DTA and Dielectric Studies of a Substance with the Nematic, Smectic A, and Smectic C Polymorphism at Ambient and Elevated Pressures

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For the first time the low frequency relaxation process in two smectic phases (smectic A and smectic C) was studied at elevated pressures with the aid of DTA and dielectric spectroscopy. The substance studied, 2-(4-hexyloxyphenyl)-5-octyl-pyrimidine (6OPB8 in short) exhibits the nematic (N) – S_A – S_C phase sequence. The *p*-*T* phase diagram was established with DTA. However, the S_A – S_C transition was not observed in the DTA, but could be detected by dielectric relaxation measurements. The dielectric relaxation time measured as function of temperature and pressure, $\tau_{\|}(p,T)$, enabled us to calculate the activation volume, $\Delta^{\#}V = RT(\partial \ln \tau/\partial p)_{\mathrm{T}}$, and activation enthalpy, $\Delta^{\#}H = R(\partial \ln \tau/\partial T^{-1})_p$. It was found that $\Delta^{\#}V(\mathrm{S_A}) > \Delta^{\#}V(\mathrm{S_C})$ and $\Delta^{\#}H(\mathrm{N}) \gg \Delta^{\#}H(\mathrm{S_A}) > \Delta^{\#}H(\mathrm{S_C})$, indicating that the molecular rotations around the short axes are more feasible in the tilted S_C than in the orthogonal S_A phase.

Key words: Liquid Crystal; Dielectric Relaxation; *p*-*T* Phase Diagram; High Pressures.

1. Introduction

The dielectric relaxation method is useful for analyzing the rotation of polar molecules in liquid crystals. In the case of rod-like molecules, rotations around the short and long molecular axes have to be distinguished. In the nematic (N) phase they are studied when the measuring field is parallel and orthogonal to the director **n**. The longitudinal μ_{l} and transverse μ_{t} dipole components are responsible for the low frequency (MHz) and high frequency (hundreds of MHz and even GHz) relaxation processes, respectively. The relaxation times $\tau_{\|}$ and $\tau_{\perp}$ are characteristic quantities describing the rates of the respective processes. In this paper we shall deal with low frequency processes only.

Dielectric relaxation studies of liquid crystals under elevated pressure were performed for several substances with the nematic [1 – 3], nematic and smectic A_d [4,5], smectic A_1 [6,7] and smectic (crystalline) E [8-10] phases. The low frequency relaxation time was analysed as function of pressure at constant temperature, yielding the activation volume $\Delta^{\#}V = RT(\partial \ln \tau/\partial p)_T$, as function of temperature at constant pressure, yielding the activation enthalpy $\Delta^{\#}H = R(\partial \ln \tau/\partial T^{-1})_p$, and as function of temperature at constant volume, yielding the activation energy $\Delta^{\#}U = R(\partial \ln \tau/\partial T^{-1})_V$. The molecules studied belong to two-ring homologous series with the alkyl or alkoxy tail at one side and the strongly polar CN or NCS group at the other side. The following results may be pointed out: The activation volume, which may be considered as the free volume the molecules need in order to perform the rotational jump over the potential barrier, is of the order of 60 – 70 cm^3/mol for the nematic and smectic E phases, whereas for the smectic A phases it is markedly lower [4, 5, 8]. Analogous features concern the behaviour of the activation enthalpy. Independently of the phase studied (nematic, smectic A_d or the crystal-like smectic E phase), the activation energy amounts to approximately half of the activation enthalpy [7, 9] which indicates that both temperature and volume effects determine the molecular rotations around the short axes in LC phases to the same extent. In the present work yet another liquid-like phase, the smectic C phase, will be studied as function of temperature and pressure. The substance chosen, 2-(4-hexyl-

