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Molecular reorientation in the nematic and rotatory phases of 4,4'-di-*n*-pentyloxyazoxybenzene

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Molecular reorientation in the nematic and rotatory phases of 4,4′-di-*n*-pentyloxyazoxybenzene

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Results of dielectric relaxation, quasielastic neutron scattering, calorimetric D.S.C. and preliminary X-ray measurements on the fifth member, POAOB, of the 4,4′-di-*n*-alkoxyazoxybenzene homologous series are presented. It has been found that POAOB exhibits two mesophases: a nematic (N) and an intermediate crystalline phase (C I) just below it. From comparison of the dielectric relaxation and quasielastic neutron scattering studies we can conclude that in the nematic phase the molecule as a whole performs rotational diffusion around the long axis ($\tau_{\perp}^{DR} \sim 150$ ps) and at the same time the two moieties perform faster independent reorientations around the N–ϕ bonds (ϕ denotes a benzene ring) with $\tau^{QNS} \sim 5$ ps. The intermediate crystal phase is identified as a solid uniaxial rotational phase in which fast molecular reorientations exist. It seems that the fast reorientations observed in the nematic phase to some extent survive to the crystal I phase. A model of molecular arrangements in the crystal I phase is proposed, and it explains the reduction of the dielectric increment observed on passing from the nematic phase to this phase.

1. Introduction

Molecular reorientational dynamics in liquid crystals has been the subject of intensive studies for about 15 years (see, e.g., [1–3]). Among various experimental techniques dielectric relaxation [2–6] and quasi-elastic neutron scattering [1, 7–12] are the two methods which have been systematically applied for this purpose. Due to the

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wide range of frequencies, from radio to microwave, the dielectric relaxation method can detect both the slow reorientation of molecules around the short axes and the fast motion around the long axes. The neutron scattering method, on the other hand, can detect only the fast molecular reorientations with characteristic times in the range of 10^{-11} to 10^{-12} s.

The dielectric relaxation method is a means for establishing that the dielectric relaxation times, $\tau_{\parallel}^{DR}$, associated with the reorientation of molecules around their short axes, obtained for the nematic, smectic A and smectic C phases; they are of the order of 10^{-7} to 10^{-8} s [2–6]. On passing to highly ordered smectic phases, such as smectic B, G and E, the process under discussion is still observed, although $\tau_{\parallel}^{DR}$ becomes longer by about one order of magnitude [2].

There exists another dielectric relaxation process observed for frequencies above ~ 100 MHz. It is characterized by the relaxation time $\tau_{\perp}^{DR}$ being of the order of 10^{-10} to 10^{-11} s [2–5], thus, it partly overlaps the range of correlation times accessible to the neutron scattering method (τ^{QNS}). There is no doubt that the high frequency relaxation process is associated with the whole molecule reorientation around long axis [3]. Until recently, neutron scattering measurements were interpreted in terms of the same reorientations [1, 11, 12]. In this later case it was commonly assumed that the molecules are rigid bodies.

However, measurements carried out for some members of the 4,4′-di-*n*-alkoxyazoxybenzene homologous series in the past few years in our group, with the use of dielectric and neutron methods, have shown that the assumption about rigidity of the molecules cannot explain the experimental results satisfactorily. As a matter of fact, the neutron correlation times are systematically shorter than the dielectric correlation times and these differences are distinctly beyond the limits of possible corrections arising from the local field factor (which enlarges, to some extent, the macroscopic relaxation time in relation to the microscopic dipole correlation time) [1, 23]. In the nematic phases of the homologues with methoxy, ethoxy and propyloxy groups, it has been found that the ratio $q = \tau_{\perp}^{DR}/\tau^{QNS}$ is of the order of 5 to 10. This fact has stimulated a new approach to the problem of the type of molecular motions that the neutron scattering method really detects [1]. Taking also into account the results of

