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Retardation of Molecular Rotations Around the Short Axes at the Transition from the Isotropic to Different Liquid Crystalline Phases[*]

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Results of the dielectric relaxation studies of several homologous series and some single compounds exhibiting different phase sequences (isotropic - nematic, isotropic - smectic A, C, B and E) are presented. Relaxation times characterizing the molecular rotations around the short axes in the isotropic and a given liquid crystalline (LC) phases were determined. Two quantities, the so-called retardation factor $g_{\mathrm{LC\text{-}Is}} = \tau_{\mathrm{LC}}/\tau_{\mathrm{Is}}$ and the activation enthalpy are analyzed. In spite of drastic changes of the *g*-factors in the case of the isotropic - crystal-like smectic phase transitions (Sm B and E) in comparison with the isotropic - liquid-like phases (N, Sm A, Sm C) transitions the activation enthalpy does not depend practically on the LC phase. This will be discussed as resulting from the coupling of the rotational and translational motions.

Key words: liquid crystals, nematics, smectics, dielectric relaxation

A wealth of liquid crystalline (LC) phases composed of the cigaro-like molecules are characterized by different orientational and positional molecular ordering. One can distinguish between the liquid-like phases (isotropic – Is, nematic – N, smectic A and smectic C – Sm A, C) and the crystal-like smectic phases (Sm B, G, H, E,...). From the point of view of rotational dynamics of molecules one can note a considerable freedom for motions around the long axes (high frequency, h. f., process) [1–3], and much more restricted rotations around the short exes (low frequency, l. f., process) [4–6]. The discussion of restrictions caused by the anisotropy of molecular interactions in LC phases has to be related to the situation taking place in the isotropic liquid, where both types of motions are simply related to largely different principal inertia moments of molecules. The dielectric relaxation method is a powerful tool for studies of the rotational motions in the case of polar substances.

In order to characterize the influence of molecular ordering on the l. f. process one has to consider substances having similar chemical structures and exhibiting a given phase sequence: Is – N, Is – Sm A, Is – Sm C, ... However, it is not easy to select sub-

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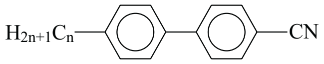
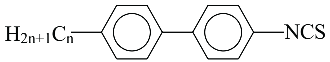
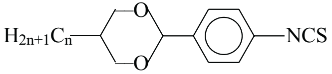
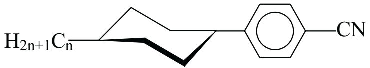
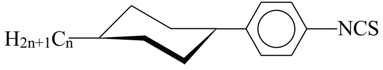
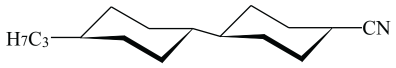
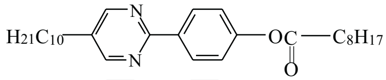
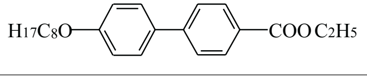
[*] Dedicated to the memory of Professor Krzysztof Pigoń.

stances fulfilling both above conditions. Two-ring compounds having strong dipole moment created by the –CN or –NCS groups attached to the benzene ring at the *para*-position seem to be the best for that purpose. Additionally, several members of a given homologous series show up the same phase sequences, which enable one to observe the dependence of analyzed properties on the molecular length. Table 1 (upper part) contains the chemical formulae, acronyms and the phase sequences of two-ring compounds, which will be considered in this paper. Because these substances do not exhibit the Is – Sm C and Is – Sm B phase sequences, we have performed dielectric relaxation studies for three new LC compounds, which are listed in the bottom part of Table 1.

Two quantities characterized the l. f. relaxation process in particular LC phases will be discussed: the so-called retardation factor introduced by Meier and Saupe [7] $g_{LC\text{-}Is} = \tau_{LC}/\tau_{Is}$, where τ_{LC} and τ_{Is} are the l. f. relaxation times measured in the LC and isotropic phase, respectively, and the activation enthalpy, $\Delta H_{l.f.} = R(\delta\tau_{l.f.}/\delta T^{-1})$. The retardation factor reflects the change of the probability of flip-flop molecular rotations, due to molecular ordering in the LC phases, whereas $\Delta H_{l.f.}$ yields information about an actual energy barrier hindering the motion.

To the best of the authors' knowledge, only a few other examples of similar analysis of the dielectric relaxation data can be found in the literature [8–12]. However, they are restricted to substances exhibiting the Is – N transition.

Table 1. Chemical formulae, acronyms and phase sequences of the substances considered in the paper. The temperatures of phase transitions in the bottom part of the table were observed in the cooling rates.

