Dielectric Behaviour of 1-(4-Isothiocyanatophenyl)-2-(4-hexyl-bicyclo[2,2,2]octane-1)ethane in Nematic and Isotropic Phases

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Static and dynamic investigations of the dielectric properties of the liquid crystal 1-(4-isothiocyanatophenyl)-2-(4-hexyl-bicyclo[2,2,2]octane-1)ethane in the nematic and isotropic phases have been carried out in the frequency region from 1 kHz to 1 GHz. Two relaxation processes, described by the Debye functions, have been observed not only in the isotropic but also in the nematic phase, when the measurements of the electric permittivity vs. frequency have been made parallel to the orientation axis of liquid crystal. These processes are related to the rotation of the permanent dipole moment around two main molecular axes. The height of the potential barrier which hinders the rotation of the liquid crystal molecule around the short axis in the ordered nematic phase and the order parameter of the liquid crystal investigated have been estimated on the basis of the relaxation time values in the nematic and isotropic phases.

Introduction

Liquid crystals are easily deformed under the influence of external factors and have therefore found wide application in various fields of the science and technology. The knowledge of their dielectric properties is substantial on the one hand for technical reasons, because in the electrooptical liquid crystal display-devices the threshold voltage, the multiplexability and other important parameters depend on the anisotropy of the electric permittivity $\Delta\varepsilon = \varepsilon_{\parallel} - \varepsilon_{\perp}$, on the other hand because dielectric measurements in static fields provide information about the relation between the dielectric anisotropy of the mesogenic substance and its molecular structure, the dipole-dipole correlation and also the symmetry of both the molecule and the liquid crystalline phase [1]. The dynamic behaviour of the molecules is investigated through measurements of the complex electric permittivity, $\varepsilon^* = \varepsilon' - i\varepsilon''$, as a function of frequency, temperature [1] and pressure [2–5]. These studies are a valuable source of information about the molecular movements in both the mesomorphic and isotropic phases.

It is well known that the anisotropy of the nematic liquid crystalline phase arises because of the tendency of the rod-like molecules to align their long axes around a certain preferred direction, described by "director", **n**. The influence of the surrounding on a molecule can be described by introducing the nematic potential which forces the molecules to become ordered. This potential hinders the molecular rotation around the short axis, and as a consequence the relaxation frequency region, observed in the direction parallel to the director ($\varepsilon_{\parallel}$), shifts towards lower values with respect to the isotropic phase.

This paper presents static and dynamic dielectric measurements on 1-(4-isothiocyanatophenyl)-2-(4-hexyl-bicyclo[2,2,2]octane-1)ethane (**1**) in the nematic and isotropic phases. This compound and its homologues were first synthesized by Dąbrowski et al. [6], and because of their low melting enthalpies they can be highly useful for obtaining low melting crystalline mixtures with a wide range of the nematic phase [6, 7].

2. Experimental

The title-compound (**1**) with the chemical structure

$$C_6H_{13} - \langle\!\!\bigcirc\!\!\rangle - CH_2CH_2 - \langle\!\!\bigcirc\!\!\rangle - NCS$$

was kindly provided by Prof. R. Dąbrowski, Military Academy of Technology, Warsaw and was used with-

out further purification. The temperatures of the phase transitions were in the substantial agreement with the literature [6] and were as follows:

(Cr) 334.8 K (N) 378.5 K (I) .

The static electric permittivity vs. temperature was measured at 10 kHz using a Wayne-Kerr 6425 bridge. The liquid crystal sample (0.6 mm thick) was placed within a plane copper capacitor with gold covered electrodes. A magnetic field ($B = 0.6$ T) was used to orient the sample in the nematic phase. The permittivity components $\varepsilon_\parallel$ and $\varepsilon_\perp$ of the ordered liquid crystal were measured with the electric field E parallel and perpendicular, respectively, to B. The accuracy of these measurements was about 0.1% and the temperature was stabilized within ± 0.01 K.

