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Megahertz dielectric relaxation process in the nematic and smectic phases of two thiol esters ($\overline{9}$S5 and $\overline{10}$S5)

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We present the results of a dielectric investigation of two members of the 4-*n*-pentylphenyl-4′-*n*-alkyloxythiobenzoate ($\bar{n}$S5) homologous series with $n = 9$ ($\overline{9}$S5) and $n = 10$ ($\overline{10}$S5), in the frequency range 0·1–10 MHz, and in the temperature range covering all of the liquid crystal phases. Some properties of the $\bar{n}$S5 substances with $n = 5$ to 10 are discussed.

1. Introduction

Thiol esters belonging to the homologous series of 4-*n*-pentylphenyl-4′-*n*-alkyloxythiobenzoates ($\bar{n}$S5) have been the subject of systematic studies in our group for more than ten years. A few experimental methods have been applied; namely adiabatic [1] and differential scanning [2] calorimetry, dielectric relaxation [2–7] and quasielastic neutron scattering [8]. The substances with $n = 5$ and 6 have only a nematic phase [6], with $n = 7$ nematic and monotropic smectic C phases [3], with $n = 8$ nematic, S_A and monotropic S_C phases, whereas those with $n = 9$ and 10 have additionally a monotropic S_Y phase (see later).

The molecules of the $\bar{n}$S5 series possess a permanent electric dipole moment and so the dielectric methods can give information about the molecular reorientations around their principal inertial axes. Reorientation around the short axes fall in the MHz frequency range, whereas the reorientation around the long axes can be observed at GHz frequencies. Here we present the results of dielectric studies of $\overline{9}$S5 and $\overline{10}$S5 at kilo and megahertz frequencies. This allows us to explore how the molecular reorientation around the short axes depend on the molecular order in the different liquid-crystalline phases. Additionally, taking into consideration the results of dielectric studies of shorter members of the $\bar{n}$S5 homologous series ($n \geqslant 5$) the dynamic parameters characterizing molecular reorientation around the short axes (relaxation time, activation barrier, dielectric increment) are compared with the clearing temperatures which show a typical odd–even effect [9].

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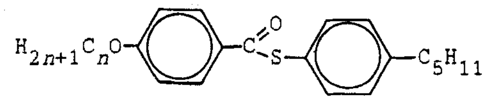
2. Experimental

The substances under study have the structure



where $\overline{9}$S5 and $\overline{10}$S5 correspond to $n=9$ and 10, respectively. They were synthesized in the Institute of Chemistry of the Agricultural and Pedagogical University at Siedlce, Poland, by the method described in [2]. Figure 1 presents the phase diagrams of both compounds, obtained with the use of a hot stage polarizing microscope. The symbols: I, N, S_A, S_C, S_Y and C stand for the isotropic, nematic, smectic A, smectic C, smectic Y [9] and polycrystalline phases, respectively.

The dielectric permittivity, ε', was measured at a single frequency of 0·1 MHz. Measurements of the dielectric loss, ε'', were carried out in the frequency range 0·1–10 MHz for the N, S_A, S_C and S_Y phases of both substances. The apparatus used is described elsewhere [3]. The accuracy of the ε' and ε'' measurements was about 2 per cent and 5 per cent, respectively. In order to obtain the proper alignment of the nematic phase a 0·6 T magnetic field was applied. Alignment of the smectic phases was attempted by very slow cooling of the nematic phase in the presence of the magnetic field. Although the degree of alignment was not checked afterwards, a good reproducibility of the results in the S_A and S_C phases indicates monodomains of similar quality. A similar procedure has been used in other studies of liquid crystals with smectic phases [10, 11].

3. Results and discussion

Figure 2 shows the temperature dependence of the permittivity ε' measured for both substances at 0·1 MHz for two orientations of the samples. For the perpendicular orientation the $\varepsilon'_\perp$ data obtained at this frequency correspond to the static $\varepsilon_{0\perp}$ values. In the case of parallel oriented samples, however, the same is true only for the nematic phase ($\varepsilon'_\parallel(0{\cdot}1\ \mathrm{MHz}) = \varepsilon_{0\parallel}$). In the smectic phases the corrections due to dispersion effects must be introduced to obtain a proper value of $\varepsilon_{0\parallel}$. This was done by taking into account the results of measurements of the dielectric losses $\varepsilon''_\parallel$ which are presented in figures 3 and 4 for $\overline{9}$S5 and $\overline{10}$S5, respectively. The experimental points are very well described by the Lorentz-type curves (the solid lines in figures 3 and 4) corresponding to the Debye formula

$$\varepsilon''_\parallel = (\varepsilon_{0\parallel} - \varepsilon_{\infty\parallel}) \frac{\omega\tau_\parallel}{1+(\omega\tau_\parallel)^2},$$

