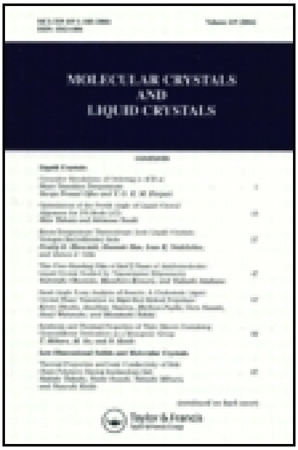

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Dielectric Relaxation in Nematic and Isotropic Phases of p-Azoxyphenetole (PAP)

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Dielectric Relaxation in Nematic and Isotropic Phases of p-Azoxyphenetole (PAP)

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Dielectric relaxation studies of the isotropic and nematic phases of 4,4′-n-diethoxyazoxybenzene (PAP) have been carried out in the radio and microwave frequency ranges. In the nematic phase two substantially different relaxation processes, with relaxation times $\tau_\parallel \sim 10^{-8}$ sec and $\tau_\perp \sim 10^{-11}$ sec, have been detected. They are connected with the reorientational motions of molecules around their short and long axes, respectively. The dielectric permittivity extrapolated to very high frequencies is markedly greater than the squared refractive index. This indicates that there might be additional relaxation process in the infra-red region. The relaxation spectrum of the isotropic phase is broad and the most probable relaxation time $\tau_0 = 2 \cdot 10^{-11}$ sec.

I. INTRODUCTION

The dielectric properties of 4,4′-*n*-diethoxyazoxybenzene (p-azoxyphenetole—PAP) had been investigated earlier by Jeżewski,[1] who found that the dielectric anisotropy at the radio frequency of 1.2 MHz was negative. Carr and Spence[2] measured the dielectric anisotropy at one microwave frequency (15.3 GHz) and it came out to be positive.

Dielectric relaxation spectra of the isotropic and liquid-crystalline phases for some members of PAA's homologous series,

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$$H_{2n+1}C_n—O—C_6H_4—N_2O—C_6H_4—O—C_nH_{2n+1},$$

have been studied extensively in the radio and microwave frequencies.[4–9] All of investigated substances ($n = 1$ (PAA), $n = 4$, $n = 6$, $n = 7$ (HOAB)) exhibit a broad relaxation spectrum in the isotropic phase characterized by the average relaxation time $\tau_{is} \sim 10^{-11}$ sec. On the other hand, the relaxation spectra of the nematic phase (and also smectic phases)[5,9] are split into two relaxation regions, the low- and high-frequency one, connected with reorientations of molecules around two principal axes: the short and the long one, respectively. As far as the low-frequency spectrum is a Debye-type process the high-frequency one exhibits distribution of the relaxation times and can be described by the Cole-Cole type formula. The complexity of the high-frequency relaxation process is strongly related to the electric structure of 4,4′-*n*-alkoxyazoxybenzenes molecules. In this case, the net dipole moment has contributions from three group dipole moments (N_2O and $-OC_nH_{2n+1}$) and it may vary due to conformational changes inside the molecule.[7,12]

If a substance has a simple electric structure of the molecule (for instance, cyanobiphenyls have a dipole moment parallel to the long molecular axis) one can easily apply Martin-Meier-Saupe theory[6] to interpret the relaxation spectra observed.[10–12] Nevertheless, this theory cannot be used for quantitative interpretation of the relaxation spectra of the alkoxyazoxybenzenes. It is due to the fact that the relaxation times, connected with the two principal molecular processes are unknown in the isotropic phase. In such a case further experimental investigations might give some hints for theoretical works. For example, there is scarce information on the temperature behavior of the high-frequency relaxation spectrum. Such investigations can be performed for substances with a wide temperature range of the nematic phase. PAP is a substance which fulfils our requirements; its nematic phase covers 31 K from 410.5 to 441.6 K.

II. RESULTS AND DISCUSSION

The dielectric properties of PAP were studied in two frequency ranges, *viz.*, 0.1 to 12.5 MHz (radio frequencies—r.f.), and for 1.99, 5.72 and 9.73 GHz (microwave frequencies—m.f.). Measurements of the complex permittivity, $\varepsilon^* = \varepsilon' - i\varepsilon''$, in the m.f. range were carried out by the standing wave technique, and in the r.f. range by a bridge technique. For the nematic phase the measurements in the r.f. range and at one gigahertz frequency (9.73 GHz) were performed on the samples oriented by means of magnetic field of 0.4 T, and the two principial components: $\varepsilon_{\parallel}^*$ ($E \mathbin{/\!/} B$)

and $\varepsilon_{\perp}^{*}$ ($E \perp B$) of the dielectric permittivity tensor have been obtained. Additionally, for all microwave frequencies the permittivity ε' and losses ε'' were measured without orientation of the sample. The temperature was changed from 410 K to 450 K, i.e., it covered the nematic phase and only a few degrees of the isotropic phase. The temperature stabilization was better than 0.5 K.

