Megahertz Dielectric Relaxation in the Nematic Phases of 4,4′-di-n-propyloxyazoxybenzene and 4,4′-di-n-pentyloxyazoxybenzene

Nguyen X. Phuc [1], W. Otowski [2], J. Chruściel [3], H. Kresse [4], S. Urban [5],
and S. Wróbel [5]

Z. Naturforsch. **40a,** 627–631 (1985); received February 22, 1985

The dielectric properties of the third (3. OAOB) and fifth (5. OAOB) members of the PAA homologous series have been investigated in the frequency range from 0.1 to 12 MHz. Negative dielectric anisotropies have been obtained in the nematic phase of both substances. For the dielectric relaxation processes observed parallel to the nematic director, the relaxation times and activation energies have been estimated and discussed.

1. Introduction

Due to anisotropic properties of both the molecular and medium structures, several reorientational processes can be observed in a nematic liquid crystal [1]. In order to investigate these relaxation processes different experimental techniques are necessary: nuclear magnetic resonance, quasielastic neutron scattering, Raman and infrared spectroscopy and dielectric relaxation measurements. By using the dielectric method one can investigate the reorientation of polar molecules around the long and short axes. In nematic liquid crystals, the former process usually appears in the GHz range and latter at about two orders of magnitude lower frequencies [2–6]. It has also been established [2–6] that the low frequency dielectric relaxation process can be well characterized by a single Debye relaxation time.

In this paper we present dielectric investigations in the MHz range on two nematogenic substances: 4,4′-di-n-propyloxyazoxybenzene (3. OAOB) and 4,4′-di-n-pentyloxyazoxybenzene (5. OAOB). It should be noted that these substances belong to the PAA homologous series, which is the subject of molecular dynamics studies carried out by the Cracow Molecular Crystal and Liquid Crystal Group [1, 5, 6].

The dielectric anisotropies of 3. OAOB and 5. OAOB have been measured earlier by Maier and Meier [2] and by de Jeu and Lethouwers [7], respectively. The measurements by Maier and Meier for 3. OAOB, performed in the frequency range from 0.1 to 1.6 MHz, have also indicated the existence of a dielectric absorption and dispersion effect in the nematic phase of this substance.

2. Experimental

In the structural formula

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

there stands $n = 3$ for 3. OAOB and $n = 5$ for 5. OAOB.

The net dipole moment has contributions from three group moments: N_2O and two OC_nH_{2n+1} groups. The substances have been synthesized in the Institute of Chemistry of the Siedlce Agricultural and Pedagogical College. The temperatures of the phase transitions are

for 3. OAOB: $T_{KN} = 388.8$ K, $T_{NI} = 396.8$ K,
for 5. OAOB: $T_{KN} = 348.8$ K, $T_{NI} = 396.3$ K,

which is in good agreement with the values obtained by Arnold [8].

The complex dielectric permittivities in the frequency range from 0.1 to 12 MHz were measured by using a multidecameter DK06 (WTW Weinheim,

---

[1] Institute of Nuclear Physics, Kraków, Poland.
[2] Institute of Physics, Cracow Technical University, Kraków, Poland.
[3] Institute of Chemistry, Siedlce Agricultural and Pedagogical College, Siedle, Poland.
[4] Institute of Chemistry, Martin-Luther University, Halle, DDR.
[5] Institute of Physics, Jagellonian University, Kraków, Poland.

Reprint requests to Dr. N. X. Phuc, Institute of Physics, Reymonta 4, 30-059 Kraków, Poland.

0340-4811 / 85 / 0600-0627 $ 01.30/0. – Please order a reprint rather than making your own copy.

Obb.). A magnetic field of 0.5 T was used to orient the samples. The temperature was varied from 345 K to 410 K to cover the whole nematic phases and a few degrees of the isotropic phases of the substances.

3. Results and Discussion

The results of our measurements are presented in Figures 1–6.

