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Dielectric studies of liquid crystals under high pressure.

IV. Static permittivity and low frequency relaxation process in 4-*n*-hexyl-4'-cyanobiphenyl (6CB)

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Dielectric studies of 4-*n*-hexyl-4'-cyanobiphenyl (6CB) were performed in the pressure range 0.1–150 MPa, the frequency range 1 kHz–13 MHz and the temperature range 290–327 K. The temperature and pressure dependencies of the static permittivity $\epsilon_{0\parallel}$ and the relaxation time τ_{\parallel} are analysed and compared with analogous data obtained recently for 5CB and 6CHBT (parts I–III of this series). It was shown that in the nematic phases of both 4-*n*-alkyl-4'-cyanobiphenyls the dipole–dipole correlations are broken by relatively low pressure.

1. Introduction

In previous parts of this series, we have presented the results of dielectric studies under high pressure (h.p.) of 4-*n*-pentyl-4'-cyanobiphenyl (5CB) [1, 2] and 4-(*trans*-4-*n*-hexylcyclohexyl)isothiocyanatobenzene (6CHBT) [3]. Both compounds have similar molecular dimensions and possess strong dipole moments directed roughly along the main molecular axes. On the other hand, they are representatives of two homologous series which show considerably different degrees of molecular association in the nematic phase. It is well established that the alkylcyanobiphenyl (*n*CB) molecules exhibit strong dipole–dipole correlations in the liquid crystalline phases ([1] and references therein), whereas in the isothiocyanatobenzene (*n*CHBT) compounds, such correlations either do not exist or are very weak ([3] and references therein).

These different behaviours of molecules are reflected in the dielectric properties at atmospheric as well as at elevated pressures. The static permittivity of 5CB exhibits markedly stronger dependence on pressure (at $T = \text{constant}$) than in the case of 6CHBT [3]. In addition, activation parameters characterizing the molecular reorientations around the short axes in the nematic phase of 5CB (activation enthalpy, energy and volume) decrease with increasing pressure [1], whereas they are practically independent of pressure in the case of 6CHBT [3]. These features of the dielectric behaviour allowed us to conclude that relatively low pressure causes breaking of the dipole–dipole correlations in the nematic phase of 5CB.

The aim of the present study was to check whether the above mentioned phenomena can also be observed in the next member of the *n*CB homologous series,

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namely, 4-*n*-hexyl-4'-cyanobiphenyl (6CB). However, for this compound no p, V, T data are available and the discussion of the results cannot be as complete as in the case of 5CB [1, 2].

2. Experimental

The sample of 6CB was obtained from R. Dąbrowski (Military Technical Academy, Warsaw). The transition points at atmospheric pressure were: 297.4 K for the melting and 302.4 K for the nematic–isotropic transitions, in good agreement with literature data [4–6].

The experimental set-up was the same as in the previous studies [1, 3]. The very low conductivity of the sample allowed us to apply the DC electric field $E \sim 300 \text{ V cm}^{-1}$ which oriented the sample parallel to the measuring field. The dielectric spectra, $\epsilon_{\parallel}^*(f) = \epsilon'_{\parallel}(f) - i\epsilon''_{\parallel}(f)$, were measured in the frequency range f from 1 kHz to 13 MHz. The conductivity contribution, ϵ''_{cond} , to the dielectric losses ϵ''_{\parallel} was fully subtracted assuming $\epsilon''_{\text{cond}} \propto \sigma_0/f$.

After filling the capacitor with the sample we carried out the measurements at atmospheric pressure in the temperature range covering the nematic and isotropic phases of 6CB. Then the pressure was increased to a (p, T) point lying near the freezing line. Most measurements were carried out with gradual decrease of pressure at constant temperature. To check the reliability of the results we repeated some runs at $T = \text{constant}$ and at $p \approx \text{constant}$. The reproducibility of the results was very good in both cases.

