DTA and Dielectric Studies under Pressure of a Smectogen Substance with a Strong Perpendicular Dipole Moment

Stanisław Urban and Albert Würflinger[a]

Institute of Physics, Jagellonian University, Reymonta 4, 30-059 Cracow, Poland
[a] Institute of Physical Chemistry II, Ruhr University, D-44780 Bochum, Germany

Reprint requests to Prof. S. U.; Fax: 0048-12-6337086; E-mail: ufurban@cyf-kr.edu.pl

Z. Naturforsch. **56a,** 489–492 (2001); received April 23, 2001

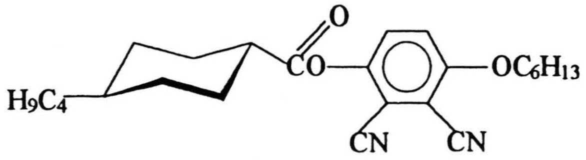
The phase diagram of a substance with two CN groups attached to the benzene ring at lateral positions (CNCN) has been obtained with differential thermal analysis (DTA). The pressure range of the smectic A phase is limited, resulting in a triple point (Cr, S_A, L) at 135 MPa and 371 K. However, the S_A-phase exists also above the triple point as a metastable phase. The transverse relaxation times $\tau_\perp$ were obtained from the dielectric spectra measured for several isotherms as a function of pressure within the S_A-phase of CNCN. The activation volume, $\Delta^{\#} V_\perp = RT\,(\partial \ln \tau_\perp/\partial p)_T$, = (52 ± 3) cm^3/mol is larger than $\Delta^{\#} V_\parallel$, recently derived from the pressure dependence of the longitudinal relaxation times for other substances in the S_A-phase. It is concluded that due to steric hindrances made by the cyano groups the molecular rotations around the long axes become strongly slowed down by pressure and the smectic phase disappears

Key words: Liquid Crystals; Smectic A; DTA; Phase Diagram; Dielectric Relaxation; High Pressure.

1. Introduction

Our recent high pressure studies of the dielectric properties of liquid crystalline (LC) substances concerned the low frequency (l. f.) relaxation process connected with the molecular reorientations around the short axes in the isotropic and different LC phases [1–4]. It is characterised by the longitudinal relaxation time $\tau_\parallel$. The rotations around the long axes are distinctly faster, and thus the corresponding relaxation process occurs in a frequency range non accessible for our experimental set-up, having a limiting frequency of 13 MHz. This high frequency (h. f.) process is characterized by the transverse relaxation time $\tau_\perp$ and can mainly be detected by time domain spectroscopy (eg. [5, 6]). Fortunately, in the case of a substance having two cyano groups attached to the benzene ring at lateral positions, the h. f. process in the smectic A phase could already be observed at megahertz frequencies [6]! This unique circumstance allow us to study, for the first time, the influence of pressure on the rotation motion of molecules around their lowest inertia moment axis.

The substance studied has the following chemical formula (abbreviated as CNCN):



It has very strong transverse and rather small longitudinal dipole components. Therefore the relaxation process connected with the molecular rotation around the long axis dominates the dielectric spectrum even in the isotropic phase [6], whereas the l. f. process is shifted to the kilohertz region, where the conductivity effects mask it considerably.

From previous dielectric studies at 1 atm [6] it was known that the smectic A phase of CNCN could be considerably supercooled. However, its pressure-temperature phase diagram was not established yet. Therefore we begun the present studies with DTA measurements as functions of *p* and *T*.

2. Experimental

The substance studied was the same as in [6]. DTA measurements have been carried out with the set-ups described in [7, 8]. Heating rates of 1 or 2 K/min were applied. Also cooling runs were performed, but a linear change of temperature could not be adjusted in that case. The substance exhibits a strong tendency to supercooling. Therefore several thermal procedures were applied. This allowed us to establish the conditions at which the transitions from the stable and metastable crystals to the smectic A phase could be detected consistently. The transition smectic A – isotropic liquid did not show a remarkable thermal hysteresis. The experimental conditions for the dielectric measurements were the same as in [3]. At a given temperature (stabilized within ±0.2 K) the pressure was increased step by step until the transition to the solid phase was observed. The complex dielectric permittivity, $\varepsilon^* = \varepsilon' - i\varepsilon''$, was measured in the frequency range of 10 kHz – 13 MHz. The sample could not be oriented since the applied bias field of ca. 600 V/cm was not large enough to influence the permittivity.

