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triazole†

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PAPER

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High-density energetic salts that contain nitrogen-rich anions and the 1-amino-1,2,3-triazole (ATZ) or 3-methyl-1-amino-1,2,3-triazole (MAT) cation were synthesized. All salts were fully characterized by IR spectroscopy, multinuclear (¹H, ¹³C) NMR spectroscopy, differential scanning calorimetry (DSC), and impact sensitivity. 1-Amino-1,2,3-triazolium 5-nitrotetrazolate, 3-methyl-1-amino-1,2,3-triazolium 5-nitrotetrazolate, and 3-methyl-1-amino-1,2,3-triazolium azotetrazolate crystallize in the triclinic space group $P\bar{I}$, as determined by single-crystal X-ray diffraction. Their densities are 1.688, 1.588, and 1.550 g cm⁻³, respectively. The measured densities of the other organic energetic salts range between 1.56 and 1.86 g cm⁻³. The detonation pressure (*P*) values calculated for these salts range from 21.2 to 37.3 GPa, and the detonation velocities (*D*) range from 7239 to 9082 m s⁻¹, making the salts potentially energetic materials.

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Energetic salts based on 1-amino-1,2,3-triazole and 3-methyl-1-amino-1,2,3-

Introduction

As controllable storage systems for relatively large amounts of chemical energy, energetic materials are widely applied in military and industrial venues. In the last decade, a unique class of high energetic compounds composed of nitrogen-containing heterocyclic anions and/or cations has been developed to meet the continuing need for improved energetic materials.¹⁻⁵ Recently, salt-based molecules have been reported to display attractive energetic properties because of special properties of ionic compounds, such as lower vapor pressures and higher densities compared with those of their atomically similar nonionic analogues.⁶⁻¹⁴ The present research is mainly directed toward the synthesis of new organic cations and anions, which exhibit high safety, performance, density, and stability.

Five-membered nitrogen-containing heterocycles are traditional sources of energetic materials; energetic salts based on C/N heteroaromatic rings with high nitrogen content (such as triazole and tetrazole) are at the forefront of high energy research.¹⁵⁻¹⁸ 1*H*-1,2,4-Triazole, 4-amino-1,2,4-triazole, and 1*H*-1,2,3-triazole were utilized to produce energetic ionic salts.^{19,20} 1,2,3-Triazole (272 kJ mol⁻¹) and 1,2,4-triazole (109 kJ mol⁻¹) have positive heats of formation. Respectively, the salts comprising protonated triazole cations paired with percholate, nitrate, or dinitramide anions were initially synthesized.^{19,21}

The incorporation of amino groups into a heterocyclic triazole ring is one of the simplest routes for enhancing thermal stability.²² The N-amino group behaves as an electron-withdrawing group in these high-nitrogen heterocycles when forming energetic salts. Many 4-amino-1,2,4-triazole and 1-methyl-4amino-1,2,4-triazole salts have already been reported.23-25 Meanwhile, salts based on 1,2,3-triazole series may possess more positive heats of formation than do salts of 1,2,4-triazole series. Studies on the chemistry and properties of energetic salts containing the former are limited possibly because of the difficulty in the purification of 1-amino-1,2,3-triazole. Although Drake et al.²⁶ reported the preparation of 3-methyl-1-amino-1,2,3-triazolium nitrate, neither the detonation performance nor impact sensitivity of the compounds were provided. A simplified process for purification of 1-amino-1,2,3-triazole (ATZ) was developed in our previous studies,^{27,28} then we investigated the energetic salts based on ATZ.

ATZ may be protonated by strong mineral acids, an approach that has been employed using classic energetic and oxidizing anions, such as NO_3^- (a) (Scheme 1). ATZ can also be quaternized at N-3 by reaction with equivalent amounts of methyl iodides under neat conditions to produce 3-methyl-1-amino-1,2,3-triazole (MAT). Compared with ATZ, MAT has an extra methyl group. Particularly, the introduction of a methyl group decreases the enthalpies of formation and densities of such compounds, as well as desensitizes them. In the present work, a series of high-nitrogen salts based on ATZ and MAT were prepared and characterized. Their thermal stabilities, detonation performance, and impact sensitivities were also investigated.

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Scheme 1 The anions we choose to pair with ATZ and MAT.

Results and discussion

Synthesis

As shown in Scheme 2, compounds 2 and 5 were prepared by treating 1-amino-1,2,3-triazole with nitric acid and nitroform (d), respectively. Given that 5-nitro-tetrazole (b) and 5-nitroimino-tetrazole (c) (Scheme 1) are strong acids (c was characterized as a dibasic acid with pK_a values of 2.5 and 6.1),²⁹ they can easily protonate ATZ and form energetic nitrogen rich salts. We also attempted to synthesize salt 6 by anion exchange between 1-amino-1,2,3-triazolium sulfate and barium azotetrazolate or anion exchange between 1-amino-1,2,3-triazolium sulfate and barium hydrochloride and silver azotetrazolate, but no desired product was formed possibly because barium azotetrazolate or silver azotetrazolate decomposes in acidic media.³⁰

Synthesis of the salts based on 3-methyl-1-amino-1,2,3-triazole was performed according to Scheme 3. Compounds 8–11 were prepared from the anion exchange of silver nitrate, silver 5-nitrotetrazolate, silver 5-nitroiminotetrazolate and silver nitroformate with 1-amino-1,2,3-triazolium iodide in methanol. Compound 12 was synthesized by anion exchange between 3-methyl-1-amino-1,2,3-triazolium sulfate and barium azote-trazolate in methanol.