3. Results

Figure 1 shows the (p, T) phase diagram of 6CB. Both transition lines, solid–nematic and nematic–isotropic, were obtained by Shashidhar and Venkatesh [7], whereas Wallis and Roy [8] measured the $T_{\text{NI}}(p)$ line only. Because both results differ markedly

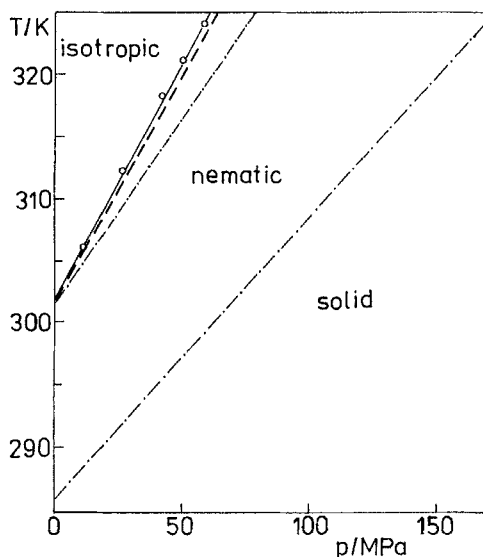


Figure 1. Temperature–pressure phase diagram for 6CB. The solid line with points was obtained in the present work, the dashed line by Wallis and Roy [8], whereas dotted–dashed lines were obtained by Shashidhar and Venkatesh [7].

we decided to reestablish the $T_{NI}(p)$ line in our studies. It was done at a few temperatures as is shown in figures 1 and 2. Near the clearing temperature we kept $T = \text{constant}$ and reduced the pressure very slowly. By measuring the capacity, we could detect the transition point rather accurately ($\pm 0.5 \text{ MPa}$, $\pm 0.3 \text{ K}$). The line obtained agrees well with the data of Wallis and Roy. Similar procedure could not be applied to the freezing line due to possible leakage of the capacitor caused by a big volume change at the nematic–solid transition [1]. Therefore we had to start with the measurements at points lying relatively far from the line reported in [7].

Figure 2 presents the static permittivity, $\epsilon_{0||}$, measured as a function of pressure at constant temperatures in the nematic and isotropic phases of 6CB. The inset of figure 2 shows the comparison of our data measured at atmospheric pressure with those obtained by other authors [4, 6]. The latter are consistently lower than our results, which may be caused by at least two important factors: (i) different degrees of orientation of the nematic phase (we used an electric field, whereas in [4, 6] magnetic fields were applied); (ii) incorrect calibrations of the capacitors—compare the results for the isotropic phase. We believe that our results are more accurate, because the strength of the orienting field corresponded to the saturation condition, and the capacitor was calibrated with the aid of many standard liquids having different permittivities. Additionally, our three-terminal capacitor has cylindrical symmetry and therefore any influence of stray capacities is much smaller than in the case of the plate capacitors used in [4–6].

Two other features of the results presented should be pointed out. There is a good consistency of the results obtained at elevated and atmospheric pressures, although they were measured during separate runs. In the isotropic phase, we always observed a small, but systematic increase of static permittivity with decreasing pressure.

