit. The small dots in Figure 8 correspond to fits where all the adjustable parameters in Eq. (9) were free in the fits. Results for other possibilities with zero values for some of the adjustable parameters have also been included in Figure 8. In arriving at Eq. (9), we have neglected the (small) dependence of the density on the order parameter and thus on t. Using density data[10] we have also made fits for the quantity

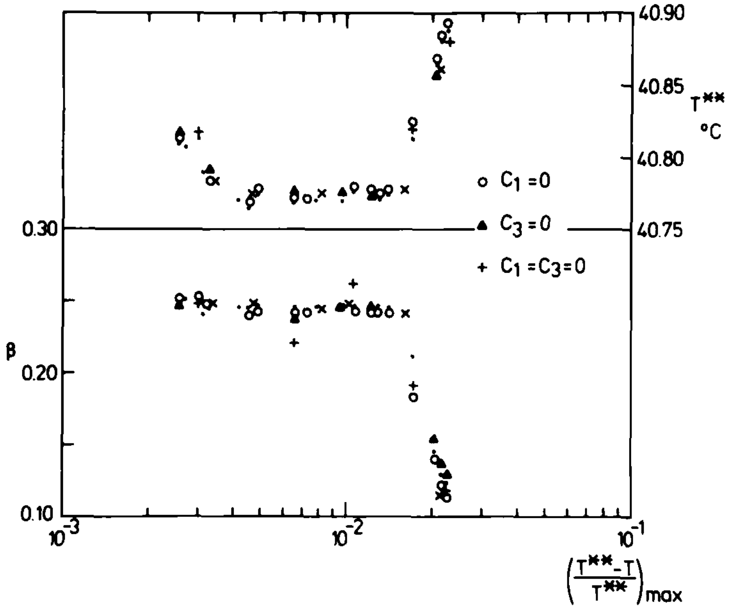

FIGURE 8 Range shrinking results for the critical exponent β and the critical temperature T^{**} from fits to the data of 8CB by means of Eq. (9).

$\Delta\varepsilon/N$. The results for T^{**} and β from these fits are given by the crosses in Figure 8. No systematic deviations from the results for $\Delta\varepsilon$ are observed. It can be seen in Figure 8 that there is essentially a constant β value for $t_m \leq 10^{-2}$. For the fit with the smallest t_m value in Figure 9, the experimental data points cover about one decade: t between 2×10^{-4} and 2×10^{-3}. For the exponent β we arrive at a best value $\beta = 0.247 \pm 0.01$. We have also carried out similar fits with Eq. (9) to the data for MHCTS (see Figure 7), where a negative dielectric anisotropy is observed. For that material we obtain $\beta = 0.252$, which is in very good agreement with the 8CB result. From an analysis by Haller[11] of the anisotropy in the refractive index for several nematogens with a simple power law for the order parameter ($S_0 = 0$ in Eq. (8)), $\beta = 0.20 \pm 0.03$ values have been found. Kneppe *et al*[12] obtained β values between 0.16 and 0.19 from simple power law fits to diamagnetic anisotropy data. When analyzed with the full-order parameter expression, Eq. (8), diamagnetic anisotropy data by Buka and de Jeu[13] give β values around 0.25. The value of 0.25 for β differs by a factor of 2 from the value 0.5 expected on the basis of the classical Landau-de Gennes[9] mean field theory. It is also not in agreement with the Ising value $\beta = 0.312$. This last value is expected for a normal second-order critical point in systems with short-range interactions (which is the case in liquid crystals). The observed β value is, however, in very good agreement with the tricritical value for this exponent, and supports the suggestion by Keyes[14] and Anisomov[15] of the quasitricritical character of this transition.

Let us now turn to the pretransitional effect for the permittivity in the isotropic phase for the compounds with cyano-end groups (see Figure 5). In these compounds with strong dipole moments, the induced polarization contributes much less to the permittivity than the orientational polarization, and it would be expected that ε in the isotropic phase (and also $\bar{\varepsilon}$ in the nematic phase) would be proportional to μ^2/kT. The normally expected behavior would thus be an increase with decreasing temperature. Instead a maximum in ε_{is} and a decrease is observed close to T_{NI}. Bradshaw and Raynes[6] have attributed this pretransitional effect to changes in the local antiparallel ordering *via* coupling with the developing short-range nematic ordering on approaching T_{NI}. This antiferroelectric short-range nematic order has been invoked by Madhusudana and Chandrasekhar[16] to explain the small jump $\delta\varepsilon$ in $\bar{\varepsilon}$ at the NI transition. On the basis of a molecular model by Longa and de Jeu,[17] this local antiparallel ordering has recently been specified in more detail. The reduced contribution of the molecular dipole moments to the polarization in compounds with strongly polar end groups is attributed to an increase of the number of dimers (with decreasing temperature) in a dynamic monomer-dimer equilibrium. The pretransitional effect in ε_{is} near T_{NI} could possibly be understood as an appreciable increase of x_D, the concentration of the dimers (with a very small effective dipole moment), on approaching T_{NI}. An aspect, which should, however, also be considered for the pretransitional effect, is the occurrence of larger and larger (nematic) fluctuations (over a certain correlation length ξ), which are at the origin of the strongly increasing light scattering[9,18] with decreasing $(T - T_{NI})$, and give the system a certain degree of heterogeneity. This kind of heterogeneity is at the origin of the theoretically[19] expected, and experimentally observed,[20] intrinsic dielectric effect near the critical solution point in binary mixtures of ordinary liquids. In these cases the temperature dependence of the static permittivity is very well described with an expression of the type

$$\varepsilon = \varepsilon_c + At^{\theta} + Bt \tag{10}$$

with $t \equiv (T - T_c)/T_c$, where T_c is the critical temperature. $\theta = 1 - \alpha_I$; with $\alpha_I = 0.11$ the heat capacity critical exponent for the Ising model, which should be applicable for the critical point in those systems. ε_c is the permittivity value at T_c and A and B are adjustable parameters. B mainly accounts for the regular (linear) background temperature dependence of ε. We have also tried to fit our data for ε_{is} for 8CB by means of Eq. (10) with the adjustable parameters ε_c, θ, A, B and T_c, where in the case of liquid crystals T_c should be identified with T^*, the lowest possible temperature for a stable isotropic phase. Very good fits to the experimental data could be obtained with a $\theta \simeq 0.45$ value, which was also quite insensitive to range shrinking. The data between T_{NI} and say 100°C are well described by the following set of parameter values: $T^* = 39.27$°C, $\varepsilon_c = 9.306$, $\theta = 0.45$, $A = 3.681$, $B = -10.22$. Fits to the data for 11CB and 5PCH (see Figure 5) resulted in similar θ values between 0.4 and 0.5. If one also makes in this case the identification of θ with $1 - \alpha$, a value $\alpha \simeq 0.5$ is obtained. This is surprisingly close to the tricritical value for this exponent, and would conform with the quasitricritical assumption.[14,15] At the moment, however, it is not clear whether this identification can be made, and that θ here should not be considered simply as an empirical factor resulting in a good description of the ε_{is} data with an expression of the type of Eq. (10). To clarify this point, additional information on the temperature dependence of the degree of antiparallel association, and thus of x_D, the concentration of the dimers, is needed.

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