Dielectric studies of liquid crystals under high pressure III. Low frequency relaxation process in 4-(*trans*-4'-*n*-hexylcyclohexyl)isothiocyanato benzene

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III. Low frequency relaxation process in 4-(*trans*-4'-*n*-hexylcyclohexyl)isothiocyanato benzene

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Dielectric studies of 4-(*trans*-4'-*n*-hexylcyclohexyl) isothiocyanatobenzene (6CHBT) were performed in the pressure range 0·1–150 MPa, the frequency range 1 kHz–13 MHz and the temperature range 295–325 K. The temperature and pressure dependencies of the static permittivity $\varepsilon_{0\parallel}$ and of the relaxation time $\tau_\parallel$ are analysed and compared with the analogous data obtained recently for 4-*n*-pentyl-4'-cyanobiphenyl (5CB) (Parts I and II of this series). Marked differences in the dielectric properties of the nematic phases of the two substances are observed. They are interpreted as a result of varying degrees of molecular association in particular compounds. It is concluded that in the nematic phase of 6CHBT dipole–dipole correlations do not exist or are very weak, whereas for 5CB they are easily broken by a relatively low pressure.

1. Introduction

Dielectric studies of liquid-crystalline substances provide important information about the molecular interactions in different phases. These interactions determine the static dielectric permittivity of a substance, they also influence the rotational dynamics of molecules in liquid crystal phases. Most of the dielectric measurements of liquid crystals were performed only as a function of temperature. However, our first studies of 4-*n*-pentyl-4'-cyanobiphenyl (5CB) under pressure have shown that relatively low pressures influence the molecular interactions considerably [1, 2]. We believe, therefore, that by changing both thermodynamic parameters, pressure and temperature, we can reach a deeper understanding of the physical properties of liquid crystal phases.

In the case of the nematic phase of 5CB the static permittivities measured under isothermal and isobaric conditions (they were near to the $\varepsilon_{0\parallel}$ values) showed a marked decrease when the nematic–isotropic transition was approached [1]. The effects were analysed with the use of the Maier–Meier equation [3] relating $\varepsilon_{0\parallel}$ to order parameter S. (The pressure and temperature dependences of other parameters entering the

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equation could be neglected in this case.) It was found that for constant p (at atmospheric as well as at elevated pressures) the static permittivities were proportional to the $(2S + 1)/T$ factor derived from the equation. However, at constant T marked divergencies from this relation were observed, especially in the vicinity of the nematic–isotropic transition line. Therefore, we have suggested that pressure markedly influences the monomer–dimer equilibrium, involving breaking of the dipole–dipole correlations between the molecules. The parameters characterizing molecular rotations around the short axes (activation enthalpy, energy and volume) decrease with increasing pressure, which supports this suggestion [1].

Nevertheless, it seemed to us that similar studies performed on a substance which does not exhibit dipole–dipole correlations in the nematic phase can throw more light on the problem. We chose 4-(*trans*-4'-*n*-hexylcyclohexyl)isothiocyanatobenzene, 6CHBT (synthesized by Dabrowski *et al.* [4]) for this purpose. Its chemical formula is
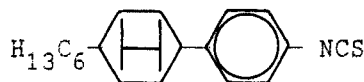
There are several reasons for this choice. (i) Similarly to 5CB the substance is also strongly polar with the dipole moment deviating only slightly from the direction of the main molecular axis [5]. (ii) Dielectric studies hitherto performed at atmospheric pressure show [6] that in the nematic phase of 6CHBT the relaxation process connected with molecular reorientations around the short axes falls in the frequency range accessible with our apparatus (up to 13 MHz). (iii) There are credible indications that dipole–dipole correlations do not play an important role (if any) in the dielectric behaviour of the substance [5]. (iv) 6CHBT is chemically very stable, and so its 'natural' conductivity is sufficiently low to prevent the appearance of instabilities, if an external electric field is applied to the sample in order to obtain a well aligned nematic phase.

Before starting the dielectric studies under pressure the (p, T) phase diagram of 6CHBT had to be known. This was established by Hartmann with the aid of the DTA method [7] and is shown in figure 1. However, no data on the pressure dependence of the order parameter and the molar volume within the nematic phase of 6CHBT are available. Therefore, the discussion of the results in terms of the theories of the nematic phase cannot be as exhaustive as was the case for 5CB [2].

