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Stanislaw Urban; Albert Würflinger; Antoni Kocot

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Phase diagram and dielectric relaxation studies of *n*-octyl-isothiocyanato-biphenyl (8BT) in the crystalline E phase under high pressure

STANISLAW URBAN*
Institute of Physics, Jagellonian University, Reymonta 4, 30-059 Cracow, Poland

ALBERT WÜRFLINGER
Institute of Physical Chemistry II, Ruhr-University Bochum, Germany

and ANTONI KOCOT
Institute of Physics, Silesian University, Katowice, Poland

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The pressure–temperature phase diagram of *n*-octyl-isothiocyanato-biphenyl (8BT) in the pressure range up to 250 MPa (2.5 kbar) and the temperature range 250–400 K was established with the aid of DTA. At 1 atm the substance exhibits exclusively CrE polymorphism. At pressures above 190 MPa, the clearing line splits showing an additional phase which is not yet identified. Dielectric relaxation measurements on the CrE phase of 8BT were performed in the pressure range 0.1–120 MPa and the temperature range 304–345 K. A Debye-type relaxation process was observed in the frequency range 100 Hz-1 MHz. The longitudinal relaxation time τ, characterizing the molecular reorientations around the short axis, was analysed with respect to the pressure and temperature, yielding the activation volume, $\Delta^{\#} V = RT(\partial \ln \tau/\partial p)_T$, and activation enthalpy, $\Delta^{\#} H = R(\partial \ln \tau/\partial T^{-1})_p$, respectively. The results are compared with analogous data obtained recently for similar compounds having other liquid crystalline phases (N, SmA).

1. Introduction

Liquid crystalline (LC) materials constituted from rod-like molecules exhibit a reduction in molecular freedom on going from the isotropic liquid state (I) through the LC phases to the crystalline (Cr) state which is characterized by long range positional and orientational order. Taking into consideration the actual degree of molecular order (orientational and/or positional) one can distinguish between the 'liquid-like' phases (isotropic, nematic, smectic A and smectic C), and the 'crystal-like' smectic phases (CrB, G, E,…) called also the 'smectic-like' soft crystal phases [1] (which have to be distinguished, however, from the plastic crystalline phases [2]). The transitions between the 'liquid-like' and the 'crystal-like' phases are accompanied by a considerable change in the rotational dynamics of the molecules [3–13]. The dielectric relaxation method is especially well suited to study this effect if the molecules possess permanent dipoles [2–5]. Generally, one can measure the low frequency (l.f.) relaxation process connected with molecular reorientations around the short axes, and the high frequency (h.f.) process connected with rotations around the long axes (and often with the intramolecular rotations). The h.f. process is practically unchanged at the phase transitions between LC phases, whereas the l.f. process is extremely sensitive to these. It should be stressed here that besides the 'liquid-like' phases, the l.f. process has been observed in practically all 'crystal-like' LC phases ([4, 6, 13] and references therein).

Our recent high pressure (h.p.) studies of the l.f. process concerned the 'liquid-like' phases (I, N, SmA) [2, 5, 7–11]. The measured longitudinal relaxation time was analysed with respect to the pressure, yielding the activation volume, $\Delta^{\#} V = RT(\partial \ln \tau/\partial p)_T$, and to the temperature, yielding the activation enthalpy, $\Delta^{\#} H = R(\partial \ln \tau/\partial T^{-1})_p$ and the activation energy, $\Delta^{\#} U = R(\partial \ln \tau/\partial T^{-1})_V$, if the density as a function of p and T was known. Due to the voluminous rotational motions

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*Author for correspondence, e-mail: ufurban@cyf-kr.edu.pl

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around the short axes, the activation volume consists of *c.* 15–20% of the molar volumes [5]. The activation energy is smaller than the activation enthalpy by a factor of *c.* 2, indicating the importance of the steric effects acting against molecular rotation. A common feature of the results obtained for cyano compounds is the decrease of the activation parameters, $\Delta^{\#}V$ and $\Delta^{\#}H$, when going away from the clearing point by changing the pressure or temperature. No such effects were detected in the case of substances having the thiocyanato, −NCS, terminal group [5, 9, 10]. This indicates the influence of dipole–dipole correlations in cyano compounds on the l.f. process, as recently discussed in [12]. In this paper we present the results of h.p. studies on *n*-octyl-isothiocyanato-biphenyl (8BT) forming the CrE phase in a broad temperature range [6]. The *p–T* phase diagram of 8BT was established by DTA. Then the dielectric relaxation measurements within the CrE phase were performed for several isotherms in the pressure range up to 120 MPa. The activation parameters are compared with analogous data obtained for the 'liquid-like' phases. Some important differences are noted and discussed.