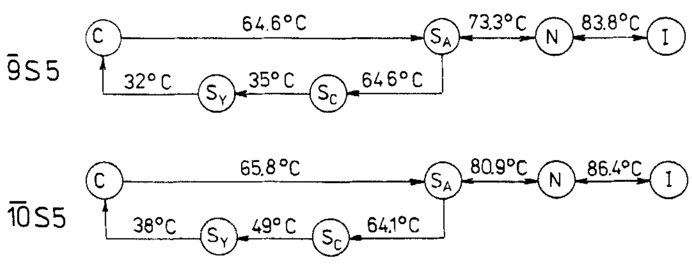


Figure 1. Phase transition temperatures for $\overline{9}$S5 and $\overline{10}$S5 as observed by polarising microscopy.

where $\tau_{\parallel}$ is the relaxation time, ω is the angular frequency and $\varepsilon_{0\parallel}$ and $\varepsilon_{\infty\parallel}$ are the static and high frequency permittivities, respectively. Two parameters were fitted to the points namely $\tau_{\parallel}$ and the dielectric increment $\delta_{\parallel} = \varepsilon_{0\parallel} - \varepsilon_{\infty\parallel}$. The values of the calculated parameters are listed in table 1. Taking $\delta_{\parallel}$, $\varepsilon'_{\parallel}(0{\cdot}1)$ and $\varepsilon''_{\parallel}(0{\cdot}1)$ at a given temperature and drawing the Cole–Cole semicircle with the radius equal to $\frac{1}{2}\delta_{\parallel}$ we can easily estimate the $\varepsilon_{0\parallel}$ value. In figure 2 a few $\varepsilon_{0\parallel}$ points obtained in this way are shown.

Looking at the temperature dependence of $\varepsilon_{0\parallel}$ we can conclude that even in the S_C phase the dielectric anisotropy, $\Delta\varepsilon_{\parallel} = \varepsilon_{0\parallel} - \varepsilon_{0\perp}$, remains positive. (The small negative

Table 1. Dielectric increments $\delta\varepsilon_{\parallel}$ and relaxation times $\tau_{\parallel}$ calculated from the dielectric loss spectra $\varepsilon''(\omega)$ obtained for liquid-crystalline phases of $\overline{9}$S5 and $\overline{10}$S5.

$\overline{9}$S5				$\overline{10}$S5			
T/°C	Phase	$\delta\varepsilon_{\parallel}$	$\tau_{\parallel} \times 10^7$/s	T/°C	Phase	$\delta\varepsilon_{\parallel}$	$\tau_{\parallel} \times 10^7$/s
81·5	N	0·535	0·98	85·0	N	0·534	1·01
76·4	N	0·618	1·79	84·0	N	0·560	1·15
72·0	S_A	0·594	3·96	81·9	N	0·585	1·64
68·0	S_A	0·561	5·68	78·2	S_A	0·565	3·73
65·3	S_A	0·531	7·96	72·1	S_A	0·489	6·79
63·2	S_C	0·513	9·67	66·9	S_A	0·470	11·39
58·8	S_C	0·502	16·25	62·3	S_C	0·457	20·55
				58·3	S_C	0·452	32·00
				43·5	S_Y	0·332	3583·00

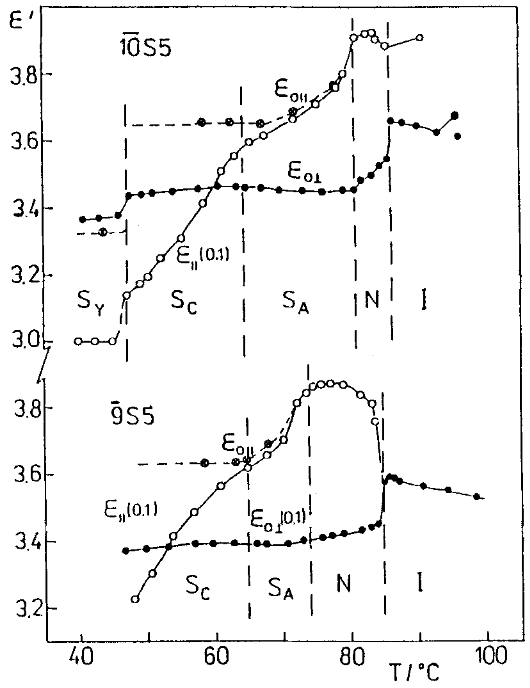


Figure 2. The temperature dependence of the permittivities $\varepsilon'_{\parallel}$ and $\varepsilon'_{\perp}$ for $\overline{9}$S5 and $\overline{10}$S5. $\varepsilon'_{\parallel}(0{\cdot}1)$ and $\varepsilon_{0\perp}$ were measured at 0·1 MHz. $\varepsilon_{0\parallel}$ was calculated taking into account the dispersion effect (see the text).

