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Technical Report ARAET-TR-05001

**STRUCTURAL FEATURES OF BIS(TRIAMINO GUANIDINIUM)
BIS(AZOTETRAZOLATE)**

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14. ABSTRACT Bis(triaminoguanidinium) bis(5, 5-azotetrazolate) an energetic high nitrogen salt known as (TAGZT) is being considered as a potential ingredient for gun propellants by this laboratory. As part of an effort to characterize TAGZT an x-ray single-crystal investigation was undertaken. TAGZT crystallizes in the centrosymmetric monoclinic space group P 2 ₁ /n with unit-cell parameters a= 3.962(1) Å, b= 15.019(2) Å, c=12.981(1) Å, and β= 95.30(2) deg. The conformation of both triaminoguanidinium cation and azotetrazolate anion as well as the crystal structure is discussed. The extensive three-dimensional network of hydrogen bonds (N-N...N) is also discussed.					
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CONTENTS

	Page
Introduction	1
Experimental	1
Results and Discussion	3
Triaminoguanidinium Cation Molecular Conformation	4
Azotetrazolate Anion Molecular Conformation	6
Crystal Structure	7
Conclusions	10
Recommendations	10
References	11
Distribution List	13

FIGURES

1	Heavy atoms and three imino H atoms of the TAG cation	5
2	ZT ² anion viewed down the axis of the unit cell with atom numbering scheme	6
3	TAGZT asymmetric unit viewed along the a axis with the atom numbering scheme	7
4	Projection of TAGZT unit cell packing on the bc plane	8
5	Three-dimensional view of packing of TAGZT along the a axis to the unit cell	8
6	Three-dimensional view of H-bonds viewed along the a axis of the TAGZT unit cell	9

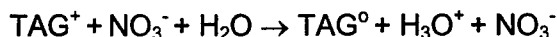
TABLES

1	Crystal data and summary of data collection and structure refinement	2
2	Atomic coordinates and equivalent temperature factors (B_{eq}/B_{iso}) and their estimated standard deviations	3
3	Bond length in Angstroms (Å) and their esd's	3
4	Bond angles in degrees and their esd's	4
5	Details of hydrogen bonds	4

INTRODUCTION

For many years propellant chemists and formulators have been interested in energetic high nitrogen molecules as potential propellant ingredients. One rationale for this interest is that propellants containing high nitrogen to carbon and oxygen concentration ratios usually burn coolly, and cool propellants normally do not erode gun barrels as much as hot propellants. However, the downside to this approach is that some of the energetic high nitrogen molecules used in the past, such as nitroguanidine, are simply not energetic enough to satisfy current and future ballistic requirements. This has resulted in a quest to find more high nitrogen molecules that are energetic enough to meet these ballistic requirements.

Another interesting property of some energetic high nitrogen molecules is that they have high gas generation or burning rates. For example triaminoguanidinium nitrate (TAGN), a fast burning compound, is being considered as a potential burning rate modifier or enhancer for composite propellants containing the slower burning RDX. Although TAGN has a moderately high impetus (1147 J/g) and a relatively low flame temperature (2568 K), its utility in gun propellants has been somewhat limited, because of its incompatibility with nitrate esters. This incompatibility occurs because TAGN is a salt of a weak base and a strong acid, which hydrolyzes in the presence of water or a strong base to form nitric acid and its freebase according to the following reaction



in which TAG^+ is a cationic acid, TAG^0 is its freebase, and $(\text{H}_3\text{O}^+ + \text{NO}_3^-)$ is free nitric acid.

A high nitrogen TAG salt presently under consideration by this laboratory as a potential propellant burning rate modifier is bis(triaminoguanidinium) bis(5, 5-azotetrazolate), which frequently is referred to as triaminoguanidinium azotetrazolate (TAGZT). The molecular formula for TAGZT is $\text{C}_4\text{H}_{18}\text{N}_{22}$ or in ionic notation $[(\text{CN}_6\text{H}_9)^+]_2 (\text{C}_2\text{N}_{10})^{2-}$. In the case of TAGZT, nitrate ester incompatibility may not be a problem because its hydrolysis product, azotetrazolic acid, is a weaker acid than nitric acid and not as strong an oxidizing agent. TAGZT may also be classified as a high hydrogen fuel.