2. Experimental

Two pieces of high pressure DTA apparatus have been used; these were designed for measurements at lower [14] and higher [15] temperatures. DTA peaks were generated at heating rates of 1 or 2 K min^{-1} and registered with a two-channel recorder. The sample was sealed in a can made with indium which limited the upper temperature to about 140°C. The CrE phase of 8BT showed a strong tendency to supercool and even prolonged annealing of the sample at *c.* −30°C led to a metastable crystal modification generating irregular melting temperatures at different pressures. The only way of obtaining the stable crystalline phase, and consequently a regular melting line, was to decrease the temperature by *c.* 20°C below this line and then have a sudden decrease of pressure. However, very often the indium cell was damaged after such a treatment, and this limited the number of points for the melting line.

The studies of the dielectric properties of 8BT in the CrE phase were performed with the use of the high pressure chamber described in [16]. For safety reasons, the upper limit of the pressure was 120 MPa and of the temperature *c.* 72°C. The complex dielectric permittivity, $\varepsilon^* = \varepsilon' - i\varepsilon''$, was measured with an HP 4192A impedance analyser in the frequency range 100 Hz–1 MHz. The temperature was stabilized within ±0.2 K. Neither magnetic nor electric fields influenced the permittivity values in the CrE phase. The high purity of the sample meant that the conductivity effect was negligible down to 100 Hz during a period of 10 days.

3. Results

Figure 1 presents the pressure–temperature phase diagram established for 8BT by DTA. With increasing pressure, a splitting of the clearing line is observed. The pressure dependence of the transition temperatures can be expressed by the following relations (*T* in °C, *p* in MPa)

$$T_{\mathrm{cl}} = 67.9 + 0.237p - 8.09 \times 10^{-5}p^2$$

$$T_{\mathrm{E\text{-}N?}} = 76.6 + 0.207p$$

$$T_{\mathrm{m}} = 22.2 + 0.241p - 1.82 \times 10^{-4}p^2.$$

The triple point corresponds to 116°C and 190 MPa. The DTA traces obtained on heating and cooling in the vicinity of the triple point and above it are shown in figure 2. The new phase is not identified yet, but a small thermal effect accompanied its transition to the isotropic liquid and this might suggest that we are dealing with a 'liquid-like' phase (nematic?).

Typical dielectric absorption spectra measured for the CrE phase at constant temperature and different pressures are shown in figure 3 (*a*), whereas figure 3 (*b*) presents the Cole–Cole plots with two spectra obtained at low and high pressures. The well known Cole–Cole modification of the Debye equation, $(\varepsilon^* - \varepsilon_\infty)/(\varepsilon_s - \varepsilon_\infty) = 1/(1 + i\omega\tau)^{1-\alpha}$, was fitted to the experimental points

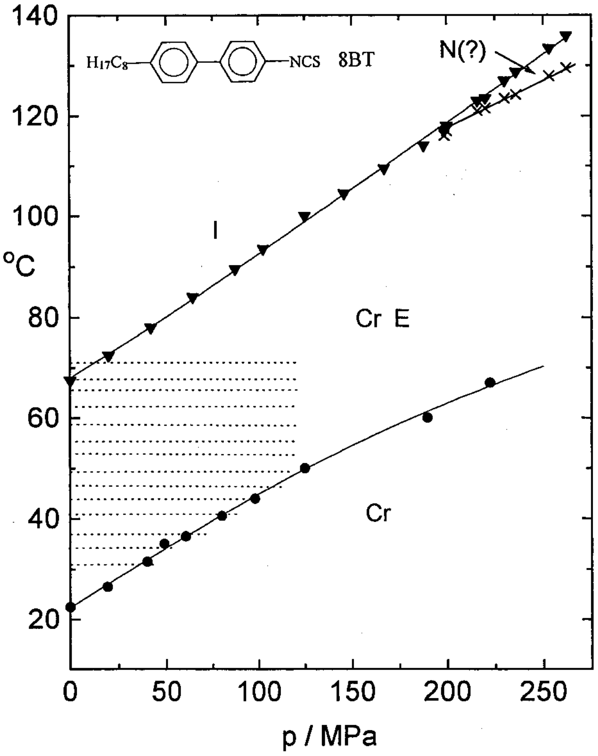

Figure 1. Pressure–temperature phase diagram for 8BT established by DTA. Dotted lines mark the temperatures at which the dielectric relaxation studies were performed.

