

# Vibrations of a Chelated Proton in a Protonated Tertiary Diamine

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## Supporting Information

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## X-Ray Structure Determination

A colorless fragment of a prism (0.16 x 0.16 x 0.01 mm<sup>3</sup>) was used for the single crystal x-ray diffraction study of [C<sub>8</sub>H<sub>21</sub>N<sub>2</sub>]<sup>+</sup>[I]<sup>-</sup> (sample tm13-no-Hsym). The crystal was mounted on to a cryo-loop glass fiber. X-ray intensity data were collected at 90(2) K on a Bruker APEX2 (version 2.0-22, **ref. 1**) platform-CCD x-ray diffractometer system (Mo-radiation,  $\lambda = 0.71073$  Å, 50KV/40mA power). The CCD detector was placed at a distance of 5.0580 cm from the crystal.

A total of 1800 frames were collected for a hemisphere of reflections (with scan width of 0.3° in  $\omega$ , starting  $\omega$  and  $2\theta$  angles at -30°, and  $\phi$  angles of 0°, 90°, and 180° for every 600 frames, 40 sec/frame exposure time). The frames were integrated using the Bruker SAINT software package (version V7.23A, **ref. 2**) and using a narrow-frame integration algorithm. Based on an orthorhombic crystal system, the integrated frames yielded a total of 6340 reflections at a maximum  $2\theta$  angle of 60.04° (0.71 Å resolution), of which 923 were independent reflections ( $R_{\text{int}} = 0.0339$ ,  $R_{\text{sig}} = 0.0215$ , redundancy = 6.9, completeness = 99.8%) and 863 (93.5%) reflections were greater than  $2\sigma(I)$ . The unit cell parameters were,  $\mathbf{a} = 8.8848(6)$  Å,  $\mathbf{b} = 10.8203(7)$  Å,  $\mathbf{c} = 11.8758(7)$  Å,  $\alpha = \beta = \gamma = 90^\circ$ ,  $V = 1141.69(13)$  Å<sup>3</sup>,  $Z = 4$ , calculated density  $D_c = 1.583$  g/cm<sup>3</sup>. Absorption corrections were applied (absorption coefficient  $\mu = 2.759$  mm<sup>-1</sup>; max/min transmission = 0.9729/0.6713) to the raw intensity data using the SADABS program (version 2004/1, **ref. 3**).

The Bruker SHELXTL software package (Version 6.14, **ref. 4**) was used for phase determination and structure refinement. The distribution of intensities and systematic absent reflections indicated three possible space groups, Cmc2(1), Cmcm, and Ama2. The space group Cmcm was later determined to be correct. Direct methods of phase determination followed by two Fourier cycles of refinement led to an electron density map from which most of the non-hydrogen atoms were identified in the asymmetry unit of the unit cell. With subsequent isotropic refinement, all of the non-hydrogen atoms were identified. There were ¼ of the cation [C<sub>8</sub>H<sub>21</sub>N<sub>2</sub>]<sup>+</sup> and ¼ of the anion [I]<sup>-</sup> present in the asymmetry unit of the unit cell. The cation [C<sub>8</sub>H<sub>21</sub>N<sub>2</sub>]<sup>+</sup> was modeled with 50%/50% disordered site occupancy ratio. The anion and disordered cation were located at the intersection of several symmetry elements; mirror planes perpendicular to the  $\mathbf{a}$ -axis and  $\mathbf{c}$ -axis, and a 2-fold axis parallel to the  $\mathbf{b}$ -axis. The NH---N hydrogen bonded H-atom was refined unrestrained and as disordered non-symmetry H-atom (25%/25% disordered site occupancy ratio). Table 7 gave the hydrogen bond distances and angle.

Atomic coordinates, isotropic and anisotropic displacement parameters of all the non-hydrogen atoms were refined by means of a full matrix least-squares procedure on  $F^2$ . The H-atoms were included in the refinement in calculated positions riding on the atoms to which they were attached, except the hydrogen bonded H-atom. The refinement converged at  $R1 = 0.0200$ ,  $wR2 = 0.0437$ , with intensity,  $I > 2\sigma(I)$ . The largest peak/hole in the final difference map was 0.546/-1.074 e/Å<sup>3</sup>.