3. Results

P-T phase diagram. Figure 1 presents the pressure-temperature phase diagram established for CNCN in the pressure range up to 220 MPa. Typical DTA traces in the heating and/or cooling runs are shown in Figure 2. The triangles in Fig. 1 correspond to the melting of a metastable crystalline phase obtained by freezing the smectic phase. If the sample was annealed at room temperature for at least 15 hours, the melting was detected at higher temperatures, as is marked by crosses. Sometimes we observed two transitions, which indicated a coexistence of the stable and metastable phases (Figure 2b). Both melting lines show markedly stronger pressure dependencies than the clearing line, which causes that all three lines merge at the same point corresponding to 135 MPa and 371 K. Above this triple point the melting points lie on the line corresponding to the lowest transition. However, when cooling the isotropic liquid, the transition occurs at p, T points lying well on the line being extrapolation of the smectic – isotropic transition. This fact, as well as a considerably smaller heat effect than the enthalpy of melting (Fig. 2c), suggests that the smectic phase exists also above the triple point as a metastable phase. The pressure dependence of the transition temperatures is presented by quadratic polynomials with the parameters in Table 1.

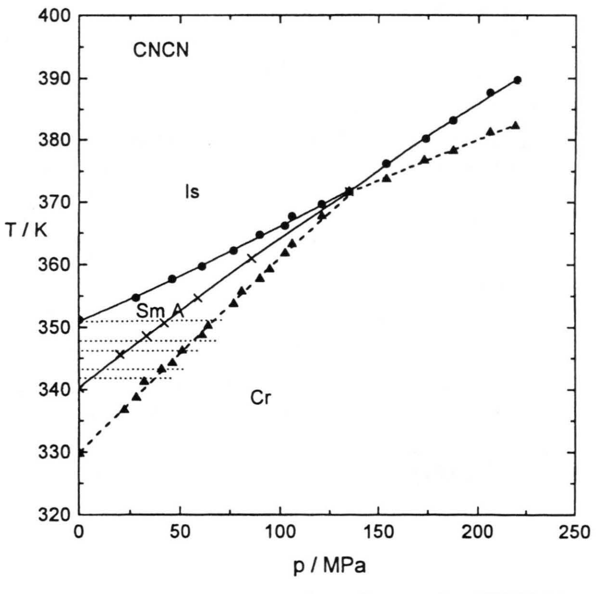


Fig. 1. Pressure – temperature phase diagram for CNCN. The transition marked by triangles was observed as the melting of a metastable crystalline phase. Long lasting annealing of the sample lead to the upper melting points marked by crosses. The dashed line presents the Is – Sm A transition observed on cooling the isotropic liquid. The horizontal dotted lines indicate the isotherms at which the dielectric measurements were performed.

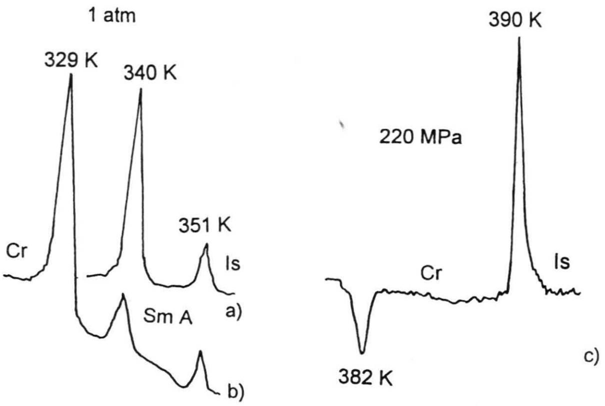


Fig. 2. DTA traces observed for CNCN at different conditions. a) The sample was annealed for a long time and the melting of the stable crystal phase was observed. b) The sample was not annealed enough and the melting of both the stable and metastable phases were detected. c) Typical trace observed above the triple point; different heat effects accompanied the upper and lower peaks.