The frequency dependences of the complex dielectric permittivities will be discussed in terms of the Debye equation

$$\varepsilon_i^* = \varepsilon_i' - j\,\varepsilon_i'' = \varepsilon_{\infty,i} + \frac{\varepsilon_{0,i} - \varepsilon_{\infty,i}}{1 + j\,\omega\,\tau_i}, \tag{1}$$

where i denotes a particular relaxation process observed for two orientations ($\parallel$ and $\perp$) of the nematic phase*, and $\varepsilon_{0,i}$ and $\varepsilon_{\infty,i}$ are, respectively, the low- and high-frequency limits of the dielectric permittivity of the i^{th} process. The inset in Fig. 1 shows, in terms of a Cole-Cole diagram, the meaning of $\varepsilon_{0,\parallel 1}$ and $\varepsilon_{\infty,\parallel 1}$.

3 a) The static dielectric constants

Temperature dependences of the dielectric permittivities measured at 0.1 and 5.4 MHz are presented in Figs. 1 and 2. As one can see, in the case of ε_{is}' and $\varepsilon_\perp'$ no dispersion effect has been observed for both substances. The measured values could then be accepted as low-frequency limits of the respective dielectric permittivities, i.e. of $\varepsilon_{0,\text{is}}$ and $\varepsilon_{0,\perp}$. However, the measurements carried out in the direction parallel to the director showed that $\varepsilon_\parallel'$ exhibits a strong frequency dependence. The $\varepsilon_\parallel'$ permittivity decreases with increasing frequency from $\varepsilon_{0,\parallel 1}$ to $\varepsilon_{\infty,\parallel 1}$. This effect is accompanied by the absorption process seen in Figs. 3, 4 and 5. The $\varepsilon_{\infty,\parallel 1}$ presented in Figs. 1 and 2 have been obtained by fitting the Debye equation (2) to the $\varepsilon_\parallel''(\omega)$ experimental points (see below).

As is seen from Figs. 1 and 2, the dielectric anisotropies $\varepsilon_{0,\parallel} - \varepsilon_{0,\perp}$ obtained for 3. OAOB and 5. OAOB are negative, which is in agreement with earlier results [2, 7].

3 b) The dynamic dielectric properties

In this section we shall discuss the relaxation process observed for the $\varepsilon_\parallel''$ component. As was

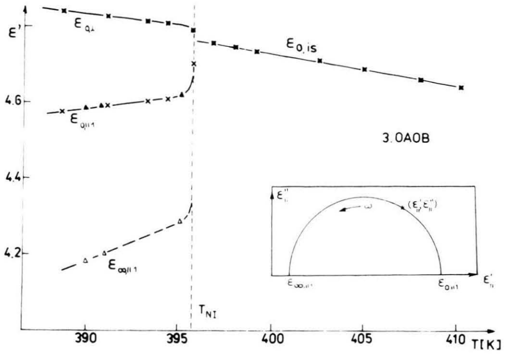

Fig. 1. Temperature dependences of the dielectric permittivities of 3. OAOB. × and ● are the experimental points measured at 0.1 and 5.4 MHz, respectively. ▲ and △ are, respectively, the low- and high-frequency limits of the dielectric permittivities obtained by fitting (2) to the absorption curves (see Figure 3).

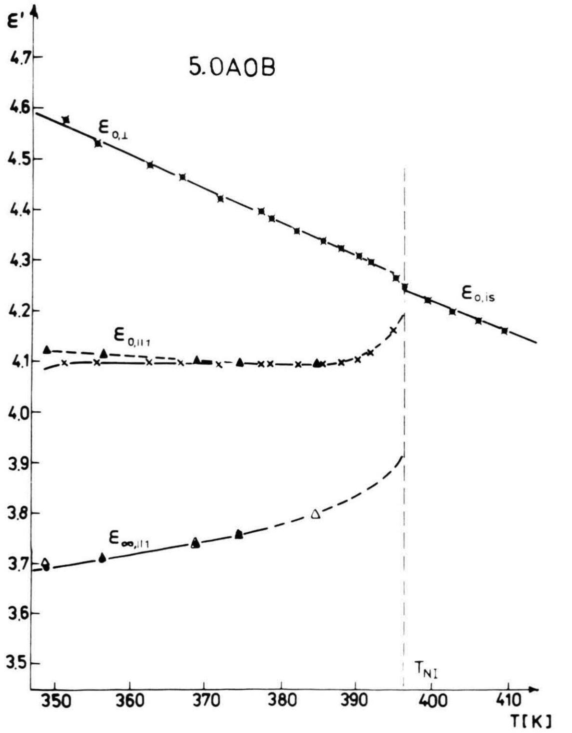

Fig. 2. Temperature dependences of the dielectric permittivities for 5. OAOB. Denotions are the same as in Figure 1.

