

QUASI-ELASTIC NEUTRON SCATTERING (QENS) STUDIES ON THE 1:1 TETRAMETHYLPYRAZINE–1,2,4,5-TETRACYANO BENZENE COMPLEX

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Dedicated to the memory of Professor Otto Exner.

The quasi-elastic neutron scattering (QENS) spectra over the temperature range 10–270 K were studied. The activation energies for the stochastic jumps of methyl groups in neat tetramethylpyrazine (TMP) and in the complex TMP·TCNB (tetracyanobenzene) were estimated to be equal to 5.0 ± 1.2 and 2.2 ± 1.1 kJ/mol, respectively, which means that the methyl groups behave in the complex more freely than in TMP. This conclusion is in good agreement with frequencies of the CH₃ torsional modes recorded in the inelastic neutron scattering (INS) spectra. They are also confirmed by the DFT calculations for the crystalline state of TMP and TMP·TCNB, although the calculations overestimate the effect of the crystalline state on the CH₃ torsional frequencies. The difference in the behavior of the methyl groups in neat TMP and TMP·TCNB is also reflected in the blue-shift of the $\nu(\text{CH})$ stretching vibration modes.

Keywords: CT complex; Tetracyanobenzene; Tetramethylpyrazine; QENS; IR spectroscopy; DFT calculations; Charge-transfer complexes.

In the search for a correlation between the molecular interaction and dynamics of the methyl group, systematic investigations of the complexes

composed of the methyl derivatives of benzene and pyrazine both of the charge-transfer and hydrogen-bond type were undertaken¹⁻⁵.

The rotational potential of methyl groups appeared to be highly sensitive to the interaction⁶. Simultaneously in several papers it was shown that this potential is best reflected in the inelastic neutron scattering experiments over a wide range of the energy and momentum transfers^{7,8}. If the potential is not very high the tunneling splitting seems to be the most sensitive parameter⁹ and then the quasi-elastic scattering, which is well observed even for a relatively high rotational barrier¹⁰⁻¹². The inelastic neutron scattering (INS) related to internal vibrational modes, to which the torsional/librational vibrations of CH₃ groups contribute, seems to be, however, the most universal tool⁸.

The 1:1 complexes of tetracyanobenzene (TCNB) with durene and tetramethylpyrazine (TMP) appeared to be interesting^{2,5}. Both durene and TMP, neat as well as in the complex with TCNB, do not show the tunneling transitions ($\hbar\omega_t \ll 1 \mu\text{eV}$), while analysis of librational modes, particularly of the CH₃ torsional mode, was successful in these studies¹³. The durene·TCNB

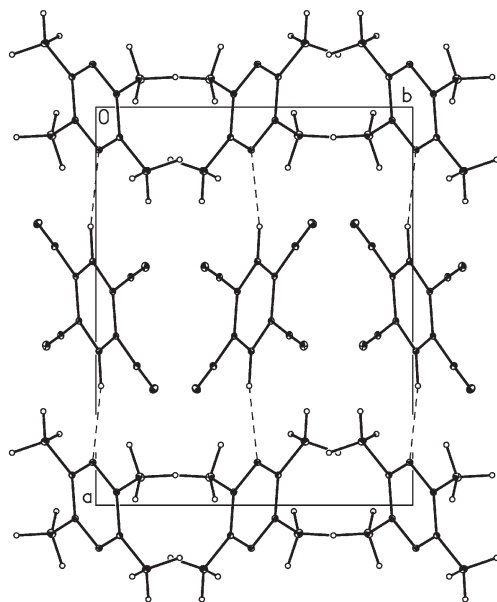


FIG. 1

Packing of molecules in the TCNB-TMP crystals; the view along the *c*-axis; according to ref.²

complex shows in the crystalline lattice stacking with alternately placed donor and acceptor molecules, thus showing a typical π - π CT interaction. However, in the case of the TMP·TCNB complex the C-H...N hydrogen bonds between TCNB and TMP molecules as well as the formation of infinite chains, as shown in Fig. 1, are a decisive packing factor.

In the present paper, we decided to investigate the rotational potential of the methyl groups in neat TMP and in the TMP·TCNB complex using QENS. The QENS technique was chosen for this investigation because through the activation energy direct information concerning the potential height can be obtained. An opinion exists that the best informative relationship, from this point of view, is the temperature dependence of QENS. Simultaneously we decided to perform a critical analysis by a comparison of the QENS results of the INS spectra in the librational region as well as of the DFT calculations of the lattice effect on the rotational potential.

