DIELECTRIC INVESTIGATIONS OF 4-*n*-PENTYLPHENYL-4′-*n*-HEPTYLOXYTHIOBENZOATE $\overline{7}$S5*

By J. Chruściel**

Institute of Chemistry, Agricultural and Pedagogical University, Siedlce***

S. Wróbel

Institute of Physics, Jagellonian University, Cracow****

J. A. Janik

Institute of Nuclear Physics, Cracow*****

J. M. Janik

Institute of Chemistry, Jagellonian University, Cracow******

H. Kresse**

Department of Chemistry, Martin Luther University, Halle*******

(Received May 5, 1980)

Dielectric relaxation studies of the isotropic and nematic phases of 4-*n*-pentylphenyl-4′-*n*-heptyloxythiobenzoate $\overline{7}$S5, m.p. 326.7 K and cl.p. 355.3 K, have been carried out in the radio and microwave frequency ranges. In the microwave frequency range, a dielectric relaxation process with the relaxation time of the order of 10^{-10} s was observed for the isotropic and nematic phases. This process is probably connected with reorientational movements of the molecules around their long axes. In the radio-frequency range a dielectric relaxation process was detected only for the nematic phase of $\overline{7}$S5. This relaxation process, originating from the reorientations of the molecules about their short axes, is characterized by a relaxation time of the order of 10^{-7} s. The temperature dependences of the relaxation times will be presented.

PACS numbers: 77.40.+i

---

* This work was partially supported by the American-Polish M. Curie-Skłodowska Foundation under Grant No INT 76-01318.

** Guest scientist at the Institute of Physics of the Jagellonian University.

*** Address: Instytut Chemii, Wyższa Szkoła Rolniczo-Pedagogiczna, 3-go Maja 54, 08-110 Siedlce, Poland.

**** Address: Instytut Fizyki UJ, Reymonta 4, 30-059 Kraków, Poland.

***** Address: Instytut Fizyki Jądrowej, Radzikowskiego 152, 31-342 Kraków, Poland.

****** Address: Instytut Chemii UJ, Karasia 3, 30-060 Kraków, Poland.

******* Address: Martin Luther Universität, Sektion Chemie, 402 Halle, Mühlpforte 1, DDR.

1. Introduction

Dielectric relaxation is one of the methods of studying the nature of molecular motions in condensed matter. So far, a number of nematic liquid crystals have been studied by means of dielectric relaxation methods [1–8, 11, 15]. It was found that in the isotropic phases of all substances studied, a complex relaxation spectrum exists which features a distribution of relaxation times. The nematic phases exhibit two well separated absorption regions, i.e. the low and high frequency regions. According to the Martin, Meier, and Saupe theory [10] this low frequency absorption is connected with the reorientations of molecules about their short axes. On the other hand, high frequency absorption involves contributions from the fast rotation around the long molecular axes as well as from different motions of the long axis itself, namely, its precessional and librational movements. This high frequency absorption can also be influenced by some possible intramolecular motions. Hence, there are reasons why the high frequency absorption region shows a distribution of relaxation times which could be characterized by a phenomenological parameter α (see Eq. (1) and (3)).

Most of the substances studied up to now, excluding mixtures [15], possess a narrow temperature range for the nematic phase, so it was difficult to study temperature dependences of the relaxation times. In this paper we deal with 4-*n*-pentylphenyl-4′-*n*-heptyloxythiobenzoate $\bar{7}$S5, which is a substance featuring a wide temperature range for the nematic phase. Its phase situation is presented in Fig. 1 [13, 14]; where the symbols: I, N, S_C, and C denote the isotropic, nematic, smectic C, and polycrystalline phases, respectively.