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

Transition	Pressure range	a	b	$c \cdot 10^4$
$S_A \rightarrow Is$	0 – 135 MPa	350.56	0.1558	0
$Cr \rightarrow S_A$	0 – 135 MPa	340.32	0.25526	–1.7333
$Cr' \rightarrow S_A$	0 – 135 MPa	329.95	0.31836	–0.7259
$Cr \rightarrow Is$	> 135 MPa	336.42	0.28930	–2.0973
$Is \rightarrow S_A'$	> 135 MPa	353.42	0.13640	–0.1850

Dielectric measurements. Considerable narrowing of the smectic A phase of CNCN with pressure caused that the dielectric relaxation studies could not be extended neither in temperature nor in pressure. In Fig. 1 the dotted lines mark the isotherms at which the measurements were performed.

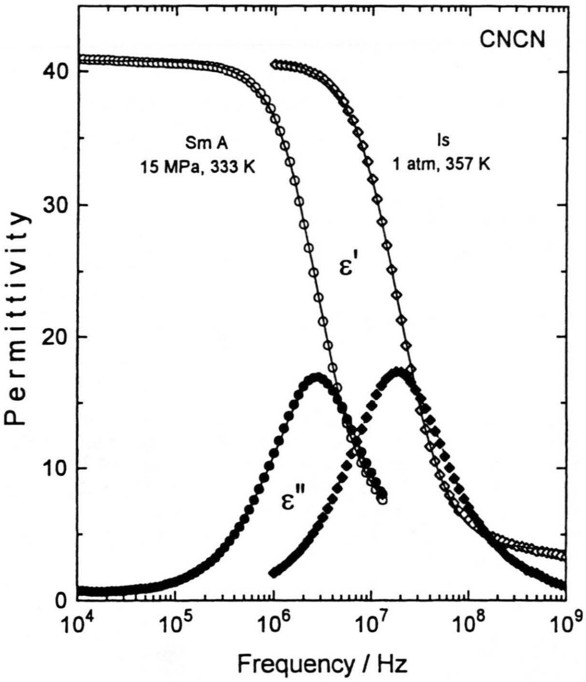


Fig. 3. Dispersion and absorption spectra measured for the smectic A and isotropic phases of CNCN. The lines are the fits of the real and imaginary parts of the Cole-Cole equation.

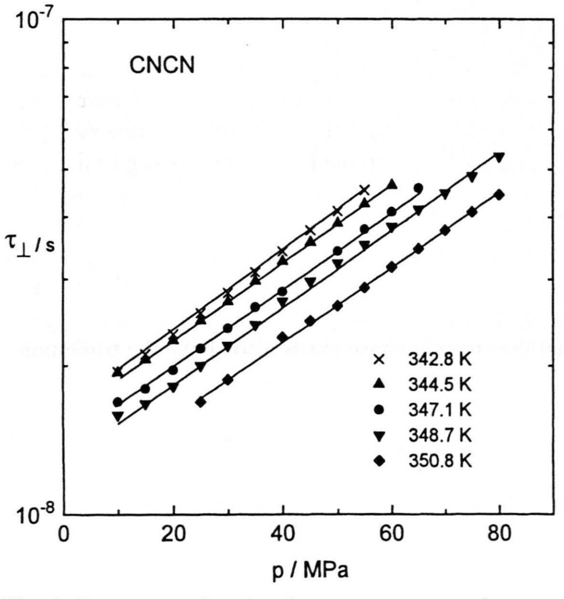


Fig. 4. Transverse relaxation time versus pressure for several isotherms within the smectic A phase of CNCN.

The static permittivities ε_s in the Sm A phase were different at particular isotherms, and they diminished slightly with increasing pressure. Typically, the ε_s-values varied between 15 and 25, i.e. they were markedly smaller than those obtained in the measurements at 1 atm (~35 in the Sm A phase and above 40 in the isotropic phase) [6]. However, when the sample was slowly cooled from the isotropic phase under small pressure of ca. 20 MPa, the permittivity within the smectic phase persisted on the large value down to the freezing. Perhaps, in such conditions the sample was oriented by the wall effects. Figure 3 shows a comparison of that relaxation spectra with those obtained by the TDS method at 1 atm in the isotropic phase [6]. One might assume that the observed large ε_s-values correspond well with the dipolar structure of the CNCN molecule. However, in spite of distinctly smaller ('polycrystalline') permittivities measured in the course of the pressure studies, the relaxation times $\tau_\perp$ calculated from the frequency corresponding to the maximum of losses, $\tau_\perp = 1/(2\,\pi\nu_{\max})$, well characterize the molecular motion around the long axes. The relaxation spectra could well be described by the Cole-Cole equation,