2. Experimental

The dielectric relaxation spectra, $\varepsilon'(\omega)$ and $\varepsilon''(\omega)$, of 6CHBT were measured with the same experimental set up as in previous studies [1, 8], except that we now used a larger capacitor with a geometrical capacity equal to 17·83 pF. The sample of 6CHBT was obtained from Dąbrowski (Military Technical Academy, Warsaw). Its high purity allowed us to apply to the sample a low frequency electric bias field (*c.* 300 V cm^{-1}). In contrast to the case of the 5CB sample, during the present measurements we did not observe any fluctuations of capacity that might be caused by an ionic current resulting from the bias field.

Most measurements of the dielectric spectra started at (p, T) points lying near the freezing line and were carried out with decreasing pressure at constant temperature. However, some points were reached by increasing the pressure at constant T or by a change of temperature at nearly constant pressure. The reproducibility of the results was very good.
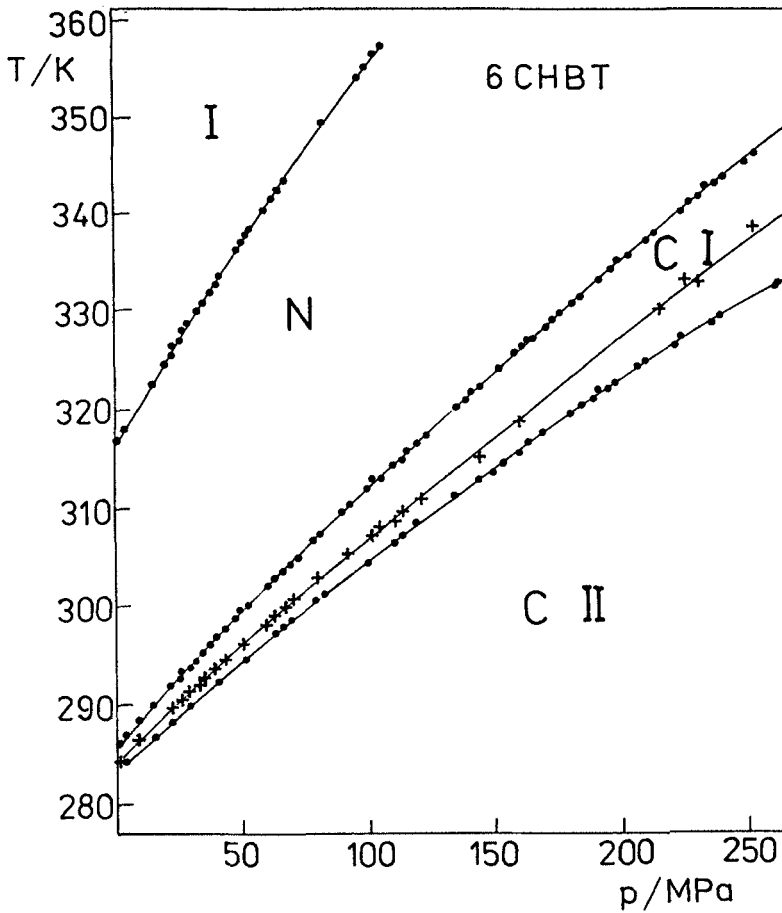
Figure 1. Temperature–pressure phase diagram for 6CHBT. The substance exhibits an additional phase transition in the solid state. Two lines separating the C I and C II phases correspond to different thermal treatment of the sample. For details see [7].

3. Results

In figure 2 the static permittivity is plotted as a function of pressure at different temperatures for the nematic and isotropic phases of 6CHBT. The inset of figure 2 shows that at atmospheric pressure there is very good agreement between the $\varepsilon_{0\parallel}$ values measured for the samples oriented by the electric (present study) and magnetic [5] fields. Additionally, we can see in figure 2 that there is a good consistency of the results obtained at elevated and at atmospheric pressures although they were measured during separate runs. Therefore, we may confirm that the static permittivity measured over the whole range of the nematic phase of 6CHBT corresponds to $\varepsilon_{0\parallel}$.