The complex electric permittivity, $\varepsilon^* = \varepsilon' - i\varepsilon''$ was measured at different temperatures in the frequency range from about 1 kHz to 1 GHz using two impedance analyzers HP 4192 A (1 kHz–13 MHz) and HP 4191 A (1 MHz–1 GHz) connected with a HP 87 computer. The measuring cell consisted of two parallel-plane capacitors located at the end of a coaxial line [8]. The homogeneous orientation of the molecules in the mesomorphic state was obtained by means of a magnetic field of 1.2 T, and the measurements were performed for $E \parallel B$. The overall uncertainty was better than 2% for ε' and 5% for ε''. The temperature of the sample was stable within ± 0.1 K.

3. Results and Discussion

Figure 1 shows the electric permittivities in the nematic ($\varepsilon_\parallel$ and $\varepsilon_\perp$) and isotropic (ε_{iso}) phases of 1 as functions of temperature. The average dielectric constant $\bar{\varepsilon} = (\varepsilon_\parallel + 2\varepsilon_\perp)/3$ in the nematic phase is also shown. The dielectric anisotropy of the liquid crystal investigated is positive, due to the strong permanent electric dipole moment of the end $-$NCS group directed almost parallel to the molecular long axis. The values of $\bar{\varepsilon}$ in the vicinity of the nematic-isotropic phase transition are slightly lower than the values of ε_{iso}. This difference is attributed to the antiparallel alignment of the molecules with the strong dipole moment in the nematic phase [9, 10]. Such association was also previously found for other liquid crystals with $-$NCS end group [11–13] and liquid crystals with $-$CN group [10, 11, 14, 15].
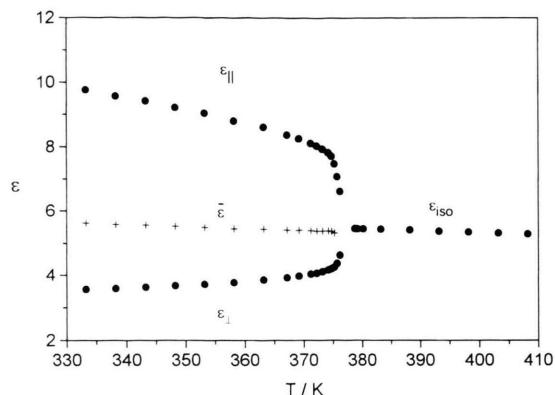

Fig. 1. Static permittivity of the nematic and isotropic phases of the title compound 1.

Figure 2 presents the real ($\varepsilon'_\parallel$) and imaginary ($\varepsilon''_\parallel$) parts of the parallel component of the electric permittivity of 1 in the nematic phase vs. frequency. A large dielectric relaxation occurs in the megahertz range. The relaxation strength decreases with increase of the temperature, and simultaneously the relaxation frequency, corresponding to the maximum of the absorption spectrum, shifts towards higher frequencies. Figure 3 shows the frequency dependence of ε' and ε'' in the isotropic phase. The dielectric spectrum is significantly broader than in the nematic phase. The relaxation strength is lower and does almost not change with temperature, and the position of the absorption maximum changes only slightly.

For some liquid crystals with molecular structures similar to that of 1, in the isotropic phase two [16–21] or three [22] relaxation processes occur. Buka et al. [21] had detected a high frequency relaxation in the dielectric spectrum of $\varepsilon_\parallel$ in the nematic phase of n-heptyl and n-heptoxy-cyanobiphenyl recorded up to 18 GHz. Some liquid crystals with the $-$NCS end group [17–19] had also shown two relaxation processes in both the isotropic and nematic phase. These two processes were described by the Debye functions. In our case we have also introduced two Debye-type components:

$$\varepsilon'(\omega) = \varepsilon_\infty + \sum_{i=1}^{2} A_i \frac{1}{1 + \tau_i^2 \omega_i^2} , \qquad (1)$$

