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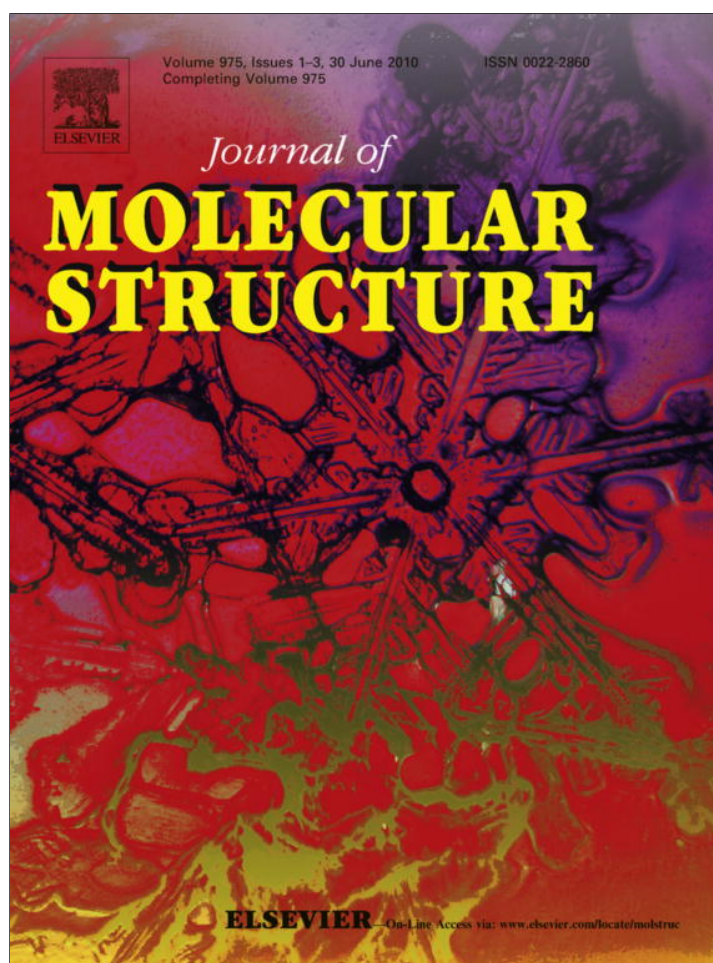


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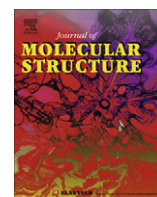
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## The (2:1) complex of picric acid with tetramethylpyrazine: The structure, IR spectra and tunnel splitting of methyl groups

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## ABSTRACT

The crystal structure of 2:1 picric acid (PAH) with tetramethylpyrazine (TMP) was determined by using X-ray diffraction studies. Two equivalent  $\text{N-H}\cdots\text{O}^-$  hydrogen bonds are formed with the length of 2.601 Å (calculated 2.640 Å). In the IR spectra very broad doublet at ca. 2000 and 2400  $\text{cm}^{-1}$  is observed, which can be interpreted as due to symmetric and asymmetric  $\text{N-H}$  vibrations. In neutron backscattering two tunnel splittings are observed, in agreement with the symmetry of 2:1 assemblies. At 4 K the tunnel peaks are located at 3.17 and 4.24  $\mu\text{eV}$ .

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## 1. Introduction

Tetramethylpyrazine (TMP) can be engaged in formation of various assemblies, first of all via hydrogen bonding. The TMP molecule is a proton acceptor that can form two hydrogen bonds. When forming a complex with a strong proton donor, ionization can proceed with proton transfer to the nitrogen atoms. With the proton donor such as chloranilic acid, the proton transfer does not take place [1,2]. There are formed  $\text{O-H}\cdots\text{N}$  hydrogen bonded chains. However, when the squaric acid  $\text{H}_2\text{SQ}$  is used as the proton donor then one of the nitrogen atoms is protonated and the second one is not ionized and the  $(\text{HSQ})_2^{2-} \cdot 2\text{TMP}\cdot\text{H}^+$  assemblies are formed [3,4].