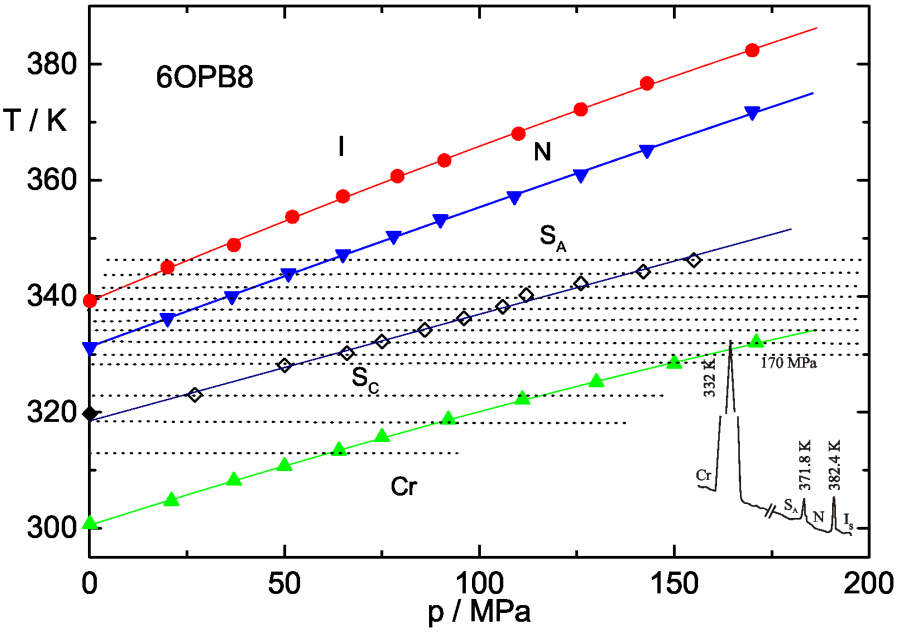
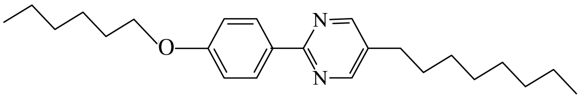


Fig. 1. Pressure-temperature phase diagram for 6OPB8. Full points: DTA results, open points: derived from the dielectric measurements (compare Fig. 6). Horizontal dotted lines indicate the isotherms at which the dielectric measurements were performed. The inset presents a typical DTA trace.



oxyphenyl)-5-octyl-pyrimidine (6OPB8 in short), exhibits the following phase sequence: crystalline (Cr) - smectic C (S_C) - smectic A (S_A) - nematic (N) - isotropic (Is). However, its molecular structure differs from those previously studied because of the presence of flexible wings at both sides of the molecule. Thus, one may expect some different behaviour of quantities characterising the molecular rotations around the short axis in particular phases.

2. Experimental

The 6OPB8 sample was synthesised in the Institute of Chemistry, Military University of Technology, Warsaw. DTA measurements have been carried out with the set-ups described in [11, 12]. Heating rates of 1 or 2 K/min were applied.

The measurements at 1 atm of the complex dielectric permittivity $\varepsilon*(f) = \varepsilon'(f) - i\varepsilon''(f)$ have been carried out in the frequency range of 10 kHz – 15 MHz (Agilent 4192A impedance analyzer) and a temperature range covering all LC phases. A parallel-plate capacitor ($C_0 \approx 50$ pF) was calibrated with the use of standard liquids. The measurements were carried out with heating and then cooling of the sample. During the collection of the spectra the temperature was stabilised within ±0.1 K. The high pressure experiment was performed at the Institute of Physics of the Silesian University, Katowice. For measurements at elevated pressure we used a Novo-Control GmbH dielectric spectrometer equipped with a Novo-Control Alpha dielectric analyzer. The sample was placed in a specially designed capacitor, with a gap $d = 0.3$ mm and $C_0 = 6.6$ pF, made from Invar. The capacitor contained 0.3 cm^3 of the sample. The pressure was transmitted to the sample by deformation of a 0.05 mm Teflon membrane [13 – 15]. The sample was always isolated from the pressurizing medium (mixture of heptane and silicon oil). The capacitor was placed in a chamber. The pressure was generated by a hydraulic press and measured by a Nova Swiss tensometric pressure meter (resolution ±0.1 MPa). Temperature was controlled within ±0.1 K by a liquid flow from a thermostatic bath. The data were analyzed by means of 6.1 ORIGIN software.