As part of an effort to characterize TAGZT, a single-crystal x-ray diffraction investigation was undertaken to determine its crystal and molecular structure.

EXPERIMENTAL

A pale yellow needle-like single crystal of TAGZT having approximate dimensions of 0.1 x 0.1 x 0.3 mm was mounted on a glass fiber with its long axis parallel to the phi axis of the goniometer of an Enraf-Nonius CAD4 x-ray scanning diffractometer. Cu $K\alpha$ X-radiation ($\lambda = 1.54184 \text{ \AA}$) was used during data collection.

Unit-cell constants and the orientation matrix for data collection were obtained from least-squares refinement using the setting angles of 25 reflections in the range $6 < \theta < 22$ deg. The x-ray data were collected at $23 \pm 1^\circ\text{C}$. The accumulated data yielded the centrosymmetric monoclinic space group $2_1/n$ (#14). The unit-cell lattice parameters are: $a = 3.962(1) \text{ \AA}$, $b = 15.019(2) \text{ \AA}$, $c = 12.981 \text{ \AA}$ (3), $\beta = 95.30(2) \text{ deg}$, and $V = 769.0 \text{ \AA}^3$. The calculated density of TAGZT based on two formula weights of TAGZT (748.8) per unit cell is 1.616 g/cm^3 (table 1).

Table 1
Crystal data and summary of data collection and structure refinement^a

Compound	C ₄ N ₂₂ H ₁₈	Crystal size, mm	0.10 x 0.10 x 0.30
Color and shape	Yellow needle	Scan type	w- θ
CCDC deposit no.		Scan width, deg	0.6 + 0.300 tan θ
Formula weight	374.34	Total reflections	1701 (1568 unique)
Temperature, °C	23 $\pm$ 1	Refls [$I > 3\sigma(I)$]	1151 ^a
Crystal system	Monoclinic	Range of h, k, l	-6 $\rightarrow$ 13, -4 $\rightarrow$ 4, -22 $\rightarrow$ 20
Space group	P2 ₁ /n (#14)	Computer programs	
2 θ max, deg	150.0	Direct methods	SIR92 ⁷
Cell constants		Structure solutions ^b	TeXsan ⁸
a, Å	3.962(1)	Graphics	ORTEP ⁹
b, Å	15.019(2)	Final max shift	0.37 σ
c, Å	12.981(3)	Function minimized	$\Sigma w(F_o - F_c)^2$
β , deg	95.30(2)		
Volume, Å ³	769.0(1)	Weights	$4F_o^2/\sigma^2(F_o^2)$
F(000)	392.00	Parameters refined	155
Z	2	R _{int}	0.038
D _{calc} , g cm ⁻³	1.620	$R = \Sigma[(F_o - F_c)/\Sigma F_o]$	0.055
μ_{calc} , cm ⁻¹	11.0		0.036
Diffractometer	Enraf-Nonius	Max peak final diff. map	0.17(4)e ⁻ /Å ³
λ (Cu K α), Å	1.54184	Min peak final diff. map	-0.17(4)e ⁻ /Å ³
Monochromator	Graphite	Extinction coefficient	5.3e ⁻⁶

^aX-ray diffraction data collected by Molecular Structure Corporation, The Woodlands, Texas.

^bCorrections: Lorentz-polarization, secondary extinction, and anomalous dispersion applied to neutral scattering factors.

A total of 1701 reflections were collected of which 1568 reflections were unique and not systematically absent. The centrosymmetric monoclinic space group P2₁/n (#14) was determined from the following systematic reflection absences

$$0k0 = 2n+1$$

$$h0l = h+1' = 2n+1$$

The four general positions for this space group are (x, y, z); ($\frac{1}{2}$ -x, $\frac{1}{2}$ +y, $\frac{1}{2}$ -z); (-x, -y, -z), and ($\frac{1}{2}$ +x, $\frac{1}{2}$ -y, $\frac{1}{2}$ +z).

