Dielectric Studies of Inter- and Intramolecular Motions in the Nematic and Isotropic Phases of 7CP5BOC

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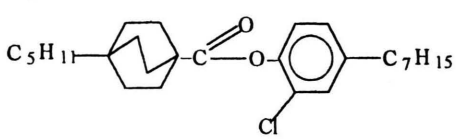
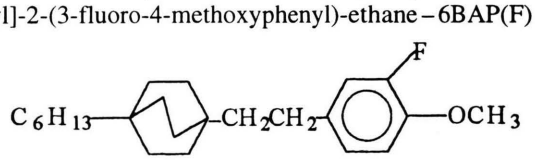
The dielectric relaxation of 7CP5BOC (2-chloro-4-heptylphenly 4-pentylbicyclo-[2,2,2]octan-1-carboxylate) in its isotropic and nematic phase has been studied. The substance has a negative dielectric anisotropy. The complex dielectric permittivity was measured in the frequency range 10 kHz – 3 GHz with the aid of an impedance analyzer and a time domain spectroscopy (TDS) method. The relaxation time, activation enthalpy and dielectric increments, characterizing the rotation of the molecules about the principal inertia axes, were obtained. It was found that the relaxation process connected with rotations about the long axis can be split into two independent motions of molecular moieties around the C–O bond in the $-\overset{\overset{O}{\parallel}}{C}-O-$ bridging group.

1. Introduction

The dielectric properties of a molecular system depend upon the polarity and the rotational freedom of the molecules and their fragments. Liquid crystalline (LC) compounds have usually complex chemical structures with dipole groups attached to a rigid molecular core as well as to more flexible wings. Thus, the observed relaxation spectrum, if measured in a sufficiently broad frequency range, can bring information about the rotations of molecules as a whole as well as about rotations of their dipolar fragments. The studies reported in this paper concern the recently synthesised [1] 2-chloro-4-heptylphenyl 4-pentylbicyclo-[2,2,2]octan-1-carboxylate–7CP5BOC



which can be compared with 1-[4-(hexylbicyclo[2,2,2]-octyl]-2-(3-fluoro-4-methoxyphenyl)-ethane – 6BAP(F)



studied recently by us [2].

Each substance has two polar groups: one connected with halogen atoms attached to the benzene rings, the second placed in different parts of the molecules (near the bridging carboxyl group in the first compound, and near the methoxy group at the terminal position of the second once). In effect, the net dipole moments are considerably inclined from the long molecular axis, and the substances have a negative dielectric anisotropy in the nematic (N) phase [1–4], $\Delta\varepsilon = \varepsilon_{\parallel} - \varepsilon_{\perp} < 0$, where $\varepsilon_{\parallel}$ and $\varepsilon_{\perp}$ are the principal permittivity components measured for the parallel and perpendicular orientation of the nematic director $\boldsymbol{n}$ (given by an external magnetic field) with respect to the measuring electric field $\boldsymbol{E}$. The present relaxation measurements cover the frequency band 10 kHz–3 GHz, so all possible dipole rotational motions should be detected.

2. Experimental

The transition temperatures of 7CP5BOC are: Cr – 18 °C – N – 43.2 °C – Is. The complex dielectric permittivity, $\varepsilon^*(f) = \varepsilon'(f) - i\varepsilon''(f)$, was measured with the aid of two experimental set-ups: an HP 4192A impedance analyzer (10 kHz–10 MHz, $\boldsymbol{E}\|\boldsymbol{n}$ geometry, $\boldsymbol{B} \sim 0.8$ T), and a time domain spectrometer (TDS) at Uppsala University [5] (20 MHz – 3 GHz, isotropic phase and $\boldsymbol{E}\perp\boldsymbol{n}$ geometry). In the TDS measurements one time window (10 ns) was used. It was proved with the aid of the thin cell [6] that the spectra collected for the N phase with an without the orienting magnetic field ($\boldsymbol{B} \sim 0.4$ T) were practically the same. Therefore, most of the TDS spectra were obtained using the open circuit

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cell [5] without orientation of the sample (this was profitable due to the rather weak dielectric response of the substance).

3. Results

The static permittivity of 7CP5BOC, $\varepsilon_{s\|}$, is ca. 3 [1, 3, 4], which indicates that the longitudinal component of the dipole moments is very small. This causes that the amplitude of the absorption spectra $\varepsilon''_{\|}$ are rather weak (see Fig. 1) and therefore the measurements were repeated three times with slightly different sample thicknesses (0.10, 0.12, 0.15 mm). They were analysed with the imaginary part of the Cole-Cole equation

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

where ε_s and ε_∞ are the static and high frequency permittivities, respectively, and α characterizes a distribution of the relaxation times. The obtained relaxation times $\tau_{\|}$ are presented in Fig. 3 as a functions of the reciprocal temperature. Due to very small increment connected with molecular motions around the short axis the corresponding relaxation process could not be detected in the isotropic phase (in the case of 6BAP(F) it was well visible in the TDS spectra [2]).

