Study of High Frequency Relaxation Processes in Three Substances with the –CN Groups at the Lateral Positions

Stanisław Urban, Bo Gestblom[a], Roman Dąbrowski[b], Jerzy Dziaduszek[b],
and Horst Kresse[c]

Institute of Physics, Jagellonian University, Reymonta 4, 30-059 Cracow, Poland
[a] Institute of Physics, Uppsala University, S-75121 Uppsala, Sweden
[b] Institute of Chemistry, Military University of Technology, 00-908 Warsaw, Poland
[c] Institute of Physical Chemistry, Martin Luther University, Halle/S., Germany

Reprint requests to Prof. S. U.; Fax: 0048-126337086; E-mail: ufurban@cyf-kr.edu.pl

Z. Naturforsch. **55a,** 733–740 (2000); received May 6, 2000

Three liquid crystalline (LC) substances with the cyano-groups attached at the lateral positions to the molecular cores were studied with the aid of dielectric spectroscopy methods. The high frequency relaxation process connected with the molecular reorientations around the long molecular axes was studied in the isotropic, nematic and several smectic phases. The dielectric spectra are rather complex, indicating a contribution from several molecular processes to the main relaxation process. The dielectric time changes smoothly at the phase transitions between "liquid-like" phases (isotropic – nematic – smectic A – smectic C), and becomes shorter at the transition to the "solid-like" smectic G phase with a lowering of the activation barrier. This indicates that the molecules perform broad angle librational motions rather than overall rotational motions in this phase. In case of a substance having two cyano groups attached to the benzene ring, a pronounced jump-wise change of the relaxation time was observed at the isotropic – smectic A transition.

1. Introduction

Dielectric spectroscopy is a powerful tool to study molecular reorientations in polar substances. In the case of liquid crystalline phases at least two well-separated relaxation processes can be observed if a sufficiently broad frequency band is covered. The low frequency (l. f.) process connected with the rotations around the short axis falls in the MHz range and is hindered by a relatively large activation barrier (60–120 kJ/mol) [1–5]. The high frequency (h. f.) process falls in the hundreds of MHz or even GHz ranges and corresponds mainly to the molecular rotations around the long axis [4–8], although the internal motions can contribute to it as well [7–9]. The activation barriers are considerably smaller for this process (~ 30 kJ/mol).

In the case of substances exhibiting smectic polymorphism the changes of the parameters characterising the molecular dynamics (relaxation time τ and activation enthalpy ΔH) depend on the actual phase sequence. The crossing of the nematic (N)-"liquid-like" smectic (SmA and SmC) border line results in a small change of the l. f. relaxation time, whereas ΔH decreases when the N-SmA transition occurs and slightly increases in the case of the N-SmC phase transition [1, 2, 10–12]. In case of the N-"solid-like" SmB transition the motion about the short axis becomes considerably slowed down with a rather small change of the barrier [1, 13, 14]. An additional big step in the relaxation time was observed when a "liquid-like" SmC-"solid-like" SmB transition occurred [15]. In constrast, the h. f. process seems to be unchanged throughout a very broad temperature range covering the isotropic, nematic and several smectic phases [6, 16–18]. This means that rotation around the long axis is not influenced by the local molecular arrangements in the smectic layers. However, hitherto performed studies of the h. f. process were done for the non-polar TBBA (neutron scattering method [16]) or for polar substances with a relatively small perpendicular component of the dipole moment [6, 17, 18]. The present study concerns three substances with strongly polar CN groups attached to the molecules at the lateral positions. One can therefore expect an intensive dielectric response connected with reorientations about the long axis of molecules, and an influence of the steric hindrances as well as the dipole-dipole interactions on the high frequency processes observed in particular phases (isotropic, nematic, smectic A, C, and G).

2. Experimental

The chemical structures and phase transitions of the substances studied are presented in Table 1. They were

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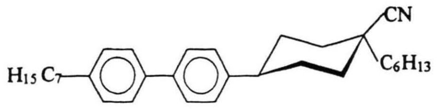
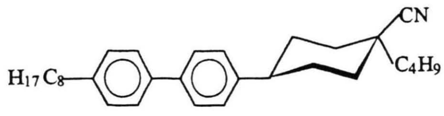
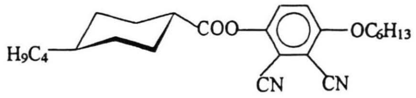
Table 1. Acronyms, chemical structures, phase transitions (cooling)/K, and enthalpy of transitions (*italics*, kJ/mol) of the substances studied.

