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QNS STUDY OF UNIAXIAL MOLECULAR REORIENTATIONS IN SOLID t-CYANOBUTANE

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The results of a quesielastic neutron scattering (QNS) investigation on a t-cyanobutane, $(CH_3)_3CCN$, sample in three solid phases are presented. It was found there is a fast uniaxial reorientation of the t-cyanobutane molecules in phase I, characterized by correlation times of the order of several picoseconds and an activation barrier $\Delta E = (0.5 \pm 0.2)$ kcal/mole. The lack of quasielastic broadening in the neutron spectra of lower-temperature phases implies that molecular rotation is then much slower or completely hindered.

1. Introduction

In organic compounds having globular molecules the transition from the normal crystal state to the liquid state takes place gradually, through a successive release — in the consecutive phase transitions — at first the rotational and then (at the melting point) translational degrees of freedom of the molecules. An example of such substances are compounds of the $(CH_3)_3CX$ type (with $X =$ Cl, Br, NO_2 or CN), which in the solid state reveal two phase transitions separating three crystal phases. In the lower-temperature phases (phase III) these compounds' molecules are orientationally ordered or perform

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relatively sparse rotational jumps about the preferred axes [12, 14]. In the intermediate phase (phase II) of *t*-butyl chloride ($X = \mathrm{Cl}$; TBC) and t-nitrobutane ($X = \mathrm{NO_2}$; TBN) quasielastic neutron scattering (QNS) investigations carried out by our group [1, 2] have shown that the molecules perform stochastic rotational jumps about frozen $\mathrm{C}-X$ axes which are characterized by correlation times of the order of picoseconds. In the case of t-butyl bromide ($X = \mathrm{Br}$) there are overall rotations of molecules in phase II, just as in the highest-temperature phases (phase I) of all threee of the mentioned compounds [3–5]. The last in this series of compounds, t-cyanobutane ($X = \mathrm{CN}$; TBCN), demonstrates a somewhat different rotational behaviour of molecules in the solid phases.

Calorimetric studies made by Westrum and Ribner [6] have shown that t-cyanobutane (also known as t-butyl cyanide, 2,2-dimethylpropanenitrile, pivalonitrile and trimethylacetonitrile) melts at 292.13 K with an entropy change $\Delta S_m = 7.60$ e. u. (cal/mole K), whereas two solid-solid phase transitions occur at 232.74 K ($\Delta S = 1.86$ e. u.) and at 213 K ($\Delta S = 0.26$ e. u.). In phase I TBCN crystallizes in the orthorhombic system with the following unit cell parameters: $a = 13.69$ Å, $b = 13.54$ Å and $c = 6.97$ Å ($Z = 8$ molecules per unit cell) [7].

Dielectric investigations [8] on TBCN have shown that the dipole moments of the molecules of this compound become frozen already at the melting point, although in phase I the dipolar axis performs librations — just as in TBN's phase II [9] — of relatively large amplitude [10]. Both, dielectric [8] and calorimetric studies [6] suggested the existence of uniaxial rotation of TBCN molecules in phase I. This conclusion has been confirmed by nuclear magnetic resonance (NMR) measurements.

El Saffar et al. [11] carried out research on TBCN, measuring the line-width, second moment and spin-lattice relaxation times T_1 in a broad range of temperatures of the solid phase. Line-width and second moment decrease in the range from 90 K to 130 K (phase III), and with continued heating of the sample and at phase transition points do not undergo any greater change. The relaxation time achieves a minimum value at a temperature of 162 K, whereas at the phase III — phase II transition point there is a slight, step-wise, shortening of T_1. At increasing temperature the relaxation time again becomes monotonically longer. The main conclusions of the authors of the paper are: (a) that already in phase III there are in TBCN two simultaneous motions of protons — the rotation of methyl groups about the C–C axis and the rotation of the whole molecule about the C–CN axis; and (b) that the one-step change of the second moment and the occurrence of a single relaxation time minimum is proof that both of these motions feature identical correlation times and activation barriers of the same height $\Delta E = (3.9 \pm 0.2)$ kcal/mole in all of TBCN's solid phases.

