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Experimental and Theoretical Study of 1,5-Diamino-4-H-Tetrazolium Perchlorate

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Abstract: The synthesis and characterization of 1,5-diamino-1,2,3,4-tetrazolium perchlorate were carried out. Experimental evidence strongly supports the protonation of a nitrogen atom of the tetrazole ring, including the structure observed in a single crystal x-ray diffraction study of the title compound. Quantum chemical calculations were performed at the CCSD(T)/6-311G(2df,p)//MP2/6-311G(d,p) level of theory to determine the relative energies of all possible N-protonated structures of the 1,5-diamino-1,2,3,4-tetrazole ring. The predicted geometry of the most stable isomer compares favorably with the experimentally observed structure.

Introduction

The field of chemistry dealing with tetrazoles has rapidly gained importance, especially in the field of biochemistry[1-7]. Tetrazoles can either be N(1) or N(2) substituted with each N-substituted isomer, having unique physical properties such as boiling points, pKa, and sensitivity to mechanical stimulii[8-26]. The synthesis of a pure N-isomer without contamination of the other N-substituted isomer is usually very difficult and often dependent upon the substituent on the carbon atom. Typically reactions involving electrophiles and tetrazoles with electron donating substituents, e.g.. 5-methyltetrazole[20], results in a majority of N(1) substituted tetrazoles, while those involving electron poor tetrazoles, e.g. 5-ethylcaboxylate-tetrazole[16] or 5-nitrotetrazole[27] react predominantly in the N(2) position. Recently there has been a considerable amount of work done with tetrazole-anion systems with examples such as 5-cyanotetrazole[8], 5-nitraminotetrazole[28, 29] and bitetrazolate based salts[30-32].

At the Air Force Research Laboratory we have pursued the synthesis and characterization of new salts, especially those defined as ionic liquids[33-40], in order to

identify the key structural features affecting physical properties, such as density and melting points. Previously we reported families of simple triazolium based salts using anions of several oxyacids finding a wide array of physical properties with slight changes in the parent triazole.[41] Acid-base reactions where the N-amino tetrazole serves as the base have not been widely reported, most likely due to the lowered basicity of these high nitrogen heterocycles, with even fewer x-ray structures of these materials. Previously a paper reported the synthesis and characterization of 1,5-diamino-1,2,3,4-tetrazole including some acid base reactions; however the authors cited the most likely site of protonation as the amino group attached to the carbon of the tetrazole ring[17]. Other authors have studied the protonation of high nitrogen heterocycles in various media citing protonation upon the nitrogen atoms of the heterocyclic ring[12-14, 42-45]. We have synthesized and characterized the previously unreported perchlorate salt of 1,5-diamino-1,2,3,4-tetrazole with vibrational, nmr spectra and DSC studies as well as a single crystal x-ray diffraction study. Theoretical calculations using MP2[46-51] and CCSD(T)[52-54] levels of theory were carried out comparing the possible protonated isomers of 1,5-diamino-1,2,3,4-tetrazole, in search of the lowest energy structure, and these results are compared to those observed experimentally.

Experimental

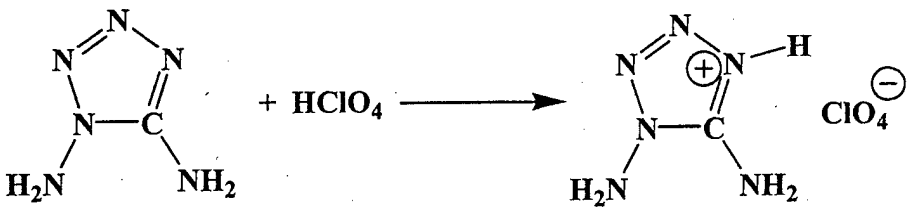
1,5-diamino-1,2,3,4-tetrazole was synthesized according to the literature route[17]. Perchloric Acid (A.C.S reagent, 70% aqueous solution) ethanol (HPLC anhydrous low water) and methanol (HPLC grade 99.93% low water) were used as received. Diethylether (A.C.S. reagent, anhydrous) was passed through a pre-activated column of alumina under nitrogen atmosphere to insure dryness. Infrared spectra were recorded as KBr disks from 4000-400 cm^{-1}, (using a KBr disk as a reference background) on a Nicolet 55XC FT-IR spectrometer. Raman spectra were recorded in pyrex melting point capillaries on a Bruker Model FRA 106/S Equinox 55 Raman spectrometer equipped with a 1.06 micron IR excitation laser. NMR experiments were carried out by dissolving the salts in CD_3CN in 5mm nmr tubes, and the ^1H and ^{13}C spectra recorded on a Bruker Spectrospin DRX 400 MHz Ultrashield™ NMR. Thermal analyses were carried out in hermetically sealed, coated aluminum pans on a Thermal Analyst 200, Dupont

Instruments 910 Differential Scanning Calorimeter. Samples were prepared and sealed inside a nitrogen-filled glove box, and once the pans were inside the DSC cell, the cell was flushed with 10 mL per minute of nitrogen gas purge during heating cycles. Elemental analyses were carried out on a Perkin Elmer Series II CHNS/O Analyzer 2400 elemental analysis instrument equipped with AD6 Autobalance.

1,5-diamino-1,2,3,4-tetrazolium perchlorate: 1,5-diamino-1,2,3,4-tetrazole, 0.4738 g, 4.73 mmoles, was placed inside a pre-weighed Schlenk flask and suspended in ethanol/methanol mixture (12mL/10mL) and stirred vigorously. Perchloric acid (0.6916 g., 4.75 mmoles) was added slowly to the stirred mixture with a disposable pipet under nitrogen purge. The diaminotetrazole dissolved rapidly, and the reaction was stirred for 30 minutes at ambient temperature; then the stir bar was removed and the volatiles removed by high vacuum for 24 hours, resulting in a sticky white solid. The solid was redissolved in 5 ml of ethanol, carefully layered with 60 ml of diethylether, and chilled to 4°C overnight. A crop of highly crystalline 1,5-diamino-1,2,3,4-tetrazolium perchlorate was recovered, washed with several aliquots of ether, and vacuum dried resulting in 0.5629 g., 2.81 mmoles of product. Melting point 125-130°C (DSC). ^{1}H nmr(CD_3CN): 5.899 (singlet, relative area = 2.000); 7.161 (singlet, relative area = 1.977); 13.098 (singlet, relative area 0.876). ^{13}C (CD_3CN): +149.471. IR(cm^{-1}): 3411, 3361, 3318, 3279, 3185, 3143, 3096, 3019, 2879, 2786, 2751, 1710, 1633, 1575, 1351, 1290, 1120, 1077, 1003, 923, 907, 748, 702, 686, 634, 627, 608, 476, 453. Raman(cm^{-1}): 3361, 3295, 3254, 3140, 1726, 1636, 1580, 1511, 1444, 1307, 1349, 1315, 1132, 1107, 1075, 1035, 1003, 935, 909, 784, 688, 625, 467, 458, 331, 305, 258, 108, 84.
Elemental analysis: %C; 5.99 (theory); 6.19 (found); %H; 2.51 (theory); 2.22 (found); %N; 41.91 (theory); 41.73 (found).