The aim of the present paper was also a comparison of the $\nu(\text{CH})$ modes of CH_3 groups for TMP and its complex with TCNB in the solid state based on the infrared studies. Our experiment is also designed to provide insight into the behavior of the low-frequency vibrations, below 500 cm^{-1} , where the deformation bands with participation of the methyl groups appear.

EXPERIMENTAL AND CALCULATIONS

The QENS spectra of TMP and the TMP·TCNB complex were measured with the time-of-flight (TOF) spectrometer, operating at the JEEP II reactor at the Institute of Energy Technology, Kjeller, Norway. Neutrons outgoing from a cold neutron source were monochromatized to the energy 4.66 meV by Bragg scattering from a pyrolytic graphite crystal. The QENS spectra measurements were performed for a scattering angle of 80° , corresponding to the momentum transfer of 1.9 \AA^{-1} . The spectra were measured at 100 – 250 K for TMP and at 150 – 270 K for the complex.

The powder sample was contained in a flat aluminum sample-holder of the size ca. $40 \times 50 \times 1\text{ mm}^3$. The spectra obtained were corrected for the sample holder scattering, the constant background of fast neutrons and for the inelastic scattering background. The multiple scattering corrections were applied as well. The instrumental resolution function was determined by measuring the spectra of both samples at 10 K . The resolution function for the TOF spectrometer could be described by a slightly distorted Gaussian function; the energy resolution of the spectrometer was $\sim 130\text{ }\mu\text{eV}$ (FWHM).

The IR spectra were recorded as previously reported². Additional experiments were performed in the high-frequency region corresponding to the $\nu(\text{CH})$ stretching vibration bands (Fluorolube suspension and CCl_4 solutions) and in the low-frequency range, below 500 cm^{-1} (Nujol suspensions). A Bruker IFS66 instrument was used.

The total energy optimization and the frequency calculations were performed based on the density functional theory (DFT) using the DMol3 program^{14,15} as a part of Materials Studio package¹⁶. The results for the crystalline state were obtained within the local density

approximation (LDA) at PWC¹⁷ functionals and within the generalized gradient approximation (GGA) at PBE¹⁸ and BLYP (Becke exchange¹⁹ plus Lee–Yang–Parr²⁰ correlation), functionals. Calculations were performed using Gaussian approximation 6-31G(d,p) (dnp) basis set as implemented in DMol3.

RESULTS AND DISCUSSION

QENS Spectra

The QENS spectra of neat TMP at 10–250 K are presented in Fig. 2. The spectra measured at 10, 100 and 130 K exhibit no quasi-elastic component. The quasi-elastic broadening begins at 150 K and increases with increasing temperature.

The spectra measured at several temperatures between 150 and 250 K could be described by the instantaneous 120° jumps of the CH₃ groups around the three-fold symmetry axis with the scattering law $S(\mathbf{Q}, \omega)$ given in refs^{10–12}

$$S(\mathbf{Q}, \omega) = \frac{1}{3} \left(1 + \frac{2 \sin(\mathbf{Q}r\sqrt{3})}{\mathbf{Q}r\sqrt{3}} \right) \delta(\omega) + \frac{2}{3\pi} \left(1 - \frac{\sin(\mathbf{Q}r\sqrt{3})}{\mathbf{Q}r\sqrt{3}} \right) \frac{\Gamma}{\Gamma^2 + \omega^2} \quad (1)$$

where \mathbf{Q} and ω are the momentum and energy transfers, respectively, $r = 1.06$ Å is the distance of the protons from the reorientation axis, $\Gamma = 3\hbar/2\tau$ and τ is the mean time between jumps. The best fit to the 120°-jump model

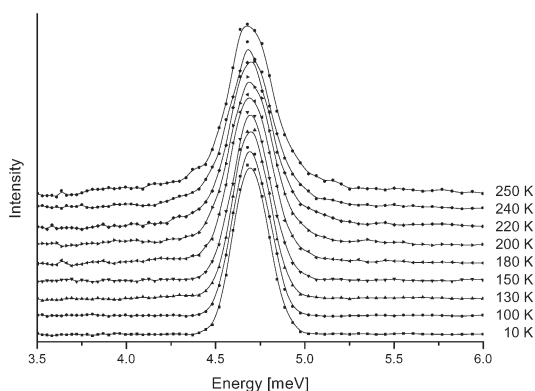


FIG. 2
QENS spectra for TMP

was achieved assuming two types of methyl groups, which differ substantially in τ . One type of motion is on the ps scale, while the other one, as very fast, is hidden by the background (of the order of 0.1–0.7 ps). An example of fitting the model to the QENS spectrum is given in Fig. 3.