The results of measurements are presented in Figures 1–5, together with the earlier data obtained by Carr and Spence for 15.3 GHz.[2] All relaxation

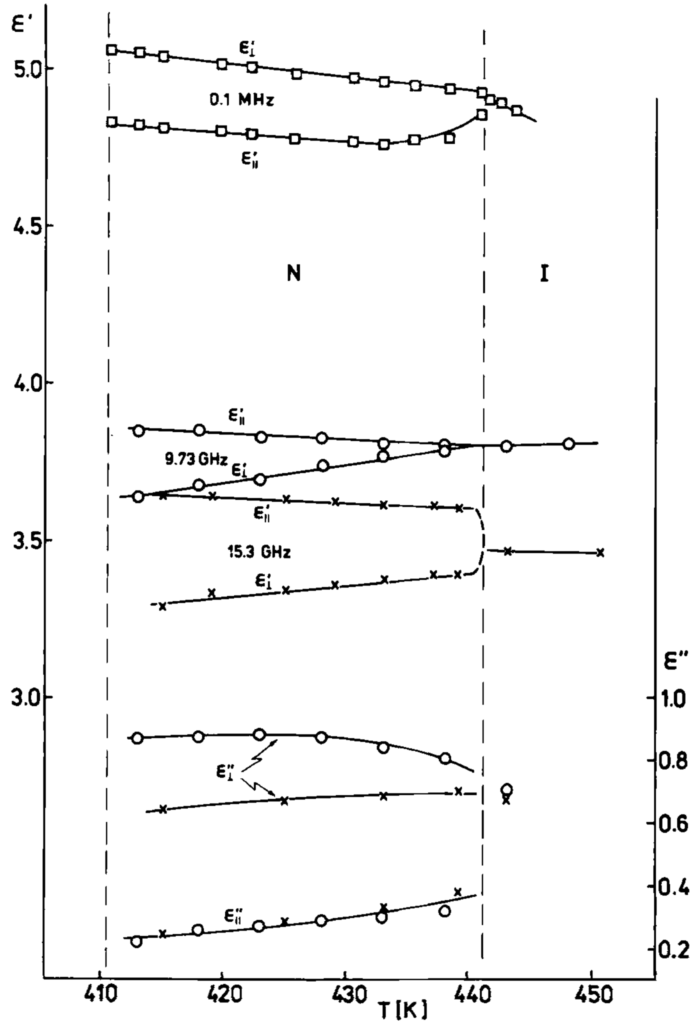

FIGURE 1 Components of the dielectric permittivity tensor measured in the megahertz and gigahertz frequency ranges.

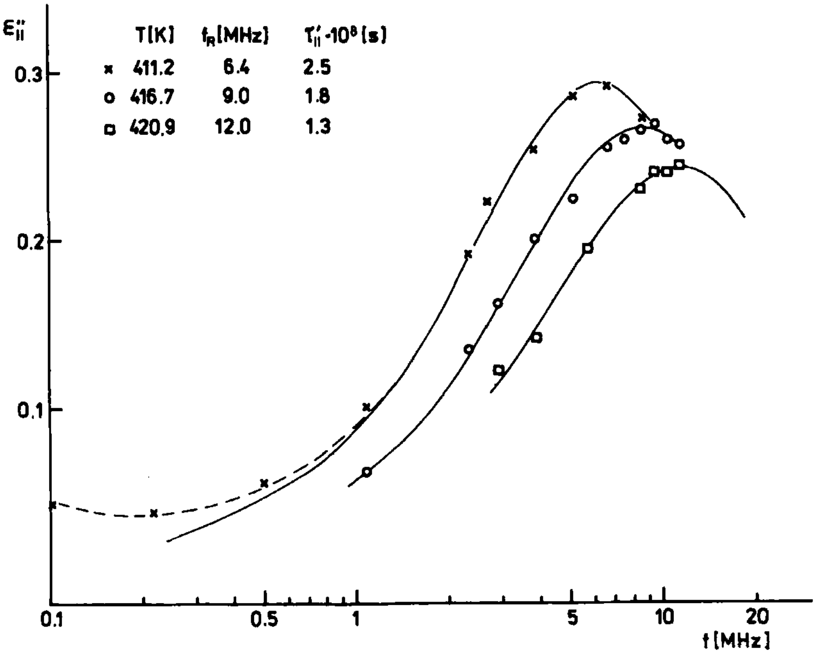

FIGURE 2 Frequency dependencies of the dielectric losses $\varepsilon''_{\parallel}$ acquired for the nematic phase in the megahertz range. Solid lines—Debye's theory, dashed line—fit to the experimental data contaminated by conductivity effects.