Scheme 2 Synthesis of the energy salts based on 1-amino-1,2,3-triazole.



Scheme 3 Synthesis of the energy salts based on 3-methyl-1-amino-1,2,3-triazole.

X-Ray crystallography

Compounds **3**, **9**, and **12** have been characterized using single crystal X-ray structure determination. Data collection was performed, and the unit cell was initially refined using APEX2 [v2.1-0].³¹ Data reduction was performed using SAINT [v7.34A]³² and XPREP [v2005/2].³³ Corrections were applied for Lorentz, polarization, and absorption effects using SADABS [v2004/1].³⁴ The structures were solved and refined with the aid of the programs in the SHELXTL-plus [v6.12] system of programs.³⁵ The full-matrix least-squares refinement on F2 included atomic coordinates and anisotropic thermal parameters for all non-H atoms. The H atoms were included using a riding model. Table 1 summarizes a selection of crystallographic data and refinement details. A comparison of selected bond lengths and angles of compounds **3**, **9** and 1-amino-1,2,3-triazole is given in Table 2. Selected bond lengths and angles of compound **12** are given in Table 3.

As expected and found in several selected structures including 1-amino-1,2,3-triazole³⁶ and its salts (**3**) and 3-methyl-1-amino-1,2,3-triazole salts (**9** and **12**) discussed in this work, the triazole ring is nearly planar, building an aromatic system, which can be seen at the torsion angle of triazole ring between $-0.247(192)^{\circ}$ and $0.611(131)^{\circ}$. The ring moieties of **3**, **9** and **12** are in agreement with the geometry observed for 1,2,3-triazole. The N–N bond lengths in triazole ring of all structures of **3**, **9**, **12** lie between 1.314 and 1.334 Å, which are typical values observed for the 1,2,3-triazole and their cations. We observed that, for the N–N bond lengths, neutral compounds 1-amino-1,2,3-triazole (1.316 Å)³⁶ are slightly shorter than their salts and their methylated salts (between 1.319 and 1.331 Å).

Compound **3** crystallizes in the monoclinic space group P2(1) with eight molecules in the unit cell (Fig. 1a), and has a density of 1.688 g cm⁻³ (at 93(2) K) (Table 2). The C–N and N–N bonds of the triazole ring are in a range similar to that observed in 1,2,3-triazole. The N1–NH₂ distances (1.3372 Å) in compound **3** are found to be shorter than the N1–NH₂ distances (1.398 Å) in 1-amino-1,2,3-triazole. The triazole ring [torsion angle N11–N12–N13–C4 0.176(185)°] is planar. In contrast to this, the amino unit [torsion angle N11–N12–N13–N14–172.435(141)°]

Table 1	Crystal data and	structure refinement	details of 3,	9, and 12
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Crystal	3	9	12
Empirical formula	$C_3H_5N_9O_2$	$C_4H_7N_9O_2$	$C_8H_{14}N_{18}$
Temperature/K	93(2)	93(2)	133(2)
Wavelength/Å	0.71073	0.71073	0.71073
Crystal system	Monoclinic	Triclinic	Monoclinic
Space group	<i>P</i> 2(1)	Pl	P2(1)/c
Unit cell dimensions	$a = 9.813(2)$ Å, $\alpha = 90^{\circ}$ $b = 10.246(2)$ Å, $\beta = 90.405(4)^{\circ}$ $c = 15.592(4)$ Å, $\gamma = 90^{\circ}$	$a = 7.736(7)$ Å, $\alpha = 100.16(1)^{\circ}$ $b = 9.684(9)$ Å, $\beta = 98.07(1)^{\circ}$ $c = 12.512(11)$ Å, $\gamma = 100.74(1)^{\circ}$	$a = 5.681(16)$ Å, $\alpha = 90^{\circ}$ $b = 7.222(2)$ Å, $\beta = 97.778(4)^{\circ}$ $c = 19.096(6)$ Å, $\gamma = 90^{\circ}$
Volume/Å ³	1567.6(6)	891.8(14)	776.3(4)
Z	8	4	2
Calculated density/g cm ⁻³	1.688	1.588	1.550
Absorption coefficient/mm ⁻¹	0.142	0.131	0.117
$F(000)^{1}$	816	440	376
Crystal size/mm	0.37 imes 0.27 imes 0.08	0.30 imes 0.17 imes 0.09	$0.40 \times 0.33 \times 0.20$
θ range for data collection	3.15° to 27.48°	3.15° to 27.48°	3.15° to 27.48°
Limiting indices	$-12 \le h \le 12, -12 \le k \le 13,$	$-9 \le h \le 9, -11 \le k \le 8,$	$-7 \le h \le 7, -9 \le k \le 8,$
	$-15 \le l \le 20$	$-14 \le l \le 14$	$-24 \le l \le 24$
Reflections collected/unique Completeness to $\theta = 27.73$	12 990/3774 [$R(int) = 0.0292$] 99.2%	6375/3388 [R(int) = 0.0436]	5842/1760 [R(int) = 0.0236]
Max, and min. transmission	0.9887 and 0.9496		
Reflections with $I > 2\sigma(I)$	3160	2052	1489
Goodness-of-fit on F^2	0.998	0.999	1.002
Final <i>R</i> indices $(I > 2\sigma(I))$	R1 = 0.0453, w $R2 = 0.0910$	R1 = 0.0472, w $R2 = 0.0995$	R1 = 0.0353, w $R2 = 0.0884$
R indices (all data)	R1 = 0.0538, wR2 = 0.0956	R1 = 0.0765, wR2 = 0.1054	R1 = 0.0450, wR2 = 0.0935
CCDC	842816	837299	837300