3. Results

3.1. P-T Phase Diagram

Figure 1 presents the temperature-pressure phase diagram established for 6OPB8 in the pressure range up to 170 MPa. Typical DTA traces are shown in the insert of Figure 1. The transition between both smec-

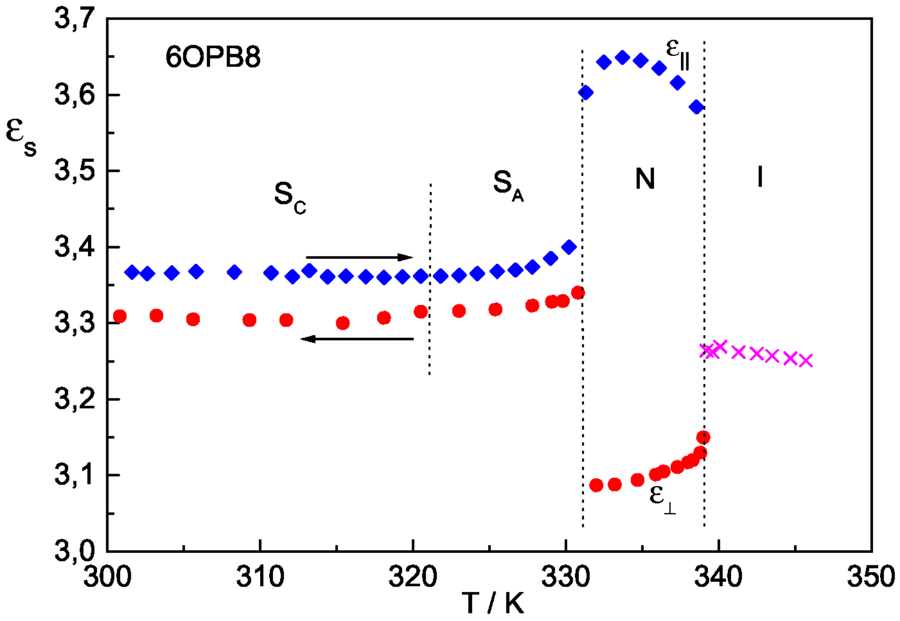


Fig. 2. Static dielectric permittivities measured in different phases of 6OPB8 for the parallel orientation (heating run) and the perpendicular orientation (cooling run) of the sample.

Table 1. The parameters of the polynomial $T/\mathrm{K} = a + b \cdot (p/\mathrm{MPa}) + c \cdot (p/\mathrm{MPa})^2$, fitted to the transition points shown in Figure 1.

Transition	*A*	*b*	$c \cdot 10^4$
N → Is	339.2	0.234	1.68
S_A → N	331.3	0.247	0.58
S_C → S_A	318.5	0.184	–
Cr → S_C	300.5	0.213	1.74

tic phases was not detected in DTA measurements. At ambient pressure this transition could be detected under a polarizing microscope equipped with a hot stage. Also the dielectric relaxation data measured as function of temperature allowed to detect this transition (see below). The open points in the phase diagram were established from the analysis of the dielectric results (see Fig. 6). The extrapolation to 1 atm of the straight line fitted to the points agrees well with the observed transition temperature T_{A-C}. The pressure dependence of the transition temperatures can be expressed by quadratic polynomials with the parameters in Table 1.

3.2. Dielectric Studies at 1 atm

At ambient pressure the 6OPB8 sample was studied in heating and then cooling runs. For the former case the sample reacted on the orienting magnetic field (0.8 T) after transition to the nematic phase only. On cooling the alignment adjusted in the N phase did not survive to the S_A phase. The results of measurements of the static permittivities $\varepsilon_{s||}$ and $\varepsilon_{s\perp}$ are shown in Figure 2. Typical absorption spectra measured in particular phases of 6OPB8 (heating rate) are presented in Figure 3a. They can be very well described by the Debye equation

$$\varepsilon'' = \frac{(\varepsilon_s - \varepsilon_\infty)\omega\tau}{1 + (\omega\tau)^2} + \frac{\sigma}{\varepsilon_0\omega}, \qquad (1)$$

where ε_s and ε_∞ are the static and high frequency permittivities, respectively, $\omega = 2\pi f$, f is the frequency, ε_0 the free space permittivity, and τ the dielectric relaxation time. At low frequencies (especially in the N phase) the conductivity term $\sigma/\varepsilon_0\omega$ was substantial (the low frequency wings in the spectra presented in Fig. 3a). The determined relaxation times $\tau_{||}$ are presented in Fig. 4 in form of the activation plot $\ln\tau_{||}$ versus T^{-1} for the heating and cooling runs. Both sets of data agree very well. The transition temperatures could be determined due to changes in the slopes of the lines fitted to the experimental points (compare Figs. 4 and 6a). On heating they correspond excellently with the points in the phase diagram, Figure 1. On cooling, however, the transition $S_A \rightarrow S_C$ was considerably shifted down from 319 K to 313 K (see Fig. 6a). The activation enthalpy $\Delta^{\#}H_{||} = R(\partial \ln\tau_{||}/\partial T^{-1})$, determined from the plots in Fig. 4 are: (173 ± 5) kJ/mol