Synthesis and Characterization

1,5-diamino-1,2,3,4-tetrazole is not a particularly strong base and will only form salts with relatively strong mineral acids ($pK_a \leq 0$) under normal conditions. Using the direct reaction of 1,5-diamino-1,2,3,4 tetrazole with concentrated perchloric acid formed the tetrazolium perchlorate. (Reaction 1)



The new salt was recovered as clear chunky crystals that were sensitive to mechanical stimuli (i.e. a heavy hammer blow) and were soluble in a wide array of polar solvents such as methanol, ethanol, acetonitrile, dimethylsulfoxide, dimethylformamide, and water. In DSC studies the material melted cleanly, 125-130°C, followed by accelerating decomposition as the temperature was increased beyond the melting point.

The proton spectrum revealed the three singlets, 5.899, relative area = 2.000; 7.161, relative area = 1.977; and 13.098, relative area 0.876, which represent the C-NH_2 protons, the N-NH_2 protons, and a proton located on the heterocyclic ring, respectively. The C-NH_2 and N-NH_2 peaks are shifted downfield and have separated significantly from those observed in the starting material, which essentially appears as a doublet (6.36 and 6.40 ppm; d_6-dmso) downfield with no other peaks observable. The shifts for the amino hydrogen environments of the protonated tetrazole ring agree well with those observed in similar N-amino high nitrogen systems previously[42-45]. The appearance of a highly deshielded broad singlet at +13.098 ppm is strong evidence of a proton located upon one of the heterocyclic nitrogen atoms. In the ^{13}C spectrum there has been a slight upfield shift of lone carbon singlet from +154 ppm to + 148 ppm upon protonation, and this agrees well with what has been observed previously in other high nitrogen heterocycles.[30-32,42-44]

In the vibrational spectra, there are significant shifts and broadening in the infrared spectral bands which are typically assigned to the NH_2 stretching environments. Typically upon N-protonation of one of the ring nitrogen atoms of a high nitrogen heterocycle with weakly basic pendant amino groups, there are blue shifts of the amino stretches typically in the range of 30-50 cm^{-1}.[13,17,41,55] Accompanying this shift there is the appearance of a broad absorbance ranging from 2600 – 2900 cm^{-1} that is strong evidence of –N-H ----N hydrogen bonding resulting from interactions in the solid state; it has been observed in many protonated cyclic and open-chained nitrogen bases

elsewhere.[56-65] One prominent band most likely assignable to C=N stretch is blue shifted in its large absorbance, which in the neutral 1,5-diamino-1,2,3,4-tetrazole, appears as a strong band centered at 1655 cm^{-1} while in the protonated species this band is shifted 50 cm^{-1} to a value of 1705 cm^{-1}. Finally, both spectra are dominataed by the powerful bands associated with the perchlorate anion, in the infrared, strong bands centered at 1120 cm^{-1} and 634 cm^{-1} and 620 cm^{-1}, while in the Raman, strong bands at 928 cm^{-1} and 467 cm^{-1} and 456 cm^{-1}, and these have been observed previously in many other perchlorate salt systems[41, 66, 67].

X-ray Crystallography. The single crystal X-ray diffraction data were collected on a Bruker 3-circle platform diffractometer equipped with a SMART CCD (charge coupled device) detector with the χ-axis fixed at 54.74° and using $MoK_{\acute{a}}$ radiation ($\acute{a}$ = 0.71073 Å) from a fine-focus tube. This diffractometer was equipped with KryoFlex apparatus for low temperature data collection using controlled liquid nitrogen boil off. The goniometer head, equipped with a nylon Cryoloop with a magnetic base, was then used to mount the crystals using PFPE (perfluoropolyether) oil. Cell constants were determined from 90 ten-second frames. A complete hemisphere of data was scanned on omega (0.3°) with a run time of ten-second per frame at a detector resolution of 512 x 512 pixels using the SMART software.[68, 69] A total of 1271 frames were collected in three sets; and final sets of 50 frames, identical to the first 50 frames, were also collected to determine any crystal decay. The frames were then processed on a PC running on Windows NT software by using the SAINT software[70, 71] to give the hkl file corrected for Lp/decay. The absorption correction was performed using the SADABS[72] program. The structures were solved by the direct method using the SHELX-90[73] program and refined by the least squares method on F^2, SHELXL-97[74] incorporated in SHELXTL New Version for Windows NT.[75, 76] All non-hydrogen atoms were refined anisotropically. For the anisotropic displacement parameters, the U(eq) is defined as one third of the trace of the orthogonalized U_{ij} tensor. The hydrogen atoms were located from difference electron density maps.

In Figure 1, the single crystal x-ray diffraction solution for 1,5-diamino-1,2,3,4-tetrazolium perchlorate is shown with details of the collection in Table 1. The salt crystallized in a monoclinic cell with $P2_1/n$ symmetry, and there is one asymmetric cation

and anion in the unit cell. There are several points of interest with the protonated cation. The proton was found attached to N(4), which neighbors the carbon atom in the 1,2,3,4-tetrazole ring. Another point of interest is the geometry of the pendant amino groups. The amino group attached to the carbon atom has a planar geometry which points to a predominantant iminium ($C=NH_2^+$) structure. The bond distance for C(1)-N(5) = 1.304(2) Å is quite short compared to a typical pendant carbon amino C-N bond distances and tetrazoles (generally around 1.32-1.35Å[29,31,32,77-81]), pointing to significant double bond character. In comparing it to the distance reported in the structural solution of the starting material, 1,5-diamino-1,2,3,4-tetrazole[77], the C-N bond distance was reported at 1.334(5) Å so protonation has significantly shortened the pendant C-N bond. The adjoining carbon-nitrogen bonds have shortened distances as well but not nearly so severe, with C(1)-N(1) = 1.3454(19) Å and C(1)-N(4) = 1.334(2) Å and are little changed from those reported for the neutral starting material[77], C(1)-N(1) = 1.342(2) Å and C(1)-N(4) = 1.329(2) Å. These are shorter than typical C-N single bonds but longer than C-N double bonds and are typical of tetrazole C-N bond distances[29,31,32,77-81].

