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DIELECTRIC STUDY OF NPOB

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In the isotropic, nematic and smectic S_A phases of NPOB a dielectric relaxation phenomenon in the GHz frequency range has been observed. Results are compared with literature data. It is proposed that the mechanism of dielectric relaxation in liquid crystalline phases of NPOB is a superposition of reorientation of the molecules about the short axes, of the movement of the long molecular axes about the director and of reorientation about the long axes. These three processes are characterized by relaxation times of the order of 10^{-8} s, 10^{-9} s and 10^{-10} s respectively in both the smectic and nematic phases. In the smectic *A* phase an effect of the thermal pseudohysteresis has been observed.

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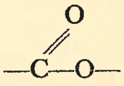
1. *Introduction*

The 4-nitrophenyl 4′-octyloxybenzoate (NPOB) under study is a liquid-crystalline compound with two mesomorphic phases: the smectic S_A phase and the nematic phase. The transition temperatures obtained by adiabatic calorimetry [4] are as follows:

	Solid *K*	↔	Smectic S_A	↔	Nematic *N*	↔	Isotropic *I*
T[K]:		323.70±0.03		334.92±0.3		341.23±0.49	

The structure of the NPOB molecule (Fig. 1) implies the existence of a permanent molecular dipole moment mainly due to the $C_8H_{17}O$-terminal group,  $-\overset{O}{\overset{\|}{C}}-O-$ central group and O_2N-second terminal group. The total dipole moment [1, 2] suggests a strong positive anisotropy of the static permittivity (Fig. 1). This has been confirmed experimentally [3, 9, 13]. The experimental value of the total electrical dipole moment

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of the NPOB molecule is approximately equal to 6.7 D, whereas the angle between the dipole vector and the axis of the highest polarisability of the molecule is about 14°.

The aim of the dielectric investigation performed in the GHz frequency range is to check whether fast molecular reorientations occur in all liquid phases of NPOB. Moreover, it is interesting to find out how the high frequency dispersion of a molecule with a large $\mu_{\|}$ component of the dipole moment supplements the dispersion corresponding to the reorientation of the molecules about their short axes examined earlier [9, 13, 7] in the MHz frequency range.

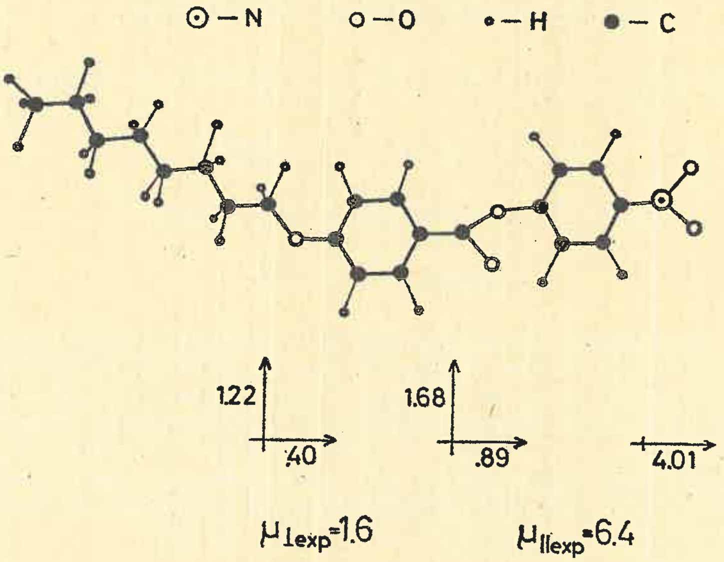

Fig. 1. NPOB molecular structure. Dipole moments in debyes

The dielectric measurements were performed on a non-oriented sample. This seems to have had little influence on the interpretation of the dielectric data from the GHz frequency range. Moreover, because of the large static dipole moment of NPOB molecules, it was rather difficult to obtain a well-oriented sample.

The NPOB samples for our investigations were synthesized in the Chemical Department of the Martin–Luther University in Halle (GDR) and used without further purification.