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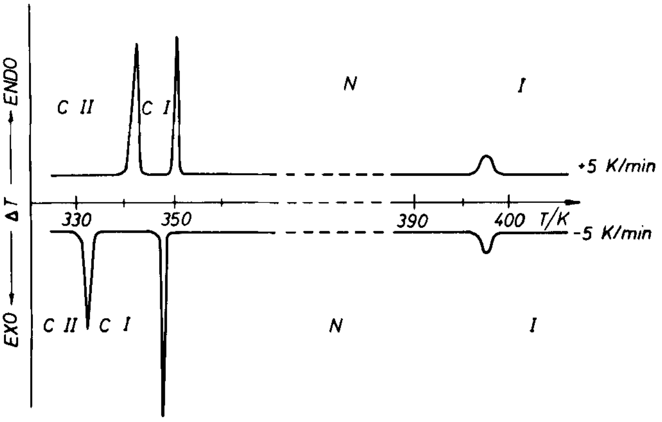

Figure 1. D.S.C. results obtained for POAOB during the cooling (EXO) and the heating (ENDO) processes. The symbols I, N, C I and C II stand for the isotropic, nematic, intermediate crystal and normal crystal phases, respectively.

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other experimental techniques and the results of quantum chemical calculations it has been suggested [1, 9, 13] that the neutron method detects reorientational motions of molecular fragments around the N–ϕ bond, where ϕ denotes a benzene ring. Unfortunately, this conclusion cannot be extended to other liquid crystals because both methods have not been applied to other mesogens. As a continuation of the systematic investigations of the 4,4′-di-*n*-alkoxyazoxybenzene homologous series we have now studied its fifth member, POAOB with the use of both methods. This substance exhibits a nematic phase (N) in a wide temperature range and an intermediate phase (C I) just below it (cf. figure 1). In this paper we present the results obtained in a wide temperature range covering the two solid phases and the nematic. Special attention is paid to the C I phase which is interpreted as a solid rotator (plastic) phase. As will be shown, the results obtained for the N and C I phases of POAOB can throw more light on the problem of different mechanisms of the molecular processes observed.

2. The substance

Both the normal (POAOB-d_0) and the chain deuteriated (POAOB-d_{22}) nematogens were synthesized [15] in the Institute of Chemistry of the Agricultural and Pedagogical University at Siedlce (Poland). The phase transitions for the undeuteriated material is presented in figure 1. As it is seen there, the sequence

$$\mathrm{C\,II} \xrightarrow[\Delta S = 7{\cdot}8R]{343\,\mathrm{K}} \mathrm{Cr\,I} \xrightarrow[\Delta S = 5{\cdot}4R]{350\,\mathrm{K}} \mathrm{N} \xrightarrow[\Delta S = 0{\cdot}45R]{397\,\mathrm{K}} \mathrm{I}$$

occurs where R is the gas constant. The transition temperatures obtained by the D.S.C. method for the deuteriated material are about 1 to 3 K lower than those of the normal compound.

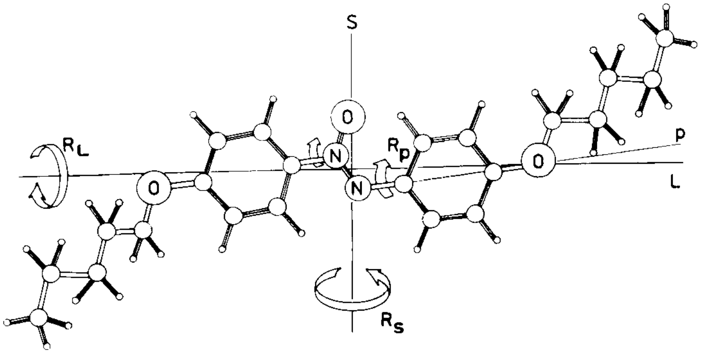

Figure 2. The molecular structure of POAOB. S, L and P stand, respectively, for the short, long and para-axes about which the reorientations (R_S, R_L and R_P) may take place.

The molecular structure of POAOB is shown in figure 2. The molecule possesses three group dipole moments concentrated at the N_2O bridging group and OC_5H_{11} end groups. The two principal axes of rotational motions of the whole molecule [32] are shown (R_L and R_S). In the later discussion the possibility of intramolecular motion of moieties about the para axes (R_P, i.e. N–ϕ bonds) is considered.