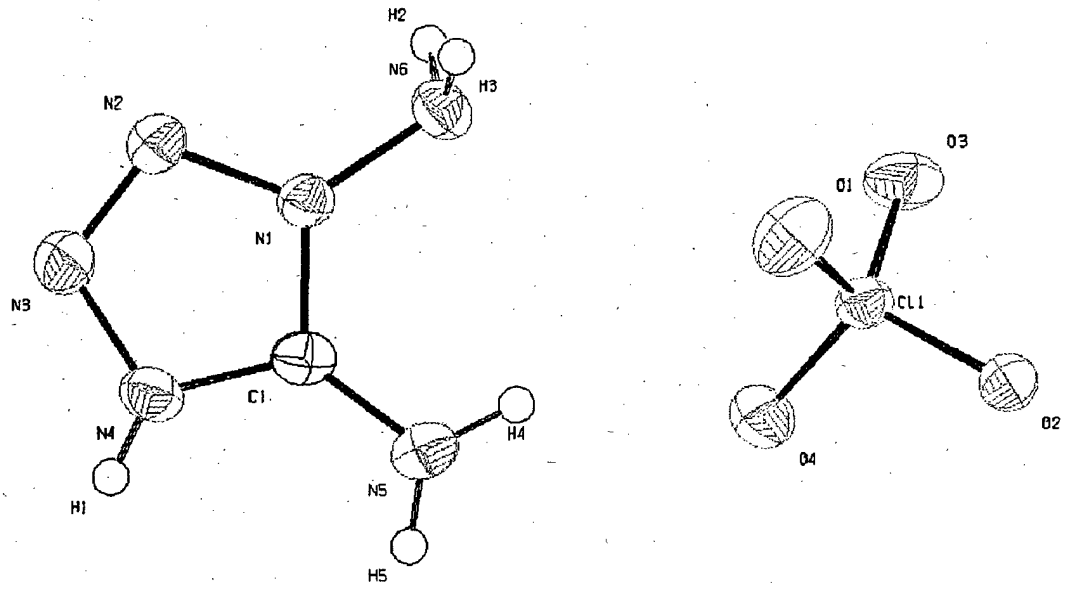


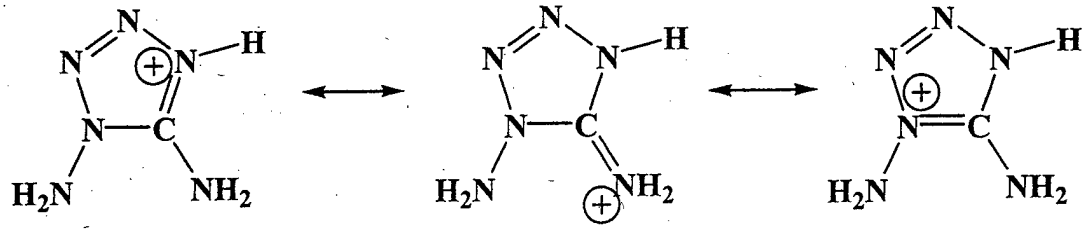
Figure 1. ORTEP (30% probability ellipsoids) showing the asymmetric cation and anion pair of 1,5-diamino-4-H-1,2,3,4-tetrazolium perchlorate.

The amino group attached to N(1) is not planar, but the expected pyramidal geometry, and saddles a mirror plane that slices through all of the carbon and nitrogen atoms of the tetrazole ring. This saddling behavior of the N-amino group has been observed in other double nitrogen substituted cation systems such as 1-substituted-4-amino-1,2,4-triazolium salts[82] and 1-amino-3-substituted-1,2,3-triazolium salts[83]. The N-N bond distance in the N-amino group, N(1)-N(6) = 1.386(2) Å, is slightly shorter than that observed for N-N single bonds in many other systems[29,31,32,77-83] but is not highly unusual. Two of the three ring nitrogen bond distances in the

Table 1. Crystal Data for 1,5-diamino-4-H-1,2,3,4-tetrazolium perchlorate

Formula	$C_1 H_5 N_6 O_4 Cl_1$
Formula Weight	200.56
Crystal System	Monoclinic
Space group	$P2_1/n$ (No. 14)
a, b, c [Å]	9.0683(8) 4.9956(4) 15.636(1)
alpha, beta, gamma [°]	90 99.857(2) 90
V[Å^3]	697.9(1)
Z	4
D(calc) [g/cm^3]	1.909
Mu(MoKa) [/mm]	0.539
F(000)	408
Temperature (K)	100
Radiation [Å]	MoKα 0.71073
Theta Min-Max [°]	2.4, 25.4
Dataset (h,k,l)	-10: 10 ; -6: 5 ; -14: 18
Tot., Uniq. Data, R(int)	3446, 1260, 0.015
Observed data [I > 2.0 σ(I)]	1226
Nref, Npar	1260, 130
R, wR2, S	0.0258, 0.0713, 1.10
Min. and Max. Resd. Dens. [e/Å^3]	-0.38, 0.21

ring, N(1)-N(2) = 1.370(2)Å, and N(3)-N(4) 1.361(2)Å, have bond distances that are slightly shorter than a typical N-N single bond distance (1.40Å) while the other N-N bond distance, N(2)-N(3) = 1.268(2) Å is close to that typically observed for N=N double bond distances and are typical of high-nitrogen azole N-N bond distances observed elsewhere[29,31,32,77-83] . In looking at resonance structures for the protonated 1,5-diamino-1,2,3,4-tetrazolium cation, several structures are possible but based on the observed crystal structure, structure B appears to be the dominant one. (Figure 2.)



A B C

Figure 2. The likely predominant resonance structures for the 1,5-diamino-4-H-tetrazolium cation based on the observed bond distances.

Other bond distances in the cation are typical and will not be discussed further. The perchlorate anion is quite normal in bond distances and angles and requires no further explanation. Hydrogen bonding is very predominant as would be expected and is depicted in Figure 3.

