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Quasielastic scattering of neutrons by a liquid crystal substance with flexible molecules

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When interpreting quasielastic neutron scattering (QNS) spectra of liquid crystals with complicated and flexible molecules, it seems absolutely necessary to take into consideration the internal reorientations. The present QNS study concerns TCDCBPh/di-(4-*n*-butyloxyphenyl) *trans*-cyclohexane-1,4-dicarboxylate. It contains a cyclohexane ring which possesses a high internal mobility. As a probing parameter we use the 'excess elasticity' p which in a way represents the elastic form-factor. We make drastic assumptions: we equalize all partial correlation times, we allow each hydrogen atom to participate in one reorientation only, and we ignore possible couplings between reorientations. Then we analyse the behaviour with temperature of the p parameter for eleven models in which either all specified molecular fragments reorient or some of them reorient and others are at rest. In the crystal, far below melting, all internal stochastic mobilities seem to be at rest. However, still 30°C below melting, the cyclohexane ring starts large angle internal deformations which have a stochastic character. It seems that some fragments in the molecules (e.g., benzene rings and/or alkyl terminal groups) start to reorient a few degrees before melting. This is connected with the formation of a 'mobile' crystal phase, just before melting. Then all internal reorientations become free, and one cannot observe much difference between the smectic A phase and the nematic phase. This study shows that the cyclohexane ring is the most mobile sub-entity in the TCDCBPh molecule. Observations by polarized microscopy seem to corroborate our claim for the existence of a "mobile" phase just before melting. The literature information about the phase sequence is C 107°C S_A 156°C N 209°C I.

1. Introduction

During the many years of studies of molecular reorientations in liquid crystals by the quasielastic neutron scattering method (QNS), too simple reorientational models have been applied. They ignored molecular flexibilities and internal reorientations in molecules. In a critical analysis which took into consideration the results of various experimental methods, a model based on reorientations of molecular fragments was suggested to interpret the QNS spectra [1, 2]. In that attempt, a modified scattering function containing an additional parameter ('excess elasticity') was introduced. The parameter played a role equivalent to that of the elastic scattering form-factor.

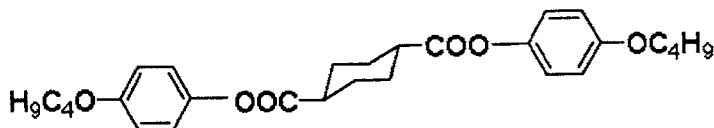
This paper presents an analysis (no doubt simplified) of internal molecular motions which may contribute to QNS in TCDCBPh (di-(4-*n*-butyloxyphenyl) *trans*-cyclohexane-1,4-dicarboxylate). In this molecule several fragments may perform reorientational movements within the time scale window of the QNS method. The cyclohexane ring is especially flexible here, so that some forms of its mobility occur with very low energy barriers.

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In the following section we present the results of quantum-mechanical calculations performed in order to obtain various conformations of the TCDCBPh molecules, the results of QNS measurements together with model fittings, and the results of microscopic observations of the phase sequence in the substance.

2. The substance. Quantum-mechanical calculations

The semistructural formula of TCDCBPh is



The phase sequence is Cr 107°C S_A 156°C N 209°C I [3].

The cyclohexane ring has (in the frame of the chair conformation) a high internal mobility, which is presented in figure 1. In this figure it is shown how easy it is to deform the terminal parts of the ring. One can see, for instance, that the barrier connected with the change of the φ -angle within the range c. 15° to c. 75° is very small [4].

Since no crystallographic data exist for TCDCBPh, we decided to perform standard quantum-mechanical calculations in order to optimize the molecular structure. The semi-empirical MINDO/3 method was used [5] for which the AMPAC-91 program for the IBM/486 computer was applied [6]. The energetically most preferred