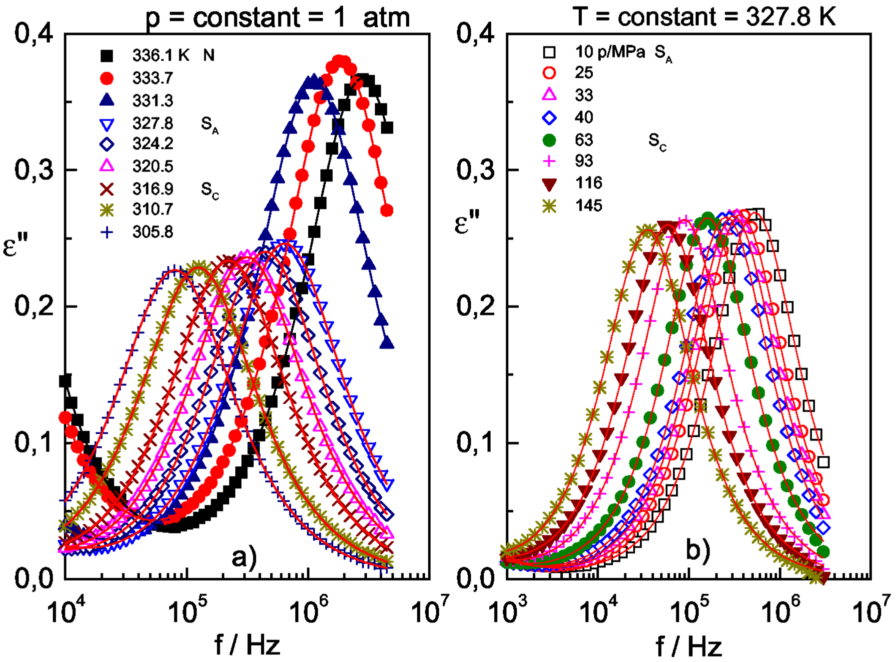


Fig. 3. Typical absorption spectra measured in the S_A and S_C phases of 6OPB8 at 1 atm as function of temperature (a), and at constant temperature as function of pressure (b). The sample could not be aligned in smectic phases, which resulted in different amplitudes of the dielectric losses. The lines are fits of the Debye equation.

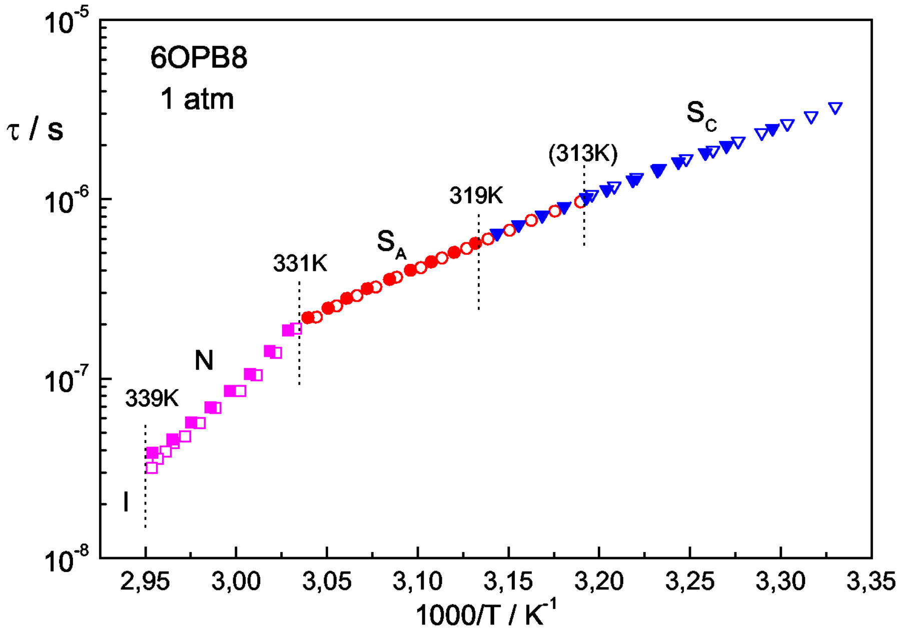


Fig. 4. Activation plot for the low frequency relaxation process in LC phases of 6OPB8 at 1 atm. Full points correspond to the heating and open points to the cooling run.

in the N phase, (83 ± 3) kJ/mol in the S_A phase, and (70 ± 3) kJ/mol in the S_C phase.

