

Structural and Theoretical Investigations of 3,4,5-Triamino-1,2,4-Triazolium Salts

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Abstract: Reactions using the high nitrogen heterocycle 3,4,5-triamino-1,2,4-triazole (guanazine) with strong acids (HNO_3 , HClO_4 , and “ $\text{HN}(\text{NO}_2)_2$ ”) resulted in a family of highly stable salts. All of the salts were characterized using spectroscopic as well as single crystal x-ray diffraction studies. The x-ray structures are compared to that obtained from theoretical calculations (MP2/6-311+G(d,p) level). Initial safety testing (impact, friction) was carried out on all of the new materials.

Introduction

The study of salts involving high nitrogen heterocycles has been the point of growing interest amongst several research groups, including species such as bitetrazolate¹⁻⁵, 3, 5-dinitrotriazoles⁶, nitrotriazalones (NTO)⁷⁻¹⁰, 5-nitrotetrazole¹¹⁻¹³, and nitramino-1,2,3-triazoles¹⁴. The majority of this work has resulted from the inherent acidity of these high nitrogen heterocycles, forming their corresponding anionic form. However, few examples have appeared where the high nitrogen heterocycles have served as bases forming cationic species, and these include salts of 3,6-dihydrazino-1,2,4,5-tetrazine¹⁵, simple triazoles¹⁶, N-amino-1,2,4-triazoles^{16,17}, and 1,5-diamino-1,2,3,4-tetrazoles^{18,19}.

Previously an x-ray study of the bromide salt of 3,4,5-triamino-1,2,4-triazole appeared in the literature²⁰, otherwise this high nitrogen molecule has been ignored. This heterocycle is somewhat unusual in that it is quite basic, in fact it is air sensitive, and forms salts readily. We undertook studies exploring reactions of this heterocycle with nitric, perchloric, and dinitramidic acids, resulting in a class of highly stable salts. These

Report Documentation Page

Form Approved
OMB No. 0704-0188

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1. REPORT DATE JUL 2004		2. REPORT TYPE		3. DATES COVERED -	
4. TITLE AND SUBTITLE Structural and Theoretical Investigation of 3,4,5-Triamino-1,2,4-Triazolium Salts				5a. CONTRACT NUMBER	
				5b. GRANT NUMBER	
				5c. PROGRAM ELEMENT NUMBER	
6. AUTHOR(S) Gregory Drake; Tommy Hawkins; Leslie Hall; Jerry Boatz; Adam Brand				5d. PROJECT NUMBER 1011	
				5e. TASK NUMBER 0046	
				5f. WORK UNIT NUMBER	
7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES) Air Force Research Laboratory (AFMC), AFRL/PRSP, 10 E. Saturn Blvd., Edwards AFB, CA, 93524-7680				8. PERFORMING ORGANIZATION REPORT NUMBER	
9. SPONSORING/MONITORING AGENCY NAME(S) AND ADDRESS(ES)				10. SPONSOR/MONITOR'S ACRONYM(S)	
				11. SPONSOR/MONITOR'S REPORT NUMBER(S)	
12. DISTRIBUTION/AVAILABILITY STATEMENT Approved for public release; distribution unlimited					
13. SUPPLEMENTARY NOTES					
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15. SUBJECT TERMS					
16. SECURITY CLASSIFICATION OF:			17. LIMITATION OF ABSTRACT	18. NUMBER OF PAGES 31	19a. NAME OF RESPONSIBLE PERSON
a. REPORT unclassified	b. ABSTRACT unclassified	c. THIS PAGE unclassified			

salts have been fully characterized by multinuclear nmr, vibrational, DSC studies, initial safety testing (impact and friction), as well as crystallographic studies of all the new salts. Quantum chemical predictions of the structure of the protonated heterocycle were found to be in good agreement with the corresponding experimental data.

Experimental

3,4,5-triamino-1,2,4-triazole was prepared according to the published procedure.²¹ Care should be exercised in handling the heterocycle and it should be manipulated under an inert atmosphere at all times as it is sensitive to air oxidation resulting in red colored polyazoles. Nitric acid, HNO₃ (69-70% by weight; H₂O solution; A.C.S. reagent grade) was purchased from Aldrich Chemical Company, and used without further purification. Perchloric acid, HClO₄ (70.0% by weight, H₂O solution; Baker Reagent grade) was used as received. Ammonium dinitramide, NH₄N(NO₂)₂, was graciously donated from ATK Thiokol, Inc., and after Raman spectroscopy showed low NO₃⁻ content, it was stored in a brown bottle inside a nitrogen filled glove box. Methanol, CH₃OH; Ethanol, CH₃CH₂OH; and 2-Propanol, (CH₃)₂CH-OH, (ACS reagent grade; distilled from sodium metal), and acetonitrile, CH₃CN (HPLC grade; distilled from calcium hydride) were purchased from Aldrich Chemical Company, and all solvents were degassed using a liquid nitrogen freeze-thaw vacuum procedure. Water was distilled and deionized using a Milli-q-reagent water system (Millipore Corporation, Inc.), and then degassed via multiple freeze-thaw processes under high vacuum. All solvents were stored inside glass vessels, which were sealed with teflon screw-cap plugs, and were equipped with #15 O-ring fittings. Infrared spectra were recorded as KBr disks (using a KBr disk as a reference background) on a Nicolet 55XC FT-IR spectrometer from 4000-400 cm⁻¹. Raman spectra were recorded in pyrex melting point capillaries on 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 d₆-dmso in 5mm nmr tubes, and the ¹H and ¹³C spectra recorded on a Bruker Spectrospin DRX 400 MHz UltrashieldTM 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 by Galbraith Laboratories, Inc. of Knoxville, TN.

3, 4, 5-triamino-1, 2, 4-triazole nitrate, [C₂H₇N₆⁺][NO₃⁻]: Inside a nitrogen filled drybox, a Schlenk flask was charged with of 3, 4, 5-triamino-1, 2, 4-triazole (1.3848 g., 12.1 mmoles). Outside the drybox, the flask was attached to a double manifold, evacuated, and then charged with dry nitrogen. Water, 12 ml, was added through a disposable syringe along with a teflon stir bar under a brisk nitrogen flow and the resultant mixture stirred vigorously. Concentrated nitric acid (1.1310 g., 12.2 mmoles) was added with a disposable glass pipet under brisk nitrogen flow. The reaction mixture, which was a colorless, homogenous solution, was stirred for one hour at ambient temperature whereupon the stir bar was removed, and the solvent was evacuated off under high vacuum overnight. The next day, the white crystalline product, 3, 4, 5-triamino-1, 2, 4-triazole nitrate remained in very high yield (2.1406 g., 12.1 mmoles, or 99.6% of theory). M.P.: 206°C by DSC.

IR (cm⁻¹): 3416, 3343, 3277, 3244, 3165, 2793, 1697, 1667, 1612, 1570, 1517, 1417, 1384, 1360, 1307, 1130, 1083, 1042, 1019, 939, 824, 800, 765, 727, 719, 650, 621, 556.

Raman (cm⁻¹) 3240, 3346, 3277, 3173, 1695, 1649, 1622, 1606, 1568, 1523, 1446, 1306, 1160, 1134, 1084, 1043, 1023, 943, 802, 771, 726, 711, 629, 578, 337, 313, 198, 126.

¹H NMR (d₆-dmsO): +5.66 (broad singlet, area = 2.29); 7.069 (broad singlet, area = 3.74); 12.46 (broad singlet, area = 1.00).

¹³C NMR (d₆-dmsO): +150.86.

Elemental analysis: Theory: %C 13.56; %H, 3.98; %N, 55.35. Found: %C 13.49; %H, 4.00; %N, 55.27.

3, 4, 5-triamino-1, 2, 4-triazole perchlorate, [C₂H₇N₆⁺][ClO₄⁻]: Inside a nitrogen filled drybox, a Schlenk flask was charged with, of 3, 4, 5-triamino-1, 2, 4-triazole (1.2758 g., 11.2 mmoles). Outside the drybox, methanol, 12 ml, was added through a disposable syringe along with a teflon stir bar under a brisk nitrogen flow and the resultant mixture stirred vigorously. Concentrated perchloric acid (1.6073 g., 11.2 mmoles) was added

with a disposable glass pipet, and the colorless, homogenous reaction mixture stirred for one hour at ambient temperature. At the end of one hour, the stir bar was removed, and the methanol evacuated off with a high vacuum overnight. The next day, the white crystalline product, 3, 4, 5-triamino-1, 2, 4-triazole perchlorate remained in very high yield (2.4180 g., 11.2 mmoles, or 100% of theory). M.P.: 194°C by DSC.

IR(cm^{-1}): 3456, 3370, 3297, 1711, 1663, 1613, 1440, 1328, 1301, 1100, 943, 903, 804, 758, 632, 559, 469.