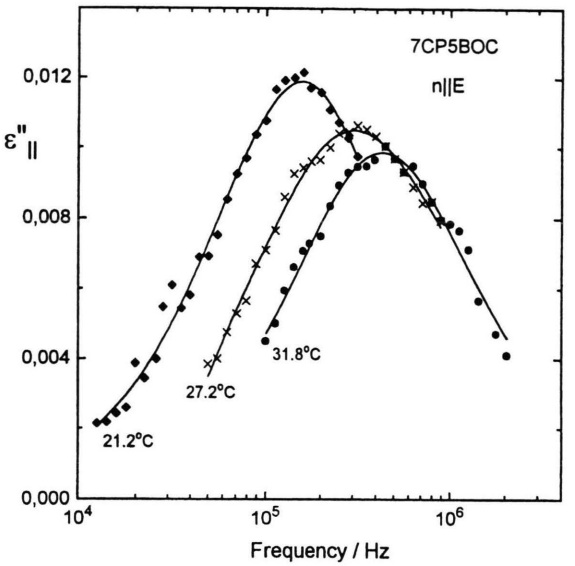

Fig. 1. Absorption spectra collected for the N phase of 7CP5BOC at the $\boldsymbol{n}\|\boldsymbol{E}$ geometry. The lines are the fits of the imaginary part of (1) to the experimental points.

Figure 2 presents the TDS spectra of the isotropic and nematic phases of 7CP5BOC. Their broad shapes indicate that at least two relaxation processes with comparable amplitudes contribute to them. In order to separate

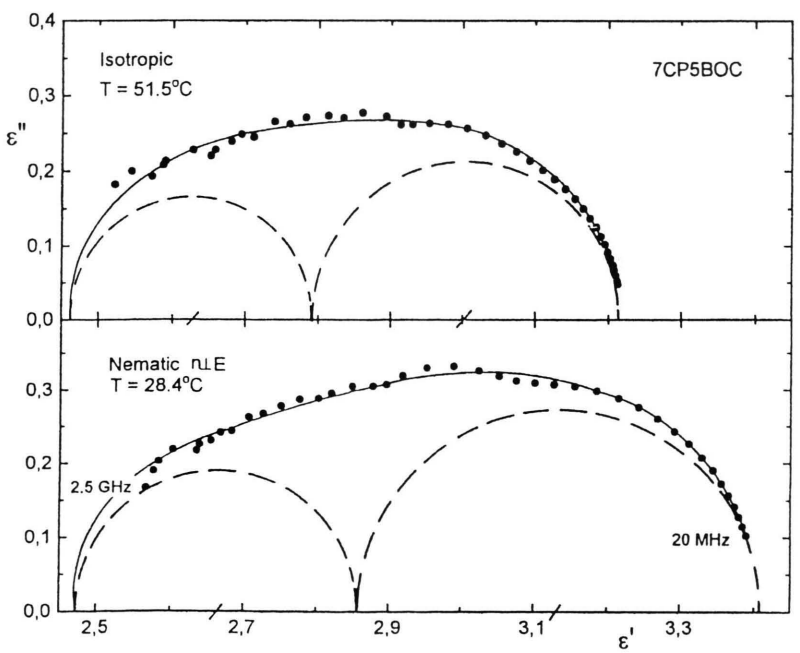

Fig. 2. Cole-Cole plots for the isotropic and nematic phases of 7CP5BOC. The solid lines are fits of (2) to the spectra. The dashed semicircles correspond to two Debye-type processes connected with the independent rotations of two molecular moieties around the C–O bond in the –C(=O)–O– bridging group.

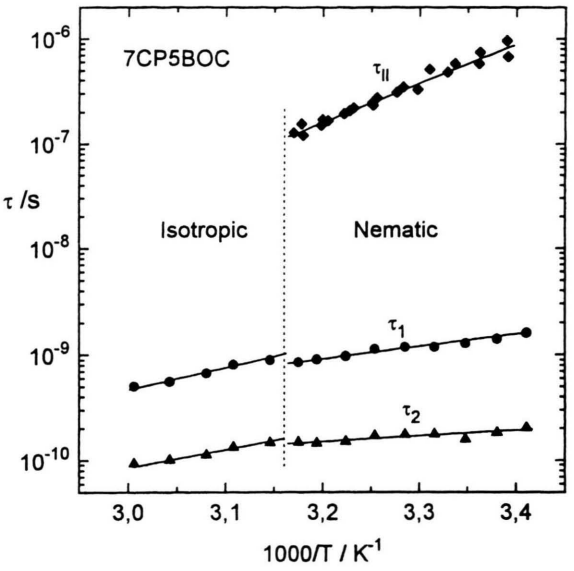

Fig. 3. Activation plots for the isotropic and nematic phases of 7CP5BOC.

