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1,3,4,5-Tetraamino-1,2,4-triazolium Cation: An Energetic Moiety

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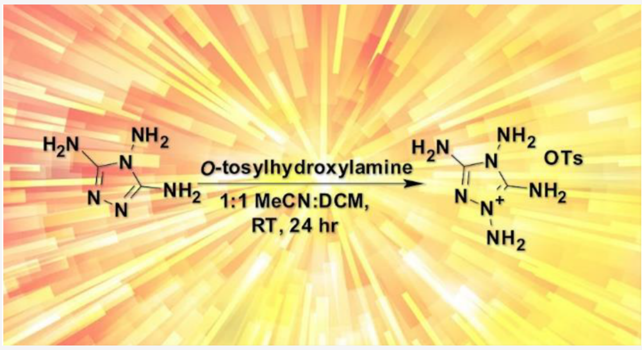

ABSTRACT: The amination of 3,4,5-triamino-1,2,4-triazole with *O*-tosylhydroxylamine yielded the nitrogen-rich 1,3,4,5-tetraamino-1,2,4-triazolium cation as its tosylate salt. Subsequent metathesis reactions produced energetic salts with various energetic anions, including perchlorate, nitrate, nitrotetrazolate, and bistetrazolate diolate. All energetic salts possess relatively high heats of formation, thermal sensitivities, and detonation velocities and pressures. The prepared energetic salts were characterized chemically using single-crystal X-ray crystallography, elemental analysis, and ^{1}H NMR, ^{13}C NMR, and IR spectroscopy and energetically by measuring their thermal, impact, and friction sensitivities. ^{15}N NMR was carried out on the tosylate salt. Energetic performances were determined by a combined experimental-computational method using calculated heats of formation and experimental crystal densities.

1. INTRODUCTION

Novel energetic materials are a subject of continuous investigation to improve upon legacy molecules. This is done to produce higher performing materials that have less environmental impact and are insensitive to undesired stimuli. There are multiple design strategies for contributing energy content to an energetic molecule. First, a molecule can feature ring or cage strain, which releases a significant amount of energy when its structure is broken.[1−3] A molecule can also contain oxidizer and fuel components within itself.[4,5] This is common within many energetic legacy materials such as 2,4,6-trinitrotoluene (TNT) and the popular secondary explosive 1,3,5-trinitro-l,3,5-triazinane (RDX).[6] Moving to modern alternatives, a nitrogen-rich molecule could be designed to have an inherently large heat of formation. During decomposition of such a molecule, the nitrogen atoms will come together forming nitrogen gas and release significant energy. These strategies are often combined, and many energetic materials derive energy content from multiple design strategies.

Recently, more developmental focus has been centered on high heat of formation energetic materials because of their relatively nontoxic postdetonation products and their ease of synthesis.[7−9] A family of energetic materials that show great promise is the nitrogen rich azoles, due to their high heat of formation resultant from their high nitrogen content within their five-membered heterocyclic ring. Specifically, both triazole and tetrazole structures have shown acceptable thermal stability and large heats of formations. However, neither molecular structure is inherently energetic and, as a result, requires the incorporation of explosophoric functionalities to be interesting.[10]

Nitro, nitramino, and azido groups have shown to improve azole detonation characteristics.[11−13] However, there is also a limit as to the number and identity of substituents which can be added to an azole. Adding multiple explosophoric groups could cause the product to become too thermally unstable or too shock or friction sensitive for practical use.[14] Alternatively, adding substituents may also limit energetic performance, such as azide groups, because the density decreases compared to what is possible with denser functional groups.[15] Therefore, there is an incentive to generate new energetic compounds by the addition of these groups to both well-known and relatively new energetic materials and to characterize these new products' performances.

One means to do this is by formation of energetic salts. The salt's overall energetic performance and stability can be readily fine-tuned by the exchanging of cations or anions. Energetic salts have been shown to be capable of possessing high energetic performances while also having lowering sensitivities to thermal and mechanical stimuli than their neutral counterparts. In addition, salts generally possess a very low vapor pressure, making them low inhalation risk and can be achieved using conventionally "green" methods. Lastly, an energetic salt may have a higher crystal density than its neutral parent species.[16]

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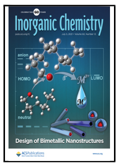

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Incorporation of *N*-amines is an effective means for developing high performing energetic materials without relying on traditional methods of functionalization (i.e., wasteful and hazardous mixed acid nitration). The formation of the N−NH_2 bond increases the molecule's heat of formation due to the thermodynamic driving force to produce stable N_2 gas. The presence of *N*-amines can dramatically improve the energetic performance of materials as seen with comparison of 5-amino tetrazole, 1-amino tetrazole, and 2-amino tetrazole. For the most part, 5-amino tetrazole is considered nonenergetic, whereas 1-amino tetrazole and 2-amino tetrazole are both much more energetic.[17] Additionally, the presence of *N*-amines acts as a powerful scaffold for further molecular modification, such as azo coupling and nitramino generation.[18,19]

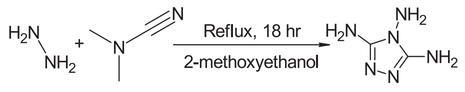
In this paper, we report on the amination of the known nitrogen-rich heterocycle 3,4,5-triamino-1,2,4-triazole (guanazine) to the novel 1,3,4,5-tetraamino-1,2,4-triazolium cation using *O*-tosylhydroxylamine. This is the only known instance of a triazole possessing four amines on the backbone and offers a unique high nitrogen cation to be considered in energetic salts. The novel 1,3,4,5-tetraamino-1,2,4-triazolium tosylate (**1**) was then used as the precursor for metathesis reactions to obtain the 1,3,4,5-tetraamino-1,2,4-triazolium cation paired with the more energetic nitrate, perchlorate, nitrotetrazolate, and bistetrazole diolate anions.