Table 2Selected bond lengths (Å) and bond angles (°) of compounds 3,9 and 1-amino-1,2,3-triazole(ATZ)

	3	9	ATZ
Bond lengths			
N(1)-C(1)	1.3242	1.3300	
N(1) - N(2)	1.3346	1.3419	
N(2) - N(3)	1.3277	1.3388	
N(3)–N(4)	1.3417	1.3511	
N(4)-C(1)	1.3186	1.3166	
N(5)-C(1)	1.4426	1.4472	
N(5)–O(1)	1.2374	1.228	
N(5)–O(2)	1.2169	1.2296	
C(3) - C(4)	1.3591	1.3693	1.359
C(3)–N(11)	1.3433	1.3480	1.363
N(11)–N(12)	1.3305	1.3190	1.316
N(12) - N(13)	1.3156	1.3264	1.345
N(13)–N(14)	1.3772	1.4038	1.398
N(13)–C(4)	1.3590	1.3469	1.343
Bond angles			
C(1)-N(1)-N(2)	103.629	102.744	
N(1)-N(2)-N(3)	109.065	109.711	
N(2)-N(3)-N(4)	109.969	109.237	
N(3)-N(4)-C(1)	102.900	102.947	
N(1)-C(1)-N(4)	114.435	115.358	
N(5)–C(1)–N(4)	123.875	122.175	
O(2)-N(5)-C(1)	118.638	117.108	
O(2)–N(5)–O(1)	124.952	124.480	
C(4)-C(3)-N(11)	106.273	105.631	
C(3)–N(11)–N(12)	112.454	113.024	
N(11)–N(12)–N(13)	103.458	103.211	
N(12)-N(13)-C(4)	113.244	113.468	
N(13)-C(4)-C(3)	104.571	104.655	
N(12)–N(13)–N(14)	119.091	121.441	
N(13)–N(14)–H(14A)	107.824	107.497	
N(13)–N(14)–H(14B)	110.084	107.483	

Table 3 Selected bond lengths (Å) and bond angles (°) of compound 12

Bond lengths			
N(1)-C(1)	1.3352	N(6)-C(3)	1.3374
N(1) - N(2)	1.3373	N(6) - N(7)	1.3343
N(2)–N(3)	1.3324	N(7) - N(8)	1.3141
N(3) - N(4)	1.3414	N(8)–N(9)	1.3938
N(4) - C(1)	1.3392	N(8) - C(2)	1.3471
N(5) - C(1)	1.4059	C(2) - C(3)	1.3624
N(5)–N(5)	1.2629	C(4) - N(6)	1.4602
Bond angles			
N(1)-N(2)-N(3)	109.175	C(2)-C(3)-N(6)	105.868
N(2)-N(3)-N(4)	109.761	C(3) - N(6) - N(7)	112.627
N(3)-N(4)-C(1)	103.892	N(6)-N(7)-N(8)	103.156
N(4)-C(1)-N(1)	112.616	N(7)-N(8)-C(2)	113.423
C(1)-N(1)-N(2)	104.555	N(8)-C(2)-C(3)	104.921
N(1)-C(1)-N(5)	118.962	N(7)–N(8)–N(9)	118.743
C(1)–N(5)–N(5)	112.845	N(7)–N(6)–C(4)	119.745

is slightly bent from the ring plane. The packing of 3 is also characterized by a three-dimensional network. The packing structure of 3 is shown in Fig. 1b.

The colorless crystals of **9** were grown by slow evaporation of a diethyl ether solution. The unit cell of **9** crystallizes with a calculated density of 1.588 g cm⁻³ (93(2) K) in the triclinic space group $P\bar{1}$. The triazole ring of **9** is nearly planar and four similar bond lengths are observed [N11–N12 1.319 Å, N12–N13 1.326 Å, N11–C3 1.348 Å, N13–C4 1.347 Å] and shows the delocalization of the positive charge from the ring (Fig. 2). The main change observed is the bond length of C3–C4 which corresponds to the N3.

Nitrogen atom undergoes protonation in 1-amino-1,2,3-triazole. Protonation results in a shortening of the C3–N11 distances (\sim 0.015 Å) and a lengthening of the C3–C4 bond



Fig. 1 (a) View of the molecular unit of **3**. Thermal ellipsoids represent 50% probability. (b) Unit cell packing of **3** (ATZ.NT 1-amino-1,2,3-triazolium 5-nitrotetrazolate).

(~0.01 A). These distances are considerably longer than C3–C4 double bonds (1.326 Å) but significantly shorter than the N13–N14 (1.404 Å) single bond. The amino and methyl unit lies in the plane of the triazole ring as clearly shown by the N11–N12–N13–N15 torsion angle of -177.43° and N13–N12–N11–C5 torsion angle of 179.27°.