Raman(cm^{-1}): 3420, 3359, 3298, 1716, 1667, 1610, 1587, 1565, 1436, 1329, 1300, 1149, 1124, 1054, 1016, 938, 900, 798, 761, 628, 561, 468, 455, 331, 320, 276, 84.

^1H NMR (d_6 -dmsO): 5.51 ppm (broad singlet, area 2.141); 7.05 (large singlet, area 4.007); 12.10 (broad, area 0.934).

^{13}C NMR (d_6 -dmsO): +150.28 ppm singlet

Elemental analysis: Theory: %C 11.19; %H, 3.28; %N, 39.16. Found: %C 11.10; %H, 3.25; %N, 38.72.

3, 4, 5-triamino-1, 2, 4-triazole dinitramide [$\text{C}_2\text{H}_7\text{N}_6^+$][$\text{N}(\text{NO}_2)_2^-$]: Inside a drybox, one Schlenk flask was charged with 3, 4, 5-triamino-1, 2, 4-triazole (1.3608 g., 11.9 mmoles), while another Schlenk flask was charged with ammonium dinitramide (1.5038 g., 12.1 mmoles). Both flasks were removed from the drybox, attached to a double manifold, evacuated, and then charged with dry nitrogen gas. Subsequent manipulations of the reaction were carried out in total darkness, with only the assistance of a red light. Methanol, 20 mL, was added to the ammonium dinitramide dissolving it. The 3, 4, 5-triamino-1, 2, 4-triazole was transferred into a 500 ml flask, and suspended in 50 ml of dry methanol, and stirred vigorously. This flask was already attached through a clamped #15 O-ring joint to a medium fritted chromatography column, which had been previously charged with a large amount of DOWEXTM strong cation exchange resin. The resin had been activated with 0.1M HCl, rinsed, and switched over to dry methanol under nitrogen atmosphere prior to the reaction. The ammonium dinitramide solution was then transferred to the top of the ion exchange column with a disposable syringe under vigorous nitrogen purge. The solution was then eluted through the column, with three aliquots, 50 ml each, of fresh methanol, which were subsequently added when the solvent

level was just above the ion exchange bed. At the end of the elution, the reaction flask was removed from the ion exchange column, and attached to a double manifold line, and the solvent removed over a 36 hour period, leaving an off white solid in high yield, 2.5140 grams, 11.4 mmoles, 95% of theory. M.P.: 145°C by DSC.

IR(cm^{-1}): 3400, 3303, 3242, 3145, 1706, 1665, 1619, 1516, 1434, 1311, 1173, 1004, 932, 871, 805, 799, 748, 692, 610, 554, 515, 447.

Raman(cm^{-1}): 3396, 3334, 3297, 3271, 1715, 1667, 1579, 1521, 1438, 1317, 1175, 1146, 1049, 1022, 960, 817, 799, 759, 630, 567, 493, 449, 345, 313, 253, 121, 103, 92, 85.

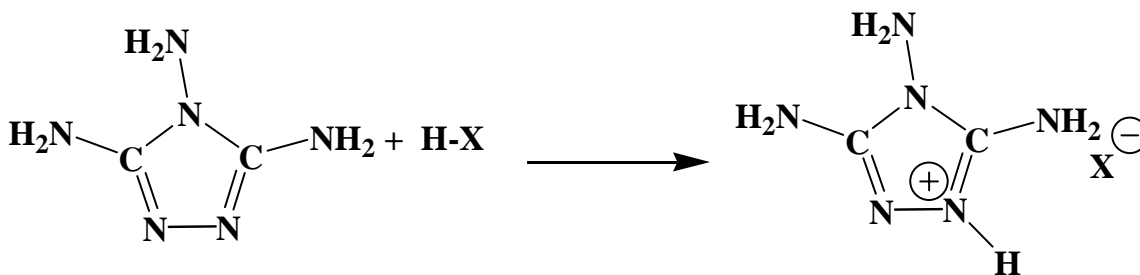
^1H NMR (d_6 -dmsO): +5.53 and 7.06 (broad singlet, area of both peaks = 6.19); 12.40 (broad singlet, area = 1.00).

^{13}C NMR (d_6 -dmsO): +150.29

Elemental analysis: Theory: %C 10.86; %H, 3.19; %N, 57.00. Found: %C 11.09; %H, 3.28; %N, 56.64.

Synthesis and Characterization

The synthesis of the perchlorate and dinitramide salts was easily accomplished by reacting the strong acid with the one equivalent of 3,4,5-triamino-1,2,4-triazole in methanol. However, for the formation of the nitrate salt the reaction had to be carried out in water due to the poor solubility of both the starting heterocycle and the product nitrate salt. (Reaction 1.)



Where $\text{H-X} = \text{HNO}_3$, HClO_4 or " $\text{HN}(\text{NO}_2)_2$ " and $\text{X}^- = \text{NO}_3^-$, ClO_4^- or $\text{N}(\text{NO}_2)_2^-$.

All of the salts were recovered as highly crystalline materials in excellent yields and purities. Unlike the starting heterocycle, there was no apparent air oxidation of any of the heterocyclic salts upon exposure to the air. The nitrate salt was only moderately soluble in water and poorly soluble in polar protic solvents, while the perchlorate and dinitramide are appreciably more soluble in polar solvents such as methanol, ethanol, and acetonitrile. DSC studies revealed a family of very stable salts with all of the salts beginning exothermic decompositions right after their respective melt. The nitrate salt melted at 205°C with decomposition beginning at 245°C, the perchlorate at 196°C with decomposition starting at 275°C and the dinitramide melted at 145°C with decomposition rapidly occurring thereafter. Thus all of the new salts have relatively high melting points for simple heterocycle salts which most likely can be attributed to the high basicity of the 3,4,5-triamino-1,2,4-triazole as well as large amounts of crystalline phase hydrogen bonding..

Multinuclear spectral information on the heterocyclic salts was strongly supportive of ring protonation upon a nitrogen atom. In the ^1H spectra, there are three separate singlets, with each assignable to the N-NH₂ and C-NH₂ peaks respectively, with relative areas of two and four, while the appearance of a highly deshielded broad singlet, appears around 12.5 ppm downfield, with a relative area of one. In the ^{13}C spectrum, there was a slight shift in the single carbon resonance upon protonation which is not unusual. These ^1H and ^{13}C shifts have been noted previously in many other high nitrogen heterocyclic systems.^{15-19, 23-34} In the vibrational spectra, there were strong indications of nitrogen protonation, with the appearance of a large broad band from 2500-2900 cm⁻¹ which is typical of N⁺-H---N interactions in the solid state and has been noted in a wide array of protonated nitrogen systems.^{16, 35-43} A significant blue shift in a band assignable to a carbon-nitrogen double bond is noted in all of the salts, and is most likely from an exocyclic C=N rather than a ring C=N bond and was noted in all three x-ray structure solutions, which is strong evidence for guanidinium like (N-C(=NH₂⁺)-N) resonance structures and has been noted previously in similar systems.^{33-35, 41} This will be discussed more in detail in the x-ray structure section below. Finally, there was strong evidence for the free oxy-anion in each of the respective salts, with vibrational bands easily assignable for nitrate^{43,44}, (1350 cm⁻¹ in the infrared, and 1043 cm⁻¹ in the Raman); perchlorate^{45,46}

(1100 cm^{-1} in the infrared, and 926 cm^{-1} in the Raman); and the dinitramide⁴⁷⁻⁵⁰ anion, $\text{N}(\text{NO}_2)_2^-$, (1530 cm^{-1} , 1445 cm^{-1} , 1345 cm^{-1} , 1183 cm^{-1} , and 1025 cm^{-1} in the infrared and 1335 cm^{-1} and 830 cm^{-1} in the Raman).

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 α radiation ($\alpha = 0.71073 \text{ \AA}$) 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.^{51, 52} 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^{53, 54} to give the hkl file corrected for Lp/decay. The absorption correction was performed using the SADABS⁵⁵ program. The structures were solved by the direct method using the SHELX-90⁵⁶ program and refined by the least squares method on F², SHELXL-97⁵⁷ incorporated in SHELXTL Suite 5.10 for Windows NT.^{58,59} 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 either from difference electron density maps or generated at calculated positions.

3,4,5-triamino-1,2,4-triazolium nitrate crystallized in a triclinic cell with P-1 symmetry and the asymmetric cation and anion are illustrated in Figure 1 with details of the x-ray study summarized in Table 1.