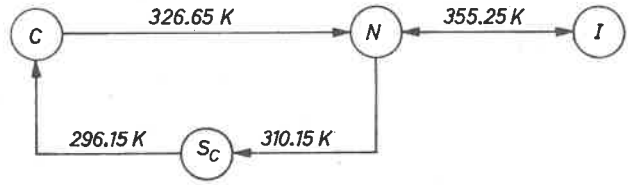

Fig. 1. Phase situation for $\bar{7}$S5 by the DSC method [14]

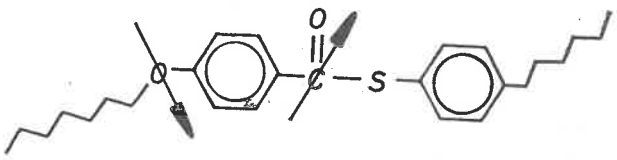

Fig. 2. Structure of $\bar{7}$S5 molecule. Group dipole moments are indicated as arrows

The molecular structure of $\bar{7}$S5 is shown in Fig. 2. As is seen, there are two permanent dipole moments (connected with two polar groups —COS—, and —OC_7H_{15}) which can contribute to dielectric absorption.

The aim of paper is to study temperature dependences of the relaxation times associated with two different types of molecular motions.

2. *Dielectric properties of $\bar{7}S5$ in the megahertz range*

A. Experimental

The dielectric permittivities $\varepsilon'_{||}$ and $\varepsilon'_{\perp}$ and parallel component of dielectric losses $\varepsilon''_{||}$ have been measured using a Multidecameter (Type DK 06), manufactured by the "Wissenschaftlich-Technischen Werkstatten" GmbH Weilheim/Obb. The apparatus can be used within the 0.1–12 MHz frequency range. One of the advantages of the DK 06 apparatus is that high accuracy can be obtained for ε' values in the region where $\varepsilon''/\varepsilon' < 0.1$. However, if the dielectric losses fulfill the relation $\varepsilon'' > 0.1\ \varepsilon'$ systematic errors in ε' measurements may appear. For this reason, frequency dependences of ε'' can be used to determine relaxation frequencies. The values in the region concerned, i.e. in the vicinity of the absorption peak, have an error $\Delta\varepsilon''/\varepsilon'' = 0.05$. Thus, the critical frequencies obtained from the experimental points must have an accuracy higher than 5%. A parallel-plate capacitor, made of silver, was used in the measurements. The apparatus constant, averaging ca. 5 pF per ε' unit, was measured with highly pure cyclohexan, and controlled with ethylbenzoate and chlorobenzene. Due to edge fields and heterogeneity of the oriented magnetic field the relative error of the dielectric anisotropy measurement is not smaller than 5%. However, the errors in $\varepsilon'_{||}$, $\varepsilon'_{\perp}$ and ε'_{is} are less than 1% at a frequency of 0.1 MHz. In order to attain the proper alignments of $\bar{7}S5$'s nematic phase a 0.5 T magnetic field was applied.

B. Results of low-frequency dielectric measurements

Measurements of the dielectric permittivities $\varepsilon'_{||}$, $\varepsilon'_{\perp}$, ε'_{is} were carried out at the following frequencies: 0.10, 0.22, 0.52, 1.1, 2.4, and 5.4 MHz. Figure 3 presents the temperature dependences of the measured dielectric permittivities. As is seen, the $\varepsilon'_{||}$ dielectric permittivity exhibits a strong frequency dependence. This effect is accompanied by pronounced absorption (Fig. 4). It was also found that the dielectric anisotropy ($\Delta\varepsilon' = \varepsilon'_{||} - \varepsilon'_{\perp}$) is positive in the kilocycle and negative ($\Delta\varepsilon' < 0$) in the megacycle range.

Having the frequency dependences of $\varepsilon'_{||}$ and $\varepsilon''_{||}$, it was possible to calculate, with the aid of the Debye-type equation

$$\varepsilon^* = \varepsilon'_{\|} - i\varepsilon''_{\|} = \varepsilon'_{\|02} + \frac{\varepsilon'_{\|01} - \varepsilon'_{\|02}}{1 + (i\omega\tau'_1)^{1-\alpha}}, \tag{1}$$

the quasi-static permittivities $\varepsilon'_{||01}$ and $\varepsilon'_{||02}$. At the same time, we made the assumption that the α-parameter is equal to zero. This means that the centers of the Cole–Cole diagrams (Fig. 5) lie on the $\varepsilon'_{||}$ axis. By fitting Debye-type absorption curves to the frequency dependences of $\varepsilon''_{||}$ obtained at different temperatures the relaxation frequencies f_R [MHz] indicated in Fig. 4 have been calculated.

