Pressure Dependence of the Dielectric Anisotropy of 5CB and 6CB

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The pressure-dependence of the dielectric anisotropy, $\Delta\varepsilon = \varepsilon_{0\parallel} - \varepsilon_{0\perp}$, of two nematogens, n-pentyl- and n-hexyl-cyanobiphenyl (5CB and 6CB) has been measured at constant temperature. For this purpose a high pressure chamber made of non-magnetic materials was constructed, allowing for the orientation of the samples by a magnetic field. The pressure dependencies of $\Delta\varepsilon_T$ were analyzed in the frame of the Maier-Meier equations for the principal permittivity components in the nematic phase. It was found that the relation between $\Delta\varepsilon$ and the order parameter S is not properly described by these equations. The Kirkwood correlation factor calculated on the basis of the present results and the Maier-Meier equations is smaller than 0.5, whereas it increases to a more realistic value (~ 0.7) if the electronic polarization is incorporated in the equations.

Key words: Nematic liquid crystals, Cyanobiphenyls, High pressure, Dielectric anisotropy.

Introduction

High pressure (h.p.) studies of liquid crystals (LCs) can bring important new information. Relatively low pressures change the properties of LCs considerably [1–3]. A few years ago, a systematic h.p. studies of LCs, especially on regards the phase transitions and dielectric relaxation, have been undertaken at the University of Bochum [3–10]. The high pressure chamber used, however, allowed for the measurement of the parallel component of the dielectric permittivity only. Therefore we constructed a new h.p. chamber made of non-magnetic materials that enabled us to apply a magnetic field for orienting the nematic samples and to measure both the parallel and perpendicular components of the static dielectric constant.

It is well known that the cyanobiphenyl homologues (nCB) exhibit strong dipole-dipole correlations in the nematic phase. Former h.p. dielectric measurements of four nCB homologues ($n = 5 \div 8$) have shown that the pressure distinctly influences the static dielectric constant $\varepsilon_{0\parallel}$ [4, 5, 7–9]. On the other hand, the effect was considerably weaker for a similar substance, 6CHBT, in which such correlations are relatively weak [6]. Also, the parameters characterizing the molecular reorientations around the short axes (activation enthalpy, energy and volume) decrease with increasing pressure, whereas they are practically independent of pressure in the case of 6CHBT. These features of the dielectric behaviour did show that relatively low pressures influence the dipole-dipole correlations in the nematic phase of cyanobiphenyls considerably.

In [4] we have discussed the change of the static dielectric constant $\varepsilon_{0\parallel}$ with increasing pressure at constant temperature in the nematic phase of 5CB using the well known Maier-Meier equations [11] relating the principal permittivity components with the dipole moment of the LC molecule and the order parameter S. However, some simplifications had to be done when theoretical predictions were confronted with the experimental results. The use of the dielectric anisotropy, $\Delta\varepsilon = \varepsilon_{0\parallel} - \varepsilon_{0\perp}$, makes such a confrontation much more straightforward.

