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K. Chłedowska[a]; D. Chruściel[b]; J. A. Janik[c]; J. M. Janik[d]; H. Kresse[e]; H. Stettin[e]; K. Otnes[f]; T. Stanek[d]; S. Urban[g]; S. Wróbel[g]

[a] Institute of Mathematics and Physics of the Technical University, Rzeszów, Poland [b] Institute of Chemistry, Agricultural and Pedagogical University, Siedlce, Poland [c] Institute of Nuclear Physics, Kraków, Poland [d] Institute of Chemistry, Jagellonian University, Krakow, Poland [e] Institute of Chemistry, Martin Luther University, Halle, GDR [f] Institute of Energy Technology, Kjeller, Norway [g] Institute of Physics, Jagellonian University, Kraków, Poland

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Dielectric relaxation and quasielastic neutron scattering study of molecular reorientation in the nematic and solid phases of 4,4′-di-*n*-butyloxyazoxybenzene

by K. CHŁĘDOWSKA†, D. CHRUŚCIEL‡, J. A. JANIK§, J. M. JANIK‖, H. KRESSE¶, H. STETTIN¶, K. OTNES*, T. STANEK‖, S. URBAN** and S. WRÓBEL**

† Institute of Mathematics and Physics of the Technical University, Rzeszów, Poland
‡Institute of Chemistry, Agricultural and Pedagogical University, Siedlce, Poland
§Institute of Nuclear Physics, Kraków, Poland
‖Institute of Chemistry, Jagellonian University, Kraków, Poland
¶Institute of Chemistry, Martin Luther University, Halle, GDR
*Institute of Energy Technology, Kjeller, Norway
**Institute of Physics, Jagellonian University, Kraków, Poland

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Dielectric relaxation measurements carried out in the nematic phae of 4,4′-di-*n*-butyloxyazoxybenzene (BOAOB) reveal fast reorientational motions of the whole molecule around the long axis ($\tau_l \sim 60$ ps) as well as slow reorientational motions of the whole molecule around the short axis ($\tau_l \sim 10^{-8}$ s). Incoherent quasielastic neutron scattering spectra obtained for nematic BOAOB, with normal and deuteriated alkoxy terminals, are interpreted as dominated by reorientation (around the C–N bonds) of moieties consisting of benzene rings coupled with alkoxy terminal chains ($\tau_l \sim 4$ ps). In addition fast conformational changes occur in these chains. Dielectric relaxation measurements reveal librations of the whole molecule in the crystal phases CI and CII accompanied by reorientation of the terminal chains in these phases. The reorientations occur on the time scale amounting to 10^{-8} s. Incoherent quasielastic neutron scattering spectra obtained for the CI and CII phases of BOAOB are interpreted as being dominated by overdamped librational motions of the moieties accompanied by fast conformational changes in the alkyl chains. The CIII phase corresponds to a normal molecular crystal.

1. Introduction

Reorientation of molecules in liquid crystal phases have been studied by various authors and by various methods (see, for example [1, 2]). Based on dielectric relaxation results it was established that in nematic phases the molecules reorientate around the short axes as well as around the long axes. These two motions differ largely in their time characteristics as the former occurs with a relaxation time of $\sim 10^{-8}$ s, whereas in the latter the relaxation time is $\sim 10^{-10}$ s. Via quasielastic neutron scattering and infrared line shape results still faster motions have been established, occurring in the region 10^{-12}–10^{-11} s. These motions have been attributed mainly to intramolecular moieties composed of the benzene rings coupled with the alkyl (or alkoxy) terminal chains. These moieties seem to be able to reorientate around single bonds connecting the benzene rings with the central bridge [1–3]. It is generally accepted that, in addition to all of these motions, conformational changes may take place in the terminal alkyl chains. These, in turn, lead to respective changes of the moment of inertia and, thus, to fluctuations of the long molecular axes with respect to the nematic director.

This picture has emerged gradually from our systematic study of the homologous series of 4,4′-di-*n*-alkyloxyazoxybenzenes ($C_nH_{2n+1}O$-ϕ-N_2O-ϕ-OC_nH_{2n+1}) carried out so far for $n = 1, 2, 3, 5$, and 7 [4–11, 16]. A new effect was then discovered for $n = 5$: in the solid phase CI, below the solid–nematic transition, both fast motions—the one revealed by dielectric relaxation measurements and that revealed by the neutrons persisted. The slow motion, connected with the reorientation of the molecule around its short axis, did not appear in this phase. All fast motions ceased below the transition to another solid phase, CII [11]. These facts are corroborated by the discussion of entropy of melting values for the series of alkoxyazoxybenzenes. In fact, the melting entropy of the $n = 5$ member has a significantly lower value than that expected from other members of the series. Thus, melting associated with some motions takes place before the transition to the nematic phase.

This paper presents an extension of our systematic study of the same series for the $n = 4$ member, i.e. for 4,4′-di-*n*-butyloxyazoxybenzene (BOAOB). We have carried out dielectric relaxation and quasielastic neutron scattering measurements for this substance in the nematic phase and in the three solid phases: CI, CII and CIII. The neutron scattering measurements were performed with a normal (d_0-BOAOB) and with an alkyl-deuteriated (d_{18}-BOAOB) substance in order to find from their comparison something about the motions in the alkyl chains. It has to be noted that the lowering of the melting entropy, mentioned previously, occurs not only for $n = 5$, but also (to a lesser extent) for $n = 4$. Therefore some of the solid phases in BOAOB may exhibit a dynamic character.

