Molecular dynamics in the nematic, S_A and S_C phases of 8S5 and 9S5 as studied by dielectric methods

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Molecular dynamics in the nematic, S_A and S_C phases of $\bar{8}$S5 and $\bar{9}$S5 as studied by dielectric methods

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Two experimental techniques—time domain spectroscopy (TDS) and a steady state frequency method—have been used to study dielectric spectra for the isotropic, nematic, S_A, S_C and S_Y phases of two thioesters (4-n-pentylphenyl-4'-n-octyloxy- and 4'-n-nonyloxythiobenzoates ($C_nH_{2n+1}O$–C_6H_4–COS–C_6H_4–C_5H_{11}, where $n = 8$ and $n = 9$) known as $\bar{8}$S5 and $\bar{9}$S5, in the frequency range from 10 Hz to 10 GHz. In the case of $\bar{8}$S5 a deuteriated sample ($\bar{8}$S5-d_{28}) has been used to study relaxation processes in the nematic and smectic phases.

1. Introduction

One of the most interesting problems in the physics of liquid crystals is molecular dynamics studied by different techniques [1]. One of the dielectric relaxation methods involves measurements of the complex dielectric permittivity, $\varepsilon^* = \varepsilon' - i\varepsilon''$, as a function of frequency for polar compounds over a wide frequency range. The dielectric spectrum of the liquid crystalline phases of 4-n-pentylphenyl-4'-n-alkoxythiobenzoates ($\bar{n}$S5) have two dielectric absorption regions showing up in the radio and microwave frequency ranges [2–6]. The first one is connected with molecular reorientations around the short axis and the second with reorientations around the long axis. In this paper, we present new results of dielectric studies of $\bar{8}$S5 and $\bar{9}$S5, using the two experimental techniques—time domain spectroscopy (TDS) [7] and a steady state frequency method [8]—for the isotropic, nematic, smectic A, smectic C and smectic Y phases, in the frequency range from 10 Hz to 10 GHz. In the case of $\bar{8}$S5, a deuteriated sample ($\bar{8}$S5-d_{28}) has been used to study relaxation processes in the nematic and smectic phases.

2. Experimental

The substances under study have the following chemical formula

$$H_{2n+1}C_nO\text{–}C_6H_4\text{–}COS\text{–}C_6H_4\text{–}C_5H_{11}$$
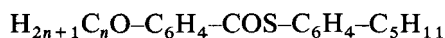
and $\bar{8}$S5 and $\bar{9}$S5 represent homologues with $n = 8$ and $n = 9$, respectively. The normal ($\bar{8}$S5 and $\bar{9}$S5) and chain deuteriated ($\bar{8}$S5-d_{28}) substances were synthesized in the

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Institute of Chemistry of the Agricultural and Pedagogical University at Siedlce (Poland) [9]. The thioesters contain two terminal groups, pentyl ($-C_5H_{11}$) and alkyloxy ($-OC_nH_{2n+1}$), connected to the benzene rings. Two groups in these molecules are polar: $-COS-$ and the alkyloxy-group, and they contribute to the net dipole moment. The phase sequences obtained by polarizing microscopy are the following:

	S_Y		S_C		S_A		N		I	Mpt
$\bar{8}$S5	●	(30°C)	●	(56°C)	●	63°C	●	86°C	●	58°C
$\bar{9}$S5	●	(38°C)	●	(60°C)	●	72°C	●	84°C	●	64°C

The transition temperatures obtained for the deuteriated $\bar{8}$S5 are about 1 to 3 K lower than those of the normal compound.

It is worth pointing out that non-symmetrical thioesters with longer alkoxy chains are of great interest as they exhibit highly ordered smectic phases (for example, S_J, S_B and S_G) [10, 11]. According to the X-ray results, the S_Y phase is identified as a highly ordered S_J phase [11].