In Figure 5 the data obtained for the low-frequency relaxation region of the nematic phase of $\bar{7}S5$ are presented in the form of Cole–Cole diagrams. As is seen, the centers of the Cole–Cole plots lie on the $\varepsilon'_{||}$ axis within the experimental error limits. This means

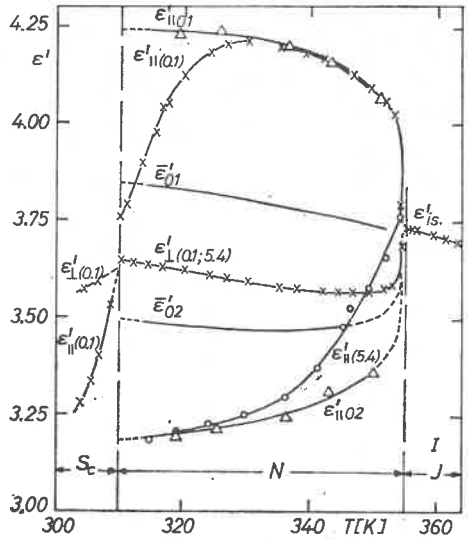

Fig. 3. Temperature dependences of dielectric permittivities measured in the r.f. range

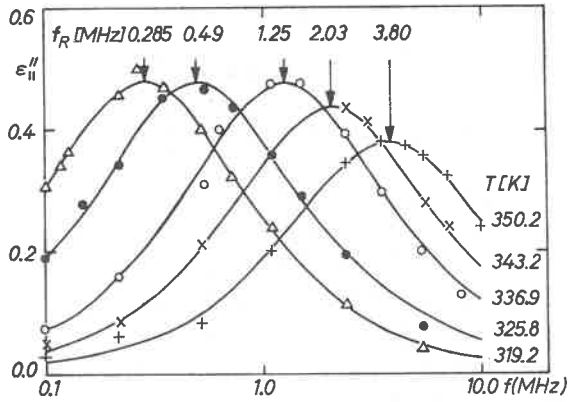

Fig. 4. Frequency dependences of $\varepsilon''_{\parallel}$ obtained at different temperatures of the nematic phase of $\overline{7}S5$

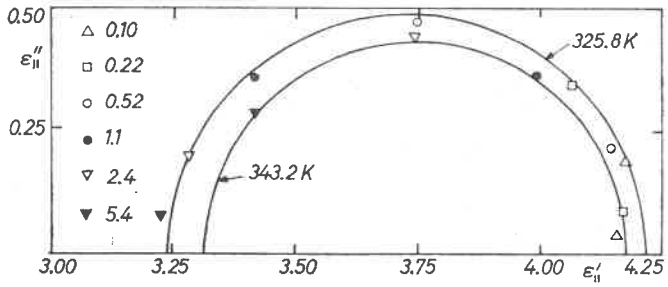

Fig. 5. The low frequency relaxation region of the nematic phase presented in the form of Cole–Cole plots

that the low-frequency relaxation region can be characterized by a single relaxation time τ_1', which is related to the relaxation frequency as follows:

$$\tau_1' = \frac{1}{2\pi f_R} . \tag{2}$$

The τ_1' values calculated for different temperatures of the nematic phase of $\bar{7}$S5 are presented in Table I.

TABLE I

Temperature dependence of the low-frequency relaxation time τ_1'

T [K]	350.2	343.2	336.9	325.8	319.2
$\tau_1' \times 10^7$ s	0.419	0.784	1.273	3.248	5.584

It is noteworthy that there was no dispersion observed for ε_{is}' or the $\varepsilon_\perp'$ component in the radio frequency range. Both quantities are frequency independent up to 12 MHz (Fig. 3).