In the present study, we also address the effect of complexation on the rotational potential of the methyl groups, using neutron backscattering at low temperatures. Two effects can contribute to the value of the tunneling splitting. The first one is related to the packing of molecules in the crystal structure, which determines the distances of the  $\text{CH}_3$  groups to either O or N atoms as well as to the  $\pi$ -electrons orbitals. The other one is due to the intermolecular charge transfer which can affect the charge distribution in the TMP ring (the occupation degree of the  $\pi$ -electron orbitals in that ring) [4]. It has been shown that a withdrawal of an electron from

the  $\pi$  orbital should strongly affect the vibrational/torsional vibrations and thus the rotational potential. However, so far it was not possible to separate these two effects in the tunneling splitting. Based on the data collected so far one can conclude that the packing is more important.

Therefore it seems desirably to protonize both nitrogen atoms in the tetramethylpyrazine molecule, which is possible by a complexation with a strong proton donor such like picric acid (PAH). The aim of the present work is formation of the TMP complex with PAH of the 1:2 composition, i.e. reaching double protonation. Then the standard X-ray diffraction and IR spectra studies will be undertaken but the main goal of this work is to carry out measurements of the tunneling transitions. The IR spectra seems also to be interesting in the fact that two  $\text{N-H}^+\cdots\text{O}^-$  hydrogen bonds are formed with a reciprocal orientation.

There is a lack of information in the literature related to the structure and properties of the TMP picrate. Searching in the literature published so far it was found that TMP forms 1:2 complex with p-nitrophenol [5]. However in this case two  $\text{O-H}\cdots\text{N}$  hydrogen bonds without proton transfer are formed. The proton transfer takes place in the complex of PAH with pyridine (1:1), which shows interesting phase transition. The results published in [6] contradict earlier report that the charge transfer complex is formed without proton transfer. The structure of pyridinium picrate was also reported in [7]. Interesting structure of 4-dimethylaminopyridinium picrate should also be mentioned [8]. Some analogy with

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the TMP complex was found in the case of 4,4'-bipyridine (1:2) complex with PAH followed by the protonation of both nitrogen atoms [9]. In the case of 2,2'-bipyridinium picrate only one nitrogen atom undergoes protonation [10].

## 2. Experimental and calculations

The title compound was prepared by mixing tetramethylpyrazine with picric acid (molar ratio 1:2) in methanol. Single crystals were grown by a slow evaporation of the solution in methanol at room temperature.

The infra-red spectra were recorded in Nujol and Fluorolube suspensions (KBr or CsI windows) using a FTIR Bruker IFS 113v spectrophotometer.

The X-ray diffraction studies were performed on a Kuma KM4 CCD  $\kappa$  axis four circle diffractometer equipped with an Oxford Cryosystem Cooler using graphite monochromated Mo K $\alpha$  radiation. The data were corrected for Lorentz and polarization effects.

The structure was solved by direct methods with SHELXS-97 [11] and refined by the full-matrix least-squares methods using the SHELXL-97 [12] program. Non-hydrogen atoms were refined with anisotropic thermal parameters. The hydrogen atoms attached to carbon were placed at calculated positions and refined, allowing them to ride on the parent carbon atom. The hydrogen atom of N–H group was located from difference map and refined. The crystal data and structure refinements are summarized in