The QENS spectra of the TMP·TCNB complex at 10–270 K are presented in Fig. 4. Also in this case one can see the quasi-elastic broadening beginning at 150 K, which increases with increasing temperature.

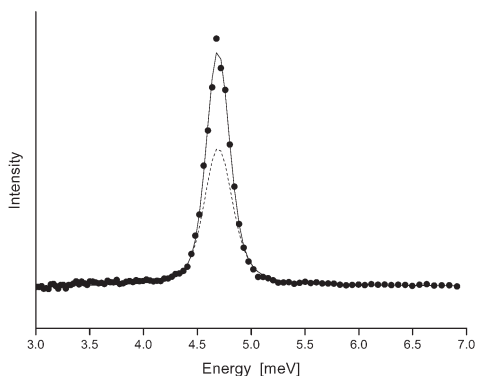


FIG. 3

Fitting of the 120°-jump model to the QENS spectra of TMP measured at 240 K. The broken line represents the quasi-elastic component

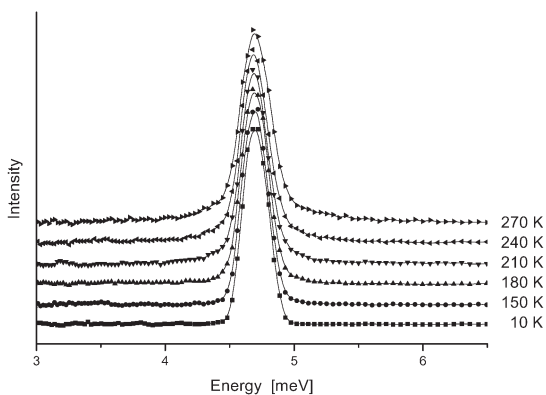


FIG. 4

QENS spectra for the TMP·TCNB complex

In the case of the complex, only the protons from the CH_3 groups of the TMP molecules take part in the fast reorientation described by the scattering function given above. As shown by the packing of molecules in the crystalline complex (see Fig. 1 and data published in ref.²) there are two different CH_3 groups, but the difference between them is negligibly small; hence, one can assume that we are dealing with one type of CH_3 groups. Two protons of the TCNB molecules contribute only to the elastic part of the spectrum and this is why the model was modified by taking into account this additional elastic contribution:

$$S_{\text{complex}}(\mathbf{Q}, \omega) = \frac{12}{14} S(\mathbf{Q}, \omega) + \frac{2}{14} \delta(\omega). \quad (2)$$

The example of fitting this model to the QENS spectrum is given in Fig. 5.

The fitted mean time between jumps, τ , changes from 32.5 ps at $T = 150$ K to 6.5 ps at $T = 250$ K for TMP and from 19 ps at $T = 150$ K to 9 ps at $T = 270$ K for the TMP·TCNB complex. The temperature dependence of the best-fit time, τ , is shown in Fig. 6 for TMP and in Fig. 7 for the TMP·TCNB complex. The data can be described by the Arrhenius formula. The fitted activation energy is 5.0 ± 1.2 kJ/mol for TMP and 2.2 ± 1.1 kJ/mol for the TMP·TCNB complex. From the fact that both τ values and activation energy are smaller for the complex than for the neat compounds, one can con-

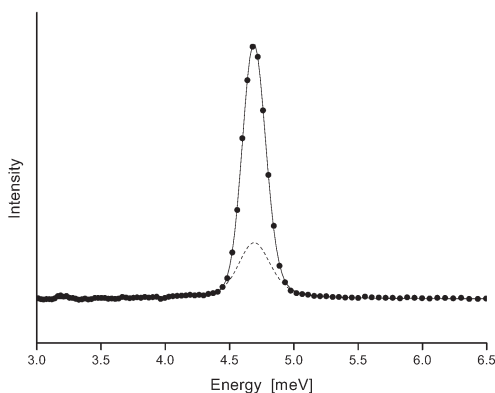


FIG. 5

Fitting of the 120° -jump model to the QENS spectra of the TMP·TCNB complex measured at 210 K. The broken line represents the quasi-elastic component

clude that the CH_3 groups reorient more freely in the complex probably because the TMP molecules are separated by the TCNB ones. A similar result was observed for hexamethylbenzene (HMB) and its complex with tetracyanoquinodimethane¹ (TCNQ) as well as for durene and durene·TCNB complex⁵.