Experimental

Figure 1 shows our high pressure vessel. It was built with non-magnetic materials at the High Pressure Center UNIPRESS, Warsaw. The main parts of the vessel are: The corps of beryllium bronze B, the electrical feed-through E, groves with packing O, the spacer of Teflon T, the parallel-plate capacitor (~ 0.2 mm distance between plates) C, two parts of the moving piston for the transmission of pressure P, the sealing of Indium I, and the gas inlet G. The minimal volume of a sample (S) is 3.5 cm³. The general idea of the vessel is based on the dielectric cell constructed by Poser and Würflinger [12]. The small gap (8 cm) between the poles (16 cm diameter) of the electromagnet used for orienting the nematic samples does not allow for
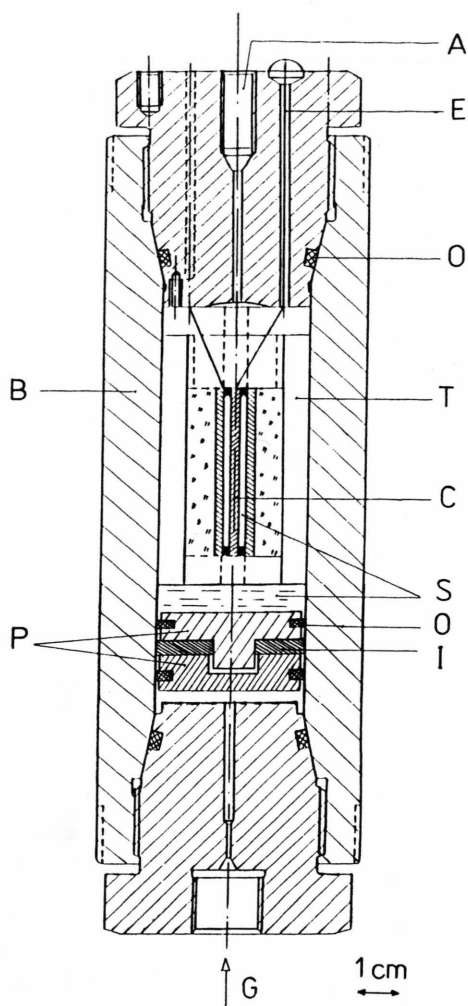

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Fig. 1. Vessel for high pressure dielectric studies of liquid crystals oriented by a magnetic field. For details see text.

in the range of 10 kHz – 13 MHz. The static permittivity ε_0 was taken to be the average of the values of ε', measured in the region of the plateau of the spectra (usually in the range of 70 – 150 kHz).

The samples of 5CB and 6CB were obtained from Prof. R. Dąbrowski, Military Technical University, Warsaw. Their transition temperatures agreed very well with the literature data. The nematic samples were oriented by a magnetic field $B \approx 0.6$ T that corresponded to the saturation effects. The orientations of the director with respect to the measuring field, ∥ and ⊥, were achieved by turning the electromagnet by 90°.

Results

Figure 2 presents the static dielectric constants, $\varepsilon_{0\parallel}$ and $\varepsilon_{0\perp}$, as functions of pressure at two temperatures within the nematic phase of 5CB and 6CB. The measurements were carried out by decreasing the pressure starting from (p, T) values close to the nematic-crystal border lines. The inset of figure shows the (p, T) phase diagrams of both substances with the temperatures of the particular runs. The results obtained in two independent runs coincide very well. The average permittivities, $\bar{\varepsilon} = (\varepsilon_{0\parallel} + 2\varepsilon_{0\perp})/3$, are practically independent of pressure and are the same at both temperatures. Additionally, $\bar{\varepsilon}$ differs very little from the values $\varepsilon_{0,\mathrm{is}}$ extrapolated from the isotropic phase. Characteristic steps observed for all cyanobiphenyls at the I-N transition point at ambient pressure [2] were not observed at $T = \mathrm{constant}$. The dielectric anisotropy $\Delta\varepsilon$ as a function of the reduced pressure, $p - p_{\mathrm{NI}}$, is shown in Figure 3.

Discussion

The static permittivity components of the nematic phase can be interpreted in terms of the Maier-Meier equations [11], which have the following simplified form for molecules having axial symmetry and the dipole moment directed along the symmetry axis:

$$\varepsilon_0 - 1 = \varepsilon_0^{-1} N_A \frac{\varrho}{M} h F$$
$$\cdot \left\{ \bar{\alpha} + \frac{2\Delta\alpha S}{3} + \frac{F\mu^2}{3kT}(1 + 2S) \right\}, \quad (1)$$

putting the vessel into an autoclave, this limiting the accessible pressures to 150 MPa. The present maximal pressure however, only 70 MPa at 40 °C due to troubles with sealing of the sample inlet A. A heating jacket around the vessel allows for temperature stabilization to ± 0.2 K. The temperature is measured by a thermocouple placed in the main corps close to the sample.