Each energetic salt was characterized chemically by elemental analysis, X-ray crystallography, and ^1H NMR, ^{13}C NMR, and IR spectroscopy. The tosylate salt was characterized by ^{15}N NMR as well. Additionally, the salts' energetic properties, including their thermal decomposition temperature, friction sensitivity, and impact sensitivity, were determined. Lastly, detonation parameters for each energetic salt were calculated using an experimental-computational method involving calculated heats of formation and experimental crystal densities.

2. RESULTS AND DISCUSSION

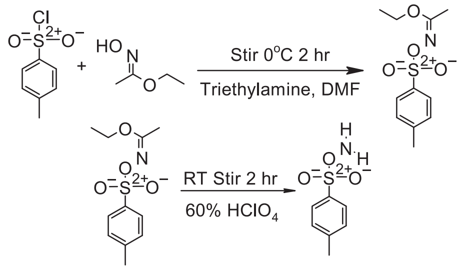
2.1. Synthesis. 3,4,5-Triamino-1,2,4-triazole (guanazine) was prepared using a modified procedure outlined by Child[20] in which anhydrous hydrazine and dimethylcyanamide were refluxed overnight in 2-methoxyethanol (Scheme 1). Once filtered and collected, guanazine was dissolved in minimal water due to insolubility in acetonitrile. Freshly prepared *O*-tosylhydroxylamine was derived from ethyl *O*-(*p*-tolylsulfonyl)-acetohydroximate (Scheme 2)[21] in dichloromethane and combined with the guanazine solution along with an equal volume of acetonitrile and stirred for 48 hr (Scheme 3).

Scheme 1. Synthesis of 3,4,5-Triamino-1,2,4-triazole

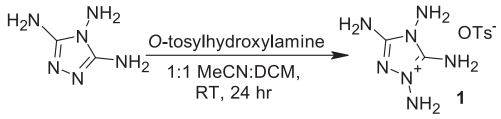


The reaction solution was then evaporated under vacuum yielding the crude tosylate salt. The salt was recrystallized in hot 2-propanol to remove impurities and residual guanazine, yielding pure **1** as fine light-salmon needles. Recrystallized **1** was then dissolved in minimal hot ethanol, and 1 equivalent of hydrobromic acid was added. The solution was removed from heat and quenched with diethyl ether yielding a beige precipitate of 1,3,4,5-tetraamino-1,2,4-triazolium bromide (**2**) (Scheme 4).

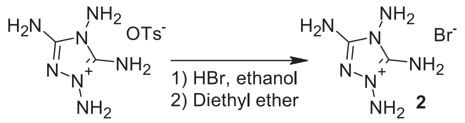
Scheme 2. Synthesis of Ethyl *O*-(*p*-Tolylsulfonyl)acetohydroximate and Fresh *O*-Tosylhydroxylamine



Scheme 3. Synthesis of 1,3,4,5-Tetraamino-1,2,4-triazolium Tosylate Salt (1)

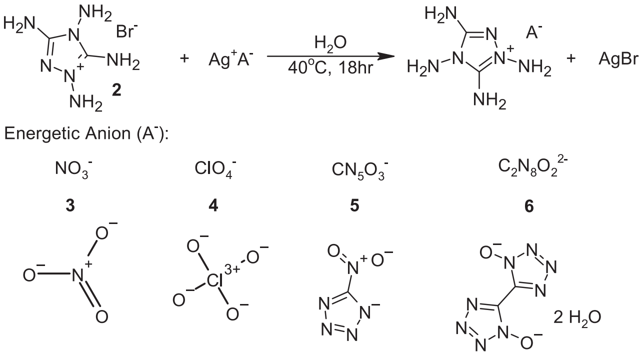


Scheme 4. Synthesis of Intermediate 1,3,4,5-Tetraamino-1,2,4-triazolium Bromide Salt (2) from 1



Equal mole amounts of **2** and a corresponding silver salt of an energetic anion were combined in aqueous solution and stirred in the dark overnight at 40 °C in minimal water (Scheme 5). The resulting solution was filtered, and the energetic crystals of the nitrate (**3**), perchlorate (**4**), nitrotetrazolate (**5**), and bistetrazole diolate (**6**) salts were collected by slow evaporation of the filtrate. Both salts **5** and **6** were isolated as hydrates, as determined from their crystal structures. Both of these salts were heated at 80 °C under vacuum (>1 mbar) overnight and crystallized from methanol. This procedure removed the water of crystallization from **5** but not **6**.

Scheme 5. Synthesis of Energetic 1,3,4,5-Tetraamino-1,2,4-triazolium Salts (3−6) from 2



2.2. Spectroscopy. The 1,3,4,5-tetraamino-1,2,4-triazolium cation was extensively characterized with multinuclear NMR spectroscopy. The cation contains two different carbons which are represented by two well-defined resonances in the ^{13}C NMR spectra (147.4 and 148.9 ppm). The more shielded carbon at 147.4 ppm corresponds to the carbon closer to the recently aminated nitrogen due to additional crowding. Guanazine only has one ^{13}C resonance at 151.3 ppm due to its symmetry. Therefore, the ring *N*-amination slightly shields the carbon atoms by approximately 2 to 4 ppm.

The cation also exhibits four distinguishable hydrogens, which is identified with four separate singlet resonances in the ^{1}H NMR spectra (7.8, 6.4, 6.0, 5.6 ppm). The 7.8 and 6.4 ppm hydrogens represent the *N*-amines, while the 6.0 and 5.6 ppm hydrogen correspond to the *C*-amines. Guanazine's ^{1}H NMR spectrum displays two unique singlet resonances at 5.15 ppm (*N*-amine) and 5.06 ppm (2 × *C*-amines).