3-Methyl-1-amino-1,2,3-triazolium azotetrazolate 12 crystallizes in the monoclinic crystal system in the space group P2(1)/c. By including two molecular moieties in the unit cell, the calculated density is 1.550 g cm^{-3} . In general, the azo-tetrazolate anions have geometries found in dihydrazinium azotetrazolate.37 Two tetrazole anions in the molecule exhibit coplanar geometry with torsion angle C1-N5-N5-C1 180.00 (99)°. This cation is nearly planar with torsion angle (N6-N7-N8-C2 -0.694(131)°) and C-N and N-N bond lengths observed between 1.314 and 1.347 Å (Fig. 3a). The negative charge is delocalized as supported by similar C-N bond lengths C1-N1 = 1.335(16) Å, C1-N41.339(17) A and a planar system, and shows the delocalization of the negative charge from the ring (Fig. 3a). Delocalization results in a shortening of the N5-N5 distances. The distances are considerably longer than N-N double bonds (1.232 Å) but significantly shorter than the N8-N9 (1.3938 Å) single bond. The packing structure of 12 is shown in Fig. 3b.



Fig. 2 (a) View of the molecular unit of **9**. Thermal ellipsoids represent 50% probability. (b) Unit cell packing of **9** (MAT.NT 1-amino-1,2,3-triazolium 5-nitrotetrazolate).

Physicochemical properties

The melting points, thermochemical, and energetic data of 2-5 and 8-12 are summarized in Table 4. The melting points of these new compounds (except for 4, 5, and 12) are below 100 °C, the accepted boundary between ionic liquids and melting salts.³⁸ The



Fig. 3 (a) View of the molecular unit of **12**. Thermal ellipsoids represent 50% probability. (b) Unit cell packing of **12** (MAT.NT 1-amino-1,2,3-triazolium 5-nitrotetrazolate).

Table 4 The physicochemical properties of 2-5 and 8-12 compared with TNT and RDX

Salt	$T_{\rm m}{}^a$	$T_d^{\ b}$	$d_{\rm c}{}^c/d_{\rm m}{}^d$	OB ^e	N^{f}	$\Delta H_{ m c}^{ m og}$	$\Delta H_{ m a}^{ m oh}$	$\Delta H_{ m L}^{{ m o}i}$	$\Delta H_{\rm f}^{{ m o}j}/\Delta H_{ m m}^{{ m o}k}$	P^{l}	D^m	IS ⁿ
2	98.6	177 7	1 64/1 75	-16	47.6	972.1	-306.4	546 5	119 3/0 81	30.5	8366	21.5
3	98.8	200.8	1.69/1.69	-28	63.3	972.1	112.8	507.8	577.1/2.90	27.0	7948	3.1
4	112.2	162.8	1.60/1.72	-43	65.8	972.1	386.1	1287.6	1042.7/3.50	28.9	8187	5.7
5	132.6	152.3	1.77/1.86	3.4	41.7	972.1	-247.7	492.1	232.3/0.99	37.3	9082	
8	87.0	241.8	1.59/1.59	-35	43.5	951.6	-306.4	528.8	116.4/0.72	23.7	7596	28.9
9	92.6	224.3	1.59/1.59	-41	59.2	951.6	112.8 (ref. 60)	490.4	574.0/2.70	23.1	7509	3.4
10	89.6	197	1.56/1.57	-59	60.1	951.6	386.1	1232.4	1056.8/3.24	23.0	7524	6.9
11	82.2	176.5	1.57/1.70	-10	39.4	951.6	-247.7	469.8	234.1/0.94	29.7	8320	
12	144.6	182.9	1.56/1.56	-66	69.6	951.6	744.6	1184.0	1463.7/4.04	21.2	7239	28.2
TNT ⁶¹	80.4	295	1.65	-25	18.5	_	_		95.3/0.42	19.5	6881	15
RDX ⁶²	204.1	230	1.82	0	37.8		_		83.8/0.38	35.2	8977	7.4

^{*a*} Melting point (°C). ^{*b*} Decomposition temperature (°C). ^{*c*} Calculated density (g cm⁻³). ^{*d*} Measured density (g cm⁻³), using an ULTRAPYC 1200, Automatic Density Analyzer. ^{*e*} CO oxygen balance (OB) is an index of the deficiency or excess of oxygen in a compound required to convert all C into CO and all H into H₂O. For a compound with the molecular formula of $C_aH_bN_cO_d$ (without crystal water), OB (%) =1600[(d - a - b/2)/ M_w], M_w molecular weight of the salt. ^{*f*} Nitrogen content (%). ^{*g*} Molar enthalpy of the formation of cation (kJ mol⁻¹). ^{*h*} Molar enthalpy of the formation of anion (kJ mol⁻¹). ^{*i*} Lattice energy (kJ mol⁻¹). ^{*j*} Molar enthalpy of the formation of salt (kJ mol⁻¹). ^{*k*} Enthalpy of the formation of salt per gram (kJ g⁻¹). ^{*l*} Detonation pressure (GPa). ^{*m*} Detonation velocity (m s⁻¹). ^{*n*} Impact sensitivity (J).

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low melting point salts show good liquid state characteristics (compounds **2**, **3**, **8**, **9**, **10**, and **11**; Table 4). Ionic liquids **2–5** have a similar 1-amino-1,2,3-triazolium cation and compounds **8–12** have a similar 3-methyl-1-amino-1,2,3-triazolium cation. Nitrotetrazolate samples **3** and **9** melt at 98.8 and 92.6 °C, respectively. For the salts with the same cations, the melting points of MAT ionic liquids (**8–12**) are generally lower than those of ATZ ionic liquids (**2–5**). The methyl group clearly helps to decrease the melting point. In comparison with 1,2,3-triazolium nitrate (Mp 110 °C),¹⁹ 1-amino-1,2,3-triazolium nitrate has lower melting point (98.8 °C). Therefore, incorporating amino groups as well as a methyl group into a heterocyclic triazole ring can decrease melting point.