3.3. Relaxation Studies at Elevated Pressures

Figure 3b presents typical absorption spectra collected at constant temperature and different pressures. In these measurements the sample was not oriented at all. The Debye formula (1) fits the spectra excellently. The relaxation times determined from the frequency corresponding to the maximum of losses $\varepsilon''_{\max}$, $\tau = 1/(2\pi f_{\max})$, are presented in Fig. 5 as $\ln \tau_{\|}$ versus p plots. The slopes of the lines fitted to the points yield

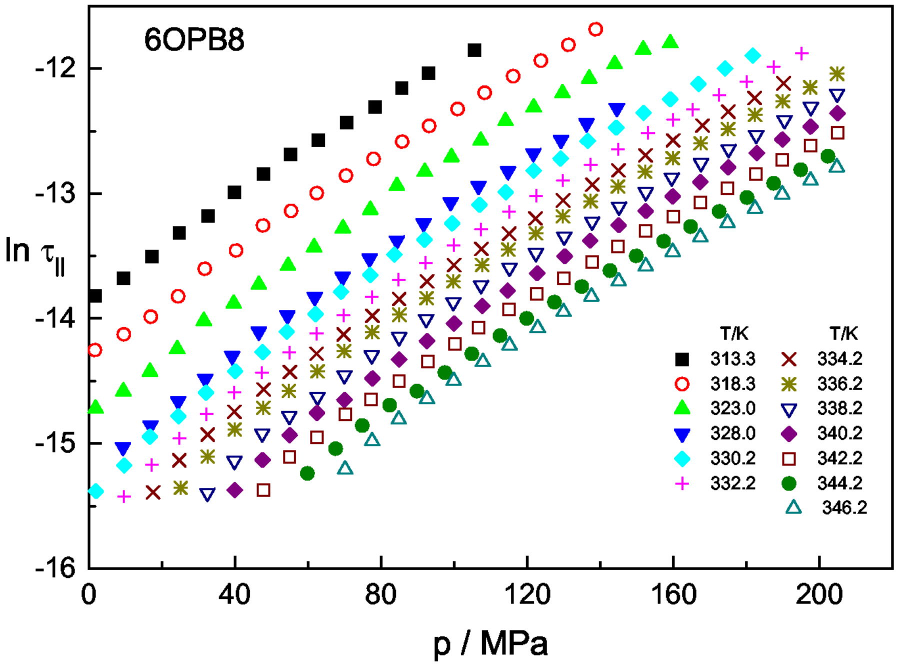


Fig. 5. Ln $\tau_{\|}$ versus pressure for all isotherms studied within the S_A and S_C phases of 6OPB8.