The real and imaginary parts of the complex electric permittivity, $\varepsilon_i^* = \varepsilon_i - i\varepsilon_i''$ for $i = \parallel$ and $\perp$, have been measured in the frequency range from 10 Hz up to 10 MHz on thin samples of $\bar{8}$S5 and $\bar{9}$S5 aligned by means of a magnetic field of 1·2 T, using a steady state frequency method described elsewhere [8]. The complex electric permittivities were also measured in the frequency range between 10 MHz and 10 GHz by applying a TDS technique [7]. This enabled us to study the two main relaxation processes that occur in the liquid crystalline phases—one connected with molecular reorientation around the short axes of the molecules and the other connected with reorientation around the long axes of the molecules. Alignment of the smectic phases was obtained by very slow cooling of the nematic phase in the magnetic field. Accurate measurements of ε' and ε'' have been made for both principal directions for the N and S_A phases, and also for the S_C and S_Y phases parallel to the director (**n**) and perpendicular to it.

The dielectric spectra obtained experimentally were proposed by fitting the Cole–Cole formula

$$\varepsilon_i^* = \varepsilon_{i\infty} + \frac{\varepsilon_{i0} - \varepsilon_{i\infty}}{1 + (i\omega\tau_i)^{1-\alpha_i}} \tag{1}$$

where $i = \parallel$ and $\perp$ depending the geometry of the measurements, $\varepsilon_{i\infty}$ is the high frequency limit of permittivity, ε_{i0} is a static dielectric permittivity, τ_i is the relaxation time and α_i is a parameter describing the distribution of the relaxation times.

3. Results and discussion

Figure 1 presents the temperature dependence of the electric permittivities (ε_{is}, $\varepsilon_{\parallel}$ and $\varepsilon_{\perp}$) measured for $\bar{9}$S5 at 0·2 MHz for two orientations of the samples. For the parallel and the perpendicular orientations, the $\varepsilon_{\parallel}$ and $\varepsilon_{\perp}$ obtained correspond to the values of the static permittivities, $\varepsilon_{0\parallel}$ and $\varepsilon_{0\perp}$, for the nematic phase.

From the fact that the static dielectric permittivity $\varepsilon_{0\parallel}$ decreases at the N–S_A phase transition and also in the S_C phase, we conclude that the layer structure of the smectic phases involves the appearance of an antiparallel dipole–dipole correlation between neighbouring molecules, and consequently, this reduces the effective dipole moments and decreases $\varepsilon_{0\parallel}$. This effect was observed for $\bar{9}$S5 below the S_A–N transition [6]. Both substances exhibit a positive dielectric anisotropy, $\Delta\varepsilon' = \varepsilon_{\parallel}' - \varepsilon_{\perp}'$, in the nematic and
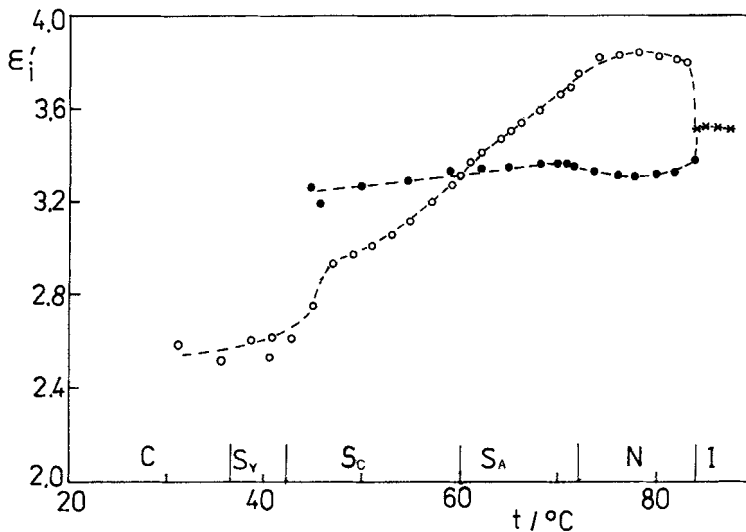
Figure 1. Dielectric permittivities (ε_{is} ($\times$), $\varepsilon_\parallel$ ($\bigcirc$) and $\varepsilon_\perp$ ($\bullet$)) *versus* temperature for $\overline{9}$S5.