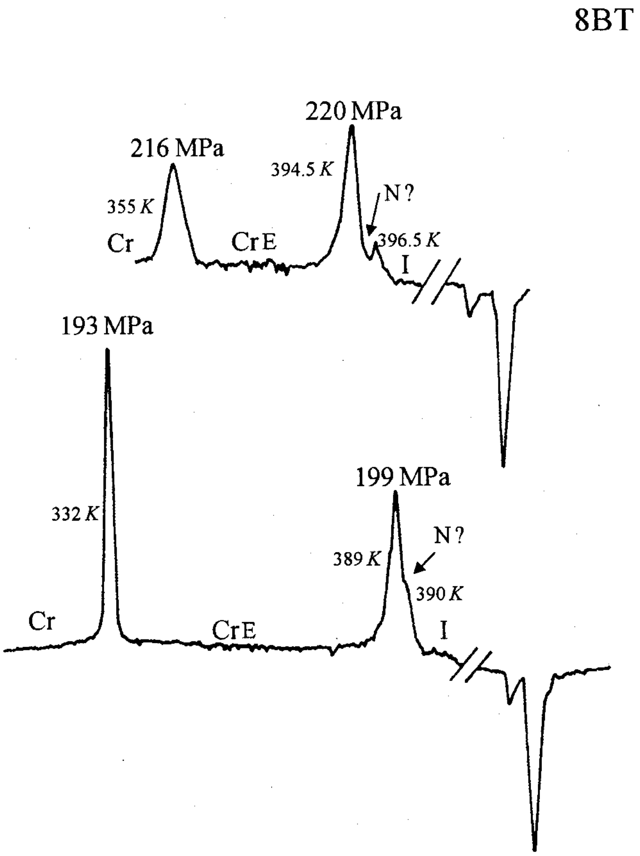

Figure 2. DTA traces on heating (left side) and cooling (right side) at pressures above the triple point (190 MPa, 116°C).

(ε_s and ε_∞ are the static and high frequency permittivities, respectively, $\omega = 2\pi\nu$, and τ is the relaxation time). The parameter α characterizing the distribution of the relaxation times was very small (*c.* 0.01–0.03), so we may consider the observed relaxation process as the Debye process. The static permittivity in the CrE phase (4.0–4.8) was markedly lower than the isotropic value (6.0 [6]). At 1 atm, ε_s was practically independent of temperature, but increased considerably with the pressure.

The dielectric relaxation time τ calculated from the fits of the imaginary part of the Debye equation to the absorption spectra measured at different temperatures and pressures are presented in figure 4 in semi-logarithmic scale. At one isotherm ($T = 335.5$ K) it was checked that the τ-values do not depend upon whether the pressure was increased or decreased. All other points were measured with increasing pressure only. Very good reproducibility of the results obtained over a week (points corresponding to the slightly different temperatures 322.7 and 322.5 K, respectively) indicates that the sample was stable over the course of the experiment. As one can see in figure 4, the points at given T can nicely be approximated by the straight lines (except the isotherm ending in the isotropic phase where deviations of the points close to the transition are observed). The slopes of the lines give the activation volumes $\Delta^{\#}V(T)$ which are presented in figure 6(*a*). By cutting the data in figure 4 at constant pressures, we have drawn the set of Arrhenius plots (figure 5) whose slopes yield the activation enthalpies $\Delta^{\#}H(p)$ that are shown in figure 6(*b*).