Lorentz and polarization corrections were applied to the reflections. No absorption correction was necessary, but a secondary extinction correction of 5.3×10^{-6} was applied (ref. 1).

A heavy-atom trial structure was determined with direct methods using 238 reflections (ref. 1). Hydrogen atom positions were located by means of the difference Fourier method. The heavy atom positions were refined anisotropically and hydrogen positions were refined isotropically with full-matrix least-squares analysis (LSQA). The final cycle of LSQA based on 1151 observed reflections [$I > 3\sigma(I)$] and 155 parameters converged with an agreement factor (R) of 0.038 and a weighted agreement factor (R_w) of 0.055.

Impetus and isochoric flame temperature values were obtained with the MCVECE thermochemical code (ref. 2).

RESULTS AND DISCUSSION

Crystal data, atomic coordinates, and equivalent temperature factors, bond lengths, and bond angles of TAGZT are presented in tables 1 through 4. Details of hydrogen bonding are given in table 5.

Table 2
Atomic coordinates and equivalent temperature factors (B_{eq}/B_{iso})
and their estimated standard deviations

Atom	x/a	y/b	z/c	B_{eq}/B_{iso}
N(1)	-0.0427(5)	0.1540(1)	0.3715(1)	3.02(4)
N(2)	-0.1949(6)	0.1955(1)	0.2817(1)	3.47(4)
N(3)	-0.2966(5)	0.2590(1)	0.4662(1)	3.04(4)
N(4)	-0.3508(5)	0.246(1)	0.5645(1)	3.38(4)
N(5)	0.0460(4)	0.1533(1)	0.5495(1)	3.11(4)
N(6)	0.2416(5)	0.0753(1)	0.5420(1)	3.75(4)
N(7)	0.4456(4)	-0.0368(1)	0.0142(1)	2.45(4)
N(8)	0.3767(5)	0.0370(1)	0.1834(1)	2.89(4)
N(9)	0.2561(5)	-0.0028(1)	0.2677(1)	3.18(4)
N(10)	0.1618(5)	-0.0866(1)	0.2506(1)	3.25(4)
N(11)	0.2226(5)	-0.1095(1)	0.1549(1)	3.01(4)
C(1)	-0.1000(5)	0.1885(1)	0.4523(0)	2.41(4)
C(2)	0.3529(5)	-0.0368(1)	0.1162(1)	2.27(4)
H(1)	0.085(6)	0.108(1)	0.368(2)	2.8(4)
H(2)	-0.285(6)	0.150(2)	0.241(2)	4.06(6)
H(3)	-0.013(6)	0.222(2)	0.244(2)	4.1(6)
H(4)	-0.395(6)	0.281(1)	0.404(2)	3.1(5)
H(5)	-0.256(6)	0.353(2)	0.571(2)	4.0(6)
H(6)	-0.59(1)	0.311(2)	0.558(3)	8.4(9)
H(7)	-0.034(7)	0.168(1)	0.613(2)	4.2(6)
H(8)	0.167(7)	0.025(2)	0.575(2)	6.0(7)
H(9)	0.470(9)	0.082(2)	0.580(2)	7.6(9)

B_{eq} is defined as one-third of the orthogonalized U_{ij} tensor and B_{iso} is defined as B_{11} .

Table 3
Bond lengths in angstroms (Å) and their esd's

Bond	Length	Bond	Length	Bond	Length
C(1)-N(1)	1.326(2)	N(1)-N(2)	1.408(2)	N(1)-H(1)	0.87(2)
C(1)-N(3)	1.319(2)	N(3)-N(4)	1.419(2)	N(3)-H(4)	0.92(2)
C(1)-N(5)	1.331(2)	N(5)-N(6)	1.413(2)	N(5)-H(7)	0.93(2)
Mean C-N	1.325(4)	Mean N-N	1.413(4)	Mean N-H	0.91(2)
N(2)-H(2)	0.92(4)	N(8)-N(9)	1.333(2)	N(7)-N(7)	1.225(3)
N(2)-H(3)	0.99(2)	N(9)-N(10)	1.325(2)	C(2)-N(7)	1.406(2)
N(4)-H(6)	0.97(4)	N(10)-N(11)	1.333(2)		
N(6)-H(8)	0.92(2)	Mean N-N	1.330(4)	C(2)-N(8)	1.335(2)
N(6)-H(4)	0.99(3)			C(2)-N(11)	1.327(2)
Mean N-H	0.96(3)			Mean C-N	1.331(4)