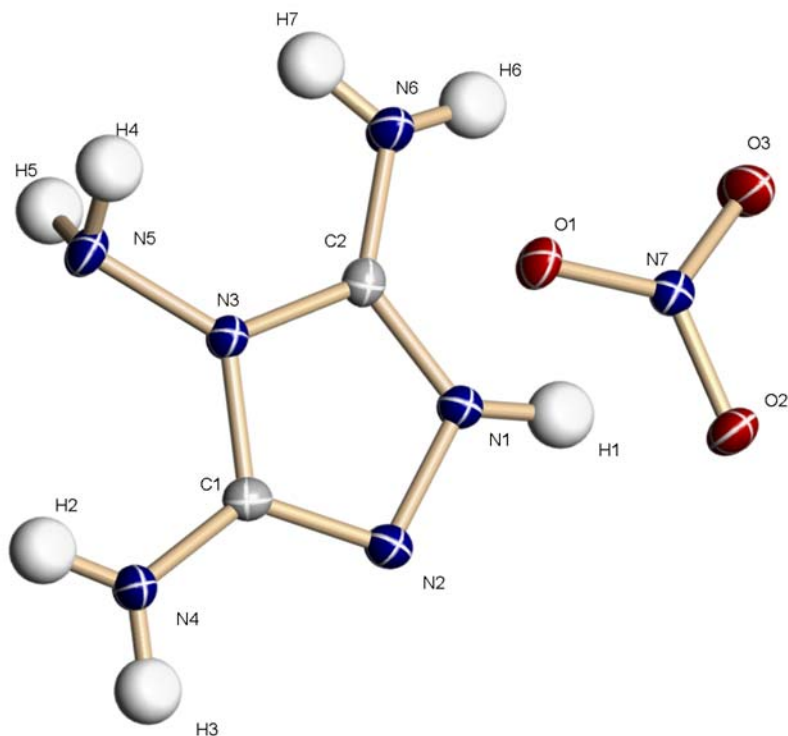


Figure 1. The single crystal x-ray diffraction structure solution of 3,4,5-triamino-1,2,4-triazolium nitrate.

Table 1. Crystal Data for 1-H-3,4,5-triamino-1,2,4-triazolium nitrate

Formula	C ₂ H ₇ N ₇ O ₃
Formula Weight	177.15
Crystal System	Triclinic
Space group	P-1 (No. 2)
a, b, c [Å]	5.523(2) 8.260(3) 8.508(3)
alpha, beta, gamma [°]	111.108(6) 103.291(6) 103.454(6)
V[Å ³]	330.4(2)
Z	2
D(calc) [g/cm ³]	1.781
Mu(MoKα) [/mm]	0.159
F(000)	184
Temperature (K)	100
Radiation [Å]	MoKα 0.71073
Theta Min-Max [°]	2.7, 28.3
Dataset	-7: 7 ; -10: 11 ; -11: 10
Tot., Uniq. Data, R(int)	3763, 1522, 0.051
Observed data [I > 2.0 σ(I)]	1428
Nref, Npar	1522, 138
R, wR2, S	0.0391, 0.0963, 1.10
Min. and Max. Resd. Dens. [e/ Å ³]	-0.43, 0.28

The proton is found on nitrogen atom N(1) of the 1,2,4-triazole ring which is the usual site of protonation in most triazoles and has been observed in several other triazole systems.⁶⁰⁻⁶² The most striking feature of the cation is the geometry of the pendant amino groups. The amino group nitrogen atom (N(6)) attached to the carbon atom C(2), closest to the site of ring protonation, is essentially coplanar with the ring and has a very short exocyclic C-N bond distance (C(2)-N(6) = 1.326(2) Å), while the amino group nitrogen atom (N(4)) attached to the other triazole ring carbon C(1) is slightly pyramidalized and has a slightly longer C-N bond distance (C(1)-N(4) = 1.349(2) Å), which is typical of amino-substituted heterocyclic carbon atoms⁶³⁻⁷⁰. These exocyclic carbon-nitrogen bond lengths are quite short pointing to significant iminium (C=NH₂⁺) character and is substantiated by the nearly planar geometries of N(4) and N(6) atoms, similar to that previously reported in the 3,4,5-triamino-1,2,4-triazolium bromide²⁰ and that observed in 1,5-diamino-4-H-tetrazolium perchlorate¹⁹. In contrast, the N-amino nitrogen (N(5)) is pyramidal with the N-amino protons, H(3) and H(4), saddling the heterocyclic ring as well as facing the side of ring protonation, with the N-N bond distance (N(3)-N(5) = 1.400(2) Å) typical of N-N single bond distances observed in several other N-amino heterocycle x-ray diffraction studies^{19, 20, 60-62}. The bond lengths within the heterocyclic ring have distances between single and double bond distances (C(2)-N(1) = 1.320(2) Å; C(1)-N(2) = 1.309(2) Å; C(1)-N(3) = 1.380(2) Å; and C(2)-N(3) = 1.360(2) Å) are typical of those observed in triazoles⁶⁰⁻⁷⁰ and will not be discussed further. The nitrate anion is planar with all of the bond lengths and angles typical of that observed in other nitrate salts.⁷¹⁻⁷⁴

3,4,5-triamino-1,2,4-triazolium perchlorate crystallized in a tetragonal cell with I41/acd symmetry and is shown in Figure 2 with details of the x-ray solution in Table 2.

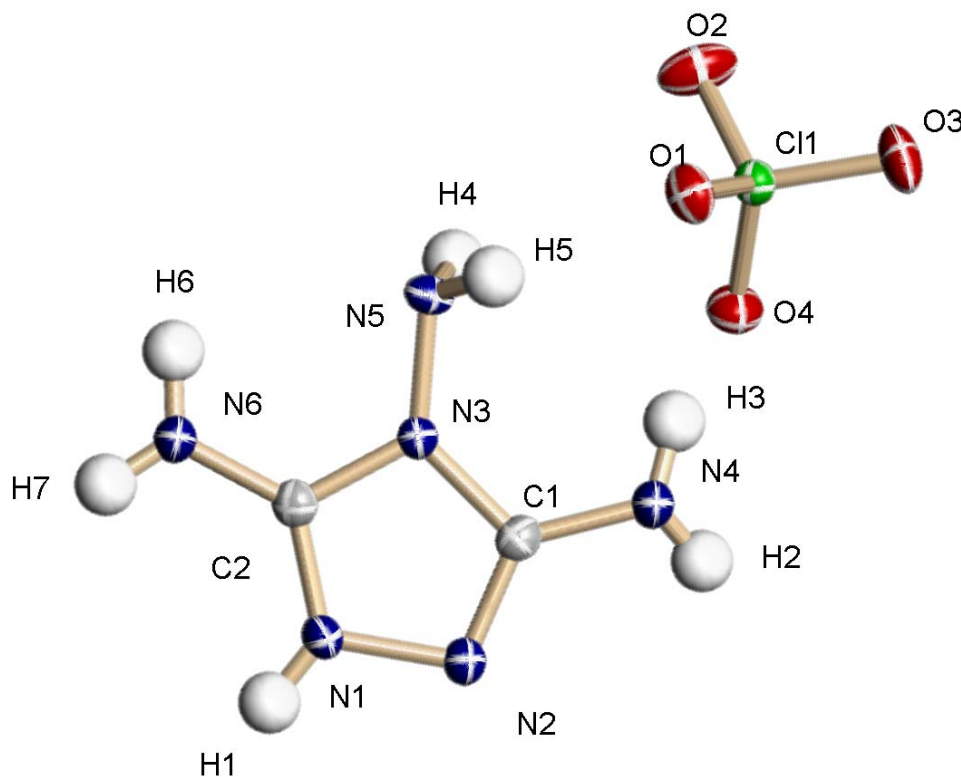


Figure 2. Single x-ray crystal diffraction study of 1-H-3,4,5-triamino-1,2,4-triazolium perchlorate.

Table 2. Crystal Data for 1-H-3,4,5-triamino-1,2,4-triazolium perchlorate

Formula	C ₂ H ₇ N ₆ Cl ₁ O ₄		
Formula Weight	214.59		
Crystal System	tetragonal		
Space group	I41/acd (No. 142)		
a, b, c [Å]	12.2899(18)	12.2899(18)	40.875(6)
alpha, beta, gamma [°]	90 90 90		
V[Å ³]	6173.8(12)		
Z	32		
D(calc) [g/cm ³]	1.847		
Mu(MoKα) [/mm]	0.494		
F(000)	3520		
Temperature (K)	100		
Radiation [Å]	MoKα 0.71073		
Theta Min-Max [°]	2.5, 28.3		
Dataset	-16: 16 ; -16: 16 ; -54: 54		

Tot., Uniq. Data, R(int)	25637, 1846, 0.043
Observed data [$I > 2.0 \sigma(I)$]	1678
Nref, Npar	1846, 146
R, wR2, S	0.0359, 0.1091, 1.11
Min. and Max. Resd. Dens. [$e/\text{\AA}^3$]	-0.42, 0.47