2. Phase situation

Figure 1 shows a thermal diagram obtained with a differential scanning calorimeter (Perkin–Elmer) in the Institute of Chemistry of the Martin Luther University, Halle/Saale, G.D.R. When starting with a fresh substance (i.e. the substance obtained by

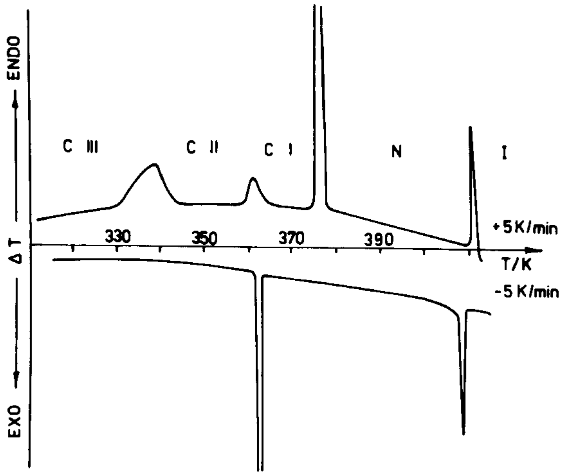

Figure 1. D.S.C. results obtained for BOAOB on heating (ENDO) and on cooling (EXO). The symbols I, N, CI, CII and CIII stand for the isotropic, nematic and the three solid phases, respectively.

crystallization from solution) two solid–solid phase transitions were revealed below the melting point. These transitions separate the three solid phases: CIII, CII and CI. However, the solid sample obtained by freezing the nematic phase does not show any transition with decreasing temperature down to room temperature. The CII and CI phases appear again after the substance has been annealed at room temperature for at least 24 hours. It seems, therefore, that the solid phase formed by freezing from the nematic phase is metastable.

Table 1. Transition temperatures T, enthalpy changes ΔH and entropy changes ΔS obtained from D.S.C. measurements on a fresh sample of BOAOB. In parentheses we give the results obtained in [12].

Transition	CIII–CII	CII–CI	CI–N	N–I
T/K	338	361	377	411
	(321)	(358)	(377)	(411)
ΔH/kJ mol^{-1}	5	1·5	21·3	1·4
	(7·2)	(1·2)	(20·3)	(1·3)
ΔS/J K^{-1} mol^{-1}	15	4	56·5	3·5
	(22·4)	(3·3)	(53·8)	(3·1)

Table 1 contains the values of the transition temperature, enthalpy and entropy changes obtained for an endothermal process starting with the fresh substance. It is worth noting that the sample annealed at room temperature shows distinctly lower transition temperatures and these agree well with the values obtained by Gruger *et al.* [12].

3. Results of dielectric studies

(*a*) *Nematic phase*

Dielectric properties of BOAOB have been studied in the same way as they were for other members of the homologous series of alkoxyazoxybenzenes [5, 6, 11, 16]. The complex dielectric permittivity, ε^* ($\equiv \varepsilon' - i\varepsilon''$) was measured in two frequency ranges: the megahertz range (0·1–12 MHz) at the Institute of Chemistry of the Martin Luther University, Halle, and the gigahertz range (1–10 GHz), at the Institute of Physics, Jagiellonian University, Krakow. This enabled us to study the two main relaxation processes that occur in liquid-crystalline phases: one connected with molecular reorientation around the short axes and the other connected with reorientation around the long axes.

Table 2. Dielectric parameters obtained for the parallel and perpendicular orientations of the nematic phase of BOAOB. The errors of the relaxation times are: ± 6 per cent for $\tau_\parallel$ and ± 10 per cent for $\tau_\perp$.

T/K	$\varepsilon_{0\parallel}$	$\varepsilon_{\infty\parallel}$	$\tau_\parallel \times 10^8$ s	$\varepsilon_{0\perp}$	$\varepsilon_{\infty\perp}$	$\tau_\perp \times 10^{12}$ s	$\alpha_\perp$
377	4·33	3·89	9·70				
379				4·66	2·50	76·0	0·25
382	4·33	3·91	6·47				
383				4·64	2·50	69·8	0·25
387				4·62	2·51	65·6	0·24
388	4·32	3·92	3·82				
393	4·31	3·93	2·33	4·58	2·52	58·3	0·22
397				4·56	2·54	54·4	0·20
401				4·54	2·54	50·6	0·21
406				4·51	2·53	46·7	0·23

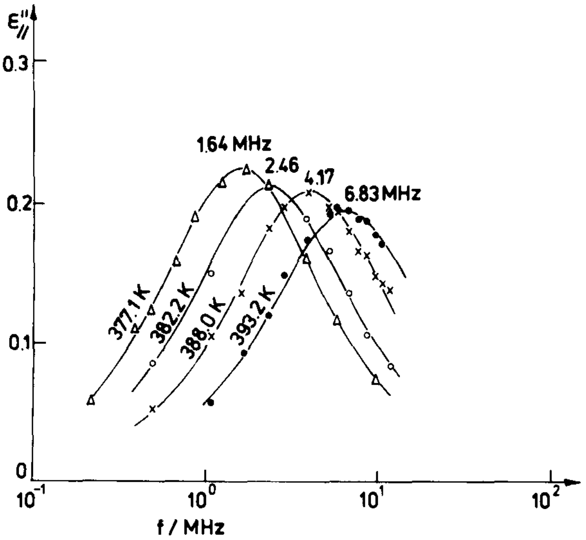

Figure 2. Dielectric losses versus the logarithm of the frequency, *f*, measured at various temperatures parallel to the director of nematic BOAOB. The curves are fitted to the experimental points using equation (1).

Figure 2 shows the frequency dependence of the dielectric losses, ε'', measured for parallel orientation of the sample (**E** $\parallel$ **B**). The experimental points satisfy very well the Debye equation

$$\varepsilon''(\omega) = 2\varepsilon''_{\max} \frac{\omega\tau_{\parallel}}{1 + (\omega\tau_{\parallel})^2}, \tag{1}$$

with $\tau_{\parallel} = 1/\omega_{\max}$. Thus the observed relaxation process is a single process and it is undoubtedly connected with the reorientation of the whole molecule around its short axis. The value of the activation barrier $E_{a\parallel}$ for this process was calculated using the Arrhenius equation and equals (112 ± 10) kJ/mole (see figure 4). It differs markedly from the value of (75 ± 3) kJ/mole obtained earlier by Mircea-Roussel and Rondelez [18].