Besides the nematic and isotropic phases, of which the $\varepsilon_{||}'$ and $\varepsilon_\perp'$ values measured on cooling as well as on heating were easily reproducible, the smectic C phase was investigated during cooling only. At first, starting from the nematic phase, the $\varepsilon_{||}'$ component was measured at the frequency 0.1 MHz. As is seen in Fig. 3, a spontaneous crystallization of the metastable smectic C phase starts at about 5K below the nematic-smectic C transition point. Then, after heating the sample up to the isotropic phase the $\varepsilon_\perp'(0.1)$ values were measured on cooling down to the S_C phase. The strong temperature dependence of $\varepsilon_{||}'(0.1)$ close to the N—S_C transition point is probably brought about by the elongation of the relaxation time τ_1' in the supercooled nematic phase; such an effect was observed for some other substances [1–8]. This means that the molecular motions about the short molecular axes become slower and slower, and in the end freeze out. On the other hand, as one can see (Fig. 3), the $\varepsilon_\perp'(0.1)$ component is not so distinctly temperature dependent within the smectic C phase. This would indicate that rotation around the long molecular axis is still very fast in this phase. Because isothermal measurements of an absorption curve (Fig. 4) last ca. 3 h, it was difficult to perform such measurements for the metastable smectic C phase. It was found that this phase is monotropic and transforms very quickly to one of the solid phases [13, 14].

3. Results of dielectric measurements in the microwave frequency range

Complex dielectric permittivity was measured by means of the standing wave method [7]. In order to attain high quality temperature stabilization ($\pm 0.2°$) a temperature controller filled with silicone oil was used. Temperature measurements were made by means of a copper-constantan thermocouple.

Dielectric investigations of $\bar{7}$S5 were performed in the microwave frequency range

at the following frequencies: 1.06, 1.86, 6.00, and 9.55 GHz. The complex dielectric permittivity ε^* ($\varepsilon^* = \varepsilon' - i\varepsilon''$) was measured for the isotropic and non-oriented ("polycrystalline") nematic phase during the cooling and heating of the samples. As is seen (Fig. 6), the nematic phase of $\bar{7}$S5 demonstrates considerable supercooling — much greater than PAA [7], MBBA [8] and other liquid crystals [2].

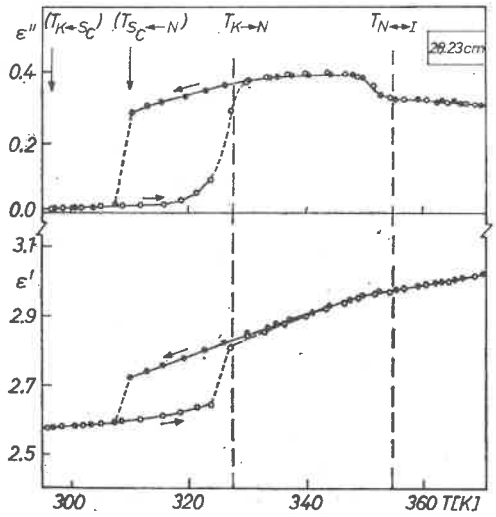

Fig. 6. Temperature dependence of ε' and ε'' obtained at a frequency of 1.06 GHz

Fig. 7 depicts the ε' and ε'' components versus temperature curves acquired for various microwave frequencies. On the basis of this plot several comments regarding the dielectric properties of $\bar{7}$S5 come to mind:

1. in the isotropic and nematic phases ε' and ε'' are frequency dependent;
2. it is seen that at the freezing point fast dipolar reorientations around the long molecular axes becomes frozen out ($\varepsilon'' \to 0$, $\varepsilon' \to \varepsilon'_\infty$);
3. it is also evident that the molecular processes affecting the microwave absorption and dispersion are practically undisturbed at the I—N transition.

In the microwave frequency range it was not possible to "see" any dipole reorientation within the smectic C phase temperature range. This is probably due to the shortness of the time the $\bar{7}$S5 sample requires to transform from the metastable S_C phase to one of its solid phases. To acquire one experimental point in the microwave frequency range by the method applied takes at least half an hour, whereas in the megahertz range ε' values are measured very quickly within 5 minutes. This is the reason why in the low frequency range it was possible to observe residual polarization (Fig. 3) in the S_C phase.