Acronym	Chemical structure	Phase transitions
7BBC6		Is – 398 – N – 390 – SmA – 346 – SmC – 328 – SmG – (296) – Cr *0.27 2.66 0 3.74 17.5* Is – 398 – N – 390.2 – SmA – 344 – SmC – (328) – SmG – 339 – Cr [19]
8BBC4		Is – 390 – N – 361.6 – SmA – 344 – SmC – 322 – SmG – (308) – Cr *2.94 1.16 0 6.65 57.8* Is – 391 – N – 361 – SmA – 344 – SmC – 322 – SmG – (308) – Cr [19, 20]
CNCN		Is – 352 – SmA – 342 – Cr Is – 349.6 – SmA – 338.2– Cr [21]

synthesised in the Institute of Chemistry, Military University of Technology, Warsaw, and have phase transitions listed in Table 1, which are practically the same as reported in [19, 20] for 8BBC4 and 7BBC6, whereas the clearing point for CNCN is a little higher than that reported in ref. [21].

The measurements of the complex permittivities, $\varepsilon^*(\nu) = \varepsilon'(\nu) - i\varepsilon''(\nu)$, of 8BBC4 and 7BBC6 for two orientations of the samples (**E** $\parallel$ **B** and **E** $\perp$ **B**, B ~ 0.8 T, **E** = measuring electric field) were carried out with the aid of an HP 4192A impedance analyser in the frequency range 10 kHz-13 MHz. A parallel plate capacitor with a capacitance of ~ 50 pF was used. The samples were cooled, starting from the isotropic phase. Beginning at the clearing point, a sample was oriented by the **B**-field, separately for each geometry. In the S_A phase of CNCN the influence of the **B**-field on the permittivity was negligibly small, so the dielectric anisotropic could not be measured in this case.

The h. f. process in the isotropic phase of all substances and in the LC phases of 7BBC6 and 8BBC4 was studied with a time domain spectrometer (TDS). The details of the instrument's parameters can be found in [22–24]. Two time windows (10 ns and 50 ns) were applied, and then the spectra were spliced. That allowed us to cover the frequency range from ca. 20 MHz to ca. 3 GHz. For the isotropic phase of CNCN the 50 ns window was used, while in the S_A phase the HP analyser was used. All measurements were done on cooling. The temperature of the samples was stabilised by a water jacket within ± 0.1 K in the range 370–295 K. Above 370 K an electrical heater was used giving stabilization within ± 1 K; therefore the spectra collected for the isotropic phase of 8BBC4 and the isotropic and nematic phases of 7BBC6 can be considered as rough results only.

3. Results

The static permittivity was taken to be the average of the values of $\varepsilon'(\nu)$ measured in the region of the plateau of the spectra (usually in the range of 50–150 kHz). The temperature dependence of the parallel, $\varepsilon_\parallel$, and perpendicular, $\varepsilon_\perp$, components of the static permittivity for 7BBC6 and 8BBC4 are presented in Figure 1. In the case of 8BBC4 both orientations established in the N phase could be kept in the whole temperature range studied. The same was true for the perpendicular orientation of 7BBC6. Unfortunately, in the case of the parallel alignment the orientation always failed at the N – S_A transition of this substance, and the permittivity $\varepsilon_\perp$ increased to a value characteristic for an unoriented sample. In the case of CNCN the static permittivity dropped considerably at the Is – S_A transition (from ca. 42 to ca. 35).