From the crystal structure solution, protonation has occurred on N(1) of the 1,2,4-triazole ring with the geometry of the 3,4,5-triamino-1,2,4-triazolium cation similar to that observed in the nitrate salt (Figure 2). The pendant amino group attached to the carbon atom C(2) neighboring the site of N-protonation (N(1)) on the triazole ring is essentially planar, having a very short exocyclic C-N bond distance (C(2)-N(6) = 1.326(2) Å) while the N-amino nitrogen (N(5)) attached to N(3) of the triazole ring has pyramidal geometry with an N-N single bond distance (N(3)-N(5) = 1.396(2) Å) typical of N-amino exocyclic heterocycle N-N bonds^{19, 20, 60-62}. In contrast to the nitrate structure, the orientation of the N-amino atom N(5) that saddles the heteroatom ring plane has the N-amino protons, H(3) and H(4), facing away from the side of ring protonation. The other pendant amino group nitrogen (N(4)) attached to carbon C(1) of the triazole ring has a high degree of planarity but is still slightly pyramidal, and has a carbon-nitrogen bond distance (C(1)-N(4) = 1.343(2) Å) and is typical of those observed in C-amino substituted heterocycles⁶³⁻⁷⁰. The bond distances in the heterocyclic cation are very similar to those observed in the nitrate structure with shortened inter-atomic ring bond distances especially N(2)-C(1) = 1.305(2) Å and N(1)-C(2) = 1.321(2) Å being observed with the longer triazole ring C-N bond distance being associated with site of N-protonation and with the carbon (C(2)) having the shortest exocyclic ring C-N bond distance. The other bonds in the ring (C(1)-N(3) = 1.387(2) Å and C(2)-N(3) = 1.354(2) Å) are within normal triazole ring distances observed elsewhere⁶⁰⁻⁷⁰. The perchlorate is tetrahedral with the bond distances and angles being typical of those observed in other perchlorate salt systems.⁷⁵⁻⁷⁸

3,4,5-triamino-1,2,4-triazolium dinitramide crystallized with one asymmetric cation and anion in a monoclinic cell with P2(1)/c symmetry and is illustrated in Figure 3 with details of the x-ray collection in Table 3. The overall structure of the cation is very similar to that observed in the previously discussed nitrate and perchlorate structures in

both distances and overall geometries and orientation of the pendant amino groups on the triazole. As was observed in the previous two structures the pendant amino groups have their own structural geometries. The amino nitrogen (N(6)) attached to carbon C(2), which neighbors the site of ring protonation, is essentially planar and has a very short C-N bond distance (C(2)-N(6) = 1.317(2) Å). The corresponding amino nitrogen atom N(4) attached to carbon C(1), that is on the far side of the ring from the site of protonation, is not quite planar and has slight pyramidalization of the nitrogen atom N(4), and has a typical carbon amino-substituted heterocyclic carbon –nitrogen bond distance (C(1)-N(4) = 1.352(2) Å). The pendant N-amino nitrogen-nitrogen bond distance (N(3)-N(5) = 1.398(2) Å) is not unusual and is typical of those observed in N-amino heterocycles.^{19, 20, 60-62} The pendant N-amino atom N(5) protons, H(4) and H(5) saddle the ring facing away from the site of ring protonation which is same as observed in the perchlorate structure.

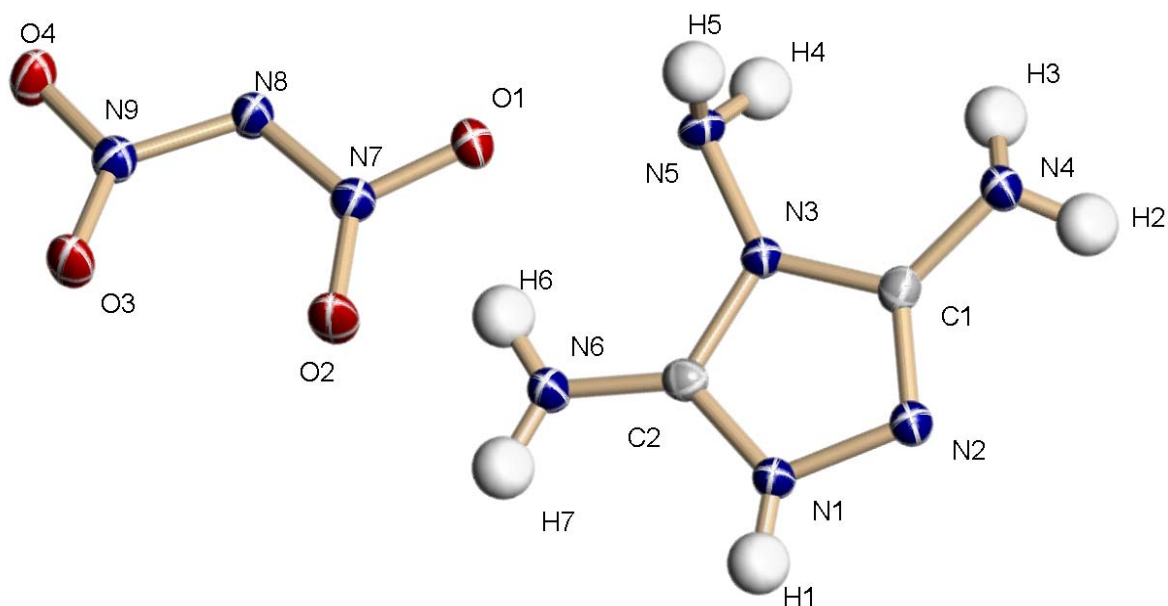


Figure 3. X-ray crystal diffraction study of 3,4,5-triamino-1,2,4-triazolium dinitramide.

The carbon nitrogen heterocyclic bond distances associated with the site of protonation (N(1)-C(2) = 1.3221(13) Å) is slightly longer than that observed on the opposite side of the ring (N(2)-C(1) = 1.3060(13) Å). This can most likely be explained

by the fact that N(1) is protonated, thereby forcing quarternization, and by the fact that the exocyclic C-N bond distance is much shorter for C(2) than that for C(1).

Table 3. Crystal Data for 1-H-3,4,5-triamino-1,2,4-triazolium dinitramide

Formula	C ₂ H ₇ N ₉ O ₄		
Formula Weight	221.17		
Crystal System	monoclinic		
Space group	P2(1)/c (No. 14)		
a, b, c [Å]	3.6438(3)	18.1307(17)	12.2872(11)
alpha, beta, gamma [°]	90 90.6060(10) 90		
V[Å ³]	881.70(12)		
Z	4		
D(calc) [g/cm ³]	1.810		
Mu(MoKα) [/mm]	0.164		
F(000)	456		
Temperature (K)	100		
Radiation [Å]	MoKα 0.71073		
Theta Min-Max [°]	2.0, 28.3		
Dataset	-4: 4; -23: 23 ; -16: 16		
Tot., Uniq. Data, R(int)	9147, 1936, 0.017		
Observed data [I > 2.0 σ(I)]	1845		
Nref, Npar	1936, 164		
R, wR2, S	0.0299, 0.0801, 1.05		
Min. and Max. Resd. Dens. [e/ Å ³]	-0.35, 0.25		

The dinitramide anion has the expected geometry with the N-NO₂ groups being slightly twisted out of expected planar structure. The N-N and N-O bond distances are not unusual with shortened N-N and N-O bonds revealing a large degree of electron delocalization in the anion, which has been observed in several other x-ray structures of dinitramide salts⁷⁹⁻⁸¹ and will not be further discussed.

Initial safety testing was carried out on all of the new salts. For impact testing, an Olin Mathieson style drop hammer test where a falling 2 kg mass is used to strike a small sample and has been described previously.¹⁶ For friction testing, a Julius Peters style friction machine incorporating pins under a known load being slid over a small sample placed on a ceramic style test tile was used and has also been described elsewhere¹⁶. 3,4,5-triamino-1,2,4-triazolium nitrate gave 5 consecutive negative responses at 200 kgcm (highest setting of machine), while for friction 5 consecutive negatives were found at 16 kg. For the perchlorate salt, 5 consecutive negatives were found at 50 kgcm for

impact and 15.2 kg for friction. Finally for the dinitramide salt, an impact value of 196 kgcm was found with a value of 15.2 kg for the friction test. In general, these salts are relatively insensitive as compared to the impact and friction values reported for similar triazolium salts.¹⁶

Theoretical Calculations of protonated 3,4,5-triamino-1,2,4-triazole

The geometry of protonated 3,4,5-triamino-1,2,4-triazole was fully optimized using second-order perturbation theory (MP2, also known as MBPT(2)⁸²⁻⁸⁷) and the 6-311+G(d,p)⁸⁸⁻⁹⁰ basis set. The optimized structure was verified as local minima via diagonalization of the matrix of energy second derivatives with respect to nuclear displacements (i.e., the Hessian matrix.) All calculations were performed using the GAMESS ab initio electronic structure program.⁹¹

The predicted geometry of the heterocyclic cation is shown in Figure 4 and is in good overall agreement with the X-ray structures of the nitrate, perchlorate, and dinitramide salts. In particular, the pendant amino group attached to C(2) is coplanar with the heterocyclic ring, the amino group attached to C(1) is only slightly pyramidalized, and the protons of the amino group attached to N(3) straddle the ring, which is consistent with the X-ray structures of the cations. Note that the N(3) amino group is oriented away from the protonated N(1) site, in agreement with the perchlorate and dinitramide X-ray structures. Several key predicted and observed bond lengths and angles are summarized in Table 4. All computed bond lengths are within 0.03 Å of the experimental values. Furthermore, the predicted bond angles generally are within 1-2 degrees of the observed values. However, the experimental C(2)-N(3)-N(5) bond angle of 127.5 degrees in the nitrate salt is approximately 5 degrees larger than the corresponding angles in the perchlorate and dinitramide salts and is 6 degrees larger than the theoretical value. Nevertheless, the agreement between the experimental observed distances and angles and those predicted by theoretical methods is very good and points to the excellent development of theory in helping out experimentalists.