Except for compound 5, which begins to decompose at 152.3 °C, the decomposition temperatures of the other salts are higher than 160 °C, showing that they are thermally stable energetic materials.³⁹ Their possible liquid ranges may reach 100 °C. In comparison with 1,2,3-triazolium nitrate, 1-amino-1,2,3-triazolium nitrate is more thermally stable (the decomposition temperature of 1,2,3-triazolium nitrate is 125 °C¹⁹ and that of 1-amino-1,2,3-triazolium nitrate is 177.7 °C). These indicate that incorporating amino groups into a heterocyclic triazole ring can also enhance thermal stability.

One of the most important physical properties of a solid energetic material is its density. The calculated and measured densities are summarized in Table 4. The densities of the ATZ and MAT salts range from 1.56 to 1.86 g cm⁻³ while salt **5** exhibiting the highest value. The measured density of 3-methyl-1-amino-1,2,3-triazolium nitrate is 1.59 g cm⁻³ while that of 1-methyl-4-amino-1,2,4-triazolium nitrate is 1.55 g cm⁻³.²³ The physical densities of 1-amino-1,2,3-triazolium salts are also higher than those of 4-amino-1,2,4-triazolium nitrate is 1.60 g cm⁻³,¹⁹ whereas that of 1-amino-1,2,3-triazolium nitrate is 1.75 g cm⁻³. The density of 1-amino-1,2,3-triazolium nitroformate (1.86 g cm⁻³) is higher than that of 4-amino-1,2,4-triazolium nitroformate (1.62 g cm⁻³)²⁵ possibly because 1,2,3-triazolium nitroformat

The heat of formation is another important parameter in evaluating the performance of energetic salts. This property of

the salts can be calculated with good accuracy (including the heat of formation of the cation and anion, and the lattice energy of salts).^{41–45} The heats of formation of these MAT and ATZ anions were calculated. Calculations were carried out using the Gaussian 03 suite of programs.⁴⁶ The geometric optimization of the structures and frequency analyses were carried out using B3-LYP functional with the 6-31 + G** basis set,⁴⁷ and single-point energies were calculated at the MP2/6-311++G** level. All of the optimized structures were characterized to be true local energy minima on the potential-energy surface without imaginary frequencies.

Based on the Born–Haber energy cycle, heats of formation of ionic salts can be simplified by eqn (1):

$$\Delta H_{\rm f}^{\rm o} (\text{ionic salts}, 298 \text{ K}) = \Sigma \Delta H_{\rm f}^{\rm o} (\text{cation}, 298 \text{ K}) + \Sigma \Delta H_{\rm f}^{\rm o} (\text{anion}, 298 \text{ K}) - \Delta H_{\rm L}$$
(1)

in which $\Delta H_{\rm f}^{\rm o}$ is the lattice energy of the ionic salts, which could be predicted by using the formula suggested by Jenkins *et al.*⁴⁸

$$\Delta H_{\rm L} = U_{\rm POT} + [p({\rm nM}/2 - 2) + q({\rm nX}/2 - 2)]{\rm RT}$$
(2)

in which nM and nX depend on the nature of the ions Mp⁺ and Xq⁻, respectively, and are equal to 3 for monoatomic ions, 5 for linear polyatomic ions, and 6 for nonlinear polyatomic ions. The equation for lattice potential energy U_{pot} has the form [eqn (3)]:

$$U_{\rm POT} \,({\rm kJ} \,\,{\rm mol}^{-1}) = \gamma (\rho_{\rm m}/M_{\rm m})^{1/3} + \delta$$
 (3)

in which $\rho_{\rm m}$ is the density (g cm⁻³) and $M_{\rm m}$ is the chemical formula mass of the ionic material (g), and the coefficients γ (kJ mol⁻¹ cm) and δ (kJ mol⁻¹) are assigned literature values.⁴⁸ The heats of formation of the cations were computed by using isodesmic reactions.⁴⁹ The heats of formation of the anion and the parent ions in the isodesmic reactions were calculated from protonation reactions ($\Delta H_{\rm f}^{0}({\rm H}^{+}) = 1528$ kJ mol⁻¹).^{49–51}

The enthalpies of the isodesmic reactions (ΔH_{r298}°) were obtained by combining the MP2/6-311++G** energy differences for the reactions, the scaled zero-point energies (B3LYP/6-31 + G**), and other thermal factors. The calculated heats of formation are summarized in Table 4. Salt **12** has the highest

value at 1463.7 kJ mo1⁻¹. The calculated heat of formation of the ATZ anion is 972.1 kJ mol⁻¹ and that of the MAT anion is 951.6 kJ mol⁻¹. All of the ATZ and MAT salts exhibit positive heats of formation, with **12** having the highest at 4.04 kJ g⁻¹ (RDX: 0.42 kJ g⁻¹; HMX: 0.38 kJ g⁻¹). For salts with the same anions, the ATZ salts show higher heats of formation than do the MAT salts (*e.g.*, **3**, 577.1 kJ mol⁻¹ versus **9**, 574 kJ mol⁻¹).

The detonation parameters were calculated by Kamlet–Jacobs (K–J) equations.^{40,49,52,53} Table 4 shows that for salts **2–5** and **8–12**, the calculated detonation pressures (*P*) fall in the range 21.2–37.3 GPa, which is comparable to that of TNT (19.5 GPa) and RDX (35.2 GPa). The detonation velocities (*D*) range from 7239 m s⁻¹ (comparable to TNT, 6881 m s⁻¹) to 9082 m s⁻¹ (comparable to RDX, 8977 m s⁻¹).