**Table 1**  
Crystal data and structure refinement for TMP(PAH)<sub>2</sub>.

Formula	C <sub>8</sub> H <sub>12</sub> N <sub>2</sub> 2(C <sub>6</sub> H <sub>3</sub> N <sub>3</sub> O <sub>7</sub> )
Formula weight	594.42
<i>T</i> (K)	100(2)
Crystal system	Monoclinic
Space group	P2 <sub>1</sub> /n
<i>a</i> (Å)	7.668(2)
<i>b</i> (Å)	20.858(3)
<i>c</i> (Å)	8.208(2)
$\beta$ (°)	114.55(2)
<i>V</i> (Å <sup>3</sup> )	1194.1(5)
<i>Z</i>	2
Crystal size (mm)	0.35 × 0.26 × 0.24
$\theta$ Range (°)	3.08 to 27.5
<i>D</i> <sub>calc</sub> (g cm <sup>−3</sup> )	1.653
Index ranges	−9 ≤ <i>h</i> ≤ 9 −27 ≤ <i>k</i> ≤ 27 −10 ≤ <i>l</i> ≤ 10
$\mu$ (Mo K $\alpha$ ) (mm <sup>−1</sup> )	0.143
No. of reflections collected	8676
No. of independent reflections	2715 ( <i>R</i> <sub>int</sub> = 0.031)
Goodness-of-fit on <i>F</i> <sup>2</sup>	1.072
Final <i>R</i> <sub>1</sub> , <i>wR</i> <sub>2</sub> indices	
[ <i>F</i> > 4 $\sigma$ ( <i>F</i> )]	0.038, 0.0838
Final <i>R</i> <sub>1</sub> , <i>wR</i> <sub>2</sub> indices (all data)	0.0447, 0.0903
$\Delta\rho_{\max, \min}$ (e Å <sup>−3</sup> )	0.280/−0.237

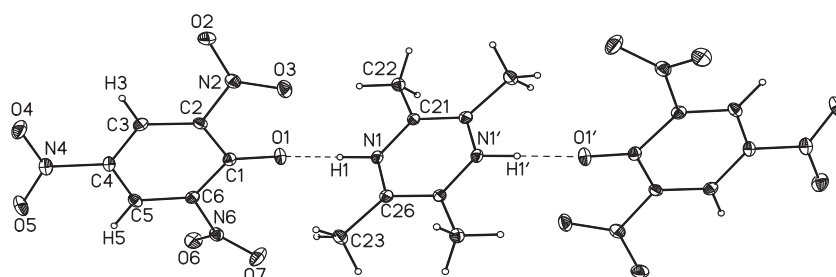
**Table 1.** Crystallographic data for the structural analysis have been deposited with the Cambridge Crystallographic Data Centre, CCDC 756,275.

High resolution neutron scattering spectra were measured on the backscattering spectrometer SPHERES [13] of the Jülich Centre for Neutron Science (JCNS) at Forschungsneutronenquelle Heinz Maier-Leibnitz (FRM II), Garching, Germany.

**Table 2**  
Selected bond lengths (Å) and angles (°) for the (2:1) complex of picric acid with tetramethylpyrazine.

	X-ray experiment	Calculated BLYP/dnp
<i>PA<sup>−</sup> anion</i>		
O(1)–C(1)	1.270(2)	1.267
O(2)–N(2)	1.237(2)	1.254
O(3)–N(2)	1.233(2)	1.248
O(4)–N(4)	1.232(2)	1.253
O(5)–N(4)	1.238(2)	1.252
O(6)–N(6)	1.229(2)	1.246
O(7)–N(6)	1.225(2)	1.249
N(2)–C(2)	1.456(2)	1.457
N(4)–C(4)	1.451(2)	1.446
N(6)–C(6)	1.468(2)	1.465
C(1)–C(6)	1.433(2)	1.454
C(1)–C(2)	1.435(2)	1.457
C(2)–C(3)	1.383(2)	1.385
C(3)–C(4)	1.379(2)	1.393
C(4)–C(5)	1.393(2)	1.403
C(5)–C(6)	1.370(2)	1.374
<i>(TMP-H<sub>2</sub>)<sup>2+</sup> cation</i>		
N(1)–C(26)	1.341(2)	1.350
N(1)–C(21)	1.343(2)	1.351
C(26)–C(21) <sup>y</sup>	1.398(2)	1.403
C(26)–C(23)	1.486(2)	1.489
C(21)–C(22)	1.485(2)	1.486
<i>(TMP-H<sub>2</sub>)<sup>2+</sup> cation</i>		
C(26)–N(1)–C(21)	125.23(13)	125.97
N(1)–C(26)–C(21) <sup>y</sup>	117.40(14)	117.02
N(1)–C(26)–C(23)	118.54(14)	118.71
C(21) <sup>y</sup> –C(26)–C(23)	124.04(14)	124.24
N(1)–C(21)–C(26) <sup>y</sup>	117.34(14)	117.00
N(1)–C(21)–C(22)	118.23(13)	118.42
C(26) <sup>y</sup> –C(21)–C(22)	124.34(14)	124.43
<i>PA<sup>−</sup> anion</i>		
O(3)–N(2)–O(2)	123.38(13)	123.72
O(4)–N(4)–O(5)	123.60(13)	123.75
O(7)–N(6)–O(6)	124.07(13)	124.30
O(1)–C(1)–C(6)	122.02(14)	121.67
O(1)–C(1)–C(2)	125.93(14)	125.41
C(6)–C(1)–C(2)	111.90(14)	112.72
C(3)–C(2)–C(1)	124.07(13)	123.14
C(4)–C(3)–C(2)	118.95(14)	119.61
C(3)–C(4)–C(5)	121.55(14)	121.34
C(6)–C(5)–C(4)	117.73(14)	118.45
C(5)–C(6)–C(1)	125.72(14)	124.65