The capacitor was calibrated with five standard liquids. The accuracy of ε'-measurements was better than 1%. A computer assisted HP 4192A impedance analyzer was used and the dielectric spectra were collected
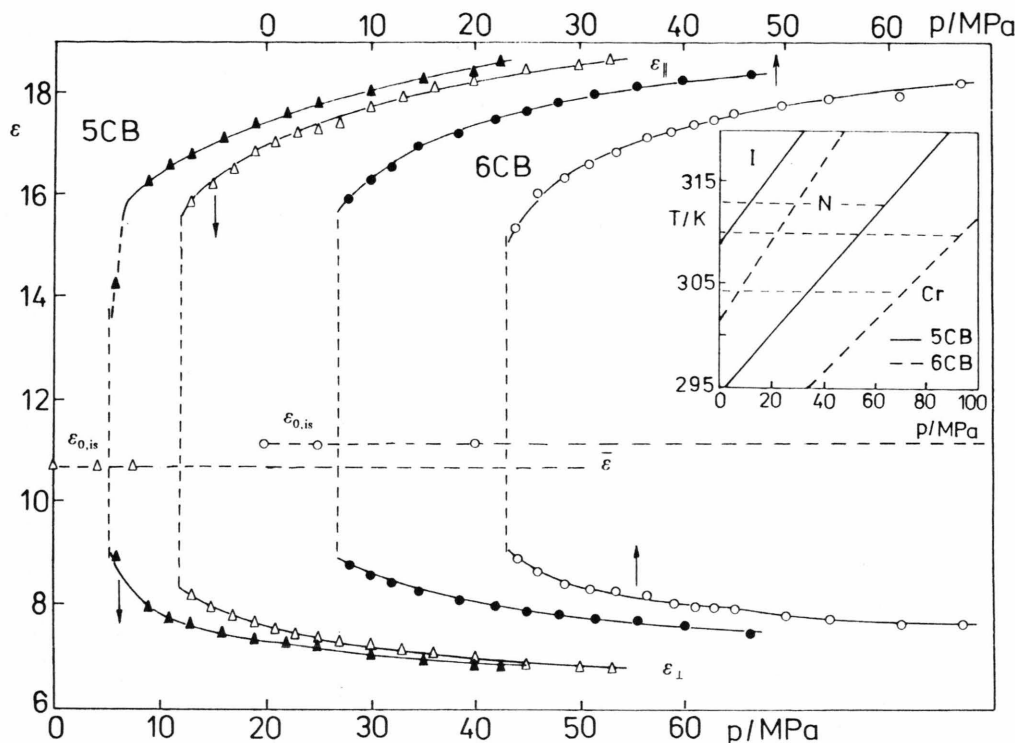
Fig. 2. Pressure dependence of the principal static dielectric permittivity in the nematic phase of 5CB (▲: 310 K, △: 313 K) and 6CB (●: 304 K, ○: 310 K) at two temperatures. Both orientations – parallel $\varepsilon_{\parallel}$ and perpendicular $\varepsilon_{\perp}$ were achieved by the magnetic field $B \sim 0.6$ T (note a shift of the pressure scale in the case of 6CB). $\bar{\varepsilon} = (\varepsilon_{\parallel} + 2\varepsilon_{\perp})/3$ is the mean dielectric constant, $\varepsilon_{\mathrm{is}}$ corresponds to the isotropic phase. The inset shows the p, T phase diagrams with marking the temperature levels of the present experiments.

$$\varepsilon_{0\perp} - 1 = \varepsilon_0^{-1} N_{\mathrm{A}} \frac{\varrho}{M} h F$$

$$\cdot \left\{ \bar{\alpha} - \frac{\Delta\alpha\, S}{3} + \frac{F\mu^2}{3kT}(1 - S) \right\}, \qquad (2)$$

$$\Delta\varepsilon = \varepsilon_{0\parallel} - \varepsilon_{0\perp}$$

$$= \varepsilon_0^{-1} N_{\mathrm{A}} \frac{\varrho}{M} h F \left(\Delta\alpha + \frac{F\mu^2}{kT} \right) S, \qquad (3)$$

where $h = 3\bar{\varepsilon}/(2\bar{\varepsilon} + 1)$ is the cavity field factor, $F = 1/(1 - \bar{\alpha}f)$ is the reaction field factor, $f = (N_{\mathrm{A}}\varrho/3\varepsilon_0 M)(2\bar{\varepsilon} - 2)/(2\bar{\varepsilon} + 1)$, ε_0 is the permittivity of free space, $\bar{\varepsilon} = (\varepsilon_{\parallel} + 2\varepsilon_{\perp})/3$ the mean dielectric constant, M the molar mass, N_{A} Avogadros number, ϱ the density, μ the dipole moment, $\Delta\alpha$ and $\bar{\alpha}$ are the polarizability anisotropy and the mean polarizability of a molecule, respectively, and S is the order parameter.