The latter of these conclusions is rather surprising, for it implies invariance of the rotational dynamics of TBCN molecules at phase transition points, in contradistinction to the situation observed in other similar compounds [1–5]. It seems, though, that the lack of changes in line-width and second moment of NMR at the phase transition points arises rather from the limited sensitivity of this method to changes in the time scale of the reorientation movements of protons. This also showed up in investigations of phase II of TBC: NMR measurements [12, 14] suggested the existence of uniaxial molecular rotation in this phase with correlation times of the order of 10^{-8} sec, whereas for the same motion QNS measurements yielded correlation times of the order of 10^{-12} sec [1]. Therefore, we decided to perform quasielastic neutron scattering measurements for all solid phases of TBCN.

2. *Experimental*

The QNS spectra were measured by the time-of-flight technique on the inverted-geometry KDSOG-1 spectrometer at the IBR-1 pulsed reactor of the Neutron Physics Laboratory, JINR, Dubna. The experimental details were the same as described in a previous paper [2]. The energy of neutrons scattered by a sample was analysed by a Be-filter-Zn (002) single crystal system. The resolution function of the spectrometer, $R(E_f)$, was measured by using a vanadium sample. Spectra for seven scattering angles 2θ were measured simultaneously, viz. 30°, 50°, 70°, 90°, 110°, 130° and 150°. The mean energy of the elastic peak was $\bar{E}_f = 5.125$ meV, while its mean spread at half peak height was $\Delta\bar{E}_f = 0.297$ meV. The average energy resolution was hence 5.8%.

The TBCN sample was produced by use of Butlerow method: melting point: 291 K (292.1 K [6]), boiling point: 378.7 K (379 K [8]), $n_D^{298} = 1.3812$ (1.3809 [8]).

3. *Results and data processing*

Since the temperature range of TBCN's phase I is quite large (59.4 K), we carried out the QNS spectrum measurements at three points of this phase: 242 K, 263 K and 283 K, in order to estimate the activation barrier for the observed proton motion. Moreover, measurements were made at one temperature each of phase II (222 K) and phase III (202 K). Also, the background of scattered neutrons was measured with the empty vessel in the cryostat (at room temperature).

Because Bragg reflections from the sample and aluminium appeared near energy E_f, only the spectra obtained at the first three (phase I) or four (phase II and III) of the scattering angles qualified for further processing. Hence, the analysed spectra corresponded to neutron momentum transfers κ of 0.82, 1.34, 1.81 and 2.21 Å^{-1}. By way of illustration, Fig. 1 shows neutron spectra for each of the three solid phases of TBCN, normalized by the spectrum of the incident neutrons.

The obtained spectra of scattered neutrons were analysed analogously as in the case of studies on TBN [2], making use of the following expression for the law of quasielastic neutron scattering:

$$S_{\mathrm{qns}}^{\mathrm{inc}}(\vec{\kappa}, \omega) = \sum_{\mathrm{H}} \left[F_{\mathrm{el}}(\vec{\kappa} \cdot \vec{r}_{\mathrm{H}}) R(E_f) + \frac{2}{\pi} \sum_{l=1}^{n} \int dE_f F_{\mathrm{qel}}^{l}(\vec{\kappa} \cdot \vec{r}_{\mathrm{H}}) R(E_f) \frac{\Gamma_l}{\Gamma_l^2 + \omega^2} \right],$$

where: $\hbar\vec{\kappa}$ is the momentum transfer and $\hbar\omega = E_i - E_f$ is the energy transfer of neutrons (E_i and E_f are the initial and final neutron energy values, respectively), $R(E_f)$ is the spectrometer's resolution function (approximated by an analytic curve being a junction of Lorentz and Gauss curves), $\vec{r}_H$ is the radius of proton rotation, and Γ_l are the half-width at half height of the Lorentz curves.