The neutron and X-ray diffraction measurements performed with the powder sample for the two solid phases of POAOB (cf. figure 3) showed that the C II phase has a triclinic structure [28, 29], while C I seems to have a monoclinic one. By comparing the intensity and the number of Bragg peaks obtained for POAOB with

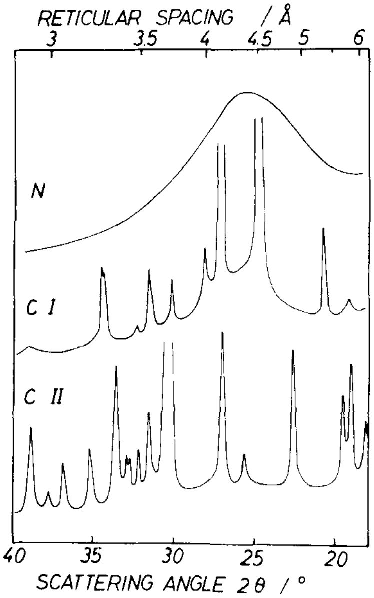

Figure 3. X-ray diffraction powder patterns for the N, C I and C II phases of POAOB at $\lambda = 1{\cdot}937$ Å.

those of TBBA [14] we conclude that the C I phase of the former is at least as ordered as the VII phase of the latter. Therefore it is quite reasonable to treat the C I phase as a solid phase (see also [17]). This statement is supported by some other arguments, such as the high entropy of the C I → N transition and the lack of reorientation around the short molecular axes (see later).

3. Dielectric study

The dielectric permittivities of POAOB have been measured at various frequency ranges as a function of temperature, covering all phases of the substance. The experimental arrangements have been described elsewhere [2, 5, 6]. The main results (see also [6, 16]) can be summarized as follows.

(1) For a parallel orientation of the nematic phase, $\mathbf{E} \parallel \mathbf{B}$, two relaxation domains ($\parallel 1$ and $\parallel 2$) have been observed. The $\parallel 1$ process is of the Debye type and is characterized by a relaxation time between 10^{-8} and 10^{-9} s. Its dielectric increment, $\varepsilon_0 - \varepsilon_\infty$, is between 0·3 and 0·4, and the activation energy is 84 kJ/mol. This dielectric process is certainly connected with 180° jumps of the molecules around their short axes (reorientation R_S in figure 2).

(2) For a perpendicular orientation of the nematic phase, $\mathbf{E} \perp \mathbf{B}$, only one relaxation process is observed and it is in the GHz frequency range. This process is characterized by a relaxation time of 10^{-10} to 10^{-11} s, the dielectric increment of about 1·8 and the activation energy of about 25 kJ/mol. It is associated mainly with the reorientation of the molecule as a whole around the long axis (reorientation R_L in figure 2). However, a distribution of the relaxation times indicates that other molecular reorientations may contribute to this high frequency relaxation process [32].

It should be noted that the dielectric relaxation times extrapolated to the N → C I transition are 6×10^{-7} s and 2×10^{-10} s for the low and the high frequency processes, respectively.

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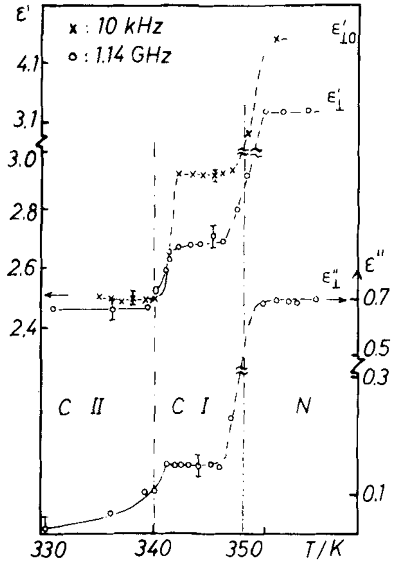

Figure 4. Temperature dependence of the dielectric permittivity ε' (the left-hand side scale) and ε'' (the right-hand side scale) obtained for POAOB at 10 kHz and 1·14 GHz.