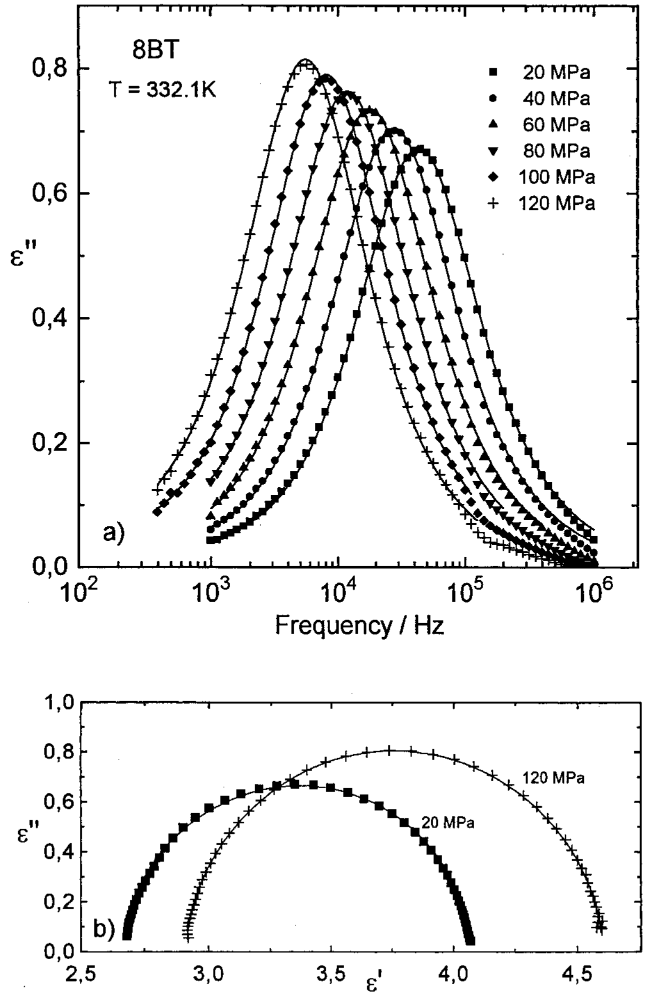

Figure 3. (*a*) Examples of the dielectric absorption spectra measured at one isotherm (332.1 K) and several pressures; the lines are fits of the Debye equation. (*b*) Cole–Cole plots for two relaxation spectra.

4. Discussion

It is well known that increase of pressure considerably influences the phase situation in LC substances. In some substances new phases are induced by pressure, in others the phases become pressure-limited [2, 5, 17–21]. Recently, Drozd-Rzoska *et al.* [22–24] have studied the discontinuity $\Delta T = T^* - T_{\text{Is-LC}}$ of the Isotropic–N, Isotropic–SmA and Isotropic–E transitions involved

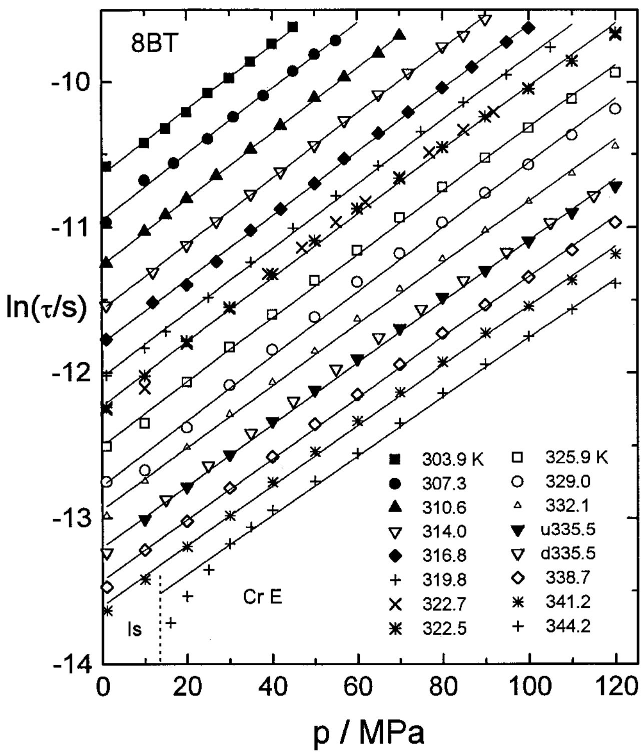

Figure 4. Logarithm of the longitudinal relaxation time versus pressure for all isotherms studied within the CrE phase of 8BT. The points at 335.5 K were obtained with increasing (u) and then decreasing (d) pressure. The data at 322.5 and 322.7 K were obtained over the time interval of one week. The straight lines fit the points that yield the activation volume.

