Quasielastic neutron scattering study of molecular reorientation in the nematic and smectic phases of 4-*n*-pentylphenyl-4'-*n*-octyloxythiobenzoate

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Quasielastic neutron scattering study of molecular reorientation in the nematic and smectic phases of 4-n-pentylphenyl-4'-n-octyloxythiobenzoate

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We report QNS investigations of the eighth member of the 4-n-pentylphenyl-4'-n-alkyloxythiobenzoate homologous series ($C_nH_{2n+1}O$–Φ–COS–Φ–C_5H_{11}, $n = 8$ and Φ denotes the benzene ring), known as $\overline{8}$S5. QNS measurements have been performed for a fully protonated sample as well as for the one with deuteriated terminal alkyl and alkoxy groups, in the phases: isotropic, nematic, smectic A and smectic C. The results obtained indicate the important role of fast reorientation within the terminal chains, including conformational changes.

1. Introduction

Molecular dynamics in liquid-crystalline phases has been investigated by many authors with various experimental techniques (e.g. [1–9]), including quasielastic neutron scattering (QNS), sensitive to fast reorientation processes, whose characteristic times are of the order of 10^{-11}–10^{-12} s. Such characteristic times are usually ascribed to intramolecular motions of benzene rings as well as to the motions within terminal alkyl or alkoxy groups (about the single bonds therein). Here we report QNS results for 4-n-pentylphenyl-4'-n-octyloxythiobenzoate, hereafter denoted as $\overline{8}$S5. The experiment was performed for both a fully protonated sample ($\overline{8}$S5-d_0), and that with deuteriated terminal chains ($\overline{8}$S5-d_{28}). We expect to find quite a number of molecular and intramolecular fast reorientation processes in $\overline{8}$S5, contributing to the quasielastic broadening of the neutron scattering peak. From what is now well established for other similar compounds, and for $\overline{7}$S5 ($C_7H_{15}O$–Φ–COS–Φ–C_5H_{11}) in particular [10–13], it follows that the $\overline{8}$S5 molecule should be especially supple as far as the central –COS–group is considered.

2. The substance

Both substances, $\overline{8}$S5-d_0 and $\overline{8}$S5-d_{28}, were synthesized at the Institute of Chemistry of the Agricultural and Pedagogical University at Siedlce (Poland) [14]. The schematic

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phase diagram of 8S5-d_0, obtained by means of differential scanning calorimetry (DSC), is
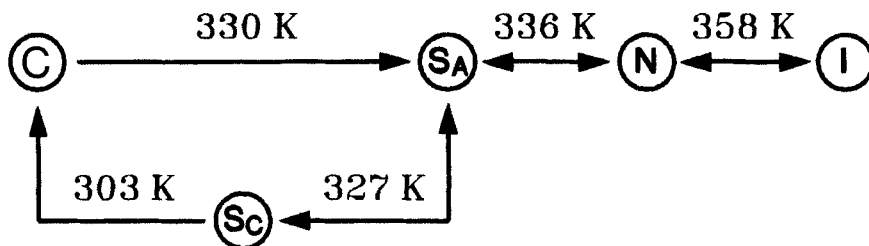
The 8S5 molecule (see figure 1) is composed of two terminal groups: pentyl (–C_5H_{11}) and octyloxy (–OC_8H_{17}), connected to their benzene rings. The latter are coupled by means of the thioester group –COS–.

Dielectric relaxation measurements, performed in both MHz and GHz regions, as well as time domain spectroscopy, detect reorientation about the short and long molecular axes with the approximate relaxation times of 10^{-8} s and 10^{-10} s, respectively [12]. Reorientation about the long axis significantly slows down upon entering the S_C phase. (from 342 ps in S_A to 517 ps in S_C) [15]. These figures suggest that both processes should not be detectable by the QNS experiment, which is sensitive to picosecond reorientations.

