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A quasielastic neutron scattering study of molecular reorientation in the nematic phases of PAP and POAB

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We present the results of Q.N.S. studies for two members of the homologous series of alkoxyazoxybenzenes, $C_nH_{2n+1}O\text{–}\phi\text{–}N_2O\text{–}\phi\text{–}OC_nH_{2n+1}$; PAP ($n = 2$) and POAB ($n = 3$). The Q.N.S. measurements were performed on the non-deuteriated (d_0-PAP and d_0-POAB) and the chain deuteriated samples, d_{10}-PAP and d_{14}-POAB. Three models were fitted to the experimental data: (1) uniaxial rotational diffusion of the molecule around the axis with the smallest moment of inertia, (2) uniaxial rotational diffusion of the two moieties of the molecule around the N–ϕ bonds, (3) 180° instantaneous jumps of the two moieties of the molecule around N–ϕ bonds. We have assumed the molecule to exist in the trans conformation. The translational diffusion of the molecules and the methyl groups' reorientation were neglected. It turned out that model (3) does not describe the experimental data well. Models (1) and (2) describe the experimental data equally well, giving no preference for the axis of rotation. However, comparison of our results with those obtained from dielectric relaxation suggests the choice of model (2) as responsible for the Q.N.S. data. The correlation times determined by fitting to both rotational diffusion models are of the order of several picoseconds. However, the correlation times determined for d_{10}-PAP and d_{14}-POAB are two or three times longer than for d_0-PAP and d_0-POAB, respectively, which indicates the existence of additional motion of the end chains.

1. Introduction

The study of stochastic reorientation in the nematic phase of 4,4′-dimethoxy-azoxybenzene or para-azoxyanisole ($CH_3O\text{–}\phi\text{–}N_2O\text{–}\phi OCH_3$) has a long history. Fast reorientation processes in the range 10^{-11}–10^{-12} s have been detected by various methods, for example, dielectric relaxation [1–3], far-infrared absorption i.r. [4–6], Raman scattering [7–9], N.M.R. [10–12] and Q.N.S. [13–23]. It was suggested by Janik *et al.* [24] that the two anisole moieties of PAA reorient separately around the N–ϕ bonds on the picosecond time scale. The molecule as a whole rotates around its long axis on a longer time scale. Recently this seems to have been confirmed by theoretical calculations [25, 26] and N.M.R. investigations [27].

Only HOAB ($n = 7$) of the homologous series of alkoxyazoxybenzenes ($H_{2n+1}C_nO\text{–}\phi\text{–}N_2O\text{–}\phi\text{–}OC_nH_{2n+1}$) (besides PAA, $n = 1$) has been studied with respect to the fast reorientation of its molecules in the liquid-crystalline phase; the methods used were dielectric relaxation [28, 29] and Q.N.S. [30]. In this paper we present the results of Q.N.S. studies for two other members of this series: PAP ($n = 2$) and POAB ($n = 3$).

2. Experimental

The Q.N.S. measurements were carried out on the neutron time-of-flight spectrometer (T.O.F.) installed at the cold source of the JEEP II reactor in the Institute for Energy Technology, Kjeller, Norway. The incident neutron energy was 4·2 meV. The energy resolution of the spectrometer was 0·15 meV. Three momentum transfers $Q = 0{\cdot}74, 0{\cdot}97$ and $1{\cdot}20\ \text{Å}^{-1}$ were covered by most of the measurements. The spectra were obtained for the solid phases (at 100°C and 70°C) and the nematic phases (at 140°C and 120°C) of PAP and POAB, respectively. The results for the solid phases were used to determine the inelastic background and the resolution function. It was checked, that the resolution function so obtained does not differ from that found from the scattering of other hydrogenous solids in which the reorientational motions either did not exist at all or were frozen at sufficiently low temperatures. The measurements were performed on the non-deuteriated (d_0-PAP and d_0-POAB) and the chain deuteriated samples (d_{10}-PAP and d_{14}-POAB). The model fittings were made on the CYBER 72 computer using the program MINUIT from the CERN Computer Library [31].