Figure 3 (*a*) presents, as an example, the dielectric dispersion, $\varepsilon'(\omega)$, and absorption spectra (after subtraction of the conductivity effect), $\varepsilon''(\omega)$, measured at 325 K for different pressures within the nematic phase and one spectrum in the isotropic phase of 6CHBT. Loss curves for the nematic phase were analysed with the aid of standard equations (Cole–Cole, Cole–Davidson, Havriliak–Negami and Jonscher). The best fits were obtained with the use of the Jonscher equation assuming $\tau_{\parallel} = 1/\omega_{max}$ [1, 8]. The
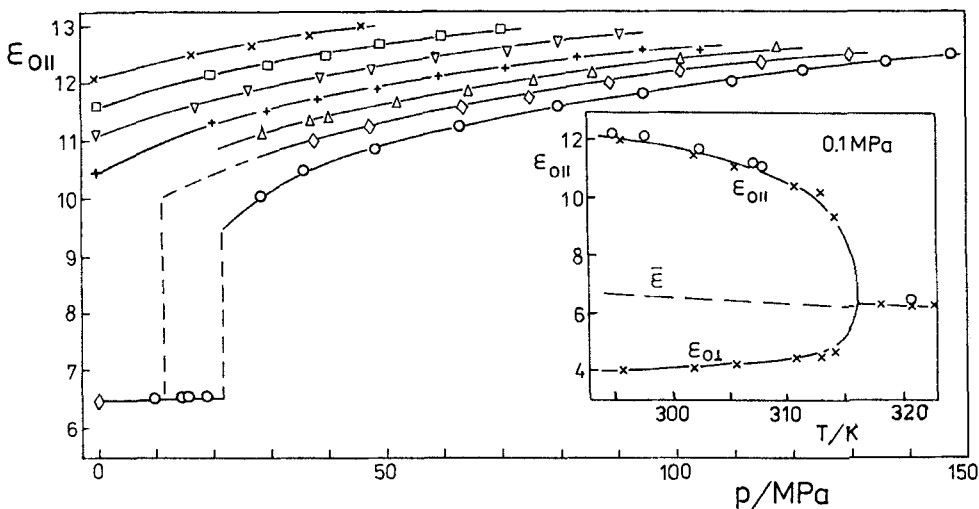
Figure 2. Dependence of the static permittivity $\varepsilon_{0\parallel}$ on pressure in the nematic phase of 6CHBT at 325 K. The inset shows the comparison of the present data (circles) with those obtained for the sample aligned by a magnetic field [5]. ×, 298 K; □, 303 K; ∇, 308 K; +, 313 K; △, 317 K; ◇, 321 K; ○, 325 K.

observed dielectric relaxation process can be described by a single Debye mechanism which is especially evident if the spectra are presented in the form of Cole–Cole plots (see figure 3 (b)). The relaxation times $\tau_\parallel$ are strongly pressure dependent (see figure 4) and it is more convenient to present them in semilogarithmic form as in figure 5.

As for 5CB [1] the relaxation time $\tau_\parallel$ is not a strictly exponential function of pressure. Neglecting this relatively small effect we have calculated the slopes $(\partial \ln \tau_\parallel / \partial p)_T$ by means of a linear regression. They are listed in the table together with the values of activation volume

$$\Delta V_\parallel = RT(\partial \ln \tau_\parallel / \partial p)_T.$$

Taking the values of $\ln \tau_\parallel$ at constant pressure from figure 5 we have calculated the activation enthalpy according to the Arrhenius equation

$$\tau_\parallel = \tau_{0\parallel} \exp(\Delta H_\parallel / RT).$$

As we can see in figure 6, the slopes $(\partial \ln \tau_\parallel / \partial 1/T)_p$ are the same over the whole range of pressure in the nematic phase of 6CHBT. The calculated activation enthalpy $\Delta H_\parallel = 63 \pm 1$ kJ mol^{-1} can be compared with 68 kJ mol^{-1} obtained by Jadzyn et al. [6] at 0·1 MPa.

