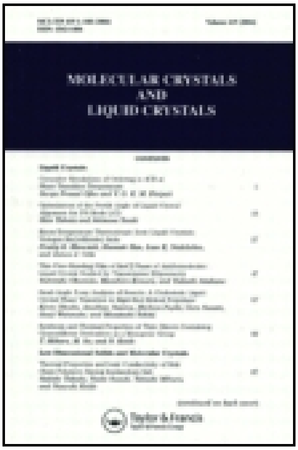

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J. Chruściel [a] , R. K. Bamezai [b] , H. Kresse [c] , S. Urban [d] & S. Wróbel [d]
[a] Institute of Chemistry, Agricultural and Pedagogical University, 3-go Maja 54, 08-110, Siedlce, Poland
[b] H. Niewodniczański Institute of Nuclear Physics, E. Radzikowskieo 152, 31-342, Kraków, Poland
[c] Sektion Chemie, Martin-Luther Universität, Mühlpforte 1, 40 20, Halle/S, GDR
[d] Institute of Physics, Jagellonian University, Reymonta 4, 30-59, Kraków, Poland

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MOLECULAR DYNAMICS IN THE NEMATIC PHASE OF $\overline{5}$S5 AND $\overline{6}$S5 AS STUDIED BY DIELECTRIC METHODS

J. CHRUŚCIEL[*], R.K. BAMEZAI[x], H. KRESSE[+], S. URBAN[#]
and S. WRÓBEL[#]
[*] Institute of Chemistry, Agricultural and Pedagogical University,
3-go Maja 54, 08-110 Siedlce, Poland
[x] H. Niewodniczański Institute of Nuclear Physics,
E. Radzikowskiego 152 31-342 Kraków, Poland
[+] Sektion Chemie, Martin-Luther Universität, Mühlpforte 1,
40 20 Halle/S, GDR
[#] Institute of Physics, Jagellonian University, Reymonta 4,
30-059 Kraków, Poland

Abstract Results of dielectric studies of two members of 4-n-pentylphenyl-4-n-alkoxytiobenzoate ($\overline{n}$ S5) homologous series, namely $\overline{5}$S5 and $\overline{6}$S5, are preseted and discussed in terms of molecular motions.

INTRODUCTION

Dielectric relaxation method is a powerful tool for investigating the reorientations of liquid crystalline molecules around their short and long axes. For nematics the former process is usually observed in MHz frequency range while the latter in GHz one. In this paper the results of dielectric investigations are presented for $\overline{5}$S5 and $\overline{6}$S5 in their nematic phases. These substances belong to the homologous series of thiol esters, viz. 4-n-pentylphenyl- 4'-n-alkoxythiobenzoate ($\overline{n}$ S5). Previously, two higher homologs of this series, viz. $\overline{7}$S5 and $\overline{8}$S5, have been investigated in our group[1,2].

EXPERIMENTAL

The substances under study have the following chemical formula:

$$H_{2n+1}C_nO-C_6H_4-COS-C_6H_4-C_5H_{11},$$

and $\overline{5}S5$ and $\overline{6}S5$ represent homologs with n = 5 and 6, respectively. They were synthesized in Siedlce (Poland). The substances are suitable for dielectric studies as their molecules are polar with two groups: -COS- and the alkoxy- one contributing to the net dipole moment.

The phase diagrams - as studied by DSC method - are the following:

Cr. - 66.1°C - N - 82.0°C - I - for $\overline{5}S5$, and
Cr. - 61.5 °C - N - 87.2°C - I - for $\overline{6}S5$.

Both principal components ($\varepsilon_{o\parallel}$ and $\varepsilon_{o\perp}$) of the static electric permittivity tensor of the nematic phase were measured at 100 kHz with the aligning magnetic field of ca. 0.5 T being, respectively, parallel and perpendicular to the electric measuring field. Measuremets of the dielectric losses, $\varepsilon''_{\parallel}$, were carried out from 0.1 to 13 MHz by using a multidecameter described elsewhere[1]. The real and imaginary parts of the complex electric permittivity, $\varepsilon^{*}=\varepsilon' - j\varepsilon''$, were also measured in the microwave frequency range, between 0.9 and 10.0 GHz, by applying a standing-wave method[3]. All measurements were carried out upon gradual cooling of the samples.