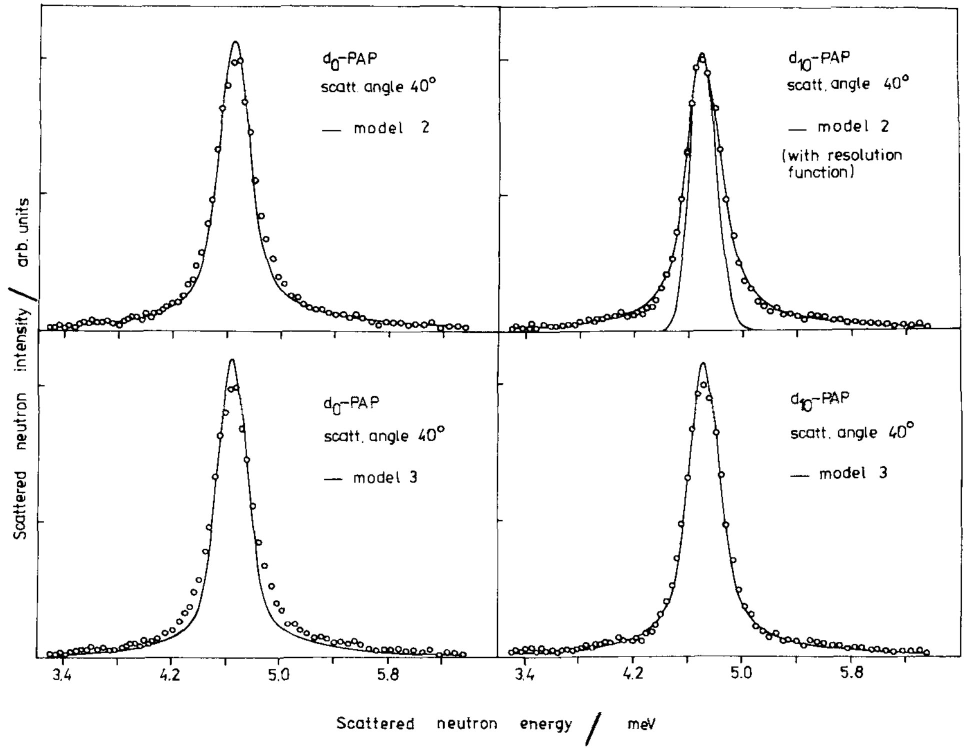

Figure 1. Examples of the fit of two reorientational models to the experimental Q.N.S. data for d_0-PAP and d_{10}-PAP in the nematic phase.

3. Results and discussion

Three models were fitted to the experimental data:

(1) uniaxial rotational diffusion of the whole molecule around the axis with the smallest moment of inertia [21], the adjustable parameter is the reorientational correlation time, τ_1;

(2) uniaxial rotational diffusion of the two moieties of the molecule around the N–ϕ bonds, the adjustable parameter is the reorientational correlation time, τ_1;

(3) 180° instantaneous jumps of the two moieties of the molecule around N–ϕ bonds [21], the adjustable parameter is the average time between jumps, τ.

We assume that the molecules exist in their trans conformations and the radii of rotation of all the protons with respect to both axes mentioned were calculated for this conformation. Examples of the fitting of the models are shown in figures 1 and 2 for