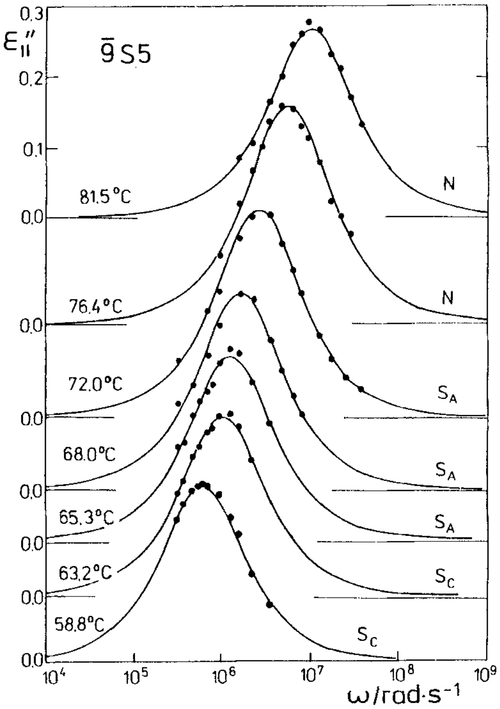


Figure 3. Dielectric losses $\varepsilon_{\parallel}''$ versus the angular frequency ω measured for the N, S_A and S_C phases of $\bar{9}$S5. The solid lines correspond to the Debye formula and were fitted to the points with the parameters listed in table 1.

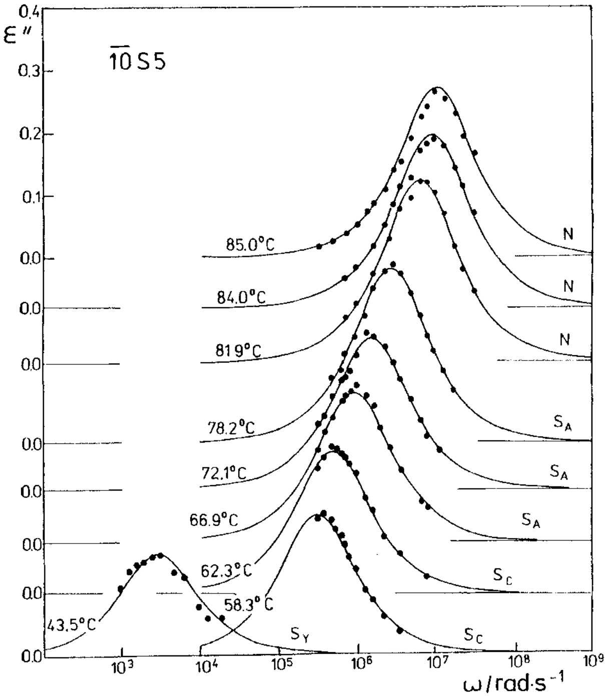


Figure 4. Dielectric losses $\varepsilon_{\parallel}''$ versus the angular frequency as measured for the N, S_A, S_C and S_Y phases of $\overline{10}$S5. The solid lines correspond to the Debye formula and were fitted to the points with the parameters listed in table 1.

$\Delta\varepsilon_{\parallel}$ in the S_Y phase of $\overline{10}$S5 is probably caused by a decrease of the sample alignment at the phase transition.) Nevertheless, a distinct discontinuous decrease of static permittivity, observed below the S_A–N transition, indicates that the layer structure of the smectic phases involves the appearance of an antiparallel dipole–dipole correlation between neighbouring molecules. This reduces the effective dipole moments and causes a decrease of $\varepsilon_{0\parallel}$. Such correlations become especially strong in the more ordered S_Y phase. Similar effects have been observed in other liquid crystals having the electric dipole moment positioned centrally in the molecules [12–14].