RESULTS AND DUSCUSSION

Figure 1 presents temperature dependences of the electric permittivities measured for $\overline{6}S5$ in the radio and microwave frequencies; similar results have been obtained for $\overline{5}S5$. As it is seen the dielectric anisotropy, $\Delta\varepsilon' = \varepsilon'_{\parallel} - \varepsilon'_{\perp}$, is positive in both frequency ranges. This effect can be interpreted by taking into account the well known Maier-Meier formula[4,5],

$$\Delta\varepsilon' = N_oFh\left\{\Delta\alpha - F\frac{\mu^2}{2kT}(1 - 3\cos^2\beta)\right\}S \qquad (1)$$

where $\Delta\alpha \sim \Delta n \equiv n_{\parallel}^2 - n_{\perp}^2$ is the polarizability anisotropy, and β stands for the angle between the total dipole moment, μ, and the long axis of molecule. From the fact that $\Delta\varepsilon'_0 > \Delta n \approx 0.4$ (at 70°C) one can conclude that $(1 - 3\cos^2\beta) \leq 0$ and hence $\beta \leq \beta_{cr} = 54.7°$. This is consistent with the results of the group dipole moment calculations[6].

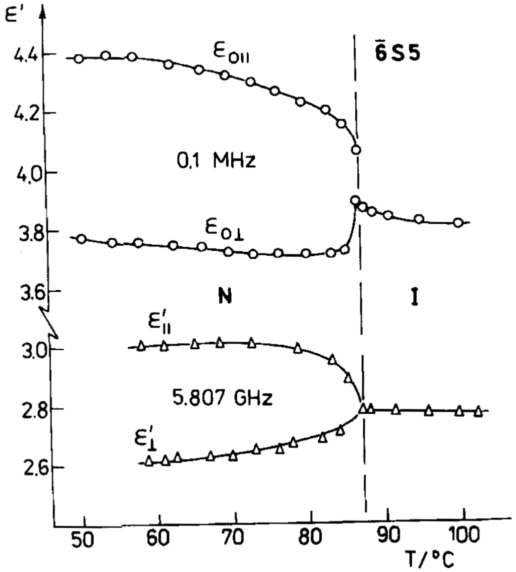

FIGURE 1. Dielectric anisotropies ($\Delta\varepsilon'$) vs. temperature for $\bar{6}S5$ obtained at the radio and microwave frequencies.

Frequency dependences of the complex electric permittivities will be discussed in terms of a Debye-type equation,

$$\varepsilon_i^* = \varepsilon_i' - j\varepsilon'' = \varepsilon_{\infty,i} + \frac{\varepsilon_{0,i} - \varepsilon_{\infty,i}}{1 + (j\omega\tau_i)^{1-\alpha_i}} \qquad (2)$$

with the α_i parameter which is commonly interpreted as a measure of a symmetric distribution of the dielectric relaxation time, τ_i. "i" denotes here one of the relaxation processes observed for two principal orientations ($\parallel$ or $\perp$) of the nematic phase.

In Figure 2 the $\varepsilon''_{\parallel}$ dielectric losses are shown as a function of frequency and temperature. The dielectric increments, $\delta\varepsilon = \varepsilon_{0\parallel} - \varepsilon_{\infty\parallel}$, as well as the dielectric relaxation times ($\tau_\parallel$) have been computed by fitting

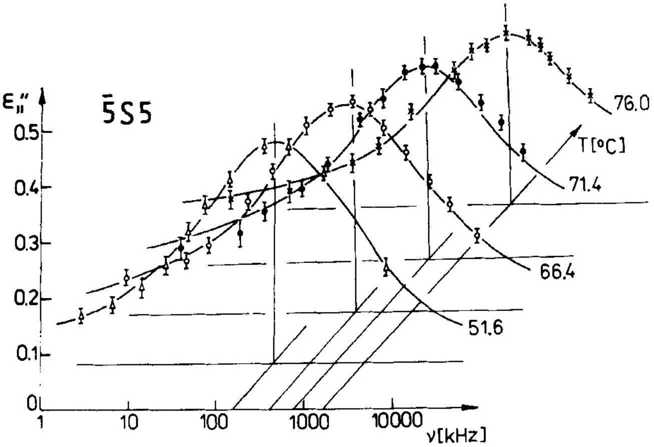

FIGURE 2. Dielectric losses ($\varepsilon_\parallel''$) vs. frequency measured for $\bar{5}$S5 at different temperatures. The solid lines are least square fits of the imaginary part of eq. (2).