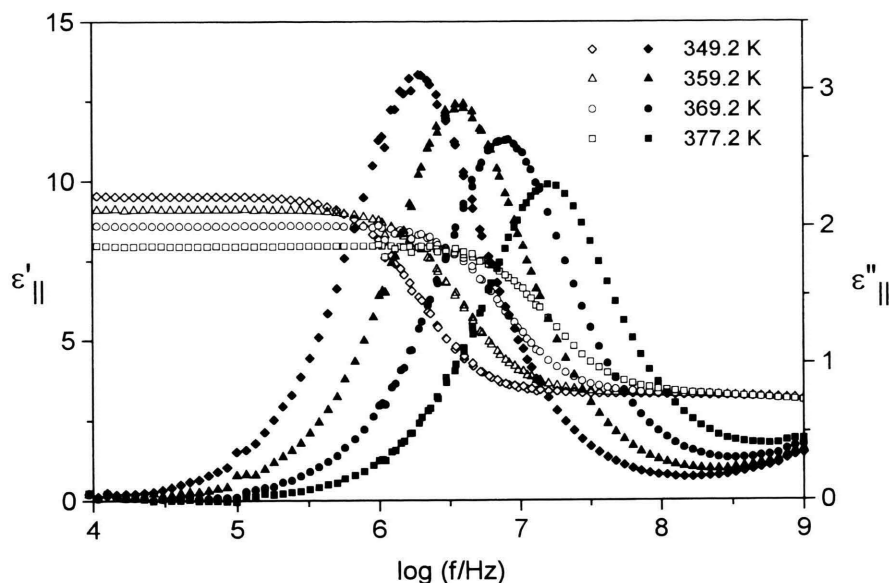$$\varepsilon''(\omega) = \sum_{i=1}^{2} A_i \frac{\tau_i \omega}{1 + \tau_i^2 \omega_i^2} , \qquad (2)$$

Fig. 2. Permittivity $\varepsilon'_\parallel$ (open) and dielectric absorption $\varepsilon''_\perp$ (filled) of **1** in the nematic phase vs. frequency.

Fig. 3. Permittivity ε' (open) and dielectric absorption ε'' (filled) of **1** in the isotropic phase vs. frequency.

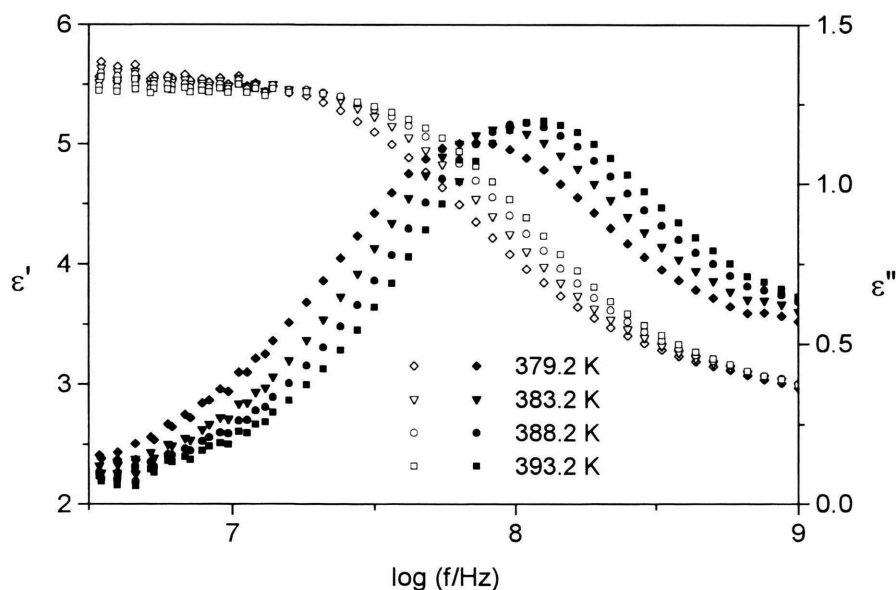where the adjustable parameters A_i and τ_i are the relaxation strength and the relaxation time, respectively.