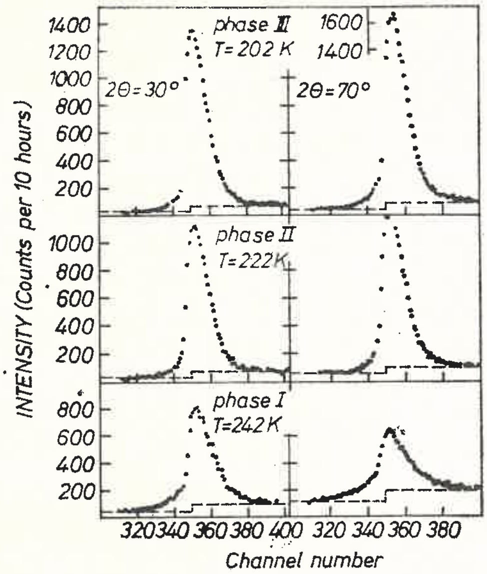

Fig. 1. Neutron spectra measured for three solid phases of TBCN in the time-of-flight scale. The dashed lines present accepted inelastic background

Quasielastic, $F_{\mathrm{qel}}(\vec{\kappa} \cdot \vec{r})$, and elastic, $F_{\mathrm{el}}(\vec{\kappa} \cdot \vec{r})$, form factors depend on the geometry of proton rotations. As in Ref. [2], the following models of proton rotation in the examined sample were considered:

— proton jumps by an angle of 120° about the C–CN axis (molecular rotational jumps),

— uniaxial rotational diffusion of molecules about the C–CN axis, and

— proton jumps by an angle of 120° about the C–C axis (intramolecular methyl group rotation).

The dependence of the form factors F_{el} and F_{qel} on the value of κr was discussed for the said models in detail in Ref. [2]. It follows from this discussion that if the quasielastic broadening appears for the smallest scattering angles (i. e. small κ values), then this means that the radius of proton rotation is relatively large. As the radius of molecular rotation in the case of the TBCN molecule is almost twice as long as the radius of the CH_3 group rotation (1.81 and 0.964 Å, respectively), it is easily predictable that the share of molecular rotation dominates in the observed spectrum of neutrons scattered quasielastically under small angles. This conclusion is corroborated by a comparison of experimental spectra with the model's curves for phase I of TBCN. As is seen in Fig. 2, the curves corresponding to the rotation of methyl groups (the solid lines) do not trace the shape of the observed spectrum at scattering angles of 30° and 50°, in contrast to the curves corresponding to molecular rotational jumps (the dashed curves). It is only at an angle approaching 70° that both models reproduce the shape of the spectrum equally well.

Figure 3 shows the spectra obtained for phase II of TBCN. In this case, the quasielastic broadening is extremely small and with the current spectrometer resolution (the solid line in the figure) it is impossible to analyse this broadening quantitatively. A comparison of the spectrum with the curve corresponding to methyl group rotation (dashed line) indicates that this small broadening may perhaps be linked with this type of rotation. The spectra for TBCN's phase III almost exactly tally with the resolution curve.

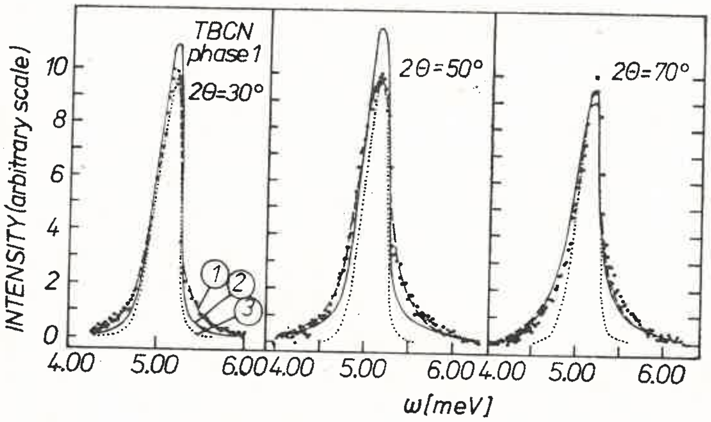

Fig. 2. Comparisons of the model's curves with the experimental QNS spectra measured at 263 K. Curve *1* corresponds to the model of molecular rotational jumps, curve *2* — to the model of methyl group rotation, curve *3* — the resolution function of the spectrometer