through the pressure for the three homologous series: *n*CB, *n*BT and *n*DBT, using the non-linear dielectric effect, NDE. (T^* is the extrapolated temperature of a hypothetical continuous phase transition, and $T_{\text{Is-LC}}$ is the clearing temperature.) The different behaviour of $\Delta T(p)$ at the transitions Isotropic–N (increase) and Isotropic–Sm (decrease) was interpreted by taking into account the influence of pressure on the molecular ordering in the particular phases. For the N phase, the increase in pressure causes an increase in the orientational ordering and hence its divergence from the isotropic liquid increases, resulting in the increase in ΔT. In smectogens the rise of pressure will probably first shift molecules along the direction of the preferred orientational ordering (an effect which might lead to a destruction of the layer structure) and consequently ΔT decreases with rising pressure [22–24]. If so, sufficiently high temperature and pressure can destroy the SmA structure and cause the appearance of a similar structure to that known as the high pressure re-entrant nematic phase (e.g. [25] and references therein). This should happen especially for smectogenic substances having long alkyl chains. However, in the case of 14CB no such effect was found up to 230 MPa [26], whereas it happens for 10DBT [21] as well as here for 8BT (figure 1).

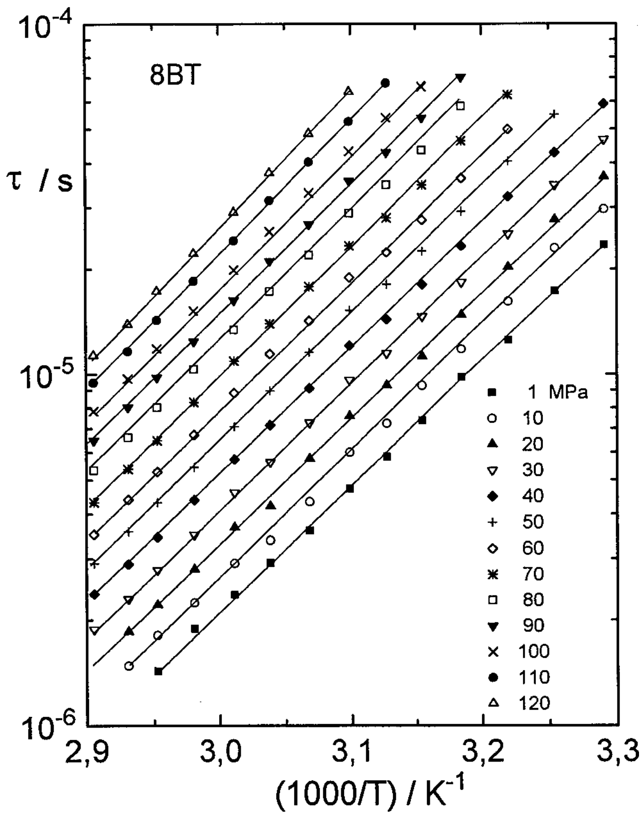

Figure 5. Arrhenius plots for several isobars within the CrE phase of 8BT that yield the activation enthalpy.

The relaxation time τ obtained is undoubtedly connected with the molecular rotations around the short axis, as in the other *n*BTs [6]. Therefore it strongly depends upon the pressure, similarly to that observed for the ‘liquid-like’ phases [5, 7–11], with the activation volume reaching *c.* 20% of the molar volume. Unlike cyano compounds [5, 7, 11], in the CrE phase of 8BT, $\Delta^{\#}V$ does not depend on temperature, figure 6 (*a*). The same was found for other thiocyanato compounds in the N [9], as well as in the SmA [10] phases, figure 7 (*a*). This might indicate an absence of dipole–dipole correlations in the thiocyanato compounds, such correlations being present in all cyano compounds. The activation enthalpy, figure 6 (*b*), shows a tendency to increase with rising pressure. This is contrary to the trends observed for many cyano compounds in the nematic, as well as in the smectic A_d phase, figure 7 (*b*), [5, 7–11]. Such a behaviour of $\Delta^{\#}H$ in the CrE phase might mean that the energy barrier hindering the molecular rotation around the short axis depends mainly on the intermolecular distances which diminish with the pressure. However, this tendency could not be further elucidated due to