2. *Experimental*

Measurements of the complex permittivity $\varepsilon^* = \varepsilon' - i\varepsilon''$ were performed on non-oriented samples by the short circuit waveguide technique [14] at the following frequencies: 1.01, 1.19, 1.50, 3.02 GHz (coaxial wave-guide) and 9.81 GHz (rectangular wave-guide). The experimental errors of ε' and ε'' were less than 0.2 and 0.1 respectively. The temperature range covered all liquid phases and the high temperature part of the solid phase of NPOB. Sample temperature was stabilized to within an accuracy of ±0.3 K by means of a water thermostat and was measured with a platinium thermometer located right at the sample. The construction of the cryostat and of the sample vessels have been described elsewhere [14].

For each frequency, from 2 to 5 independent measurements were made, each of them on a new sample. The measurement vessel was filled with the sample at a temperature of 350 K (isotropic phase) and then was quickly cooled (at a rate of 5 K/min) to the solid phase, i.e. to 300 K. The ε^* measurements were performed both while the sample was being slowly heated and while it was slowly cooled. The temperature was stabilized every 3 K.

Reproduction of the ε'' values obtained during various experimental runs was very good. The ε' values were more varied but even so the discrepancies were smaller than the experimental error. Subsequent analysis employed the $\varepsilon'(T)$ and $\varepsilon''(T)$ curves which were closest to the average ones.

3. Results and discussion

3.1. Thermal effects

The temperature dependence of ε' and ε'' for the frequency of 1.01 GHz obtained during heating and cooling the sample is presented in Fig. 2. The temperature plots for all frequencies obtained while the sample was being heated are shown in Fig. 3. Transitions between different liquid phases are to be seen only in the ε'' vs. temperature curves. The ability of the smectic phase to become supercooled has been observed.

Interesting thermal pseudohysteresis in the smectic phase S_A has been observed. The ε'' values obtained from heating the sample are larger than those obtained while it was being cooled; in the $\varepsilon'(T)$ curves the effect is much weaker. The magnitude of this effect diminishes as the frequency of the measuring field increases. Substantial differences between the $\varepsilon''(T)$ curves obtained in successive heating processes have also been observed (Fig. 2): curve (1) corresponds to the heating process following quick cooling of the sample from the liquid phase, whereas curve (3) to heating after slow cooling. For successive cooling runs the ε'' values are always the same, regardless of what the thermal history of the sample has been. In the nematic and isotropic phases the differences between the ε' and ε'' values obtained while the sample was being heated and cooled are smaller than the experimental error.

A similar thermal pseudohysteretic effect was observed earlier for an externally unoriented sample in the smectic C phase of HOAB [15]. In this case the sign of the difference between the ε'' values was opposite to that observed in the smectic A phase of NPOB (see Fig. 2). As the dielectric loss depends on the ordering of the dipole liquid-crystalline molecules, it seems that an externally unoriented sample orients itself during the transition between the nematic and smectic phases. The difference between the pseudohysteretic effect for NPOB and HOAB is consistent with this hypothesis, for the substances have opposite anisotropies of the static permittivity [3, 9, 7, 15]. For a molecular system with positive anisotropy (such as NPOB) the dielectric loss in the GHz frequency range decreases as the degree of ordering of the molecules increases. For HOAB, with its negative