Sensitivity deserves closer attention by researchers because this is closely linked with the safety of handling and applying explosives. In the present study, impact sensitivity was tested on a type 12 tooling according to the "up and down" method. Listed in Table 4 are the impact sensitivities of sensitive compounds 3, 4, 9, and 10 (ranging between 3 and 6 J) as well as those of relatively less sensitive compounds 2, 8, and 12 (between 20 and 30 J). Because of the extremely deliquescent nature of compounds 5 and 11, the sensitivity tests could not be carried out with accuracy given that water is extremely efficient at reducing the sensitivity of energetic materials. The properties of the new ATZ and MAT salts were compared; ATZ salts have superior detonation properties because methyl groups have a significant negative effect on density. Incorporating methyl groups into 1-amino-1,2,3-triazole rings can also lead to enhanced thermal stability and lower impact sensitivity compared with that observed for 1-amino-1,2,3-triazolium salts.

These ATZ and MAT compounds have high nitrogen content, some of them exceeding 50% and reaching as high as 60%. Polynitrogen compounds are of significant interest as high-energy materials for propulsion or explosive applications.^{54–59} In the past several years, a large number of salts with polyazide cations have presented considerable competitiveness as materials with the highest nitrogen content.^{3,54–59} Compared with such compounds, however, the ATZ and MAT salts have superior thermal stabilities, suggesting promise for practical applications.

Conclusions

A family of energetic salts based on nitrogen-rich anions and the ATZ or MAT cation were prepared and fully characterized. The structures of 3, 9, and 12 were confirmed by single-crystal X-ray diffraction, which showed that there are extensive hydrogenbonding interactions between the cation and anion in these salts. The densities of the ATZ and MAT salts, measured with an automatic density analyzer (ULTRAPYC 1200), fall within the range 1.56(12) to $1.86 \,\mathrm{g \, cm^{-3}}(5)$, which places them in a class of relatively dense compounds. Using K-J equations, we calculated their detonation pressures and velocities; these fall in the range 21.2-37.3 GPa and 7239–9082 m s^{-1} , respectively. Salt 5, with a detonation pressure and velocity of 37.3 GPa and 9082 m s⁻¹, is comparable to HMX (35.2 GPa and 8977 m s⁻¹). Except for the impact sensitivities of 5 and 11, those of the ATZ and MAT salts range from 3 to 30 J. Based on rather high detonation properties and superior stabilities, the ATZ and MAT salts have potential as energetic materials.

Experimental

Caution: although we experienced no difficulties in handling these materials, with such high positive heats of formation some could be unstable. Therefore, all of them should be treated with care and with appropriate safety precautions.

General methods

All materials were commercially available and used as received. Melting point was determined using an XT4 microscope melting point apparatus. IR spectra were recorded by using KBr pellets for solids on a Bruker tensor 27 spectrometer. ¹H and ¹³C NMR spectra were recorded on a Bruker 400 MHz spectrometer operating at 400 MHz, respectively, with [D₆]-DMSO as the locking solvent unless otherwise stated. ¹H and ¹³C NMR chemical shifts are reported in ppm relative to TMS. DSC measurements were performed on a TA-DSC Q2000 calorimeter equipped with an Autocool accessory, and calibrated by using indium. Measurements were carried out by heating from 50 °C. Densities were measured by using an Automatic Density Analyzer, ULTRAPYC 1200. Detonation pressure and velocity were predicted by the Kamlet-Jacobs equations. Computations were performed by using the Gaussian 03 (Revision D.01) suites of programs.⁴⁶ We used the B3LYP/6-31G** method to calculate the molecular volumes for the energetic triazolium salts. The volume of each ion was defined as inside a contour of 0.001 electrons bohr⁻³ density that was evaluated using a Monte Carlo integration. The geometric optimization and the frequency analyses were carried out using B3LYP functional analyses with the 6-311 + G** basis set.⁴⁷ Single energy points were calculated at the MP2/6-311++G** level. All of the optimized structures were characterized to be true local energy minima on the potential energy surface without imaginary frequencies.

X-Ray crystallography

Crystals suitable for X-ray crystallographic analysis were obtained as mentioned above. The crystal structure was determined by a Rigaku RAXIS IP diffractometer and SHELXTL crystallographic software package of molecular structure. The single crystals of compounds **3**, **9**, and **12** were mounted on a Rigaku RAXIS RAPID IP diffractometer equipped with a graphite-monochromatized MoK α radiation ($\lambda = 0.71073$ Å). Data were collected by the ω scan technique. The structure was solved by direct methods with SHELXS-97 and expanded by using the Fourier technique. The non-hydrogen atoms were refined anisotropically. The hydrogen atom was determined with theoretical calculations and refined with an isotropic vibration factor.

1-Amino-1,2,3-triazole (1)

In a 500 mL round-bottom flask equipped with an over-head stirrer, 14.46 g (168 mmol) of glyoxal bishydrazone was dispersed in 225 mL acetonitrile at 20 °C. Manganese dioxide 30.00 g (348 mmol) was added portion-wise over a few minutes to the vigor-ously stirred solution. The reaction was stirred for 40 min while additional manganese dioxide 20.00 g (232 mmol) was added. Thin layer chromatography revealed through a plug of Celite.