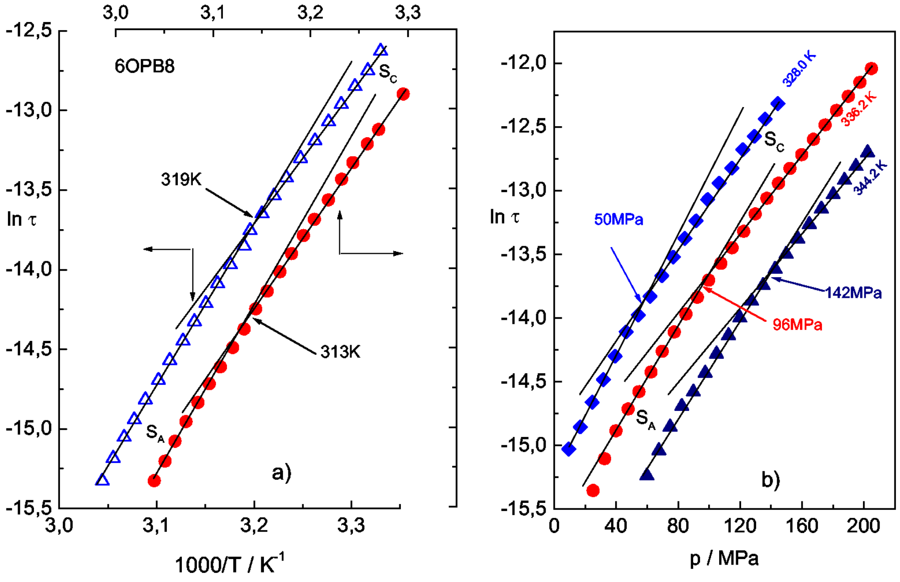


Fig. 6. The vicinity of the $S_A - S_C$ transition observed: (a) at 1 atm for the heating (full points) and cooling (open points) runs (in order to separate both sets of points the reference axes were shifted – compare Fig. 4); (b) at three isotherms from Figure 5. The straight lines, fitted to the low and high temperature (a), and the low and high pressure (b), allow for calculation of the activation volume for both smectic phases, and from intersection of the lines to determine the transition pressures indicated in Fig. 1 as open points.

the activation volume $\Delta^{\#}V_{\|} = RT(\partial \ln \tau_{\|}/\partial p)_T$. Looking at the activation plots in Figs. 4 and 6a, one could expect that in the pressure studies some differences in the behaviour of the relaxation time $\tau_{\|}$ in both smectic phases would be seen as well. Figure 6b shows that the transition between the S_A and S_C phases is really visible as the change of the slopes of straight lines fitted to the low and high pressure parts of the data. The transition pressures taken as the crossing point of the lines were put on the phase diagram (Fig. 1) and marked by the open points. As one can see, they lie on a straight line which intercepts the $p = 0$ axis close to the transition point determined by the optical observation at 1 atm. This happens because the measurements were done while increasing the pressure (that corresponds to rising temperature).

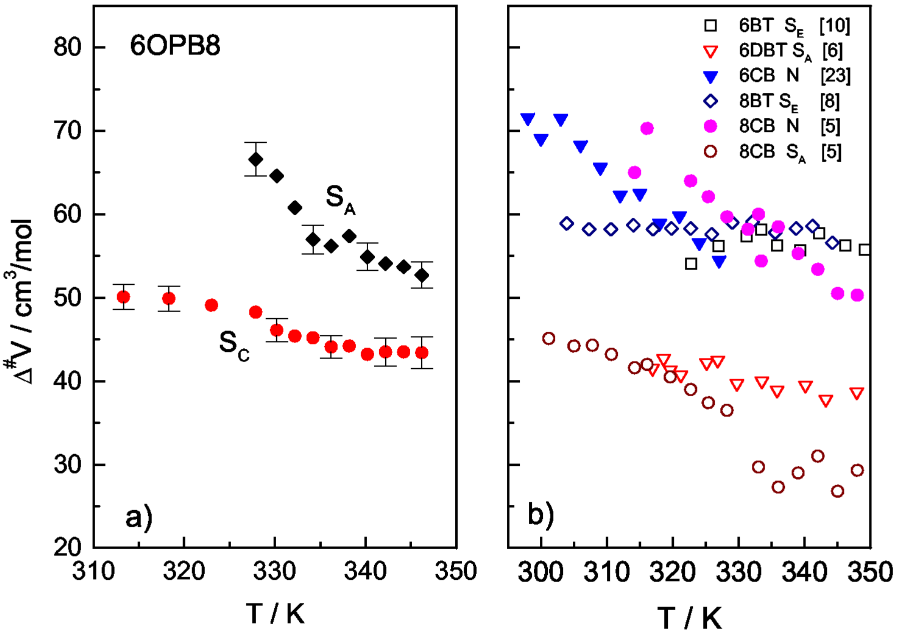


Fig. 7. Activation volumes versus temperature a) determined for 6OPB8 in the S_A and S_C phases, and b) obtained for several alkyl - two-ring - CN or NCS compounds in different phases.