Chemical formula	Acronym	Phase sequence	
	***n*CB**	Is – N Is – N – SmA_d	*n* = 5 ÷ 7 *n* ≥ 8
	***n*BT**	Is – Sm E	*n* ≥ 2
	***n*DBT**	Is – Sm A_1	*n* ≥ 2
	***n*PCH**	Is – N	*n* ≥ 3
	***n*CHBT**	Is – N	*n* ≥ 6
	**3CCH**	Is – 79.5°C – N – 51.5°C – Sm B – 44.8°C – Cr	
	**10PBE8**	Is – 66.8°C – Sm C – 50.3°C – (Sm X) – Cr	
	**8BBE2**	Is – 109.3°C – Sm B – 93.3°C – Sm E – 85°C – Cr	

RESULTS AND DISCUSSION

Most of the relaxation times and activation enthalpies analyzed in this paper come from recent papers [6,13–16]. As an example, in Fig. 1 the l. f. relaxation times obtained for 6th members of several homologous series are presented. These data are now enriched by new results for substances shown in the bottom part of the Table 1. However, the SmB phase in 3CCH is separated from the isotropic phase by the N phase, whereas the molecular structures of 10PBE8 and 8BBE2 differ from the other substances. All substances were synthesized in the Military Technical University, Warsaw. As in previous studies the relaxation spectra of LC phases, $\varepsilon^* = \varepsilon' - i\varepsilon''$, were measured with a HP 4192A analyzer, and that of the isotropic liquid were collected with the aid of a time domain spectroscopy (TDS) method as described in [17]. Time windows 10 ns, 50 ns or 100 ns or their combinations were applied depending on the rates of relaxation processes in particular substances and phases. TDS measurements were also done for the N phase of 3CCH because of shifting of the spectra beyond the limit of the HP analyzer (13 MHz). Typical examples of the absorption spectra obtained for particular phases of 3CCH are presented in Fig. 2. All spectra were analyzed with the Cole-Cole modification of the Debye equation,

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

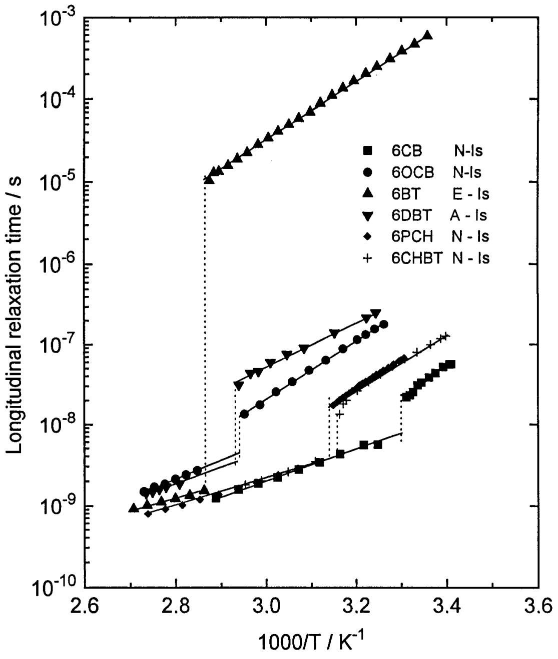


Figure 1. Longitudinal relaxation times in the isotropic and LC phases for the 6th members of several homologous series. The data were taken from ref. [6] – 6BT, [13] – 6OCB, [14] – 6DBT, [15] – 6CB and 6PCH, [16] – 6CHBT.

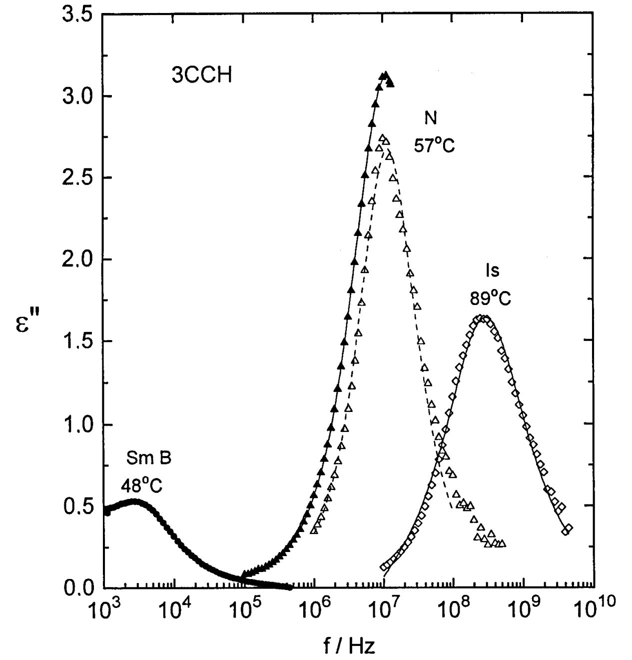


Figure 2. Dielectric absorption spectra collected for 3CCH with the aid of a HP analyzer (full symbols) and TDS method (open symbols). Lower values of ε″ measured in the N phase with TDS in comparison with HP results were caused by too weak orienting electric field (~1500 V/cm in relation to ~3500 V/cm). The lines are fits of the imaginary part of (1) with $\alpha = 0$ for N and B phases, $\alpha \sim 0.10$ for the Is phase.