Using a saturated solution of salt **1**, ^{15}N NMR spectroscopy identified seven unique peaks corresponding to the 1,3,4,5-tetraamino-1,2,4-triazolium cation which contains seven nitrogen atoms, shown in Figure 1. The azolium nitrogen atom without an attached *N*-amine (N_a) and its adjacent nitrogen (N_b) corresponds to −156.2 and −218.8 ppm, respectively. The third azolium nitrogen (N_c) is well resolved at −242.9 ppm. For the amines, the least shielded nitrogen corresponds to *N*-3 (N_d) of the 1,3,4,5-tetraamino-1,2,4-traizolium cation, resonating at −335.0 ppm. *N*-1, *N*-4, and *N*-5 amines unfortunately are indistinguishable; however, they resonated at −308.2, −321.4, and −322.1 ppm. Darwich et al. conducted ^{15}N spectroscopy on the precursor 3,4,5-triamino-1,2,4-triazole in 2007.[22] Due to the symmetry of the molecule, they found four unique nitrogen resonances at −156.5 (azole, *N*-1 and *N*-2), −238.1 (azole, *N*-4), −326.3 (amine, *N*-4), and −340.7 (amine, *N*-3, *N*-5) ppm. By comparing the chemical shifts before and after the amination, one can see that the newly aminated ring nitrogen exhibited the largest chemical shift of over 60 ppm, while all other nitrogen exhibited much lower shifts (<20 ppm).

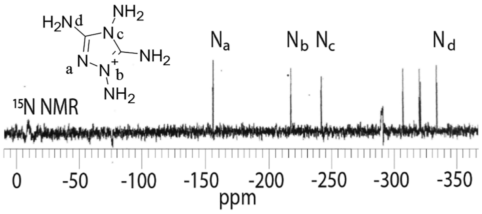


Figure 1. ^{15}N NMR spectrum of the 1,3,4,5-tetraamino-1,2,4-triazolium cation.

Using mass spectrometry, the 1,3,4,5-tetraamino-1,2,4-triazolium cation ($C_2N_7H_8^+$) for all salts appeared at 130.2 *m*/*z* (ESI$^+$). The salts respective anions or anionic complexes appeared at 171.1 (**1**, $C_7H_7SO_3^-$), 289.8 (**2**, $C_2N_7H_8Br_2^-$), 62.0 (**3**, NO_3^-), 328.1 (**4**, $C_2N_7H_8(ClO_4)_2^-$), 114.0 (**5**, $CN_5O_2^-$), and 169.0 (**6**, $C_2N_8O_2^-$) *m*/*z* (ESI$^-$).

2.3. Single-Crystal X-ray Analysis. Single crystals of the investigated compounds **1**, **3**, **4**, **5**, and **6** were coated with a trace of Fomblin oil and were transferred to the goniometer head of a Bruker Quest diffractometer with kappa geometry, a Cu Kα wavelength (λ = 1.54178 Å) I-μ-S microsource X-ray tube, a laterally graded multilayer (Goebel) mirror for monochromatization, and a Photon III C14 area detector. The instrument was equipped with an Oxford Cryosystems low temperature device, and examination and data collection were performed at 150 K. Data were collected, reflections were indexed and processed, and the files were scaled and corrected for absorption using APEX3[23] and SADABS.[24] The space groups were assigned using XPREP within the SHELXTL suite of programs[25,26] and solved by direct methods using ShelXS[26] and refined by full matrix least-squares against F^2 with all reflections using Shelxl2018[27] using the graphical interface Shelxle.[28] H atoms attached to carbon, boron, and nitrogen atoms as well as hydroxyl hydrogens were positioned geometrically and constrained to ride on their parent atoms. C−H bond distances were constrained to 0.95 Å for aromatic and alkene C−H and to 0.98 Å for CH_3 moieties, respectively. Amine and water H atom positions were refined. For compound **6**, N−H and O−H distances were restrained to target values of 0.88(2) and 0.84(2) Å, respectively. For compound **3**, U_{iso}(H) values were freely refined. For all other structures, they were set to a multiple of U_{eq}(C/N) with 1.5 for CH_3 and OH and 1.2 or 1.5 for NH_2 units, respectively. Complete crystallographic data, in CIF format, have been deposited with the Cambridge Crystallographic Data Centre. CCDC 2063169, 2063170, 2063171, 2063172, and 2063173 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Figures 2−6 show the novel crystal structures containing the 1,3,4,5-tetraamino-1,2,4-triazolium cation. Densities of all crystals were determined at 150 K (Table 1) and at ambient temperature (Table 2). Each salt crystal was colorless. Tosylate salt **1** (Figure 2) and nitrate salt **3** (Figure 3) both crystallized in the monoclinic space group $P2_1/c$ with 4 formula units in the unit cell. **1** exhibited a density of 1.469 g-cm^{-3} at 150 K and 1.434 g-cm^{-3} at ambient temperature. **3** featured a density of 1.632 g-cm^{-3} at 150 K and 1.600 g-cm^{-3} at ambient temperature. Perchlorate salt **4** (Figure 4) crystallized in a monoclinic space group $P2_1/n$ with 4 formula units in the unit cell. **4** had the highest densities of all the salts, 1.808 g-cm^{-3} at 150 K and 1.763 g-cm^{-3} at ambient temperature. Nitrotetrazolate salt **5** (Figure 5) crystallized in the monoclinic space group $C2/c$ with 8 formula units per unit cell and a density of 1.694 g-cm^{-3} at 150 K and 1.606 g-cm^{-3} at ambient temperature. Lastly, the bistetrazole diolate salt **6** (Figure 6) crystallized in the triclinic space group $P\bar{1}$ with 1 formula unit per unit cell and two waters of hydration. This dihydrated salt featured a density of 1.680 g-cm^{-3} at 150 K and 1.651 g-cm^{-3} at ambient temperature. None of the produced salts yielded densities close to RDX (1.82 g-cm^{-3} at ambient temperature).[29]

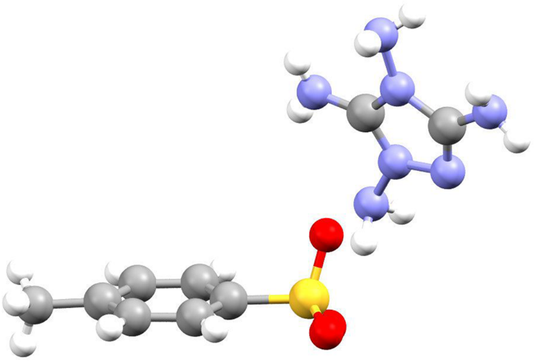


Figure 2. Molecular unit of 1,3,4,5-tetraamino-1,2,4-triazolium tosylate (**1**). Ellipsoids are drawn at the 50% probability level.