In the frequency range up to a few MHz large conductivity effects, caused probably by the mobility of the proton nearest to the CN group, superimposed a weak relaxation given by a small longitudinal component of the dipole moment of the 7BBC6 and 8BBC4 molecules. This made impossible a separation of the l. f. relaxation process from the measured absorption spectra for both samples. Therefore only the spectra collected with the aid of the TDS method will be analysed. Typical spectra obtained for particular phases of all three substances stud-

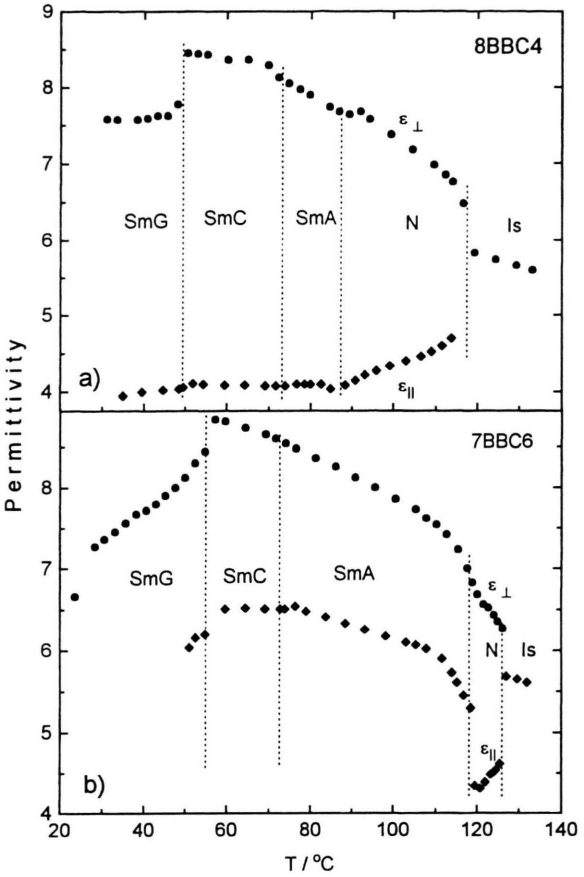


Fig. 1. Principal permittivity components versus temperature measured a) for 8BBC4, and b) for 7BBC6 (cooling runs). In the case of 7BBC6 the parallel alignment established in the N phase was always failed at the transition to the SmA phase.

ied are presented in Figs. 2, 3, and 4 in the form of Cole-Cole plots.

Three well known formulae can be useful for the analysis of the spectra: Cole-Cole [24] (1), Davidson-Cole [25] (2), and Jonscher (imaginary part) [26] (3):

$$\frac{\varepsilon^* - \varepsilon_\infty}{\varepsilon_s - \varepsilon_\infty} = \frac{1}{1 + (i\omega\tau_{CC})^{1-\alpha}}, \tag{1}$$

$$\frac{\varepsilon^* - \varepsilon_\infty}{\varepsilon_s - \varepsilon_\infty} = \frac{1}{(1 + i\omega\tau_{DC})^{\beta}}, \tag{2}$$

$$\frac{\varepsilon'' - \varepsilon_\infty}{\varepsilon_s - \varepsilon_\infty} = \frac{1}{(\omega / \omega_p)^{-m} + (\omega / \omega_p)^{1-n}}, \tag{3}$$

where ε_s and ε_∞ are the static and high frequency permittivities, respectively, τ is the relaxation time and ω_p a characteristic frequency in the neighbourhood to the frequency of maximum loss ν_{max}. The phenomenological parameters α, β, n, and m characterise the distributions of relaxation times about a principal value τ caused by specific interactions or cooperative phenomena. According to Würflinger [27]

$$\tau_{CC} = \tau, \quad \tau_{DC}/\tau = \cot\left(\frac{\pi/2}{\beta+1}\right),$$

$$\omega_{max}/\omega_p = \left(\frac{m}{1-n}\right)^{1/(m+1-n)}.$$

For the LC phases of 8BBC4 the best fits were obtained with the assumption of a superposition of two Debye-type processes [(1) with $\alpha = 0$], characterised by the relaxation times τ_1 and τ_2, which are presented in Figure 6a. However, the dipole structure of the compound (one polar group, Table 1) does not allow a clear assignment of two relaxation processes, especially a process occuring at high frequencies with a relatively small increment. On the other hand, the fits of (2) gave unreasonably small β-values (less than 0.5) which could not be accepted. Therefore we used additionally the Jonscher equation (3) for localizing the frequency ν_{max} corresponding to the maximum loss. Examples of fits are shown in Fig. 5 (solid lines) with $\tau_{max} = 1/\omega_{max}$ presented in Fig. 6a as well.