3. Results and discussion

The QNS measurements were carried out on a time-of-flight spectrometer, using the cold neutron source at the JEEP II reactor in Kjeller, Norway. 4·67 meV neutrons were collected under scattering angles of 30° and 40°, corresponding to the momentum transfer of 0·78 Å^{-1} and 1·03Å^{-1}, respectively. The spectrometer energy resolution was about 0·13 meV. For both 8S5-d_0 and 8S5-d_{28}, QNS spectra have been collected for the nematic, smectic A, smectic C, and crystalline phases. The latter were used as
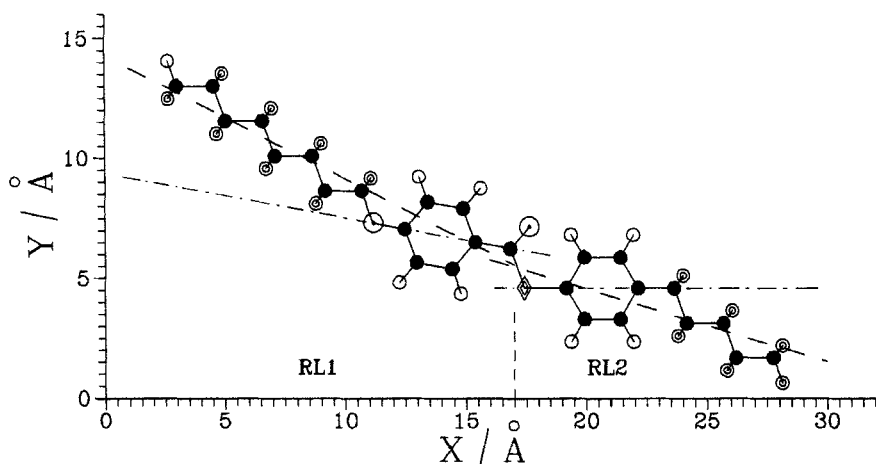

Figure 1.   Molecular structure of 8S5—a projection on the XY plane. Dashed lines show the principal axes of the smallest moments of inertia of the two moieties. (cf. version (iii).) The moieties extend sideways from the C–S bond. The dotted lines are the para axes of the benzene rings. (●) C; (○) H; (◉) O; (◇) S.

instrument or resolution functions. With this energy resolution, QNS can be used to investigate molecular reorientation processes, whose characteristic times are between a few and a few tens of picoseconds. It is believed that, in $\bar{8}S5$, this condition is fulfilled by independent reorientation of molecular fragments, e.g. the RL1 and RL2 moieties (see figure 1), and by fast conformation changes within the terminal chains (cf. [8, 9]).

In processing the experimental data it was assumed that the reorientation processes, however complex they may really be, can be satisfactorily described in terms of stochastic jumps over the closely located potential minima, i.e. rotational diffusion [8, 9]. The measured QNS spectrum is proportional to the convolution of the instrument function $G(\omega)$ with the so-called scattering law $S(\kappa, \omega)$

$$\sigma_{\text{inc}} \frac{k_i}{k_f} \exp\left(\frac{\hbar\omega}{k_f T}\right) S(\kappa, \omega) * G(\omega), \tag{1}$$

where σ_{inc} is the incoherent neutron scattering cross section for hydrogen. The rotational diffusion model leads to the expression

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

for the scattering law [2]. For a non-oriented sample, the f_k coefficients are

$$f_k(\kappa) = \frac{1}{2} \sum_j \int_{-1}^{+1} J_k^2(|\kappa| d_j \sin\beta) \, d\cos\beta. \tag{3}$$