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The results for the solid phases of POAOB are presented in figure 4 which shows the temperature dependencies of the dielectric constant ε' and losses ε'' obtained at 10 kHz and 1·14 GHz. The C I phase was obtained by cooling the perpendicularly aligned nematic phase. As can be seen in the C II phase the kHz and GHz measurements give approximately $\varepsilon' = n^2$ and $\varepsilon'' = 0$, which corresponds to a complete freezing out of the molecular reorientation in this phase.

At the C II → C I transition pronounced steps in the dielectric permittivities measured at all frequencies have been observed. This observation evidently shows that in the C I phase a dielectric relaxation process does exist. This process is characterized by the dielectric increment $\varepsilon_0 - n^2 \cong 0{\cdot}5$. In the frequency range from 10 kHz to 100 kHz ε' does not show any dispersion and ε'' remains equal to zero. This means that on passing from the nematic to the C I phase the reorientation of the molecules around the short axes are frozen out. It is worth mentioning that the low frequency relaxation process was observed even for highly ordered smectic phases such as smectic B, G and E [2]. On the other hand, at MHz and GHz frequencies the dielectric permittivity ε' exhibits a strong dispersion which is accompanied by dielectric losses ε'' (cf. figure 4). Unfortunately, poor accuracy of the measurements in the solid phases (especially for ε') and a large gap in the frequencies used make a detailed analysis of the relaxation processes which take place in the C I phase, rather difficult. Figure 5 shows ε'' values measured at two MHz (1·1 and 10 MHz) and four GHz frequencies (1·1, 1·8, 7·4 and 9·4 GHz). If the existence of only one Debye relaxation process is assumed in this phase a critical frequency of *c*. 5×10^8 Hz ($\tau^{DR} \sim 3 \times 10^{-10}$ s) should be obtained and the dielectric increment of about 1·9. Since the latter value is considerably larger than the observed value ($\varepsilon_0 - n^2$), it is reasonable to say that the dielectric spectrum in the C I phase does not correspond to a single Debye relaxation but is rather complex. One possible treatment of this spectrum would be, for instance, to separate it into two dielectric processes as shown, as an example, in figure 5. In

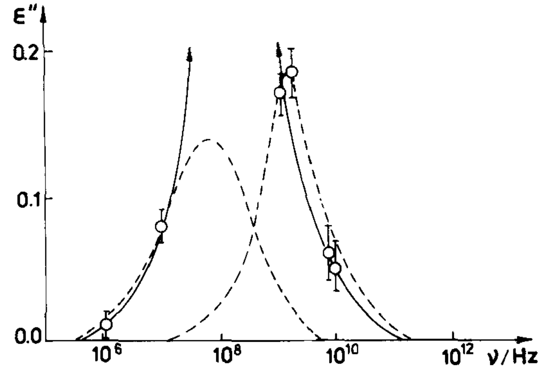

Figure 5. Dielectric loss ε'' measured in C I phase of POAOB at 1·1 and 10 MHz, and 1·14, 1·8, 7·4 and 9·4 GHz. The solid line corresponds to the case when one Debye relaxation process is assumed to exist. The dashed lines show a possible guess of a separation of the relaxation spectrum into two processes.

any event the results of the dielectric measurements allow us to conclude that fast molecular reorientation around the long axis does exist in the C I phase.

This seems to be the first case where such a high frequency dielectric process has been observed for the solid phase of a mesogen. Only some very low frequency dielectric relaxation processes have been observed previously [19, 22].

4. Quasi-elastic neutron scattering study

The neutron scattering experiments were carried out on two neutron spectrometers: (1) on the inverted-geometry spectrometer (KDSOG) installed at the pulsed reactor IBR-30 at Dubna, U.S.S.R., and (2) on the time-of-flight (TOF) spectrometer at the JEEP II reactor at Kjeller, Norway. The incident neutron energies were 5·11 meV and 4·63 meV for the KDSOG and TOF spectrometers, respectively. The energy resolution for both spectrometers was approximately 0·20 meV. The spectra were measured at the following scattering angles: 30°, 40° and 50° at Kjeller, and 50° at Dubna. The measurements were performed for the C II phase (290, 323 and 332 K), C I phase (341, 343 and 344 K) and nematic phase (353, 363 and 374 K). The spectra obtained for the C II phase (evidently with no quasi-elastic component) were used to determine the resolution and to subtract the inelastic background [7]. The model scattering law $S(\mathbf{Q},\omega)$ was convoluted with the resolution function before being fitted to the experimental data. The fitting process was made on a CYBER-72 computer using the MINUIT programme from the CERN library.

