

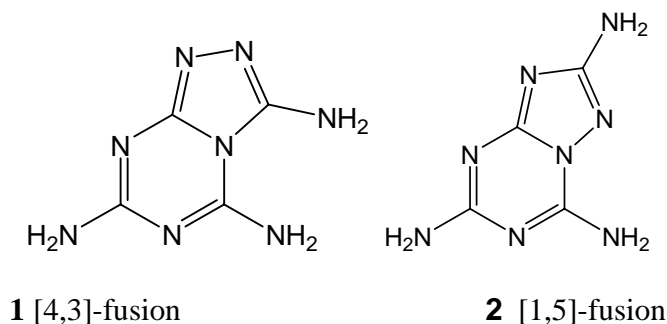
## TriazoloAminoTriazinylTetrazine (TATTz) Salts: Insensitive Propellant Ingredients

### Abstract

A series of high-energy salts were prepared by the reaction of TATTz, an acidic polycyclic heterocycle, with amine bases that have a high-nitrogen content. Guanidine and its amino-substituted congeners form salts with good thermal stability and insensitivity on the standard safety tests. TATTz itself is a relatively strong N-H acid that is friction sensitive and has a heat of formation of 700 cal/g (127 kcal/mol). Its salt, prepared by neutralization with triaminoguanidine, was used in a test gun propellant formulation. An increase in performance was observed when the TATTz salt was used as a partial replacement for RDX in a closed-bomb burning rate test.

### Introduction

Reviews of synthetic efforts to prepare new energetic molecules indicate that there is a growing interest in the use of aromatic heterocycles as synthetic frameworks for achieving the desired properties of insensitivity and performance in candidate ingredients for explosives and propellants<sup>1,2,3</sup>. The combustion of energetic heterocycles can also produce highly stable byproducts that stabilize the burning process<sup>4</sup>. Our interest in energetic materials based on the 1,3,5-triazine ring has focused on the products of the fusion of this ring with the 1,2,4-triazole ring. Of the two isomeric forms of the triamino triazolotriazines, **1** and **2**, the [4,3] ring junction compound was of the highest interest based on molecular modeling that showed higher energy content and higher density<sup>5</sup>. The proximity of the triazole and triazine amine groups in **1** causes steric strain and rotation of the amine attached to the triazole out of the plane of the ring system, according to the molecular modeling results. These spatial factors contribute to the formation of TATTz on diazotization of the triazole amine of **1**.



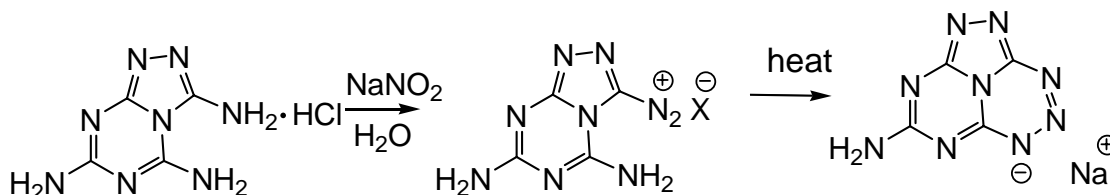
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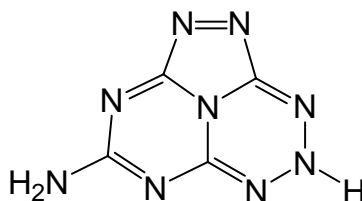
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### TATTz Synthesis and Properties

The reaction of 2-hydrazino-4,6-diaminotriazine with BrCN gives **1** as the hydrochloride salt. Treatment of an aqueous suspension of the salt with NaNO<sub>2</sub> at R.T. and then at 65 °C gives the sodium salt of TATTz (red crystals) in 88% yield. The intermediate diazonium salt can be isolated in good yield also if the temperature is not raised.



The free N-H acid, TATTz, is isolated by protonation of the salt in dilute sulfuric acid to give a yellow powder<sup>6</sup>. This imbedded 1,2,3,5-tetrazine ring has few precedents in the literature, and none with only a CHN composition.



