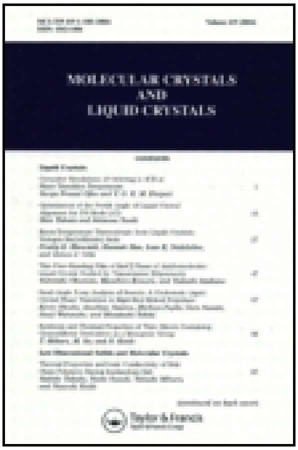

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NEUTRON SCATTERING BY A LIQUID CRYSTAL SUBSTANCE WITH A "CUBIC" PHASE

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Abstract The applicability of the rotational diffusion model around the long molecular axes in liquid crystalline phases is being questioned.

INTRODUCTION

All liquid crystals exhibit broad components of quasi-elastically (incoherently) scattered neutrons (QNS). As examples may serve: PAA and some next members of its series[1,2,3], TBBA (see for inst.[4]), IBPBAC and related substances (see for inst. [5]). In all these examples the QNS components were interpreted via the model of uniaxial rotational diffusion around the long molecular axes. It should be pointed out that the so obtained (by fitting) reorientational correlation times happened to be surprisingly small especially for liquid crystals with low dimensional order. For instance: τ_1 correlation time for the nematic PAA is ca. 2 psec, for the nematic TBBA it is ca. 5 psec, for the nematic IBPBAC it is ca. 7 psec. As these correlation times are approximately those needed for performing a reorientation by one radian, it is worth while to compare them with times needed for changing the orientation by one radian via the free rotation process. These latter times happen to be of the order of several psec. Thus the reorientation is approximately as fast as the free rotation, which is improbable.

In the present work we give an even more drastic argument against the interpretation of QNS components via the uniaxial reorientation of the rigid stretched molecule. The molecule in question is one of the 1,2-bis-(′4-n-alkyloxybenzoyl)-hydrazines, with n = 10:

The substance was described by Demus et al.[6] The authors give the following information about the sequence of phases:

$$\mathrm{CrIII} \xleftrightarrow{124\ C} \mathrm{CrII} \xleftrightarrow{128\ C} \mathrm{CrI} \xleftrightarrow{143\ C} \mathrm{Cubic}$$

$$\mathrm{Cubic} \underset{143\ C}{\overset{154\ C}{\rightleftarrows}} S_c \xleftrightarrow{165\ C} \mathrm{Is}$$

With this substance we carried out the QNS measurements at the TOF spectrometer installed at the JEEP 2 reactor of the Institute of Energy Technology, Kjeller, Norway.

QNS RESULTS

The QNS results, after isolation from the inelastic background, were subjected to model fitting. The model was that of rotational diffusion around the long molecular axis of inertia. The scattering law formula for this model is:

$$S_{inc}(Q,\omega) = \langle J_0^2(Q \cdot r)\rangle \delta(\omega) + \frac{2}{\pi}\sum_{l=1}^{\infty} \langle J_l^2(Q \cdot r)\rangle \frac{1/\tau_l}{(1/\tau_l)^2 + \omega^2}$$

where Q and ω are neutron momentum and energy transfers, J_l are cyllindrical Bessel functions, r is the gyration radius of the proton under consideration and τ_l are the reorientational correlation times mutually interconnected by the formula $\tau_l = \tau_1/l^2$. The averaging is over all orientations of molecules. When applying the formula, only protons are taken into consideration because of their large (dominant) incoherent scattering cross-section.

For our molecule, different protons have different radiuses of gyration; this fact was taken into consideration in the fitting calculations.

Fig. 1 shows the QNS results for various phases of the substance. It may be seen that a QNS component shows up even in the Crystal III (although it is quite weak). Starting from the Crystal II the QNS component is very pronounced and it broadens only a little when going from CrII, through CrI, "cubic" to smectic C phase. The results of the fitting are presented in Tab.I.