The relaxation time $\tau_{\parallel}$ characterizes the molecular reorientation around the short axes. Two main factors determine their values in the liquid-crystalline phases: the potential barrier caused by the neighbouring molecules and the moment of inertia of

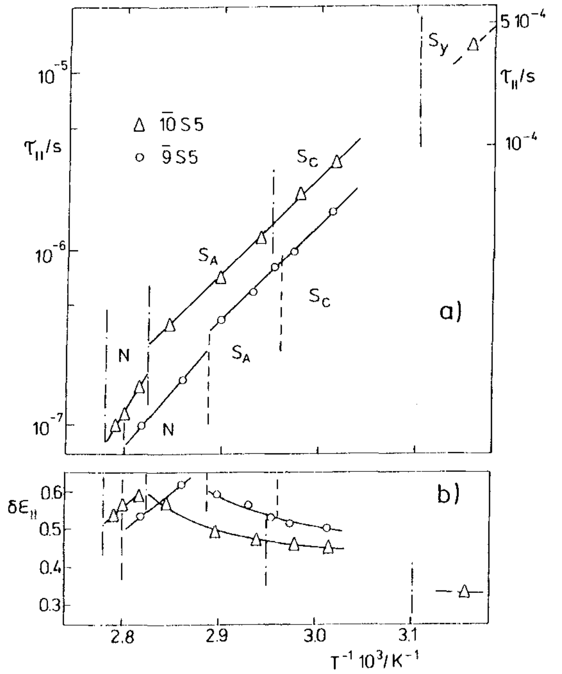


Figure 5. The relaxation time $\tau_{\parallel}$ (*a*) and the dielectric increment $\delta\varepsilon_{\parallel}$ (*b*) of $\overline{9}$S5 and $\overline{10}$S5 as a function of the reciprocal temperature.

Table 2. Activation enthalpy $\Delta H_{\parallel}$ obtained for the $\bar{n}$S5 homologous series.

	$\Delta H_{\parallel}/\mathrm{kJ\,mol^{-1}}$			
n	N	S_A	S_C	S_Y
5	77	—	—	—
6	74	—	—	—
7	78	—	†	—
8	92	92	110	—
9	122	103	103	†
10	168	106	106	†

† Could not be obtained due to rapid crystallization of the samples.

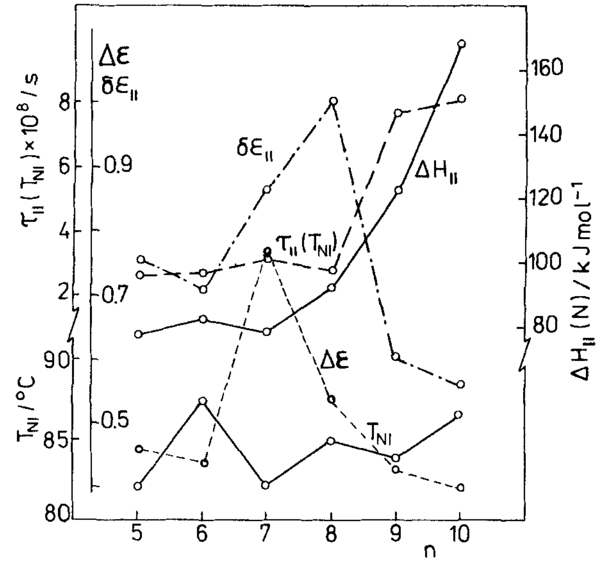


Figure 6. The nematic–isotropic transition temperature T_{NI}, relaxation time $\tau_{\parallel}$ taken at T_{NI}, activation enthalpy $\Delta H_{\parallel}$, dielectric anisotropy $\Delta\varepsilon$ and dielectric increment $\delta\varepsilon_{\parallel}$ taken at T_{NI} -4°C as a function of the number of carbon atoms in the alkyloxy chain of the $\bar{n}$S5 compounds (nematic phase).

the molecule with respect to the short axes. Therefore, we can expect that $\tau_{\parallel}$ should change at the phase transition between liquid-crystalline phases and should depend on the molecular length along a homologous series. Some examples of such behaviour have been discussed in [12] (phase transitions) and in [15–17] (homologous series). Here, we expect similar effects for the $\bar{n}$S5 homologous series. Figure 5(*a*) shows the Arrhenius plots for both substances over a broad temperature range covering all liquid-crystalline phases (for the monotropic S_Y phase we succeeded with the measurement of the relaxation spectrum only once because of rapid crystallization of the samples). The following facts should be noted.

(i) At the S_A–N transition the relaxation time increases by the factor $p=\tau_{\parallel}(S_A)/\tau_{\parallel}(N)=1{\cdot}3$ and $1{\cdot}4$ for $\bar{9}$S5 and 10S5, respectively. It is a characteristic feature of the substances with a narrow nematic range and is connected with pretransitional effects [12].