Symmetry code: (')  $-x + 1, -y, -z$ .



**Fig. 1.** The structure and numbering scheme of double protonated tetramethylpyrazine (TMPH<sub>2</sub>)<sup>2+</sup> and deprotonated picric acid (PA<sup>−</sup>). Displacement ellipsoids are shown at the 35% probability level. Symmetry code (')  $-x + 1, -y, -z$ .

The total energy optimization and the frequency calculations have been performed based on density functional theory (DFT) using the DMol3 program [14,15] as a part of Materials Studio package [16]. The results have been obtained for the crystalline state with the local density approximation (LDA) within the generalized gradient approximation (GGA) at BLYP (Becke exchange [17] plus Lee–Yang–Parr correlation functional [18]). Calculations have been performed using DNP basis set as implemented in DMol3.

**Table 3**  
Possible hydrogen bonds and short contacts for TMP(PAH)<sub>2</sub>.

D–H...A	D–H (Å)	H...A (Å)	D...A (Å)	<DHA (°)
N(1)–H(1)...O(1)	0.98(2)	1.62(2)	2.601(2) <sup>a</sup>	179(2)
N(1)–H(1)...O(3)	0.98(2)	2.56(2)	2.913(2) <sup>b</sup>	101(2)
C(3)–H(3)...O(2)	0.93	2.44	2.715(2)	97
C(3)–H(3)...O(4)	0.93	2.46	2.741(2)	97
C(5)–H(5)...O(5)	0.93	2.42	2.697(2)	97
C(5)–H(5)...O(6)	0.93	2.64	2.817(2)	91
C(3)–H(3)...O(6) <sup>i</sup>	0.93	2.67	3.346(2)	130
C(5)–H(5)...O(2) <sup>ii</sup>	0.93	2.39	3.311(2)	170
C(22)–H(21)...O(1) <sup>iii</sup>	0.96	2.68	3.620(2)	167
C(22)–H(21)...O(7) <sup>iii</sup>	0.96	2.93	3.574(2)	125
C(22)–H(22)...O(5) <sup>iv</sup>	0.96	2.78	3.340(2)	117
C(22)–H(22)...O(6) <sup>v</sup>	0.96	2.73	3.307(2)	118
C(22)–H(22)...O(7) <sup>v</sup>	0.96	2.75	3.448(2)	130
C(22)–H(23)...O(4) <sup>vi</sup>	0.96	2.56	3.311(2)	136
C(23)–H(26)...O(1)	0.96	2.68	3.365(2)	128
C(23)–H(26)...O(7)	0.96	2.63	3.572(2)	167
C(23)–H(24)...O(5) <sup>i</sup>	0.96	2.64	3.211(2)	118
C(23)–H(24)...O(6) <sup>vii</sup>	0.96	2.58	3.277(2)	130
C(23)–H(25)...O(7) <sup>viii</sup>	0.96	2.71	3.419(2)	131

<sup>i</sup> Symmetry code:  $x + 0.5, -y + 0.5, z - 0.5$ .

<sup>ii</sup> Symmetry code:  $x, y, z + 1$ .

<sup>iii</sup> Symmetry code:  $-x, -y, -z$ .

<sup>iv</sup> Symmetry code:  $-x + 0.5, y + 0.5$ .

<sup>v</sup> Symmetry code:  $x, y, z - 1$ .