At microwave frequencies a distinct relaxation process has been observed for the perpendicular orientation of the sample (**E** $\perp$ **B**). This is a complex process and was interpreted according to the Cole–Cole modification of the Debye equation, namely,

$$\frac{\varepsilon^*(\omega) - \varepsilon_\infty}{\varepsilon_0 - \varepsilon_\infty} = \frac{1}{1 + (i\omega\tau_\perp)^{1-\alpha_\perp}}, \tag{2}$$

where the parameter $\alpha_\perp$ is commonly interpreted as a measure of a symmetric distribution of the dielectric relaxation times $\tau_\perp$.

Figure 3 presents the Cole–Cole diagrams for both orientations of the sample in the nematic phase and for the isotropic phase. The experimental points obtained by Axmann [19] are also included. From such diagrams obtained for various temperatures the relaxation times were calculated. Figure 4 presents these relaxation times versus $1/T$. The value of the activation barrier, $E_{a\perp}$ of (23 ± 4) kJ/mol, is similar to that found for other members of this homologous series [4–7].

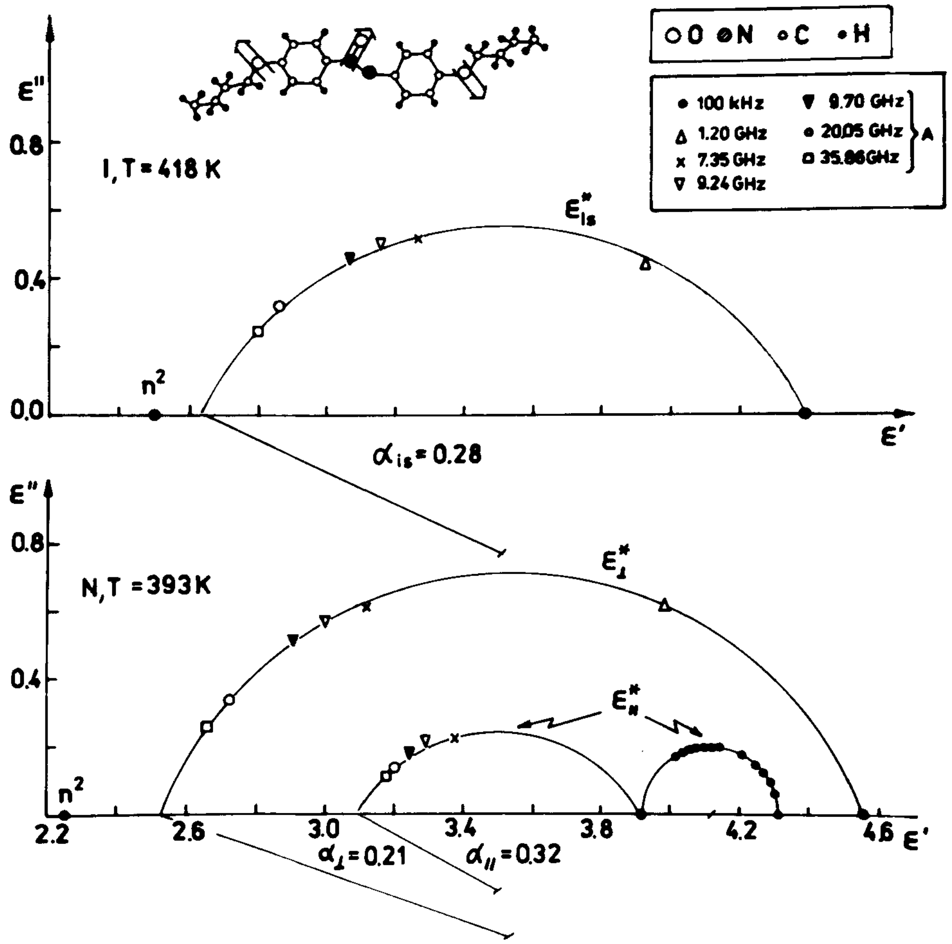

Figure 3. Cole–Cole plots for the isotropic and for the nematic phase of BOAOB (two orientations). The experimental points obtained by Axmann (A) [19] are also included. The insert shows the positions of the dipole moments in the molecule.

(*b*) *Solid phases*

In figure 5 the results of the dielectric permittivity measurements are shown. Starting from the nematic phase ε_0 and ε' fall at the freezing point to values which are distinctly higher than the square of the refractive index. With further lowering of the temperature down to room temperature these values continuously decrease. Only at one measurement the ε_0 show a small step, at about 346 K which perhaps reflects the phase change CI–CII. At room temperature the permittivities decrease slowly with time and after about 24 hours (sometimes even longer) a constant value of about 2·6 was reached. On heating, the permittivities start to increase at the CIII–CII phase transition but with no change at the CII–CI phase transition. The dielectric parameters of solid BOAOB do not depend on the magnetic field strength ($B = 0{\cdot}5\,\mathrm{T}$).