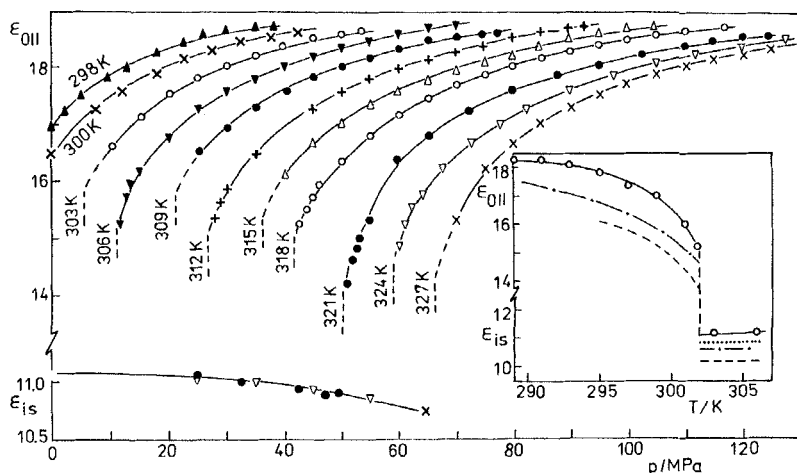


Figure 2. Dependence of the static permittivity on pressure in the nematic and isotropic phases of 6CB. The points for the isotropic phase were obtained by reducing the pressure at constant temperature, except the point at $p=0$ (really at 0.1 MPa) which was measured when the temperature was increased. Dashed vertical lines correspond to the nematic–isotropic transition. The inset shows the comparison of the present data (solid lines with points) with those obtained by Ratna and Shashidhar [4] (dashed lines), and by Dunmur *et al.* [6], (dotted–dashed lines). For the isotropic phase, the data obtained by Menu [10] are also shown (dots).

Figure 3(a) presents the dispersion, $\epsilon'_\parallel(f)$, and absorption, $\epsilon''_\parallel(f)$, spectra of 6CB obtained at atmospheric pressure, whereas in figure 4(a), the spectra obtained at one temperature and at different pressures are shown. In both cases, the observed dielectric relaxation process can be described by a single Debye mechanism which is well seen if the spectra are presented in the form of Cole–Cole plots (see figures 3(b) and 4(b)). The relaxation times τ_\parallel were calculated in the same way as in the previous studies [1, 3], i.e. from the frequencies of maximum losses: $\tau_\parallel = 1/(2\pi f_{\max})$.

At atmospheric pressure the relaxation times τ_\parallel are the following: 6.35, 5.49, 4.61, 3.86, 3.30, 2.51 and 2.16×10^{-8} s at 291, 293, 295, 297, 299, 301 and 302 K, respectively. The activation enthalpy calculated with the use of the Arrhenius equation is

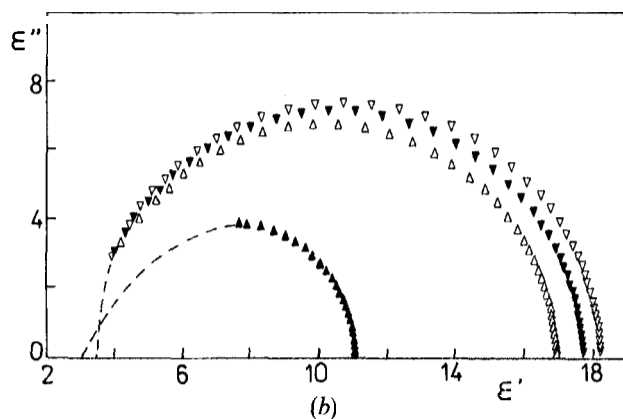
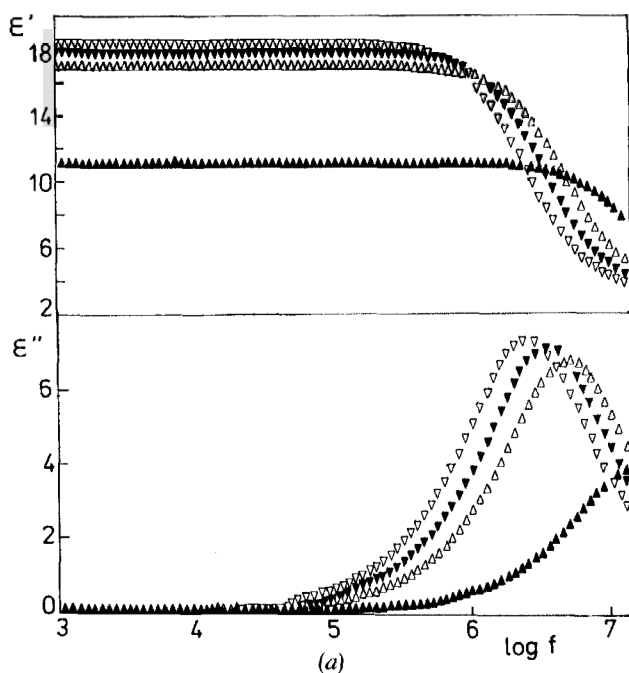


