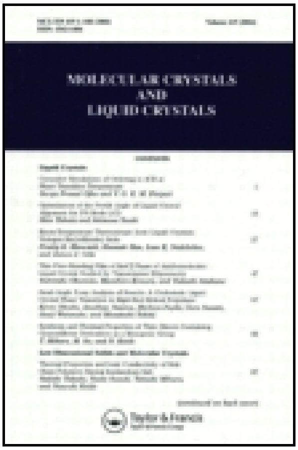

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Dielectric Studies of 4-n-Pentylphenyl-4-Octyloxythiobenzoate

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Dielectric Studies of 4-n-Pentylphenyl-4-Octyloxythiobenzoate†

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Measurements of the complex dielectric permittivity for the isotropic, nematic and smectic phases (S_A and S_C) of the 4-n-pentylphenyl-4-n-octyloxythiobenzoate ($\bar{8}S5$) have been performed in the radio frequency range and at one microwave frequency of 9.38 GHz. The dielectric anisotropy of $\bar{8}S5$ is positive in both the radio and microwave frequency regions. However, in the smectic C phase there is a change of sign of the dielectric anisotropy which might be connected with dipole-dipole correlations. The low frequency relaxation process exhibits a Debye-type behaviour in all liquid-crystalline phases. The temperature dependence of the dielectric relaxation time will be discussed in terms of the Arrhenius law.

I. INTRODUCTION

So far a number of liquid crystals has been studied by means of dielectric relaxation methods. In this paper we deal with one of the thiol esters, viz., 4-n-pentylphenyl-4-n-octyloxythiobenzoate $\bar{8}S5$, which possesses nematic and two smectic phases (S_A and S_C). Thiol esters have been synthetized quite recently[4,5] and are the subject of exten-

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sive X-ray investigations[6] as the higher members of this homologous series ($\overline{12}$S5 and $\overline{14}$S5) exhibit highly ordered smectic phases. The seventh member of the series ($\overline{7}$S5) has been studied in our group by means of calorimetric[3] and dielectric methods.[1,2]

The aim of this paper is to present some dielectric results obtained for $\overline{8}$S5 and compare them with those acquired for $\overline{7}$S5. The molecular structure of $\overline{8}$S5 is shown in Figure 8. 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 most striking feature of dielectric behaviour of liquid crystals is that the reorientation around the short molecular axis gives a Debye-type absorption in the radio frequency range, whereas fast rotation about the long axis contributes to the absorption at microwave frequencies which has a more complicated nature.[1,2] This paper is mainly devoted to the low-frequency relaxation process in the liquid crystalline phases of $\overline{8}$S5.

II. EXPERIMENTAL

The last step of the synthesis of $\overline{8}$S5 is shown in Figure 1. As is seen the final product was obtained by means of condensation (in the

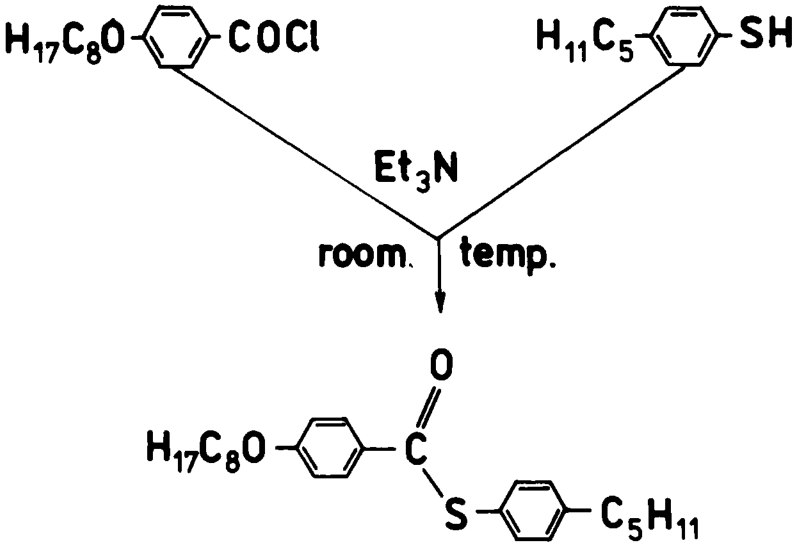

FIGURE 1 Schematic diagram of the synthetic route of $\overline{8}$S5.

presence of Et_3N) of octyloxybenzoic acid chloride and pentylthiophenol.[4] The substance was eventually recrystallized three times from absolute ethyl alcohol.