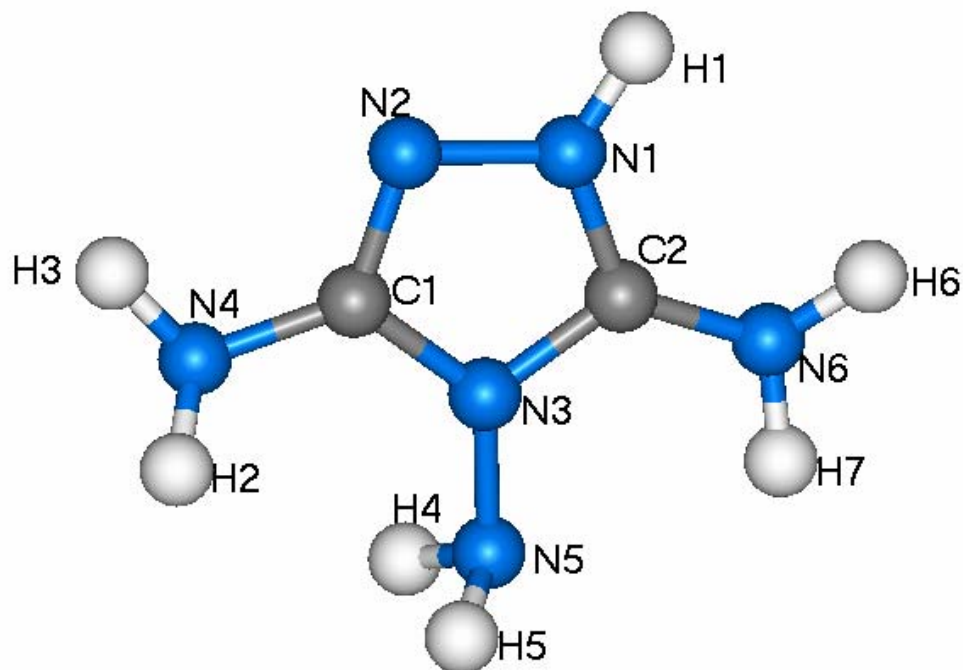


Figure 4. MP2/6-311+G(d,p) gas-phase optimized structure of protonated 3,4,5-triamino-1,2,4-triazole.

<u>Bond</u>	<u>Theory(Å)</u>	<u>NO₃⁻ salt(Å)</u>	<u>ClO₄⁻ salt(Å)</u>	<u>N(NO₂)₂⁻ salt(Å)</u>
N(1)-N(2)	1.377	1.402(2)	1.404(2)	1.402(2)
C(1)-N(2)	1.311	1.309(2)	1.305(2)	1.306(2)
C(1)-N(4)	1.367	1.349(2)	1.343(2)	1.352(2)
C(1)-N(3)	1.397	1.380(2)	1.387(2)	1.385(2)
N(3)-N(5)	1.391	1.399(2)	1.396(2)	1.398(2)
N(3)-C(2)	1.357	1.360(2)	1.354(2)	1.359(2)
C(2)-N(6)	1.338	1.326(2)	1.326(2)	1.317(2)
C(2)-N(1)	1.333	1.320(2)	1.321(2)	1.322(2)

<u>Angle</u>	<u>Theory(°)</u>	<u>NO₃⁻(°)</u>	<u>ClO₄⁻(°)</u>	<u>N(NO₂)₂⁻(°)</u>
N(1)-C(2)-N(3)	105.1	106.0(1)	106.3(2)	105.9(8)
N(1)-C(2)-N(6)	130.4	129.4(2)	130.2(2)	129.9(9)
C(2)-N(3)-C(1)	107.3	107.1(1)	107.1(2)	107.3(8)
C(2)-N(3)-N(5)	121.4	127.5(1)	122.3(2)	122.2(8)
N(3)-C(1)-N(4)	121.5	122.0(1)	121.2(2)	122.2(9)
N(3)-C(1)-N(2)	110.5	110.7(1)	111.0(2)	111.0(9)
C(1)-N(2)-N(1)	104.1	104.1(1)	103.9(1)	104.0(8)
N(2)-N(1)-C(2)	113.0	111.7(1)	111.7(2)	111.9(8)

Table 4. Comparison of gas phase theoretical MP2/6-311+G(d,p) bond distances and angles of protonated 3,4,5-triamino-1,2,4-triazole versus those observed in the corresponding 3,4,5-triamino-1,2,4-triazolium salts.

Conclusions

A new family of highly stable salts based on protonated 3,4,5-triamino-1,2,4-triazole with various oxyanions has been synthesized and characterized using spectral as well as single crystal x-ray diffraction studies. In all cases, the 3,4,5-triamino-1,2,4-triazole ring is protonated at N(1) of the 1,2,4 triazole ring. The pendant amino groups attached to the carbon atoms display a high degree of iminium type behavior with shortened C-N bond distances and planar geometries. The N-amino nitrogen is pyramidal and saddles the major plane of the ring with the orientation of the pendant protons apparently influenced by the anion, in the nitrate salt they face the N(1) position, but in the perchlorate and dinitramide salts the pendant N-amino protons point away from the protonated N(1) position. Theoretical calculations carried out at the MP2/6-311+G(d,p) level reveal a structure which compares very well to that observed in the perchlorate and dinitramide salts in overall geometry as well as bond distances and angles. Initial safety testing revealed that all three salts were relatively insensitive to mechanical stimuli (friction and impact), giving hope of these new salts of finding possible applications.

Acknowledgements

The authors would like to thank Michael Berman (AFOSR), Mike Huggins (AFRL/PRS), Ronald Channell and Wayne Kallioma (AFRL/PRSP) for their financial support as well as their encouragement of this work. The authors gratefully acknowledge the support of the Department of Defense High Performance Computing Modernization Program via grants of IBM SP time from the Aeronautical Systems Center, Wright-Patterson Air Force Base, Dayton, Ohio, and Cray SV1 time from the Arctic Region Supercomputing Center, Fairbanks, Alaska.