For the isotropic phase the frequency range accessible in our bridge (up to 13 MHz) allowed us to measure only the rising part of the loss curves (compare figure 3 (a)). However, taking into account the shifts of the dispersion and absorption spectra induced by pressure as well as the results of measurements at atmospheric pressure presented in [6] we were able to estimate the slope $(\partial \ln \tau_{is}/\partial p)_T$ at 325 K. The value for the slope of 0·013 MPa^{-1} and the activation volume ΔV_{is} of 35 cm^3 mol^{-1} are comparable to those obtained for 5CB in the isotropic phase [1].
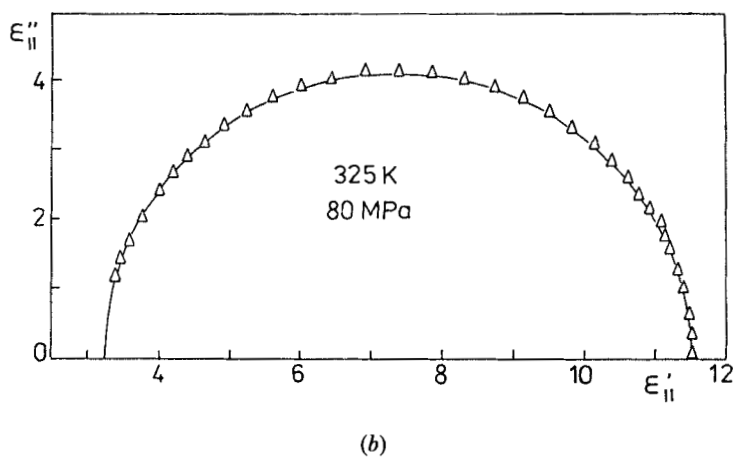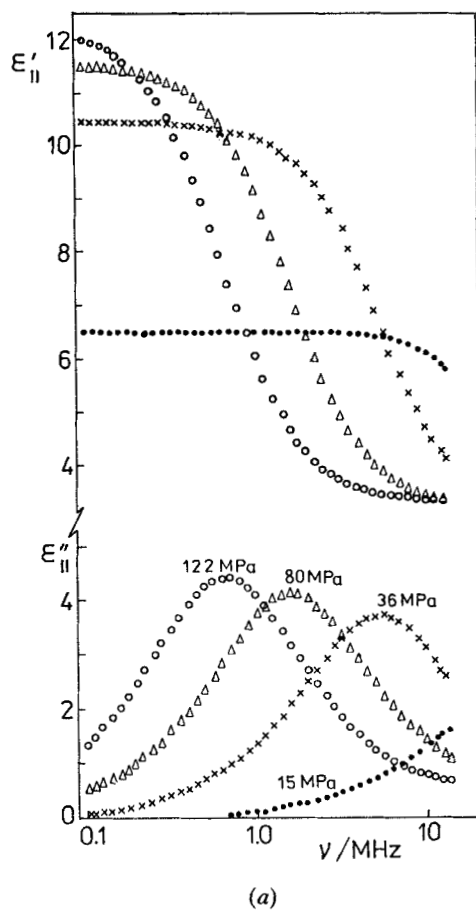
Figure 3. (*a*) Dispersion and absorption spectra obtained for the nematic (122, 80 and 36 MPa) and isotropic (15 MPa) phases of 6CHBT at 325 K. (*b*) Cole–Cole plot for one spectrum from (*a*).
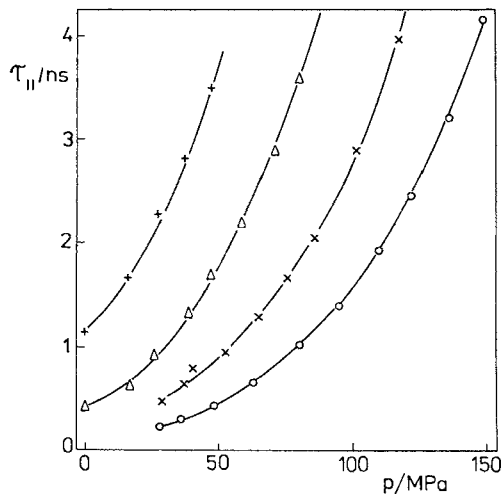
Figure 4.   Pressure dependence of the relaxation time $\tau_{\parallel}$ at different temperatures in the nematic phase of 6CHBT. +, 298 K; D, $\triangle$, 308 K; ×, 317 K; O, 325 K.
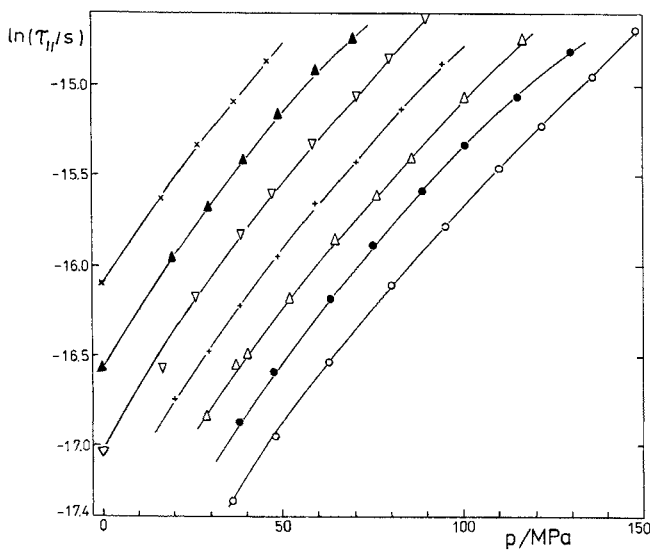