Table 1. Crystallographic Data and Structure Refinement Details for Salts 1, 3, 4, 5, and 6

	1	3	4	5	6
formula	$C_9H_{15}N_7SO_3$	$C_2H_8N_8O_3$	$C_2H_8N_7ClO_4$	$C_3H_8N_{12}O_2$	$C_6H_{20}N_{22}O_4$
FW [g mol^{-1}]	301.34	192.16	229.60	244.21	464.44
crystal system	monoclinic	monoclinic	monoclinic	monoclinic	triclinic
space group	$P2_1/c$	$P2_1/c$	$P2_1/n$	$C2/c$	$P\bar{1}$
a [Å]	15.0951 (8)	5.5461 (2)	5.6741 (2)	24.9631 (17)	6.5034 (4)
b [Å]	9.6374 (6)	8.4679 (3)	11.0488 (4)	3.7996 (3)	7.9023 (5)
c [Å]	9.4354 (4)	16.6593 (9)	13.4960 (5)	20.8866 (14)	10.1915 (7)
α [deg]	90	90	90	90	458.98 (4)
β [deg]	97.114 (3)	90.817 (3)	94.6549 (12)	104.791 (3)	105.162 (3)
γ [deg]	90	90	90	90	111.469 (3)
V [$Å^3$]	1362.07 (13)	782.30 (6)	843.30 (5)	104.791 (3)	458.98 (5)
Z	4	4	4	8	1
ρ [g cm^{-3}]	1.469	1.632	1.808	1.694	1.680
T [K]	150	150	150	150	150
crystal shape	plate	fragment	block	plate	block
color	colorless	colorless	colorless	colorless	colorless
crystal size (mm)	0.04 × 0.03 × 0.002	0.25 × 0.15 × 0.11	0.23 × 0.20 × 0.15	0.21 × 0.08 × 0.03	0.13 × 0.10 × 0.07
R_1	0.046	0.040	0.040	0.034	0.041
wR_2	0.130	0.117	0.117	0.096	0.127
S	1..06	1.09	1.16	1.05	1.09
no. of reflections	2893	1605	1786	2048	1913
parameters	207	151	152	179	176
restraints	0	0	0	0	10
CCDC	2063173	2063169	2063170	2063172	2063171

Table 2. Energetic Properties and Calculated Detonation Parameters for Salts 3–6 and RDX

	3	4	5	6	RDX[29]
formula	$C_2H_8N_8O_3$	$C_2H_8N_7ClO_4$	$C_3H_8N_{12}O_2$	$C_6H_{20}N_{22}O_4$	$C_3H_6N_6O_6$
FW (g/mol)	192.14	229.58	244.17	464.39	222.12
Ω^a (%)	−41.64	−27.88	−32.76	−62.01	−21.6
$T_d{}^b$ (°C)	156	163	137	177	239
ρ^c (g-cm^{-3})	1.600	1.763	1.606	1.651	1.858 (90 K)[47]
ρ^{calcd} (g-cm^{-3})	1.662	1.788	1.656	1.732	
$\Delta_fH_m{}^{oe}$ (kJ/mol)	61.3	144.0	518.0	909.7	92.6
IS^f (J)	7.0	6.0	2.0	>40	7.4
FS^g (N)	8.4	11.2	8.0	14.4	120
calculated values by EXPLO5					
$\Delta_{Ex}U^{oh}$ (kJ/kg)	4034	4852	4103	4214.8	5355
$T_{det}{}^i$ (°C)	2484	3150	2866	2436.9	3959
ρ^j (GPa)	23.9	28.9	23.6	27.4	33.7
$V_{det}{}^k$ (m/s)	8209	8410	8198	8795	8710
$V_o{}^l$ (cm^3/g)	0.486	0.436	0.486	0.476	0.734

[a] Oxygen balance. [b] Temperature decomposition. [c] Density from X-ray diffraction (25 °C). [d] Calculated density. [e] Calculated molar enthalpy of formation. [f] Impact sensitivity. [g] Friction sensitivity. [h] Total energy of detonation. [i] Detonation temperature. [j] Detonation pressure. [k] Detonation velocity. [l] Volume of detonation products.

2.4. Thermal Behavior. All energetic salts decomposed at elevated temperatures between 137 and 177 °C, as shown in Table 2. Intermediate salts **1** and **2** decomposed at 177 and 189 °C, respectively. Each salt displayed one exotherm during incremental heating, representing the decomposition point. The temperatures were recorded at the onset temperature of the exothermic process. The highest energetic salt decomposition temperature was bistetrazolate diolate **6** at 177 °C, while the lowest was the nitrotetrazolate **3** at 137 °C. The hydrated salt **6** also displayed an endotherm around 100 °C, corresponding to the loss of its crystal water. The amination of the 3,4,5-triamino-1,2,4-triazole reduces the decomposition temperature of the salt. In 2010, Liang et. al determined the decomposition point of 3,4,5-triamino-1,2,4-triazolium nitrate to be near 220 °C.[30] By comparing to our nitrate salt **3** (T_{dec} = 157 °C), our results indicate the decomposition temperature of the triazolium moiety drops over 60 °C with one additional *N*-amine. All salts have lower decomposition temperatures than RDX (205 °C).[29]

2.5. Detonation Parameters. Only salts **3**, **4**, **5**, and **6** were studied for energetic performance. Intermediate salts **1** and **2** were not tested for energetic performance because their anions are not considered energetic. All calculated detonation characteristics were calculated using the theoretical heat of formation and experimental X-ray crystallography room temperature density.