For the isotropic phase (I) of $\bar{7}$S5 the Cole–Cole plots (Fig. 8) are circular arcs with centers lying below the ε'_0 axis. The ε'_0 values are the static dielectric permittivity acquired in the r.f. range. By fitting the Cole–Cole formula

$$\varepsilon^* = \varepsilon'_\infty + \frac{\varepsilon'_0 - \varepsilon'_\infty}{1 + (i\omega\tau_0)^{1-\alpha_{is}}} \tag{3}$$

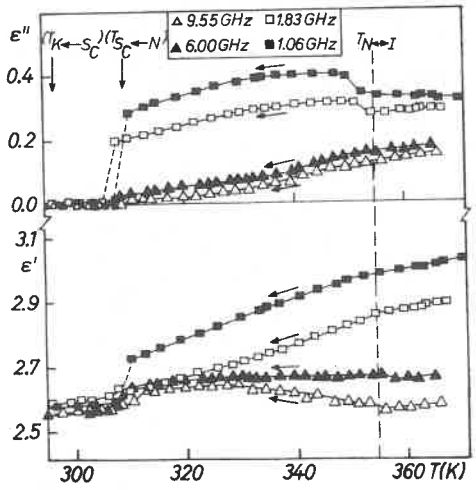

Fig. 7. Temperature dependences of ε' and ε'' acquired at various microwave frequencies

to the experimental data we obtained the following parameters: ε'_∞, ε'_0, α_{is}, τ_0. The τ_0 values acquired for the isotropic phase are of the order of 10^{-10} s (Table II). This relaxation time is the most probable relaxation time and is mainly connected with the fast reorientational movements of the molecules around their long axes.

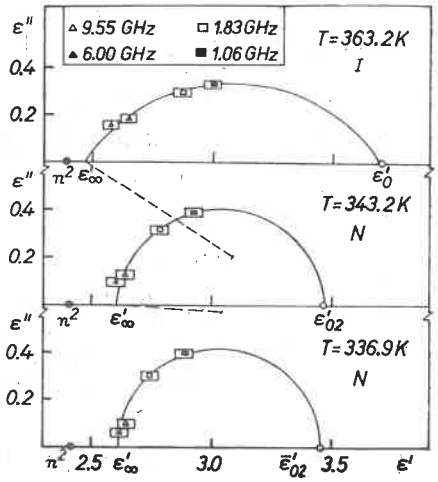

Fig. 8. The high frequency relaxation region presented in the form of Cole-Cole plots

In the case of the nematic phase, the Cole–Cole plots are nearly semicircles (Fig. 8) with centers lying below, but close to, the ε' axis. The $\bar{\alpha}$ parameter, accounting for the distribution of the relaxation times, is now of the order of 0.05 or even smaller (Table II). Roughly speaking, there is only one molecular process involved, i.e. the fast rotation of the molecules about their long axes.

TABLE II

High frequency relaxation region parameters (ε'_0, ε'_∞, τ_0, τ_1, and α)

Phase	T [K]	ε'_0	ε'_∞	$\tau_0 \times 10^{10}$ s	$\bar{\alpha}$
	365.0	3.688	2.469	2.122	0.35
	363.0	3.700	2.466	2.212	0.36
isotropic	361.0	3.701	2.470	2.225	0.35
(I)	359.0	3.716	2.476	2.416	0.36
	357.0	3.728	2.476	2.545	0.36
	355.0	3.737	2.500	2.691	0.34
Phase	T [K]	$\bar{\varepsilon}'_{02}$	$\bar{\varepsilon}'_\infty$	$\tau_1 \times 10^{10}$ s	$\bar{\alpha}$
	353.0	3.548	2.530	1.917	0.24
	350.0	3.503	2.569	1.829	0.13
	347.0	3.492	2.585	1.883	0.09
	343.0	3.483	2.606	1.995	0.05
	340.0	3.478	2.612	2.084	0.03
	336.9	3.475	2.627	2.186	0.00
	334.0	3.475	2.628	2.317	0.00
nematic	331.0	3.476	2.628	2.457	0.00
(N)	328.0	3.477	2.628	2.577	0.00
	325.8	3.484	2.627	2.724	0.00
	324.0	3.481	2.629	2.817	0.00
	319.2	3.486	2.623	3.170	0.00
	316.0	3.488	2.621	3.417	0.00
	313.0	3.493	2.618	3.673	0.00

In Fig. 9 the complete relaxation spectrum obtained for the nematic phase of $\bar{7}S5$ is presented. The points in the r.f. range represent mean values of dielectric permittivity and dielectric losses calculated from the formulae:

$$\bar{\varepsilon}' = \tfrac{1}{3}(\varepsilon'_\parallel + 2\varepsilon'_\perp), \tag{4a}$$

$$\bar{\varepsilon}'' = \tfrac{1}{3}(\varepsilon''_\parallel + 2\varepsilon''_\perp). \tag{4b}$$

As shown in Fig. 9 the nematic phase of $\bar{7}S5$ exhibits two well separated relaxation regions: (*i*) the megacycle region characterized by $\tau'_1 \sim 10^{-7}$ s, and (*ii*) the microwave region with $\tau_1 \sim 10^{-10}$ s.