The filtrate was stripped down under reduced pressure leaving a viscous oil that was sublimed, yielding 12.30 g (88%) of highly pure 1-amino-1,2,3-triazole (yield: 79.8%). Mp 49–50 °C; IR (KBr) v: 3292, 3123, 1624, 1482, 1319, 1224, 1171 cm⁻¹; ¹H NMR (acetonitrile- d_6) δ : 7.65 (s, 1H), 7.56 (s, 1H), 5.97 ppm (s, 2H); ¹³C NMR (acetonitrile- d_6) δ : 132.2, 124.0 ppm; Anal. calcd for C₂H₄N₄: C 28.57, H 4.80, N 66.64; found C 28.56, H 4.75, N 67.07%.

1-Amino-1,2,3-triazolium nitrate (2)

Acetonitrile (20 mL) was mixed with 1-amino-1,2,3-triazole (1.72 g, 20 mmol) and nitric acid (30 wt%, 4.2 g, 30 mmol). The mixture was stirred for 30 min at room temperature; the solvent was evacuated under vacuum to produce a white solid (**2**) (2.56 g), 87% yield. Mp 98.6 °C; IR (KBr): 3297, 3166, 2823, 2703, 1614, 1572, 1443, 1384, 1311, 1163, 1119, 1089, 1037, 932, 791, 691, 629 cm⁻¹; ¹H NMR (DMSO-*d*₆): δ : 8.12 (s, 1H), 7.72 (s, 1H), 9.7 ppm (s, 3H); ¹³C NMR (DMSO-*d*₆) δ : 132.44, 124.61 ppm.

1-Amino-1,2,3-triazolium 5-nitro-tetrazolate (3)

A 50 mL beaker was charged with 1-amino-1,2,3-triazole (0.50 g, 6 mmol), ether (20 mL), and 5-nitrotetrazole (0.68 g, 6 mmol). The mixture was stirred for 30 min at room temperature. The solvent was evacuated under vacuum to produce a white solid (3) in 97% yield (1.15 g). Mp 98.8 °C; IR (KBr): 3427, 3281, 3155, 3119, 1633, 1540, 1446, 1420, 1318, 1188, 1168, 1029, 924, 837, 800, 670 cm⁻¹; ¹H NMR (DMSO-*d*₆): δ : 8.75 (s, 1H), 8.58 (s, 1H), 8.28 (s, 1H), 4.23 ppm (s, 2H); ¹³C NMR (DMSO-*d*₆) δ : 185.24, 131.98, 127.32 ppm.

1-Amino-1,2,3-triazolium 5-nitroiminotetrazolate (4)

5-Nitroiminotetrazole (390 mg, 3 mmol) was dissolved in 20 mL ether, and 1-amino-1,2,3-triazole (504 mg, 6 mmol) was added to the solution. The mixture was stirred for 60 min at room temperature. After evaporation of the ether in vacuum, a poorly water-soluble white powder was obtained, which could be recrystallized from methanol to produce 861 mg of (2.89 mmol, 96% yield) **4**. Mp 112.2 °C; IR (KBr): 3279, 3189, 3151, 3097, 2986, 1614, 2886, 2842, 2750, 1535, 1489, 1433, 1389, 1348, 1325, 1230, 1157, 1091, 1029, 932, 867, 809, 690 cm⁻¹; ¹H NMR (acetone-*d*₆) δ : 7.23 (s, 6H), 7.75 (s, 2H), 7.87 ppm (s, 2H); ¹³C NMR (DMSO-*d*₆) δ : 179.32, 132.51, 120.76 ppm.

1-Amino-1,2,3-triazolium nitroformate (5)

A 50 mL beaker was charged with 1-amino-1,2,3-triazole (0.50 g, 6 mmol), methanol (20 mL), and nitroform (0.39 g, 3 mmol). The mixture was stirred for 30 min at room temperature. The solvent was evacuated under vacuum to yield a yellow solid, which could be recrystallized from methanol to produce compound **5** at 89% yield (0.87 g). Mp 132.6 °C; IR (KBr): 3407, 3252, 3142, 2807, 1621, 1547, 1465, 1403, 1192, 1084, 1050, 1032, 795, 697, 601, 509 cm⁻¹; ¹H NMR (acetone- d_6) δ : 9.21 (s, 3H), 8.14 (s, 1H), 8.09 ppm (s, 1H); ¹³C NMR (DMSO- d_6): δ : 150.36, 130.83, 125.31 ppm.

3-Methyl-1-amino-1,2,3-triazolium iodide (7)

1-Amino-1,2,3-triazole 5.00 g (59.5 mmoles) was dissolved and stirred vigorously in 100 mL of acetonitrile at 20 °C, whereupon methyl iodide 50 g (352 mmoles) was added. The reaction was stirred in darkness, being periodically monitored by thin layer chromatography until all 1-amino-1,2,3-triazole was consumed. As the reaction progressed, white crystals of 1-amino-3-methyl-1,2,3-triazolium iodide precipitated. The product salt was filtered and washed with several aliquots (120 mL total) of diethyl ether. The mother liquor was concentrated by distillation under reduced pressure resulting in a second crop of crystals that were filtered, washed with diethyl ether combined with first crop and dried under high vacuum, resulting in a good yield 12.1 g (93%) of 1-amino-3-methyl-1,2,3-triazolium iodide. Mp 146-147 °C; 1H NMR (DMSO-d₆) δ: 8.71 (s, 1H), 8.76 (s, 1H), 8.27 (s, 2H), 4.23 ppm (s, 3H); ¹³C NMR (DMSO- d_6) δ : 131.4, 126.9, 39.7 ppm. Anal. calcd for C₃H₇N₄I: C 15.94, H 3.12, N 24.79; found: C 16.22, H 3.20, N 24.66%.