The results obtained evidently show that in both, the CII and the CI, phases a dielectric relaxation process occurs. Its dielectric increment, $\varepsilon_0 - n^2 \approx 0{\cdot}5$, is about the same as that observed earlier for the CI phase of 4,4′-di-*n*-pentyloxyazoxybenzene (POAOB) [11]. However, for BOAOB, in contrast to POAOB, we did not observe any

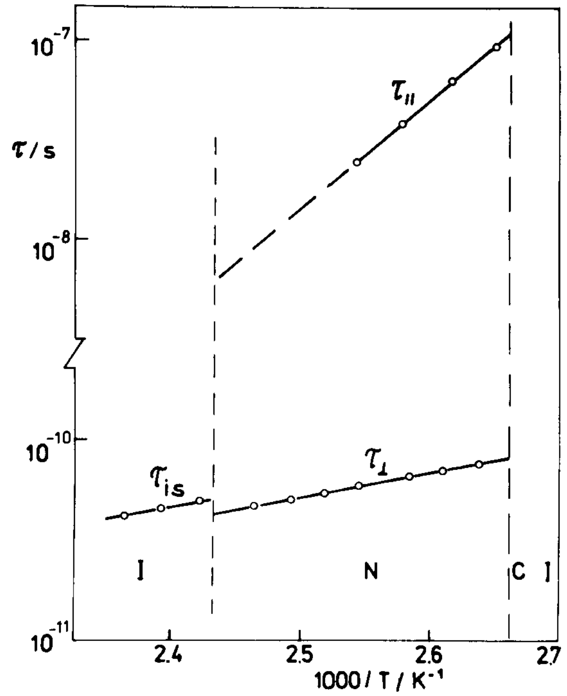

Figure 4. Dielectric relaxation times versus reciprocal temperature for the isotropic and nematic phases of BOAOB. The lines are obtained by fitting to the Arrhenius equation.

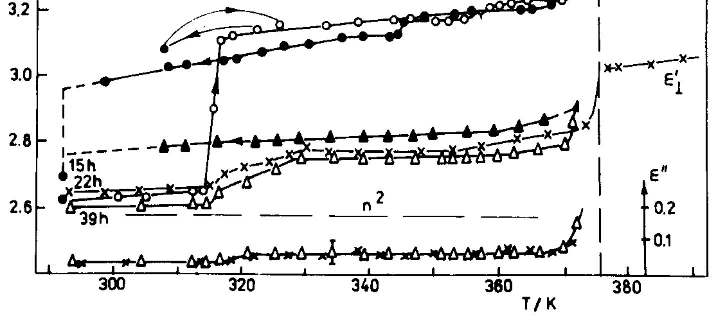

Figure 5. Results of dielectric investigations of the solid phases of BOAOB at megahertz and gigahertz frequencies.

relaxation process at microwave frequencies. As can be seen in figure 5 the dielectric losses ε'' are very small and do not depend on frequency in the range between 1·2 GHz and 9·2 GHz. At the same time, again in contrast to POAOB, we observe a relaxation process at megahertz frequencies in both the CI and the CII phases of BOAOB.

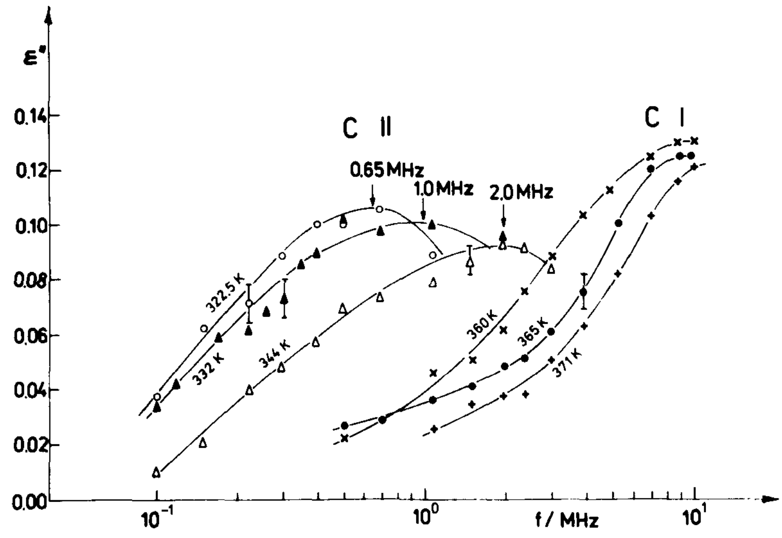

Figure 6. Dielectric losses versus the logarithm of the frequency measured at different temperatures of solid CII and CI phases of BOAOB. The curves are guides to the eye only.

Figure 6 shows the broad $\varepsilon''(f)$ spectra with well defined maxima. As we can see the $\varepsilon''_{\max}$ values and the critical frequencies f_c ($\equiv 1/2\pi\tau$) exhibit a distinct change at the phase transition. Assuming that they are both Debye-type relaxation processes we can estimate the respective dielectric increments $\varepsilon_0 - \varepsilon_\infty = 2\varepsilon''_{\max}$. These increments are equal to ~0·20 in the CII phase and ~0·27 in the CI phase. As it may be seen from figure 5, these values are about half of the $\varepsilon_0 - n^2$ values, but in addition they are nearly equivalent to the values of $\varepsilon_0 - \varepsilon'(f/\mathrm{GHz})$ where $\varepsilon'(f/\mathrm{GHz})$ denotes the permittivity measured at microwave frequencies. It seems therefore that the relaxation process taking place in the megahertz region is well separated from that appearing at much higher frequencies.

The megahertz relaxation process observed in the CI and CII phases of BOAOB is characterized by a relaxation time, whose value is very close to that obtained at megahertz frequencies for the **E** ∥ **B** orientation of the nematic phase (compare figures 6 and 2). It is tempting to suppose hence that in these phases reorientation of molecules around their short axes takes place. However, if these phases were not solid but only smectic, a distinct increase of the relaxation times $\tau_\parallel$ in comparison with the nematic phase would be observed [17]. Also the ε' values would not change so drastically at the transition. Moreover, a preliminary X-ray study shows that at least the CII phase of BOAOB is a crystalline solid with well defined sharp Bragg peaks. Taking all these facts into account we exclude the possibility of molecular reorientation around the short axis in these phases. Thus, the observed megahertz relaxation process seems to be connected with the side dipole reorientation around perhaps the N-phenyl bonds (see the insert in figure 3). Such a motion seems possible due to a lattice expansion at the CIII–CII phase transition. The CII–CI transition facilitates this motion and because of this a small but distinct jump in relaxation times is observed at the CI–CII transition.