Table 4
Bond angles in degrees and their esd's

Atoms	Angle	Atoms	Angle	Atoms	Angle
N(1)C(1)N(3)	119.8(2)	C(1)N(3)H(4)	117.(1)	H(8)N(6)H(9)	100.(2)
N(1)C(1)N(5)	120.3(2)	N(4)N(3)H(4)	124.(1)	N(7)C(2)N(8)	127.3(2)
N(3)C(1)N(5)	119.9(2)	N(3)N(4)H(5)	109.(1)	N(7)C(2)N(11)	120.3(2)
C(1)N(1)N(2)	117.9(2)	N(3)N(4)H(6)	104.(2)	N(8)C(2)N(11)	112.6(2)
C(1)N(1)H(1)	120.(1)	H(5)N(4)H(6)	99.(2)	C(2)N(7)N(7)	113.8(2)
C(1)N(3)N(4)	118.4(2)	C(1)N(5)N(6)	118.(1)	C(2)N(8)N(9)	103.9(1)
N(2)N(1)H(1)	122.(1)	C(1)N(5)H(7)	120.(1)	N(8)N(9)N(10)	109.8(1)
N(1)N(2)H(2)	105.(1)	N(6)N(5)H(7)	120.(1)	N(9)N(10)N(11)	109.2(1)
N(1)N(2)H(3)	108.(1)	N(5)N(6)H(8)	116.(2)	C(2)N(11)N(10)	104.5(1)
H(2)N(3)H(3)	106.(2)	N(5)N(6)H(9)	111.(2)		

Table 5
Details of hydrogen bonds
Donor atoms are designated as D and acceptor atoms as A.
Distances are in angstroms (Å) and angles are in degrees.

D-H.....A	D-H, Å	H...A, Å	D.....A, Å	>DHA (deg)	D symmetry
N(1)-H(1)...N(6)	0.9(3)	2.3(7)	2.665(4)	105(5)	x, y, z
N(1)-H(1)...N(9)	0.9(3)	2.3(5)	3.010(2)	144(6)	3/2-x, -1/2+y, 1/2-z
N(2)-H(2)...N(8)	0.9(6)	2.32(3)	3.2(4)	162(2)	1/2-x, -1/2+y, 1/2-z
N(2)-H(3)...N(4)	1.0(5)	2.49(3)	3.2(7)	132(2)	1/2+x, 1/2-y, -1/2+z
N(3)-H(4)...N(2)	0.93(2)	2.3(5)	2.7(7)	106(2)	x, y, z
N(3)-H(4)...N(11)	0.93(2)	2.19(2)	2.955(2)	139.7(2)	x, y, z
N(4)-H(5)...N(7)	0.96(3)	2.39(3)	3.215(2)	144(2)	1+x, y, z
N(4)-H(5)...N(8)	0.96(3)	2.31(3)	3.133(2)	145(2)	1-x, 1-y, 1-z
N(5)-H(7)...N(10)	0.94(3)	2.25(2)	2.968(3)	133.2(8)	1/2+x, 1/2-y, 1/2+z
N(6)-H(8)...N(6)	0.93(3)	2.60(3)	3.095(8)	114.2(2)	2-x, y, 1-z
N(6)-H(9)...N(9)	1.00(3)	2.47(3)	3.216(5)	131(2)	3/2-x, 1/2-y, 1/2+z

Triaminoguanidinium Cation Molecular Conformation

The heavy atoms and three imino H atoms of the TAG cation (fig. 1) are essentially coplanar. Both the imino N(5) and H(7) atoms have the greatest deviations from the TAG cation least-squares-plane, which are -0.033(2) Å, and -0.17(3) Å, respectively. Although the three amino hydrogen atom-pairs are intersected by the molecular plane of the cation, the hydrogen atoms are not equidistant from the plane. With the exception of the amino hydrogen atoms, the TAG cation displays C_{3h} point-group symmetry.