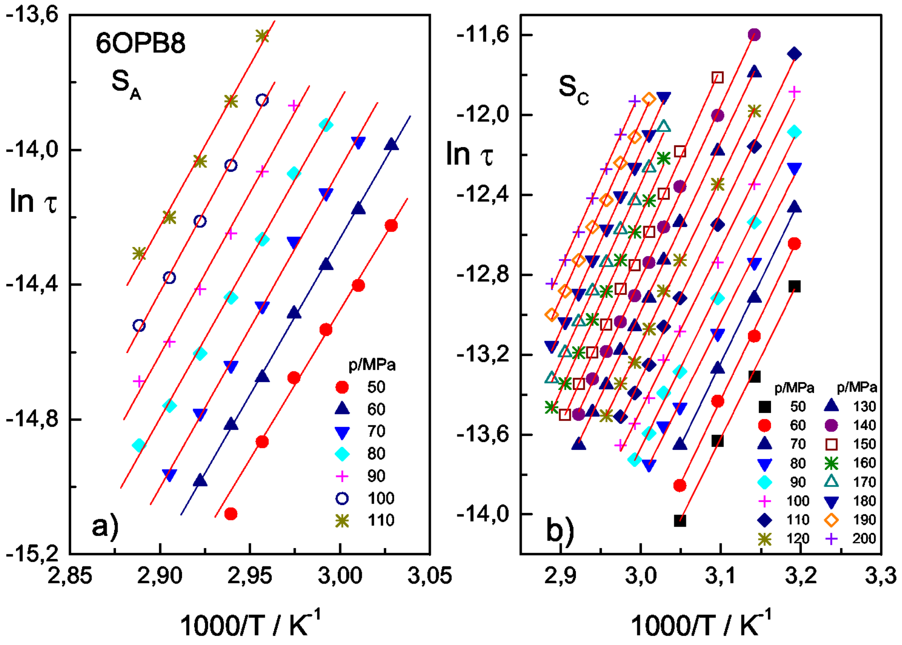


Fig. 8. Activation plots for several isobars within the S_A and S_C phases of 6OPB8. The points were taken from the data in Fig. 5 using interpolations shown in Figure 6.

The values of the activation volume determined for both smectic phases of 6OPB8 are presented in Fig. 7a and compared with the data obtained recently for several other compounds (Fig. 7b).

The establishment of the $S_A \rightarrow S_C$ transition line allows us to analyse the relaxation times as function of the inverted temperature at constant pressures separately for the S_A and S_C phases. Figures 8a,b show that the points lie nicely on straight lines in a broad range of pressures. The slope of the lines yield the activation enthalpy $\Delta^{\#}H_{\|} = R(\partial \ln \tau_{\|}/\partial T^{-1})_p$ that are presented in Fig. 9a and compared with the data obtained for other two-ring compounds in different phases (Fig. 9b).

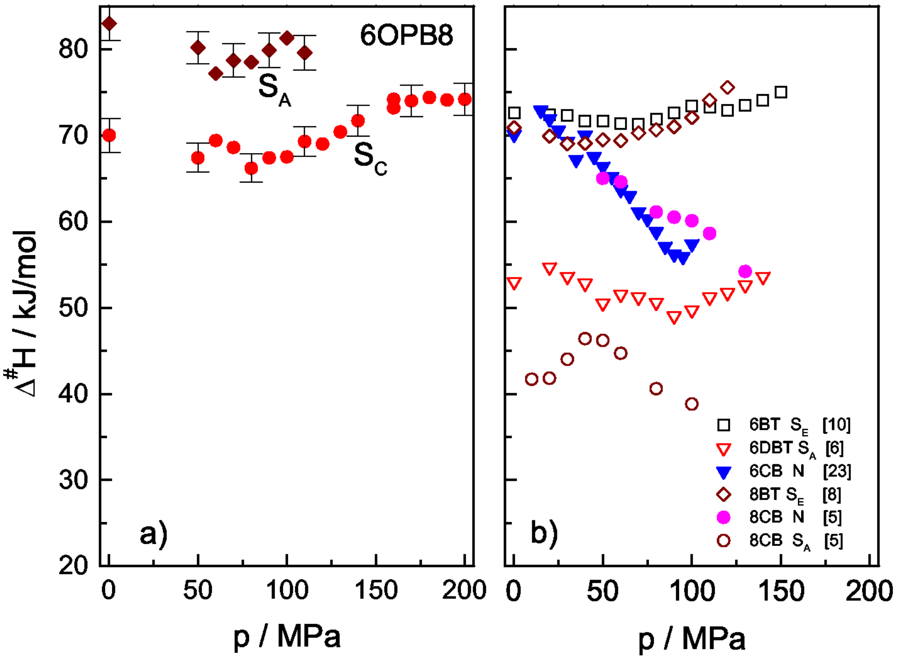


Fig. 9. Activation enthalpy versus pressure determined for 6OPB8 in the S_A and S_C phases a), and obtained for several alkyl - two-ring - CN or NCS compounds in different phases b).