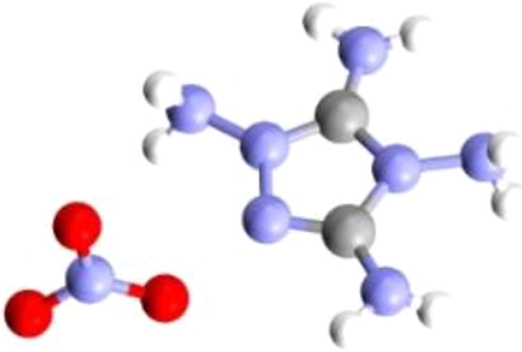


Figure 3. Molecular unit of 1,3,4,5-tetraamino-1,2,4-triazolium nitrate (**3**). Ellipsoids are drawn at the 50% probability level.

Figure 4. Molecular unit of 1,3,4,5-tetraamino-1,2,4-triazolium perchlorate (**4**). Ellipsoids are drawn at the 50% probability level.

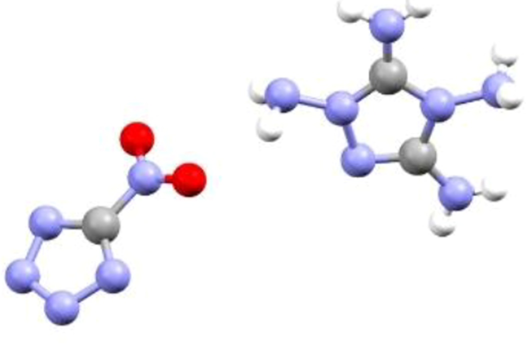


Figure 5. Molecular unit of 1,3,4,5-tetraamino-1,2,4-triazolium nitrotetrazolate (**5**). Ellipsoids are drawn at the 50% probability level.

The energetic properties of each of the compounds are shown in Table 2. The method of Byrd and Rice (based on properties of individual energetic compounds derived from quantum mechanics) provided the heats of formation[31] and densities[32,33] of all compounds. These calculated densities agreed within 3% with those measured via X-ray crystallography at 150 K. The Gaussian09 program package[34] and the B3LYP spin-restricted Kohn−Sham density functional theory (KS-DFT)[35−38] with the 6-31G** Pople Gaussian basis set[39−41] were used to determine gas phase geometries of each compound. Using these geometry data, the G3MP2-(B3LYP)[42] electronic energy was determined which is required to compute the heat of formation. The Gutowski method[43] provided the heat of sublimation as determined from the molecular volume of each compound. The EXPLO5 V6.05.02 software package[44,45] provided the detonation performance data from the calculated heats of formation based on observed X-ray diffraction crystal densities at ambient temperature.

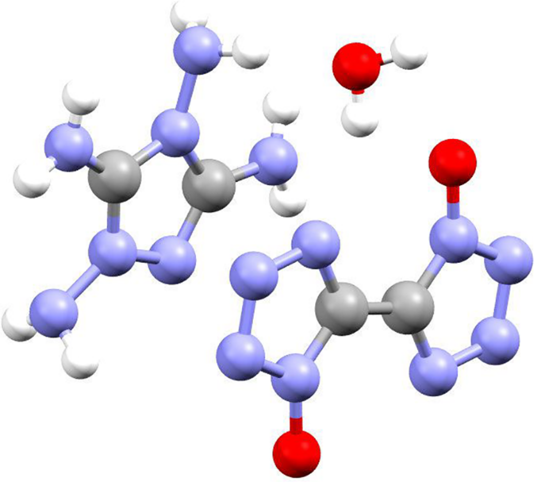


Figure 6. Molecular unit of 1,3,4,5-tetraamino-1,2,4-triazolium bistetrazole diolate dihydrate (**6**). Ellipsoids are drawn at the 50% probability level.

Salt **6** showed the highest heat of formation (909.7 kJ/mol) of the 1,3,4,5-tetraamino-1,2,4-triazolium salts. This high heat of formation can be attributed to its nitrogen-rich bistetrazole diolate anion. Additionally, **6** displayed a calculated detonation velocity of 8795 m/s, which surpasses RDX performance (8710 m/s). If the nonhydrated salt of **6** was produced, meaning solely two tetraamino-triazolium cations per bistetrazole diolate anion, the calculated heat of formation and calculated density would change to 1381.6 kJ/mol and 1.655 g-cm^{-3}. This theoretical salt has a slightly larger heat of formation and slightly smaller density than its hydrated form **6**, so it can be assumed that its performance is similar to **6**'s parameters.

The perchlorate salt **4** achieved the second best characteristics (V_{det} = 8410 m/s, $\Delta_{\mathrm{Ex}}U^{\circ}$ = 4852 kJ/kg, ρ = 28.9 GPa), despite a low heat of formation (144.0 kJ/mol). **4**'s higher performance values (especially the detonation pressure) are most likely due to its higher density and greater oxygen balance than the other salts (1.763 g-cm^{-3}). Dense crystal formation is important to achieve high energetic performance.[46] Salts **3**, **4**, and **5** do not surpass RDX detonation performance. This may be attributable to their lower crystal density and oxygen balance compared to RDX.