In the former h.p. dielectric studies of 5CB [4], (1) was used for the analysis of the relationship between the measured permittivities (which were obtained for an unperfectly oriented sample, however) and the order parameter known form optical measurements [4, 13]. Assuming other quantities to be constant and neglecting the induced polarization, the approximate relation

$$\varepsilon_{0\parallel} - 1 \propto (2S + 1)/T \qquad (4)$$

was discussed. It described well the data measured at $p = $ const, whereas at $T = $ const this was not the case. The factor $(2S(p) + 1)_{\mathrm{T}}$, normalized to the permittivity at high pressure, differed much from that at low pressures. Especially close to the N-I transition the permittivity decreased more strongly than according to (4). Because of this effects, together with a systematic decrease with pressure of the activation parameters characterizing the molecular reorientations around the short axes, it was concluded that a relatively low pressure breaks the dipole-dipole correlations in the nematic phase of 5CB. This statement was then supported by further studies of nCB compounds [5, 7–9].
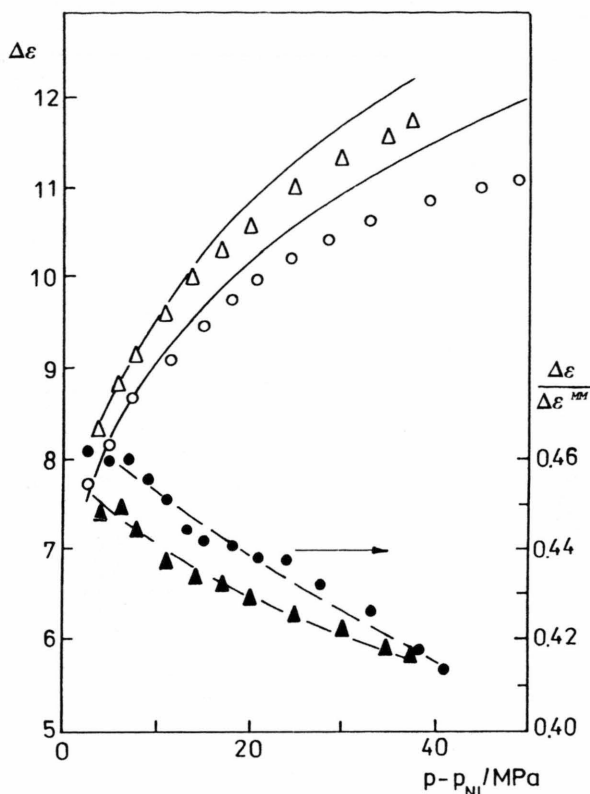
Fig. 3. Dielectric anisotropy $\Delta\varepsilon$ as a function of the reduced pressure in the nematic phase of 5CB: $\triangle$ (310 K) and 6CB: $\circ$ (310 K). The lines are the order parameters S normalized to the three points close to the N-I transition. Right hand scale: 5CB – pressure dependence of the ratio $\Delta\varepsilon(\text{experimental})/\Delta\varepsilon^{MM}$ ($\blacktriangle$: 310 K, $\bullet$: 313 K).