**TATTz**

#### **4H-1,2,3,4,5,6,8,8b-Octaaza-acenaphthylen-7-ylamine**

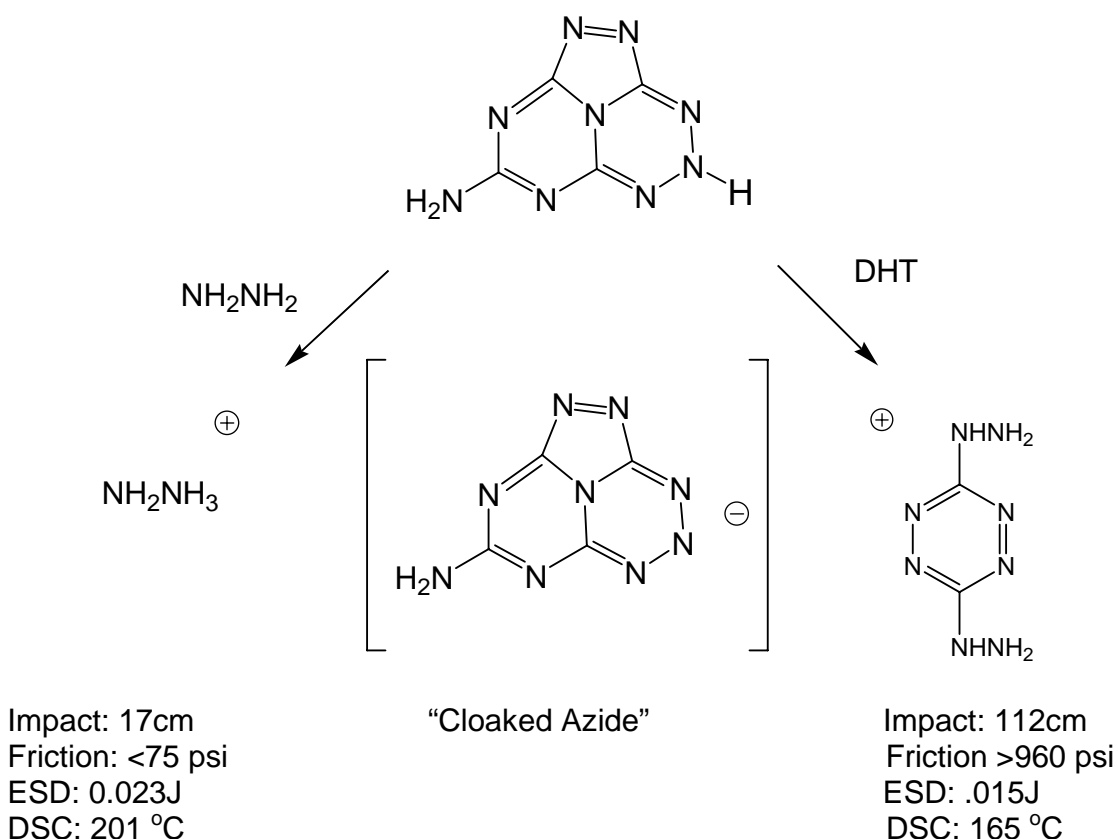
The density was determined by gas pycnometry since no crystals could be isolated for X-ray crystallography. The density of 1.77 g/cc is very high for a CHN compound. The composition of C<sub>4</sub>H<sub>3</sub>N<sub>9</sub> gives a nitrogen content of 71%. It has low solubility in water so that its pK was not determined. Molecular modeling<sup>7</sup> gives an estimated value of -5.14 (gas phase). For comparison, the values obtained for dinitramidic acid, HN(NO<sub>2</sub>)<sub>2</sub>, are -5.6 (gas phase) and 3.4 (measured). TATTz thus appears to have remarkable acidity for a CHN compound. Its ionized structure is interesting in that it can be regarded as a highly delocalized azide ion that is “cloaked” within a heterocyclic ring system. Its protonation can occur at any of the nitrogens in the 3-atom chain. The parent acid thus can theoretically consist of three tautomeric forms. The heat of formation of TATTz calculated from its combustion data is 700 cal/g (127 kcal/mol). The DSC shows a very sharp decomposition point at 213 °C. The sensitivity data are the following:

Impact H<sub>50</sub> = 17cm  
Friction = <30 psig  
ESD = 0.0085J

The impact data is comparable to RDX, but this material is very sensitive to friction and static electricity. Fortunately, this level of sensitivity is not found in the salts formed from guanidine and its amino-substituted congeners.