The remaining part of the dielectric increment, i.e. of the $\varepsilon'(f/\mathrm{GHz}) - n^2$ value, can then be attributed to a motion of the central dipole moment of the molecule. The lack of the ε' dispersion and practically zero values of ε'' at microwave frequencies (see figure 5) indicate that it is not a normal relaxation process. Similar behaviour has been observed for some uniaxial plastic-crystalline phases [20, 21] and interpreted as a result of broad angle dipole librations in potential wells (the so called librational phases).

Summarizing, we are inclined to interpret the dielectric properties of solid phases of BOAOB as follows. In the CIII phase all dipole moments of the molecules are frozen out. A lattice expansion taking place at the CIII–CII phase transition makes enough room for reorientational motions of the molecular terminal groups with simultaneous broad angle librations of the molecule as a whole. The next phase transition facilitates these motions but does not change their character.

4. Quasielastic neutron scattering results for nematic BOAOB

The incoherent quasielastic neutron scattering method makes use of the exceptionally large cross-section for scattering of neutrons by hydrogen. If hydrogen atoms perform stochastic reorientations or/and overdamped librations around an axis, the scattered neutron energy transfer distribution, being peaked around zero energy transfer, shows a quasielastic component besides an elastic one. The width (or rather shape) of the quasielastic component provides information concerning the time characteristics of the motion in question, whereas the ratio of the elastic or quasielastic (or what is normally used—the ratio of the elastic to total) intensities provides information concerning the model by which the motion in question can be approximated. It should be stressed once more that the quasielastic neutron scattering method responds to hydrogen atom motions. If a part of the molecule is deuteriated, it appears to be masked, since the incoherent cross-section for deuterium is only about 2 b, compared with approximately 80 b for hydrogen. It should also be pointed out that the detection window of the neutron method is in the characteristic time range 10^{-12}–5×10^{-11} s (at least for our data); the faster motions give quasielastic components which are so broad that they cannot be distinguished from the inelastic background, whereas the broading produced by the slower motions are so small that the spectrum cannot be distinguished from the instrumental resolution function.

The neutron scattering measurements were carried out on the neutron time-of-flight spectrometer installed at the cold source of the JEEP II reactor in the Institute for Energy Technology, Kjeller, Norway. The incident neutron energy was 4·67 meV. The energy resolution of the spectrometer was 0·13 meV. Two scattering angles 30° and 40° corresponding to the momentum transfers of 0·78 and 1·03 $Å^{-1}$, respectively, were used in the measurements. The time-of-flight spectra were converted to an energy scale. The sample was mounted in an oven with a temperature control. The measurements were carried out for the CIII (293 K), CII (343 K), CI (362 K and 371 K) and nematic (394 K) phases.

The inelastic background was estimated and drawn as a smooth line through the ends of the quasielastic wings of the spectra. The values of this line were subtracted in order to obtain the isolated quasielastic plus elastic components. The elastic peak of the CIII phase was used to determine the resolution function of the instrument. The model spectra were convoluted with the resolution function before being fitted to those of the experiment. The model fittings were made on a CYBER 72 computer using the program MINUIT from the CERN Computer Library [14]. By using a χ^2 test the best fit values of the adjustable parameters of the model were obtained.

It has to be pointed out that it is rather difficult to formulate an accurate statement concerning the way the molecules are reorienting. One reason is that the quasielastic neutron scattering experiment is often not sufficiently sensitive to distinguish between various reorientational models; the second reason is connected with an uncertainty concerning the distribution of conformations in the alkyl chains. This latter factor makes it impossible to calculate correctly the reorientation radii of all hydrogen atoms involved in reorientation, which leads to errors in the correlation time determination. Taking this into account, the assumption that the alkyl chains are in the trans-conformation, must be considered to be rather arbitrary.

We have decided to perform fittings of three models to our experimental scattering data:

Model 1 assumes reorientation of the whole molecule via rotational diffusion around the long molecular axis, taken as the axis associated with the smallest value of the moment of inertia. The possible existence of other motions which are fast and so detectable by neutrons, is evidenced via the negative p-parameter, which represents the reduction of the elastic component due to these motions. The fitted function is

$$F(\kappa, \omega) = \sigma_{\text{inc}} \frac{k_f}{k_i} \exp\left(\frac{\hbar\omega}{k_B T}\right) [p\delta(\omega) + (1 - p)S(\kappa, \omega)] * G(\omega), \qquad (3)$$

where σ_{inc} is the incoherent neutron scattering cross-section for hydrogen, k_f and k_i are the scattered and initial neutron wave vectors respectively, and

$$\hbar\omega = E_f - E_i$$

and

$$\hbar\boldsymbol{\kappa} = \hbar(\mathbf{k}_f - \mathbf{k}_i)$$

are the neutron energy and momentum transfers, respectively. p is the parameter which represents the deviation of the elastic part of the scattering from the applied model. $G(\omega)$ is the spectrometer instrumental function.

The model scattering function is (for references see, for instance, [2])

$$S(\kappa, \omega) = f_0(\kappa)\delta(\omega) + \frac{2}{\pi} \sum_{k=1}^{\infty} f_k(\kappa) \frac{\Gamma_k}{\Gamma_k^2 + (\hbar\omega)^2}, \qquad (4)$$

where $\Gamma_k = \hbar k^2/\tau_1$, and

$$f_k(\kappa) = \frac{1}{2} \sum_i a_i \int_{-1}^{1} J_k^2(\kappa d_i \sin\beta) d\cos\beta; \qquad (5)$$

here a_i is the fraction of hydrogen atoms (in the molecule) whose radius of reorientation is d_i and J_k are the cylindrical Bessel functions. The procedure contained in equation (5) presents averaging over various director orientations (β), since our nematic sample was not oriented. In the model the d_i values (obtained with the assumption of the trans conformation of the alkyl chains) are contained in the interval between ~0·6 Å and ~2·6 Å.