It seems that the present results should allow one for a more straightforward comparison of the experimental data with the predictions of Maier-Meier theory. In Fig. 3 the order parameter $S(p)_T$, taken from [13] (5CB) and [14] (6CB), are normalized to the $\Delta\varepsilon$ values at pressures close to the N-I transition. The disagreement between both quantities, when the pressure is increased, is evident. The order parameter changes more strongly than the permittivity anisotropy, an effect which may be caused, however, by the change of the density. In the case of 5CB it is possible to check the influence of the density changes on that discrepancy. Taking $S(p)$ and $\varrho(p)$ from the optical anisotropy data [13], $\Delta\alpha$ from [15] and μ from [16] it is possible to calculate the dielectric anisotropy $\Delta\varepsilon^{MM}$ as a function of pressure according to the Maier-Meier formula (3). As one can see in Fig. 3 (right hand

scale) the ratio $\Delta\varepsilon(\text{experimental})/\Delta\varepsilon^{MM}$ exhibits considerable dependence on the pressure. This indicates that the Maier-Meier formulae give only a rough description of the dielectric properties of the nematic phase. This could be expected since in the derivation of the cavity and reaction field factors the intrinsic field is treated as isotropic, characterized by the mean electric permittivity $\bar\varepsilon$. Such an approximation cannot be true for substances with a large dielectric anisotropy [11, 17, 18] like the cyanobiphenyls. Bordewijk [20] has extended this theory taking into account the anisotropy of the nematic medium, but the derived relations were obtained with other not very realistic assumptions.

Neglecting a small contribution to $\Delta\varepsilon$ from the anisotropy of the induced polarization (see (3)) one can write

$$\Delta\varepsilon/\Delta\varepsilon^{MM} \approx \mu_{\text{eff}}^2/\mu^2 = g, \qquad (5)$$

where $\Delta\varepsilon_{MM}$ is the anisotropy calculated according to (3) by taking μ obtained from the measurements in dilute solutions, whereas μ_{eff} is an effective dipole moment of a molecule calculated from the experimental $\Delta\varepsilon$ values with the use of (3). The Kirkwood g-factor is commonly used for a characterization of the dipole-dipole correlations between molecules in liquid crystalline phases [15–17, 19–21]. Its value is distinctly smaller than unity (compare Fig. 3 and (5)), which indicates that the dipole-dipole correlations are very effective in the nematic phase of 5CB. However, in the light of the above objections concerning the validity of (3) in case of the compounds under study its analysis as a function of pressure seems to be unreliable.

An interesting extension of the Maier-Meier theory has been done by Sharma [21]. He treated a polar LC material as a mixture of unpaired molecules with a finite dipole moment and antiparallel pairs with a zero dipole moment. The molecules interact with each other through a combination of the generalized Maier-Saupe pseudo-potential for nematic mixtures and a reaction field energy term calculated from an extension of the Maier-Meier theory. Additionally, it was assumed that a molecule with dipole moment μ is embedded in a spherical cavity of dielectric permittivity n^2, which is surrounded by a medium of average dielectric permittivity $\bar\varepsilon$. In that case the expressions for the cavity field factor h and the reaction field factor f are given by $h = 3\bar\varepsilon/(2\bar\varepsilon + n^2)$, $f = (N_A\varrho/3\varepsilon_0 M)$ $(2\bar\varepsilon - 2n^2)/n^2(2\bar\varepsilon + n^2)$. The calculations performed for 5CB and 7CB gave reasonable agreement with the

overall behaviour of the dielectric permittivity in the nematic phase. The mole fraction of the 'associated' pairs seems to be relatively small ($\sim 10\%$), and the association energy does not exceed $2kT$ [21]. Because the author did not obtain analytical expressions for the permittivity components, we used (3) with new h and F factors to calculate the g-factor. Now it appears to be ca. 0.7, a value which seems to be more realistic than the previous one (< 0.5).

In conclusion one can say that the results of measurements of the dielectric anisotropy in the nematic phase of LC substances performed as a function of pressure at constant temperature make easier an analysis of the Maier-Meier equations. It is due to the fact that pressure influences the parameters which are simply factors in the equations. The presented analysis shows that the equations do not relate properly the permittivity anisotropy with the order parameter in the two cyanobiphenyls studied. The Kirkwood g-factor calculated from the $\Delta\varepsilon$ data seems to be more realistic if the electronic polarization is taken into account when the internal electric field for the nematic phase is calculated.

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