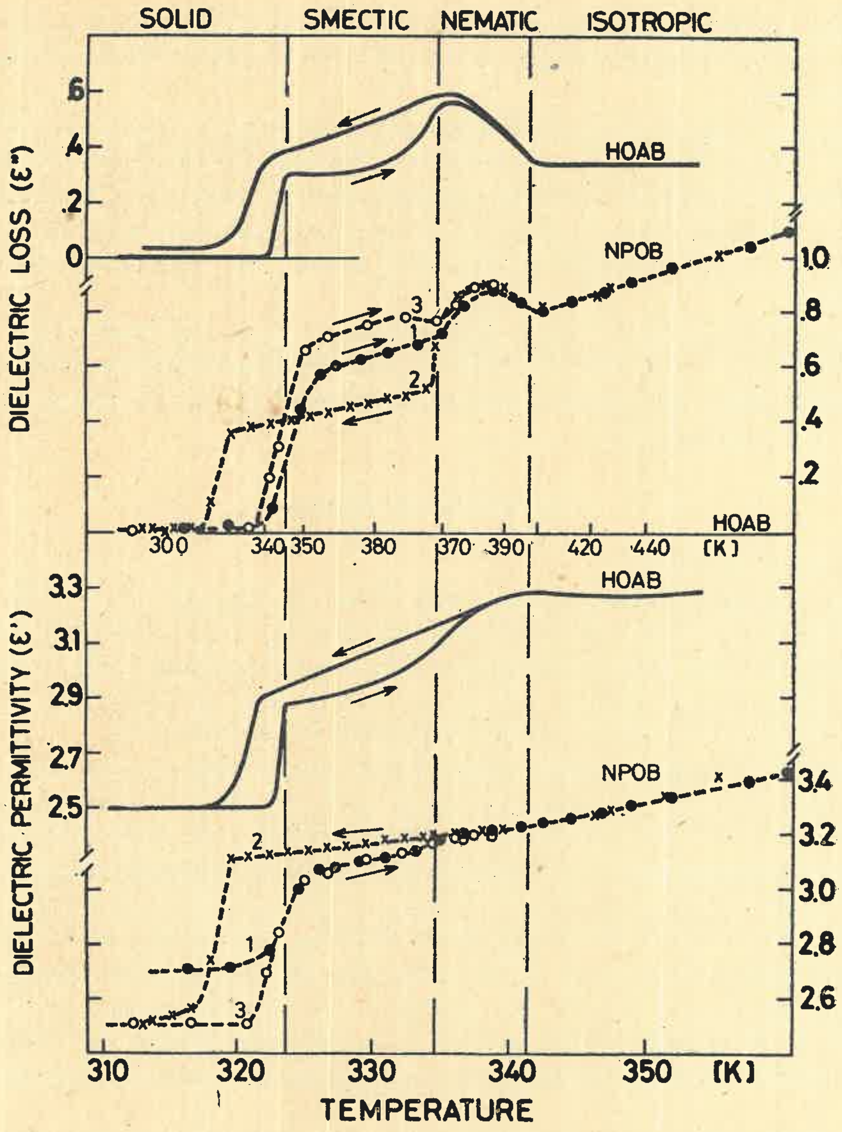

Fig. 2. ε' and ε'' vs T at 1 GHz. Dotted curves are for NPOB: 1 — during heating after fast freezing of the sample, 2 — during slow cooling, 3 — during heating after slow cooling. Solid curves are for HOAB

anisotropy, the behaviour of ε'' in the GHz frequency range should be the opposite. $\varepsilon''(T)$ suggests that the degree of arrangement of NPOB permanent dipole moments perpendicular to the coaxial vessel walls (i.e. parallel to the measuring field and temperature gradient in the sample as well) is larger in the S_A obtained by cooling the nematic phase than in S_A obtained by heating the solid phase. At the same time it was found by thermal microscopy [11] that the nematic phase of NPOB has a strong tendency to homeotropic orientation which remains in the smectic state. The explanation of the pseudohysteretic effect by the ordering action of the measuring fields is difficult to support on account of their small values (about 10 μV/cm). A detailed explanation of the mechanism of this effect, however, requires further studies. The difference between ε'' values obtained in successive heating processes (1 and 3) does not seem to be connected with thermal pseudohysteresis and can be explained as the result of the different texture of the solid phases antecedent to the respective smectic phases (corresponding to the curves 1 and 3).