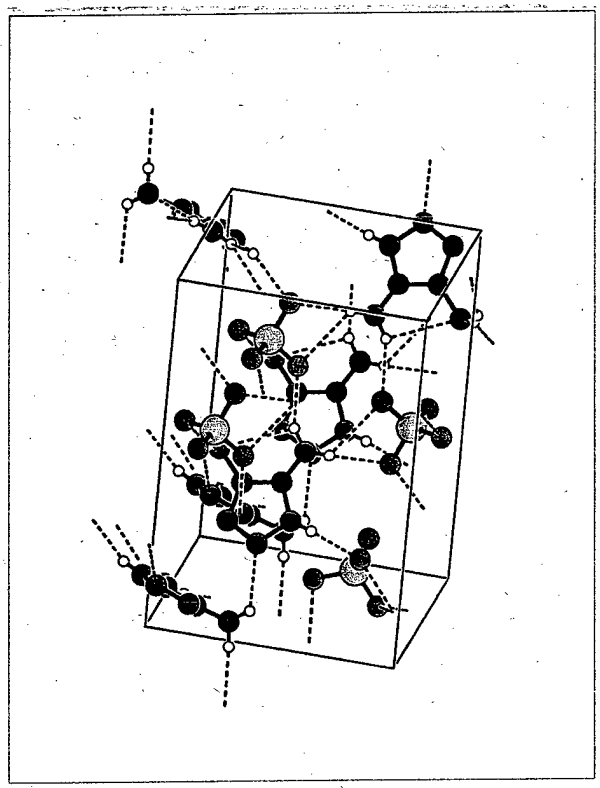
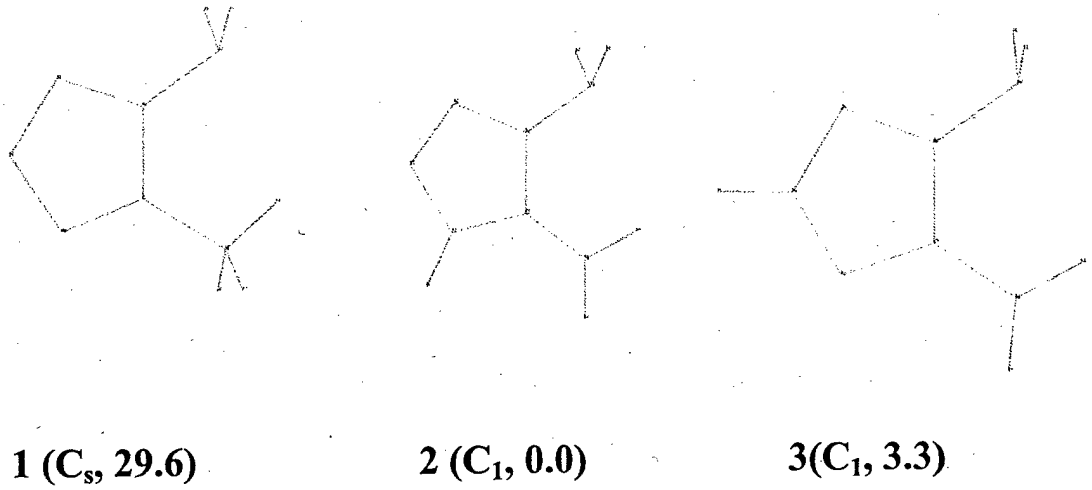


Figure 3. Unit cell of 1,5-diamino-4-H-1,2,3,4-tetrazolium perchlorate illustrating hydrogen bond contacts as dotted lines.

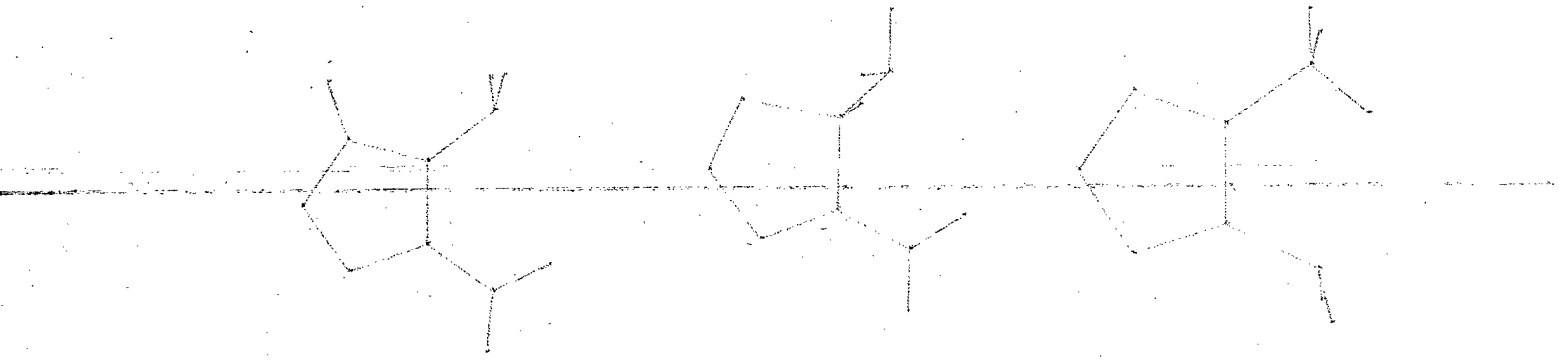
Theoretical Methods

The geometries of the six possible N-protonated isomers of 1,5-diamino-1,2,3,4-tetrazole were fully optimized using second-order perturbation theory (MP2, also known as MBPT(2)[46-51]) and the 6-311G(d,p)[84, 85] basis set. All structures were verified as local minima via diagonalization of the matrix of energy second derivatives with respect to nuclear displacements (i.e., the Hessian matrix.) Relative energies were computed using single-point coupled cluster singles and doubles with perturbative estimates of triples (CCSD(T)[52-54]) method and the 6-311G(2df,p)[84, 85] basis set, denoted as CCSD(T)/6-311G(2df,p)//MP2/6-311G(d,p). All calculations were performed using the GAMESS ab initio electronic structure program.[86]

The predicted structures of all possible N-protonated 1,5-diamino-1,2,3,4-tetrazoles are shown in Figure 4, including their point group symmetries and relative energies (in kcal/mol) which include zero-point vibrational energy corrections obtained from scaled[87] MP2/6-311G(d,p) harmonic vibrational frequencies. The lowest energy structure **2**, where the proton is located on N(4) of the 1,2,3,4-tetrazole ring, agrees with what is observed experimentally. (It should be noted, however, that structure **3** in which the proton is attached to N(3) is only 2.8 kcal higher in energy than **2.**) Furthermore, the overall structure and bond distances predicted by theory for **2** are in good agreement with the observed X-ray structure. The amino group attached to the carbon atom is essentially coplanar with respect to the tetrazole ring, and the N-amino group saddles the ring with the protons pointed away from the C-amino group. Two views of the theoretically predicted lowest energy structure are shown in Figure 5, and a comparison of calculated versus bond distances and angles is shown in Table 2. As can be seen in the right side of Figure 5, the C-amino group is nearly coplanar with the tetrazole ring, with only a slight degree of pyramidalization about the N atom. All predicted N-N and C-N bond lengths are within 0.02 Å of the experimental values.



1 (C_s, 29.6) **2 (C_1, 0.0)** **3(C_1, 3.3)**



4 (C_1, 16.8) **5 (C_1, 45.6)** **6 (C_s, 38.0)**

Figure 4. Possible protonated structures of 1,5-diamino-1,2,3,4-tetrazole and their relative CCSD(T)/6-311G(2df,p)//MP2/6-311G(d,p) energies (including zero-point vibrational energy corrections) in kcal/mol.

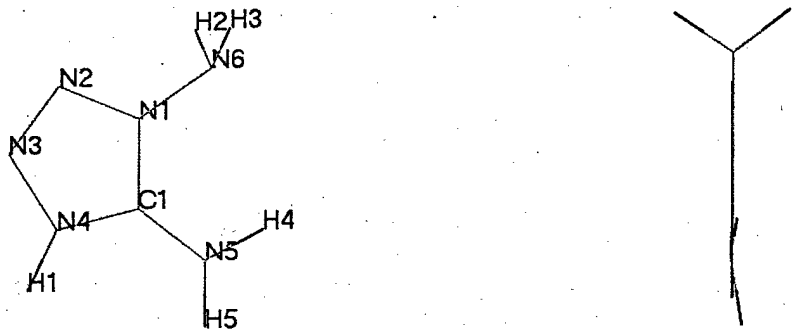


Figure 5. MP2/6-311G(d,p) optimized geometry of 1,5-diamino-1,2,3,4-tetrazolium cation.