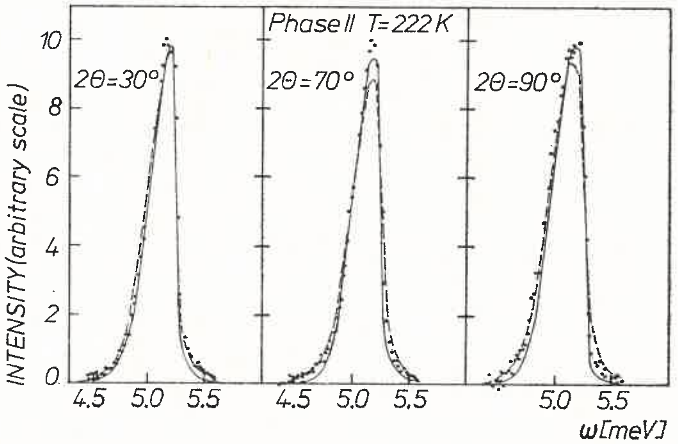

Fig. 3. QNS spectra obtained for phase II of TBCN. Solid line — the resolution function of the spectrometer, dashed lines — the curve corresponding to model of methyl group rotation

Subsequent analysis of the neutron patterns obtained for phase I was performed in order to decide which of the molecular rotation models reproduces the observed quasielastic broadening better. To this aim use was made of the "χ^2 test" described elsewhere

[2]. Figure 4 shows the dependence of χ^2 on the half-width of the Lorentz curve Γ for all three proton rotation models. Since comparatively the best fit was obtained for the model of molecular rotational jumps, only this model was taken into account when analysing

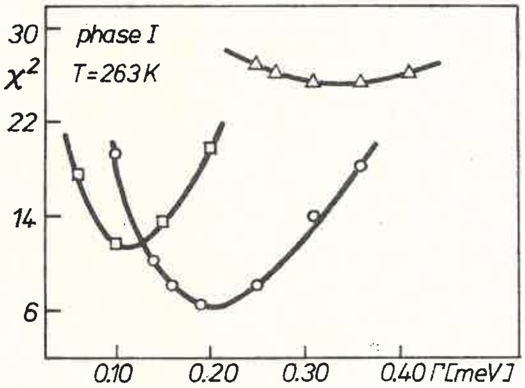

Fig. 4. χ^2 test for three models of proton rotation in TBCN's phase I: ○ – model of molecular rotational jumps, □ – uniaxial rotational diffusion, △ – methyl group rotation

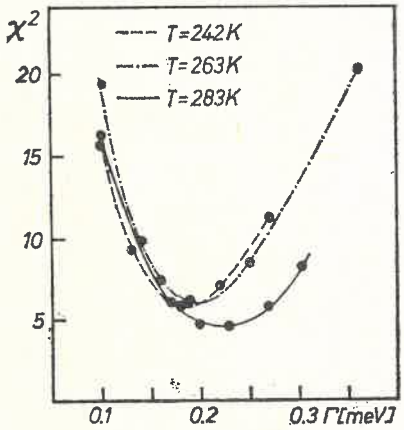

Fig. 5. $\chi^2(\Gamma)$ for three temperatures of TBCN's phases I (the molecular rotational jumps model)

TABLE I

The values of half-width at half maximum of quasielastic Lorentz curve Γ, mean time between proton jumps τ, and correlation time τ_1 for three temperatures of phase I of t-cyanobutane

T (K)	Γ (meV)	$\tau \cdot 10^{-12}$ sec	$\tau_1 \cdot 10^{-12}$ sec
242	0.190±0,01	5.2±0.2	1.7±0.2
263	0.205±0.01	4.8±0.2	1.6±0.2
283	0.220±0.01	4.5±0.2	1.5±0.2

the temperature dependence of the size of the quasielastic broadening of neutron spectra in phase I of TBCN. Figure 5 presents the $\chi^2(\Gamma)$ dependence for all three temperatures of the substance's phase I. The values of Γ read for the curve minima and the corresponding mean values of time between proton jumps τ and the correlation times τ_1($\tau = 3\hbar/2\Gamma$, $\tau_1 = \hbar/2\Gamma$ [13]) are arranged in Table I.