Figure 2. Low frequency dielectric spectra obtained for $\overline{9}$S5 in its isotropic, nematic, smectic A and smectic C phases.

smectic phases. However, the anisotropy is distinctly reduced in the smectic phases due to the dipole–dipole correlations. Reduction of the absolute value of $|\Delta\varepsilon|$ with decreasing temperature is unexpected from the Maier and Saupe theory [12], which predicts that $|\Delta\varepsilon|$ increases with decreasing temperature ($\Delta\varepsilon \sim S/T$), where S is the order parameter and T is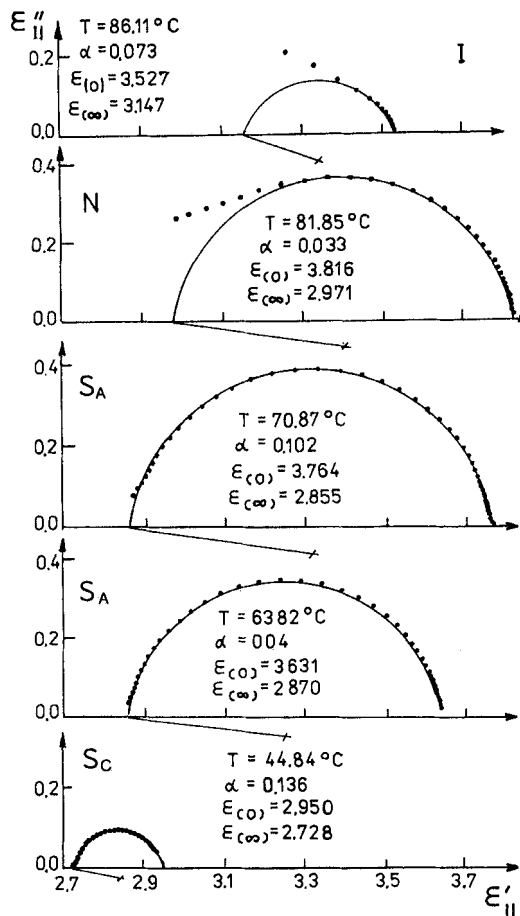 the temperature. One of the reasons for the $\varepsilon'_{\parallel}$ component decreasing with decreasing temperature is connected with the fact that reorientation about the short molecular axis becomes slower in smectic phases, as has been suggested before [13] in terms of the theory of Nordio–Rigatti and Segre [14].

Figure 2 shows the low frequency dielectric spectra for $\overline{9}$S5 in the nematic, smectic A and smectic C phases, and also the isotropic phase. The shape of the Cole–Cole plot shows that there is a large influence of the reorientation of the terminal alkoxy chains upon the dielectric spectrum of $\overline{9}$S5; this is also seen in QNS studies [15].

In figure 3 the relaxation times $\tau_{\parallel}$ are shown as a function of $1/T$ for low frequency relaxation processes in the I, N, S_A and S_C phases of $\overline{9}$S5. The values of $\tau_{\parallel}$ change over a wide range from $\tau_{\parallel} = 0.01 \times 10^{-6}$ s for the I phase to $\tau_{\parallel} = 2.5 \times 10^{-6}$ for the S_C phase (see table 1). There is a weak dielectric relaxation in the S_Y phase, which seems to be a highly ordered S_J phase [11]. On going from the liquid-like order in the layer of the S_C phase to the two dimensional order in the S_J phase, there is a large change in both the relaxation times and the dielectric increments. The same effect was observed for 4-*n*-pentyloxybenzylidene-4'-*n*-hexylaniline [16].

High frequency relaxation spectra in the form of Cole–Cole plots obtained for the I, N, S_A and S_C phases of $\overline{8}$S5-d_0 and $\overline{8}$S5-d_{28} are shown in figure 4. As is seen, the dielectric spectrum is complex, and for both substances is dominated by the reorientation of the molecules around their long axes. In the I, N and S_A phases, reorientation around the short axes gives a small contribution to the low frequency side. In the S_C phase, the reorientation does not depend on reorientation of the molecules around their short axes. The spectrum in the S_C phase results from two intermolecular processes: (*a*) non-homogeneous reorientation around the molecular
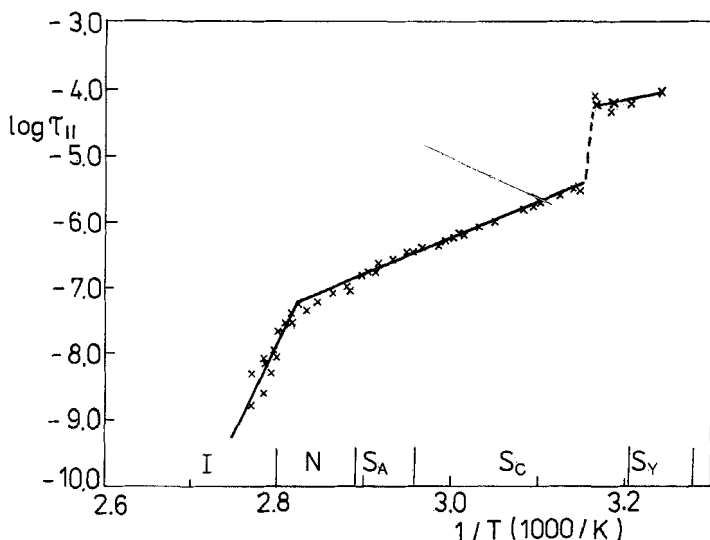