In the case of 7BBC6, (1) gave quite good fits in the Is, N, and S_A phases with $\alpha \approx 0.05$. The same was done for the S_C and S_G phases taking into account a limited range of frequencies (up to ca. 250 MHz, compare Fig. 3). The second relaxation band could also be fitted here, but the results were not consistent as a function of temperature. Fig. 6b presents the relaxation times calculated with (1) only. For the S_A phase of CNCN, (1) could be fitted to the points measured in a relatively broad frequency range up to ca. 5 MHz. The obtained relaxation

Table 2. Activation enthalpies $\Delta H = R \cdot \partial \ln \tau / \partial\,(1/T)$ calculated from the Arrhenius plots presented in Fig. 6 for particular substances.

Substance	Phase	ΔH/kJ mol^{-1}
7BBC6	N, S_A, S_C	38 ± 3
	S_G	39 ± 3
8BBC4	N, S_A, S_C	29 ± 3 from τ_1 15 ± 5 from τ_2 34 ± 3 from τ_{max}
CNCN	Is	52 ± 2
	S_A	54 ± 2

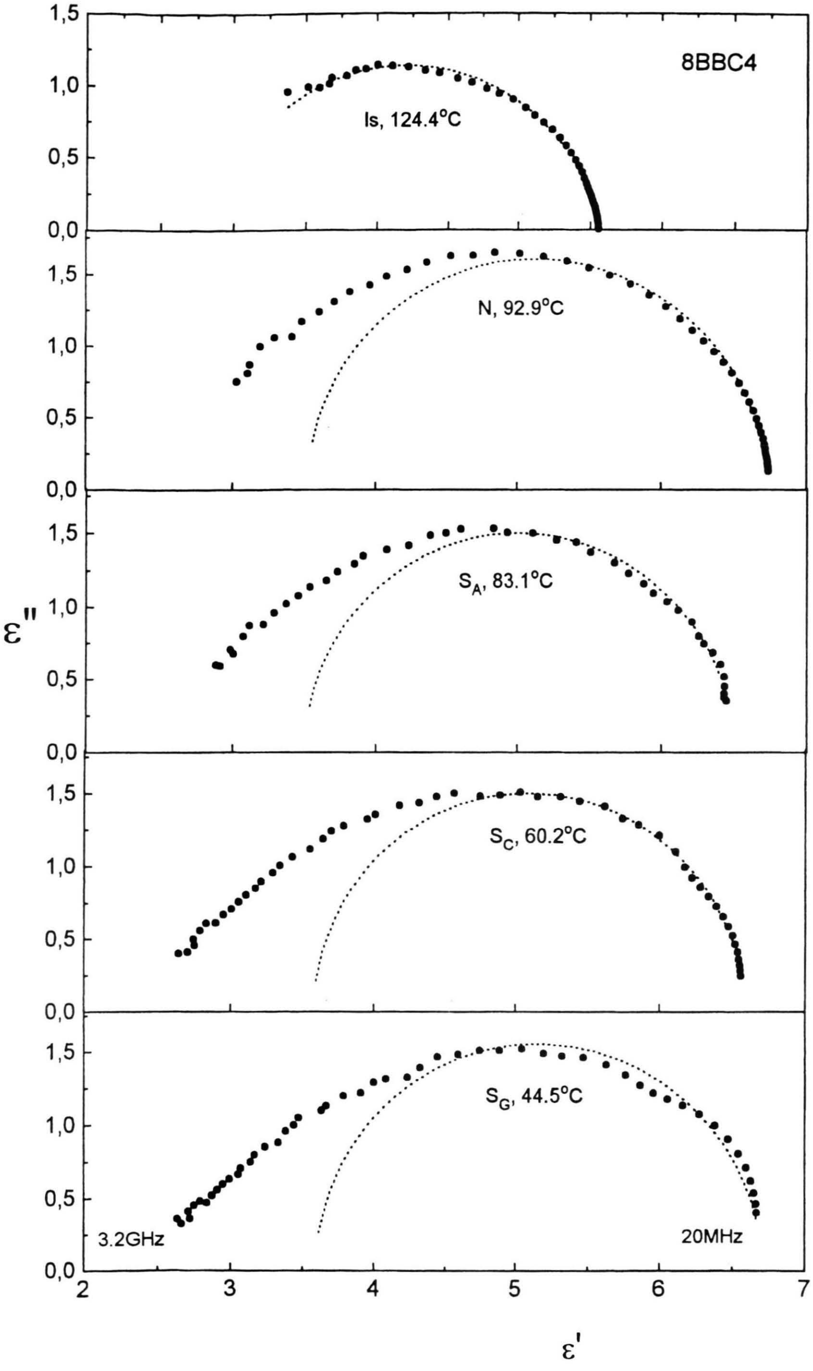


Fig. 2. Cole-Cole plots from the TDS spectra in different phases of 8BBC4. In the Is and N phases the spectra were measured with 10 ns time window. In case of the S_A, S_C, and S_G phases two times windows, 10 ns and 50 ns, were applied, and then the spectra were spliced in the range of ca. 100–450 MHz. The circular arcs are fits of (1) to the low frequency part of the spectra including the points of maximum loss.