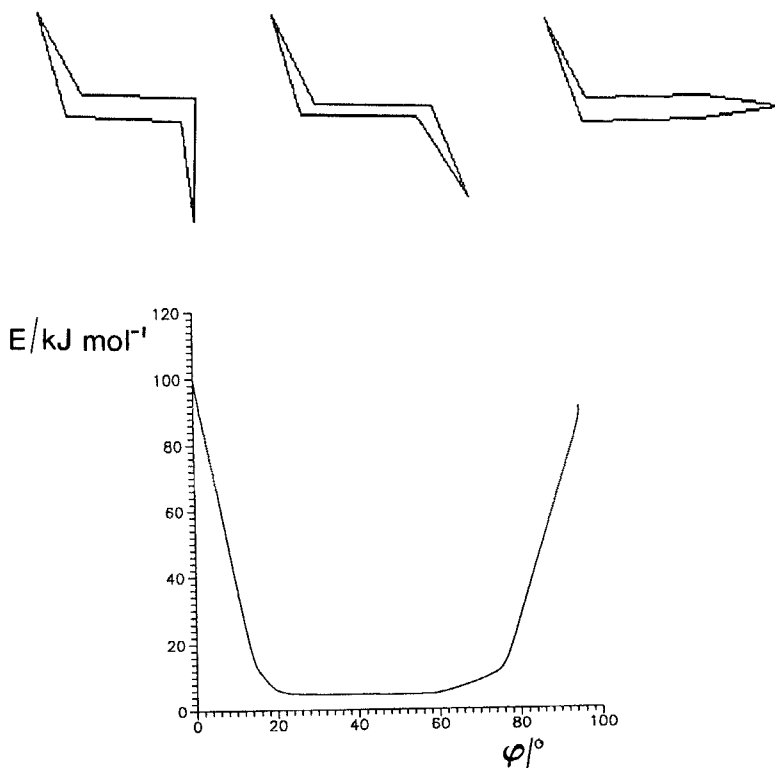


Figure 1. Top: Variation of the chair conformation of the cyclohexane ring with the angle φ , (a) $\varphi = 0^\circ$, (b) $\varphi = 35^\circ$ and (c) $\varphi = 90^\circ$. Bottom: constitution energy versus angle φ .

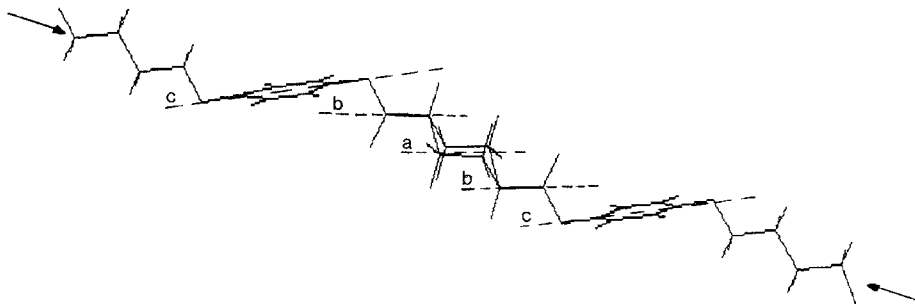


Figure 2. The energetically most preferred conformation of the TCDCBPh molecule. Lines *a*, *b*, and *c* denote the reorientational axes of the molecular fragments, as suggested in model variants 1–11. Arrows indicate the long molecular axis.

molecular conformation was obtained and this is shown in figure 2. We are in possession of all coordinates of atoms resulting from these calculations. These coordinates were then used for model calculations connected with QNS results.

3. QNS measurements. Remarks concerning the analysis of data

The QNS measurements were carried out on the TOF neutron spectrometer installed at the JEEP II reactor of the Institutt for energiteknikk, Kjeller, Norway. The energy resolution was $137 \mu\text{eV}$. A mono-energetic neutron beam of 4.61 meV was used. The scattering angle was 30° , which corresponded to the neutron momentum transfer 0.736 \AA^{-1} .

The non-oriented TCDCBPh sample was placed in a standard Al sample holder inside a furnace. The measurements were made for the following temperatures: 40, 74, 91, 100.3, 101, 103, 104.2, 105, 105.7, 106, 110, 116.5, 124.5, 132, 140, and 160°C . The isotropic phase was not included, because of the danger of decomposition of the substance at such a high temperature.