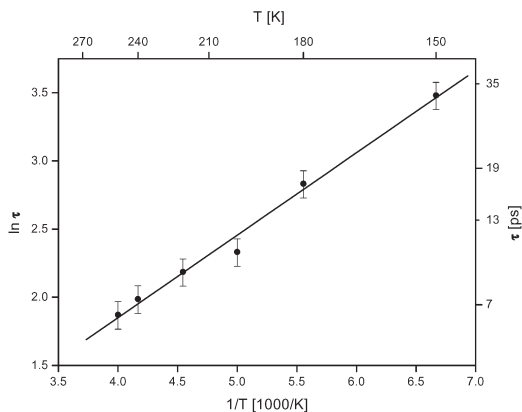


FIG. 6
Arrhenius plot for TMP; τ in ps

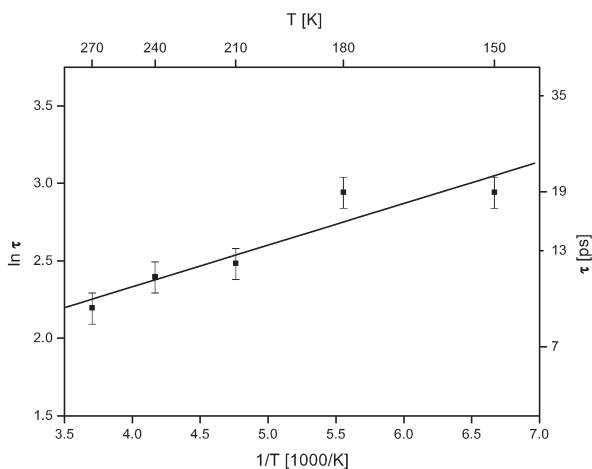


FIG. 7
Arrhenius plot for the TMP·TCNB complex; τ in ps

Infrared Spectra

From the viewpoint of interactions with participation of methyl groups one can expect substantial spectroscopic changes in the low-frequency deformation modes and high-frequency stretching $\nu(\text{CH})$ frequencies. In the latter case, as expected from rich literature²¹, we are dealing with a blue-shift. In the low-frequency region the modes related to the methyl group rotation (torsional modes) are particularly sensitive to the intermolecular interaction⁸. As it has been shown we are dealing with an unusual shift to higher frequencies analogous to the deformation IR bands of proton donor groups in hydrogen bonds.

In Fig. 8, we compared the IR spectra (in Nujol) of neat TMP and TCNB and the TMP·TCNB complex. Let us emphasize first a lack of bands in the spectra ascribed to the methyl torsional vibrations due to either selection rules or extremely low intensity. This is in agreement with earlier analysis¹³. Thus, only two bands assigned to C-CH₃ bending and C-CH₃ wagging vibrations are observed in the spectrum. A negligible shift of these bands towards higher frequencies takes place in comparison to those present in the spectra of the neat components of the complex. Generally one can say that we observe the sum of constituents assigned separately to TMP and TCNB. This result shows once more the advantages of the INS spectra, which almost perfectly demonstrate the behavior of methyl groups in torsional vibrations.

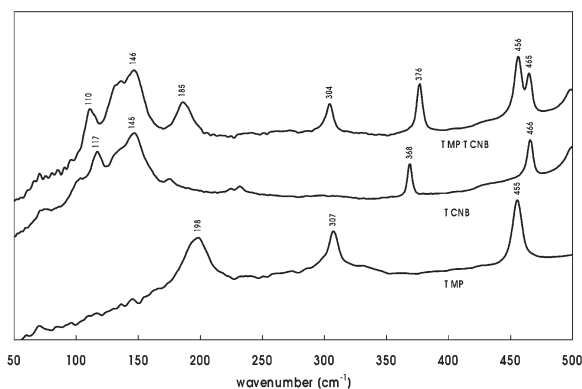


FIG. 8

Infrared spectra in the region below 500 cm⁻¹ in Nujol for TMP, TCNB and the TMP·TCNB complex

Let us look now at the behavior of methyl groups in the range of $\nu(\text{CH})$ stretching vibrations. According to theoretical DFT analysis of normal modes in IR spectra, four bands are present as depicted in Fig. 9. The ratios of intensities of particular bands can change upon the chemical environment. The comparison presented in Table I allows to state unequivocally that the frequencies measured for the complex are lower than for neat TMP and TMP in CCl_4 solution. In terms of the blue-shift concept this implies that the interactions in the crystalline complex are weaker than in neat crystalline TMP. It is not clear why the frequencies are higher in CCl_4 solution than in neat TMP but one can assume that we are dealing in this case with relatively strong $\text{C-H}\cdots\text{Cl}$ interactions.