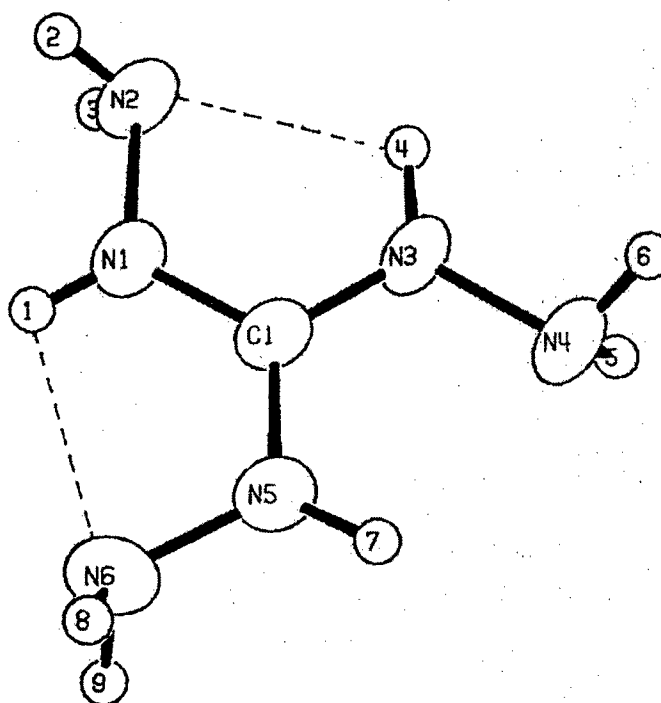


Figure 1
Heavy atoms and three imino H atoms of the TAG cation

All the imino C-N bonds are significantly shorter than the accepted C-N single bond length of 1.472(5) Å and are considered partial C-N double bonds. Specifically, the C-N bond lengths (table 2) are for C(1)-N(1), C(1)-N(3), and C(1)-N(5) are 1.326(2) Å, 1.319(2) Å, and 1.331(2) Å, respectively. Although the measured bond lengths do differ by as much as 0.012 Å, they are statistically equivalent with a mean bond length of 1.325 ± 0.004 Å. The observed shortening of the C-N bond is a consequence of pi-electron de-localization that occurs when the C-N double bond of the triaminoguanidine molecule is protonated to form the TAG cation. The average imino N-C-N angle is 120.0(2) deg, which is indicative of sp^2 bonding.

The N-N bonds are equivalent single bonds. N(1)-N(2), N(3)-N(4), and N(5)-N(6) are 1.408(2) Å, 1.419(2) Å, and 1.413(2) Å, respectively. The mean N-N bond length is 1.413 ± 0.004 Å. The mean C-N-N bond angle is 120 ± 3 deg, which is indicative of planar sp^2 bonding. The mean H-N-H bond angle in the pyramidal amino groups is 101 ± 3 deg, and the mean N-N-H bond angle is 109 ± 3 deg. These bond angles suggest sp^3 type bonding. All the bond lengths and bond angles agree with those observed in other TAG salts such as TAGN (ref. 3), TAG azide (ref. 4), and bis(triaminoguanidinium) bis(5-aminotetrazolate) (ref. 5).

Two out of three of the imino nitrogen atoms form intra-molecular N-H...N hydrogen bonds (H-bonds), with nitrogen atoms of their neighboring amino groups as depicted in figure 1. The mean H-bond distance is 2.682 ± 0.018 Å. Specifically, N(1)...N(6) and N(3)...N(2), and N(5)...N(4) are 2.665(4) Å, and 2.7(7) Å, respectively. The mean N-H-N bond angle is $105.5 \pm$

0.5 deg, with N(1)-H(1)...N(6), and N(3)-H(4)...N(2) of 105(5) and 106(2) deg, respectively. In addition these atoms also form bifurcated inter-molecular H-bonds with N(9) and N(11) of the anion.