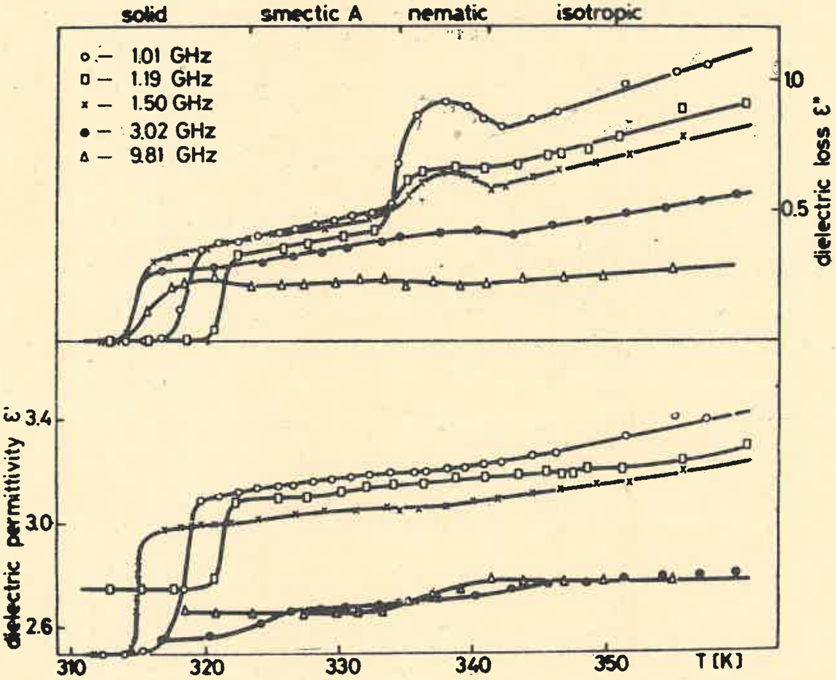

Fig. 3. Temperature dependence of ε' and ε'' in GHz range (during heating). The lack of a substantial discrepancy between the ε' values obtained at the two highest frequencies is probably due to a systematic error caused by the different geometries of the measurement on the coaxial and rectangular wave-guides

In the nematic phase of NPOB an anomalous behaviour of the ε'' has been observed (Fig. 2). There are no corresponding anomalous changes of ε'. It seems that the ε'' anomaly may be caused by the near-transitional effects superposing the dielectric relaxation phenomenon.

3.2. Dielectric relaxation

In the GHz frequency range examined a pronounced dielectric dispersion is observed (Fig. 3). In Fig. 4 the results presented above (points) and those of earlier MHz studies[1] [9] (crosses) are ploted on a complex (ε', ε'') plane. The dielectric dispersion for NPOB pre-

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[1] In fact the MHz investigations of NPOB [9] have been made on oriented samples. We use these results after averaging them to the case of an unoriented sample.

sented by means of Cole–Cole diagrams shows that the relaxation process for all phases studied is rather complex. For an unoriented sample the total dielectric dispersion in the nematic phase seems to be the superposition of three parts produced by:

(1) — reorientation of the molecules about the short molecular axes,
(2) — movement of the long molecular axes about the director and
(3) — reorientation of the $\mu_\perp$ component of the NPOB dipole moment [8, 9, 1].

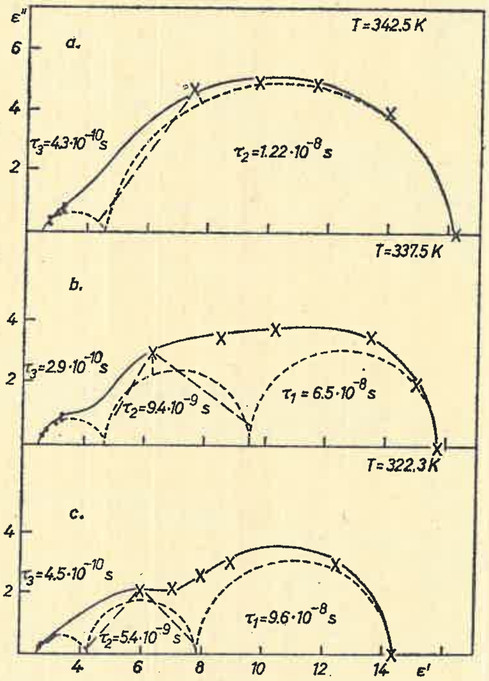

Fig. 4. Representative Cole–Cole plots for isotropic (a), nematic (b) and smectic S_A (c) phases: ● — present data, x — data from 0.05 MHz to 25 MHz [9]. The figures show the shape of the resulting relaxation spectrum together with component Cole–Cole arcs. The example of decomposition procedure is given: points of an equal frequency on arcs and their sum, the experimental points of identical frequency are joined with dashed lines