The complex relaxation spectrum of the nematic phase can be described by a phenomenological formula. In the case of oriented nematic liquid crystals the complex dielectric permittivities measured parallel and perpendicular to the nematic order axis can be given by:

$$\varepsilon^*_\parallel(\omega) = \varepsilon'_{\parallel\infty} + (\varepsilon'_{\parallel 0} - \varepsilon'_{\parallel\infty})\left(\frac{g_{\parallel 1}}{1+i\omega\tau'_1} + \frac{g_{\parallel 2}}{1+(i\omega\tau_1)^{1-\alpha_\parallel}}\right), \tag{5a}$$

$$\varepsilon^*_\perp(\omega) = \varepsilon'_{\perp\infty} + (\varepsilon'_{\perp 0} - \varepsilon'_{\perp\infty})\left(\frac{g_{\perp 1}}{1+i\omega\tau'_1} + \frac{g_{\perp 2}}{1+(i\omega\tau_1)^{1-\alpha_\perp}}\right), \tag{5b}$$

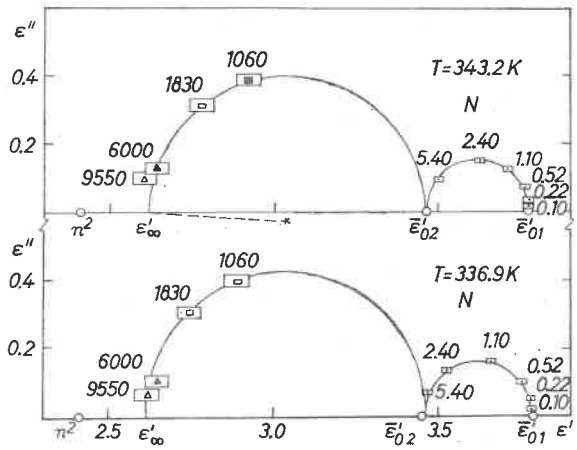

Fig. 9. The entire relaxation spectrum of the nematic phase of $\bar{7}$S5

where $\varepsilon_{||\infty} = n_{||}^2$, $\varepsilon_{\perp\infty} = n_{\perp}^2$, $\varepsilon_{||0}$ and ε_{10} are the static dielectric permittivities. The weight factors, $g_{||1}$ and $g_{||2}$, $g_{\perp 1}$ and $g_{\perp 2}$, introduced in these equations, are interrelated as

$$g_{\|1}+g_{\|2} = 1 \quad \text{and} \quad g_{\perp 1}+g_{\perp 2} = 1.$$

The molecular structure of the $\bar{7}$S5 molecule (Fig. 2) shows that the net permanent dipole moment is in this case inclined to the long molecular axis, so $g_{\perp 1} = 0$, which is consistent with the fact that perpendicular to the director only low frequency absorption was observed (Fig. 3). If one is dealing with an unoriented nematic phase ("polycrystalline sample") equations (5a) and (5b) could be replaced by:

$$\bar{\varepsilon}^* = \bar{\varepsilon}'_\infty + (\bar{\varepsilon}'_{01} - \bar{\varepsilon}'_\infty)\left(\frac{g_1}{1+i\omega\tau'_1} + \frac{g_2}{1+(i\omega\tau_1)^{1-\bar{\alpha}}}\right), \tag{6}$$

where

$$g_1 = (\bar{\varepsilon}'_{01} - \bar{\varepsilon}'_{02})/(\bar{\varepsilon}'_{01} - \bar{\varepsilon}'_\infty) \quad \text{and} \quad g_2 = \frac{\bar{\varepsilon}'_{02} - \bar{\varepsilon}'_\infty}{\bar{\varepsilon}'_{01} - \bar{\varepsilon}'_\infty}.$$