A smooth inelastic background was subtracted from all spectra. This procedure always introduces a certain subjective element to the data processed. It is unavoidable and, of course, it produces some error, especially when the inelastic spectrum is peaked in the low energy transfer region (i.e. in the region of QNS wings). We took as the instrumental function the spectrum of the same substance at room temperature, at which there were no indications of any quasielastic component. Both the inelastic background subtraction and the fittings of models were made on an IBM/486 personal computer.

The procedure of the inelastic background subtraction leads to the isolation of the quasielastic component and of the purely elastic component. Both components are of course convoluted with the instrumental function. The QNS component must be composed of several sub-components, since various hydrogen atoms (which are the main neutron scatterers) take part in various partial internal molecular motions. The experiment, however, does not allow us to separate these sub-components. Therefore, we have to make drastic simplifications in our analysis. Firstly, we shall assume that a hydrogen atom participates in only one reorientational motion, although various hydrogen atoms may participate in various such motions. Owing to this assumption we avoid having to deal with too many convolutions in the calculations. Secondly, we

shall assume that all partial reorientational motions have the same effective correlation time. This is superimposed by the energy resolution (of c. 100 μeV) and amounts to several picoseconds. Thirdly, we shall neglect possible couplings between the reorientational motions in the molecule. These, we repeat, drastic simplifications in the models have the advantage of leading to one global QNS component, characteristic of the model. It should be emphasized that the parameter analysed in this procedure will not be the correlation time but the 'excess elasticity' parameter, which we introduce as follows.

Normally, one introduces the following form of the scattering function to be fitted to experimental data (after background subtraction)

$$F(\boldsymbol{\kappa}, \omega) = \sigma^{\text{inc}} \frac{\mathbf{k}_f}{\mathbf{k}_i} \exp(\hbar\omega/k_B T) S(\boldsymbol{\kappa}, \omega) \otimes G(\omega),$$

where σ^{inc} is the hydrogen cross-section for incoherent neutron scattering, \mathbf{k}_f and \mathbf{k}_i are the wave vectors of the scattered (f) and incident (i) neutrons, $\hbar\boldsymbol{\kappa} = \hbar\mathbf{k}_f - \hbar\mathbf{k}_i$ is the neutron momentum transfer, $\hbar\omega = E_f - E_i$ is the neutron energy transfer, $G(\omega)$ is the instrumental function, \otimes denotes the convolution operation, and $S(\boldsymbol{\kappa}, \omega)$ stands for the so-called scattering law which is characteristic of the model. For the rotational diffusion model the scattering law has the form [7]

$$S(\boldsymbol{\kappa}, \omega) = f_0(\boldsymbol{\kappa})\delta(\omega) + \frac{2}{\pi} \sum_{i=1}^{\infty} f_i(\boldsymbol{\kappa}) \frac{\Gamma_i}{\Gamma_i^2 + (\hbar\omega)^2}$$

where Γ_i is the partial lorentzian half width related to the partial reorientational correlation time via the formula $\Gamma_i = \hbar/\tau_i$ in which $\tau_i = \tau_1/i^2$. The geometrical formfactor $f_i(\boldsymbol{\kappa})$ is given by the formula

$$f_i(\boldsymbol{\kappa}) = \frac{1}{2} \sum_j a_j \int_{-1}^{+1} J_j^2(\kappa r_j \sin \beta) d \cos \beta,$$

where a_j are the fractions of the overall number of hydrogen atoms with reorientational radii r_j , J_j are the cylindrical Bessel functions, and β describes various orientations of the molecules in the sample. A somewhat simpler formula can be written for the scattering law corresponding to a model in which reorientations occur via instantaneous angular jumps [7].

Now, we introduce a modification. It is a new fitted function $\mathbf{F}(\boldsymbol{\kappa}, \omega)$ [8]

$$\mathbf{F}(\boldsymbol{\kappa}, \omega) = \sigma^{\text{inc}} \frac{\mathbf{k}_f}{\mathbf{k}_i} \exp(\hbar\omega/k_B T) [p\delta(\omega) + (1 - p)S(\boldsymbol{\kappa}, \omega)] \otimes G(\omega),$$

where p is the 'excess elasticity' parameter. Its interpretation is the following. If $p = 0$, it means that the model applied for the calculation of $S(\boldsymbol{\kappa}, \omega)$ leads to an agreement with the experiment (which does not mean automatically that the model is adequate). If $p > 0$, it means that we took into consideration too many motions in the model; in reality there are fewer motions in the system. If $p < 0$, it means that we took into consideration too few motions in the model; in reality there are more motions in the system.