<sup>vi</sup> Symmetry code:  $x - 0.5, -y + 0.5, z - 0.5$ .

<sup>vii</sup> Symmetry code:  $x + 1, y, z$ .

<sup>viii</sup> Symmetry code:  $-x + 1, -y, -z + 1$ .

<sup>a</sup> Calculated 2.640 Å.

<sup>b</sup> Calculated 2.943 Å.

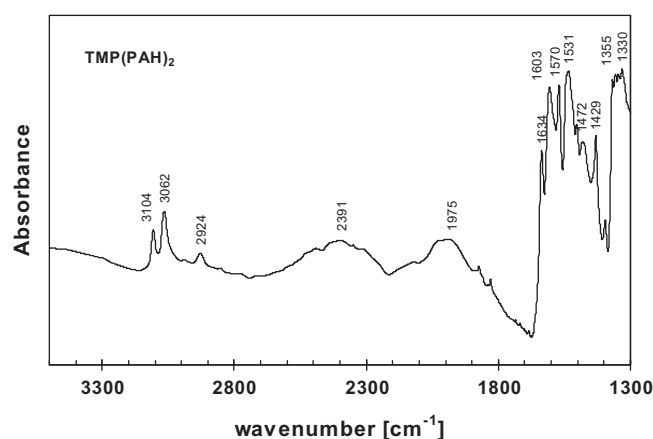
### 3. Results and discussion

#### 3.1. X-ray diffraction studies

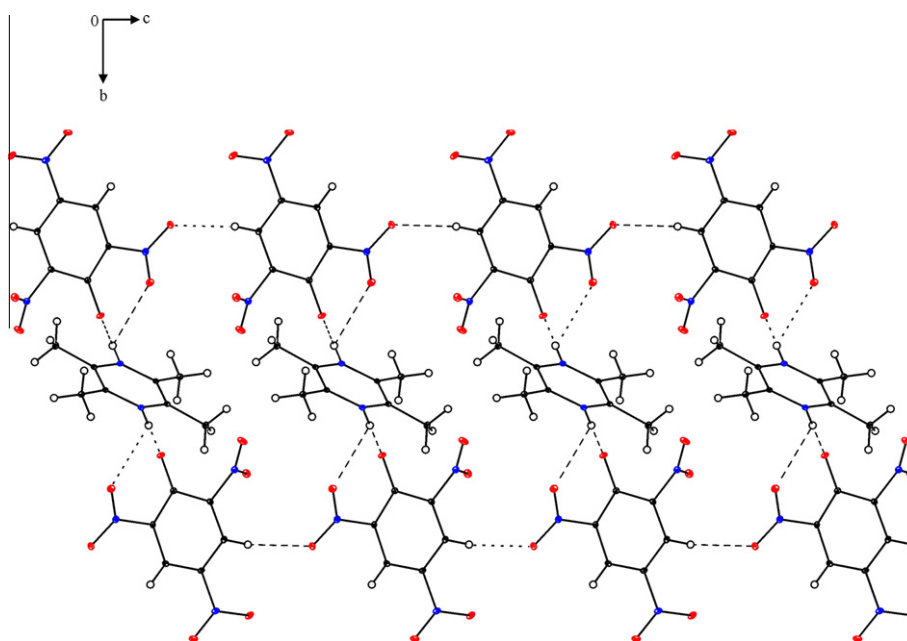
The asymmetric unit of the TMP(PAH)<sub>2</sub> crystal structure consists of one picrate anion and half TMP cation. The TMP cation lies on a crystallographic center of inversion. The TMP molecule appears in crystalline lattice as double protonated cation, while the PA molecule is present as deprotonated anion. The structure with atom numbering scheme is shown in Fig. 1.

The selected bond lengths and angles are presented in Table 2.

The loss of a proton in the picrate anion is confirmed by the length of the C–C bonds adjacent to the phenolic group (the C1–C2 and C1–C6 distances are equal to 1.435(2) and 1.433(2) Å, respectively). We have also observed an increase of the value of both C1–C2–C3 and C1–C6–C5 angle in the benzene ring to 124.07(13)° and 125.72(14)°, respectively, and a decrease of the C6–C1–C2 angle to 111.90(14)°.