2.6. Mechanical Sensitivity. The four energetic salts underwent sensitivity testing, and the results are found in Table 2. Impact sensitivity was performed according to STANAG 4489 and modified according to instruction[48] on an OZM drop hammer by the BAM method.[49] Friction sensitivity was carried out in accordance with STANAG 4487[50] and modified according to instruction[51] using a BAM friction tester. The nitrotetrazolate salt **5** was the most sensitive for both friction and impact (8.0 N, 2.0 J), while the hydrated bistetrazole diolate salt **6** was the least sensitive (14.4 N, >40 J). Hydrated energetic materials are often less sensitive to various stimuli, which most likely increased its resistance to detonating.[52] If the anhydrous form of salt **6** was achieved, it can be predicted to be much more sensitive. Salts **3**, **4**, and **5** exhibited more sensitive behavior than RDX (7.4 J, 120 N).[29]

3. CONCLUSIONS

In summary, a new energetic 1,3,4,5-tetraamino-1,2,4-triazolium cation was created by reacting the strong aminating agent ethyl *O*-(*p*-tolylsulfonyl)acetohydroximate with nitrogen-rich 3,4,5-triamino-1,2,4-triazole. The novel energetic cation was then paired with other energetic anions using metathesis reactions to form distinct energetic salts. None of the salts exhibited remarkable energetic performance, with all salts having detonation parameters around or below RDX. We theorize that the low performance is mostly due to the salts' low densities. However, the successful amination of guanazine to the first ever 1,3,4,5-tetraamino-1,2,4-triazolium cation is still important as a new high nitrogen moiety and will lead to more energetic compounds in the future.

4. EXPERIMENTAL SECTION

4.1. General. All reagents and solvents were used as received unless otherwise specified (Sigma-Aldrich, Fluka, Acros Organics, Fisher Scientific Co LLC). Decomposition temperatures were acquired using a TA Instruments SDT Q600 TGA/DSC using heating rates of 5 °C min^{-1}. Salt characterization using Elemental Analysis was conducted using an Elementar Vario EL cube. All NMR (^{1}H, ^{13}C, ^{15}N) spectroscopy was collected with a Bruker AV-III-500-HD (5 mm BBFO Cryoprobe Prodigy) Avance DRX NMR spectrometer. All chemical shifts for ^{1}H and ^{13}C spectra are relative to TMS. Salt **1** was used for the ^{15}N NMR spectrum. ^{15}N chemical shifts are relative to CH_3NO_2. Infrared spectra were measured with a PerkinElmer Spectrum Two FT-IR spectrometer. Transmittance values are described as "strong" (s), "medium" (m), and "weak" (w). Mass spectra were obtained using an Agilent 1260 Infinity II Quaternary LC instrument. The BAM (Bundesanstalt für Materialforschung) friction tester from Reichel & Partner Gmbh and the OZM BAM Fall Hammer BFH-10 were used to acquire sensitivity data.

4.2. WARNING. This paper's salts and many of their intermediates are considered energetic materials that could be detonated by various stimuli. During our experiments, we did not encounter issues while handling the materials. However, personal protective equipment (face shield, body armor, Kevlar gloves, grounded equipment) should be used at all times.

4.3. 1,2,3,4-Tetraamino-1,3,5-triazolium Tosylate (1). Ethyl *O*-(*p*-tolylsulfonyl)acetohydroximate (2.2 g, 8.7 mmol) was stirred in 60% perchloric acid (40 mL) for 2 hr at RT. The solution was then poured into ice water. The white aminating agent was extracted from the water using dichloromethane. In a separate container, 3,4,5-triamino-1,2,4-triazole (1.0 g, 8.7 mmol) was dissolved in a minimal amount of water. The water (25 mL) and dichloromethane solutions (125 mL) were combined with an equal volume acetonitrile (125 mL) and stirred at RT for 24 h. The resultant aqueous layer was evaporated to yield a purple-red solid consisting of 3,4,5-triamino-1,2,4-triazole and **1**. To increase purity, the solid was stirred in hot 2-propanol for 2 hr. A hot vacuum filtration was performed to separate the two compounds. Pure pink **1** (1.67 g) precipitated and was collected via vacuum filtration and allowed to dry (yield = 64%). DSC: 177 °C (dec.). IR: $\tilde{\nu}$ = 3471 (w), 3316 (m), 3277 (m), 3215 (m), 3167 (m), 2920 (w), 1726 (m), 1674 (m), 1588 (m), 1537 (w), 1495 (w), 1453 (m), 1395 (w), 1361 (w), 1302 (w), 1189 (s), 1177 (s), 1122 (s), 1109 (m), 1035 (s), 1009 (s), 940 (m), 897 (m), 816 (m), 799 (m), 773 (w), 711 (m), 683 (s), 631 (m), 566 (s), 514 (s) cm^{-1}. ^{1}H NMR ([D$_6$]DMSO): δ = 7.8 (s, 2H, $N^+{-}N{-}C{-}NH_2$), 7.5 (d, 2H, $CH{-}C{-}SO_3^-$), 7.1 (d, 2H, $CH{-}C{-}CH_3$), 6.4 (s, 2H, $N^+{-}C{-}NH_2$), 6.0 (s, 2H, $N{-}NH_2$), 5.6 (s, 2H, $N^+{-}NH_2$), 2.3 (s, 3H, CH_3). ^{13}C NMR ([D$_6$]DMSO): δ = 148.9 (1C, $N{-}C{-}N^+$), 147.4 (1C, N−C−N), 146.3 (1C, $C{-}CH_3$), 138.1 (1C, $C{-}SO_3^-$, 128.5 (2C, $CH{-}C{-}CH_3$), 126.0 (2C, $CH{-}C{-}SO_3^-$), 21.2 (1C, CH_3). ^{15}N NMR ([D$_6$]DMSO): δ = −156.2 (2*N*-azolium), −218.8 (1*N*-azolium), −242.9 (4*N*-azolium), −308.2 (1*N*-amine, 4*N*-amine, 5*C*-amine), −321.4 (1*N*-amine, 4*N*-amine, 5*C*-amine), −322.1 (1*N*-amine, 4*N*-amine, 5*C*-amine), −335.0 (3*C*-amine). MS (ESI$^+$): *m*/*z* = 130.2 ($C_2N_7H_8^+$); MS (ESI$^-$): *m*/*z* = 171.1 ($C_7H_9SO_3^-$). $C_9H_{15}N_7SO_3$ (301.32): calcd. C 35.87, H 5.02, N 32.54; found C 35.90, H 5.02, N 32.52.

