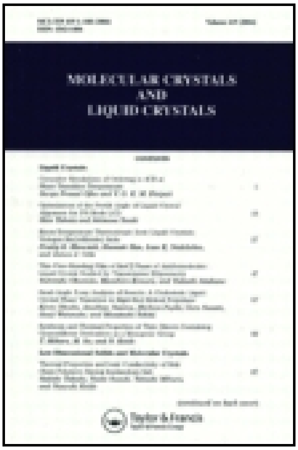

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Quasielastic Neutron Scattering Study of Reorienting di-heptyloxyazoxybenzene (HOAB) Molecules in the Nematic and Smectic C Phases

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Quasielastic neutron scattering (QNS) measurements carried out for heptyloxyazoxybenzene (HOAB) revealed the existence of fast molecular reorientation in the nematic and smectic C phases. The correlation time of this process, derived by fitting to a uniaxial rotational diffusion model, is of order of 10–20 ps in both liquid crystal phases. An explanation of the reasons for the disagreement between the correlation time values obtained by methods based on QNS and dielectric relaxation in the microwave region is suggested.

INTRODUCTION

Incoherent quasielastic neutron scattering (QNS) provides information concerning the stochastic motions of protons. Using spectrometers with a resolution of ~0.1 meV, these stochastic motions must occur on a time scale of 10^{-11}–10^{-12} s in order to be detected. In particular the QNS technique is very suitable for determining the reorientational correlation times of molecules containing hydrogen atoms. Because the cross-section of hydrogen is mainly incoherent, this method provides information concerning *self-motion* of the molecules, i.e., the correlation times obtained using the QNS technique are *single particle* correlation times.

Similar information concerning time scale and the single particle behavior can be obtained by the IR and Raman contour methods, but a competing process, namely vibrational relaxation, very often causes a considerable nuisance in correlation time determinations.

The microwave dielectric relaxation method provides information relating to the time scale range 10^{-9}–10^{-11} s. This information is usually contaminated by the *many particle* response and therefore does not correspond to self-motion alone.

Finally the NMR relaxation method provides results in which very often a slower molecular process dominates and masks a faster one. Thus good agreement between the NMR method and other methods is usually observed for substances, for which only one, single molecular relaxation process exists. However, this is seldom the case for substances consisting of complicated molecules. For the mesogenic 4,4′-di-*n*-heptyloxyazoxybenzene (HOAB), the following experimental results concerning the *fast* relaxation processes of the molecules were reported: the microwave dielectric relaxation study[1] gave a correlation time of ~100–200 ps for both smectic C and nematic phases and of ~60 ps for the isotropic phase. This correlation time is attributed to the reorientation of the molecules around their long axis. The NMR study[2] gave the correlation time of ~300 ps, with a similar interpretation. On the other hand the IR-contour study[3] gave a very short correlation time (5 ps) for the same motion, but this value should rather be attributed to vibrational relaxation, which the authors neglected. A much more careful Raman profile study,[4] which takes into account both the reorientational and vibrational relaxations, gave a reorientational correlation time for the isotropic phase of ~20 ps. Therefore if we exclude the IR value, which we assume to be incorrect, all other data seem to agree roughly, although we believe that at least in the liquid crystal phases, they correspond to the *long*-time behavior of the reorientational correlation function. It must be stressed that because of the complications listed before, the accuracy of all these methods is poor. Therefore values of the correlation times which differ by a factor of three may still be considered not to disagree.

Our aim was to determine the reorientational correlation time connected with the *short*-time part of the correlation function for HOAB, using the incoherent QNS method for this objective. To be able to distinguish between the motion of the central part of the molecule and that of the aliphatic tails, we carried out measurements on two samples: d_0-HOAB and d_{30}-HOAB. Because deuteriation of the alkyl chains masks the contribution of the tails, the latter sample provided information concerning the motions of the central part of the molecule only.

EXPERIMENTAL AND DATA PROCESSING

The QNS measurements were carried out on the neutron time-of-flight spectrometer (TOF) installed at the cold source of the JEEP II reactor in the Institute for Energy Technology, Kjeller, Norway. The incident neutron energy was 4.66 meV. The energy resolution of the spectrometer was 0.19 meV. Four scattering angles 20°, 30°, 40° and 50° corresponding to the momentum transfers 0.52, 0.78, 1.03 and 1.27 $Å^{-1}$ respectively were covered by the measurements. The time-of-flight spectra were converted to the energy scale.