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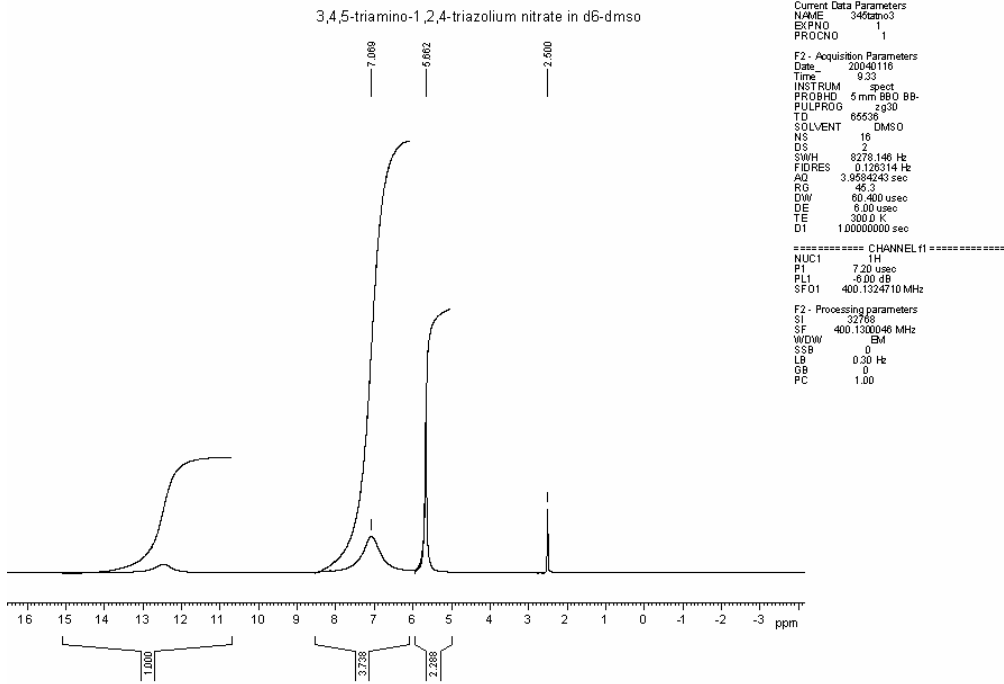
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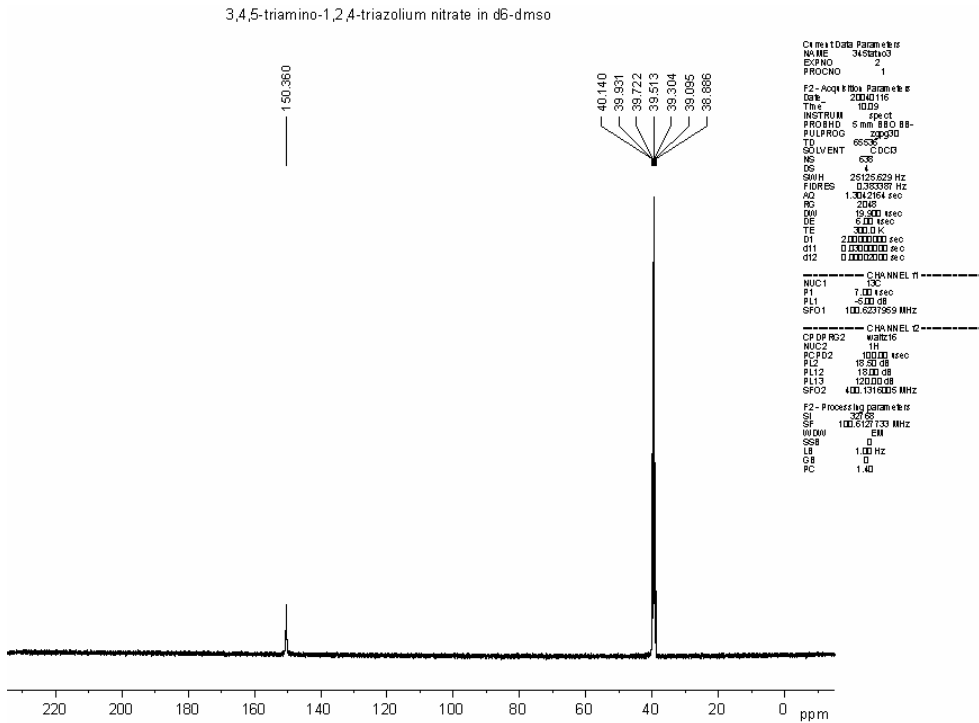
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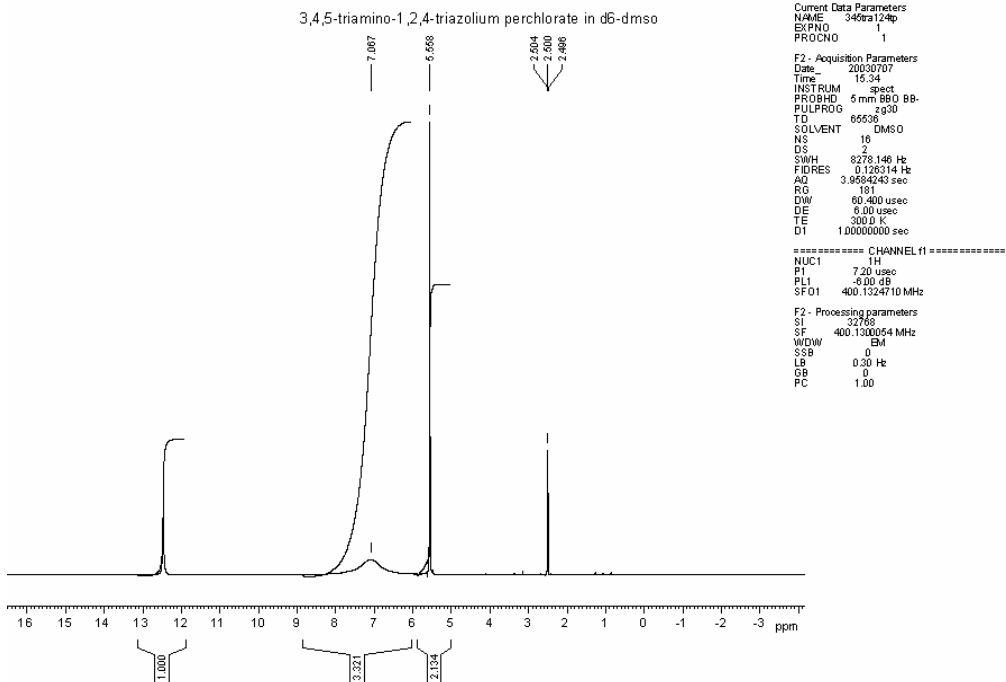
Supplemental Data



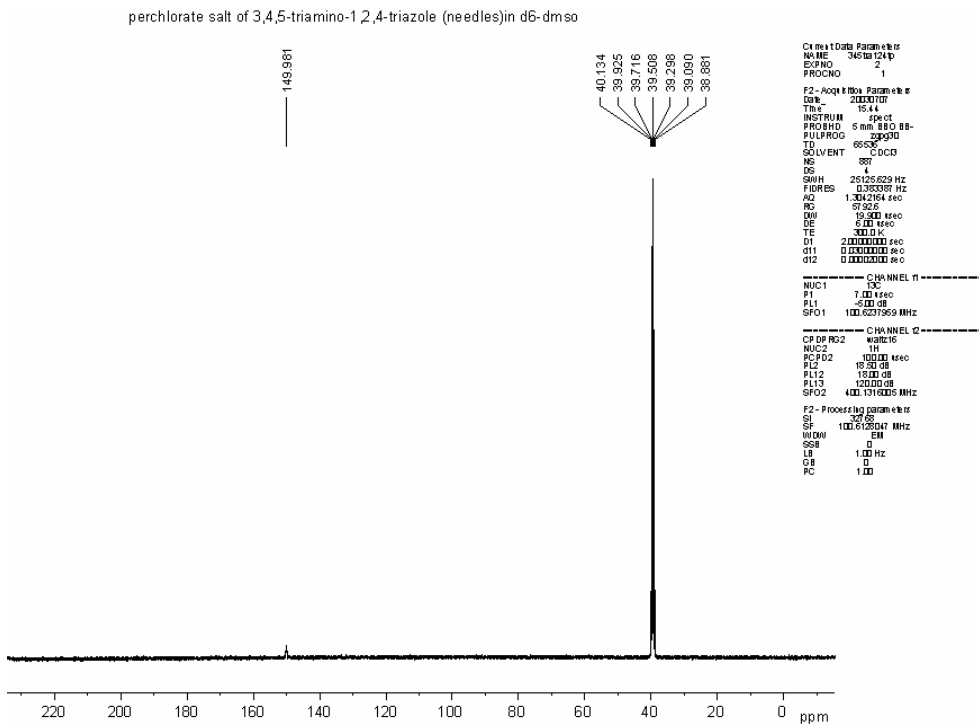
The ¹H spectrum of 3,4,5-triamino-1,2,4-triazolium nitrate.



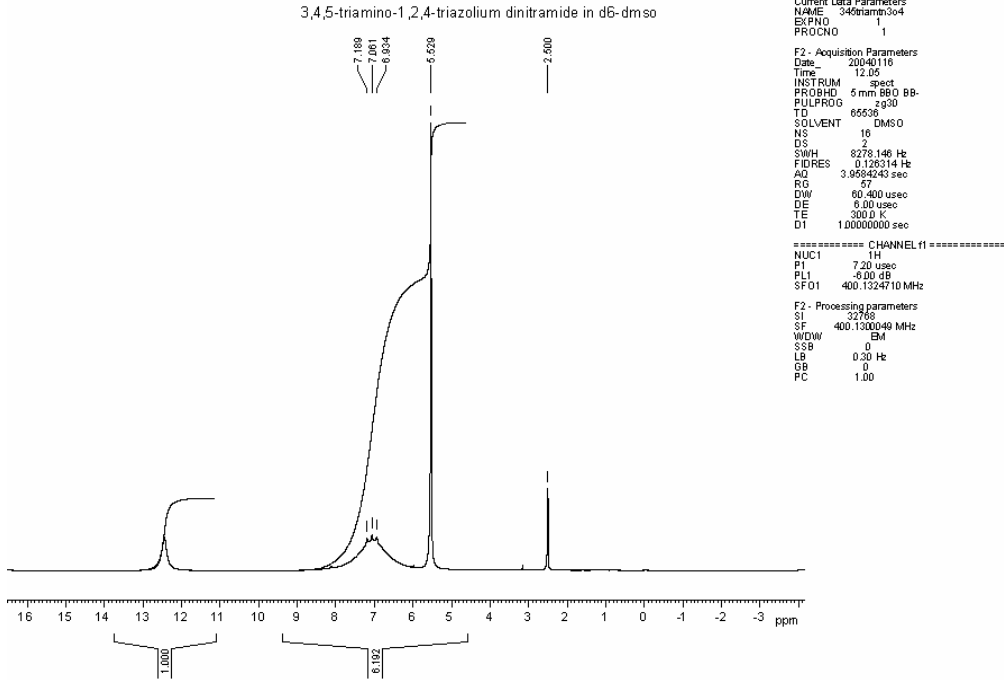
The ¹³C spectrum of 3,4,5-triamino-1,2,4-triazolium nitrate.