Figure 5. $\ln \tau_{\parallel}$ versus p plots for the nematic phase of 6CHBT at different temperatures. ×, 298 K; ▲, 303 K; ▽, 308 K; +, 313 K; $\triangle$, 317 K; ●, 321 K; O, 325 K.

Temperature dependence of the activation volume $\Delta V_\parallel$ for the nematic phase of 6CHBT.

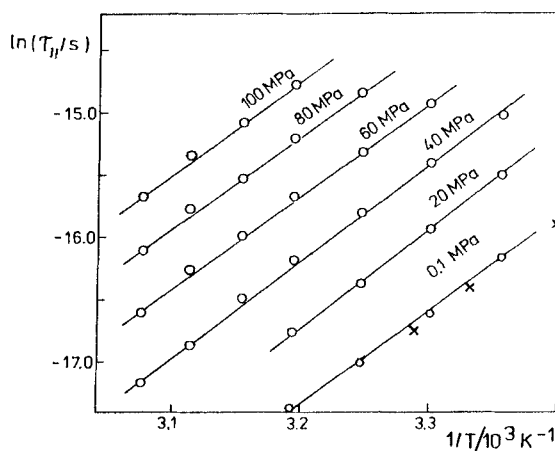| T/K	$(\partial \ln \tau_\parallel / \partial p)_T / \mathrm{MPa}^{-1}$	$\Delta V_\parallel / \mathrm{cm}^3 \, \mathrm{mol}^{-1}$	r
298	0·0244	60·67	0·9995
303	0·0256	64·82	0·9979
308	0·0262	67·45	0·9974
313	0·0251	65·61	0·9985
317	0·0236	62·60	0·9982
321	0·0225	60·46	0·9969
325	0·0230	62·54	0·9974

Figure 6. $\ln \tau_\parallel$ versus $1/T$ plots for the nematic phase of 6CHBT at different pressures. The points marked by $\times$ correspond to $\tau_\parallel$ values obtained in [6].

4. Discussion

It is well established that liquid-crystalline substance having a strongly polar group in the para position (for example –CN or –NO$_2$) exhibit a considerable tendency to form antiparallel dimers [9]. This must lead to a distinct reduction of the dielectric anisotropy, $\Delta \varepsilon' = \varepsilon'_\parallel - \varepsilon'_\perp$, which has been proved experimentally and theoretically, especially for the 4-*n*-alkyl-4'-cyanobiphenyl (*n*CB) homologous series [10–13]. The anti-parallel associations of molecules are found to be reflected in other dielectric properties as well. For all *n*CB compounds it has been found that at the nematic–isotropic transition a marked difference between the extrapolated ε_{is} and $\bar{\varepsilon} = (\varepsilon_\parallel + 2\varepsilon_\perp)/3$ of the nematic phase exists [10–12]. Above the nematic–isotropic transition a characteristic increase in ε_{is} with increasing temperature is observed [11, 12, 14].

The results of our dielectric studies of 5CB under pressure suggest [1] that increase in pressure breaks the dipole–dipole correlations in the nematic phase of this substance very effectively. This is reflected in a strong $\varepsilon_{0\parallel}(p)_T$ dependence and also in the reduction of the activation parameters characterizing the molecular rotation around

the short axes. We have checked [1] that the $\varepsilon_{0\parallel}(T)_p$ values do, while the $\varepsilon_{0\parallel}(p)_T$ values do not obey the approximate relation $\varepsilon_{0\parallel} - 1 \propto (2S+1)/T$ predicted by the Maier–Meier theory [3].