Consequently, the Cole–Cole equation [16] for the case of an unoriented liquid-crystalline sample would take the form:

$$\varepsilon^* - \varepsilon_{\infty 3} = \sum_{i=1}^{3} \Delta_i / [1 + (j\omega\tau_i)^{1-\alpha_i}],$$

where index i denotes the type of the relaxation mechanism mentioned above, $\Delta_i = \varepsilon_{0i} - \varepsilon_{\infty i}$ is the so-called dielectric increment and ε_0 and ε_∞ have their conventional meaning for each of the three dispersion regions. τ_i and α_i denote relaxation time and the so-called Cole–Cole parameter describing the distribution of the relaxation times for each of the mechanisms.

TABLE

Dielectric relaxation time τ and dielectric increments Δ for three dispersion regions of NPOB

Phase T [K]	Dielectric relaxation time τ [10^{10} s]			Dielectric increment Δ^a							
				Δ_1		Δ_2			Δ_3		
	τ_1	τ_2	τ_3	*A*	*B*	*B*	*C*	*D*	*B*	*C*	*D*
isotropic 342.5		122	4.3 ($\alpha_3 = 0.35$)			11.7		12.5	2.0		1.1
nematic 337.5 $S = 0.35$ [10]	650	94	2.9 ($\alpha_3 = 0.21$)	6.2	6.5	4.9	4.9 ($x_2 = 1.5$)	5.8 ($x_2 = 0$)	2.0	1.6 ($x_2 = 1.5$)	0.8 ($x_2 = 0$)
smectic 322.3 $S = 0.57$	960	54	4.5 ($\alpha_3 = 0.25$)	6.6	6.5	3.5	3.4 ($x_2 = 1.6$)	4.2 ($x_2 = 0$)	1.7	1.8 ($x_2 = 1.6$)	0.8 ($x_2 = 0$)

[a] from: fit to the experimental data from 0.05 MHz to 25 MHz [9] (*A*), Cole–Cole fit (*B*), Tsvetkov's method (with different x_2 value) (*C*), (*D*).

The above formula has been fitted to the experimental data from both the GHz and MHz frequency ranges [9] by the least-squares method [17] not only in the nematic but also in the smectic and isotropic ($i = 2, 3$) phases. The results of that fit, i.e. Δ_i, τ_i, and α_i for representative temperatures of the isotropic, nematic and smectic phases are collected in Table I. Fits are presented on the (ε', ε'') plane in Fig. 4. The singled out Cole–Cole arcs corresponding to the relaxational processes already mentioned are also given.

For the present case of an unoriented sample the Δ_i values for the mechanisms denoted by (1), (2) and (3) are proportional, respectively, to the following formulas [1, 5, 8, 9]

(1) $\frac{1}{3}\mu_{\parallel}^2(1+2S)$,

(2) $\frac{2}{3}\mu_{\parallel}^2(1-S)$,

(3) $\mu_{\perp}^2$.

The values of Δ_1 calculated from earlier MHz experimental data [9] and Δ_2 and Δ_3 estimated using the above formulas (2) and (3) are presented in Table I. In Tsvetkov's model [9] formula (1) is corrected by the factor $(1+X_1)$ and formula (3) by the factor $(1+X_2)$ to account for the anisotropy of the hindered molecular rotation (1) and (3) respectively. The application of $X_2 \neq 0$ improves agreement with Cole–Cole fits (Table I) but it should be mentioned that the physical meaning of Tsvetkov parameters does not seem to be clear enough.

The amount of experimental data which could be taken into account in our separation procedure was small. Hence, the results actually give a qualitative picture of the dynamical behaviour of the NPOB molecules in liquid phases. The dielectric relaxation time τ for all liquid phases presented in Table I are estimated to within an error of about 30%. Our τ_1 value for the slowest relaxation process differs by about 50% from values accepted in literature [13].