The sample was mounted in a cryostat/oven with temperature control. The measurements were carried out for the solid (333 K), smectic C (359 K) and nematic (378 K) phases. The spectra obtained for the solid phase were used to determine the inelastic background. This was done in the following way: a smooth line was drawn through the ends of the quasielastic wings of the spectra. The values of this line were subtracted from the liquid crystal spectra after being normalized to the same monitor counts. The elastic peak of the solid phase spectra was used to determine the resolution function of the instrument. The model spectra were convoluted with the resolution function before being fitted to the experimental spectra.

The model fittings were made on the CYBER 72 computer using program MINUIT from the CERN Computer Library.[5] By using the χ^2 test, the best fit values of the adjustable parameters of the model were obtained.

RESULTS OF THE MEASUREMENTS AND MODEL FITTINGS

The qualitative features of the QNS spectra of d_{30}-HOAB and d_0-HOAB may be summarized as follows:

(1) The QNS spectra obtained for d_{30}-HOAB in the smectic C and nematic phases are practically identical (Figure 1). This means that the central groups in both phases reorient in the same way.

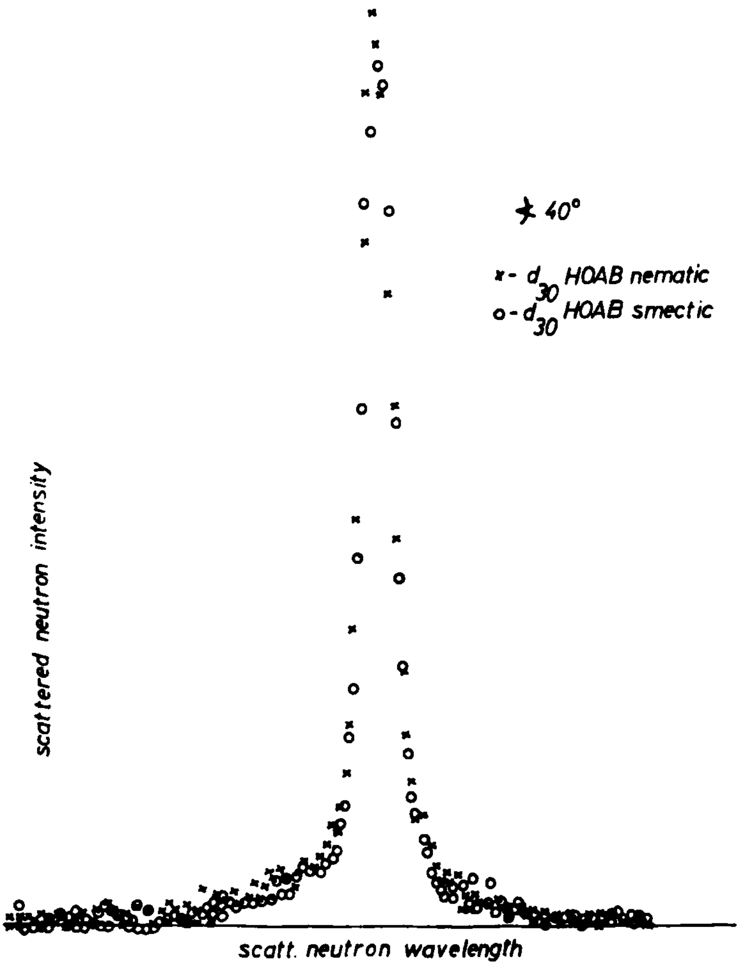

FIGURE 1 Comparison of the QNS spectra obtained for the nematic and smectic C phases of d_{30}-HOAB.

(2) The QNS spectra obtained for d_0-HOAB in the nematic phase have a somewhat more pronounced quasielastic component than those for the smectic C phase (Figure 2). This may be due to the fact that in the nematic phase there are a greater number of molecules which have configurations deviating from the trans-configuration than in the smectic C phase. Therefore in the nematic phase a greater number of protons have larger radii of reorientation.

(3) The QNS spectra of d_0-HOAB in both phases have more pronounced quasielastic components than those of d_{30}-HOAB (Figure 3).