A comparison of spectra obtained for different phases is shown in figure 6. The spectrum measured for the C II phase has only the elastic component, whereas the spectra obtained for C I and nematic phases exhibit distinct quasi-elastic broadening which is practically the same for both normal and chain-deuteriated materials.

The spectra were analysed quantitatively by using models which assume that the molecules are in an all-trans configuration, and the protons perform uniaxial reorientation. Two models of proton motions have been applied.

Model I. The protons perform instantaneous jumps by 180° (180°-jump model). The scattering law for this model is

$$S(\mathbf{Q},\omega) = \frac{1}{2}\sum_i a_i\left[\left(1+\frac{\sin 2Qr_i}{2Qr_i}\right)\delta(\omega)+\frac{1}{\pi}\left(1-\frac{\sin 2Qr_i}{2Qr_i}\right)\frac{\Gamma}{\Gamma^2+\omega^2}\right], \quad (1)$$

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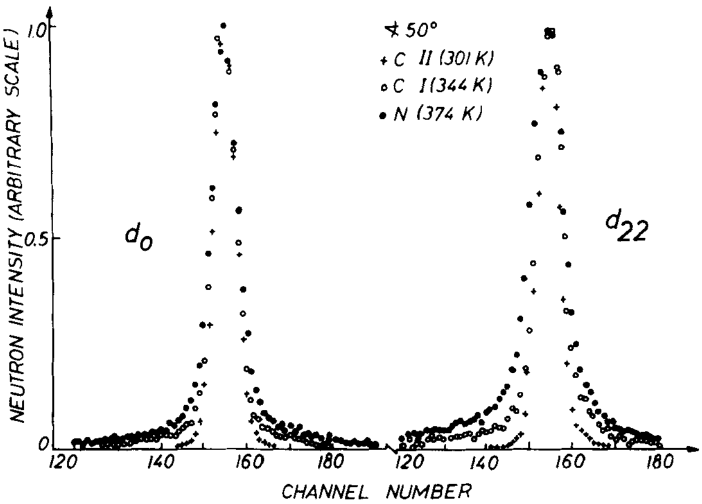

Figure 6. A comparison of neutron scattering spectra obtained for the N, C I and C II phases of POAOB-d_0 and d_{22} (Kjeller data).

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where $\hbar\omega$ and $\hbar\mathbf{Q}$ are the energy and momentum transfers, respectively, a_i is the fraction of the protons in the molecule whose giration radii are r_i. The half-width of the lorentzian curve, Γ, is an adjustable parameter and is connected with the average residence time τ by $\Gamma = 2\hbar/\tau$.

Model II. The protons perform a random walk with infinitesimal steps (diffusion model). The scattering law for this model is

$$S(\mathbf{Q},\omega) = f_0(Qr)\,\delta(\omega) + \frac{2}{\pi}\sum_{n=1}^{\infty} f_n(Qr)\,\frac{\Gamma_n}{\Gamma_n^2+\omega^2}, \tag{2}$$

$$f_n(Qr_i) = \sum_i a_i \langle J_n^2(Qr_i)\rangle, \tag{3}$$

where $\langle J_n^2\rangle$ are the averages of the squares of the cylindrical Bessel functions. The correlation time τ_1 is an adjustable parameter of the model and is connected with Γ_n by $\tau_1 = n^2\hbar/\Gamma_n$.

Two sets of giration radii corresponding to two axes of reorientation (namely, axes P and L in figure 2) have been used in the fitting process. For the P axis the r_i values for 30 protons are: 2·14 Å (8 protons in the benzene rings), 4·0 Å (6 protons in the methyl groups) and 1·81, 0·55, 3·07 and 1·82 Å (each for 4 protons in the methylene groups). The radii with respect to the long molecular axis L are different for each proton, e.g. for 8 protons of the benzene rings the r_i are 2·17, 1·87, 2·00, 2·31, 1·58, 1·80, 2·65 and 2·43 Å. The first set of radii (the P axis) corresponds to a rotation of the two molecular moieties around the N–ϕ bonds. The second set (the L axis) corresponds to a rotation of the whole molecule about the long axis. We have also assumed that the 120° jumps of the CH_3 groups around the C_3 axes and the translational diffusion of molecules do not contribute significantly to the form of the scattering law.