where ε_s and ε_∞ are the static and high frequency permittivities, respectively, $\omega = 2\pi f$, and α characterizes a distribution of the relaxation times τ. The second part of (1) corresponds to the conductivity effects, which often influence the absorption spectra $\varepsilon''(\omega)$ at low frequencies. The relaxation times $\tau_{\mathrm{l.f.}}$ presented in Fig. 3 were calculated from the frequency f_m corresponding to the maximum of losses $\tau_{\mathrm{l.f.}} = 1/(2\pi f_m)$. Fig. 4 shows typical absorption spectra in the Is and SmC phases of 10PBE8. In the SmC phase a conductivity effect is seen, which was subtracted from the losses in the calculations of τ-values. The spectra of the isotropic phase show a high frequency wing due to the h. f. relaxation process. In the case of the isotropic phase of 8BBE2 the l.f. and h.f. processes are not well separated and they were analyzed assuming a superposition of two Debye-type processes (Fig. 5a). The spectra of the SmB phase of 8BBE2 can be described by the well known Debye formula (eq. (1) with $\alpha = 0$) (Fig. 5b). The l. f. relaxation times obtained for both substances are presented in Fig. 6. It is necessary to note that all spectra measured in the smectic phases were strongly depressed in comparison with that of other phases. External electric and/or magnetic fields applied to the samples did not influence the permittivities at all.

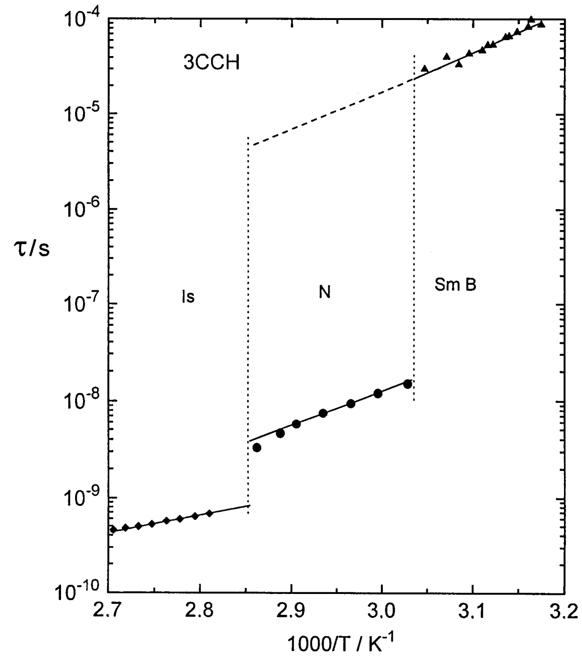


Figure 3. Longitudinal relaxation times determined for 3CCH in particular phases. The lines extrapolated to the transition points (dotted vertical lines) yield the retardation factors listed in Table 2.

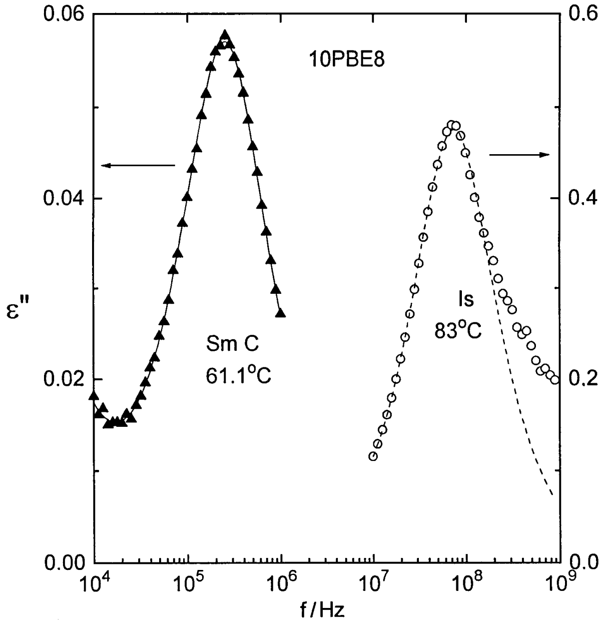


Figure 4. Examples of spectra measured for the Is and Sm C phases of 10PBE8. The lines are fits of (1) to the spectra (in the case of the Is phase a few points above f_{max} were taken only in fitting).