The 6CHBT molecule also has a strong dipole moment ($\mu = 3\cdot5$ D) which makes an angle of about $23°$ with the long molecular axis [5]. Therefore, the possible appearance of dipole–dipole correlations in the nematic phase of this substance has to be considered carefully. The authors of previous dielectric studies performed on 6CHBT [5, 6, 15] do not mention any effect characteristic of the substances with significant degrees of molecular association. Moreover, Baran *et al.* [5] did not observe such effects in other members of the nCHBT homologous series. The dielectric studies of a binary mixture of 6CHBT and 5CB show that antiparallel complexes $(5CB)_2$ vanish as the concentration of 6CHBT increases [16]. The results of X-ray studies of smectic phases in substances with the –CN and –NCS groups have shown that exchange of –NC by –NCS leads to the cancelling of two-molecule layers, whereas substituting the hexyl for a phenyl ring in the mesogens with the –CN group does not affect such layers [9, 15]. Therefore, it seems to be proved that in the nematic phase of 6CHBT dipole–dipole correlations either do not exist or are very weak.

By comparing the results of dielectric studies of 5CB [1] and 6CHBT under pressure we notice distinct differences in the dielectric properties of the nematic phases of the two substances. Figure 7 shows how the static permittivities of the two
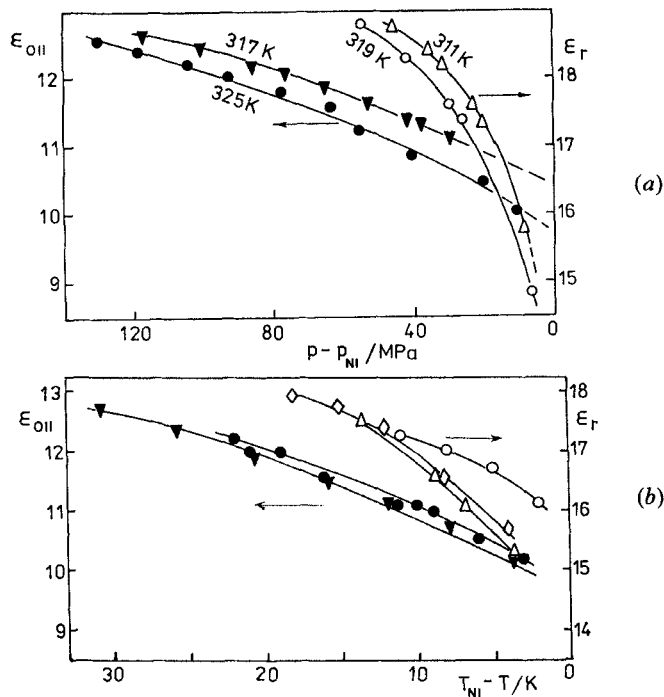

Figure 7. Comparison of the pressure (*a*) and temperature (*b*) dependences of the static permittivity in the nematic phases of 5CB and 6CHBT. (*a*) ▼, ●, 6CHBT; △, ○, 5CB. (*b*) 6CHBT: ●, 0·1 MPa; ▼, 30 MPa. 5CB: ○, 0·1 MPa; △, 30 MPa; ◇, 60 MPa.

substances change while going into the nematic phase along the isothermal (see figure 7 (*a*)) and isobaric (see figure 7 (*b*)) lines. In both presentations the static permittivity of 5CB is influenced by pressure much more than 6CHBT. Furthermore, in the pressure range 0·1 to 100 MPa the activation enthalpy $\Delta H_{\parallel}$ is constant for 6CHBT (63 $\pm$ 1 kJ mol^{-1}, see figure 6), whereas it gradually decreases with increasing pressure for 5CB [1]. It is characteristic that the observed reduction of $\Delta H_{\parallel}$ within the nematic phase of 5CB (from *c.* 62 at 0·1 MPa to *c.* 50 kJ mol^{-1} at 100 MPa) coincides well with the value of the association energy (9 $\pm$ 4 kJ mol^{-1}) estimated for the *n*CB homologous series (*n* = 5–8) on the basis of dielectric studies [15]. The activation volume $\Delta V_{\parallel}$ behaves similarly: for 6CHBT there is some scatter of values calculated at different temperatures (see the table) but no systematic decrease with increasing temperature is observed, in contrast to 5CB [1].

All of these facts seem to corroborate the conclusion put forward in Part I [1] that relatively low pressure causes breaking of the dipole–dipole correlations in the nematic phase of 5CB. In this context it would be extremely interesting to perform high pressure dielectric studies of other substances with a –CN terminal group, especially those exhibiting the so-called reentrant nematic phases induced by pressure. The appearance of such phases has been explained by a model assuming the persistence of strong dipole–dipole correlations well above 100 MPa [17, 18].

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