The correlation times obtained by fitting the two sets of giration radii to the same spectra are presented in table 1. We can see that the two axes lead to almost equal correlation times. From now on we shall concentrate on the case of the para axis

Table 1. Influence of the choice of the axis of reorientation on the neutron correlation times (in ps).

Phase	POAOB-d_0	POAOB-d_{22}	Axis
N	5·1	7·0	P
(374 K)	6·6	7·0	L
C I	6·2	5·6	P
(344 K)	6·2	5·4	L

Table 2. Correlation times, τ^{QNS}, and square of the deviation, χ^2, obtained by fitting the rotational diffusion and 180°-jump models to spectra of POAOB (P axis).

Scattering angle 2θ	Nematic phase (374 K)				C I phase (344 K)				Remarks
	Diffusion		180° jumps		Diffusion		180° jumps		
	τ/ps	χ^2	τ/ps	χ^2	τ/ps	χ^2	τ/ps	χ^2	
				POAOB-d_0					
30°	3·9	16	4·3	50	0·4	154	4·2	41	Kjeller
40°	4·8	86	4·3	411	0·5	579	4·7	26	Kjeller
50°	5·5	273	4·2	1224	13·7	30	6·2	23	Kjeller
50°	3·6	103	3·4	346	11·8	31	5·5	31	Dubna
Average	4·5	120	4·1	508	6·6	199	5·2	28	
				POAOB-d_{22}					
30°	3·2	37	5·2	44	0·4	321	2·1	151	Kjeller
40°	4·1	63	4·5	68	—	—	—	—	Kjeller
50°	7·0	50	4·5	361	14·1	65	5·6	36	Kjeller
Average	4·8	50	4·7	158	7·3	193	3·9	94	

which, we believe, corresponds to the rotation which is seen by the neutron scattering method. The results of the fitting are presented in table 2. Figures 7 and 8 show examples of fits for the spectra measured on the TOF and KDSOG spectrometers, respectively.

The results in table 2 show that for the nematic phase the diffusion model seems to be a little better than the 180°-jump model, whereas for the C I phase the situation is reversed. This statement is based on the smaller χ^2 values as well as on the smaller scatter of correlation times. The change of geometry of motion from uniaxial rotational diffusion (nematic phase) to 180° jumps when the degree of order of the phase becomes large has been observed for other substances [11, 12]. The agreement between correlation times obtained from the spectra measured on different instruments seems to be fairly good.

The correlation times are practically the same for both the normal and chain-deuteriated substances as seen from table 2. This means that the reorientational motions of the benzene rings are as fast as those of whole molecular moieties, which is in agreement with the results of studies of other members of the 4,4′-di-*n*-alkoxy-azoxybenzene homologous series [1, 7, 8]. In addition for the C I phase of POAOB each moiety as a whole reorients about the N–ϕ bond with a correlation time of about 5 ps. At the N → C I transition no significant change in τ was observed.

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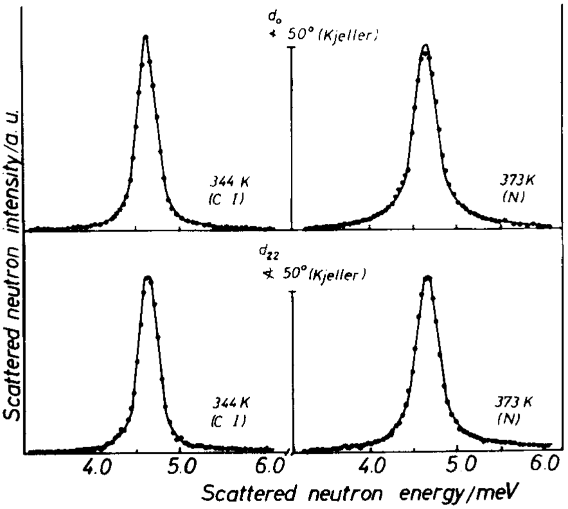

Figure 7. Examples of the fitting of the 180°-jump model (C I phase) and rotational diffusion model (N phase) to the neutron scattering spectra of POAOB-d_0 and d_{22} (Kjeller data).