(ii) There is no change of $\tau_{\parallel}$ at the S_C–S_A transition.

(iii) A distinct increase of $\tau_{\parallel}$ at the S_Y–S_C transition is observed ($p \approx 20$). It results probably from a quasi-crystalline structure of the S_Y phase.

(iv) The activation enthalpy, $\Delta H_{\parallel}$, in the nematic phase is larger than in the smectic phases (see table 2) despite the existence of stronger dipole–dipole correlation in the smectic phase which is manifest in the reduction of the dielectric increments (see figure 5(*b*)).

Let us summarize the results of the studies of the low frequency relaxation process in the $\bar{n}$S5 series with *n* ranging from 5 to 10. Table 2 gathers the values of the activation enthalpy $\Delta H_{\parallel}$ (calculated with the aid of the Arrhenius equation) for the liquid-crystalline phases whereas figure 6 shows how some quantities obtained for the nematic phase (T, $\tau_{\parallel}$ at T_{NI}, $\delta\varepsilon_{\parallel}$ and $\Delta\varepsilon$ at $T_{NI}-4°$, and $\Delta H_{\parallel}$) depend on the number of carbon atoms in the alkyloxy group of $\bar{n}$S5 substances. On this basis we can state the following.

(i) The nematic–isotropic transition temperature T_{NI} shows an alternation (an odd–even effect) typical of many homologous series [12, 18]. According to the Marcelja theory [19] this effect is caused by a strong variation at T_{NI} of the order parameter which, in turn, is connected with the different shape of the end groups in a molecule when odd or even carbon atoms are attached.

(ii) The relaxation time $\tau_{\parallel}$ does not show a marked alternation for small n and it rapidly increases for the two highest homologues. For the 4,4′-di-n-alkyloxyazoxybenzene series the relaxation time exhibits a stronger alternation at T_{NI} as well as at $T_{NI}-10°C$ [15] with an amplitude opposite to the $T_{NI}(n)$ alternation ($1 \leqslant n \leqslant 7$). Similar behaviour was observed for other homologous series [17, 20].

(iii) The activation energy being almost constant for small n increases rapidly for larger n. For the 4,4′-di-n-alkyloxyazoxybenzene series $\Delta H_{\parallel}$ systematically increases with $n(4 \leqslant n \leqslant 9)$ [21], whereas for the cyanobiphenyls it remains constant [17]. However, for the biphenyl esters the values of $\Delta H_{\parallel}$ is constant for low n and increases for higher homologues exhibiting a smectic phase at lower temperatures [20] similar to the substances under study.

(iv) The dielectric increment $\delta\varepsilon_{\parallel}$ and the dielectric anisotropy $\Delta\varepsilon = \varepsilon_{\parallel} - \varepsilon_{\perp}$ taken at $T_{NI}-4°C$ behave rather astonishingly: it does not show any regularity with increasing n, contrary to some homologous series with the cyano end group where a continuous decrease of $\Delta\varepsilon$ with increasing chain length has been observed [16]. On the other hand for compounds with small positive dielectric anisotropy $\Delta\varepsilon$ exhibits an alternation similar to $T_{NI}(n)$ [12, 20, 22]. The values of $\delta\varepsilon_{\parallel}$ and $\Delta\varepsilon$ are determined by the projections of the net dipole moment of the molecule on the long, and the short, axes [23]. The molecules of the $\bar{n}$S5 series have two polar groups: –COS– and –OC_nH_{2n+1} giving $\mu \approx 2{\cdot}25$ D directed at about 50° to the long axis [24]. The group dipole moment calculations have shown that μ does not depend on the length of the alkyloxy group [25]. It seems reasonable to assume that $\delta\varepsilon_{\parallel}$ and $\Delta\varepsilon$ obtained for $n=5$ and 6 correspond to $\mu_l \approx 1{\cdot}5$ D and $\mu_t \approx 1{\cdot}7$ D resulting from the above data. Therefore, the large increase of the dielectric parameters observed for $n=7$ and 8 and then the decrease for $n=9$ and 10 against the reference value must be connected with the dipole–dipole correlations between neighbouring molecules in the nematic phase (parallel for $n=7$ and 8, and antiparallel for $n=9$ and 10). Two facts: small values of dipole moments of both polar groups and their localization in the different parts of the molecule allow us to conclude that these correlations have a steric origin rather than the real dipole–dipole interactions observed, for example, in many compounds with the cyano groups (e.g. [11, 26]).

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