4.4. 1,2,3,4-Tetraamino-1,3,5-triazolium Bromide (2). Tosylate **1** (0.486 g, 1.61 mmol) was dissolved in a minimal amount of hot ethanol (20 mL). Hydrobromic acid (48%, 0.415 g, 5.129 mmol) was added to the solution. The bromide salt precipitated out of solution at RT. To further reduce solubility, diethyl ether (100 mL) was added and placed in the fridge overnight. The solid beige product was separated from the solution via vacuum filtration and dried to yield 0.332 g, 1.58 mmol of **2** (yield = 98%). DSC: 189 °C (dec.). IR: $\tilde{\nu}$ = 3375(w), 3320 (m), 3294 (m), 3174 (m), 3121 (m), 2750 (w), 1728 (m), 1650 (s), 1622 (m), 1607 (m), 1569 (m), 1445 (m), 1380 (w), 1341 (w), 1311 (w), 1221 (w), 1152 (w), 1079 (m), 1009 (w), 949 (s), 892 (m), 799 (w), 765 (w), 710 (m), 671 (w), 630 (m), 599 (s), 491 (s) cm^{-1}. ^{1}H NMR ([D$_6$]DMSO): δ = 7.8 (s, 2H, $N^+{-}N{-}C{-}NH_2$), 6.4 (s, 2H, $N^+{-}C{-}NH_2$), 6.0 (s, 2H, $N{-}NH_2$), 5.6 (s, 2H, $N^+{-}NH_2$). ^{13}C NMR ([D$_6$]DMSO): δ = 148.9 (1C, $NH_2{-}N{-}C{-}N^+{-}NH_2$), 147.4 (1C, $NH_2{-}N{-}C{-}N$). MS (ESI$^+$): *m*/*z* 130.2 ($C_2N_7H_8^+$); MS (ESI$^-$): *m*/*z* = 78.9 (Br^-),210.1 ($C_2N_7H_8Br$), 289.9 ($C_2N_7H_8Br_2^-$). $C_2H_8N_7Br$ (210.0): calcd. C 11.44, H 3.84, N 46.68; found C 11.84, H 3.88, N 46.38.

4.5. 1,2,3,4-Tetraamino-1,3,5-triazolium Nitrate (3). Silver nitrate (0.087 g, 0.512 mmol) was dissolved in a minimal amount of water (10 mL). Bromide salt **2** (0.105 g, 0.500 mmol) was dissolved in a separate container in a minimal amount of water (10 mL). The two solutions were combined and stirred overnight at 40 °C in darkness. The solution then underwent a Celite filtration. The filtrate was allowed to evaporate to dryness to yield 0.076 g of nitrate salt **3** (yield = 79%). DSC: 156 °C (dec.). IR: $\tilde{\nu}$ = 3320 (w), 3234 (w), 3196 (w), 3134 (w), 2949 (w), 1728 (w), 1667 (m), 1632 (m), 1596 (w), 1530 (w), 1458 (w), 1437 (w), 1371 (s), 1337 (m), 1316 (m), 1235 (m), 1182 (w), 1148 (m), 1073 (m), 1054 (m), 963 (w), 903 (m), 825 (m), 774 (m), 720 (m), 710 (m), 670 (w), 656 (m), 630 (m), 522 (s), 463 (s) cm^{-1}. ^{1}H NMR ([D$_6$]DMSO): δ = 7.8 (s, 2H, $N^+{-}N{-}C{-}NH_2$), 6.4 (s, 2H, $N^+{-}C{-}NH_2$), 6.0 (s, 2H, $N{-}NH_2$), 5.6 (s, 2H, $N^+{-}NH_2$). ^{13}C NMR ([D$_6$]DMSO): δ = 148.9 (1C, $NH_2{-}N{-}C{-}N^+{-}NH_2$), 147.4 (1C, $NH_2{-}N{-}C{-}N$). MS (ESI$^+$): *m*/*z* = 130.2 ($C_2N_7H_8^+$); MS (ESI$^-$): *m*/*z* = 62.0 (NO_3^-). $C_2H_8N_8O_3$ (192.14): calcd. C 12.50, H 4.20, N 58.32; found C 13.20, H 4.17, N 57.40. BAM impact: 7.0 J; BAM friction: 8.4 N.

4.6. 1,2,3,4-Tetraamino-1,3,5-triazolium Perchlorate (4). Silver perchlorate (0.208 g, 1.00 mmol) was dissolved in a minimal amount of water (10 mL). Bromide salt **2** (0.204 g, 0.97 mmol) was dissolved in a separate container in a minimal amount of water (10 mL). The two solutions were combined and stirred overnight at 40 °C in darkness. The solution then underwent a Celite filtration. The filtrate was allowed to evaporate to dryness to yield 0.199 g, 0.87 mmol of perchlorate salt **3** (yield = 89%). TGA: 171 °C (dec.). IR: $\tilde{\nu}$ = 3439 (m), 3408 (m), 3376 (m), 3364 (m), 3288 (m), 3153 (w), 1730 (m), 1651 (s), 1614 (m), 1463 (m) 1346 (w), 1245 (w), 1154 (w), 1063 (s), 942 (m), 910 (m), 862 (m), 771 (s), 715 (s), 657 (m), 619 (s), 562 (s), 469 (m) cm^{-1}. ^{1}H NMR ([D$_6$]DMSO): δ = 7.8 (s, 2H, $N^+{-}N{-}C{-}NH_2$), 6.4 (s, 2H, $N^+{-}C{-}NH_2$), 6.0 (s, 2H, $N{-}NH_2$), 5.6 (s, 2H, $N^+{-}NH_2$). ^{13}C NMR ([D$_6$]DMSO): δ = 148.9 (1C, $NH_2{-}N{-}C{-}N^+{-}NH_2$), 147.4 (1C, $NH_2{-}N{-}C{-}N$). MS (ESI$^+$): *m*/*z* = 130.2 ($C_2N_7H_8^+$); MS (ESI$^-$): *m*/*z* = 98.9 (ClO_4^-), 327.9 ($(C_2N_7H_8)(ClO_4)_2^-$). $C_2H_8N_7ClO_4$ (229.58): calcd. C 10.46, H 3.51, N 42.71; found C 10.62, H 3.54, N 40.91. BAM impact: 6.0 J; BAM friction: 11.2 N.