4. Discussion

The 6OPB8 molecule consists of two dipolar groups: the pyrimidine ring and the hexyloxy tail. According to Kresse [16] the longitudinal component of the dipole moment $\mu_l = 1.5$ D, whereas the transverse component $\mu_t = 1.2$ D. The permittivity components in the N phase, shown in Fig. 2, reflect roughly the dipole structure of the molecule ($\varepsilon_\parallel - \varepsilon_\infty \sim \mu_l^2$, $\varepsilon_\perp - \varepsilon_\infty \sim \mu_t^2$, with $\varepsilon_\infty \approx 2.8$). The experimental geometry ($\boldsymbol{E} \parallel \boldsymbol{B}$) and the available frequency range (up to 10 MHz) allow for the study of the low frequency relaxation process only.

Figures 4 and 5 show that the l. f. relaxation time does not change stepwise at the transitions between all liquid-like phases, in accordance with other studies done for substances with the same phase sequence [17–20]. As usually, a large decrease of the activation barrier hindering molecular rotation around the short axis when the nematic phase transforms to the smectic A phase, is observed, Fig. 4 and refs. [1,5,17–24]. Madhusudana et al. [23,24] have suggested that such lowering of the activation barrier is due to the anisotropic packing effects: the volume expansion mainly causes an expansion within the smectic layer, whereas the layer spacing hardly varies with temperature, this favours a lowering of the activation energy in the smectic A phase. It is characteristic that the activation barrier is even smaller in the tilted than in the orthogonal smectic phase. Similar behaviour was noted for other smectogens [17–20].

Figure 7a shows that the activation volume diminishes with raising temperature (and thus with increasing pressure, compare Figs. 1 and 5). A similar effect was noted for several cyanobiphenyls (Fig. 7b) [1, 5, 25] and was interpreted as a result of the breaking of the dipole-dipole associations with pressure. In the case of 6OPB8 one can rather suppose that the increasing pressure favours less extended conformers of the hexyloxy and octyl tails which reduces the total molecular length. In the orthogonal smectic A phase the effect is stronger than in the tilted smectic C phase. The values of $\Delta^{\#}V$ in the smectic phases of 6OPB8 (Fig. 7a) are larger than those found in other smectics studied (Fig. 7b), which may be connected with different lengths of the molecules.

The nematic phase of 6OPB8 was not studied under pressure in this work, but one can assume that the value of the activation enthalpy $\Delta^{\#}H \approx 170$ kJ/mol determined at ambient pressure cannot change markedly with pressure. Thus, the reduction of the barrier hindering the molecular rotation around the short axes in the smectic A phase with respect to the nematic phase is much greater in the case of 6OPB8 than for 8CB (octyl- cyanobiphenyl) (Fig. 9).

5. Summary

The presented high pressure studies of the low frequency relaxation process in liquid crystalline phases for the first time concern a substance with a tilted smectic C phase. The phase sequence N - S_A - S_C observed for 6OPB8 enables us to observe how the parameters describing the rotational motion of molecules change at the phase transition between the orthogonal and tilted phase in the same substance. Additionally, some interesting observations arise from comparing the present results with those obtained recently for the cyano and isothiocyanato two-ring compounds in different phases.

The *p*-*T* phase diagram of 6OPB8 is typical for LC substances [1]. In the pressure range studied it does not exhibit any special features like a pressure induced or pressure limited phases observed for other substances [1, 7 – 9, 25, 26]. In the DTA measurements the melting and the $S_A \rightarrow$ N and N $\rightarrow$ Is transitions are easily detected, whereas the $S_C \rightarrow S_A$ transition is not visible at all. However, it cannot be considered as a second order phase transition because of its strong supercooling observed at ambient pressure. This transition can, however, be determined by texture observation and by the changes in the activation plots.

The low frequency relaxation time passes smoothly through the transitions between the liquid-like LC phases. However, both, the activation volume and the activation enthalpy, which characterise the molecular rotations around the short axes, change in the following way: $\Delta^{\#}V(S_A) > \Delta^{\#}V(S_C)$, and $\Delta^{\#}H(\mathrm{N}) \gg \Delta^{\#}H(S_A) > \Delta^{\#}H(S_C)$. At the same time they are markedly larger than those observed in the same phases for compounds with one tail and the CN or NCS groups. Both activation parameters are smaller in the tilted than in the orthogonal phase of 6OPB8. The activation volume in both smectic phases diminishes with raising temperature (and pressure), which can be interpreted as an indication of shortening of the effective molecular length due to conformation motions of the tails.

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