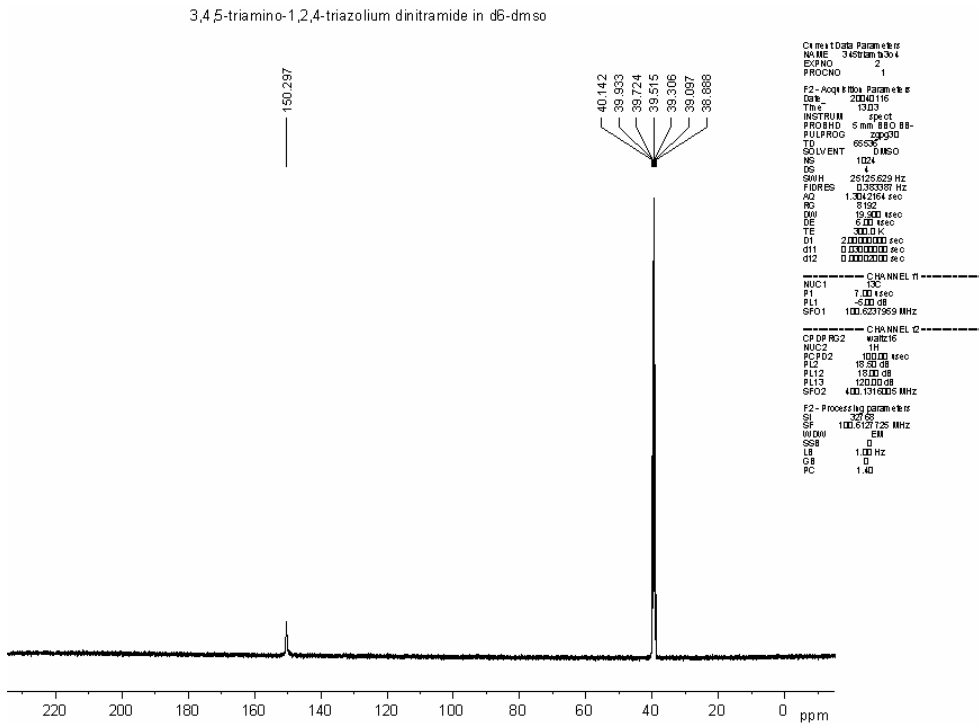
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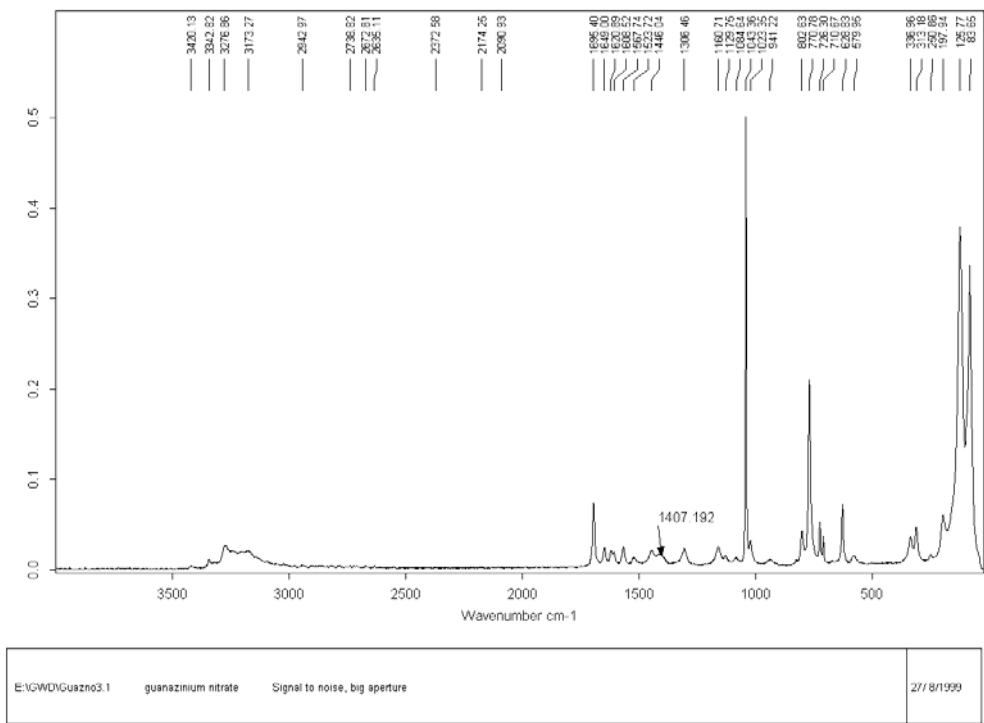
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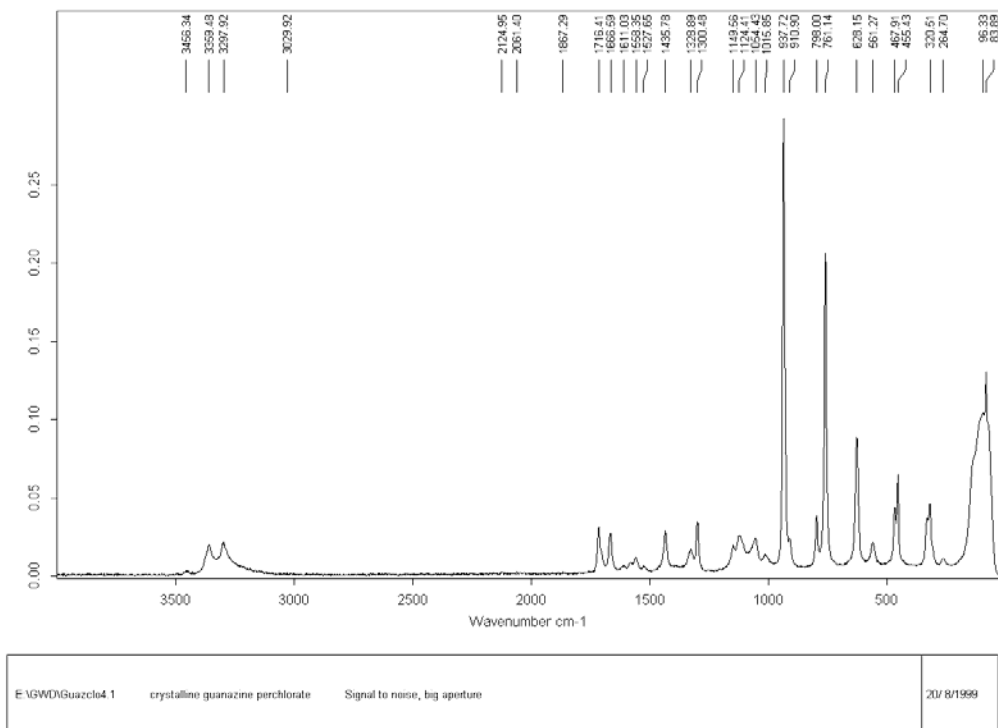
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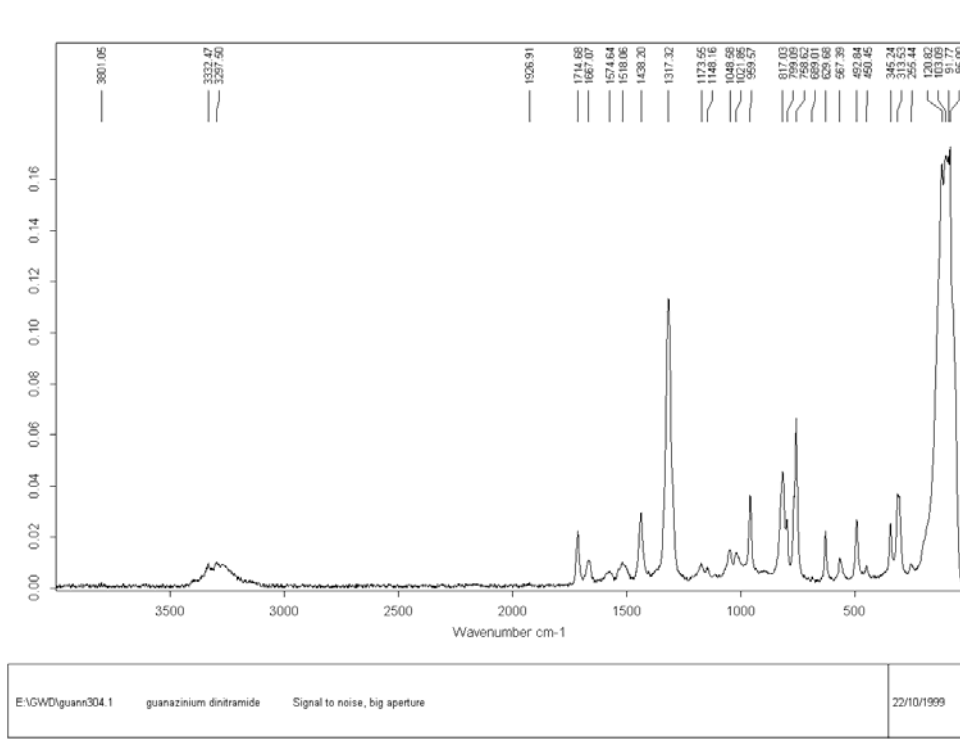
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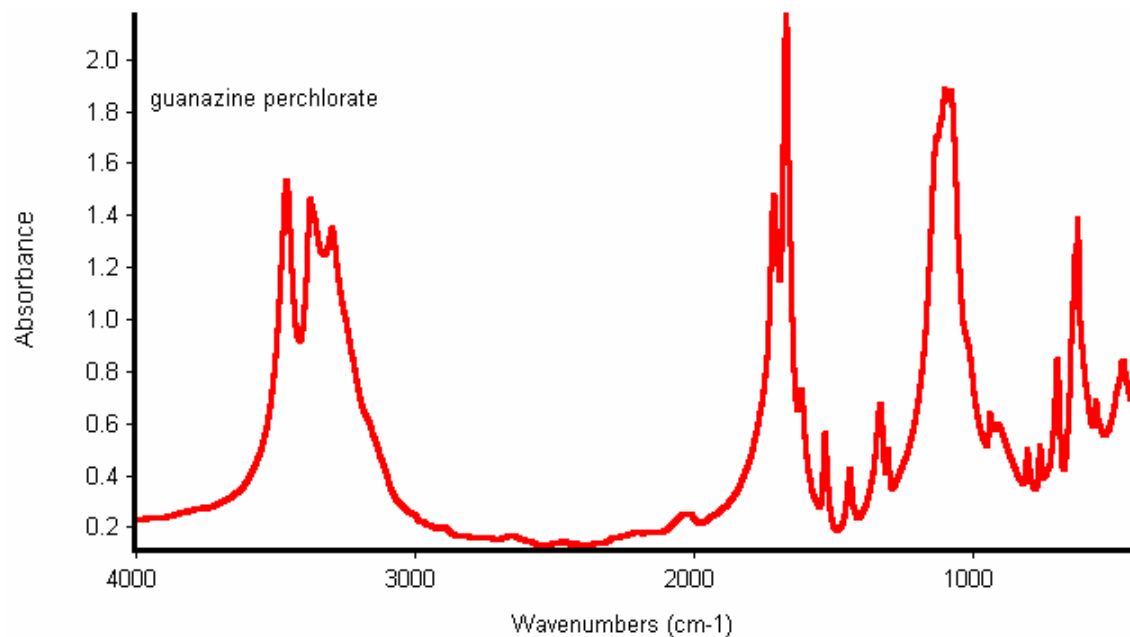