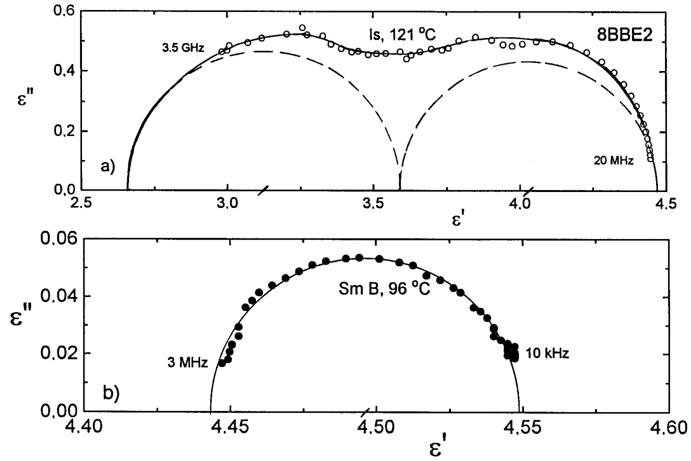


Figure 5. Cole-Cole plots from the spectra of 8BBE2: a) Isotropic phase – a superposition of two Debye-type processes was assumed marked by dashed semicircles. b) Sm B phase.

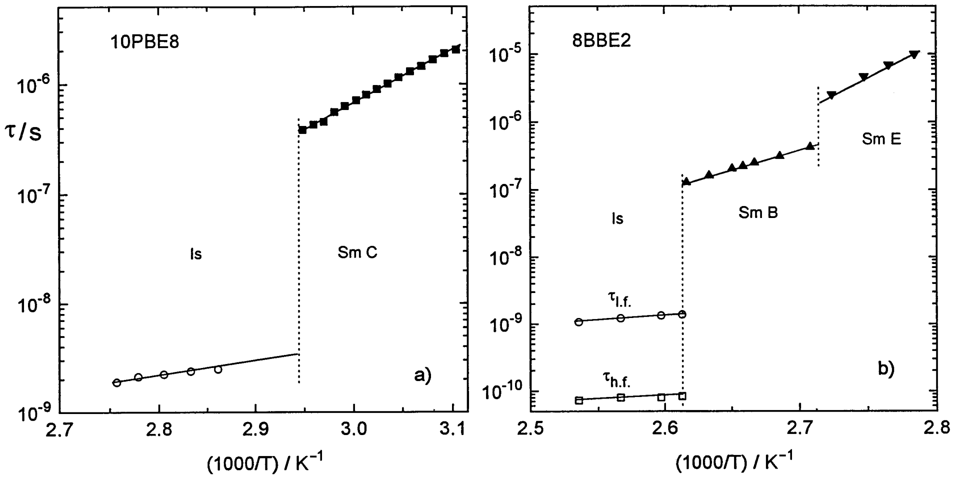


Figure 6. Longitudinal relaxation times determined for 10PBE8 (a) and 8BBE2 (b).

The calculated retardation factors and activation enthalpies are presented in Table 2 and Figs. 7a,b.

The studies of the l. f. relaxation process under high pressures [18] have shown that the barrier hindering the molecular motions around the short axes in different LC phases is about two times larger when it was calculated from the relaxation times measured at constant pressure (activation enthalpy $\Delta H_{l.f.}$) than at constant volume or density (activation energy $\Delta U_{l.f.}$). This indicates that the contributions from the thermal and steric effects to the barrier are roughly of the same importance. That means that the flip-flop molecular motions must be treated as a cooperative process. This fact has to be taken into consideration in the discussion of the observed effects.