In Figures 2 and 3 the results of scanning calorimetry measurements are presented where the symbols: I, N, S_A, S_C and Cr stand for the isotropic, nematic, smectic A, smectic C and polycrystalline phases, respectively.

The dielectric permittivity (ϵ') was measured for the isotropic, nematic and smectic phases at one radio frequency of 0.1 MHz. Measurements of the dielectric loss ($\epsilon''_{\parallel}$) have been carried out in the radio frequency range (0.1 ÷ 10 MHz) for the nematic, S_A and S_C phases of $\bar{8}$S5. Additionally, ϵ^* was measured at one microwave frequency of 9.38 GHz (λ_0 = 3.2 cm). The low-frequency measurements were done by means of a standard method described elsewhere.[8] The accuracy of measurements of ϵ' and ϵ'' were about 2% and 5%, respectively. In order to attain the proper alignment of $\bar{8}$S5 nematic phase a 0.5 T magnetic field was applied. Orientation of the smectic phases was obtained by very slow cooling of the nematic phase in the

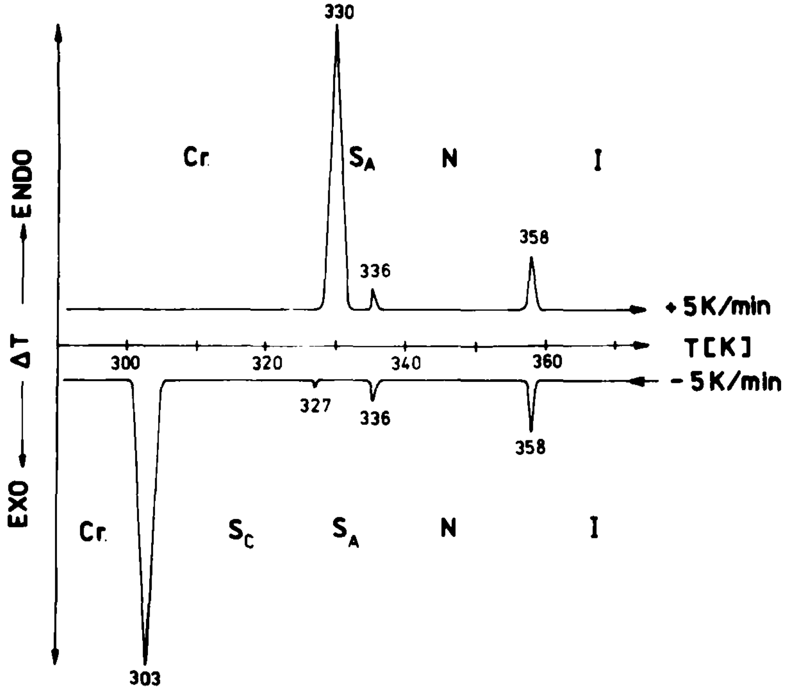

FIGURE 2 Results of the scanning calorimetry investigation of $\bar{8}$S5.

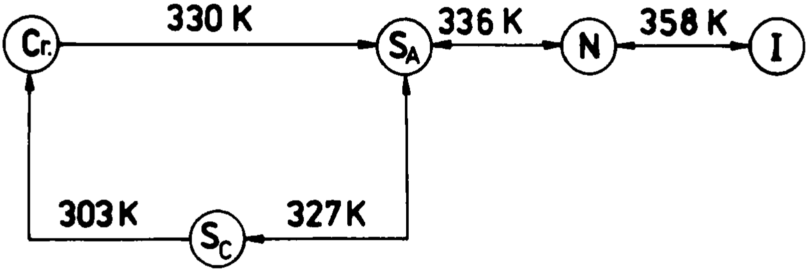

FIGURE 3 Phase diagram of $\bar{8}$S5.

presence of the magnetic field. Measurements at the microwave frequency were carried out by means of the standing wave method. The orientation conditions were the same as at low-frequency measurements.