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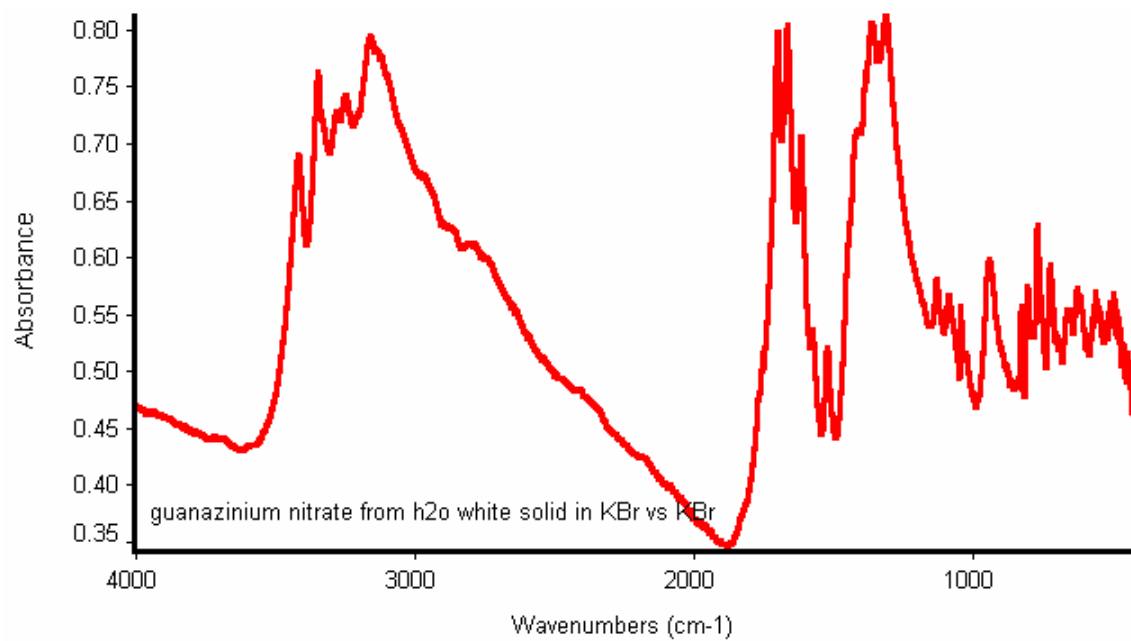
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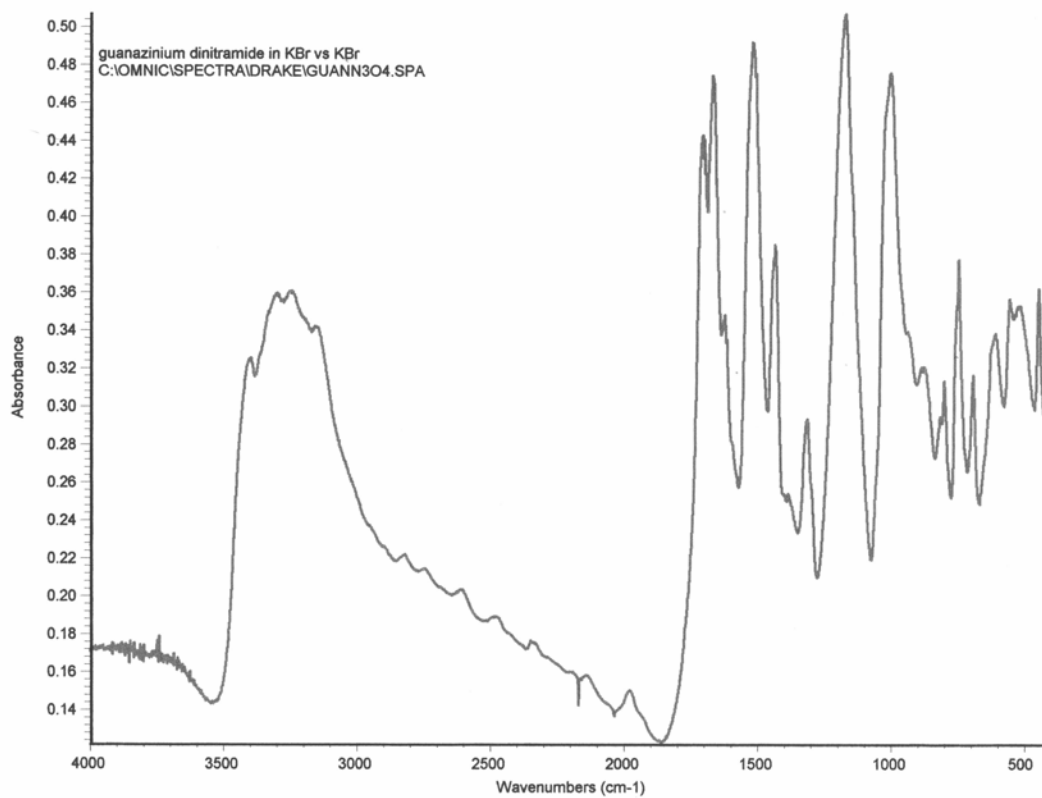
The Raman spectrum of 3,4,5-triamino-1,2,4-triazolium dinitramide.



The infrared spectrum of 3,4,5-triamino-1,2,4-triazolium perchlorate.



The infrared spectrum of 3,4,5-triamino-1,2,4-triazolium nitrate.



The infrared spectrum of 3,4,5-triamino-1,2,4-triazolium dinitramide.