It should be pointed out, that similar fitting attempts were made with an assumption that the molecules are not in the trans configuration but that the aliphatic chains exhibit a kink at C_5. This attempt was stimulated by the work of Grande et al.[7], who observed a marked decrease of the local order parameter for segments with $n \geqslant 5$. However, the τ_1 correlation times were only slightly higher in this attempt: from 4.7 psec to 2.2 psec, when going from CrII to SmC.

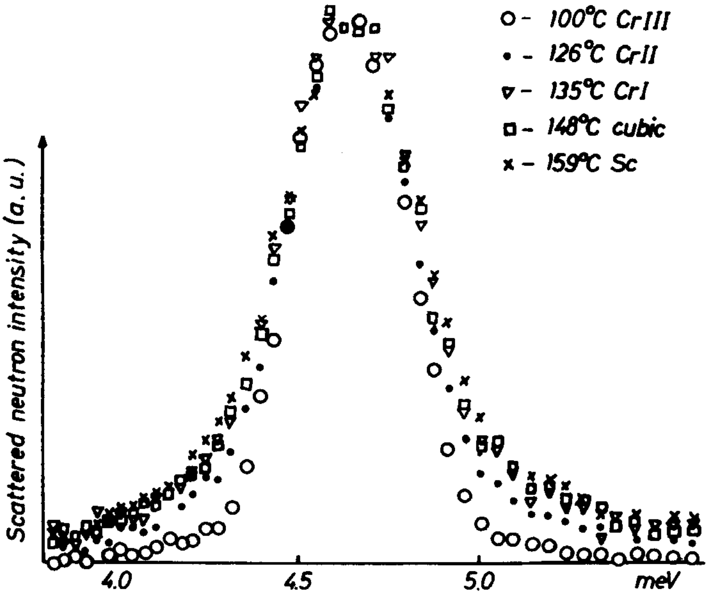

FIGURE 1. QNS data (sc.angle 50°) for $C_{10}H_{21}$ OØCONHNHCOØOC$_{10}H_{21}$ in various phases.

TABLE I Reorientational correlation times for $C_{10}H_{21}O\phi CONHNHCO\phi OC_{10}H_{21}$ molecules in trans configurations

Temp. C	Phase	Sc.angle	Q, Å^{-1}	τ_1, psec
126	CrII	30°	0.773	3.2 ± 0.3
126	CrII	50°	1.261	3.5 ± 0.3
135	CrI	30°	0.773	2.6 ± 0.2
135	CrI	50°	1.261	2.3 ± 0.1
148	Cubic	30°	0.773	2.2 ± 0.1
148	Cubic	50°	1.261	2.1 ± 0.1
159	SmC	30°	0.773	2.3 ± 0.1
159	SmC	50°	1.261	2.0 ± 0.1

DISCUSSION

We believe that the values of τ_1 as listed in Table I are highly improbable if they are to be interpreted as reorientational correlation times of rigid molecules in their stretched (or nearly stretched) configuration. They are too small and suspiciously too close to the free rotation periods.

Fast configuration changes of the aliphatic chains (as a cause of QNS broadening) seem improbable. The barriers to rotation of the particular segments are rather high[8], except those for the final CH_3 groups (whose contribution would anyway be negligible). And indeed the QNS spectra measured for liquid crystals with deuterated and non-deuterated aliphatic chains have been reported as very similar[1,9].

Therefore we are inclined to believe, that the two benzene rings (with the respective aliphatic chains attached) may reorient via an internal rotation around the CC bonds of the central bridge. Such a possibility was suggested by us in one of our previous papers[10], and recently it has been discussed in details via the quantum-mechanical estimations of the barriers to benzene rings internal rotation by Volino et al.[11]. These barriers are quite low for an isolated molecule and they gradually increase when going through various liquid crystal phases to the solid ones.

It seems, that for our particular substance that rather loose molecular arrangement being characteristic for the "cubic" phase is preserved in at least two crystal phases (I and II). That in turn is responsible for the low barrier values to internal rotation of the two molecular "halves".

We would like also to point out, that the substance subjected to this study is the first one in which the QNS component showed up not only in liquid crystal phases but also in solid phases. So far, in all other liquid crystal forming substances the solid scattered neutron spectrum was purely elastic and the QNS part showed up above the melting point.

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