The parameters obtained by fitting this model were the reorientational correlation time τ_1 and the factor of deviation of the elastic component from the rotational diffusion model, p.

Model 2 assumes reorientation of molecular moieties consisting of the benzene rings together with the alkoxy chains coupled (at least on the neutron time scale) with the rings. Reorientation occurs around the single bonds connecting the rings with the azoxy groups (C–N bonds), via rotational diffusion. The possible existence of other motions is evidenced via the p-parameter, as in model 1. The corresponding fitted function is the same as in model 1. In this model the d_i values are contained in the interval between ~0·6 Å and ~2·9 Å. The parameters obtained from the fitting are τ_1 and p.

Model 3 assumes the reorientation of molecular moieties via instantaneous 180° angular jumps around the same axis as in model 2. The possible existence of other motions is evidenced via the p parameter, as in models 1 and 2. The d_i values are the same as in model 2. The corresponding scattering function is (for references see [2])

$$S(\kappa, \omega) = \frac{1}{2}\sum_i a_i\left[\left(1 + \frac{\sin 2\kappa d_i}{2\kappa d_i}\right)\delta(\omega) + \frac{1}{\pi}\left(1 - \frac{\sin 2\kappa d_i}{2\kappa d_i}\right)\frac{\Gamma}{\Gamma^2 + (\hbar\omega)^2}\right], \tag{6}$$

where $\Gamma = \hbar/\tau$, and τ is the residence time between two successive instantaneous angular jumps. The parameters obtained in the fitting are τ and p.

It should be pointed out that the reorientation radii of the hydrogen atoms of the extended parts of the alkyl chains are, especially for models 2 and 3, quite large. It may be therefore that the reorientation of the moieties is connected with conformational changes in the alkyl chains, which are taken care of approximately by the parameter p of the model. This is no doubt only a very primitive way of describing all the complicated motions that take place.

Figure 7 presents examples of the neutron scattering spectra obtained in the nematic phase and at one particular scattering angle (40°), for BOAOB-d_0 and BOAOB-d_{18}. The fitted curves can be attributed equally well to any of the three models. Thus the quality of fits (represented by the χ^2 values) cannot be used for a model choice and so we must find other arguments leading to such a choice.

Table 3 lists the p and τ_1 (or τ) values obtained for all experiments in the nematic phase via the three models. We can see that the characteristic times are not very different for the three models and, in addition, are practically the same for both, BOAOB-d_0 and -d_{18}. This can be interpreted firstly, as evidence of a fast reorientational motion with a characteristic time of several picoseconds and, secondly, as an indication that the alkoxy chains are coupled with the benzene rings for a time longer than the long time limit of the neutron scattering detection window which is approximately 5×10^{-11} s. The latter statement follows from the fact that masking the alkyloxy chains (by deuteriation) and focusing our attention on the benzene rings does not lead to any change in the effective characteristic time.

Table 3. p and τ_1 (or τ) parameters obtained in fitting the three models to the quasielastic neutron scattering results for nematic BOAOB-d_0 and -d_{18} at 394 K.

		Model 1		Model 2		Model 3	
Substance	Scattering angle	p (per cent)	τ_1/ps	p (per cent)	τ_1/ps	p (per cent)	τ/ps
BOAOB-d_0	30°	−74	3·9	−15	4·2	−27	6·5
BOAOB-d_0	40°	−56	4·1	−13	4·8	−36	6·1
BOAOB-d_{18}	30°	14	3·3	14	3·2	6	5·4
BOAOB-d_{18}	40°	8	5·2	11	4·9	−3	6·4

Moreover, we can see that for the undeuteriated substance the elastic peak is quite considerably reduced ($p \sim -60$ per cent) for model 1; this reduction takes place, although to a lesser extent, for models 2 and 3 ($p \sim -14$ per cent and -30 per cent, respectively). We believe that such a great reduction disqualifies model 1. The moderate reduction obtained in models 2 and 3 seems much more realistic. Model 2, for instance, would mean therefore that the molecular moieties reorient with a correlation time of 4–5 ps and that in addition, there exist relatively frequent conformation changes in the alkyl chains, responsible for the reduction of the elastic component by about 14 per cent. (Needless to say such conformational changes must lead to rapid changes of the long molecular axes, which is another way of discussing these phenomena).

The fact that the deuteriated substance (in which the alkyl chains are masked) does not show any reduction of the elastic peak corroborates the statement that the additional motion in question occurs in the chains. However, the p-value is now not zero (which would correspond to pure rotational diffusion) but it amounts to $\sim +12$ per cent (or at least several per cent for model 3). This can be understood if we remember that deuterium has a non-negligible incoherent scattering cross-section amounting to 2 b. That gives 36 b as compared to about 600 b for the eight hydrogens. This, together with the contribution from the aluminium sample holder and the oven, can explain approximately the positive p. It should be added that it is natural that models 1 and 2 are practically undistinguishable for BOAOB-d_{18}. As a matter of fact, when the alkyl chains are masked, the two models represent practically the same situation for the hydrogen atoms belonging to the benzene rings.

Summarizing we may conclude that in nematic BOAOB the motion dominating the quasielatic neutron scattering spectra is the moieties reorientation, occurring either via rotational diffusion or via jumps on a time scale of several picoseconds. Additionally, fast conformational changes occur in the alkyl chains.

5. Quasielastic neutron scattering results for the solid phases of BOAOB

As we can see from figure 8 the neutron scattering spectra of CI and CII phases of BOAOB show wings besides the elastic component. Originally we were tempted to believe that in the two phases, CI and CII, the moieties have a considerable freedom of reorientation around the C–N axes and thus the spectra can be well described by equation (3) with S given by either equation (4) or (6). Formally this is possible, as we can see from a comparison of the model curves with the experimental points in figure 8. It is, however, quite evident that the p parameter values obtained by the fitting cannot now be regarded as more corrections of reorientational models (see table 4). These (now positive) p values are about 50 per cent which means that the elastic component is 50 per cent larger than what could be expected from a reorientational model. We should note here that it is formally possible to understand such strong elastic components (for instance on the basis of an equation similar to (6)) if we assume that the molecules perform no real reorientation (180° angular jumps) but angular jumps confined to an angle considerably smaller than 180°. Then the jump length is reduced, which formally leads to a stronger elastic part as compared to the quasielastic component, and as indeed seen in our spectra.