TABLE I Relaxation times and dielectric increments calculated for different temperatures in the nematic phases of $\bar{5}$S5 and $\bar{6}$S5.

$\bar{5}$S5			$\bar{6}$S5		
T[°C]	δε	$\tau_\parallel \cdot 10^6$[s]	T[°C]	δε	$\tau_\parallel \cdot 10^6$[s]
76.0	0.654	3.68	80.8	0.639	0.36
71.4	0.767	6.01	75.5	0.709	0.63
66.4	0.803	8.83	68.0	0.765	1.04
61.6	0.882	12.13	64.6	0.795	1.42

the imaginary part of eq. (2) with $\alpha_{\parallel} = 0$ to the experimental points. Solid lines in Figure 2 represent the theoretical fits.
In Table I the dielectric parameters, obtained by the fitting procedure for the low frequency relaxation, are gathered for both substances studied. One can conclude that the low frequency relaxation process observed for parallel orientation of the nematic phase is a monodispersive one.

Making use of the Arrhenius equation the activation energies ($E_{\parallel}$) have been calculated as equal to 80 and 82 kJ/mole (± 2 kJ/mole) for $\bar{5}S5$ and $\bar{6}S5$, respectively. From the geometry of measurements as well as from the fact that the values of the relaxation times and activation energies are high, one can conclude that the relaxation process observed is connected with reorientations of molecules around their short axes.

Measurements of the complex electric permittivity for perpendicular orientation were performed in the microwave range from 0.9 to 10 GHz. As an example, Fig. 3 shows the Cole-Cole plot for the nematic phase of $\bar{6}S5$. The $\tau_{\perp}$ relaxation times, calculated by fitting of eq. (2) to the experimental points obtained at 70°C, are $2.4 \cdot 10^{-10}$ s and $2.2 \cdot 10^{-10}$ s ($\pm 0.2 \cdot 10^{-10}$ s) for $\bar{5}S5$ and $\bar{6}S5$, respectively. The corresponding activation energies ($E_{\perp}$) are equal to 14 and 16 kJ/mole (± 2 kJ/mole), respectively, for $\bar{5}S5$ and for $\bar{6}S5$.

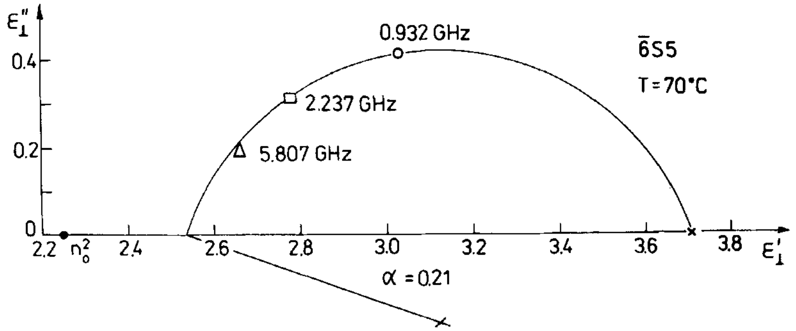

FIGURE 3. Cole-Cole plot for the nematic phase of $\bar{6}S5$.

Large values of the $\alpha_{\perp}$ parameters (≈ 0.20) show that there are many relaxation processes which contribute to the high frequency dielectric spectra. It is commonly assumed that the high frequency relaxation process, observed for the perpendicular alignment of the nematic phase, is mainly connected with reorientation of molecule as a whole around its long axis[5]. However, other molecular processes like internal reorientations, conformational changes in the end groups and stochastic precession of the long axis around the director, lead to the distribution of the relaxation times.

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