Table 1. Activation enthalpy ΔH (kJ/mol) obtained according to the Arrhenius equation for particular relaxation processes observed in the nematic and isotropic phases of 7CP5BOC and 6BAP(F) [2].

Phase	Relaxation	7CP5BOC	6BAP(F)
Nematic	$\|$	70±5	73.4±2
	$\perp$ 1	20±3	30.0±2
	2	10±3	
Isotropic	1	36±3	
	2	29±3	
	l		55.0±3
	t		23.6±2

these processes we used a superposition of two Debye equations,

$$\varepsilon^* - \varepsilon_\infty = \frac{\delta_1}{1 + i\omega\tau_1} + \frac{\delta_2}{1 + i\omega\tau_2}, \qquad (2)$$

where $\delta_1 = \varepsilon_s - \varepsilon_{s2}$ and $\delta_2 = \varepsilon_{s2} - \varepsilon_\infty$, are the strengths (increments) of the two relaxation processes. In both phases studied the increment δ_1 corresponding to the slower process is larger than δ_2 characterizing the faster process. The calculated relaxation times are shown in Fig. 3 in the form of Arrhenius plots. The activation enthalpies calculated for particular relaxation processes observed are listed in Table 1. They are compared with the analogous results obtained for 6BAP(F) [2].

4. Discussion

In nematic phase one can distinguish two main relaxation processes connected with rotations of the elongated molecules around the principal inertia axes. The movement around the short axis is strongly hindered by the nematic potential and viscosity effects and falls in the MHz freqency range (the low frequency, l.f., process). It is well visible in measurements with the $\boldsymbol{E}\|\boldsymbol{n}$ geometry. A considerably faster movement around the long axis is detected for the $\boldsymbol{n}\perp\boldsymbol{E}$ geometry and falls into the hundreds of MHz range (the high frequency, h.f., process). It does not depend on the nematic potential and is practically unchanged at the N – Is transition [2].

The results obtained for 7CP5BOC indicate that the parameters characterizing the l.f. process ($\tau_{\|}$, $\Delta H_{\|}$) can only treated as typical for nematics [2, 7]. The h.f. relaxation process in the N phase of 7CP5BOC, unlikely to other nematics [2, 8], is split into two independent processes with different relaxation times τ_1 and τ_2, and slightly different increments and activation enthalpies (compare Figs. 2 and 3 and Table 1). Both these processes are also observed in the isotropic phase (Figs. 2 and 3), although the activation enthalpies become higher in the non-ordered phase (Table 1). The increment δ being proportional to μ^2 [9], one can suppose that the corresponding motions have to be ascribed to the molecular fragments having similar polarity. Looking at the chemical structure of the molecule one can suggest that two moieties perform independent motions around the –CO–O bond. According to [10], Table 10, one can estimate the ratio of the perpendicular components of the dipole moments of the chlorophenyloxy (ClØO) and the phenylbicyclooctylcarbonyl (RCO) group. This leads to $\mu^2_{\text{ClØO}}/\mu^2_{\text{RCO}} \approx 0.69$, which can be compared with the ratio $\delta_2/\delta_1 \approx 0.73$ (isotropic phase) and ≈ 0.66 (nematic phase). Thus, the process named '1' has to be ascribed to the 4-pentylbicyclo[2,2,2]octyl-1-carbonyl moiety, whereas process '2' is ascribed to the 4-heptyl-2-chlorophenyl moiety. The discussed processes must be distinguished from those observed for 6BAP(F) [2] in the isotropic phase, which were connected with the whole molecule rotations around the short axis (δ_l-process) and around the long axis (δ_t-process).

In conclusion one should stress that the 7CP5BOC molecule performs intramolecular motions of two moieties around the C–O bond in the $-\overset{\overset{O}{\|}}{C}-O-$ bridging group. A similar behaviour was observed for the *p*-azoxynisole (PAA) homologous series, where two moieties rotate

around the Ø-N_2O bond in the bridging group [11, 12]. Rjumtsev and Kovshik reported about the superposition of intra and intermolecular rotational motions in the dielectric spectra of a three-ring compound having two laterally attached chlorine atoms [13].

Acknowledgements

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