Table I

Wavenumbers (in cm^{-1}) of stretching vibration $\nu(\text{CH})$ bands of tetramethylpyrazine (TMP) and its complex with 1,2,4,5-tetracyanobenzene (TCNB)

CCl_4 solution	2866	2921	2953	2995
TMP in Fluorolube suspension	2864	2921	2950	2986
TMP in the TMP-TCNB complex (Fluorolube)	2853	2917	2946	^a

^a Band of TCNB overlapped with the $\nu(\text{CH})$ vibration.

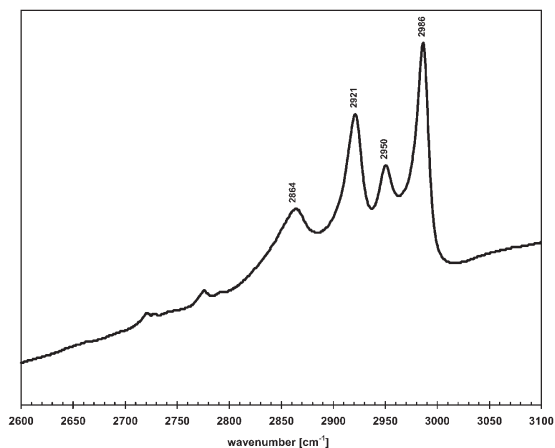


FIG. 9
Infrared spectrum in the $\nu(\text{CH})$ frequency region for TMP in Fluorolube

INS Spectra

Taking into account that the INS spectra in the region of torsional vibrations are those of the most sensitive probes of the methyl group interactions⁶⁻¹⁰, we decided to analyze the manifestation of these modes in neat TMP and the TMP·TCNB complex.

As shown¹³, four modes related to the torsional vibrations, namely at 120, 122, 140 and 156 cm⁻¹, appear in the isolated TMP molecule. From the data presented in Table II it results that experimental frequencies are markedly higher both for neat crystalline TMP and the TMP·TCNB complex. For the complex, the experimental wavenumbers are lower than those for neat TMP, which corresponds to a lowering of the rotational barrier.

TABLE II
Wavenumbers (in cm⁻¹) of CH₃ torsional modes of INS experimental data compared with the calculated ones for tetramethylpyrazine (TMP) and its complex with 1,2,4,5-tetracyanobenzene (TCNB)

	TMP			
INS experimental ^a	171	171	190	190
Calculated for isolated molecule (B3LYP)	120	122	140	156
Calculated for the crystalline state				
BLYP(dnp)	191	202	264	266
PBE(dnp)	224	232	310	315
PWC(dnp)	215	221	243	251
	TMP·TCNB			
INS experimental ^a	140	162	172	187
Calculated for isolated molecule (B3LYP)	120	122	140	156
Calculated for the crystalline state				
BLYP(dnp)	155	158	185	196
PBE(dnp)	186	189	204	212
PWC(dnp)	215	221	243	251

^a Taken from ref.²

We decided to perform calculations of frequencies of particular modes for the crystalline states of TMP and the TMP·TCNB complex on the DFT level applying three selected functionals. The results of such calculations are included in Table II. These data clearly show that simulated frequencies for TMP are markedly higher than those for the TMP·TCNB complex. The theoretically overestimated frequencies independently of the applied functionals are a separate problem. The results obtained by using the BLYP(dnp) approach are the closest ones to the experimental data. It is difficult to formulate far-reaching conclusions based on these observations. The disagreement can be due to several factors. One of them could be a result of the limited basis set that arises from computational limitations. The most probable reason for the discrepancy is the assumption of the harmonicity of vibrations in the applied methods that is far from the reality, particularly in the case of librational modes.

CONCLUSIONS

Based on the QENS studies over the broad temperature range for neat TMP and the TMP·TCNB complex it was possible to evaluate the activation energy for the stochastic jumps of methyl groups. This activation energy is for the complex markedly lower than for neat TMP. Because in this case the charge transfer between the components can be neglected, the direct contacts of hydrogen bonds to the adjacent molecules in the lattice seem to be a unique reason for the reduction of the rotational barrier. This fact finds some reflection in the blueshift of the $\nu(\text{CH})$ stretching vibration bands in the IR spectra. The frequencies of all the four modes in the IR spectra are higher for neat crystalline TMP than in the TMP·TCNB complex. The results obtained in this paper are in agreement with earlier INS studies in the region of torsional modes of CH_3 groups. The frequencies of the four modes observed in the INS spectra are markedly higher in TMP than for the complex. Additional calculations performed in this paper by using the DFT methods applied to crystalline states fully confirm the differences in the behavior of methyl groups in TMP and in the complex. An open question remains with respect to the accuracy of the applied theoretical methods.

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