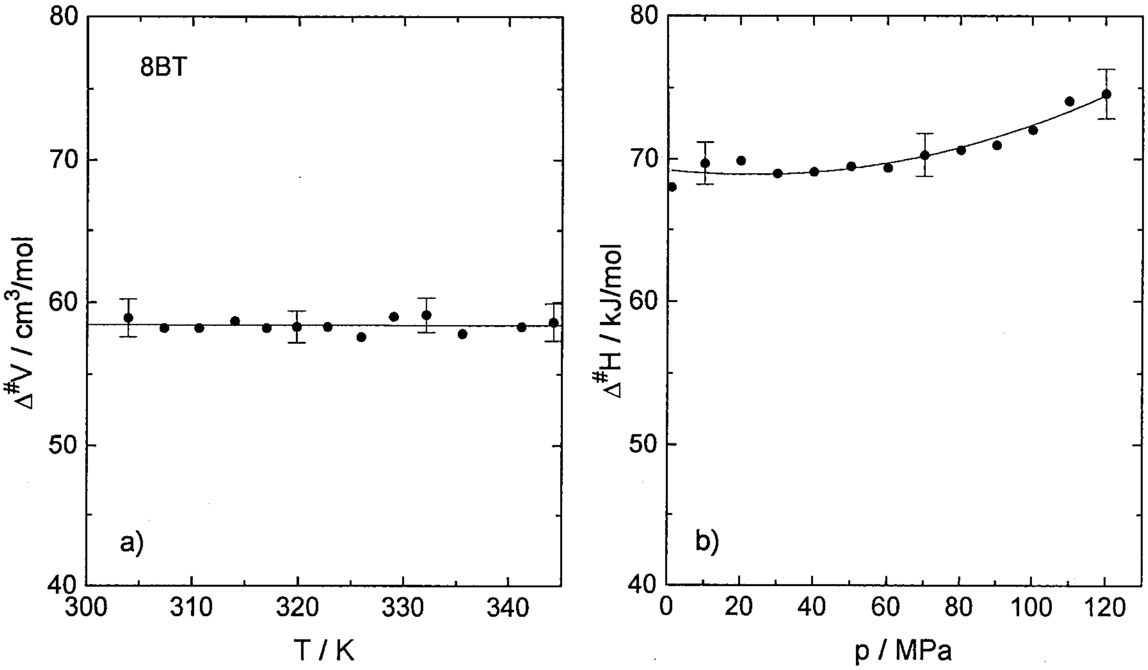

Figure 6. Activation volume versus temperature (*a*) and activation enthalpy versus pressure (*b*) calculated from the plots in figures 4 and 5, respectively.

