

## SUPPORTING INFORMATION

# Structure and Tunneling Splitting Spectra of Methyl Groups of Tetramethylpyrazine in Complexes with Chloranilic and Bromanilic Acids

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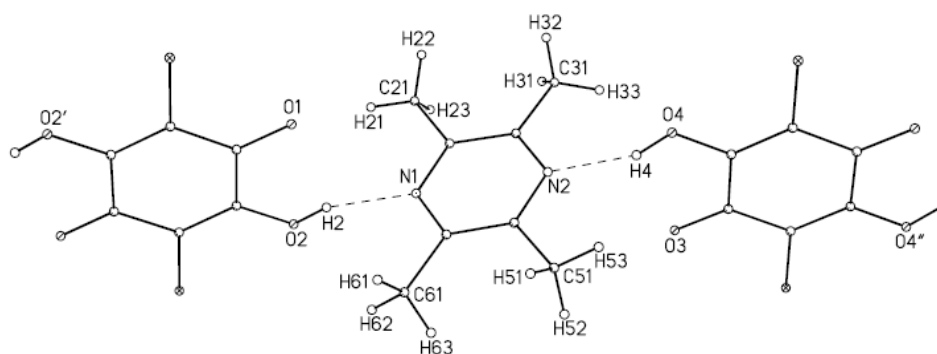
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**Tab. S1.** Hydrogen bonds and short contacts for TMP CLA (at 14 K).

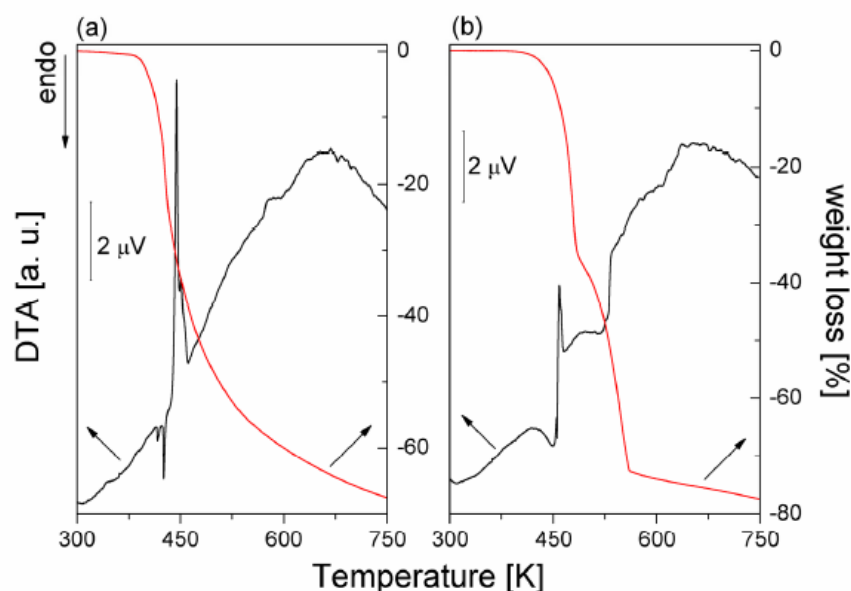
D-H...A (Å)	D-H (Å)	H...A (Å)	D...A (Å)	< D-H...A (°)
O(2)-H(2) ...N(1)	0.85(3)	1.90(3)	2.714(2)	159(3)
O(4)-H(4) ...N(2)	0.87(4)	1.84(4)	2.668(2)	158(3)
C(21)-H(21) ...O(1)	0.92(3)	2.93(4)	3.558(3)	126(3)
C(21)-H(21) ...O(1) <sup>i</sup>	0.93(3)	2.62(4)	3.158(3)	117(3)
C(31)-H(33) ...O(4)	0.95(4)	2.89(4)	3.484(3)	122(3)
C(31)-H(33) ...O(4) <sup>i</sup>	0.95(4)	2.78(4)	3.332(3)	118(3)
C(31)-H(32) ...O(1) <sup>ii</sup>	0.99(3)	2.66(4)	3.364(3)	135(3)
C(51)-H(53) ...O(4)	0.97(3)	2.81(4)	3.556(3)	134(3)
C(51)-H(53) ...O(3) <sup>iii</sup>	0.97(3)	2.55(3)	3.383(3)	144(3)
C(61)-H(62) ...O(2)	0.98(4)	2.84(4)	3.455(3)	121(3)
C(61)-H(61) ...O(2) <sup>iii</sup>	0.94(4)	2.78(4)	3.697(3)	166(3)
C(61)-H(62) ...Cl(2) <sup>iv</sup>	0.98(4)	2.92(3)	3.742(3)	143(3)
C(61)-H(63) ...O(3) <sup>v</sup>	0.96(4)	2.77(4)	3.371(3)	121(3)
Symmetry code: ( <sup>i</sup> ) x, y-1, z, ( <sup>ii</sup> ) -x+1/2, y-1/2, -z+1/2, ( <sup>iii</sup> ) x, y+1, z, ( <sup>iv</sup> ) x-1/2, -y+1/2, z-1/2, ( <sup>v</sup> ) -x-1/2, y+1/2, -z+1/2				