Bond	Theory (Å)	Obsd. (Å)	Angle	Theory (°)	Obsd (°)
N(1)-N(2)	1.356	1.370(2)	N(2)-N(1)-N(6)	126.2	126.0(1)
N(1)-N(6)	1.380	1.386(2)	N(2)-N(1)-C(1)	110.9	110.2(1)
N(1)-C(1)	1.348	1.341(2)	N(6)-N(1)-C(1)	122.9	123.7(1)
N(2)-N(3)	1.284	1.268(2)	N(1)-C(1)-N(5)	125.5	126.7(1)
N(3)-N(4)	1.367	1.361(2)	N(1)-N(2)-N(3)	107.4	107.4(1)
N(4)-C(1)	1.341	1.329(2)	N(4)-C(1)-N(5)	131.3	129.6(2)
N(5)-C(1)	1.326	1.304(2)	N(2)-N(3)-N(4)	107.6	108.4(1)
N(4)-H(1)	1.014	0.76(3)	N(1)-C(1)-N(4)	103.2	103.7(1)
N(5)-H(4)	1.013	0.85(2)	N(3)-N(4)-C(1)	110.9	110.4(1)
N(5)-H(5)	1.009	0.78(3)			
N(6)-H(2)	1.017	0.85(3)			
N(7)-H(3)	1.017	0.84(3)			

Table 2. Comparison of predicted gas phase bond distances and angles to those observed in the crystalline state of 1,5-diamino-4-H-1,2,3,4-tetrazolium perchlorate.

Finally, the calculated infrared vibrational spectrum of the 1,5-diamino-4-H-1,2,3,4-tetrazolium cation is compared with the observed spectrum of the perchlorate salt and matches fairly well (Figure 6). It must be pointed out that the gas phase structure spectrum differs mainly in the fact that strong hydrogen bonding interactions affect the entire spectrum, especially those bands associated with hydrogen modes. As well the perchlorate anion heavily dominates the region around 1100 cm^{-1}, making some of the cation bands undiscernable.

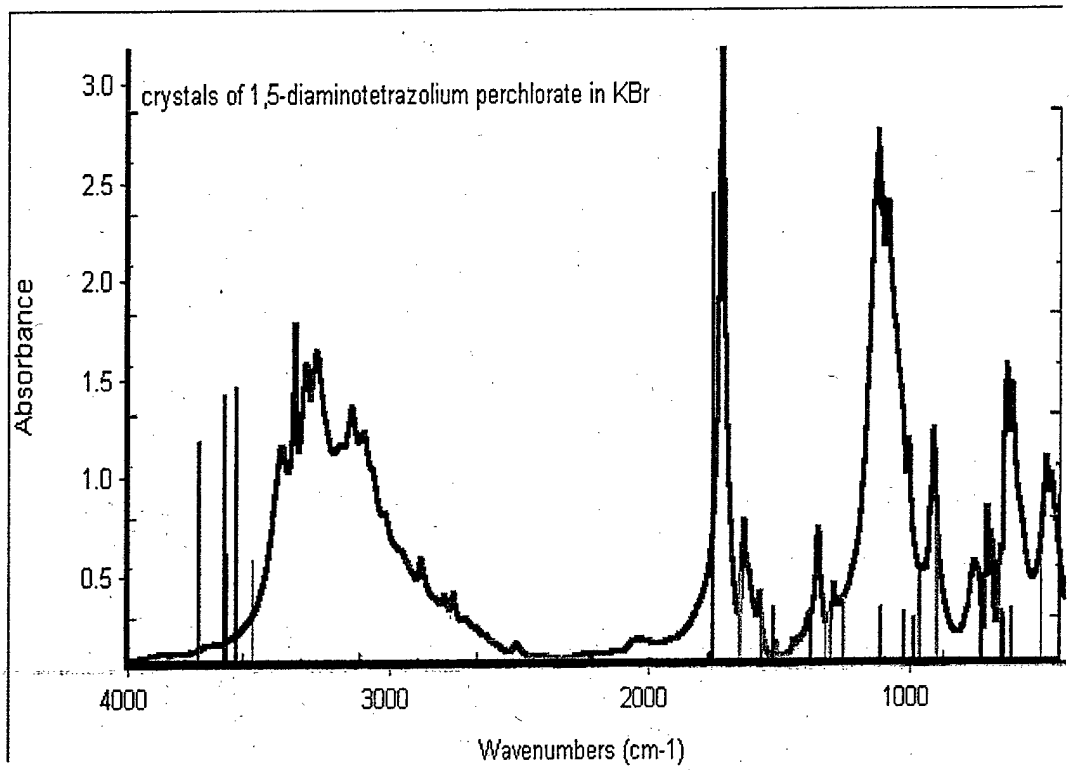


Figure 6. Overlay of calculated infrared spectrum (gas phase cation only) versus the observed spectrum for 1,5-diamino-4-H-1,2,3,4-tetrazolium perchlorate.

Conlusions

The synthesis and characterization of 1,5-diamino-1,2,3,4-tetrazolium perchlorate was carried out using several forms of spectroscopy, including a single crystal x-ray diffraction study confirming protonation of the tetrazole ring at nitrogen atom 4. Calculations carried out at the CCSD(T)/6-311G(2df,p)//MP2/6-311G(d,p) level of theory found the lowest energy structure to be that of protonation of ring nitrogen 4 of the tetrazole as well. The predicted structure of this isomer, including the geometries and orientations of the pendant amino groups with respect to the tetrazole ring, is in excellent agreement with experimental findings.