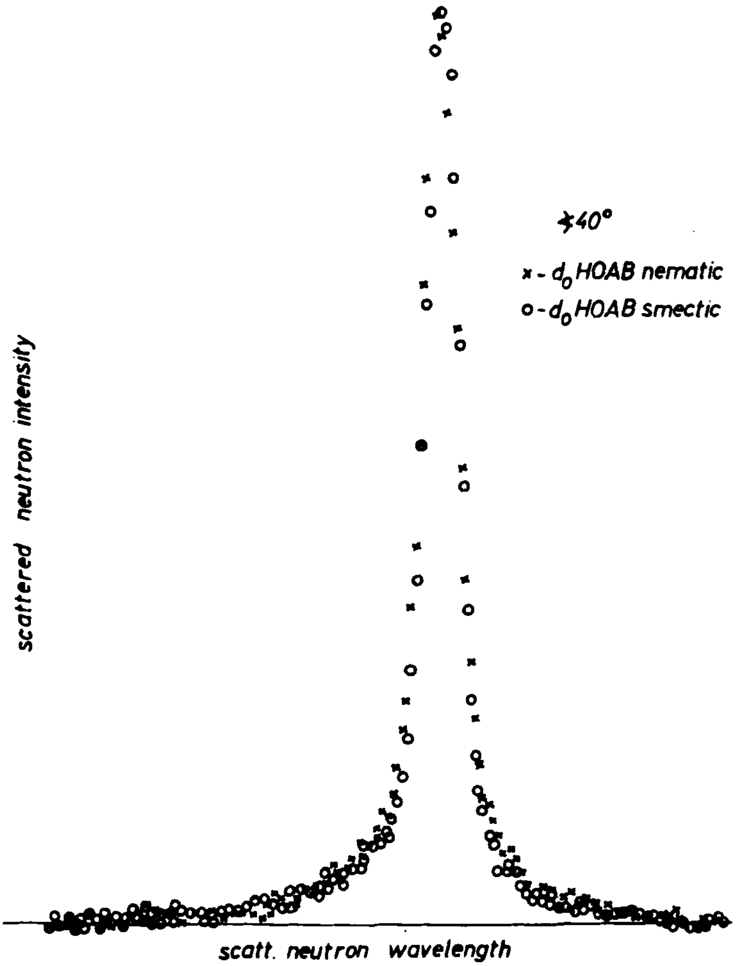

FIGURE 2 Comparison of the QNS spectra obtained for the nematic and smectic C phases of d_0-HOAB.

This can be explained by noting that the protons of segments of the tails more remote from the rings have trajectories with larger radii than the protons of the central group.

A quantitive description of the results was obtained by using a model assuming that the whole molecule (1) is rigid, (2) is in the trans-configuration, (3) is performing uniaxial rotational diffusive motions around the long axis. The correlation time τ_l is the adjustable parameter of the model. The scattering law for this model is[6]