Figure 3. (a) Dispersion and absorption spectra obtained at atmospheric pressure for the nematic (∇] 291, \blacktriangledown] 295 and \triangle] 299 K) and isotropic (\blacktriangle] 303 K) phases of 6CB. (b) Cole–Cole plots for these spectra. Pressure = 0.1 MPa.

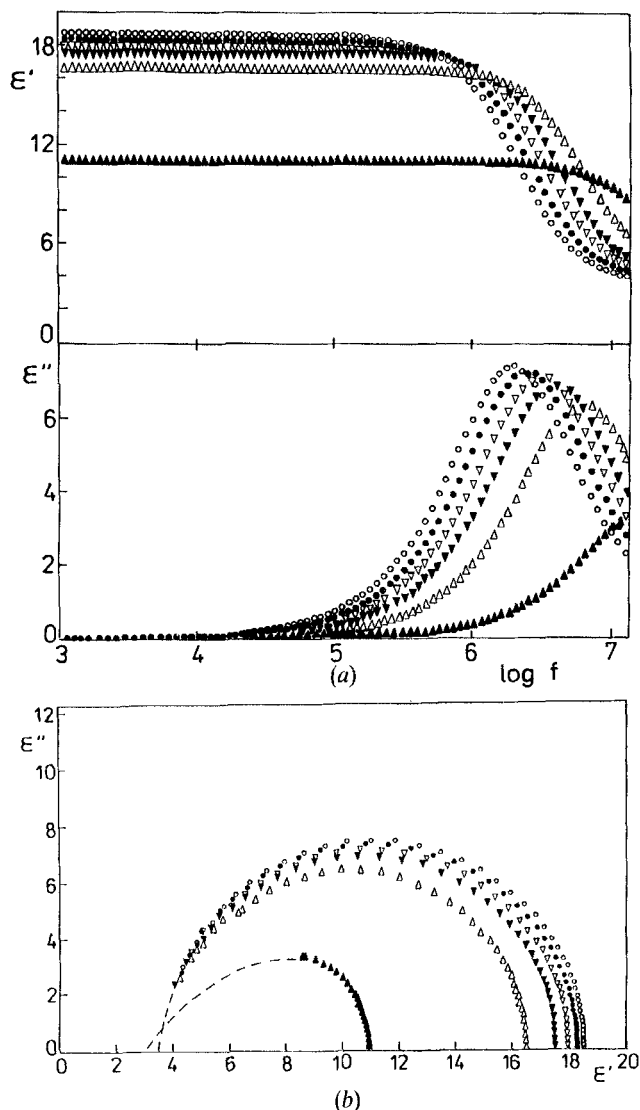


Figure 4. (a) Dispersion and absorption spectra obtained at constant temperature (312 K) and different pressures for the nematic (\circ] 80, \bullet] 70, ∇] 60, \blacktriangledown] 50, and \triangle] 35 MPa) and isotropic (\blacktriangle] 25 MPa) phases of 6CB. (b) Cole-Cole plots for these spectra.