### Formation of TATTz Salts and Properties

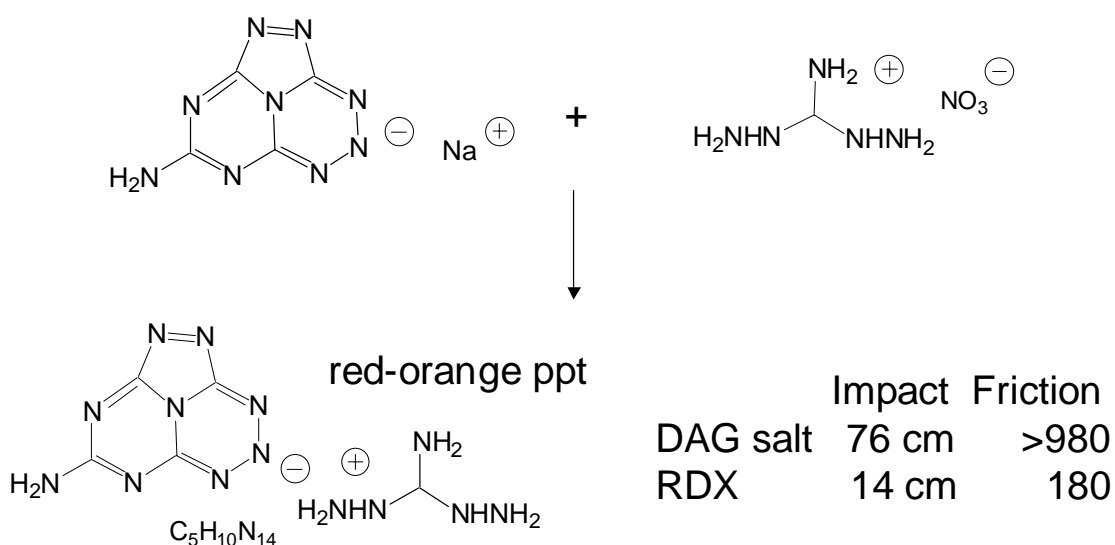
The TATTz acid forms stable salts with amine bases such as ammonia and hydrazine. In the case of the weakly basic hydrazine groups on 3,6-dihydrazino-1,2,4,5-tetrazine (DHT) the salt may actually not consist of fully dissociated TATTz and protonated DHT. The C-13 NMR of the DHT-TATTz compound shows C-13 shifts for the anion that are different from those of other TATTz salts. This compound decomposes violently at 165 °C in a capillary mp determination with an audible sound.



The hydrazinium salt precipitated from the neutralization reaction as red crystals (74%). Capillary melting point determination: 200 °C, (dec). The related ammonia salt was similarly prepared to give red crystals (74%), mp >300 °C.

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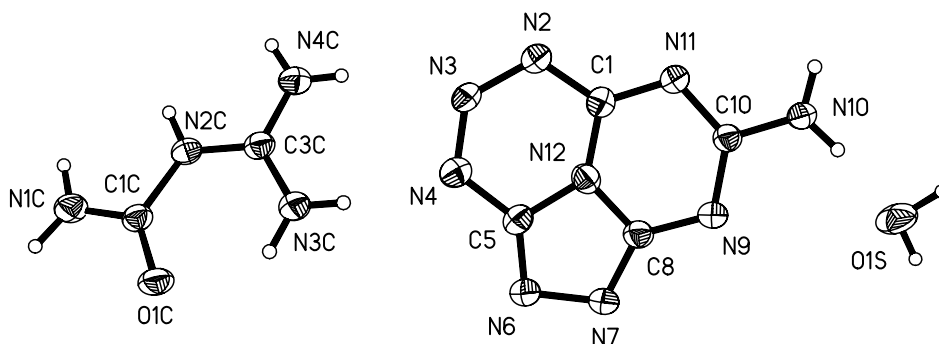
The sodium salt initially isolated in the synthesis of TATTz can also be used to generate new salt derivatives by metathesis reactions in water. The soluble sodium salt will precipitate a TATTz-M product from solution on addition of a soluble MX salt, where M<sup>+</sup> is a heavy metal ion or an ammonium ion such as the diaminoguanidinium (DAG) ion.