4. Discussion

The α parameter, accounting for the distribution of the relaxation times, has a relatively high value in the case of the isotropic phase of $\bar{7}$S5 (Table II). This means that there are many contributions to the dielectric increment connected with different molecular motions, namely:

(*i*) reorientation of the whole molecule about the short axes (η or ξ); (*ii*) rotation of the molecule around the long axis (ζ), and probably (*iii*) reorientation of the end heptyloxy group aboud the para-axis of the benzene ring. Previously, the latter molecular process has never been observed clearly in a liquid crystalline substance.

Assuming that $\bar{7}$S5 molecules are ellipsoidal in shape one can write the following expression for ε^* [12]:

$$\varepsilon^* = \varepsilon'_\infty + \frac{\Delta\varepsilon_1}{1+i\omega\tau_\eta} + \frac{\Delta\varepsilon_2}{1+i\omega\tau_\xi} + \frac{\Delta\varepsilon_3}{1+i\omega\tau_\zeta}, \tag{7}$$

which in the complex plane should give at least two different ($\tau_\eta \cong \tau_\xi$) semicircles. What we obtain from the experiment is a circular arc having a center much below the ε' axis (Fig. 8). This means that the system studied exhibits a broad distribution of relaxation times. According to formula (7) there should be at least two kinds of overlapped relaxation spectra. However, experimentally we can only get most probable relaxation time τ_0, which for the isotropic phase of $\bar{7}$S5 is of the order of 10^{-10} s (Table II).

One of the prime advantages of these studies is the wide temperature region of the nematic phase of $\bar{7}$S5, which allowed proper temperature dependences of both relaxation times to be obtained. Such studies have been performed lately [15] on mixtures of some nematic liquid crystals, but they only concerned low-frequency relaxation. Another thing is that these mixtures had a large positive dielectric anisotropy, in which case the low-frequency relaxation spectrum occurs in both principal directions of the nematic phase. The relaxation spectrum as a whole is much more complicated in the case of mixtures due to the presence of different types of molecules.

The shortening of τ_1 at the I—N transition point corroborates the assumption [9] that rotation around the long molecular axis is less hindered in the nematic phase of $\bar{7}$S5

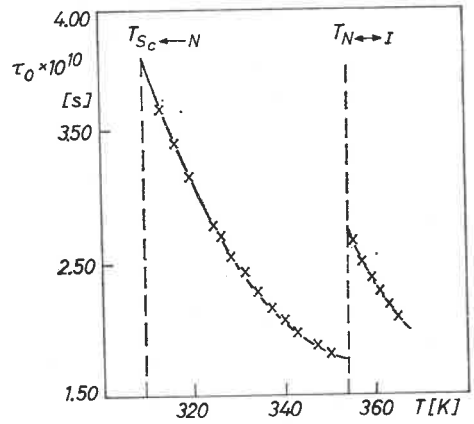

Fig. 10. Temperature dependence of the higth frequency relaxation time

than in the isotropic phase (Fig. 10). The slope of the straight line, as in Fig. 11, enables one to calculate the activation energy. Values of the activation energy connected with rotation around the short molecular axis have been found for the nematic phase $\Delta H_{\tau'_1}$, as well as the activation energy connected with rotation around the long molecular axis in the nematic phase $\Delta H^{N}_{\tau_1}$, in the supercooled nematic phase $\Delta H^{NS}_{\tau_1}$ and in the isotropic phase $\Delta H^{I}_{\tau_0}$. The activation energy values determined are presented in Table III. The calcula-