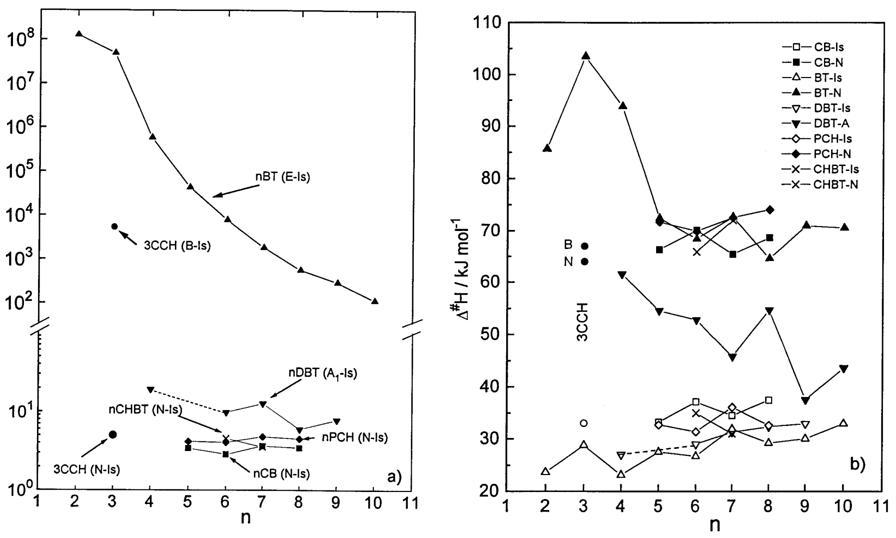


Figure 7. a) Retardation factors for several two-ring homologous series as a function of the length of the alkyl chain. b) The activation enthalpy in the Is and LC phases *versus n* for the same substances. The data come from the references mentioned in Fig. 1, except that for 7CHBT, which were taken from ref. [11].

Table 2. The values of the activation enthalpy and retardation factors for particular phases of three substances.

Substance		3CCH	10PBE8	8BBE2
$\Delta H_{l.f.}$ [kJ/mol]				
	Is(l.f.)	33 ± 2	21 ± 3	27 ± 3
	Is(h.f.)		—	14 ± 3
	N	64 ± 3		—
	Sm C	—	90 ± 3	—
	Sm B	67 ± 4	—	106 ± 4
	Sm E			198 ± 6
$g_{LC\text{-}Is}$				
	N – Is	5	—	—
	Sm C – Is	—	110	—
	Sm B – Is	5400	—	95
	(N – Sm B)	1500	—	—

Let us first consider substances built with two rings and having a strong dipolar group at one side. Figs. 1, 3 and 7a show that the retardation of the molecular motions around the short axes when passing the clearing point strongly depends on the type of LC phase (note the logarithmic scale at the y-axis). The drop of the l. f. relaxation time is much greater in the case of crystal-like smectic B and E phases than this happens for liquid-like phases (N, Sm A). Such effect should be expected – the more ordered LC phase the less probable the molecular jumps between the potential minima separated by 180°. On the other hand, the barriers hindering these motions (Fig. 7b) are close in the isotropic phase (*ca.* 25 ÷ 35 kJ/mol) as well as in both types of LC phases (*ca.* 65 ÷

75 kJ/mol). Exceptions concern the Sm A phase, for which the barrier is always smaller than in the N phase (*eg*. [18,19]), and three shortest members of the *n*BT series – see ref. [6]. One can conclude, therefore, that for two-ring compounds having strongly polar group at one end and the alkyl tail at the second end the energy barrier hindering the molecular motions around the short axes is determined mainly by the side-by-side interactions. However, the probability of jumps, which is proportional to τ^{-1}, depends upon the degree of molecular order in LC phases. In order to perform a jump over 180° a molecule must have sufficient room created by the fluctuations of the positions of neighbouring molecules, which are markedly slowed down for the crystal-like phases.

The above conclusions may not be, however, simply related to the molecules having other chemical structures. The results obtained for 10PBE8 and 8BBE2 (Fig. 6a,b, Table 2) indicate that there is practically no difference between properties of the liquid-like SmC and crystal-like SmB phase. Perhaps, the flexible wings at both sides of molecules establish other conditions for molecular dynamics.

CONCLUSIONS

The presented results of studies of the low frequency relaxation process in the isotropic and several LC phases allow us to formulate the following conclusions:

- Molecular rotations around the short axes take place in the liquid-like phases (N, Sm A, Sm C) as well as in the crystal-like phases (Sm B, Sm E, ...).
- This motion is much stronger retarded at the transition from the isotropic liquid to the crystal-like phases than that happens at the transition from the isotropic liquid to liquid-like phases. Thus, one can note a drastic change of the probability of the rotational jumps between the liquid-like and crystal-like phases.
- In spite of the above, the corresponding activation enthalpies in both types of LC phases are close for similar substances. That might indicate that the energy barrier for flip-flop molecular rotations in LC phases is mainly created by the side-side interactions, which are similar for all two-ring compounds having a strong dipole moment along the long axis.
- The above conclusions may not be, however, simply related to molecules having the alkyl or alkoxy chains at both sides.
- In order to overcome the energy barrier a molecule must have a sufficient room created by transverse fluctuations of its neighbours.

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