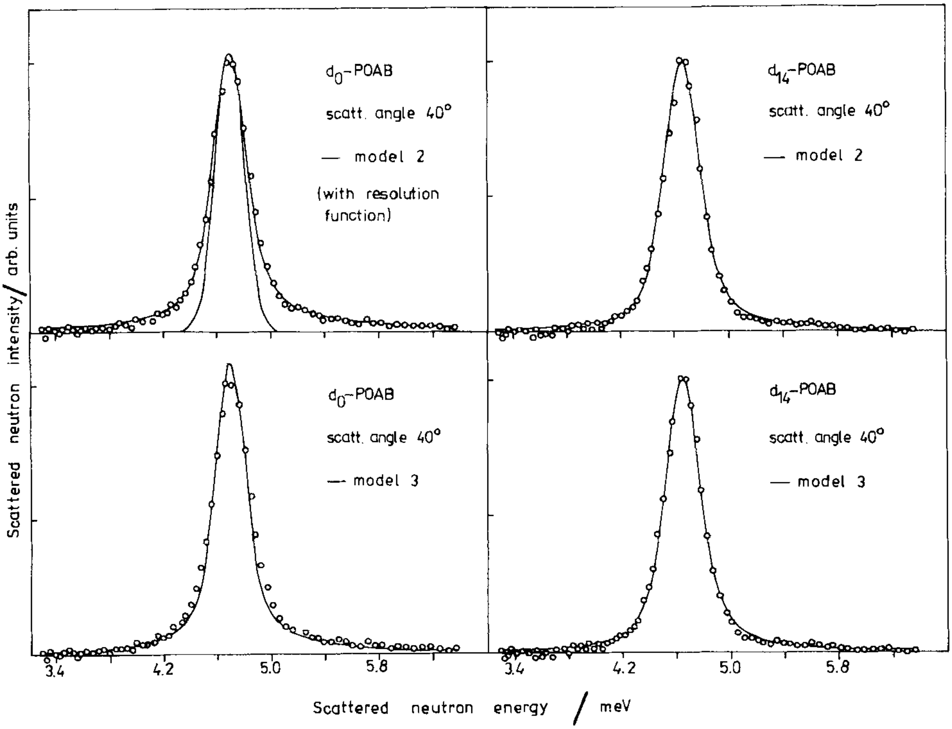

Figure 2. Comparison of two reorientational models with the experimental Q.N.S. data for d_0-POAB and d_{14}-POAB in the nematic phase.

Table 1. The values of the characteristic times and the sum of the squares of the deviations, χ^2, for the models described in the text for the nematic phase of PAP.

		Model 1		Model 2		Model 3	
	Q/Å^{-1}	τ_1/ps	χ^2	τ_1/ps	χ^2	τ/ps	χ^2
	0·74	2·6	1·4	3·7	0·9	4·7	12·7
d_0-PAP	0·97	2·3	10·6	2·3	5·6	3·9	13·5
	1·20	2·2	18·2	2·2	10·2	3·6	32·1
	Average	2·4	10·1	2·7	5·6	4·1	19·5
	0·74	4·3	2·3	4·2	2·3	5·8	2·9
d_{10}-PAP	0·97	5·2	1·8	5·4	1·7	4·9	8·2
	1·20	5·4	5·4	5·8	5·4	3·9	24·2
	Average	5·0	3·2	5·1	3·1	4·9	11·8

Table 2. The values of the characteristic times and the sum of the squares of the deviations, χ^2, for the models described in the text for the nematic phase of POAB.

		Model 1		Model 2		Model 3	
	$Q/\text{Å}^{-1}$	τ_1/ps	χ^2	τ_1/ps	χ^2	τ/ps	χ^2
d_0-POAB	0·97	2·7	5·0	3·7	1·5	4·4	7·0
	1·20	2·6	4·0	3·8	1·9	3·8	13·4
	Average	2·7	4·5	3·8	1·7	4·1	10·2
d_{14}-POAB	0·97	8·2	1·8	8·7	1·8	7·5	2·1
	1·20	9·0	1·6	9·4	1·6	4·7	3·1
	Average	8·6	1·7	9·0	1·7	6·1	2·6

PAP and POAB, respectively. In tables 1 and 2 the values of the characteristic times for all the models are listed. As we can see from figures 1 and 2 the diffusion models describe the experimental data much better than the model of 180° jumps around the para axes. Taking into account the results obtained by Chledowska *et al.* [34] it may be said that this model does not apply for the description of the pico-second reorientation of the molecules in liquid-crystalline phases.

The diffusion models describe the experimental data quite well for POAB but for PAP the fit is slightly worse. There are two reasons which may explain this discrepancy. First of all translational diffusion of the PAP molecules was not taken into account as the diffusion coefficient is not known. For PAA, translational diffusion (the diffusion coefficient, D, is $4{\cdot}1 \times 10^{-6}\,\text{cm}^2\,\text{s}^{-1}$) influences the spectra and it must be considered when fitting the model scattering law to the PAP neutron data. The diffusion coefficient for PAP should be less than for PAA as the molecules are larger, but the diffusion process may still influence the Q.N.S. spectra. We believe that for POAB translational diffusion may already be neglected in describing our neutron data.