The salt is isolated in 71% yield and has a dec. point of 196 °C. The related guanidinium salt is isolated also from a metathesis process in water as red crystals in 73% yield. It is a monohydrate with a mp of 263 °C(dec). The aminoguanidinium salt was prepared from neutralization of TATTz with aminoguanidine bicarbonate to give red crystals (81%) with mp 227 °C (dec). The remaining amino-guanidine congener was made by a metathesis reaction of triaminoguanidine nitrate and Na-TATTz. The red crystalline product (71%) was a monohydrate and had mp 195 °C (dec), and after a recrystallization, 203 °C (dec). A TGA analysis also confirmed a monohydrate by detection of the expected 6% weight loss at 68 – 82 °C.

A preparation of the guanyl urea salt was key to establishing the structure of the TATTz anion by X-Ray crystallography. Suitable single crystals were not obtained from the other salts or from TATTz itself. An aqueous solution of guanyl urea (obtained by NaOH neutralization of N-guanyl urea sulfate) was added to a stirred aqueous suspension of TATTz at 25 °C. After 2h the solution was cooled to 5 °C and red crystals of a monohydrate were collected in 96% yield: mp>300 °C.

The X-ray data showed the atoms in the anion were in a planar array



Guanyl Urea Salt of TATTz, as a Monohydrate

The sensitivity properties and the heats of combustion were determined on a selected number of the TATTz salts. The heats of combustion were converted to heats of formation, which were used to rank the salts shown in Table 1.

Cation	Impact (cm)	Friction (psi)	ESD (J)	DSC	%N	$\Delta H_f$ (cal/g)
DHT+	112	>960	0.015	165	74.6	1102
TAG+	282	>960	0.165	206	70.2	1060
H+	17	<30	0.0085	213	63.3	721
NH <sub>2</sub> NH <sub>3</sub> <sup>+</sup>	17	<75	0.023	201	73.7	689
NH <sub>4</sub> <sup>+</sup>	>320	>960	0.095	--	64.9	611
DAG+	76	>960	0.095	206	73.7	384

Table1. TATTz and its Salts: Sensitivity and Energy Content

The salt derived from the combination of the energetic 1,2,4,5- and 1,2,3,5-tetrazine compounds DHT and TATTz is quite insensitive, while being the most energetic of the salts. The TAG salt is also clearly more energetic than the remaining salts while also being very insensitive. In this case it is likely that its water of hydration is at least partly responsible. The simple amine salts of ammonia and hydrazine offer a striking contrast in sensitivity to mechanical

energy input, while being in the same energy range. The data show some interesting trends and contrasts in energy content and sensitivity as the TATTz anion is coupled with various cations. For the purpose of obtaining burn rate data the TAG salt was selected for its overall energy, sensitivity, and thermal stability characteristics.

### Evaluation in a Propellant Formulation

TAG-TATTz was tested in a gun propellant formulation together with other candidate burning-rate modifiers by replacing a portion of the RDX normally present with the material being tested. Most of the materials were high-nitrogen heterocycles that were used to replace ~25% of the RDX, so that they were present as 20% by weight of the formulation. With 20% TAG-TATTz present, the formulation had the following sensitivity values (compared to RDX):

		<u>RDX</u>
Impact:	16 cm	26 cm
Friction	>980 psig	100 psig
ESD	0.853 J	0.095 J

The TAG-TATTz formulation, together with seven other burning-rate modifier formulations<sup>8</sup> and the baseline formulation with the undiminished amount of RDX, were ignited in a closed bomb test of burning rate vs. pressure. The extruded grains were ignited with a standard match composition. In the case of TAG-TATTz, the test sample size was smaller due to insufficient sample. This accounts for a negative slope during the last portion of the burn. The burning rate values (inches/sec) for all of the samples at the 30,000-psi point are given in Table 2. The figure of merit for the formulations was chosen at this pressure because it represents a typical barrel pressure for a gun.

Burn rate at 30Kpsi In/sec	
Sample 1	9.34
Sample 2	7.43
Sample 3	6.96
TAG-TATTz	6.81
Sample 4	6.67
Sample 5	5.53
Sample 6	4.75
Sample 7	4.70
Baseline	4.13

Table 2. Burning rate of TAG-TATTz in relation to other modifiers

Figure 1. shows the plots of the data from the combustion experiments. The baseline composition with only RDX as the energetic ingredient is exceeded in burning rate by all of the samples of Table 2, shown in the blue line plots. The TAG-TATTz composition in red is seen to taper off in rate as the sample grain reaches the end of its combustion.