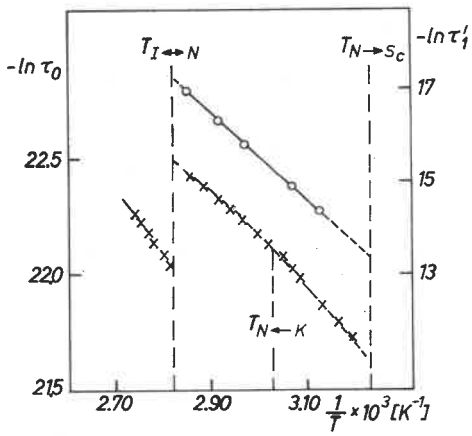

Fig. 11. Temperature dependence of τ_1' (open circles) and τ_0 (crosses)

tion error $\delta(\Delta H)$ is ± 0.5 kJ/mol in the microwave frequency range and ± 0.2 kJ/mol in the megahertz range. The coefficient of correlation R, which is a quality measure for matching the Arrhenius model to the temperature dependence of relaxation time, is near 1 (if $R = 1$, the fitting is perfect, if $R = 0$ no fitting occurs). The coefficient of correlation

TABLE III

The activation energy for the isotropic phase, nematic phase and for the supercooled nematic phase

Phase	ΔH (kJ/mol)	$\delta(\Delta H)$ (kJ/mol)	Coefficient of correlation R
Isotropic	$\Delta H^{I}_{\tau_0} = 26.1$	± 0.5	0.98
Nematic	$\Delta H^{N}_{\tau_1} = 13.1$	± 0.5	0.97
	$\Delta H_{\tau'} = 77.1$	± 0.2	0.99
Nematic supercooled	$\Delta H^{NS}_{\tau_1} = 20.0$	± 0.5	0.99

values near 1 are proof of good matching. The activation energy value for the supercooled nematic phase surpasses the one for the nematic phase $\Delta H^{NS}_{\tau_1} > \Delta H^{N}_{\tau_1}$ (Table III). The observed effect may perhaps be due to the existence of cybotactic groups in the supercooled nematic phase.

5. *Conclusions*

(*i*) The dielectric relaxation spectrum observed for the isotropic phase of $\bar{7}$S5 is greatly influenced by the molecular structure of elongated molecules;

(*ii*) The nematic phase of $\bar{7}$S5 possesses two well separated relaxation regions described

by a Debye-type model. The relaxation spectrum of this phase is affected by the anisotropic potential produced by the long-range orientational order.

(*iii*) The temperature dependence of the relaxation time τ_1 is stronger in the supercooled nematic phase than in its high temperature region. The effect is probably due to the existence of cybotactic groups in the pretransitional region.

REFERENCES

[1] W. Maier, G. Meier, *Z. Naturforsch* **16a**, 1200 (1961).

[2] W. H. de Jeu, Supplement to *Solid State Physics* **14**, 109–195; Liquid Crystals, Academic Press, New York, San Francisco, London 1978.

[3] X. P. Nguyen, S. Urban, S. Wróbel, H. Kresse, *Acta Phys. Pol.* **A54**, 617 (1979).

[4] H. Kresse, D. Demus, S. König, *Phys. Status Solidi* **K17**, 41a (1978).

[5] H. Kresse, D. Demus, A. Wiegeleben, *Phys. Status Solidi* **50a**, K181 (1978).

[6] L. Bata, G. Molnar, *Chem. Phys. Lett.* **33**, 535 (1975).

[7] S. Wróbel, J. A. Janik, J. K. Mościcki, S. Urban, *Acta Phys. Pol.* **A48**, 215 (1975).

[8] J. Mościcki, X. P. Nguyen, M. Rachwalska, S. Urban, S. Wróbel, J. A. Janik, *Mol. Cryst. Liq. Cryst.* **40**, 177 (1977).

[9] V. N. Tsvetkov, *Viestnik of Leningrad State University*, No 4, 26 (1970); *Kristallografiya* **14**, 681 (1968).

[10] A. Martin, W. Meier, A. Saupe, *Faraday Symposia*, No 5 (1971).

[11] J. P. Parneix, A. Chapoton, E. Constant, *J. Phys.* **36**, 1143 (1975).

[12] C. F. J. Böttcher, P. Bordewijk, *Theory of Electric Polarization*, Elservier Scientific Publishing Company, Amsterdam, Oxford, New York 1978.

[13] L. Richter, A. Wiegeleben, private information.

[14] J. Chruściel, L. Richter, M. Rachwalska, to be published in *Mol. Cryst. Liq. Cryst.*

[15] V. N. Tsvetkov, Y. I. Ryumtsev, S. G. Polushin, A. P. Kovshik, *Acta Phys. Pol.* **A56**, 871 (1979).