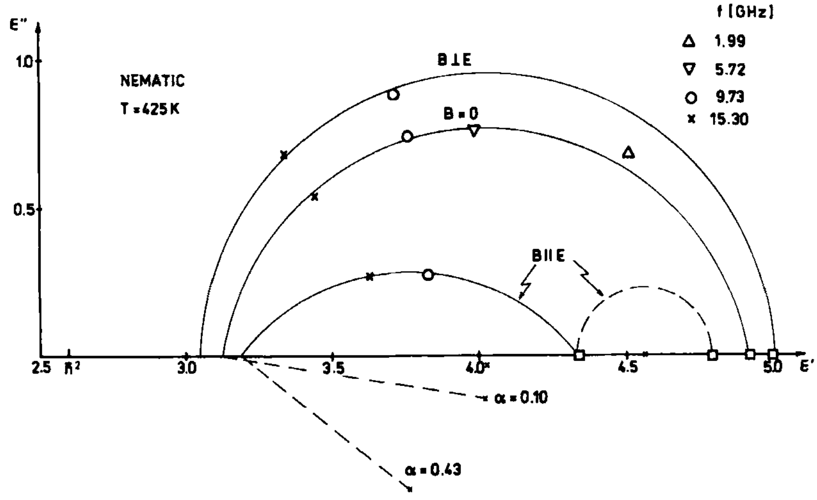

FIGURE 3 The Cole-Cole plots obtained for the nematic phase of PAP.

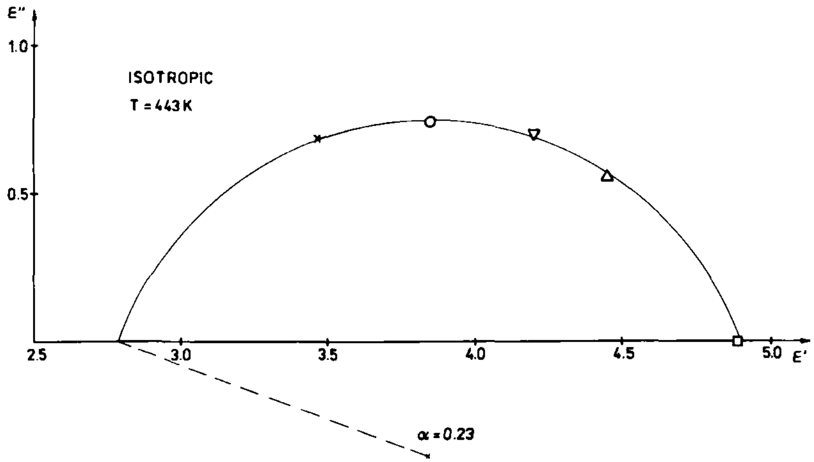

FIGURE 4 The Cole-Cole diagram of the isotropic phase of PAP. (Marks are the same as in Figure 3.)

processes were interpreted on the basis of Cole-Cole modification of the Debye equation:

$$\varepsilon^* = \varepsilon_\infty + \frac{\varepsilon_0 - \varepsilon_\infty}{1 + (i\omega\tau)^{1-\alpha}} \tag{1}$$

where $\omega = 2\pi f$ is a circular frequency, α is an empirical parameter interpreted as a measure of a symmetric distribution of the relaxation times, and τ is the most probable relaxation time. $\varepsilon_0 - \varepsilon_\infty$ is dielectric increment connected with respective relaxation process. Below we shall discuss three main problems which arise from our investigations.