Figure 3.   Arrhenius plot for the low frequency processes observed for the I, N, S_A, S_C and S_Y phases of $\overline{9}$S5.

Table 1. Dielectric parameters $\tau_\parallel$, $\varepsilon_{\parallel 0}$, $\varepsilon_{\parallel \infty}$ and $\alpha_\parallel$ for the liquid-crystalline phases of $\overline{9}$S5.

	$T/°C$	$\tau_\parallel \times 10^{-6}$ s	$\alpha_\parallel$	$\varepsilon_{\parallel 0}$	$\varepsilon_{\parallel \infty}$
C	31·2	38·143	0·23	2·61	2·58
S_Y	38·6	64·693	0·43	2·69	2·58
S_C	40·8	48·020	0·40	2·69	2·60
	42·8	44·091	0·40	2·75	2·60
	44·8	3·428	0·14	2·95	2·73
	46·8	2·530	0·06	3·41	2·87
	48·9	1·944	0·05	3·49	2·87
	50·9	1·653	0·08	3·52	2·87
	52·8	1·356	0·01	3·52	2·88
	54·7	1·100	0·09	3·55	2·86
	56·8	0·883	0·06	3·56	2·87
	58·9	0·714	0·05	3·58	2·87
	59·8	0·644	0·05	3·59	2·87
S_A	60·9	0·570	0·02	3·60	2·88
	62·0	0·508	0·01	3·61	2·88
	63·8	0·423	0·04	3·63	2·87
	64·9	0·385	0·04	3·64	2·87
	65·8	0·348	0·04	3·65	2·87
	67·8	0·284	0·04	3·68	2·88
	69·9	0·222	0·04	3·72	2·88
	70·9	0·188	0·10	3·76	2·86
	71·7	0·166	0·02	3·79	2·91
N	73·8	0·100	0·10	3·85	2·89
	75·8	0·084	0·01	3·84	2·98
	77·9	0·066	0·02	3·85	3·00
	79·9	0·052	0·02	3·84	3·01
	81·9	0·038	0·03	3·82	2·97
	81·8	0·039	0·03	3·82	2·97
	82·7	0·034	0·04	3·77	2·97
I	83·7	0·027	0·04	3·77	2·99
	83·9	0·014	0·05	3·53	3·15
	84·7	0·013	0·08	3·53	3·13
	84·8	0·013	0·05	3·53	3·15
	85·8	0·013	0·07	3·53	3·18
	86·1	0·013	0·07	3·53	3·15
	87·2	0·008	0·13	3·53	3·06

long axis and (*b*) stochastic precession in relation to the 'director' [13]. The Cole–Cole diagram for the S_C phase shows that some contributions from the intramolecular processes are visible on the high frequency side. The reorientation around the long axis significantly slows down upon entering the S_C phase (from 164 ps in I to 241 ps in N and from 342 ps in S_A to 517 ps in S_C).