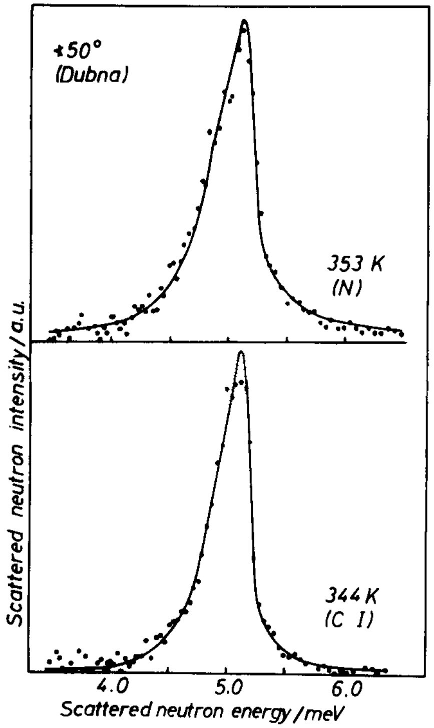

Figure 8. Examples of the fitting of the 180°-jump model (C I phase) and rotational diffusion model (N phase) to the neutron scattering spectra of POAOB-d_0 (Dubna data).

5. Discussion

Table 3 contains the correlation times acquired by our group for the nematic phase from the dielectric ($\tau_{\perp}^{DR}$) and neutron (τ^{QNS}) measurements for four members of the 4,4′-di-*n*-alkoxyazoxybenzene homologous series. These correlation times were

Table 3. Comparison of the correlation times obtained from the dielectric relaxation ($\tau_{\perp}^{DR}$) and quasi-elastic neutron scattering (τ^{QNS}) measurements for four members of the 4,4′-di-*n*-alkyloxyazoxybenzene homologous series in nematic phase.

Substance†	$T_{NI}-T$	$\tau_{\perp}^{DR}$/ps	τ^{QNS}/ps	$q = \tau_{\perp}^{DR}/\tau^{QNS}$	References
PAA (1)	10°	23	4	6	[23]
PAP (2)	10°	27	4	7	[5, 8]
PrOAOB (3)	6°	50	9	5,5	[16, 8]
POAOB (5)	10°	90	4	22	—

† The number in parentheses gives the number of carbon atoms in the alkyl chain.

obtained when the molecular rotational diffusion around the long axis (L) was assumed to be responsible for the results of both sets of measurements. It is characteristic that $\tau_{\perp}^{DR}$ increases with the length of the end groups in the molecule, whereas τ^{QNS} is practically independent of this length. It is remarkable that the q value for POAOB is distinctly larger than those at other compounds. There is evidently a large disagreement between the values of both correlation times and it cannot be explained either by an influence of the local field factor on the $\tau_{\perp}^{DR}$ values or by the experimental errors. Thus, we must conclude that the two methods detect different reorientational motions of the molecules.

The dielectric high frequency process originates, no doubt, mainly from the reorientation of a molecule as a whole about its long axis. This is confirmed by comparison of the experimental dielectric increment with that estimated on the basis of the Maier–Meier theory [24]. As there is a distribution of dielectric relaxation times, we can admit an influence of intramolecular and other motions on the relaxation process observed [16].

The process seen by the neutron scattering method is supposed to originate from the reorientation of the molecular moieties around the N–ϕ bonds. This assumption is supported by quantum chemical calculations [33] as well as by the results of proton and deuterium N.M.R. measurements [13] for 4,4′-dimethoxyazoxybenzene. It seems that the two moieties perform such motion independently. Thus, in the nematic phase of the members of the 4,4′-di-*n*-alkoxyazoxybenzene homologous series the molecule as a whole performs rotational diffusion around the long axis and at the same time the two moieties perform faster independent reorientations around the N–ϕ bonds.