The existence of a third imino nitrogen intra-molecular H-bond [N(5)...N(4)] is questionable. The N(5)...N(4) distance is 2.659(5) Å, which, in itself, is well within the accepted distance range for N...N H-bonds. However, the bond angle range for defining H-bonds is 100 deg or greater, but because the bond angle [99.9(5) deg] is quite close to the cut-off point, the possibility of intra-molecular H-bonding between N(5)...N(4) is duly noted.

Azotetrazolate Anion Molecular Conformation

The divalent ZT anion, whose coordinates are listed in table 1, is composed of two identical co-planar five-membered aromatic tetrazolate heterocyclic rings that are connected at the C atoms with an azo group (N-N). The two rings are related to each other by two-fold rotational symmetry (fig. 2). The azo group is bisected by a two-fold rotation axis that is normal to its molecular plane. The two tetrazolate rings are also off-set from each other by 1.146 Å. The azo N(7)-N(7) distance is 1.255(3) Å, which is indicative of a N=N double bond, and the two identical C(2)-N(7) bonds [1.1406(2) Å] are shortened single bonds. The two azo N(7) atoms have the greatest deviation of 0.018(2) Å from the least-squares plane of the ZT anion. The anion is also inclined 122 deg to the TAG cation.

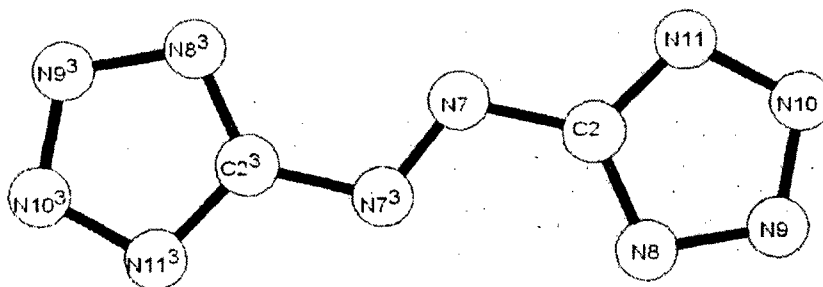


Figure 2
ZT²⁻ anion viewed down the axis of the unit cell with atom numbering scheme

Symmetry related equivalent atoms are labeled with the exponent 3. All atoms are drawn with spheres of arbitrary radii.

Within each identical tetrazolate ring there are two equivalent C-N partial double bonds with a mean bond length of 1.331 ± 0.004 Å, [C(2)-N(8) and C(2)-N(11) are 1.335(2) Å and 1.327(2) Å, respectively]. The N(8)-C(2)-N(11) bond angle is 112.7(2) deg. Each tetrazolate ring also contains three equivalent N-N partial double bonds with a mean bond length of 1.330 ± 0.004 Å. N(9)-N(10), N(8)-N(9), and N(10)-N(11) bond lengths are 1.325(2) Å, 1.333(2) Å, and 1.333(2) Å, respectively. The average N-N-N bond angle is 109.5 ± 0.5 deg. These shortened bond lengths indicate pi-electron delocalization. This highly conjugated planar conformation has been observed in a previous investigation of triaminoguanidinium bis(aminotetrazolate monohydrate) (ref. 5).

The small deviations from planarity in both anion and cation are probably due to the extensive H-bonding and molecular packing.

Crystal Structure

Although TAGZT is a salt composed of two planar monovalent TAG cations and one planar divalent ZT anion, the repeating asymmetric unit shown in figure 3 consists of one TAG cation and one-half of a ZT anion.