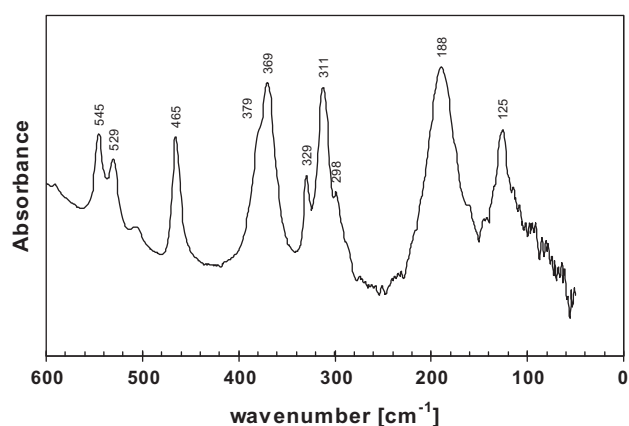


**Fig. 3.** Infra-red spectrum in Fluorolube suspension of the TMP(PAH)<sub>2</sub> complex over frequency range 1300–3200 cm<sup>−1</sup>.



**Fig. 2.** The packing of the (TMPH<sub>2</sub>)<sub>2</sub><sup>2+</sup>(PA<sup>−</sup>)<sub>2</sub> assemblies in the crystalline lattice. The hydrogen bonds N1–H1...O1 and C5–H5...O2<sup>ii</sup> are shown as dashed lines.





**Fig. 4.** Low frequency range of the spectrum of TMP(PAH)<sub>2</sub> recorded in Nujol suspension in the range 50–600 cm<sup>−1</sup>.

**Table 4**

Experimental infra-red peaks confronted with calculated frequencies by using BLYP/dnp approach (cm<sup>−1</sup>).

Experimental	Calculated	Assignment
125	125	Ring tors
188	193	C–NO <sub>2</sub> bend
298	295	C=O bend
311	313	C–CH <sub>3</sub> bend overlapped with C–NO <sub>2</sub> bend
329	327	ring def
369	373	C–CH <sub>3</sub> wagg
380	382	C–NO <sub>2</sub> wagg
465	466	ring def
529	531	C–CH <sub>3</sub> bend
545	544	NO <sub>2</sub> rock

The protonation of the nitrogen atoms on both sides of TMP by picric acid, presented in Table 3, finds a confirmation in the DFT calculations for the crystalline state. Thus the calculated <sup>+</sup>N–H bond length equals to 1.065 Å, while the distance between the hydrogen and oxygen atoms of deprotonated picric acid equals to 1.575 Å. These values differ a little from those in Table 3 but it is commonly known that the location of hydrogen atoms by using the X-ray diffraction method is not correct; the difference between experimental and calculated position of hydrogen atom equals to ca 0.1 Å. The calculations provide more correct data.

In the picrate anion the nitro group at the 4-position is twisted from the phenyl ring by a dihedral angle of only 8.5(2)°, whereas the nitro groups at the 2- and 6-positions are significantly twisted (by dihedral angles of 30.3(2)° and 49.2(1)°, respectively) out of the plane of the benzene ring. The methyl group (C(22)H<sub>3</sub>) in the TMP cation is displaced significantly (by −0.104(3) Å) from the pyrazine plane. The phenolic O1 atom is about −0.132(2) Å out of the picrate anion plane. The angle between the picrate and tetramethylpyrazine ring is 82.9(1)°.

The packing of molecules in the lattice is determined by conventional and unconventional C–H...O hydrogen bonds. Their parameters are presented in Table 3. The arrangement of the molecules in the unit cell is depicted in Fig. 2.