Using the Arrhenius activation equation, $\tau = \tau_0 \exp(\Delta E/RT)$, the value of the activation barrier hindering uniaxial rotation of TBCN molecules in phase I was calculated; it was found to be $\Delta E = (0.5 \pm 0.2)$ kcal/mole, i. e. it is comparable with the thermal energy RT.

4. *Discussion*

The results of quasielastic neutron scattering measurements made on t-cyanobutane sample in its three solid phases presented here exhibit an essential difference in the magnitude of the quasielastic broadening of phase I and that of the other phases. This indicates either that reorientation motions of the molecules are frozen below the "phase I — phase II transition", or that the correlation times become distinctly elongated jump-wise after transition to the lower-temperature phases. This conclusion contradicts the results of NMR studies mentioned in the Introduction, which suggest invariance of correlation times and activation barrier at the various phase transitions. Moreover, the activation barrier for molecular rotation in TBCN's phase I evaluated in our research is considerably lower than that obtained in the NMR studies. The latter, in turn, is approximately equal to barriers for methyl group rotations in similar compounds obtained from NMR measurements [12, 14]. Whence it can be concluded that both of the methods mentioned, NMR and QNS, recognize — at least as far as TBCN's phase I is concerned — the different processes of proton reorientation.

Analysis of the quasielastic broadening of the spectrum of neutrons scattered by the TBCN sample in phase I gives preference to the model of 120° jumps of the trimethyl groups about the C–CN axis. However, owing to the small range of neutron momentum transfers, this conclusion cannot be unambiguous. For an analysis of the form factors $F_{\text{qel}}(\vec{\kappa} \cdot \vec{r})$ for the jump model and the rotational diffusion model (cf. [2]) indicates that these two models become decidedly discernible only when κr is greater than about 2.5 (in our case, $\kappa r = 2.21$ for the scattering angle of 70°).

Recapitulating, it may be stated that the quasielastic neutron scattering experiments we made on a t-cyanobutane sample in three solid phases have shown that:

— in the substance's phase I the molecules perform stochastic rotational jumps about the frozen C–CN axis;

— this rotation is almost free; and

— in phases II and III molecular reorientation is either frozen or takes place much more slowly than in phase I.

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REFERENCES

[1] P. S. Goyal, W. Nawrocik, S. Urban, J. Domosławski, I. Natkaniec, *Acta Phys. Pol.* **A46**, 399 (1974).
[2] J. Mayer, I. Natkaniec, J. Ściesiński, S. Urban, *Acta Phys. Pol.* **A52**, 665 (1977).
[3] S. Urban, J. A. Janik, J. Lenik, J. Mayer, T. Waluga, S. Wróbel, *Phys. Status Solidi* (a) **10**, 271 (1972).
[4] S. Urban, J. Lenik, J. Mościcki, S. Wróbel, *Acta Phys. Pol.* **A48**, 787 (1975).
[5] S. Urban, *Acta Phys. Pol.* **A49**, 741 (1976).
[6] E. F. Westrum, A. Ribner, *J. Phys. Chem.* **71**, 1216 (1967).
[7] S. Urban, J. Domosławski, Z. Tomkowicz, to be published.
[8] C. Clemett, M. Davies, *Trans. Faraday Soc.* **58**, 1705 (1962).
[9] P. Freundlich, J. Kalenik, E. Narewski, L. Sobczyk, *Acta Phys. Pol.* **A48**, 701 (1975).
[10] P. Freundlich, private information.
[11] Z. M. El Saffar, P. Schultz, E. F. Meyer, *J. Chem. Phys* **56**, 1477 (1972).
[12] D. E. O,Reilly, E. M. Peterson, C. E. Scheie, E. Seyfarth, *J. Chem. Phys.* **59**, 3576 (1973).
[13] J. A. Janik, J. M. Janik, K. Otnes, K. Rościszewski, *Physica* **83B**, 259 (1976).
[14] E. O. Stejskal, D. E. Woessner, T. C. Farrar, H. S. Gutowsky, *J. Chem. Phys.* **31**, 55 (1959).