---

* In the case of parallel orientation of molecules with respect to the measuring field the dielectric relaxation process observed in the present work will be denoted as "∥1" in order to distinguish it from the "∥2" process observed in the GHz range [3–6].

mentioned above, the frequency dependences of $\varepsilon''_{\parallel}(\omega)$ were measured for both substances (Figs. 3, 4 and 5). Making use of the Debye equation (1) one gets the following formula for the dielectric loss factor:

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

which is a Lorentzian curve. By fitting (2) to the absorption curves we found the dielectric increments $(\varepsilon_{0,\parallel 1} - \varepsilon_{\infty,\parallel 1})$ and the $\tau_{\parallel 1}$ relaxation times (see Table 1). The fitted curves are presented in Figs. 3 and 4. The errors of the estimation of relaxation times are about 10–15% for 5. OAOB and 15–30% for 3. OAOB.

In the case of 3. OAOB we have measured the temperature dependence of the dielectric loss factor at the frequency $f = 12$ MHz (Figure 5). Because the maximum value of $\varepsilon''_{\parallel}$ shows up at 390.2 K, the corresponding relaxation time, as shown by Schallamach [9], should be

$$\tau_{\parallel 1}(390.2\ \mathrm{K}) = 1/2\pi \cdot f = 13.2 \times 10^{-9}\ \mathrm{s}.$$

Table 1. The relaxation times and dielectric increments estimated for different temperatures in the nematic phases of 5. OAOB and 3. OAOB.

5. OAOB					
T [K]	348.8	356.2	368.5	374.2	384.2
$\tau_{\parallel 1} \cdot 10^9$ [s]	469	298	107	72.8	33.5
$\varepsilon_{0,\parallel 1} - \varepsilon_{\infty,\parallel 1}$	0.42	0.40	0.35	0.34	0.30

3. OAOB			
T [K]	390.2 ± 0.5	390.0	395.2
$\tau_{\parallel 1} \cdot 10^9$ [s]	13.26	13.9 ± 1.8	8.51 ± 3.9
$\varepsilon_{0,\parallel 1} - \varepsilon_{\infty,\parallel 1}$	–	0.38	0.31

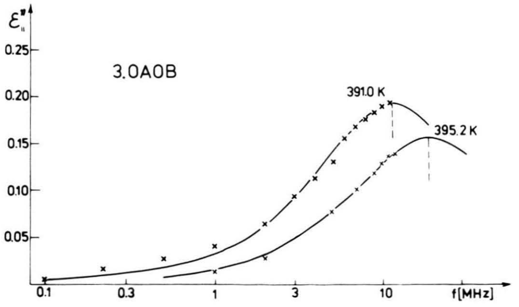

Fig. 3. Dielectric absorption curves measured at two temperatures in the direction parallel to the nematic director of 3. OAOB. × are the experimental points to which the solid curves are the fitted (see text).