Figures 4 and 5 show examples of the decomposition of the dielectric absorption spectra into two components in the nematic ($T = 369.2$ K) and isotropic ($T = 388.2$ K) phase, respectively. The obtained values of A_i and τ_i at various temperatures are plotted in Figure 6. At the nematic-isotropic phase transition significant changes occur only for A_1 and τ_1, describing the low-frequency relaxation process. This means that this process is connected with the rotation of the
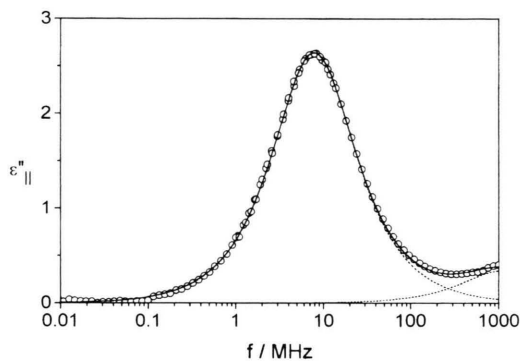
Fig. 4. Frequency dependence of $\varepsilon''_\parallel$ of **1** at $T = 369.2$ K (nematic phase). o: experimental points, dashed curves: resolved Debye-type components, solid curve: sum of components.
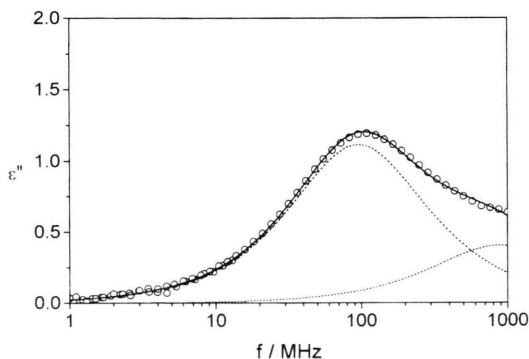

Fig. 5. Frequency dependence of $\varepsilon''_\parallel$ of **1** at $T = 388.2$ K (isotropic phase). o: experimental points, dashed curves: resolved Debye-type components, solid curve: sum of components.
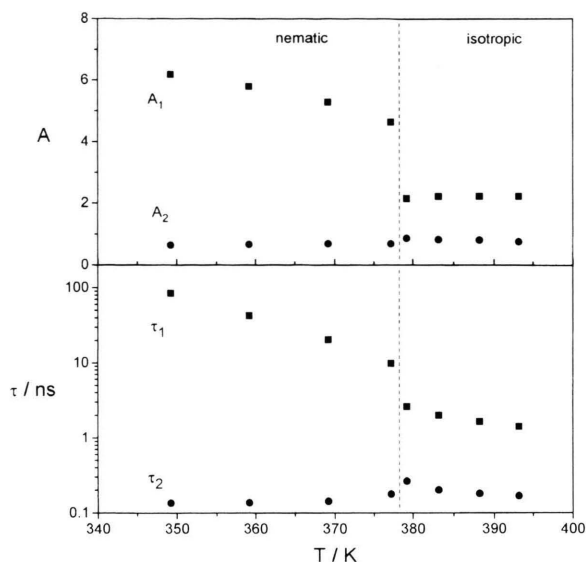

Fig. 6. Relaxation strengths, A_i and relaxation times, τ_i vs. temperature in the nematic and isotropic phases of **1**.

Table 1. Relaxation time τ_0, retardation factor $g_\parallel$, height of potential barrier q for rotation around the molecular short axis, and the order parameter $\langle P_2 \rangle$ for **1**.