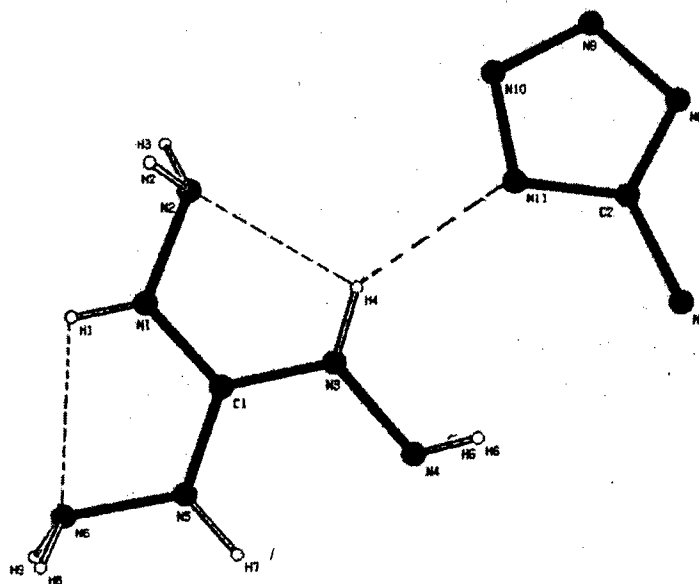


Figure 3
TAGZT asymmetric unit viewed along the a axis with the atom numbering scheme
(All atoms drawn as spheres of arbitrary radii)

In addition to electrostatic interactions in the asymmetric unit there is also an inter-molecular H-bond, N(3)...N(11), which has a bond length of 2.955(2) Å, and a bond angle of 139.7(2) deg]. The TAG cation and the tetrazolate ring rather than being co-planar are inclined to each other by 122 deg.

The molecular packing presented in figure 4 reveals that each cation is surrounded by three nearest-neighbor anions, and conversely each anion is surrounded by six nearest-neighbor cations. Furthermore, it can be seen in figure 5 that the cations are stacked one upon the other along the a axis and that the anions are positioned in separate juxtaposed stacks. The minimum inter-planar non-hydrogen bonded distance between the heavy atoms of ions along the a axis is 3.962(2) Å. This seemingly unusual ion packing is observed in other triaminoguanidinium salts such as TAGN (ref. 4) and triaminoguanidinium chloride (ref. 6).

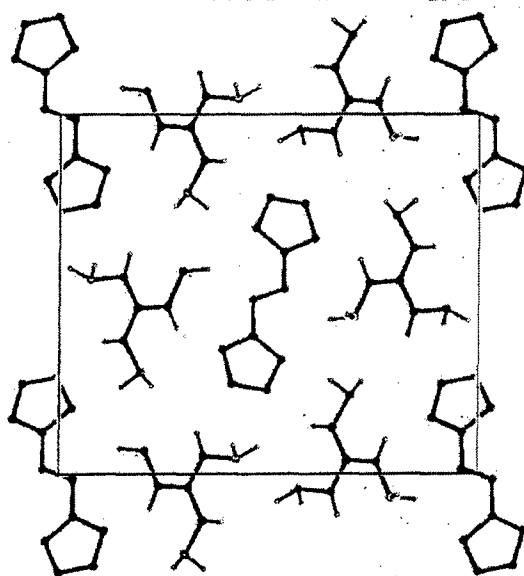


Figure 4
Projection of TAGZT unit cell packing on the bc plane

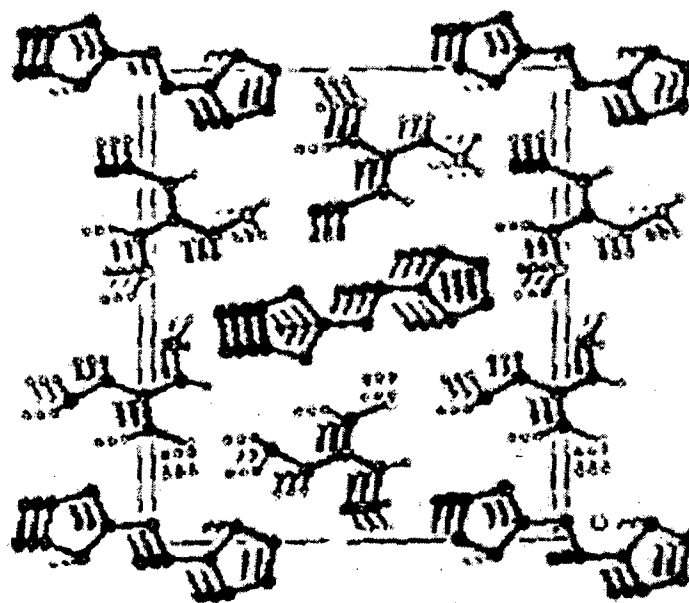


Figure 5
Three-dimensional view of packing of TAGZT along the a axis to the unit cell

The ions are bound together by an infinite three-dimensional network of intermolecular H-bonds (fig. 6). The amino N(6) atom of each cation forms bifurcated inter-molecular H-bonds with N(6) of its nearest neighbor cation and with N(9) of its nearest neighbor anion. The bond lengths of N(6)...N(6), and N(6)...N(9) are 3.095 Å, and 3.216(3) Å, respectively. Their respective H-bond angles are 114.1(2) and 131(2) deg.