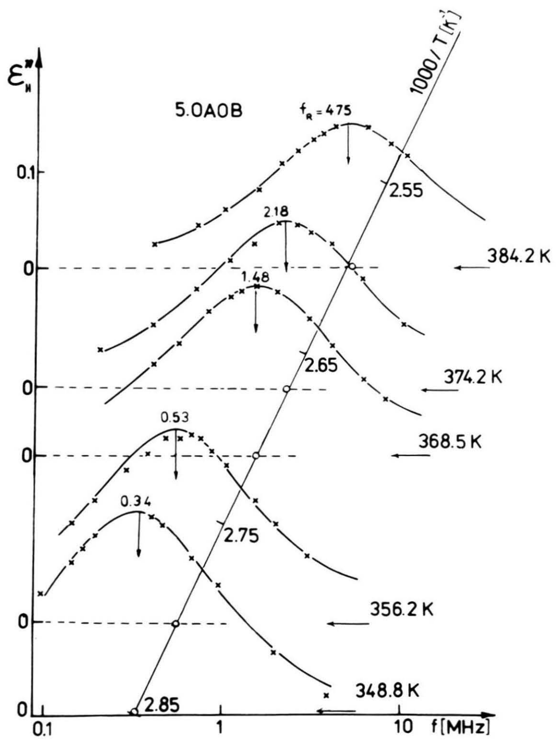

Fig. 4. Dielectric absorption curves measured at different temperatures in the direction parallel to the nematic director of 5. OAOB. The curves are representated in the reciprocal scale of temperature and in the logarithmic scale of frequency. The denotions are the same as in Figure 3.

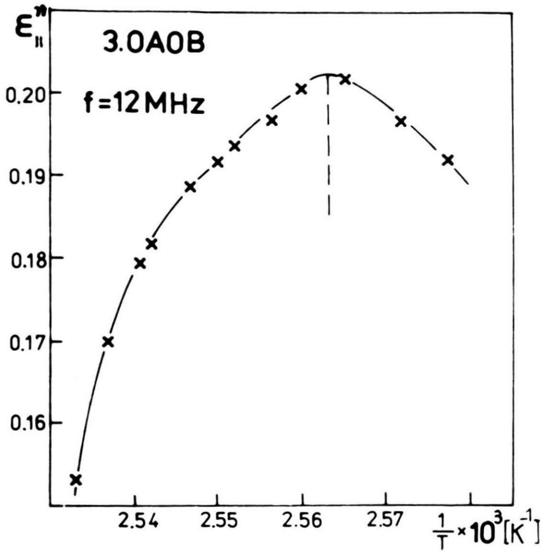

Fig. 5. Temperature dependence of the dielectric loss factor of 3. OAOB measured at the frequency $f = 12$ MHz.

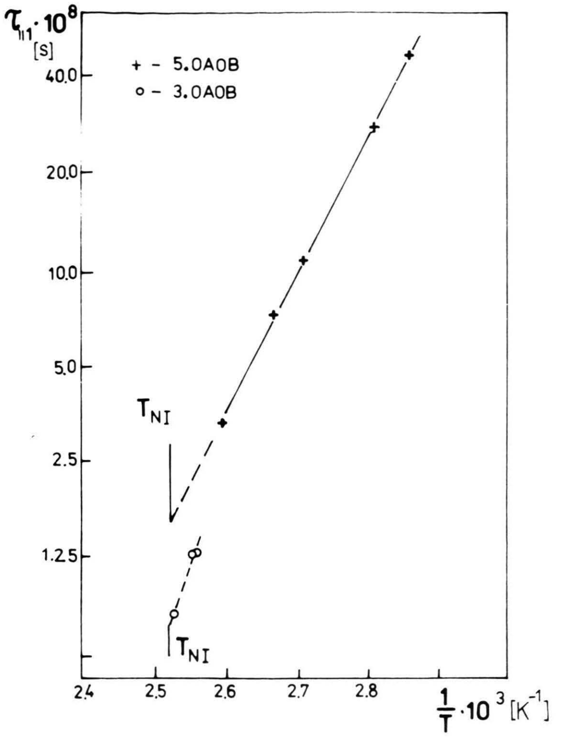

Fig. 6. Dielectric relaxation times vs. $1/T$ of the low-frequency relaxation process in the nematic phase of 3. OAOB and 5. OAOB.

The temperature dependences of the relaxation times obtained for 5. OAOB and 3. OAOB are presented in Figure 6. On assuming the Arrhenius law

$$\tau_{\parallel 1} = \tau_0 \exp(E/RT) \tag{3}$$

we found the activation energies $E \simeq 84$ kJ/mol for 5. OAOB and $E \simeq 146$ kJ/mol for 3. OAOB.