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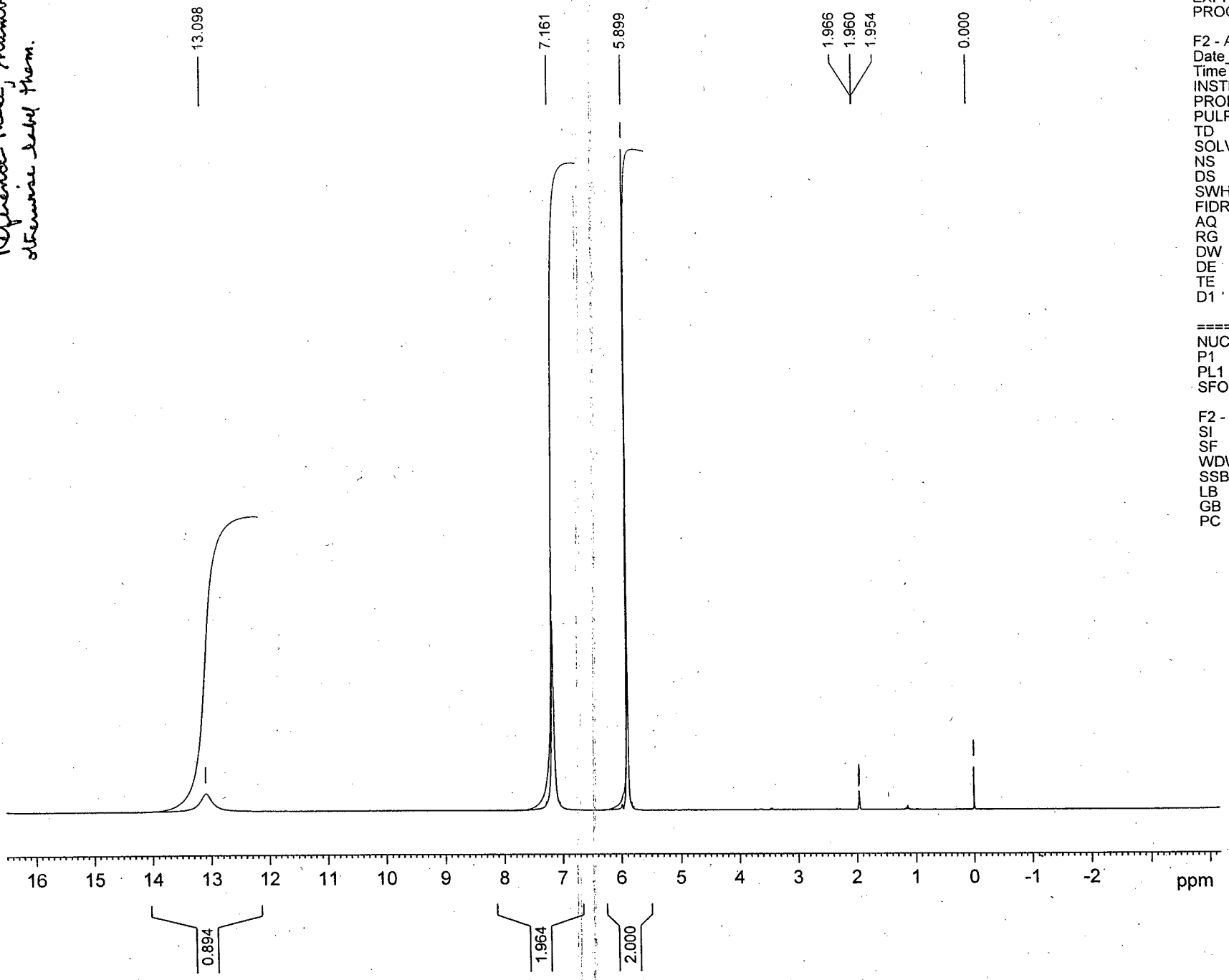
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crystals of 1,5-diaminotetrazolium perchlorate in CD3CN



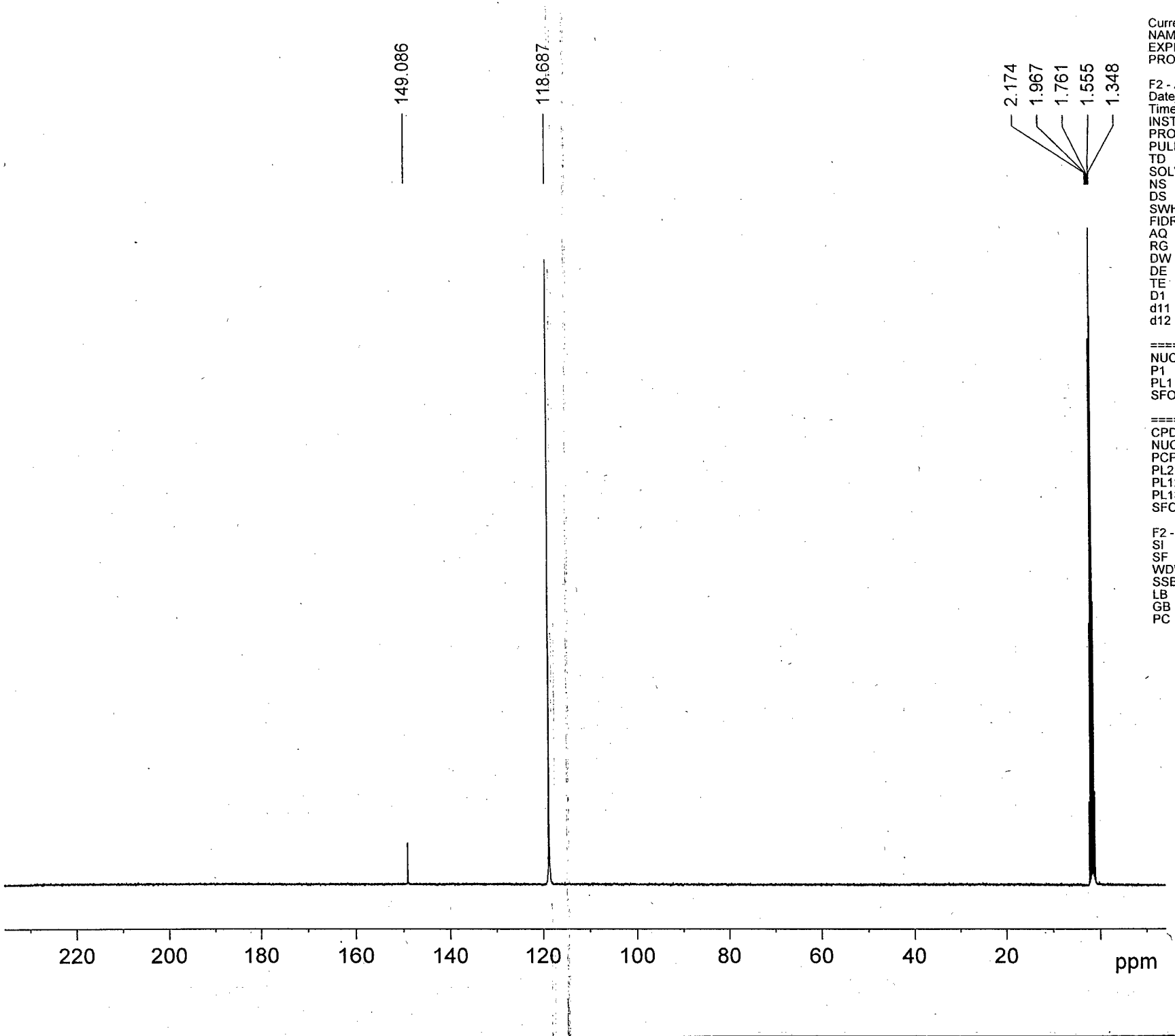
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LB 0.30 Hz
GB 0
PC 1.00

1,5-Diaminotetrazolium perchlorate in CD3CN



Current Data Parameters
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PROCNO 1

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DE 6.00 usec
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d11 0.03000000 sec
d12 0.00002000 sec