4.7. 1,2,3,4-Tetraamino-1,3,5-triazolium Nitrotetrazolate (5). Sodium nitrotetrazolate dihydrate (0.200 g, 1.16 mmol) and silver nitrate (0.199 g, 1.17 mmol) were dissolved in water (20 mL) and stirred for 2 h in the dark. Silver nitrotetrazolate (0.193 g, 0.87 mmol) was collected and dried via vacuum filtration (yield = 75.3%). Bromide salt (0.166 g, 0.79 mmol) **2** was dissolved in water (10 mL). The silver nitrotetrazolate was added slowly into the solution and stirred overnight at 40 °C in darkness. The solution then underwent a Celite filtration. The filtrate was allowed to evaporate to dryness to yield the hydrated nitrotetrazolate salt **5**. The hydrated salt was then baked under vacuum for 24 h and redissolved in methanol. Anhydrous

5 (0.089 g, 0.36 mmol) was obtained by letting the methanol solution evaporate to dryness slowly (yield = 46%). DSC: 137 °C (dec.). IR: $\tilde{\nu}$ = 3360 (w), 3230 (m), 3139 (w), 2999 (w), 2951 (w), 2846 (w), 2458 (w), 1722 (m), 1660 (s), 1635 (m), 1573 (w), 1532 (s), 1504 (m), 1457 (w), 1439 (s), 1418 (s), 1358 (w), 1342 (w), 1317 (s), 1239 (w), 1183 (m), 1168 (m), 1152 (w), 1118 (w), 1079 (w), 1051 (w), 1030 (w), 946 (w), 900 (m), 839 (s), 759 (m), 735 (m), 701 (m), 672 (m), 623 (m), 596 (s), 528 (s), 451 (m) cm^{-1}. ^1H NMR ([D_6]DMSO): δ = 7.8 (s, 2H, $N^+{-}N{-}C{-}NH_2$), 6.4 (s, 2H, $N^+{-}C{-}NH_2$), 6.0 (s, 2H, $N{-}NH_2$), 5.6 (s, 2H, $N^+{-}NH_2$). ^{13}C NMR ([D_6]DMSO): δ = 169.2 (1C, $N{-}C{-}NO_2$), 148.9 (1C, $NH_2{-}N{-}C{-}N^+{-}NH_2$), 147.4 (1C, $NH_2{-}N{-}C{-}N$). MS (ESI^+): m/z = 130.2 ($C_2N_7H_8^+$); MS (ESI^-): m/z = 114.0 ($CN_5O_2^+$), 228.8 ($H{-}(CN_5O_2)_2^+$). $C_3H_8N_{12}O_2$ (244.17): calcd. C 14.76, H 3.30, N 68.84; found C 14.83, H 3.21, N 68.49. BAM impact: 2.0 J; BAM friction: 8.0 N.

4.8. 1,2,3,4-Tetraamino-1,3,5-triazolium Bistetrazole Diolate Dihydrate (6). Diammonium bistetrazolate diolate (0.195 g, 0.96 mmol) and silver nitrate (0.327 g, 1.93 mmol) were dissolved in water and stirred for 2 h. The resultant precipitant silver bistetrazole diolate was collected and dried via vacuum filtration (0.260 g, 0.73 mmol). The silver bistetrazole diolate (0.242 g, 0.68 mmol) was redissolved in hot water (50 °C). Bromide salt **2** (0.280 g, 1.33 mmol) was dissolved in a separate container in a minimal amount of water. The two solutions were combined and stirred overnight at 40 °C in darkness. The solution then underwent a Celite filtration. The filtrate was allowed to evaporate and then dried under vacuum to yield 0.243 g (0.52 mmol) of the bistetrazole diolate salt **6** (yield = 78%). TGA: 100 °C (H_2O removal), 186 °C (dec.). IR: $\tilde{\nu}$ = 3334 (m), 3279 (m), 3220 (m), 3113 (m), 2955 (w), 2927 (w), 2850 (w), 1740 (m), 1660 (s), 1626 (m), 1524 (w), 1454 (m), 1411 (m), 1349 (m), 1266 (w), 1228 (m), 1174 (m), 1130 (m), 1100 (m), 1056 (m), 997 (m), 944 (w), 865 (m), 771 (m), 735 (s), 714 (m), 689 (m), 659 (m), 630 (s), 619 (s), 562 (s), 495 (s), 468 (s) cm^{-1}. ^1H NMR ([D_6]DMSO): δ = 7.8 (s, 2H, $N^+{-}N{-}C{-}NH_2$), 6.5 (s, 2H, $N^+{-}C{-}NH_2$), 6.0 (s, 2H, $N{-}NH_2$), 5.7 (s, 2H, $N^+{-}NH_2$). ^{13}C NMR ([D_6]DMSO): δ = 148.9 (1C, $NH_2{-}N{-}C{-}N^+{-}NH_2$), 147.4 (1C, $NH_2{-}N{-}C{-}N$) 134.4 (2C, $N{-}C{-}C{-}N$). MS (ESI^+): m/z = 130.2 ($C_2N_7H_8^+$); MS (ESI^-): m/z = 169.0 ($C_2N_7HO_2^-$). $C_4H_{10}N_{15}O_3$ (316.22): calcd. C 15.19, H 3.19, N 66.44; found C 16.10, H 4.32, N 67.68. BAM impact: >40 J; BAM friction: 14.4 N.

■ ASSOCIATED CONTENT

SI Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acs.inorgchem.1c00877.

IR, ^1H NMR, ^{13}C NMR, ^{15}N NMR, DSC-TGA, and MS spectra (PDF)

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CCDC 2063169−2063173 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/data_request/cif, or by emailing data_request@ccdc.cam.ac.uk, or by contacting The Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033.

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Notes

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