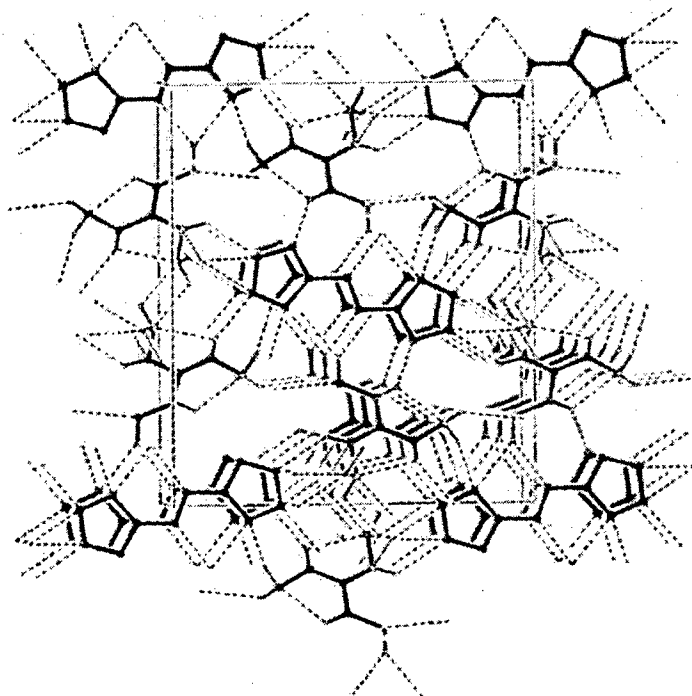


Figure 6

Three-dimensional view of H-bonds viewed along the a axis of the TAGZT unit cell (the H-bonds are drawn as dashed lines)

The imino N(1), N(3), and N(5) atoms of the cation form inter-molecular H-bonds with N(9), N(11), and N(10) of the anion. The bond lengths for N(1)...N(9), N(3)...N(11), and N(5)...N(1) are 3.010(2) Å, 2.995(2) Å, and 2.968(3); as previously stated N(1) and N(3) form bifurcated intra-molecular H-bonds.

The amino N(2) atom of the cation forms an inter-molecular H-bond with N(8) [N(2)...N(8) is 3.2(7) Å]. The amino N(4) atom forms a bifurcated H-bonds with N(7) and N(8), where N(4)...N(7) is 3.215(2) Å and N(4)...N(8) is 3.133(2) Å with bond angles 144(2) and 145(2) deg, respectively.

CONCLUSIONS

1. Triaminoguanidinium azotetrazolate (TAGZT) is a salt with a limiting density of 1.616 g/cm³.
2. TAGZT has an infinite three-dimensional network of inter-molecular hydrogen bonds, which may enhance TAGZT stability.

RECOMMENDATIONS

1. Other energetic high nitrogen compounds should be screened for potential use as fuels, burning rate enhancers and or cool burning propellants. Some possible candidates are: bis(triaminoguanidinium) bis(5,5-tetrazolate), bis(guanidinium) bis(5,5 azotetrazolate, and bis (5,5-tetrazole).
2. Determine the pH of 0.01 M solutions of the candidate salts as a preliminary test for hydrolysis.
3. Determine the crystal and molecular structures of the candidate compounds.
4. Perform impact tests on triaminoguanidinium azotetrazolate, bis(triaminoguanidinium) bis(5,5-tetrazolate), bis(guanidinium). bis(5,5-azotetrazolate, and bis(5,5-tetrazole).

These data are needed to better understand the impact trigger mechanism.

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