III. RESULTS OF THE MEASUREMENTS

The dielectric results obtained at radio frequencies are presented in Figures 4 and 5. The static dielectric permittivities ($\epsilon_{\text{ois.}}$, $\epsilon'_{\parallel}$ and $\epsilon'_{\perp}$) were measured only at one frequency of 0.1 MHz. It was found that the dielectric anisotropy is positive at the radio frequency (Figure 4). However, there is a change of sign of $\Delta\epsilon$ in the S_C phase.

As is seen in Figure 5 all liquid crystalline phases of $\bar{8}$S5 exhibit the well known low-frequency absorption. The critical frequencies of the absorption curves depend strongly on temperature. Making use of the Debye equations:

$$\epsilon' = \epsilon'_{\infty} + \frac{\Delta\epsilon_{\parallel}}{1 + (\omega\tau'_{\parallel})^2} \tag{1a}$$

$$\epsilon'' = \frac{\Delta\epsilon_{\parallel}\omega\tau'_{\parallel}}{1 + (\omega\tau'_{\parallel})^2} \tag{1b}$$

Lorentzian curve fits to the experimental data have been done. In this way the dielectric increments $\Delta\epsilon_{\parallel}$ as well as the relaxation times $\tau'_{\parallel}$ were computed as functions of temperature. The results of measurements of ϵ' and ϵ'' at the microwave frequency of 9.38 GHz are presented in Figures 6 and 7, respectively. As one can see the dielectric anisotropy is positive in all liquid crystalline phases.

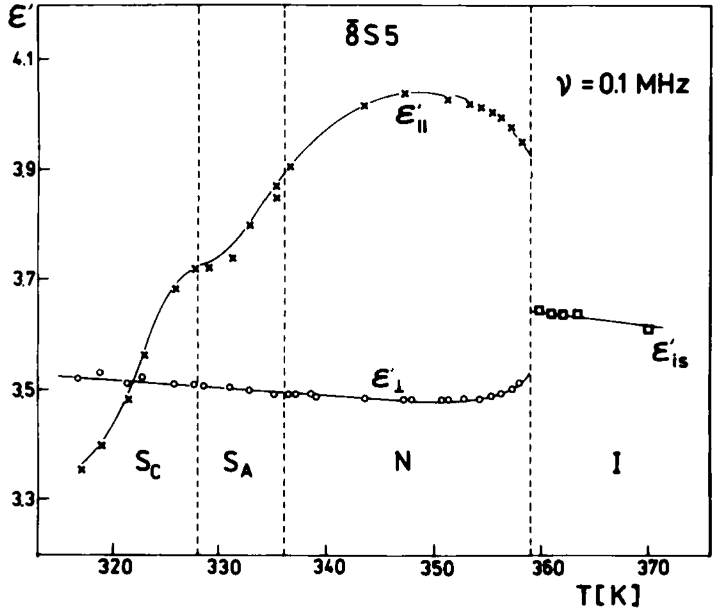

FIGURE 4 Temperature dependence of the dielectric permittivities measured at low frequency of 0.1 MHz.