3-Methyl-1-amino-1,2,3-triazolium nitrate (8)

Compound 7 (2.26 g, 10 mmol) was dissolved in 15 mL distilled water. While stirring, a solution of 1.72 g (10 mmol) of silver nitrate in 10 mL distilled water was added dropwise. The pale yellow suspension was stirred for 30 min, filtered, and rinsed with 10 mL distilled water. The solvent was removed under reduced pressure to produce a white solid (8) at 91% yield (1.47 g). Mp 87.0 °C; IR (KBr): 3151, 3070, 3014, 2935, 1762, 1629, 1538, 1485, 1386, 1323, 1241, 1188, 1081, 1050, 987, 825, 815, 713, 626 cm⁻¹; ¹H NMR (DMSO-*d*₆) δ : 4.21 (s, 3H), 8.29 (s, 2H), 8.60 (s, 1H), 8.75 ppm (s, 1H); ¹³C NMR (DMSO-*d*₆) δ : 133.45, 126.93 ppm.

3-Methyl-1-amino-1,2,3-triazolium 5-nitro-tetrazolate (9)

Silver 5-nitro-tetrazolate (2.44 g, 11 mmol) was added to a solution of 2.26 g (10 mmol) of compound **7** dissolved in 70 mL distilled water. The solution was stirred for 2 h, filtered in the dark, and then rinsed with 25 mL distilled water. The resulting solid was recrystallized from methanol, yielding 1.81 g of **9** at 91%. Mp 92.6 °C; IR (KBr): 3284, 3260, 3166, 3153, 3024, 2838, 1620, 1538, 1438, 1417, 1373, 1316, 1266, 1229, 1200, 1158, 1095, 1023, 993, 839, 802, 672, 630, 548 cm⁻¹; ¹H NMR (DMSO-*d*₆) δ : 8.76 (s, 1H), 8.62 (s, 1H), 8.30 (s, 2H), 4.23 ppm (s, 3H); ¹³C NMR (DMSO-*d*₆) δ : 188.08, 132.01, 127.32, 42.37 ppm.

3-Methyl-1-amino-1,2,3-triazolium 5-nitroiminotetrazolate (10)

A mixture of compound 7 (2.26 g, 10 mmol) and silver 5-nitroiminotetrazolate (10 mmol) in water (70 mL) was stirred for 60 min at room temperature. The AgI was filtered and rinsed with 25 mL distilled water. The clear filtrate was evaporated to dryness under reduced pressure to produce a pale yellow solid product, at 88% yield. Mp 89.6 °C; IR (KBr): 3417, 3318, 3150, 3124, 3070, 3014, 1619, 1537, 1485, 1399, 1300, 1241, 1222, 1188, 1140, 1081, 1028, 986, 816, 763, 730, 633, 483 cm⁻¹; ¹H NMR (DMSO-*d*₆) δ : 8.32 (s, 6H), 8.13 (s, 2H), 7.82 (s, 2H), 4.52 ppm (s, 3H, CH₃); ¹³C NMR (DMSO-*d*₆) δ : 182.27, 133.46, 126.27, 42.62 ppm.

3-Methyl-1-amino-1,2,3-triazolium nitroformate (11)

Compound 7 (1356 mg, 6 mmol) was dissolved in 20 mL methanol. While stirring, a solution of 1548 mg (6 mmol) of silver nitroformate dissolved in 10 mL methanol was added dropwise. The pale yellow suspension was stirred for 30 min, filtered, and then rinsed with 20 mL methanol. The yellow solvent was removed under reduced pressure to provide a yellow solid (11) at 82% yield (1.22 g). Mp 82.2 °C; IR (KBr): 3178, 3152, 3124, 3105, 3070, 3015, 2865, 1697, 1630, 1537, 1513, 1422, 1384, 1323, 1279, 1147, 1107, 984, 815, 794, 733, 631, 483 cm⁻¹; ¹H NMR (DMSO- d_6) δ : 9.10 (s, 2H), 8.63 (s, 1H), 8.50 (s, 1H), 4.23 ppm (s, 3H); ¹³C NMR (DMSO- d_6) δ : 150.53, 131.68, 127.36, 49.01 ppm.

3-Methyl-1-amino-1,2,3-triazolium azotetrazolate (12)

A mixture of 3-methyl-1-amino-1,2,3-triazolium sulfate salt (1.47 g, 5 mmol) and barium azotetrazole (1.81 g, 6 mmol) in methanol (100 mL) was stirred at room temperature. BaSO₄ was filtered and rinsed with 25 mL methanol. The clear filtrate was evaporated to dryness under reduced pressure to obtain a yellow solid product at 90% yield. Mp 144.6 °C; IR (KBr) v: 3426, 3248, 3148, 3124, 3063, 2930, 2808, 1627, 1548, 1486, 1389, 1315, 1250, 1196, 1180, 1106, 1029, 800, 729, 628, 560, 482 cm⁻¹; ¹H NMR (DMSO- d_6) δ : 8.77 (s, 1H), 8.62 (s, 1H), 8.32 (s, 2H, NH₂), 4.22 ppm (s, 3H, CH₃); ¹³C NMR (DMSO- d_6) δ : 171.86, 130.78, 127.73, 39.86 ppm.

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