$$(\varepsilon^* - \varepsilon_\infty)/(\varepsilon_s - \varepsilon_\infty) = 1/[1 + (i\,\omega\tau)^{1-\alpha}]$$

with the distribution parameter $\alpha \approx 0.08$ and $\varepsilon_\infty \approx 5.3$. Figure 4 presents the logarithm of the transverse relaxation time $\tau_\perp$ versus pressure. As in the case of the longitudinal relaxation times [1–4], the points lie nicely on the straight lines. The slopes of the lines yield the activation volume, $\Delta^\# V_\perp = RT\,(\partial \ln \tau_\perp/\partial p)_T$. Surprisingly, the mean value $\Delta^\# V_\perp = (52 \pm 3)$ cm^3/mol is even larger than the values of the activation volumes $\Delta^\# V_\parallel$ obtained recently for other substances in the smectic A phase [3, 4]. However, $\Delta^\# V_\parallel$ characterises the rotations of molecules around the short axes, which motion needs usually much larger room than the rotation around the long axes. Due to limited range of temperature available in the experiment, the activation enthalpy $\Delta^\# H_\perp = R\,(\partial \ln \tau_\perp/\partial T^{-1})_p$, can only be roughly estimated from the data. It equals to $\Delta^\# H_\perp = (52 \pm 6)$ kJ/mol and agrees with the value (54 ± 2) kJ/mol obtained at 1 atm [6].

4. Discussion

The presented results of pressure studies of CNCN in the smectic A phase indicate an anusual behaviour of this substance. The attachment of two strongly polar CN groups to the benzene ring at lateral positions results in a limited $p\ (T)$ range of the smectic A phase at relatively low pressures, and in a considerable slowing down of the rotation of molecules around the long axes. In the substances having one halogen atom attached to the benzene ring at the *meta-* or *para-* positions, the transverse relaxation times are of the order of 10^{-10} s in the isotropic phase and 10^{-9} s in the nematic phase [5, 9]. For CNCN the corresponding relaxation times are two orders of magnitude longer [6]. The activation enthalpy $\Delta^{\#}H_{\perp}$, being 30 kJ/mol or less for the former substances, is now increased to ≥ 50 kJ/mol for CNCN. Furthermore, the activation volume of the smectic A phase points to the role of the steric effects concerning the hindrances for the rotational motions of CNCN molecules around the long axes (and perhaps around the short axes, but this could not be studied). Thus, by applying hydrostatic pressure the space needed for molecular motions becomes strongly reduced, and finally the smectic phase disappears.

Acknowledgement

The presented work was supplied by The Project for Bilateral Cooperation in Science and Technology, POL 99/011, sponsored by DLR (Germany) and KBN (Poland).

[1] S. Urban and A. Würflinger, Adv. Chem. Phys. **98,** 143 (1997).
[2] S. Urban, A. Würflinger, D. Büsing, T. Brückert, M. Sandmann, and B. Gestblom, Polish J. Chem. **72,** 241 (1998).
[3] P. Markwick, S. Urban, and A. Würflinger, Z. Naturforsch. **54a,** 275 (1999).
[4] S. Urban and A. Würflinger, Z. Naturforsch. **54a,** 455 (1999).
[5] S. Urban, B. Gestblom, and R. Dąbrowski, Z. Naturforsch. **54a,** 545 (1999).
[6] S. Urban, B. Gestblom, R. Dąbrowski, J. Dziaduszek, and H. Kresse, Z. Naturforsch. **55a,** 733 (2000).
[7] N. Pingel, U. Poser, and A. Würflinger, J. Chem. Soc. Faraday Trans. I **80,** 3221 (1984).
[8] C. Schmidt, M. Rittmeier-Kettner, H. Becker, J. Ellert, R. Krombach, and G. M. Schneider, Thermochim. Acta **238,** 321 (1994).
[9] S. Urban, B. Gestblom, R. Dąbrowski, and H. Kresse, Z. Naturforsch. **53a,** 134 (1998).