The sum runs over all hydrogen atoms in the molecule, J_k is a cylindrical Bessel function; $\hbar\omega$ and $\hbar\kappa = (\mathbf{k}_f - \mathbf{k}_i)$ are the energy and momentum transfers, repectively, d_j denotes the radius of reorientation of the jth hydrogen atom and Γ_k is proportional to the reciprocal correlation time: $\Gamma_k = (\hbar k^2/\tau)$. Following [9], we replace in formula (1) the scattering law $S(\kappa, \omega)$ with the expression:

$$p\delta(\omega) + (1-p)S(\kappa, \omega). \tag{4}$$

The free parameter p, referred to as the excess elasticity, modifies the contribution of the elastic part to the observed QNS spectrum. Not only is it intended to account for the small effects of neutron scattering on the sample holder, but it also becomes a means of estimating the adequacy of the assumed reorientation model, [9] provides a more detailed discussion. An attempt was made to fit the rotational diffusion model in the three following versions:

(i)   a rigid molecule reorienting about the axis of its smallest moment of inertia;

(ii)   independent rotation of the RL1 and RL2 moieties (see figure 1) about the para axes of the corresponding benzene rings;

(iii)   independent rotation of the RL1 and RL2 moieties about their own smallest moment of inertia axes.

It can be argued that the proposed analysis of the spectra at our disposal, makes little sense due to the energy resolution being too poor to resolve elastic and quasielastic components with the naked eye. Consequently, any conclusions going beyond the obvious predictions, should be highly suspect. Indeed, from among the above three approaches, none can be undoubtedly considered superior within any reasonable level of confidence (in terms of a usual statistical reasoning). Clearly, no quantitative conclusions can be drawn. Nevertheless, the spectra can still be a source of qualitative information, complementary to the results of other experimental techniques.

Version (i) proved definitely inadequate, which is a correct result in view of the time domain spectroscopy measurements [16]. This approach was made just to test the data processing technique. With regard to the two other versions, no clear preference can be given to either of them. Version (ii), successfully applied in previous QNS studies of the homologous 4,4'-di-n-alkyloxyazoxybenzene series, this time failed to provide a high quality fit to the data. Such reorientation of the long terminal chains is probably obstructed by lack of enough free volume around the molecule. Table 1 gives the results. Version (iii) leads to the best fits, (see table 2), although the p parameter takes on large negative values. Figure 2 shows the sample QNS spectra fitted with this model.

An attempt was also made to fit both version (ii) and version (iii) to the spectra of the chain deuteriated sample. In this case, for both molecular moieties, one average correlation time was assumed. Correlation times obtained for $\overline{8}$S5-d_{28}, are systematically somewhat longer than those in $\overline{8}$S5-d_0. Moreover, the values of the excess elasticity, p are much higher (and positive). This seems to confirm the assumption that in the investigated compound, the terminal chains are by no means rigid. On the contrary, they are undergoing fast conformation changes (within the picosecond region) which are reflected by the negative p value obtained in $\overline{8}$S5-d_0. Definitely positive excess elasticity in $\overline{8}$S5-d_{28} suggests the presence of strongly damped librations, involving the benzene rings. The motions about the C–S bond in the central bridge can be mentioned in this context.

Table 1.　Characteristic times and excess elasticity for fully protonated (H) and deuteriated (D) $\overline{8}$S5. Version (ii), rotation of the RL1 and RL2 moieties about the para axes of their benzene rings.

Phase	Scattering angle/°	τ_1/ps	τ_2/ps	p_H	τ_D/ps	p_D
N	30	7·5	7·4	0·15	5·9	0·23
	40	4·8	6·7	−0·20	5·5	0·33
S_A	30	7·9	8·6	0·09	6·2	0·25
	40	6·5	7·7	−0·18	5·7	0·36
S_C	30	9·6	9·5	0·22	9·7	0·36
	40	8·3	8·7	0·27	8·8	0·47

(In this version, the RL1 and RL2 moieties are indistinguishable for a chain deuteriated sample; hence τ_D has a sense of a mean value.)

Table 2.　Characteristic times and excess elasticity for fully protonated $\overline{8}$S5. Version (iii) rotation of the RL1 and RL2 moieties about their smallest moment of inertia axes.