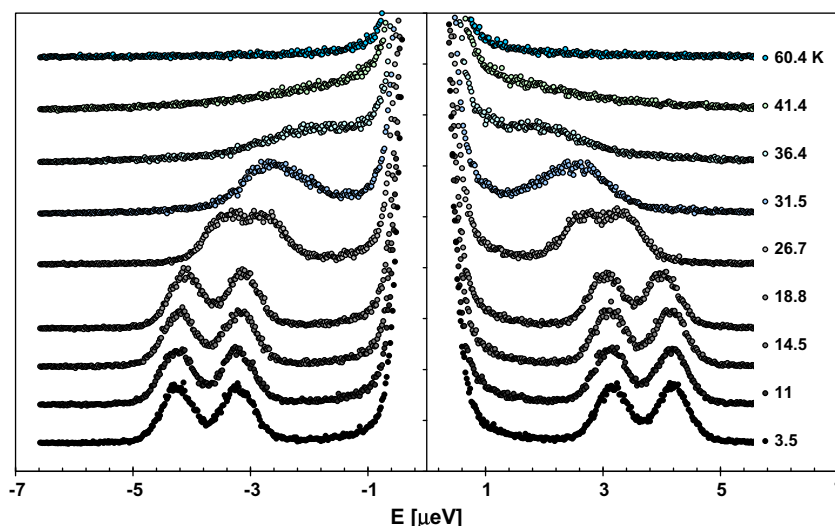
The pyrazine N1 atom forms bifurcated hydrogen bonds, N1–H1...O1 and N1–H1...O3, with the picrate anion. The corresponding N–H...O distances are equal to 2.601(2) and 2.913(2) Å.

In addition to the conventional hydrogen bonds the short C–H...O intramolecular contacts between C3–H3 or C5–H5 and nitro groups are observed. This is an important feature in all aromatic picrate complexes. Moreover, the C5–H5 groups and O2 atoms, forming hydrogen bonds, create an infinite chain running along the c-axis.

In Table 3 the chosen C–H...O contacts with the nitro group oxygen atoms are also listed. They may affect a shape of rotational potential of methyl groups as well. There are possible two such interactions for two a little different methyl groups, C(23)H<sub>3</sub> and C(22)H<sub>3</sub>. Their C–H...O distances lie in the range between 3.211(2) and 3.574(2) Å. It is difficult to assess, which groups are more strongly engaged in attraction with oxygen atoms, because this depends not only on the C–H...O distance but also on the C–H...O angle. In our opinion it is worth to mention that two of four methyl groups in the TMP molecule are identical, whereas two others are different but the difference between them is small.

### 3.2. Infra-red spectra

The IR spectra in the low frequency and high frequency regions are shown in Figs. 3 and 4. In the high frequency region one can distinguish two sharp peaks at 3062 and 3104 cm<sup>−1</sup>, which can be ascribed to the C–H stretching vibrations of C(3)–H(3) and C(5)–H(5) groups. Most interesting is broad doublet with maxima at ca. 2000 and 2400 cm<sup>−1</sup>, which without doubts should be ascribed to the stretching vibrations of the <sup>+</sup>N–H hydrogen bonded



**Fig. 5.** The tunnel splitting recorded for varying temperature 4–70 K.

groups. The components of this doublet correspond to symmetric and asymmetric vibrations. The low frequency infra-red peaks can be compared with calculated frequencies by using the BLYP/dnp method applied to the crystalline state. The corresponding data with the assignment are listed in Table 4. The agreement is very good. The calculations performed for isolated compounds, i.e. for  $\text{TMP}\cdot\text{H}_2^{++}$  and  $\text{PA}^-$ , do not lead to satisfactory results.

### 3.3. Inelastic neutron scattering in the region of tunneling splitting

We have measured neutron backscattering at low temperatures in order to investigate the rotational tunneling of the four  $\text{CH}_3$  groups in the  $\text{TMP}(\text{PAH})_2$  complex. The tunneling of a  $\text{CH}_3$  group is expected to result in a pair of inelastic peaks at  $\pm E_i$ , corresponding to scattering with energy gain and loss [19].

Fig. 5 shows some of the spectra we recorded in the energy range between  $-7$  and  $7$   $\mu\text{eV}$  for several temperatures between  $4$  and  $70$  K. Two pairs of peaks are resolved. At  $4$  K, they are located at  $E_1 = 3.16$   $\mu\text{eV}$  and  $E_2 = 4.24$   $\mu\text{eV}$ . Both pairs of peaks comprise

about the same integral intensity. Thus each of them can be attributed to the tunneling of two equivalent  $\text{CH}_3$  groups. This is consistent with the crystallographic result that there are two pairs of identical methyl groups.