As shown in table 2, the relaxation times obtained for a deuteriated sample ($\overline{8}$S5-d_{28}) are longer, but there is no hint that the spectrum could be split into, for instance, two components. The difference in molar mass between the fully protonated sample ($\overline{8}$S5-d_0) and that with deuteriated terminal alkyl and alkoxy chains ($\overline{8}$S5-d_{28}) is 6·8 per cent, with reference to the undeuteriated sample. Moreover, the differences in the transition temperatures are probably due to the difference in polarizibility of the C–D
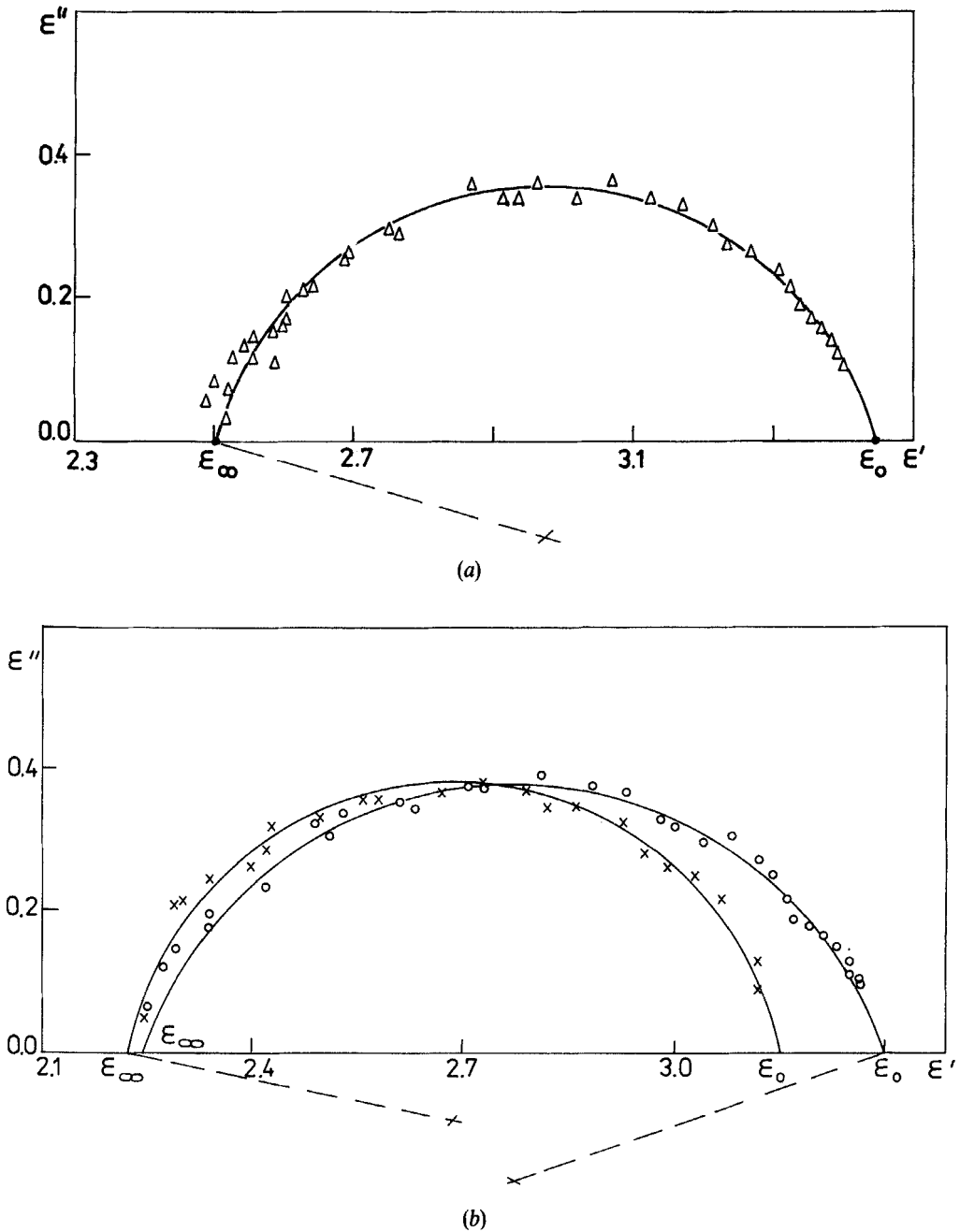
(a)

(b)

Figure 4.   High frequency dielectric spectra obtained for $\overline{8}$S5. (a) $\overline{8}$S5-d_0 in the S_C phase at 45°C with $\tau = 5{\cdot}2 \times 10^{-10}$ s and $\alpha = 0{\cdot}18$. (b) $\overline{8}$S5-d_{28} in the N phase at 77°C (○) with $\tau = 2{\cdot}1 \times 10^{-10}$ s and $\alpha = 0{\cdot}21$, and in the S_C phase at 42°C (×) with $\tau = 5{\cdot}5 \times 10^{-10}$ s and $\alpha = 0{\cdot}12$.