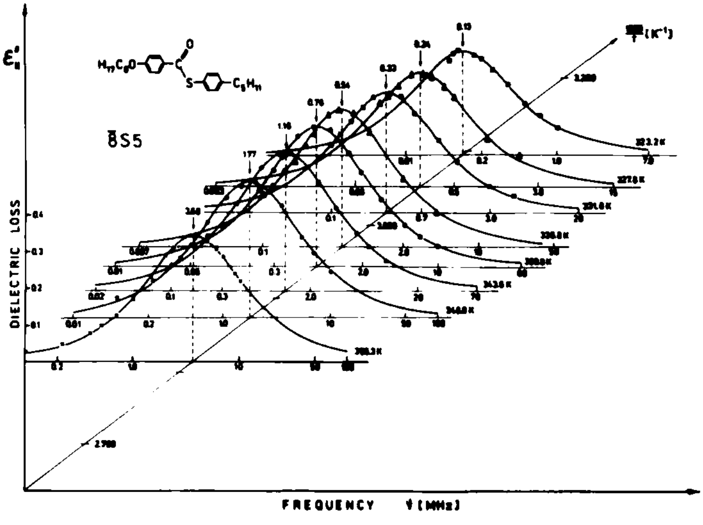

FIGURE 5 The dielectric loss ($\epsilon''_{\parallel}$) versus frequency acquired at different temperatures of the nematic, smectic A and smectic C phases of $\bar{8}$S5. Solid lines are Lorentzian curve fits.

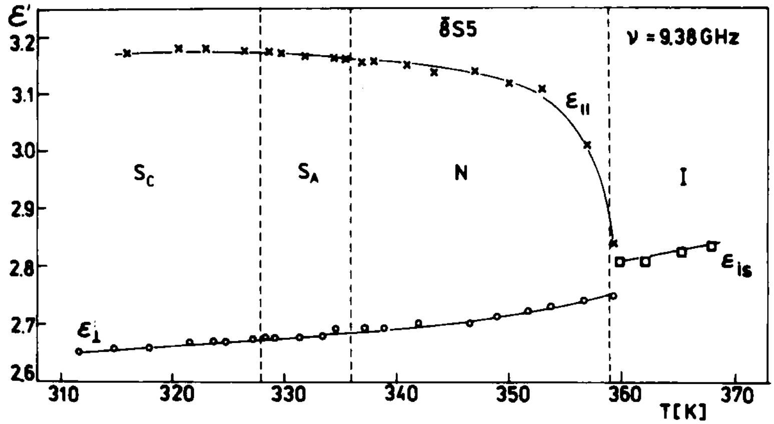

FIGURE 6 The dielectric permittivities as functions of temperature obtained for $\bar{8}$S5 at the microwave frequency of 9.38 GHz (3.2 cm).

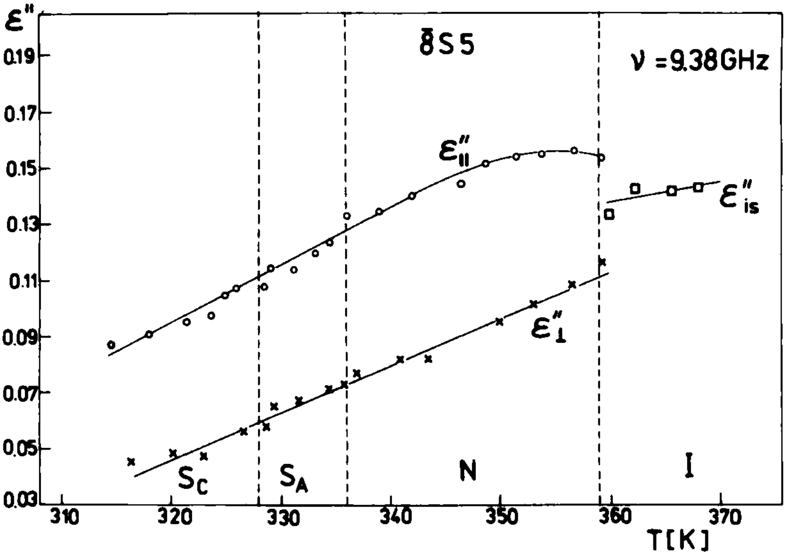

FIGURE 7 The dielectric loss factors versus temperature measured for $\bar{8}$S5 at the microwave frequency of 9.38 GHz.