The second reason that the Q.N.S. spectra predicted by the diffusion models deviate from the experimental results is that we have not considered the possible reorientation of the six terminal protons of the alkyl chains. For PAA such a reorientation on the picosecond time scale (120° jumps of the terminal protons around the threefold symmetry aixs of the CH_3 groups) was found to occur independently of the reorientation of the whole molecule [21, 23]. It has a significant influence on the Q.N.S. spectra (6 protons out of 14 reorient in this way) although the radius of such reorientation is smaller ($\sim$ 1 Å) than that of the protons of the benzene ring (2·4 Å). For d_0-PAP (6 protons out of 18 reorient by 120° jumps) and d_0-POAB (6 protons out of 22 perform 120° jumps) the methyl group reorientation contributes less to the Q.N.S. scattering law than for d_0-PAA but the effect may still be quite pronounced. This second reason for the deviation of the model fit from experiment for PAP, applies, of course, only to the non-deuteriated samples. Indeed, we note that the agreement between the model fit and experimental data is much better for d_{10}-PAP than for d_0-PAP (cf. figure 1).

We believe that in view of all these uncertainties it is more informative to fit the data with only one adjustable parameter rather than two or three.

From tables 1 and 2 we see that both diffusion models provide an equally good description of the data, giving no preference for the axis of reorientation. The correlation times determined for d_{10}-PAP and d_{14}-POAB are two or three times longer than for d_0-PAP and d_0-POAB, respectively, which indicates the existence of an additional motion of the end chains. This conclusion must be regarded as very qualitative and of limited value only. It is possible that the shortening of the effective correlation times observed for the d_0 species, as compared with d_{10} (or d_{14}) species, is only an *apparent* shortening due to a change of the principal inertial axis via the conformational change. Such a change of the inertial axis leads, of course, to a change in the radii of proton trajectories which would have to be taken into consideration in a more quantitative treatment. It should, however, be noted that a similar (although smaller) shortening of correlation times has been reported recently for other liquid crystals by researchers using the infrared lineshape method [35].

Table 3. Comparison between Q.N.S. and dielectric relaxation times for the nematic phase of four members of the homologous series of alkoxyazoxybenzenes.

Substance	Neutron determined uniaxial diffusion correlation time $\tau_\parallel$/ps	Dielectrically determined uniaxial diffusion correlation time $\tau_\parallel$/ps	
PAA	4	22	[21, 3]
PAP	5	30	[32]
POAB	9	50	[33]
HOAB	12	110	[30, 29]

In table 3 we list the Q.N.S. $\tau_\parallel$ correlation times for diffusion around the para axis for the four members of the homologous series of alkoxyazoxybenzenes. In the same table we give the $\tau_\parallel$ correlation times obtained from dielectric relaxation experiments. An order of magnitude difference between $\tau_\parallel$ obtained by these two methods is evident. Either (indirectly) it indicates a preference of the model 2 as representing the Q.N.S. data (whereas the reorientation of the whole molecule, i.e. model 1, is responsible for dielectric relaxation) or it is a result of a failure of the simple models in describing dielectric and neutron data for liquid crystals.

Several things have to be noted here, in connection with the conclusion. The possibility of internal molecular rotations of the two molecular moieties in liquid crystals was suggested several years ago [24] by our group; its serious treatment, however, started a few years later, when quantum chemical calculations [25, 26] proved that such rotations, at least in an isolated molecule, are indeed possible, since the respective barriers are low. Recently, an N.M.R. study of nematic order parameters obtained from the quadrupolar splittings [27] provided further confirmation of this hypothesis.

It is true that our neutron data, presented in this paper, do not give any preference between the models of the whole molecule reorientation, on the one hand, and the two moieties reorienting on the other. However, the substances studied (together with those investigated by our group previously [21, 30]), are the only ones so far subjected to *both* neutron and dielectric relaxation measurements. The large discrepancy observed between the two sets of data is no doubt real. Hence the conclusion that the two methods observed are in fact two different motions: the dielectric method is dominated by the motion of the permanent dipole moment, which is located in the azoxy bridge and reorients with the molecule as a whole, whereas the neutron method sees (within its observation window) a much faster motion of the two moieties. This motion evidently exists not only in an isolated liquid crystal molecule, but also in the nematic phase, being frozen (in most of the cases) in the crystalline phases.

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