$71 \pm 3 \text{ kJ mol}^{-1}$; thus it is distinctly larger than the 54 kJ mol^{-1} reported in [5]. The relaxation times τ_{\parallel} obtained at elevated pressures are presented in semi-logarithmic scale in figure 5. Again, one can confirm very good consistency of the results obtained at elevated and atmospheric pressures, and good reproducibility of the relaxation times measured for different runs. As for 5CB [1, 2] and 6CHBT [3], the relaxation time τ_{\parallel} is not a strictly exponential function of pressure. Neglecting this small effect, we have calculated the slopes $(\partial \ln \tau_{\parallel} / \partial p)_{\text{T}}$ by means of linear regression, and then the activation volumes ΔV_{\parallel} from the relation

$$\Delta V_{\parallel} = RT(\partial \ln \tau_{\parallel} / \partial p)_{\text{T}}. \quad (1)$$

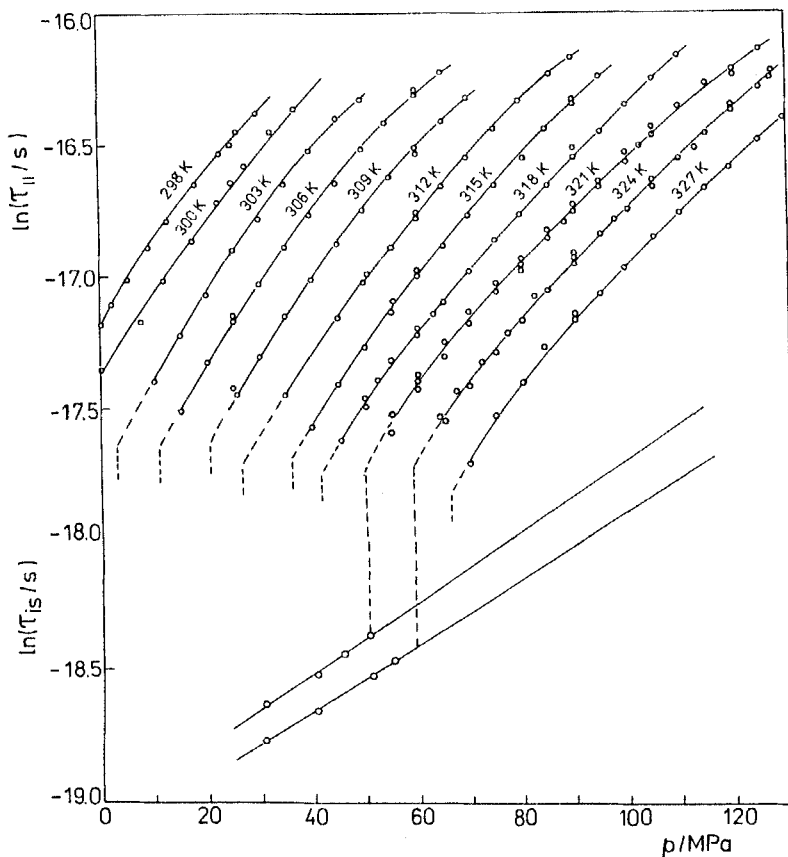


Figure 5. $\ln \tau_{||}$ and $\ln \tau_{is}$ versus p plots for the nematic and isotropic phases of 6CB at different temperatures.

The values obtained are presented in figure 6 as a function of temperature. Taking the values of $\ln \tau_{||}$ at constant pressures from figure 5, we have calculated the activation enthalpy according to the Arrhenius equation

$$\tau_{||} = \tau_{0||} \exp(\Delta H_{||}/RT)_p. \quad (2)$$

The values of $\Delta H_{||}$ calculated at different pressures are shown in figure 6.

The dielectric spectra measured for the isotropic phase of 6CB were analysed in the same way as the spectra of 5CB [1], i.e. we assumed that they showed the distribution of the relaxation times τ_{is} which could be described by the Cole–Davidson skewed arc (see figures 3(b) and 4(b)). This assumption is based on the results of dielectric studies of the *n*CB substances in the isotropic phase carried out over a much broader frequency range [9]. The relaxation times at atmospheric pressure are the following: 10.67, 9.50 and 7.06 ns at 303, 306 and 312 K, respectively, which leads to the activation enthalpy $\Delta H_{is} = 36.4 \pm 2 \text{ kJ mol}^{-1}$, in comparison with 28.5 kJ mol^{-1} obtained for 5CB [1]. The pressure dependence of τ_{is} was measured at 321 and 324 K. The results are shown in figure 5. The corresponding activation volumes ΔV_{is} are 34.8 and $32.5 \text{ cm}^3 \text{ mol}^{-1}$ at 321 and 324 K, respectively. These values are a bit larger than those obtained for the isotropic phase of 5CB [1] at similar $T - T_{NI}$ values.