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PL1 -5.00 dB
SFO1 100.6237959 MHz

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PL12 18.00 dB
PL13 120.00 dB
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F2 - Processing parameters
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SSB 0
LB 1.00 Hz
GB 0
PC 1.40

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SUPPLEMENTARY MATERIAL

BELONGING TO THE PAPER

by

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for: sad

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for: sad

1,5-diamino-4-h-1,2,3,4-tetrazolium clo4.sup

Table S1 - Crystal Data and Details of the Structure Determination
for: sad

Crystal Data			
Formula			Cl O4, C H5 N6
Formula Weight			200.56
Crystal System			Monoclinic
Space group		P21/n	(No. 14)
a, b, c [Angstrom]	9.0683(8)	4.9956(4)	15.6355(13)
alpha, beta, gamma [deg]	90	99.857(2)	90
V [Ang**3]			697.86(10)
Z			4
D(calc) [g/cm**3]			1.909
Mu(MoKa) [/mm]			0.539
F(000)			408
Crystal Size [mm]		0.00 x 0.00 x 0.00	
Data Collection			
Temperature (K)			173
Radiation [Angstrom]		MoKa	0.71073
Theta Min-Max [Deg]			2.4, 25.4
Dataset		-10: 10 ; -6: 5 ; -14: 18	
Tot., Uniq. Data, R(int)		3446, 1260, 0.015	
Observed data [I > 2.0 sigma(I)]			1226
Refinement			
Nref, Npar			1260, 130
R, wR2, S		0.0258, 0.0713, 1.10	
w = 1/[\s^2^(Fo^2^)+(0.0409P)^2^+0.3295P] where P=(Fo^2^+2Fc^2^)/3			
Max. and Av. Shift/Error			0.00, 0.00
Min. and Max. Resd. Dens. [e/Ang^3]			-0.38, 0.21

Table S2 - Final Coordinates and Equivalent Isotropic Displacement Parameters of the non-Hydrogen atoms
for: sad

Atom	x	y	z	U(eq) [Ang^2]

Cl1	0.78841(4)	0.04709(7)	0.60378(2)	0.0227(1)
O1	0.92969(13)	-0.0528(3)	0.58854(8)	0.0339(4)
O2	0.67467(13)	-0.0046(3)	0.52914(8)	0.0354(4)
O3	0.79723(15)	0.3269(2)	0.62203(9)	0.0413(4)
O4	0.74583(12)	-0.0938(2)	0.67739(7)	0.0275(3)
N1	0.77373(13)	0.1819(2)	0.13455(8)	0.0218(4)
N2	0.76682(15)	0.3839(3)	0.19297(9)	0.0272(4)
N3	0.89650(15)	0.4097(3)	0.23781(9)	0.0290(4)
N4	0.98842(16)	0.2279(3)	0.20894(9)	0.0259(4)
N5	0.95983(19)	-0.1106(3)	0.10003(10)	0.0315(5)
N6	0.65415(15)	0.0793(3)	0.07672(9)	0.0267(4)
C1	0.91308(17)	0.0826(3)	0.14474(10)	0.0223(4)

U(eq) = 1/3 of the trace of the orthogonalized U Tensor

Table S3 - Hydrogen Atom Positions and Isotropic Displacement Parameters
for: sad

Atom	x	y	z	U(iso) [Ang^2]
H1	1.068(3)	0.207(4)	0.2322(14)	0.036(6)
H2	0.588(3)	0.034(4)	0.1064(15)	0.037(6)
H3	0.620(3)	0.199(5)	0.0408(16)	0.040(6)
H4	0.896(2)	-0.177(4)	0.0599(15)	0.034(5)
H5	1.043(3)	-0.156(5)	0.1118(14)	0.039(6)

==========

The Temperature Factor has the Form of Exp(-T) Where
T = 8*(Pi**2)*U*(Sin(Theta)/Lambda)**2 for Isotropic Atoms

Table S4 - (An)isotropic Displacement Parameters
for: sad

Atom	U(1,1) or U	U(2,2)	U(3,3)	U(2,3)	U(1,3)	U(1,2)
Cl1	0.0216(2)	0.0252(3)	0.0215(2)	0.0000(1)	0.0039(2)	-0.0029(1)
O1	0.0231(6)	0.0439(8)	0.0369(7)	-0.0039(5)	0.0110(5)	-0.0031(5)
O2	0.0306(6)	0.0470(7)	0.0258(6)	0.0042(5)	-0.0030(5)	-0.0075(5)
O3	0.0528(8)	0.0247(7)	0.0472(8)	-0.0018(5)	0.0107(6)	-0.0047(5)

O4	0.0239(6)	0.0344(6)	0.0246(6)	0.0059(4)	0.0057(4)	0.0000(5)
N1	0.0217(6)	0.0252(7)	0.0185(6)	0.0000(5)	0.0032(5)	0.0028(5)
N2	0.0274(7)	0.0287(7)	0.0259(7)	-0.0033(5)	0.0055(5)	0.0023(6)
N3	0.0285(7)	0.0325(7)	0.0262(7)	-0.0034(6)	0.0050(5)	-0.0008(6)
N4	0.0190(7)	0.0330(7)	0.0250(7)	0.0011(5)	0.0017(5)	0.0009(6)
N5	0.0249(8)	0.0364(8)	0.0333(8)	-0.0049(6)	0.0054(6)	0.0069(7)
N6	0.0236(7)	0.0343(8)	0.0210(7)	0.0010(6)	0.0000(6)	-0.0007(6)
C1	0.0226(7)	0.0254(8)	0.0197(7)	0.0056(6)	0.0058(6)	0.0013(6)

==========

The Temperature Factor has the Form of Exp(-T) Where
T = 8*(Pi**2)*U*(Sin(Theta)/Lambda)**2 for Isotropic Atoms
T = 2*(Pi**2)*Sumij(h(i)*h(j)*U(i,j)*Astar(i)*Astar(j)), for Anisotropic Atoms. Astar(i) are Reciprocal Axial Lengths and h(i) are the Reflection Indices.