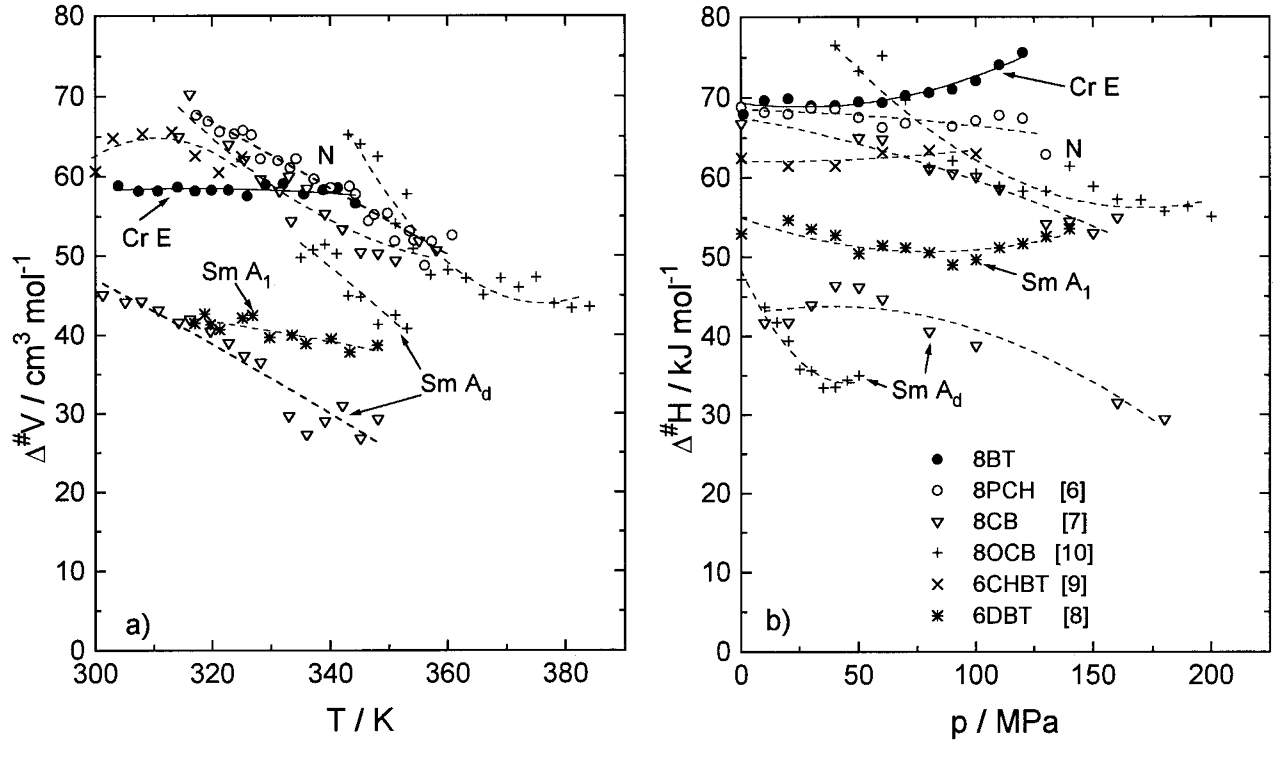

Figure 7. Comparison of the activation volumes (*a*) and activation enthalpies (*b*) in different LC phases for several substances having comparable molecular shapes. The lines are guides for the eye only.

the limited range of pressure accessible in the present experiment (the same relates to the h.p. experiment for 6DBT [10]).

Striking features of the activation data gathered in figure 7 are: (i) the activation volumes $\Delta^{\#}V$ and enthalpies $\Delta^{\#}H$ are close for such different phases as nematic

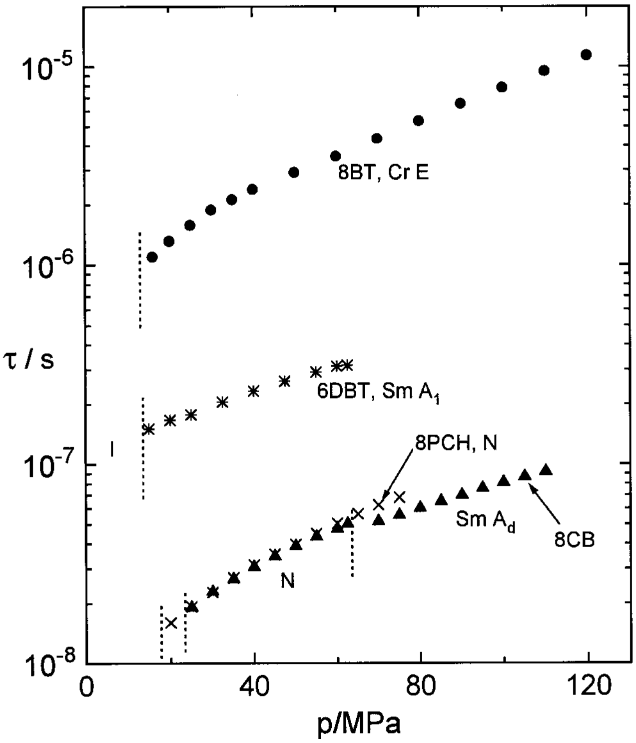

Figure 8. Comparison of the pressure dependence of the longitudinal relaxation times in several LC substances. The vertical dotted lines mark the transition pressures.

and crystalline E, and (ii) the values of both activation parameters are markedly lower in the smectic A phases. Surprisingly, this happens in spite of the very large difference in the values of the longitudinal relaxation times between particular phases which is illustrated in figure 8. This might indicate that the energy barrier in the LC phases is mainly created by the side–side interactions which are similar for all two-ring compounds. However, the rotational freedom of molecules in the orthogonal smectic A phases is additionally increased due to a lack of any arrangement of the molecular centres of mass in the layers. In order to overcome the energy barrier a molecule must have sufficient room created by the transverse fluctuations of its neighbours. Considering the relaxation time as the mean residence time in the two-well potential model [27], one can note a drastic change in the probability of rotational jumps between the 'liquid-like' and 'crystal-like' phases.

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