## REFERENCES

1. *APEX 2*, version 2.0-22, Bruker (2004), Bruker AXS Inc., Madison, Wisconsin, USA.
2. *SAINT*, version V7.23A, Bruker (2003), Bruker AXS Inc., Madison, Wisconsin, USA.
3. *SADABS*, version 2004/1, Bruker (2004), Bruker AXS Inc., Madison, Wisconsin, USA.
4. *SHELXTL*, version 6.14, Bruker (2008), Bruker AXS Inc., Madison, Wisconsin, USA.

Table 1. Crystal data and structure refinement for *N, N, N', N'*-tetramethylputrescinium iodide

Identification code	tm13-no-hsym	
Empirical formula	C8 H21 I N2	
Formula weight	272.17	
Temperature	90(2) K	
Wavelength	0.71073 Å	
Crystal system	Orthorhombic	
Space group	Cmcm	
Unit cell dimensions	a = 8.8848(6) Å	α = 90°.
	b = 10.8203(7) Å	β = 90°.
	c = 11.8758(7) Å	γ = 90°.
Volume	1141.69(13) Å <sup>3</sup>	
Z	4	
Density (calculated)	1.583 Mg/m <sup>3</sup>	
Absorption coefficient	2.759 mm <sup>-1</sup>	
F(000)	544	
Crystal size	0.16 x 0.16 x 0.01 mm <sup>3</sup>	
Theta range for data collection	2.97 to 30.02°.	
Index ranges	-12 ≤ h ≤ 12, -15 ≤ k ≤ 15, -16 ≤ l ≤ 14	
Reflections collected	6340	
Independent reflections	923 [R(int) = 0.0339]	
Completeness to theta = 30.02°	99.8 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.9729 and 0.6713	
Refinement method	Full-matrix least-squares on F <sup>2</sup>	
Data / restraints / parameters	923 / 35 / 55	
Goodness-of-fit on F <sup>2</sup>	1.091	
Final R indices [I > 2σ(I)]	R1 = 0.0200, wR2 = 0.0437	
R indices (all data)	R1 = 0.0230, wR2 = 0.0446	
Largest diff. peak and hole	0.546 and -1.074 e.Å <sup>-3</sup>	

Table 2. Atomic coordinates ( $\times 10^4$ ) and equivalent isotropic displacement parameters ( $\text{\AA}^2 \times 10^3$ ) for tm13-no-Hsym.  $U(\text{eq})$  is defined as one third of the trace of the orthogonalized  $U^{ij}$  tensor.

	x	y	z	$U(\text{eq})$
I(1)	5000	6950(1)	7500	18(1)
C(1)	6429(7)	6195(5)	3999(6)	20(1)
C(2)	3760(6)	6640(5)	4074(5)	22(1)
N(1)	5222(5)	7029(2)	3603(2)	14(1)
C(3)	5566(4)	8345(3)	3865(3)	20(1)
C(4)	4745(5)	9263(3)	3117(3)	22(1)

Table 3. Bond lengths [ $\text{\AA}$ ] and angles [ $^\circ$ ] for tm13-no-Hsym.

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C(1)-N(1)	1.478(6)
C(1)-H(1A)	0.9800
C(1)-H(1B)	0.9800
C(1)-H(1C)	0.9800
C(2)-N(1)	1.476(6)
C(2)-H(2A)	0.9800
C(2)-H(2B)	0.9800
C(2)-H(2C)	0.9800
N(1)-C(3)	1.490(4)
N(1)-H(1)	0.86(6)
C(3)-C(4)	1.519(5)
C(3)-H(3A)	0.9900
C(3)-H(3B)	0.9900
C(4)-H(4A)	0.9600
C(4)-H(4B)	0.9600
C(2)-N(1)-C(1)	110.1(3)
C(2)-N(1)-C(3)	111.9(3)
C(1)-N(1)-C(3)	111.6(3)
C(2)-N(1)-H(1)	110(2)
C(1)-N(1)-H(1)	111(2)
C(3)-N(1)-H(1)	102(4)
N(1)-C(3)-C(4)	113.9(3)
N(1)-C(3)-H(3A)	108.8
C(4)-C(3)-H(3A)	108.8
N(1)-C(3)-H(3B)	108.8
C(4)-C(3)-H(3B)	108.8
H(3A)-C(3)-H(3B)	107.7
C(3)-C(4)-H(4A)	105.9
C(3)-C(4)-H(4B)	105.8
H(4A)-C(4)-H(4B)	106.2

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Symmetry transformations used to generate equivalent atoms:

Table 4. Anisotropic displacement parameters ( $\text{\AA}^2 \times 10^3$ ) for tm13-no-Hsym. The anisotropic displacement factor exponent takes the form:  $-2\pi^2 [ h^2 a^{*2} U^{11} + \dots + 2 h k a^* b^* U^{12} ]$

	$U^{11}$	$U^{22}$	$U^{33}$	$U^{23}$	$U^{13}$	$U^{12}$
I(1)	14(1)	16(1)	24(1)	0	0	0
C(1)	16(2)	19(3)	26(2)	0(2)	-4(2)	3(2)
C(2)	18(2)	26(3)	22(2)	2(2)	-2(2)	-3(2)
N(1)	10(3)	15(1)	18(1)	0(1)	1(1)	-1(1)
C(3)	20(1)	18(2)	22(2)	-5(1)	0(1)	0(1)
C(4)	23(4)	14(1)	28(2)	-4(1)	-1(1)	3(1)

Table 5. Hydrogen coordinates ( $\times 10^4$ ) and isotropic displacement parameters ( $\text{\AA}^2 \times 10^{-3}$ ) for tm13-no-Hsym.

	x	y	z	U(eq)
H(1A)	6207	5347	3760	31
H(1B)	6487	6228	4822	31
H(1C)	7393	6457	3677	31
H(2A)	3559	5780	3862	33
H(2B)	2961	7172	3776	33
H(2C)	3788	6709	4897	33
H(1)	5180(20)	7040(50)	2880(50)	17
H(3A)	6663	8479	3787	24
H(3B)	5294	8510	4660	24
H(4A)	5100	10065	3339	26
H(4B)	3707	9224	3339	26

Table 6. Torsion angles [°] for tm13-no-Hsym.

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C(2)-N(1)-C(3)-C(4)	-78.8(4)
C(1)-N(1)-C(3)-C(4)	157.3(4)

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Symmetry transformations used to generate equivalent atoms:

Table 7. Hydrogen bonds for tm13-no-Hsym [ $\text{\AA}$  and °].

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D-H...A	d(D-H)	d(H...A)	d(D...A)	<(DHA)
N(1)-H(1)...N(1)#1	0.86(6)	1.79(6)	2.648(6)	171(2)

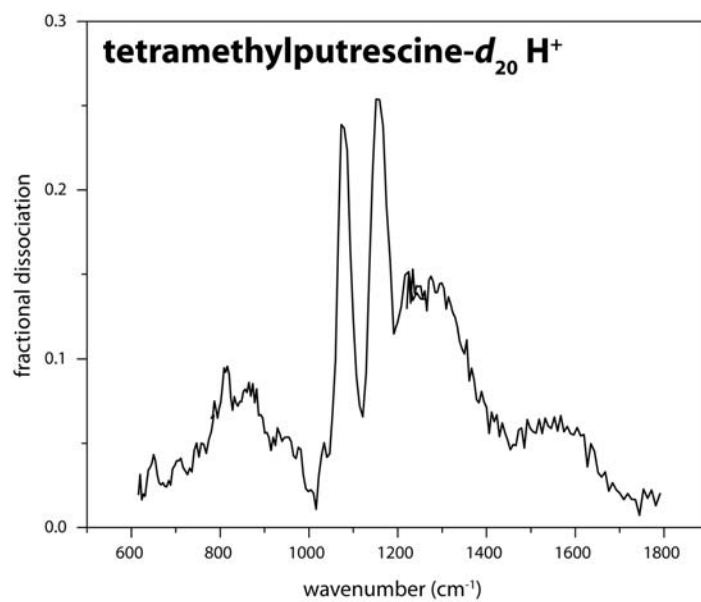
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Symmetry transformations used to generate equivalent atoms:

#1 -x+1,y,-z+1/2

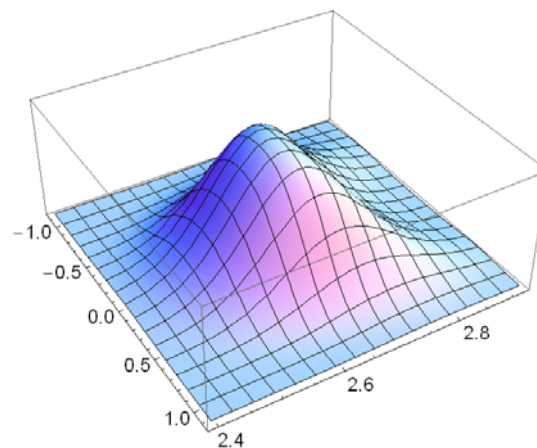


**Figure 13.** IRMPD of protonated *N, N, N, N*-tetramethylputrescine- $d_{20}$

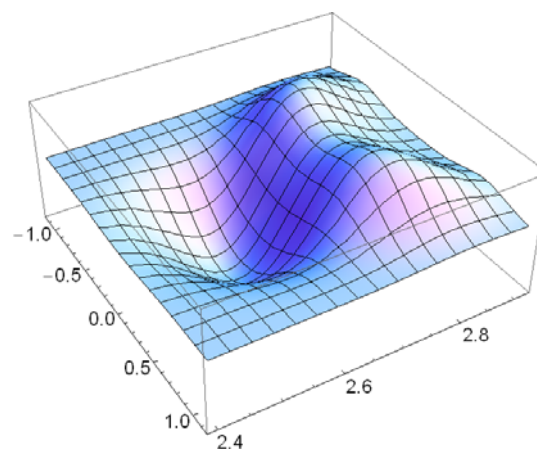


**Figure 14.** Wavefunctions for protonated tetramethylputrescine.

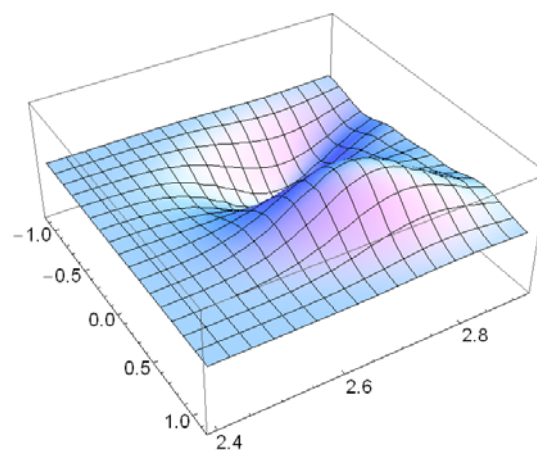
Zero point wavefunction for ion **1a**



NN stretch wavefunction for ion **1a** ( $\nu=1$ )

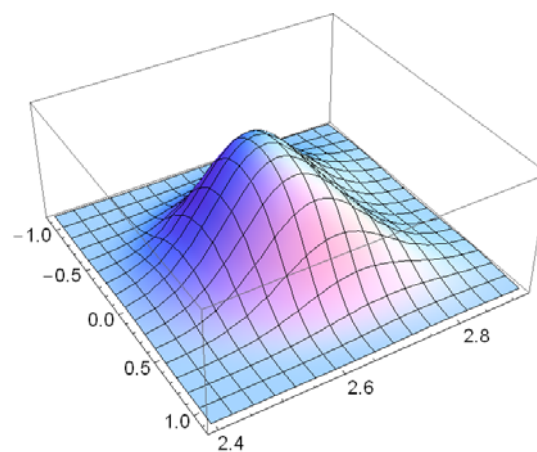


NHN asymmetric stretch wavefunction for ion **3a** ( $\nu=1$ )

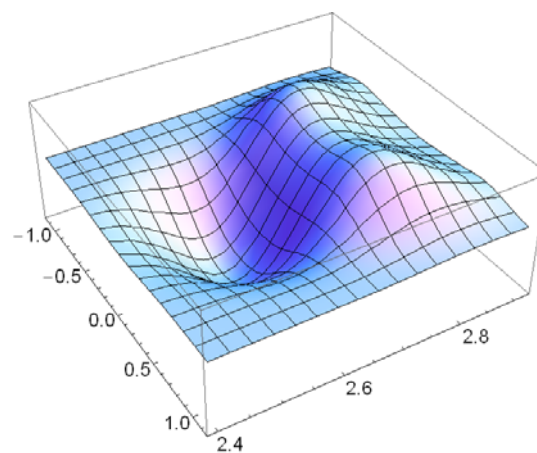


**Figure 14.** Wavefunctions for protonated hexamethylcadaverine.

Zero point wavefunction for ion **3a**



NN stretch wavefunction for ion **3a** ( $\nu=1$ )



NHN asymmetric stretch wavefunction for ion **3a** ( $\nu=1$ )