**Fig. S1:** The fragment of the chain in the crystal of TMP CLA complex at  $T = 14$  K. Projection along  $b$ -axis.

### Thermal properties

Fig. S2 presents the results of simultaneous thermogravimetric analysis (TGA) and differential thermal analysis (DTA) of a TMP BRA (a) and TMP CLA (b) complexes between 300 and 750 K. The results show that title compound (TMP BRA) is stable up to about 390 K, while TMP CLA complex up to 420 K ( $\sim 1.5\%$  mass loss). Further heating, above these temperatures, lead to a continuous decomposition of the samples.



**Fig. S2:** Simultaneous thermogravimetric analysis (TGA) and differential thermal analysis (DTA) of a TMP BRA (a) and TMP CLA (b) complexes between 300 and 750 K.

### INS spectra

In case of the TMP molecule we have four methyl positions ( $n = 1, 2, 3$  and  $4$ ) and the threefold symmetry of the methyl groups which leads to the following scattering function<sup>1-4</sup> (eq. 1):

$$S(Q, \omega) = \left( 2 \left( \frac{5}{3} + \frac{4}{3} j_0(Qd) \right) + r(Q) \right) \delta(\omega) + \sum_{n=1}^4 \left( \frac{2}{3} - \frac{2}{3} j_0(Qd) \right) \{ \delta(\omega + \omega_{tn}) + \delta(\omega - \omega_{tn}) \} \quad (\text{eq. 1})$$

with momentum transfer  $\hbar Q$  and energy transfer  $\hbar\omega$ . On the right-hand side,  $d$  is the H-H distance in the methyl group, and  $\hbar\omega_t$  is the ground state tunnel splitting. The term  $r(Q)$  stands for the elastic scattering by the rest of the molecule. It is dominated by incoherent scattering from the two non-methyl protons; therefore, in first approximation  $r(Q) = 2$ . For fully resolved tunneling bands Eq. 1 implies an intensity ratio:<sup>3</sup>

$$\frac{I_{inel}}{I_{el}} = \frac{4 - 4j_0}{10 + 8j_0 + 3r} \quad (\text{eg. 2})$$

which shall be compared to the experiment below.

The fittings of the spectra were carried out with a standard model consisting of a Dirac component for the elastic scattering and Loretzians for the tunnelling excitations. The theoretical curves are convoluted with the instrumental resolution function obtained during the present experiment using vanadium.

At higher temperatures, thermal fluctuations of the lattice become significant causing a softening and a broadening of the tunnelling transitions. The frequencies  $\omega_m(T)$  become temperature dependent, and the Dirac distributions in eq. (1) must be replaced by Lorentzians with linewidth  $\Gamma_n(T)$ . It was well established<sup>1,2</sup> that usually an Arrhenius expression provides a reasonable first approximation for the broadening

$$\Gamma_n = \Gamma_{0n} \exp\left(\frac{E_{\Gamma n}}{kT}\right) \quad (\text{eq. 3})$$

For the softening of the peaks the following Arrhenius expression may be applied

$$\hbar\omega_n = \hbar\omega_n(T=0) \left[ 1 - A_n^{sin} \exp\left(\frac{E_n^{sin}}{kT}\right) \right] \quad (\text{eq. 4})$$

The activation energies  $E_{\Gamma n}$  represent the distance from the pocket groundstate to the first librational level. The sinusoidal coupling coefficients  $A_n^{sin}$  and the activation energies  $E_n^{sin}$  describe the interaction between the methyl group and the heat bath. From the temperature dependence of the positions,  $\Delta E_i = \hbar\omega_i(T=0) - \hbar\omega_i$ , we have estimated the  $E_{01}$  value using Eq. (4). The plot  $\ln \Delta E_i = \ln[\hbar\omega_i(T=0) - \hbar\omega_i]$  versus  $1000/T$  for the TMP CLA complex is shown in Fig. 7(b).

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