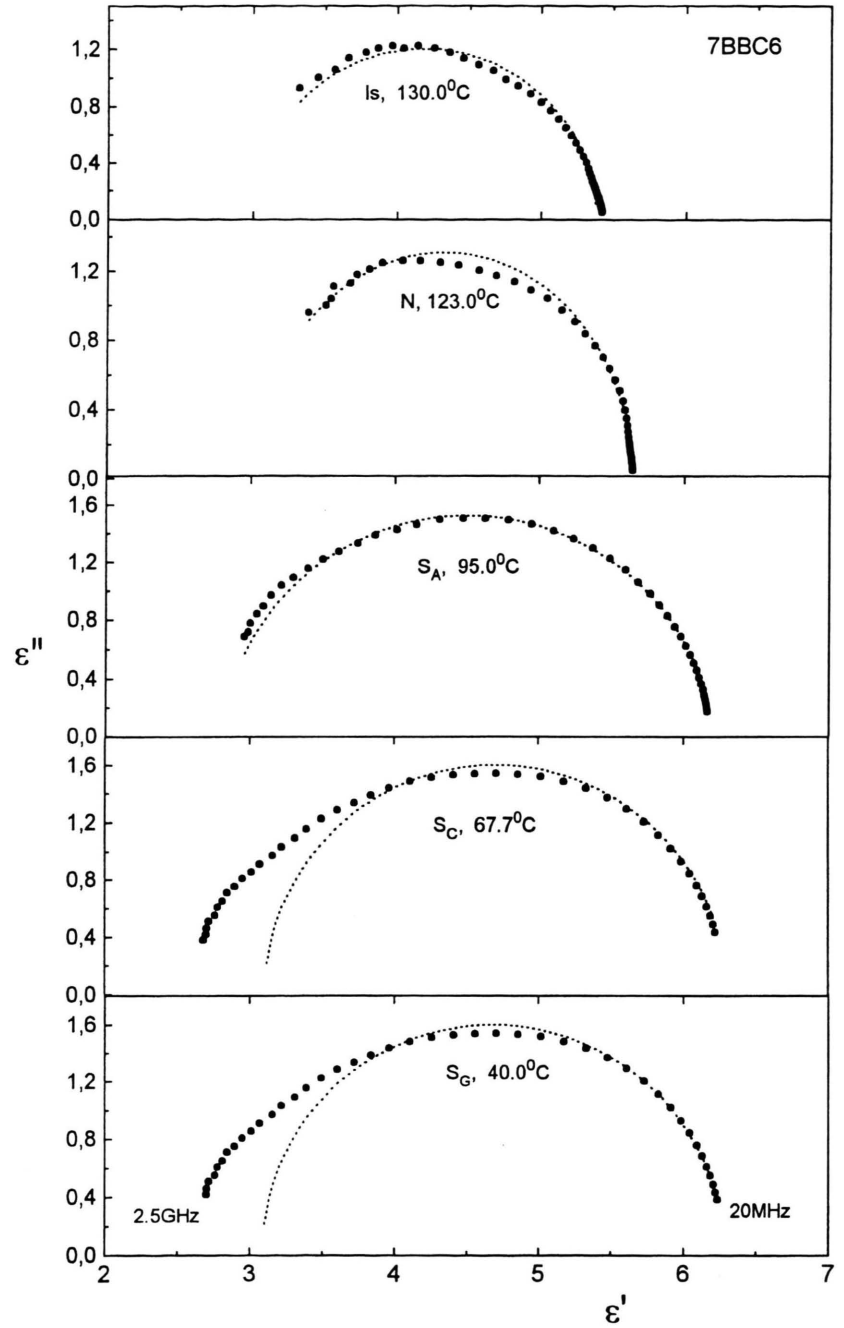


Fig. 3. Cole-Cole plots from the TDS spectra collected for different phases of 7BBC6. In the Is, N, and S_A phases the spectra were measured with 10 ns time window. In case of the S_C and S_G phases two times windows, 10 ns and 50 ns, were applied, and then the spectra were spliced in the range of ca. 100 – 450 MHz. The circular arcs are fits of (1) to the low frequency parts of the spectra including the points of maximum loss.

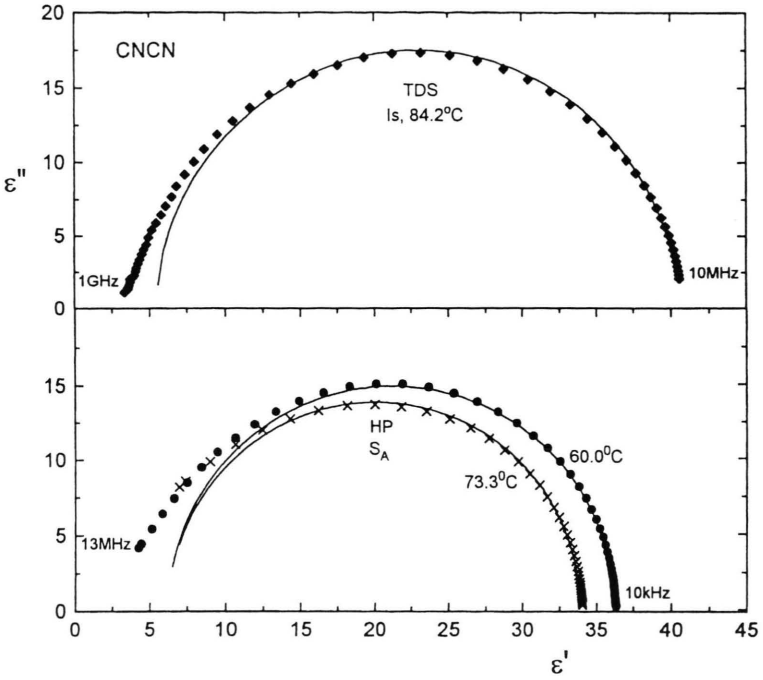