A. The dielectric anisotropy

As it is seen from Figure 1, the dielectric anisotropy, $\Delta\varepsilon = \varepsilon'_\parallel - \varepsilon'_\perp$, has negative value in r.f. and positive one in the m.f. range. This effect can be easily explained on the basis of Meier-Maier theory.[3] Taking into account the parallel ($\mu_\parallel = 1.1$ D) and perpendicular ($\mu_\perp = 2.2$ D) components of the net dipole moment μ of PAP's molecule one can see that at low frequencies the $\varepsilon'_\perp$ component is greater than the $\varepsilon'_\parallel$ one. On the contrary, in the microwave range $\varepsilon'_\parallel$ is greater than $\varepsilon'_\perp$ which is due to the dispersion effects discussed in this paper later on. Dispersion of the $\varepsilon'_\perp$ component takes place in the m.f., where the perpendicular component of the dipolar polarizability ($\mu_\perp^2/3k_BT$) decreases with increasing frequency and it is the

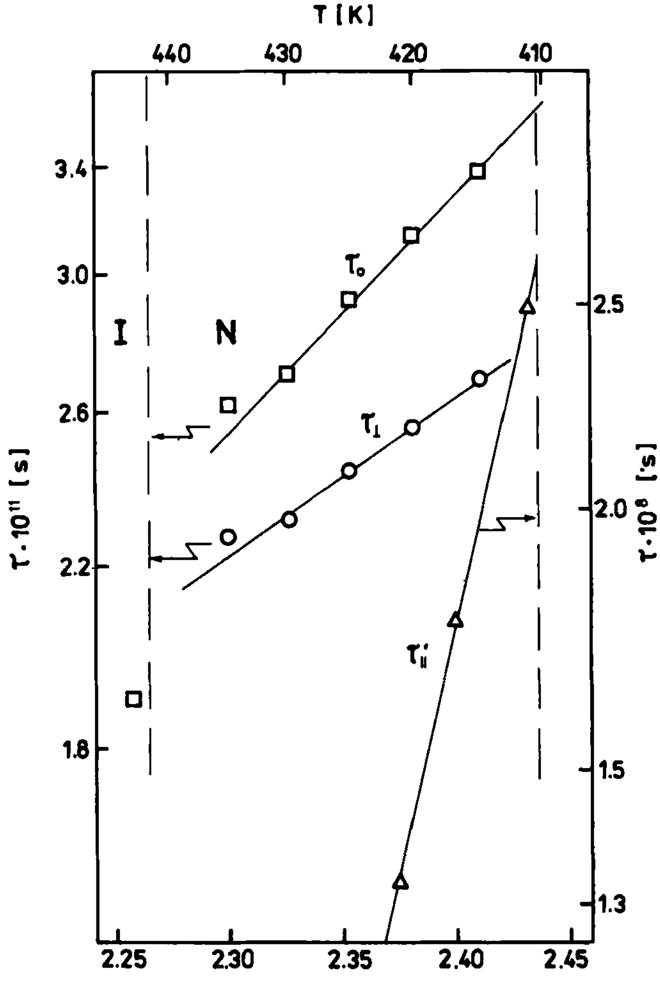

FIGURE 5 Arrhenius plots for the dielectric relaxation times: $\tau_{\|}$, $\tau_{\perp}$, τ_o.

main reason for changing sign of dielectric anisotropy from negative to positive. By comparing the results obtained by us at 9.73 GHz with those by Carr and Spence at 15.3 GHz (Figure 1), one can see that the dielectric anisotropy becomes greater with increasing frequency. It is also seen that close to the clearing point the 9.73 GHz is an isotropic f_0-frequency for which the $\Delta\varepsilon$ value becomes zero.

B. Low-frequency relaxation

The measurements in r.f. range showed strong frequency dependence of $\varepsilon_{\parallel}'$ which was accompanied by pronounced absorption maxima (Figure 2). This spectrum can be described by the formula (1) with parameter $\alpha = 0$. It means that we observe a single relaxation process connected most probably with 180°-jumps of molecules around their short axes. Taking into account the critical frequencies f_R the relaxation times $\tau_{\parallel}'$ could be calculated ($\tau_{\parallel}' = 1/2\pi f_R$) at given temperatures. The obtained values of $\tau_{\parallel}'$ are seen in Figure 2, and in Figure 5 on a logarithmic scale. The activation energy estimated from that is given in Table I. It is less than the value obtained for nematic phase of HOAB,[9] as could be expected by taking into account the length of end groups in both compounds.

C. High-frequency relaxation spectrum

The complex relaxation spectrum, presented in the form of Cole-Cole diagrams in Figure 3, shows that the nematic phase of PAP exhibits two well separated relaxation regions: one falling within the r.f. range ($\tau_{\parallel}' \sim 10^{-8}$ sec), and the other one appearing in the m.f. range with the relaxation times $\tau_{\perp} \sim 2.5 \cdot 10^{-11}$ sec. However, there is an additional relaxation process characterized by the relaxation time $\tau_{\parallel} \sim 1.4 \cdot 10^{-11}$ sec. $\tau_{\parallel}$ and $\tau_{\perp}$ are the most probable relaxation times obtained from the formula (1) applied to the high-frequency relaxation processes seen parallel and perpendicularly to the director, respectively.