IV. DISCUSSION

By fitting Debye-type absorption curves (Lorentzian) to the frequency dependences of $\epsilon''_\parallel$, acquired at different temperatures (Figure 5), the critical frequencies, f_c[MHz], indicated at the tops of the curves, have been obtained. Because the Lorentzian curves fit perfectly to the experimental data in all liquid crystalline phases of $\bar{8}$S5 one can conclude that the low frequency relaxation region can be characterized by a single relaxation time $\tau'_\parallel$, which is connected with the f_c frequency by the formulae: $\tau'_\parallel = (2\pi f_c)^{-1}$. The activation barriers calculated by means of the Arrhenius equation are about the same for both the nematic and smectic A phases ($\Delta E_{S_A} \cong \Delta E_N = 92$ kJ/mol). It means that one has in this case a smectic A_1 phase. It is a well known fact[1,2] that such a high value of the activation energy can be only connected with the end-over-end exchange of elongated molecules around the *S* axis of the molecular principal axes frame (Figure 8). This molecular process becomes more restricted in the S_C phase for the respective activation energy seems to be larger ($\Delta E_{S_C} = 110$ kJ/mol).

There is a strong variation of the relaxation times as well as activation energies within the thio-esters homologous series. The relaxation times discussed in this paper for $\bar{8}$S5 (table I) are longer than those obtained for $\bar{7}$S5.[1,2] In the case of the nematic phase of $\bar{7}$S5 the activation energy, connected with the reorientation around the short molecular axis, equals: $\Delta E_N = 77$ kJ/mol and it is distinctly lower than that obtained in this paper for $\bar{8}$S5.

Another important result of this study is that the dielectric anisotropy changes its sign in the smectic C phase of $\bar{8}$S5. A question

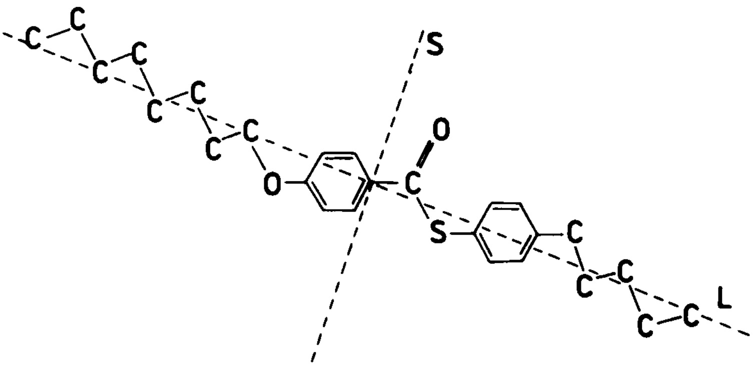

FIGURE 8 The principal axes frame for $\bar{8}$S5 molecule.

TABLE I

The relaxation time, $\tau'_{\parallel}$, acquired for $\bar{8}$S5 at different temperatures.

T[K]	354.2	346.7	342.2	338.2	335.2	330.2	325.2	322.2
$\tau'_{\parallel} \times 10^8$ [s]	4.1	8.0	13.3	20.9	28.4	46.1	66.3	109.8

may arise whether it is caused by the dipole-dipole correlations[7] and/or by the dispersion effect.[1,2] In the case of the monotropic smectic C phase of $\bar{7}$S5 the sign of $\Delta\epsilon$ also changes,[2] but we would rather interpret this effect as a result of slowing down of the molecular process in the S_C phase. To solve this problem one should study the frequency dependence of $\Delta\epsilon$ at low radio and acoustic frequencies.

Finally, the dielectric measurements at the microwave frequency (Figures 6 and 7) show very clearly that there is no dipole-dipole correlation leading to antiparallel alignment of the perpendicular components of molecular dipole moments in the S_C phase of $\bar{8}$S5. Measurements are being done for lower microwave frequencies. At the moment we can only say that the relaxation time connected with the rotation around the *L* axis (Figure 8) is of the order of 10^{-10} s.

V. CONCLUSIONS

1. The dielectric anisotropy is positive at the radio and microwave frequencies in the nematic and smectic A phases of $\bar{8}$S5.

2. In all phases the low-frequency relaxation is a Debye-type process characterized by a single relaxation time of the order of $\tau'_{\parallel} \sim 10^{-7}$ s.

3. The barriers to reorientation around the short axis are nearly the same in the nematic and smectic A phases ($\Delta E_N \cong \Delta E_{S_A} = 92$ kJ/mol). It means that we are dealing here with the smectic A_1 phase.

4. The estimated relaxation time connected with the rotation around the long molecular axis is of the order of 10^{-10} s for all phases studied.

Acknowledgments

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