Fig. 4. Examples of the spectra collected for the Is and S_A phases of CNCN. The spectra in the Is phase were collected with 50 ns time window. In the S_A phase the HP analyser was used. The circular arcs are fits of (1) to the low frequency parts of the spectra including the points of maximum loss.

times are presented in Figure 6c. The corresponding activation energies are gathered in Table 2.

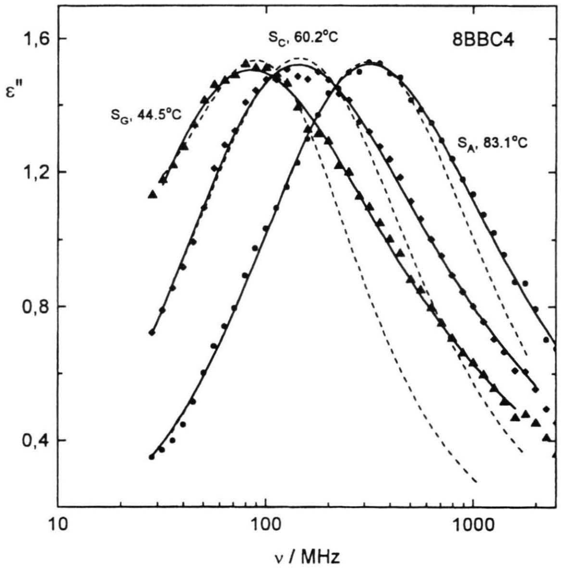


Fig. 5. Examples of fits of (3) to the loss spectra in three phases of 8BBC4 (full lines). The fit of imaginary part of (1) to the low frequency part of the spectra is shown for comparison.