Table 2. Dielectric parameters ε_0, ε_∞, $\tau_\perp$ and α for $\overline{8}$S5-d_0 and $\overline{8}$S5-d_{28}.

$T/°C$	ε_0	ε_∞	$\tau_\perp/\mathrm{ps}$	α
89(I, -d_0)	3·38	2·42	164	0·21
86(I, -d_0)	3·42	2·42	178	0·23
86(I, -d_{28})	3·33	2·35	204	0·19
77(N, -d_{28})	3·30	2·24	209	0·21
72(N, -d_{28})	3·19	2·09	233	0·20
70(N, -d_0)	3·33	2·53	241	0·18
67(S_A, -d_{28})	3·17	2·15	265	0·17
58(S_A, -d_0)	3·36	2·53	342	0·21
56(S_A, d_{28})	3·16	2·19	385	0·15
45(S_C, -d_0)	3·45	2·50	517	0·18
42(S_C, -d_{28})	3·15	2·23	551	0·12
20(S_Y, -d_0)	2·43	2·43	No relaxation,	solid phase
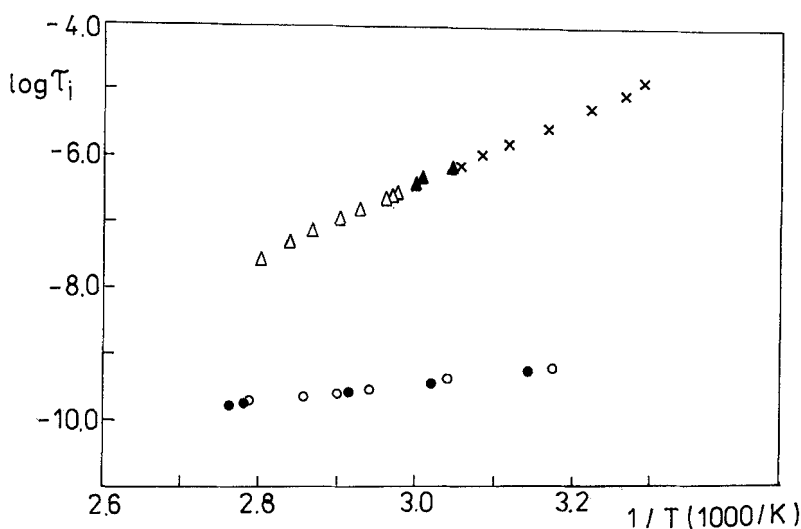
Figure 5. Arrhenius plot for the low and high frequency processes $\tau_\parallel$ for the nematic ($\triangle$), smectic A ($\blacktriangle$) and smectic C ($\times$) phases for $\overline{8}$S5 and $\tau_\perp$ for $\overline{8}$S5 ($\bullet$) and $\overline{8}$S5-d_{28} ($\bigcirc$).

and C–H bonds [17]. Similar effects, i.e. lower transition temperatures for the deuteriated compounds, have been observed for the homologous series of symmetrically substituted azoxybenzenes [18]. Generally, the differences in the mesomorphic properties of normals and deuteriated $\overline{8}$S5 do not play a significant role in the molecular reorientation in all the liquid-crystalline phases (see table 2).

Figure 5 shows the dependence of the relaxation times $\tau_\parallel$ and $\tau_\perp$ for the low and high frequency ranges (from 10 Hz to 10 GHz) for the liquid crystal phases of $\overline{8}$S5. The relaxation time $\tau_\parallel$, characterizing the molecular reorientation around the short axes, increases from the nematic to the S_C phase and exists in the highly ordered S_Y phase. The values of the relaxation times are in good agreement with those found by another dielectric method [19]. The reorientation around the long axes ($\tau_\perp$) does not show any changes at the phase transitions. The character of the molecular motions is therefore similar in the nematic and smectic phases in the high frequency range.

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