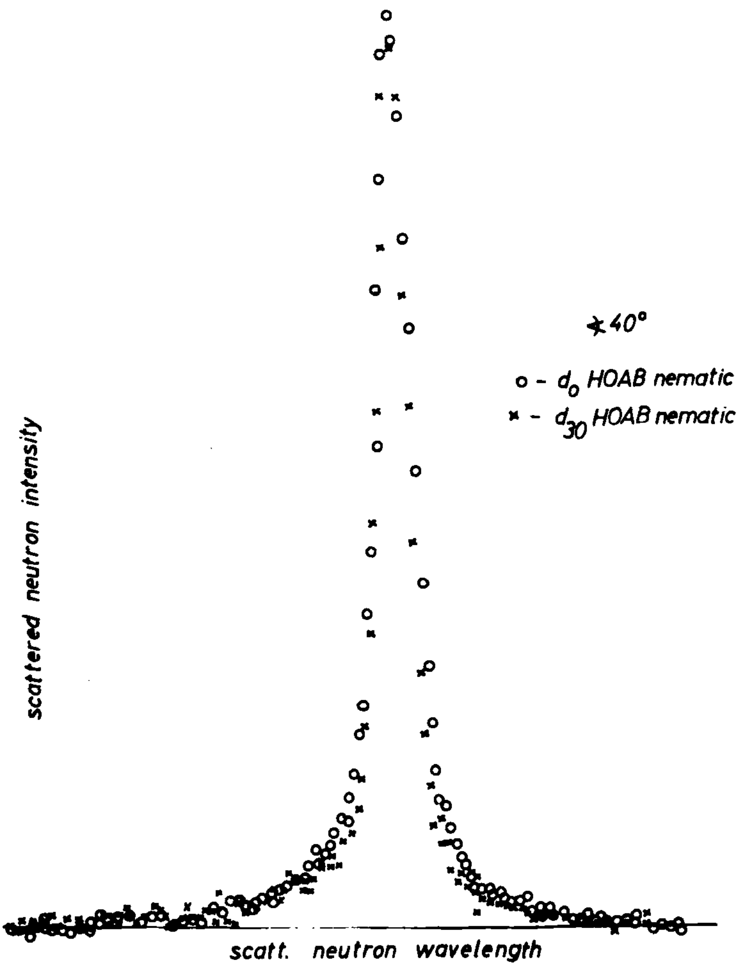

FIGURE 3 Comparison of the QNS spectra obtained for the nematic phases of d_0-HOAB and d_{30}-HOAB.

$$S(\kappa,\omega) = f_0(\kappa)\delta(\omega) + \frac{2}{\pi}\sum_{k/1}^{\infty} f_n(\kappa)\,\frac{\Gamma_k}{\Gamma_k^2+\omega^2}, \tag{1}$$

where $\Gamma_k = k^2/\tau_1$, $\hbar\omega$ and $\hbar\kappa$ are the energy and momentum transfers and

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

In Eq. (2), a_i is the fraction of protons in the molecule whose radius of reorientation is d_i. The d_0-HOAB molecule was too complicated to calculate exact position of the long molecular axis. We have therefore assumed that the long axis is not very different from the *para*-axis of the phenyl rings. With this assumption, we were able to calculate the radius of reorientation for all 38 protons in the molecule: 8 of them reorient with a radius of 2.14 Å (protons in the rings), 6 with a radius of 5.43 Å (protons in the CH_3 end-groups) and 4 protons in each segment of the tails reorient with radii of 1.81, 0.55, 3.07, 1.82, 4.34 and 3.09 Å respectively. The 120° jumps of the CH_3 end-groups were not taken into consideration because the radius of these jumps is small, and a relatively small fraction (6/38) of protons take part in this process; therefore its contribution is negligible. Translational diffusion is omitted, because we did not observe any κ-dependent broadening of the elastic component. This is not unexpected: a typical value of the translational diffusion coefficient for the nematic phase (about 10^{-6} cm^2/s) corresponds to a broadening of about 0.01 meV for the largest scattering angle. This broadening is negligible in comparison with the energy resolution of our spectrometer (0.19 meV).

We must point out that we are well aware of the fact that such a simple reorientational model may be far from reality. In particular, it is hard to believe that the reorientations have really uniaxial symmetry. It might well be that the angular range of the rotational Brownian motion is limited due to steric reasons (see for instance Ref. 7). Nevertheless, we believe that the parameter τ_1 of the model applied gives a rough characteristic of the short time behavior of the reorientational correlation function.

The results of the fittings are presented in Table I, and Figure 4 shows several examples of the fittings.

DISCUSSION

First of all we should note that in general the accuracy of the measured correlation times is poor; an agreement within a factor of three cannot be considered as bad. Therefore we may say that the values of the correlation times in d_0-HOAB and d_{30}-HOAB are the same. The apparent difference between the QNS spectra of d_{30}-HOAB and d_0-HOAB is caused by the difference in the effective radius of the proton trajectories. The correlation time τ_1 is nearly the same for both liquid crystal phases of HOAB and amounts to 10–20 ps.