4. Discussion

The lateral positions of strongly polar CN groups result in a negative dielectric anisotropy of the substances studied (in the case of CNCN the parallel component of the permittivity in the S_A phase could not be measured). Therefore the observed relaxation processes characterise exclusively the molecular reorientations around the long axes, even in the isotropic phase and non-oriented LC phases. Looking at the Cole-Cole plots in Figs. 2, 3, and 4 one can note characteristic differences between the spectra collected for particular phases, as well as between different substances. Let us first compare the spectra obtained for 8BBC4 (Fig. 2) and 7BBC6 (Fig. 3). In order to render conspicuous the observed effects, the Debye semicircles were fitted to the low frequency parts of the spectra (including the points at maximum absorption). For the first substance a characteristic skewing of the $\varepsilon''(\varepsilon')$ plots at the high frequency side is observed, beginning from the N phase, whereas for the second substance this begins from the S_C phase only and is substantially less pronounced. The spectra in the S_A phase of CNCN are only slighty deformed at high frequencies, similarly to the spectra of the isotropic phase (Figure 4).

Looking at Figs. 6a and 6b one can conclude that in spite of using different formulae to fit the relaxation spec-

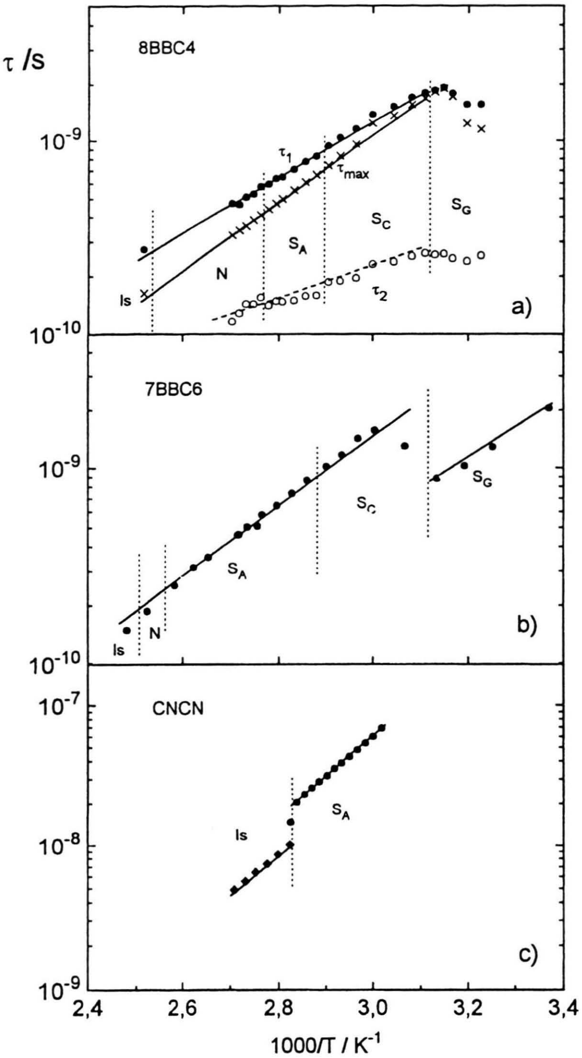


Fig. 6. Arrhenius plots from the relaxation times at different phases of the substances studied. a) τ_1 (full points) and τ_2 (open points) were obtained by fitting two Debye-type equations to the spectra (except the Is phase), τ_{max} (crosses) was calculated from the maximum of losses using (3). b) τ comes from the fits of (1) to the spectra; in case of the S_C and S_G phase a limited frequency range was taken into account (up to ca. 700 MHz). c) in both phases (1) was fitted to the spectra in limited frequency ranges.

tra, the calculated relaxation times for the main relaxation process observed change smoothly throught the isotropic and all "liquide-like" LC phases. The same has been observed in other studies as well [6–8, 16–18, 28]. Surprisingly, the transition to the monoclinic S_G phase [1] results in a jump-wise *fastening* of the relaxation process accompanied by a decrease of the activation barrier (it is well seen for 7BBC6; in the case of 8BBC4 the sample transformed to the crystalline phase in the course of measurements).