For the temperature range $(T_{\mathrm{NI}} - 40\,\mathrm{K}) < T < (T_{\mathrm{NI}} - 10\,\mathrm{K})$ of the nematic phase of 5. OAOB, the good fit of the Lorentzian function to the experimental points (Fig. 4) suggests that there is only one relaxation process. The activation energy of this process is almost temperature independent. Its estimated value, $E \simeq 84$ kJ/mol, is similar to those obtained for the second and seventh member of the same homologous series [6].

From the values of the activation energies as well as from the geometry of the measurements one may conclude that the low-frequency relaxation process observed is connected with the reorientations of the molecules around their short axes.

It should be noted that in the case of 3. OAOB, due to the restricted frequency range available, we could measure the relaxation times only for three points in the temperature range of 10 K below the clearing point, i.e. $(T_{\mathrm{NI}} - 10\,\mathrm{K}) < T < T_{\mathrm{NI}}$ (Figures 3, 6). Except for an inaccuracy arising from the small number of experimental points and the small temperature range [13], the value $E \simeq 146$ kJ/mol obtained for the activation energy seems to be too large for 3. OAOB which is shorter than 5. OAOB. We explain this by supposing that in the temperature range quite near to the clearing point, where the order parameter S varies rapidly with T, the dielectric relaxation time of the low frequency process decreases more and more quickly with increasing temperature. This effect has recently been observed by Zeller [11] who connected it with the density change. Noack et al. [10], however, suggest that in the pretransitional range beside the molecular motions showing up in the lower temperature range there must be an additional molecular motion known as fluctuation of the order parameter. In our present measurements we could only note a small deformation from the symmetric form of the absorption curve (Figure 5).

Because the two substances investigated have almost the same clearing temperatures, one can compare directly their relaxation times at any temperature in the nematic phase. As it could be noted from Fig. 6, the extrapolated relaxation time of 5. OAOB is about 2 times larger than that obtained for 3. OAOB at the same temperature. This fact appears to be related to the difference in the moments of inertia of the two molecules [13].

4. Conclusions

From the dielectric measurements in the frequency range of 0.1 – 12 MHz we could deduce the following conclusions:

1) In the direction parallel to the nematic director of 3. OAOB and 5. OAOB a dielectric relaxation has been observed, which is connected with the reorientation of the molecules around the short axes.

2) In the temperature range from 349 to 384 K of the nematic phase of 5. OAOB the observed dielectric relaxation process seems to be uninfluenced by other motional processes.

3) The behaviour of the low frequency dielectric relaxation process in the pretransitional range is more complicated. Our results suggest that the slope of the temperature dependence of the relaxation times in this region is larger than that in the lower temperature region.

Acknowledgements

The authors wish to express their grateful thanks to Prof. J. A. Janik for his interest in this work and valuable discussions.

[1] J. A. Janik, T. Grochulski, M. Godlewska, A. Kocot, E. Ściesińska, J. Ściesiński, and W. Witko, Mol. Cryst. Liq. Cryst. **98,** 67 (1983).
[2] W. Maier and G. Meier, Z. Naturforsch. **16 a,** 1200 (1961).
[3] A. Axmann, Z. Naturforsch. **21 a,** 615 (1966).
[4] H. Kresse, Fortschr. Physik **30,** 507 (1982).
[5] X. P. Nguyen, S. Urban, S. Wróbel, and H. Kresse, Acta Phys. Pol. **A 54,** 617 (1978).
[6] S. Urban, S. Wróbel, K. Chłędowska, J. Chruściel, J. A. Janik, and H. Kresse, Mol. Cryst. Liq. Cryst. **100,** 57 (1983).
[7] W. H. de Jeu and Th. W. Lathouwers, Z. Naturforsch. **29 a,** 905 (1974).
[8] H. Arnold, Z. Phys. Chem. **226,** 146 (1964).
[9] A. Schallamach, Trans. Faraday Soc. **42,** 495 (1946).
[10] G. Nagel, W. Wolfel, and F. Noack, Israel J. Chem. **23,** 380 (1983).
[11] H. R. Zeller, Phys. Rev. A **26,** 1785 (1982).
[12] S. Wróbel, Mol. Cryst. Liq. Cryst. in print.
[13] H. Kresse, A. Wiegeleben, and D. Demus, Kristall u. Technik **15,** 341 (1980).