Finally, we must add that the 'excess elasticity' is not a molecular parameter. Its value depends on the momentum transfer, as does the value of the elastic form-factor, which the 'excess elasticity' replaces. The discussion of the behaviour of this parameter will concern various models, but one scattering angle only. It is our opinion that the

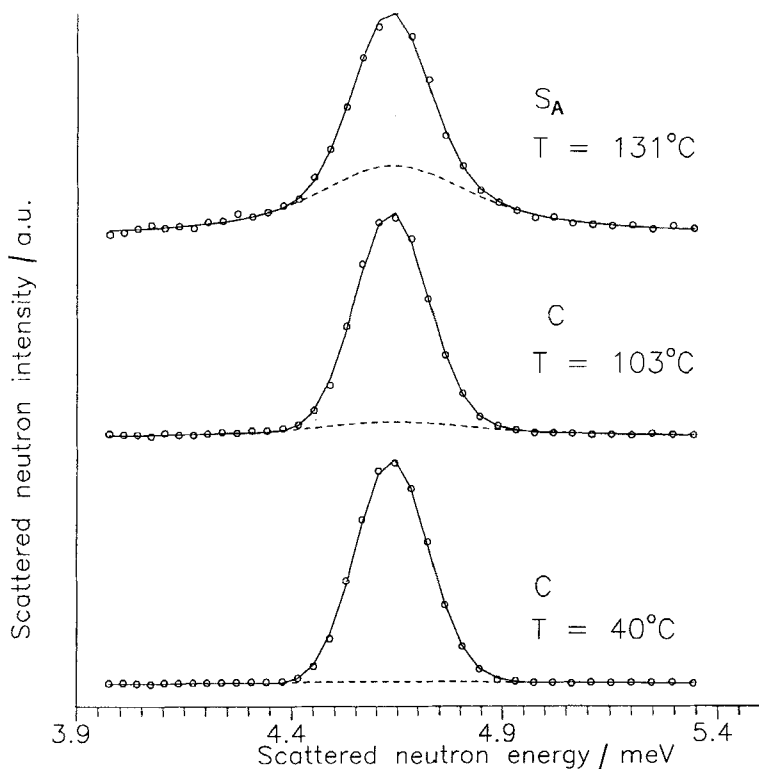


Figure 3. Examples of QNS spectra and examples of model fitting. The solid lines represent model variant 3, the broken lines the QNS components as derived from the fitting procedure. The spectrum at 40°C is nearly elastic and hence very close to the instrumental function. Scattering angle 30°.

gain which could be obtained by using more angles would be illusory, because of complications connected with contributions of various motions in the molecule. Figure 3 shows an example of the quality of fittings.

4. Discussion of the thermal behaviour of various reorientational models

The crucial problem is how to take into consideration the deformational motion of the central cyclohexane group, the motion which we have introduced in §2. We suggest considering instead, a fictitious reorientation of cyclohexane around an axis passing through the planar part of the ring. Within this approximation, we consider the ring as rigid. It should be noted that the reorientational radii of hydrogen atoms around the fictitious axis are nearly equal to those found when the deformation of the ring occurs. It should also be noted that the fictitious reorientation implies a breaking of the bonds connecting the cyclohexane with the rest of the molecule. This is artificial and purely formal.

Now, we introduce the following model variants:

- (1) Cyclohexane performs a fictitious reorientation around the axis dividing into two the planar part of the ring (axis *a* of figure 2). Other molecular fragments, taken as rigid wholes, reorient around the axes: carbon (cyclohexane)–carbon (carboxyl group) (axis *b*). All reorientations occur via rotational diffusion.