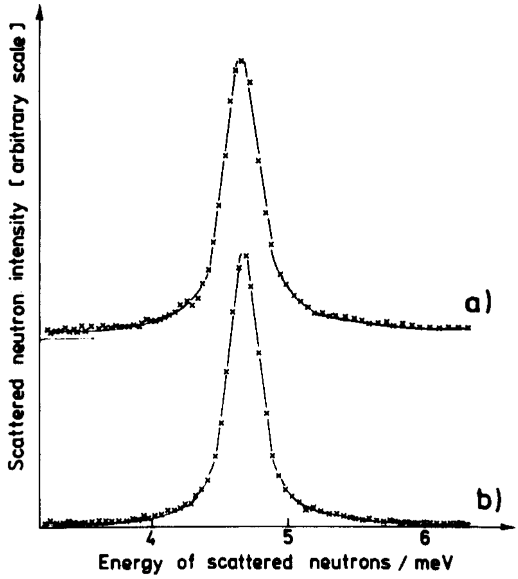

Figure 7. Incoherent quasielastic scattering spectra of nematic BOAOB; temperature 394 K. Scattering angle 40°. The solid line represents the results of model fitting. Models 1, 2 and 3 give indistinguishable curves. (*a*) BOAOB-d_0 (*b*) BOAOB-d_{18}.

Table 4. p and τ parameters obtained by formal fitting of equation (6) to the neutron scattering for BOAOB-d_0 and -d_{18} in CI and CII phases.

			Model 3	
Substance	Temperature (phase)	Scattering angle	p (per cent)	τ/ps
BOAOB-d_0	371 K (CI)	40°	41	5·7
BOAOB-d_0	363 K (CI)	40°	41	2·6
BOAOB-d_0	343 K (CII)	30°	61	7·2
BOAOB-d_0	343 K (CII)	40°	59	7·1
BOAOB-d_{18}	371 K (CI)	30°	58	3·2
BOAOB-d_{18}	371 K (CI)	40°	65	4·3

Note: Similar p and τ values are obtained when models 1 and 2 are formally applied for such fitting.

Let us point out however that such a confinement to smaller angles either in models 2 or 3 is in fact practically indistinguishable from overdamped librations of the moieties in question. Indeed, the analysis of the neutron spectra of hydrogen atoms performing librations gives as a result a spectrum with two satellite peaks (one corresponding to energy gain and the other to energy loss) besides the elastic peak when the damping is small, and a quasielastic spectrum (peaked at zero energy transfer) when the damping is large (see, for instance, [15]). The spectrum in this latter case can be described as consisting of an elastic part plus a lorentzian to which the quasielastic component is approximated. This is, in fact, the reason why equation (6) can be formally used. Another equivalent treatment would be via a formula derived by Dianoux and Volino [22] for a random motion of a uniaxial rotator in an N-fold cosine potential.

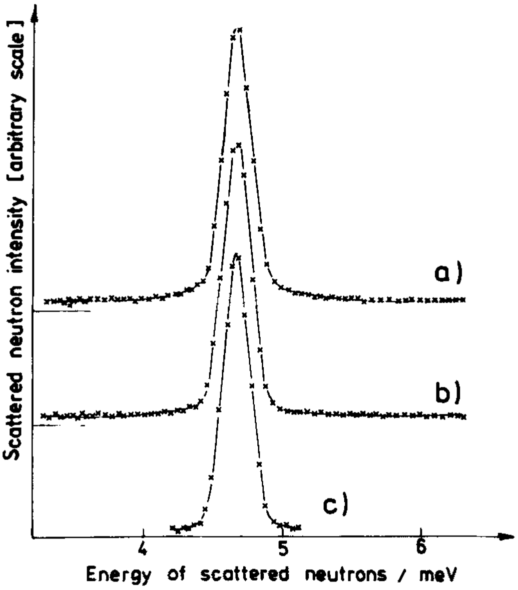

Figure 8. Incoherent neutron quasielastic scattering spectra of solid BOAOB-d_0; scattering angle 40°. Solid line represents the result of formal model fitting. Models 1, 2 and 3 give indistinguishable curves. (*a*) CI phase at 371 K. (*b*) CII phase as 343 K. (*c*) CIII phase at room temperature (these data represent the instrumental resolution).

The interpretation of the time parameter τ is perhaps not so simple in the overdamped librational picture. Roughly, it can be understood as the life time of a libration or the time between successive jumps confined to an angle smaller than 180°. This time is longer for the CII phase than for the CI, which is natural. Moreover, it is practically the same for BOAOB-d_0 and -d_{18}, which probably means that the alkyl chains move together with the benzene rings (within the neutron time scale) forming the moieties.

The fact that the p value for BOAOB-d_{18} is larger than that for BOAOB-d_0 (for the CI phase it amounts to about 60 per cent as compared to approximately 40 per cent) may mean that the motion additional to the librations of the moieties exists in the alkyl chains. This motion is perhaps connected with conformational changes in the alkyl chains, as discussed for the nematic phase.

Since the quasielastic neutron scattering components of the solid spectra are weak, many of the statements concerning the results for the CI and CII phases have a somewhat qualitative character. Nevertheless, summarizing, we are inclined to believe that the motion dominating in spectra for BOAOB in the CI and CII phases is an overdamped libration of the moieties. This seems to be corroborated by the dielectric relaxation measurements as described previously. An indication of occurrence of fast conformational changes in the alkyl terminals also seems to exist.

The neutron scattering spectrum of the CIII phase cannot be distinguished from the instrumental resolution function.