Before discussing this behaviour, let us mention the results of some other studies of substances with a rich smectic polymorphism. Schacht et al. [18] have studied two isomeric compounds, 4-undecyloxy-4′-carboxyethyl-*trans*-stilbene (11Et) and 4-dodecyloxy-4′-carboxymethyl-*trans*-stilbene (12Me), exhibiting the SmA, SmB, and SmE polymorphism (SmB and SmE phases have hexagonal and orthorhombic structures, respectively [1]). In the case of 12Me the molecular rotations around the long axis persist continuously through the Is, SmA, and SmB phases. At the SmB → SmE transition the relaxation frequency $\nu_R = 1/(2\pi\tau)$ *increases* and shows non-Arrhenius behaviour within the SmE phase. This was assigned to the coupling of the molecular rotations around the short and long axes resulting from the biaxiality of the SmE phase. On the other hand, in 11Et the relaxation frequency decreases at the same transition, with diminishing of the activation barrier in the SmE phase (the process has then a continuation in the crystalline phase). The authors related this behaviour to the intramolecular reorientation of a polar group. In the case of *p*-phenyl-benzelidene-*p*′-buthylaniline [29] the SmB – SmE transition was accompanied by a considerable increase of the barrier for rotation around the long axis (25 kJ/mol in SmB and 60 kJ/mol in SmE phase).

The jump of the relaxation time at the SmC → SmG transition of 8BBC4 and 7BBC6 resembles the situation observed for 12ME. However, taking into account the fact that the molecules have one polar group and that the permittivity diminishes at the transition (compare Fig. 1), it seems reasonable to attribute the relaxation process observed in the SmG phase to broad angle molecular librations rather than to overall rotations of molecules around the long axis.

Steric hindrances made by two –CN groups attached to the benzene ring at lateral positions in the CNCN molecule cause a considerable slowing down of the rotation around the long axis even in the isotropic phase in comparison to the three-ring compounds studied (compare Figs. 6a, b and Fig. 6c). Pronounced retardation of the h.f. relaxation process is observed at the Is → S_A phase transition which can be characterised by the retardation factor $g = \tau_{SmA}/\tau_{Is} \approx 1.9$. Rather opposite trends have been observed at the same phase transition in substances without such steric hindrances [28].

The skewings of the Cole-Cole arcs observed in most of the phases indicate that some dipolar process, in addition to the molecular rotations around the long axes, occur. It seems reasonable to suggest that due to steric hindrances caused by the CN groups the molecules perform broad angle librations before jumping by, say, an angle π. The shorter butyl tail in 8BBC4 compared to the hexyl tail in 7BBC6 causes a shiftening of the characteristic frequencies to higher values, and the skewings become more pronounced. Such interpretation seems to be supported by the large difference in the values of the activation enthalpy corresponding to both processes in 8BBC4 (see Table 2).

However, yet another factor can influence the measured spectra. The compounds 8BBC4 and 7BBC6 may exist in two conformers: one more stable, wherein the cyano group is in the axial position and the neighboring alkyl group in the equatorial position of the cyclohexane ring, and the less stable second one, wherein both groups are attached at the opposite positions to the above ones. The longer the alkyl group, the more prefered is the first conformer. The equilibrium between them can in part be responsible for the complicated character of the observed dielectric spectrum.

5. Concluding Remarks

The analyses of the results of the dielectric relaxation studies of three LC compounds with the CN group attached to the molecular cores at lateral positions enable us to formulate the following conclusions:

i) The reorientation of molecules about the long axes in the isotropic, nematic and several smectic phases could be exclusively studied.

ii) For CNCN the transition from the isotropic to SmA phase results in a slowing down of the motion, whereas the activation barrier persists practically unchanged (Fig. 6c, Table 2); no such retardation was observed in the case of substances with a smaller perpendicular component of the dipole moments [28].

iii) No marked changes of the relaxation times at the transitions between liquid-like smectic phases were observed.

iv) A step-wise decrease of the relaxation time and the activation barrier at the transition from the SmC to the solid-like SmG phase indicates that closely packed molecules perform broad angle librational motions around the long axes.

v) It might be that the complex shapes of the relaxation spectra are due to contributions both from libration (faster) and reorientation (slower) processes, as well as by different conformers formed by the group attached to the cyclohexane ring.

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