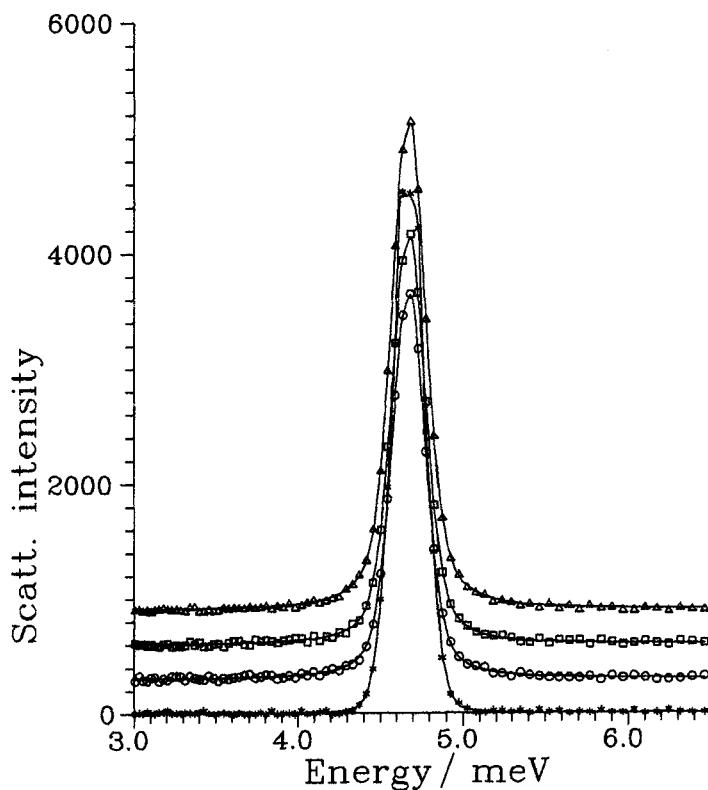| Phase	Scattering angle/°	τ_1/ps	τ_2/ps	p
N	30	6·0	5·2	−0·23
	40	6·9	4·9	−0·22
S_A	30	7·2	6·1	−0·16
	40	8·4	6·7	−0·18
S_C	30	8·7	7·4	−0·11
	40	8·3	6·6	−0·17

Figure 2. The QNS spectra of $\bar{8}S5$-d_0, collected for the scattering angle of 30°. Solid lines are the results of the least squares fits of version (iii). (Independent rotational diffusion of the RL1 and RL2 moieties about their principal axes). ($\triangle$) Nematic; ($\square$) smectic A; ($\bigcirc$) smectic C; ($*$) solid.

The geometry of motion influences the scattering law via the coefficients f_k (see equation (3)). Even if it is very complicated, or unknown in general, we can still believe in rotational diffusion philosophy, and try to estimate the few first f_ks by treating them as free parameters.

Generally, the f_k coefficients obtained vanish for $k > 1$. Practical lack of higher order terms is a reliable result (the numerical procedures have been carefully tested). It suggests that there are so many various reorientation processes going on in the substance investigated that they can be effectively described by a single lorentzian, or by its convolution with a gaussian. This conclusion is exactly what we would expect, knowing the reports on a number of elegant QSN experiments performed on long chain liquid crystals at ILL, Grenoble. Numerous kinds of motions have been proved to influence the QNS spectra, including diffusive and localized translation, conformational changes, fluctuations of the long axis spatial orientation. The results obtained for TBBA by Volino, Dianoux and co-workers (e.g. [17] and references therein), and for IBPBAC obtained by Leadbetter, Richardson and coworkers (e.g. [18]), should be cited in this context. See also [14–27] in [2], and [19].

Well founded physical arguments have made us treat picosecond reorientation processes in $\bar{8}S5$ in terms of rotational diffusion. However, no uniaxial reorientation

can be considered predominant. Consequently, any model fitting of QNS spectra for similar compounds must be performed very cautiously. A frequently encountered argument, intended to discourage one from doing so, that any reorientation model would give equally good results (within the error limits), seems too strong. Even the spectra of rather poor resolution are good enough to reject oversimplified approaches to intramolecular reorientation.

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