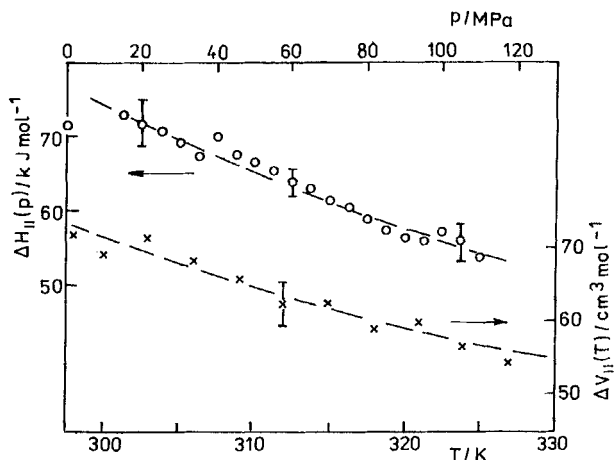


Figure 6. Comparison of the activation parameters characterizing the molecular reorientations around the short axes in the nematic phase of 6CB: enthalpy $\Delta H_{||}$ (open circles) as a function of pressure, and volume $\Delta V_{||}$ (crosses) as a function of temperature. T -scale corresponds roughly to the p -scale. The lines are drawn as guides for the eye only.

4. Discussion

The dielectric properties of particular members of the n CB homologous series were hitherto studied at atmospheric pressure by many authors. However, little attention was paid to the study of 6CB [4–6, 10]. The results obtained by us differ markedly from the literature data. This concerns both the static permittivity $\varepsilon_{0||}(T)$ [4, 6] (see figure 2) as well as the dielectric relaxation [5]. In the latter case a big difference in the values of the activation enthalpy, 70 kJ mol^{-1} instead of 54 kJ mol^{-1} in [5], may partly arise from a lower quality of formerly measured relaxation spectra.

Figure 2 shows that the static permittivity $\varepsilon_{0||}$ changes strongly with temperature and pressure reaching values of $c. 15$ near T_{NI} and $c. 18.7$ near the freezing point. Thus, the assumptions accepted in [1] for the reduction of the Maier–Meier [11] formula linking $\varepsilon_{0||}$ with the order parameter S to the simplified relation, $\varepsilon_{0||} - 1 \propto (2S + 1)/T$, seem to be fulfilled, as in the case of 5CB [1]. To check this relation for 6CB we have taken the $S(p, T)$ data obtained from the NMR measurements by Wallis and Roy [8]. Unexpectedly, the temperature and pressure dependencies of the $(2S(p, T) + 1)/T$ factors calculated in this way are markedly stronger than the experimental $\varepsilon_{0||}(T)_p$ and $\varepsilon_{0||}(p)_T$ dependencies. At the same time, $\varepsilon_{0||}$ changes with p and T more strongly for 5CB than for 6CB, whereas the corresponding order parameters behave in the opposite way.

Looking at figures 3 and 4, one notices an evident similarity of the spectra measured while changing the temperature and pressure. From these figures, as well as from figure 5, it may be deduced that a decrease in temperature by 1 K or an increase in pressure by $c. 3 \text{ MPa}$ changes the relaxation time $\tau_{||}$ by the same value.