In the temperature range between  $3.5$  and  $20$  K the positions of the peaks are almost independent of temperature. On heating above  $20$  K, both pairs of peaks shift toward the elastic line. The temperature dependence of the tunneling splittings,  $E_i$ , is presented in Fig. 6a. Fig. 6b shows an Arrhenius plot of the peak shifts.

From the Arrhenius relationship the activation energy,  $E_{as}$ , may be estimated.

$$\Delta E = E(0\text{ K}) - E(T) = A \exp\left(-\frac{E_{as}}{kT}\right) \quad (1)$$

where  $E(0\text{ K})$  is a tunneling splitting approximated to  $0$  K.

Using the peak shifts observed between  $15$  and  $35$  K, we obtain activation energies of  $6.9$  and  $6.3$  meV for peak 1 and 2, respectively. Because the peaks overlap at higher temperatures, a quantitative analysis of line widths is practically impossible.

Tunneling spectroscopy is an extremely sensitive probe of local potentials. The fact that both tunneling splittings are of the same order of magnitude indicates that the environments of the two inequivalent pairs of  $\text{CH}_3$  groups differ only slightly. This is supported also by the similar values of activation energy estimated from the temperature shifts of the peaks. It is worth to mention that all these conclusions drawn from neutron measurements are consistent with our crystallographic results.

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MATERIALS STUDIO package was used under POLAND COUNTRY-WIDE LICENSE.

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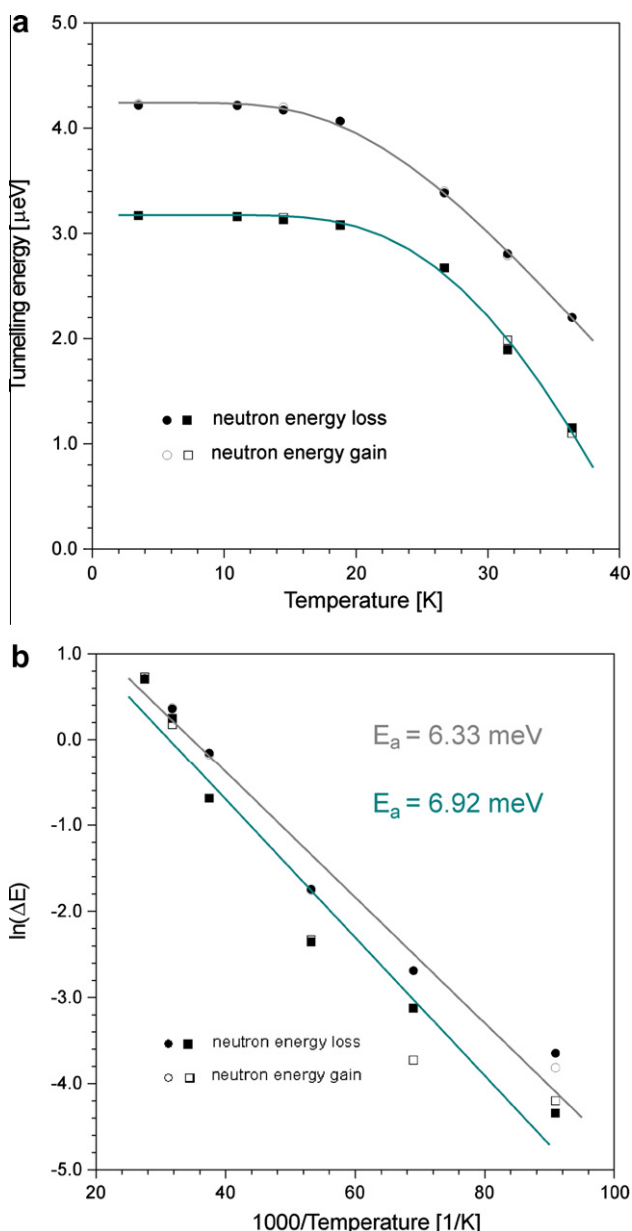


Fig. 6. (a) The temperature dependence of the position of tunneling lines, (b) the Arrhenius plot of the peak shifts.