When going from the nematic to the C I phase, fast reorientations of these moieties seem still to exist (cf. figure 6, and table 2) but the large reduction of the static dielectric constant (cf. figure 4) suggests that the dipole reorientation is qualitatively changed at the transition. It should be noted that similar dielectric behaviour has been observed in highly ordered smectics [2, 22] and is interpreted as an effect of the appearance of dipole–dipole correlations between neighbouring molecules.

An analysis of the dipole correlations in the C I phase of POAOB would be possible if the molecular arrangement in the crystal lattice were known. Preliminary X-ray measurements [25] indicate that the C I phase has a layered structure. Such a structure has also been found in the solid phase of 4,4′-di-*n*-heptyloxyazoxybenzene which melts to a smectic C phase [27]. Let us assume that the molecules in the C I phase are packed in alternate sheets consisting of pairs of molecules in an antiparallel head-to-tail configuration with their N → O dipoles opposed attractively so that the molecules are displaced relative to each other along their long axes by a few Å [27]. Since the C I phase is a rotational phase we suppose that the packing of molecules is

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not so tight as in the normal crystal and that the molecules can reorient around their long axes rather easily. However, such a molecular arrangement should cause an antiparallel correlation of the dipole moments of the molecules in pairs. This fact should then strongly influence the value of the static dielectric constant. According to the Fröhlich–Kirkwood equation suggested for solids [31]

$$(\varepsilon_0 - \varepsilon_\infty) = \frac{3\varepsilon_0(\varepsilon_\infty + 2)}{2\varepsilon_0 + \varepsilon_\infty} \frac{N_0}{9kT} \mu^2 g, \tag{4}$$

where μ is the molecular dipole moment and other symbols have their usual meanings. The dipole correlation factor g is defined as

$$g = 1 + z\langle\cos\theta\rangle, \tag{5}$$

where θ is the angle between a chosen dipole and one of its nearest neighbours, and $\langle \ldots \rangle$ means averaging over orientations of all dipoles considered. If the dipoles have a tendency to antiparallel orientations the value of $\langle\cos\theta\rangle$ is negative, which leads to $g < 1$ and then to a reduction of the ε_0 value. Assuming equation (4) to be applicable to the nematic and C I phases and supposing a lack of dipole correlations in the nematic phase, we can estimate a value of the g factor in C I phase, from the experimental ε_0 values on both sides of the transition. We find $g \cong 0{\cdot}23$ for $z = 2$ and subsequently $\theta \cong 113°$ which means that in the C I phase the orientations of the dipole moments in pair are not completely antiparallel.

Figure 5 shows that the relaxation process detected in our dielectric measurements for the C I phase consists of several molecular motions. More detailed analysis is impossible, since the dielectric increment is small and there is a large gap in the measuring frequencies. We suppose that all fast molecular motions existing in the nematic phase survive to some extent to the C I phase.

We are inclined to classify the C I phase of POAOB as a uniaxial rotational phase [20]. It should be noted that the existence of plastic-like phases in liquid-crystalline materials was suggested by de Gennes and Sarma [26].

6. Conclusions

POAOB exhibits a phase diagram which is not typical of liquid-crystalline materials: beside the nematic phase it has a mesomorphic intermediate solid phase (C I).

For the nematic phase the dielectric relaxation method reveals the existence of fast molecular motion with the relaxation time $\tau_\perp^{\mathrm{DR}} \sim 10^{-10}$ to 10^{-11} s. This relaxation time is mainly associated with the reorientation of the molecule as a whole around its long axis. As there is evidence of some distribution of the relaxation times we are inclined to suggest an influence of the intramolecular motion of the moieties on this relaxation process.

The neutron scattering method shows, however, that in the nematic phase there exists fast molecular motion with a correlation time of the order of 10^{-12} s, which on the basis of quantum chemical calculations we believe is associated with the reorientation of molecular moieties about the para-axes.

The C I phase is very like the uniaxial rotational phase of plastic crystals. The neutron scattering measurements reveal the existence of the reorientation of molecular moieties. The dielectric relaxation measurements show that all motions existing in the nematic phase most probably survive to the C I phase. They become frozen out on passing to the C II solid.

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