Both activation parameters characterizing the reorientations of 6CB molecules around the short axes, $\Delta H_{||}$ and $\Delta V_{||}$ (see figure 6), are similar to those obtained for 5CB and they diminish when the system changes to the nematic phase, as was the case for 5CB [1]. The difference in the values of the activation enthalpy at atmospheric pressure and at $c. 100 \text{ MPa}$ equals $c. 10 \text{ kJ mol}^{-1}$, and again this value is consistent with the value of the association energy of molecules in the nematic phase of the n CB

homologous series [12]. Simultaneously, the activation volume $\Delta V_{\parallel}(T)_p$ systematically decreases on changing to the nematic phase along the isochoric paths. The analogous behaviour observed for 5CB has been interpreted as a result of changes in the degree of dimerization of the molecules in the nematic phase [1]. Such effects have not been observed in the case of 6CHBT [3]. Thus, it can be concluded that the pressure causes breaking of the dipole-dipole correlations in the nematic phases of both *n*CB compounds.

It is commonly assumed [5, 13, 14] that the activation enthalpy ΔH_{\parallel} consists of two parts

$$\Delta H_{\parallel} = W_{\eta} + q, \quad (3)$$

where W_{η} accounts for the viscosity effects, whereas q is the so-called 'nematic potential', introduced by Maier and Saupe [15] in their mean-field theory of the nematic state. Using the data of figure 5 and the formula for the retardation factor g_{\parallel} derived by Meier and Saupe [16]

$$g_{\parallel} = \tau_{\parallel}/\tau_0 = (RT/q)(\exp(q/RT) - 1), \quad (4)$$

we could calculate the q values as a function of pressure at 321 and 324 K, and as a function of temperature at atmospheric pressure. Similarly to the previous calculations [2], the relaxation times $\tau_0(p, T)$ (corresponding to $q=0$) were estimated by extrapolation of $\tau_{\parallel}(p, T)$ to the nematic phase (see figure 5). Figure 7 shows the comparison of q values obtained in this way with the order parameters S calculated from the data quoted in [5]. One notices rough proportionality of both quantities: $q = \varepsilon S$, with the coefficient $\varepsilon = 7.5 \pm 1 \text{ kJ mol}^{-1}$, in comparison with $11 \pm 1 \text{ kJ mol}^{-1}$ in the case of 5CB [2].

Figures 6 and 7 show that the activation enthalpy ΔH_{\parallel} and the nematic potential q behave in the opposite way with pressure. This should mean, consequently, that the activation energy W_{η} characterizing the viscosity in the nematic phase is a decreasing function of pressure! This physically doubtful effect may be avoided if a third component to equation (4) is added

$$\Delta H_{\parallel} = W_{\eta} + q + W_{dd}, \quad (5)$$

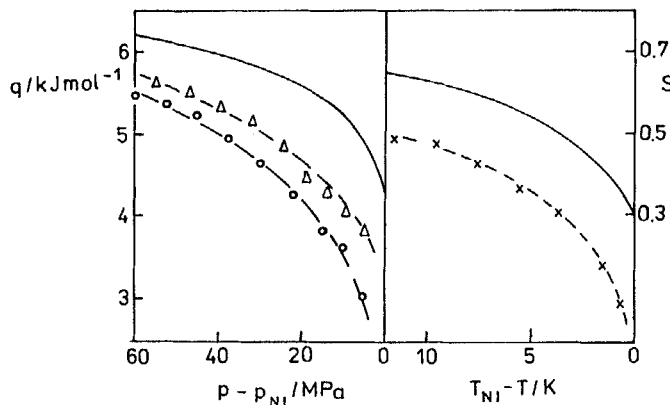


Figure 7. Comparison of the nematic potential q (points) and the order parameter S (solid lines) in the nematic phase of 6CB ($S(p)$ values corresponding to different T are indistinguishable on this scale). T_{NI} and p_{NI} correspond to the nematic-isotropic transition. (○), 321 K; (△), 324 K; (×), 0.1 MPa.

where W_{dd} corresponds to the dipole–dipole association energy. This seems to be the only component in that energy balance which really decreases with the increase of pressure due to the breaking of the dipole–dipole correlations between molecules. This explanation can apply to the 5CB case as well.

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