- (2) Cyclohexane performs a fictitious reorientation (axis *a*). Other fragments reorient around the *para*-axes of the benzene rings (axis *c*). All reorientations occur via rotational diffusion.
- (3) Motions as in model (2), but they all occur via instantaneous 180° jumps.
- (4) The whole molecule, regarded as rigid, performs rotational diffusion around the long axis.
- (5) Cyclohexane does not move. Other fragments perform rotational diffusion around the *para*-axes of the benzene rings (axis *c*).
- (6) Motions as in model (5) but they all occur via instantaneous 180° jumps.
- (7) Cyclohexane does not move. Benzene rings do not move. Alkyl terminal groups (regarded as rigid) perform rotational diffusion around the *para*-axes of the benzene rings (axis *c*).
- (8) Cyclohexane performs a fictitious reorientation (axis *a*). Benzene rings reorient around their *para*-axes (axes *c*). Alkyl terminal groups do not move. All reorientations occur via rotational diffusion.
- (9) Motions as in model (8), but they all occur via instantaneous 180° jumps.
- (10) Cyclohexane performs a fictitious reorientation (axis *a*) via rotational diffusion. Other molecular fragments do not move. hence, only cyclohexane is mobile.
- (11) Motion as in model (10), but it occurs via instantaneous 180° jumps. Again, only cyclohexane is mobile.

Remark I: none of the variants takes into consideration the interconformational jumps inside the alkyl terminal groups.

Remark II: variant (4), although formally adequate in a certain temperature range, should be rejected *a priori*, since the rotation of the molecule as a whole is too slow (10^{-10} s [2]) for the observation window of our QNS experiments.

Let us now look at the behaviour of the 'excess elasticity' parameter p with temperature in our QNS experiments with the TCDCBPh sample (see figure 4). At 40°C (i.e. for the crystal) all model variants give p values which are positive and large (+80–+50 per cent). This means that we have ascribed to the sample motions which do not show up in reality (too much mobility). At 74°C (i.e. also for the crystal) most model variants give p values which are positive and large (+70–+40 per cent). But the models 10 and 11 suddenly shift to values close to zero (as a matter of fact, even to slightly negative ones). This may mean that the cyclohexane ring affords some mobility before melting. We believe that, in this temperature region, the ring deformation motions which we have discussed in §2 become free. At 100.3°C and then at 101°C we observe a systematic decrease of p . For model variants 1–9, the p values remain positive (c. +30 per cent), which means that we ascribed too many motions to our sample. On the other hand, models 10 and 11 give p c. –30 per cent, which means that the fictitious motion introduced in cyclohexane neglects some mobilities, which is not strange in view of the primitive nature of the model. At 103°C, models 10 and 11 give p values of c. –75 per cent. We shall not discuss these any more, since other degrees of freedom start to become free. For instance, variants 7–9 give p values of c. +15 per cent (i.e. not far from zero) which may mean that other fragments (besides the cyclohexane ring) become free, perhaps gradually. At 104°C, all models give a sudden drop of p and this looks like a phase transition, since all variants give a drop of p at the same temperature. We are inclined to believe that this phase