6. Discussion and conclusions

The study of a substance with different experimental methods provides complementary information on the molecular processes taking place. This sort of study is especially important for such complicated systems as liquid crystalline materials. The results of dielectric relaxation and quasielastic neutron scattering measurements, presented in this paper, show that although these methods respond to molecular reorientational motions differently it is possible to find a consistent picture of the dynamic processes taking place. The confrontation of both types of results leads to a deeper understanding of the nature of molecular motions in all of the phases.

In the nematic phase of BOAOB the molecules perform two main reorientational motions: one around the short and the other around the long molecular axis. The dielectric relaxation method can investigate them both, whereas quasielastic neutron scattering can in principle detect only the faster motion. However, in BOAOB a distinct difference between the dielectric relaxation time $\tau_{\perp}^{DR}$ and the neutron correlation time τ_{l}^{QNS} has been observed similar to the findings of the previous investigations [2, 11]. The ratio $\tau_{\perp}^{DR}/\tau_{l}^{QNS}$ at 394 K is approximately 11, as for other compounds, and cannot be explained by experimental errors or by an influence of intermolecular correlation effects on $\tau_{\perp}^{DR}$; this problem has been discussed in detail in [6]. The conclusions are the following: each method responds to a different motion, the reorientation of the whole molecule around the long axis is seen in dielectric relaxation studies, while the reorientations of the molecular moieties around the N-phenyl bonds are evidenced in neutron scattering measurements. Moreover, the existence of faster intramolecular motions is clearly observed in the dielectric relaxation results. As we can see in figure 3, for the **E** ⊥ **B** geometry, the $\alpha_{\perp}$ parameter is about 0·20 which means that there is a distribution of relaxation times. This distribution is partly caused by the conformational changes of the alkyl chains but predominantly by the fact that partial dipole moments of the molecule take part in reorientational motions with various rates.

Thus, we can conclude that in the nematic phase of BOAOB the molecule as a whole reorients around the long axis with characteristic time of approximately 60 ps, and in the same time the moieties perform faster intramolecular rotations around the N-phenyl bonds with $\tau_l \approx 6$ ps. These two motions are influenced by the conformational changes of the terminal alkyl chains.

The properties of solid BOAOB seem to be unusual for liquid-crystalline materials. D.S.C. as well as dielectric measurements show that polymorphism of the solid samples may occur only in a fresh or annealed sample. Freezing the nematic phase leads to a metastable solid which slowly transforms to a stable one. The kinetics of this transformation have not yet been established. Both experimental techniques used in these investigations detect molecular reorientational motions in the two solid phases, CI and CII, whereas the CIII phase is a normal crystal. It is natural to compare the properties of CI and CII phases of BOAOB with the properties of the plastic-crystalline phase (CI) of the next member in this series, POAOB [11]. It should be pointed out once more that the dielectric properties of the phases in both substances differ in the sense that in the latter case the dielectric losses attain noticeable values and depend on frequency, whereas in the former the losses are negligibly small up to 10 GHz. The broad $\varepsilon''(f)$ spectrum obtained for the plastic phase of POAOB ranges from ~10 MHz to ~10 GHz, which suggests the existence of two overlapping relaxation processes: one (slower) associated with the reorientation of the central dipole moment and the other (faster) associated with the reorientations of the terminal dipole moments. In the BOAOB case, however, the slower process is indeed seen at megahertz frequencies (see figure 6) but the faster seems to be limited to broad angle dipole librations. Such confined librations of a dipole moment do not produce dielectric losses, since they have a resonant character rather than a relaxational one.

The analysis of the small quasielastic broadening of the quasielastic neutron scattering spectra measured in the CI and CII phases of BOAOB corroborates the interpretation of the dielectric relaxation studies. However, rather large systematic errors in the dielectric measurements caused by inhomogeneities in the solid sample obtained when freezing from a liquid, on the one hand, and the rather poor resolution of the spectrometer used in neutron studies, on the other do not leave room for the speculations about the angle to which the librational motions are confined.

Summarizing we can conclude that in the CI and CII phases of BOAOB the moieties take part in confined librational motions and from time to time they are able to reorient. The bridging part of a molecule also librates but without any detectable losses at microwave frequencies.

We must admit, however, that our picture emphasizing two motions (rotation around the long axis and that of the moieties) is no doubt oversimplified and has to be treated as a tentative only. Perhaps nearer the truth is the more qualitative picture, which may be described as follows. In the nematic phase there exist many types of molecular motions with the whole spectrum of correlation times. The quasielastic component of the neutron scattering spectrum is, therefore, a result of many components. The latter statement is enhanced by the fact that various hydrogen atoms reorientate with different gyration radii, thus leading to different quasielastic components. When performing neutron scattering experiments with various energy resolutions, some region of correlation time is emphasized at each resolution. Therefore, the conclusions derived from the magnitude or comparison of correlation times are not very convincing. This is the reason why we suggest in this paper an analysis of another parameter connected with fitting quasielastic neutron scattering spectra, i.e. the parameter p representing the excessive elasticity (negative or positive). The approximate adequacy of a model (no doubt too simple) is then based upon an observation that the p parameter is for it nearly equal to zero, or at least it is nearer to zero than the other model. This is why we give in this paper a preference of the moieties reorientation above the whole molecule reorientation as dominating (but *only* dominating) the neutron scattering spectra, in the nematic phase.

In a similar way, our conclusions derived from the dielectric relaxation experiments are tentative. Here, we certainly have the right to say that the GHz relaxation region is complex and consists of the whole spectrum of correlation times. This statement is similar to that derived from neutron scattering and is based on the lowering of the Cole–Cole diagram. It is no doubt true, when expressed in such a qualitative form. More specific statements, however, being based upon a discussion of connections between the molecular dipole moments and the respective dielectric increments, are much less certain. In particular this applies to conclusions about reorientational motions of molecular fragments.

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