TABLE I

The reorientational correlation times (τ_l) and the sum of the squares of deviations (χ^2) for HOAB

scattering angle	nematic phase τ_l [ps]	nematic phase χ^2	smectic C phase τ_l [ps]	smectic C phase χ^2
d_{30}-HOAB				
20°	10.9	18	14.2	17
30°	21.0	12	13.2	13
40°	6.0	6	8.5	6
50°	9.4	7	11.0	7
average	12.0	11	12.0	11
d_0-HOAB				
20°	16.2	22	15.4	21
30°	16.6	9	26.2	19
40°	17.7	9	15.4	15
50°	7.1	6	16.5	17
average	12.9	12	18.4	18

Compared with the values obtained by the NMR and microwave dielectric relaxation methods[1,2] which are ~100 ps or more, the value of the correlation time measured by the QNS technique is *significantly* smaller. This may be due to the difference in the characteristic observation time for the methods. Of course, if the reorientational process were simple, with an exponentially decaying correlation function, each method would give the same correlation time. However, if for instance the short-time part of the correlation function were decaying more rapidly than the long-time part, the QNS method would give smaller values of τ_l than the microwave dielectric relaxation method. A possible explanation of the long-time behavior is suggested to be the reorientation of the molecule around the long axis with the dipole moment moving on a circle. But this motion does not possess uniaxial symmetry, and it may well be that the normal component of the dipole moment for some time remains confined within a certain angular range in which it reorients. This confined Brownian motion is a kind of stochastic libration which corresponds to the short-time part of the correlation function and hence to the smaller τ_l value which is measured by the QNS method. Occasional jumps over the confinement limits or their slow reorientation would thus correspond to the dielectric relaxation values of the correlation time. However, results of QNS studies performed for a few other liquid crystals do not support such a suggestion.[9,10]

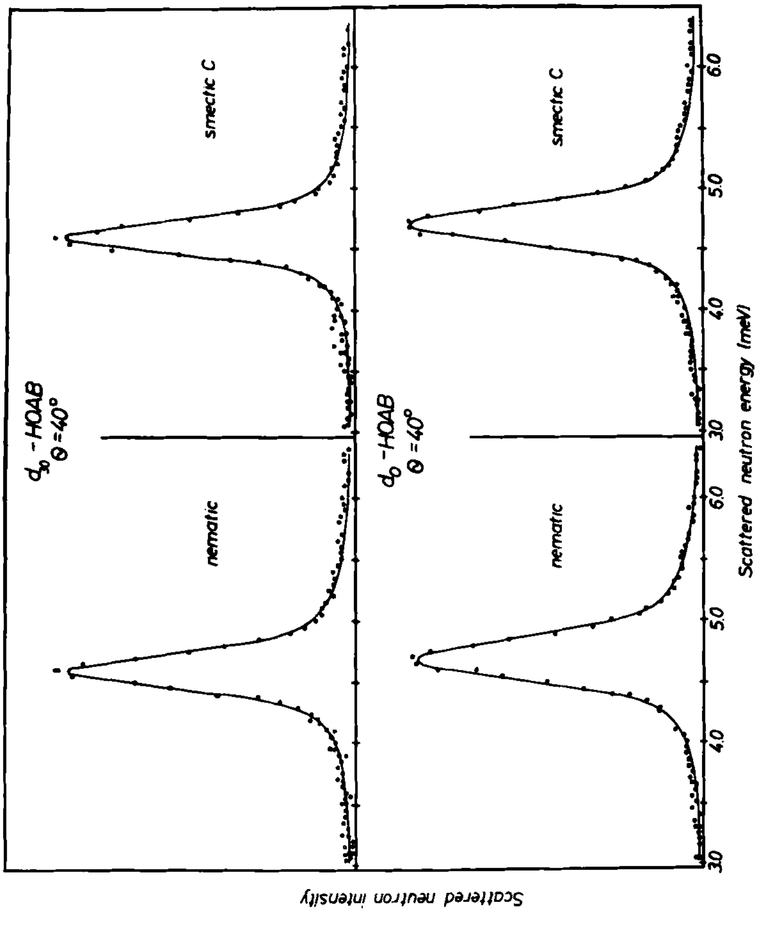

FIGURE 4 Examples of the fittings of the model explained in the text to the QNS spectra of HOAB.

If this simplified explanation is true, we may expect that the QNS and the Raman contour experiments would give the same results. Indeed the Raman scattering experiment[4] carried out for the isotropic phase of HOAB gives a correlation time of ~20 ps which is close to our results for the nematic and smectic C phases. If there exist stochastic librations of the molecules around their long axes, we would also expect the existence of Poley absorption in the far IR. Evidence for this was indeed reported for HOAB and for other homologes of PAA.[8]

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