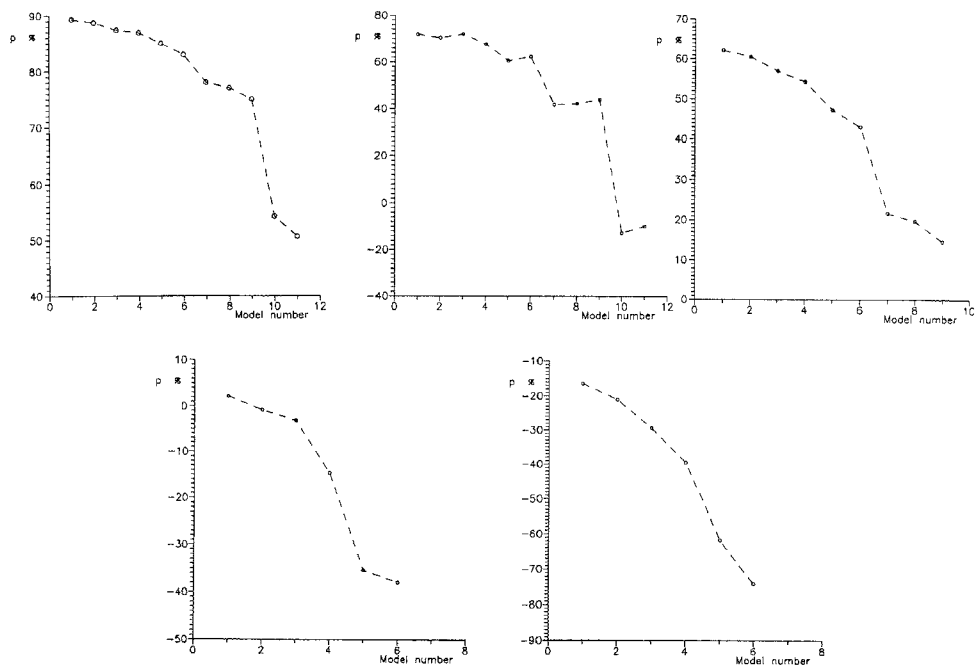


Figure 4. 'Excess elasticity' values for various model variants. (a) 40°C, $p > 0$ for all variants; the crystal is less mobile than suggested by the models. (b) 74°C, $p > 0$ for all models except those with mobile cyclohexane; cyclohexane ring starts moving well before melting. (c) 103°C (crystal), $p > 0$ for some models; but it is close to zero for models 7–9, which may mean that the benzene rings and the alkyl terminal groups have started moving. (d) 104°C (phase X), all molecular fragments move. (e) 132°C (smectic A), all fragments move, but as $p < 0$ it is clear that the substance is more mobile than the models suggest.

transition takes place before melting, and that above this transition all degrees of freedom as discussed in the models are free. Further temperature increase gives a further systematic decrease of p to more negative values, which means that in reality the set of stochastic motions in the sample is richer than that suggested in the models. This is not surprising, since for instance, the inter-conformational motions in the alkyl terminal groups were completely neglected in the model variants. No doubt, the flexibility of the molecule permits a variety of motions.

Let us emphasize once more the fact that a sudden drop of p takes place at 104°C, three degrees below the nominal melting at 107°. Is it or is it not too risky to conclude from this that there exists a new phase before the smectic A phase? Perhaps this difference of three degrees is illusory, an experimental artefact, and in reality, the release of motions which we have ascribed to the new phase occurs on melting. The answers to these questions may be: firstly, such a large error in temperature reading is improbable. Secondly, when compared with that of other members of the homologous series, there exists, only for TCDCBPh, a minimum of the melting entropy. This may mean that some degrees of freedom were released ('melted') before the proper melting [9]. To investigate this matter we carried out studies of the phase sequence in TCDCBPh by using polarized light microscopy.



Figure 5.

5. Phase sequence in TCDCBPh as studied by polarization microscope

Observations were made using a MNP-1 microscope (Polish made), in which a table with an automatically operating thermostat (Linkam Instruments) was installed. A video camera was connected with the system. Observations were made on cooling; hence the temperatures of phase transitions are not correct, due to undercooling effects. However, we were able to see the proper phase sequence and in all runs which started from the nematic phase we were able to observe, at first the marbled texture characteristic of the nematic [10] and then the phase transition to typical focal-conic texture characteristic of the smectic A [10]. On further cooling we observed (in all runs) a new texture lasting over a short range (within the limits of 1.5°C), and not described in the literature [10, 11]. At still lower temperatures, a texture of a crystal appeared. Figure 5 presents three of the textures. On the basis of this observation we conclude that just below the melting of TCDCBPh there (probably) exists a 'mobile' crystalline phase.

6. Conclusions

Analysis of the 'excess elasticity' parameter of the QNS data obtained for the mesogenic substance TCDCBPh seems to reveal the following points:

- (1) Stochastic deformational motions in the cyclohexane ring are released well below the melting, and before other molecular motions are made free.
- (2) A gradual release of other motions in the molecule starts at $c. 103^\circ$.
- (3) At 104°C a phase transition probably occurs. The majority of reorientational motions in the molecule are being released. This occurs before melting.
- (4) After melting, a further increase in mobility in the molecules takes place, but without sudden changes.
- (5) Microscopic observations confirm the existence of an additional 'mobile' crystal phase, as mentioned in point (3).

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Figure 5. Microscopic observation of the TCDCBPh sample, on cooling: (a) moment of transition smectic A-phase X?, (b) unknown type of texture of phase X and (c) the crystal texture.

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