As one can see in Figure 3, the high-frequency relaxation spectrum shows up in both orientations. By fitting formula (1) to the experimental data the following relaxation times and respective α parameters have been calculated: ($\tau_{\perp}, \alpha_{\perp}$), ($\tau_{\parallel}, \alpha_{\parallel}$) and ($\tau_0, \alpha_0$) (index "o" refers to nonoriented sample). It must be pointed out that all three relaxation times ($\tau_{\perp}$, $\tau_{\parallel}$ and τ_0) are of the same order of magnitude (Figure 5), but there is a big difference

TABLE I

Activation energies obtained for different relaxation processes observed in PAA[7], PAP and HOAB[9] (in kJ/mole)

Substance	PAA	PAP	HOAB
Low-frequency relaxation	—	$\Delta E_{\parallel} = 93.6$	$\Delta E_{\parallel} = 107.8$
High-frequency relaxation	$\Delta E_0 = 13.0$	$\Delta E_0 = 20.5$ $\Delta E_{\perp} = 15.0$	$\Delta E_0 = 20.9$

in $\propto$ parameters. As it is seen, the $\tau_\perp$ is mostly affected by the molecular rotation around the long axis, because $\propto = 0$ (only close to the clearing point $\propto$ is about 0.08). On the other hand, the relaxation process observed for parallel orientation, and also for non-oriented sample, is influenced by many molecular processes, namely, reorientations around the long molecular axes and librational movements about the long and short axes.

In the case of the isotropic phase the Cole-Cole plot (Figure 4) is a circular arc with rather big value of $\propto$ parameter. It is obvious that all molecular processes mentioned above give contributions to the relaxation spectrum of the isotropic phase.

In the nematic phase (Figure 3) there is a big difference between ε'_∞ and the mean square of refractive index: $\varepsilon'_\infty - n^2 \cong 0.5$. A similar effect was observed for PAA.[7] In this case it was assumed that the effect might be caused either by the existence of fast intramolecular reorientations of $-OCH_3$ groups around para-axes or by librational movements of the whole molecule around its long and short axes. The former interpretation should be excluded in view of the results of neutron scattering (QNS) investigations[15] which show that methoxy terminals cannot rotate faster around para-axes than the molecular body around the long axis. Therefore, the dielectric increment discussed seems to be connected with so-called Poley absorption observed for some liquid crystals in the far infrared region.[16-18]

Making use of the Arrhenius equation the activation barriers for respective molecular reorientations have been estimated. The log-plots are presentd in Figure 5, and the values of the barriers, together with the data gathered for PAA[7] and HOAB,[9] are listed in Table I. One can see that the barriers to molecular reorientations increase with the length of side chains. This effect cannot be explained on the basis of macroscopic viscosity coefficients, which in the case of PAP are smaller than for PAA.[13]

It is worthwhile to point out that the relaxation time τ_0 as well as the activation barrier ΔE_0, measured for non-oriented sample, are a bit greater than the corresponding values acquired for perpendicular orientation. Nevertheless, it seems that the measurements of dielectric relaxation process in microwave frequency range on non-oriented sample in nematic phase may be treated as an approximate representative for molecular reorientations around the long axes.[7-9]

III. CONCLUSIONS

(i) In the nematic phase of PAP there are two substantially different relaxation processes with relaxation times: $\tau'_\parallel \sim 10^{-8}$ sec and $\tau_\perp \sim 10^{-11}$ sec. In the low temperature region of the nematic phase these relaxation processes can be described by Debye-type theory ($\alpha = 0$). It means that we are dealing with two well defined relaxation processes, i.e. with the reorientations of molecules around their short and long axes, respectively. The third relaxation process characterized by $\tau_{\|} \sim 10^{-11}$ sec and a very big α parameter ($\alpha_{\|} \cong 0.4$) is affected by several reorientations of molecules.

(ii) The difference between ε'_{∞} and n^2 can be explained by the existence of additional absorption processes in the infrared region.

(iii) The isotropic phase of PAP exhibits a complex relaxation spectrum influenced by many molecular motions.

(iv) The activation barriers increase with the length of molecule within the PAA's homologous series.

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