Despite the structural differences between smectic and nematic phases the dynamics of the NPOB molecules seems to be similar in both (Fig. 4b, c). The process of reorientation about the short axes is of the Debye type and has almost identical τ_1 and dielectric increment Δ_1, in both phases. The next type of dispersion due to the reorientation of the long molecular axis about the director has τ_2 values of the same order of magnitude in both phases but the dielectric increment Δ_2 is smaller in the smectic than in the nematic phase. This behaviour is in agreement with theory: the dielectric increment Δ_2 grows with the decreasing S parameter. Also in good agreement with theory is the fact that the values of the dielectric increment Δ_3 connected with the third process (i.e. with reorientation of $\mu_{\perp}$) are much smaller than the first two. This process, which occurs in all liquid phases, is not of the Debye type and has nearly the same τ_3 values and a constant dielectric increments Δ_3 independent of the S parameter in all phases.

In the liquid phase of NPOB (Fig. 4a) we can note an apparent existence of two dispersion regions to be associated with isotropic reorientation of long molecular axes i.e. with the reorientation of $\mu_{\parallel}$ and rotation about the long molecular axes i.e. reorientation of $\mu_{\perp}$. In the nematic phase two dielectric relaxation regions connected with $\mu_{\parallel}$ motion are due to the nematic potential. In comparison with the isotropic phase the region denoted by (1) is shifted to lower and the region denoted by (2) to higher frequencies (Fig. 4a, b). (In the smectic phase (Fig. 6c) these shifts seems to be larger.) The singling out of these two regions allows us to estimate the retardation factors $g_{\parallel}$ and $g_{\perp}$ defined as

$$g_{\parallel} = \frac{\tau_{1\ \mathrm{nematic}}}{\tau_{2\ \mathrm{isotropic}}}, \quad g_{\perp} = \frac{\tau_{2\ \mathrm{nematic}}}{\tau_{2\ \mathrm{isotropic}}}.$$

The values of $g_{\parallel}$ and $g_{\perp}$ for the nematic phase of NPOB are 5.33 and 0.77 respectively which is quite reasonable in comparison to the theoretical values accepted in literature [6]. The nematic potential for NPOB leading to these $g_{\parallel}$ and $g_{\perp}$ factors is not higher than 10 kJ/mole.

We are especially interested in the relaxation phenomenon connected with the reorientation of $\mu_{\perp}$. The effective relaxation time τ_3 for this process is of the order of 10^{-10} s in all phases. It is longer than for PAA (τ_3 (403 K) $= 2 \cdot 10^{-11}$ s) but similar to the values for MBBA (τ_3 (305 K) $= 1.5 \cdot 10^{-10}$ s) and HOAB (τ_3 (308 K) $= 1.1 \cdot 10^{-10}$ s).

The ε^* behaviour in the temperature near the melting point, i.e. $\varepsilon'' \approx 0$, and the abrupt fall of ε' (Fig. 4) indicate the freezing of the three rotational motions mentioned above. The disagreement between $\varepsilon_{\infty 3} \approx 2.6$ (Fig. 4) and $n^2 = 2.4$ [7, 10] (n — refractive index) does not rule out another higher frequency molecular movement. For example a ^{13}C-NMR study [12] of the so-called shift-tensor anisotropy for various C positions in the NPOB molecule in the smectic *A* phase shows that the last three segments of the tails reorient faster than the segments which are close to the body and seem to be coupled with it. There also is some evidence that reorientations of the molecular chain are independent of the movement of the molecular body in other liquid crystalline compounds [18, 19].

4. *Conclusions*

The electric permittivity results from GHz together with former data from the MHz frequency range give the full spectrum of dielectric relaxation in liquid phases of NPOB. The decomposition of the spectrum into three parts associated with the following processes: reorientation of the molecules about the short axes, the movement of the long axes about the director, and reorientation of the molecules about the long axes seems to be reasonable. The three processes are characterized by relaxation times of the order of 10^{-8} s, 10^{-9} s and 10^{-10} s respectively. For each process the relaxation time does not change much with the nematic-smectic phase transition. In the isotropic phase only two dispersion regions connected with reorientations of the $\mu_{\parallel}$ and $\mu_{\perp}$ of the molecule are observed.

In the smectic *A* phase of NPOB an effect of thermal pseudohysteresis has been observed. It seems to be related to the self-orientation of the sample during the transition from the nematic to smectic phase.

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