T [K]	τ_0 [ns]	$g_\parallel$	q		$\langle P_2 \rangle$
			[eV]	[kJ/mol]	
349.2	4.97	16.98	0.154	14.80	0.65
359.2	4.14	10.28	0.135	12.99	0.59
369.2	3.32	6.17	0.111	10.74	0.50
377.2	2.65	3.74	0.088	8.47	0.40

permanent electric dipole moment around the molecular short axis, which is strongly affected by the nematic potential. The second relaxation process is probably related to the rotation around the long axis, which indicates that the liquid crystal has a transversal component of the dipole moment. The nematic packing improves the conditions for rotation of the molecules around the long axes in comparison with their random rotation in the isotropic phase. Therefore, the relaxation time τ_2 in the nematic state is slightly lower than in the isotropic one.

The main dielectric relaxation process observed for the parallel component of the permittivity may be interpreted by the Martin-Meier-Saupe model [23]. These authors had showed that the relaxation time τ_1 is larger than the relaxation time τ_0 in the absence of the nematic potential by a factor

$$g_\parallel = \tau_1/\tau_0 , \qquad (3)$$

called the retardation factor.

Of course, for the nematic phase τ_0 is a hypothetical value. In our experiment we have determined it through the extrapolation of the relaxation times measured vs. temperature in the isotropic phase to a given temperature in the nematic state. Knowing the retardation factor $g_\parallel$, one can estimate the barrier height of the nematic potential q, using the plot given by Martin et al. [23]. The values of τ_0, $g_\parallel$, and q obtained for **1** at four temperatures are gathered in Table 1. For easier comparison of our data with data given in the literature, the q value are given in two different units. It is seen that the height of the potential barrier decreases

with increasing temperature, which means that the orientational order of the liquid crystal molecules, resulting from the existence of the nematic potential, becomes smaller.

The orientational order parameter, defined by [24]

$$\langle P_2 \rangle = \tfrac{1}{2} \langle 3 \cos^2 \theta - 1 \rangle , \qquad (4)$$

can be determined on the basis of the q value through the distribution function of the nematic order $f(\theta)$, having the form [23, 25]

$$f(\theta) = C \exp\left(- \frac{q}{kT} \sin^2 \theta \right), \qquad (5)$$

where θ is the angle between the nematic director $\mathbf{n}$ and the long axis of the liquid crystal molecule, and

$$\langle \cos^2 \theta \rangle = \frac{\int\limits_0^\pi \cos^2 \theta \, f(\theta) \sin \theta \, d\theta}{\int\limits_0^\pi f(\theta) \sin \theta \, d\theta} . \qquad (6)$$

The values of $\langle P_2 \rangle$ are given in Table 1. It has been estimated that the uncertainty in the determination of the order parameter was ± 0.01.

Now let us compare the values of the order parameter obtained for **1** from our dielectric relaxation time measurements with those determined using other methods: optical birefringence, Δn, dielectric anisotropy, $\Delta \varepsilon$ and anisotropy of absorption R, measured for the dichroic dye dissolved in the liquid crys-

Table 2. Comparison of the order parameter of **1** obtained by using different experimental methods.

T [K]	$\langle P_2 \rangle^{\mathrm{a}}$	$\langle P_2 \rangle^{\mathrm{b}}$	$\langle P_2 \rangle^{\mathrm{c}}$	$\langle P_2 \rangle^{\mathrm{d}}$
349.2	0.65	0.53	0.62	0.53
359.2	0.59	0.50	0.57	0.50
369.2	0.50	0.45	0.50	0.45
377.2	0.40	0.32	0.41	0.32

[a] this paper, [b] from Δn [27], [c] from $\Delta \varepsilon$ [27], [d] from R [27].

talline host ("guest-host" effect [26]). The latter data are taken from [27] and are listed together with our results in Table 2. It is seen that the values of $\langle P_2 \rangle$ determined from the relaxation time measurements are quite close to those obtained from the dielectric anisotropy, but significantly higher than the results arising from Δn and R. The difference within 20% had been noticed previously for many liquid crystalline compounds [18, 28–31]. However, the character of the changes of the order parameter with temperature observed **1** by using all mentioned methods is similar and agrees quite well with the predictions of the Maier-Saupe mean-field theory of nematics [32].

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