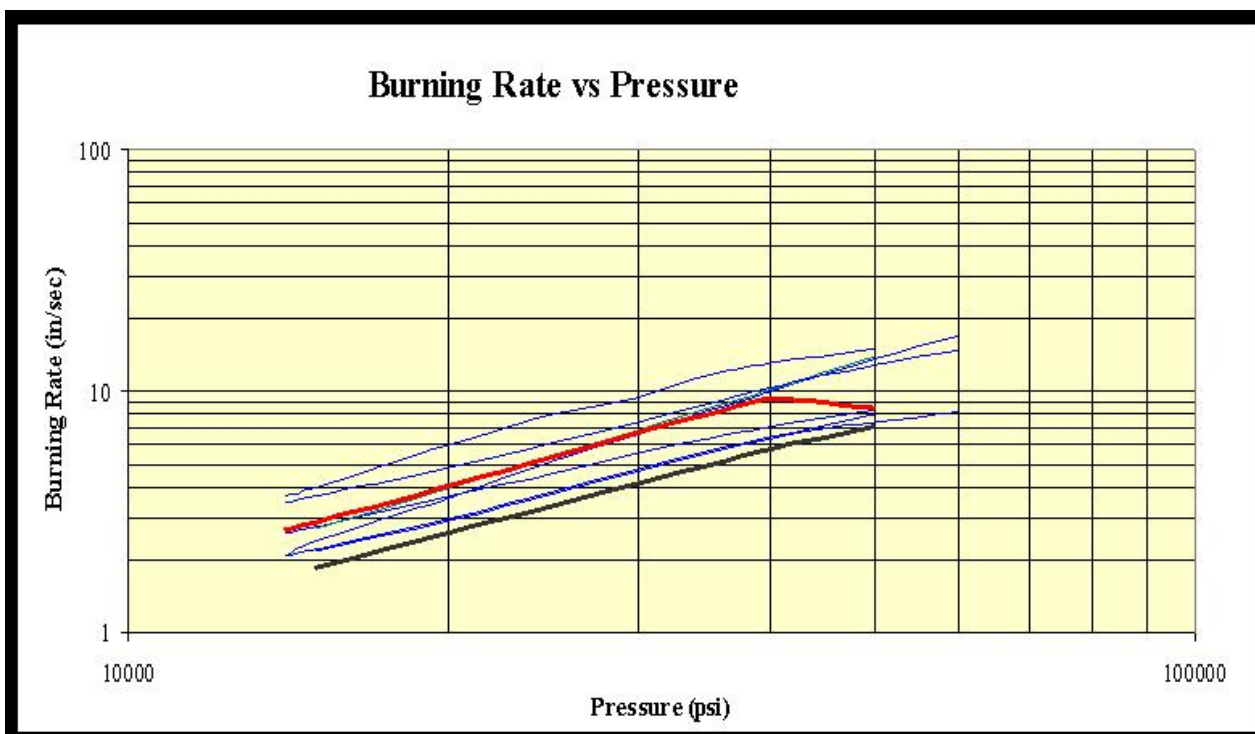


Figure 1. Plot of combustion tests. TAG-TATTz (red), Baseline (green), other High-Nitrogen Samples (blue).

## Summary

A new fused, tricyclic ring system, TATTz, has a high heat of formation. Due to its remarkable acidity as a CHN heterocycle, it forms a wide variety of salts with high-nitrogen bases. Some of these are quite insensitive. The triaminoguanidinium salt, TAG-TATTz, demonstrated performance comparable to other high performance burning rate modifiers in a closed-bomb combustion test. The potential exists for further enhancement of the energy content of this type of material via modification of the acid and the generation of new acid-base pairs.

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6. W. Koppes and M. Sitzmann, "Triazolyl-aminotriazine compositions, including salts", U.S. Patent 6,846,926, January 25, 2005.
7. Personal communication from Dr. Peter Politzer, U. of New Orleans.
8. The unspecified seven burning rate modifiers are being evaluated in a continuing program to improve gun propellant performance at this time. The structures are not revealed here at the request of the investigators of this program, Dr. Christine Michienzi and Ms. Christine Knott.