Table S5 - Bond Distances (Angstrom)
for: sad

Cl1	-O1	1.4324(13)	N3	-N4	1.361(2)
Cl1	-O2	1.4423(13)	N4	-C1	1.329(2)
Cl1	-O3	1.4262(11)	N5	-C1	1.304(2)
Cl1	-O4	1.4565(11)	N4	-H1	0.76(3)
N1	-N2	1.3697(18)	N5	-H4	0.85(2)
N1	-N6	1.3858(18)	N5	-H5	0.78(3)
N1	-C1	1.341(2)	N6	-H2	0.85(3)
N2	-N3	1.268(2)	N6	-H3	0.84(2)

Table S6 - Bond Angles (Degrees)
for: sad

O1	-Cl1	-O2	109.82(7)	N3	-N4	-H1	121.3(16)
O1	-Cl1	-O3	110.71(8)	C1	-N4	-H1	127.7(16)
O1	-Cl1	-O4	109.19(7)	C1	-N5	-H4	116.4(13)
O2	-Cl1	-O3	110.19(8)	H4	-N5	-H5	125(2)
O2	-Cl1	-O4	107.65(7)	C1	-N5	-H5	118.6(17)

O3	-Cl1	-O4	109.20(7)	N1	-N6	-H2	106.8(16)
N2	-N1	-N6	125.98(12)	N1	-N6	-H3	109.3(18)
N2	-N1	-C1	110.06(12)	H2	-N6	-H3	110(2)
N6	-N1	-C1	123.83(12)	N1	-C1	-N5	126.58(15)
N1	-N2	-N3	107.43(13)	N4	-C1	-N5	129.54(16)
N2	-N3	-N4	108.14(14)	N1	-C1	-N4	103.87(13)
N3	-N4	-C1	110.49(14)				

Table S7 - Torsion Angles (Degrees)
for: sad

N6	-N1	-N2	-N3	175.98(13)
C1	-N1	-N2	-N3	0.00(17)
N2	-N1	-C1	-N4	-0.40(16)
N2	-N1	-C1	-N5	-179.80(16)
N6	-N1	-C1	-N4	-176.49(13)
N6	-N1	-C1	-N5	4.1(2)
N1	-N2	-N3	-N4	0.41(17)
N2	-N3	-N4	-C1	-0.69(18)
N3	-N4	-C1	-N1	0.65(17)
N3	-N4	-C1	-N5	-179.97(16)

Table S8 - Contact Distances(Angstrom)
for: sad

Cl1	.H3_a	3.08(3)	O4	.H1_i	2.75(2)
Cl1	.H4_b	3.13(2)	O4	.H5_d	2.31(3)
Cl1	.H1_c	2.96(2)	N1	.O2_k	3.1036(18)
Cl1	.H5_d	2.98(3)	N1	.N2_a	3.1565(19)
O1	.N6_a	3.156(2)	N1	.N3_a	3.0446(19)
O1	.N6_e	3.147(2)	N2	.N1_b	3.1565(19)
O1	.N4_c	3.2463(19)	N2	.N2_a	3.114(2)
O2	.C1_a	3.397(2)	N2	.N2_b	3.114(2)
O2	.N5_b	2.932(2)	N2	.N3_a	3.086(2)

O2	.N5_d	3.076(2)	N2	.N3_b	3.288(2)
O2	.O2_g	3.1432(17)	N2	.C1_b	3.392(2)
O2	.N1_a	3.1036(18)	N3	.N1_b	3.0446(19)
O2	.N6_a	3.217(2)	N3	.N2_a	3.288(2)
O3	.O4_h	3.0789(15)	N3	.N2_b	3.086(2)
O4	.N5_d	3.049(2)	N3	.N6_b	3.130(2)
O4	.N4_c	2.8193(18)	N4	.O4_m	3.0704(18)
O4	.O3_j	3.0789(15)	N4	.O1_l	3.2463(19)
O4	.N4_i	3.0704(18)	N4	.O4_l	2.8193(18)
O1	.H1_c	2.90(2)	N5	.O4_o	3.049(2)
O1	.H2_f	2.79(2)	N5	.N6	2.893(2)
O1	.H3_e	2.66(3)	N5	.O2_n	2.932(2)
O1	.H3_a	2.35(2)	N5	.O2_o	3.076(2)
O2	.H4_b	2.17(2)	N6	.O1_k	3.156(2)
O2	.H3_a	2.75(3)	N6	.N5	2.893(2)
O2	.H5_d	2.55(2)	N6	.N3_a	3.130(2)
O3	.H5_i	2.81(3)	N6	.O1_p	3.147(2)
O3	.H2_e	2.78(3)	N6	.O2_k	3.217(2)
O4	.H1_c	2.09(2)	N3	.H2_b	2.49(2)

Table S8 - Contact Distances(Angstrom) (continued)
for: sad

N6	.H4	2.592(19)	H3	.O1_k	2.35(2)
C1	.O2_k	3.397(2)	H3	.O2_k	2.75(3)
C1	.N2_a	3.392(2)	H3	.O1_p	2.66(3)
H1	.H5	2.60(3)	H4	.N6	2.592(19)
H1	.Cl1_l	2.96(2)	H4	.Cl1_n	3.13(2)
H1	.O1_l	2.90(2)	H4	.O2_n	2.17(2)
H1	.O4_l	2.09(2)	H5	.H1	2.60(3)
H1	.O4_m	2.75(2)	H5	.Cl1_o	2.98(3)
H2	.N3_a	2.49(2)	H5	.O2_o	2.55(3)

H2	.O1_q	2.79(2)	H5	.O3_m	2.81(3)
H2	.O3_p	2.78(3)	H5	.O4_o	2.31(3)
H3	.Cl1_k	3.08(3)			

Table S9 - Hydrogen Bonds (Angstrom, Deg)
for: sad

N4	-- H1	.. O4	0.76(3)	2.09(2)	2.8193(18)	163(2)	3_756
N6	-- H2	.. N3	0.85(3)	2.49(2)	3.130(2)	132(2)	2_645
N6	-- H3	.. O1	0.84(2)	2.35(2)	3.156(2)	161(2)	2_655
N6	-- H3	.. O1	0.84(2)	2.66(3)	3.147(2)	118(2)	4_454
N5	-- H4	.. N6	0.85(2)	2.592(19)	2.893(2)	102.4(15)	.
N5	-- H4	.. O2	0.85(2)	2.17(2)	2.932(2)	149.4(18)	2_645
N5	-- H5	.. O2	0.78(3)	2.55(3)	3.076(2)	126(2)	4_544
N5	-- H5	.. O4	0.78(3)	2.31(3)	3.049(2)	158(2)	4_544

Translation of Symmetry Code to Equiv.Pos

a =[2645.00] = 3/2-x,-1/2+y,1/2-z
b =[2655.00] = 3/2-x,1/2+y,1/2-z
c =[3756.00] = 2-x,-y,1-z
d =[4445.00] = -1/2+x,-1/2-y,1/2+z
e =[4555.00] = 1/2+x,1/2-y,1/2+z
f =[4545.00] = 1/2+x,-1/2-y,1/2+z
g =[3656.00] = 1-x,-y,1-z
h =[1565.00] = x,1+y,z
i =[4455.00] = -1/2+x,1/2-y,1/2+z
j =[1545.00] = x,-1+y,z
k =[2655.00] = 3/2-x,1/2+y,1/2-z
l =[3756.00] = 2-x,-y,1-z
m =[4554.00] = 1/2+x,1/2-y,-1/2+z
o =[4544.00] = 1/2+x,-1/2-y,-1/2+z
p =[4454.00] = -1/2+x,1/2-y,-1/2+z
q =[4444.00] = -1/2+x,-1/2-y,-1/2+z