



Oxygen-containing Tetrazole Salts of 3-Hydrazino-4-amino-1,2,4-triazole (HATr): Nitrogen-rich Ionic Materials with High Thermal Stability

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Abstract: Energetic salts of doubly-protonated 3-hydrazino-4-amino-1,2,4-triazole (**2-4**), and mono-protonated 3-hydrazino-4-amino-1,2,4-triazole (**5-7**), have been prepared in high yields from the corresponding oxygen-containing tetrazoles by (i) reaction of free acids and neutral 3-hydrazino-4-amino-1,2,4-triazole, or (ii) metathesis reactions of 3-hydrazinium-4-amino-1*H*-1,2,4-triazolium di-chloride with the silver salts of the corresponding oxygen-containing tetrazoles. All of these energetic salts were fully characterized by single-crystal X-ray diffraction, FT-IR and DSC measurements. All of the structures are dominated by extensive hydrogen bonds due to amino groups, hydrazino groups and oxygen atoms in the molecules. These salts exhibit good thermal stability, especially the salt 3-hydrazinium-4-amino-1*H*-1,2,4-triazolium 1*H*,1'*H*-5,5'-bitetrazole-1,1'-diolate (**4**), which exhibits a measured onset of decomposition temperature of 237 °C. Quantum chemical calculations, carried out using the Gaussian 03 suite of programs and based on the experimental densities were used to calculate the detonation pressures and velocities of all of the salts .

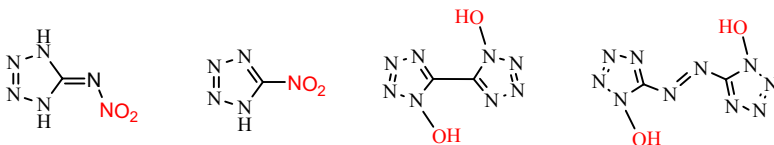
Keywords: energetic salts, thermal stability, oxygen-containing tetrazoles, 3-hydrazino-4-amino-1,2,4-triazole

1 Introduction

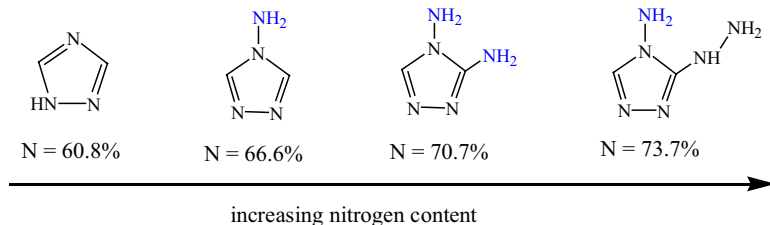
There has been significant progress in the development of nitrogen-rich materials in the field of new energetic compounds and their applications as pyrotechnics, propellants and explosives [1-4]. Energetic salts are generally considered as an

unique class of highly energetic materials and have attracted considerable interest over recent decades, since salt-based energetic derivatives often possess the advantages of lower vapour pressure (less toxic vapour in handling), enhanced thermal stability and higher heats of formation compared to their atomically similar non-ionic analogues [5, 6]. Furthermore, their properties can be readily improved and optimized through the suitable combination of different component ions [7-12]. It is a powerful methodology that could enable the design and synthesis of energetic materials for specific purposes [5, 13-15].

Azole-based compounds represent promising structures for novel energetic materials since they generally show positive heats of formation, resulting from cleavage and rearrangement of highly energetic nitrogen bonds, and high densities [16-18]. One of the most promising energetic fragments for the tailoring of energetic molecules is the tetrazole ring, since tetrazoles show the outstanding property of often combining a high nitrogen content with good thermal and kinetic stability (due to aromaticity). The introduction of oxygen-containing groups (such as nitro, nitramine, and hydroxyl) are of particular interest since these derivatives generally show higher densities and even greater energy output [19-24]. Several, structurally analogous, energetic oxygen-containing tetrazoles are well known, such as 5-nitrimino-tetrazole, 5-nitro-tetrazole, 1*H*,1'*H*-5,5'-bi-tetrazole-1,1'-diol and 1*H*,1'*H*-5,5'-azotetrazole-1,1'-diol (Scheme 1) [15, 25-28].



Scheme 1. Oxygen-containing tetrazoles



Scheme 2. Structures of triazoles

It is known that introducing amino groups into a molecule tends to generate more hydrogen bonds (especially hydrogen bonds between the $-NH_2$ group

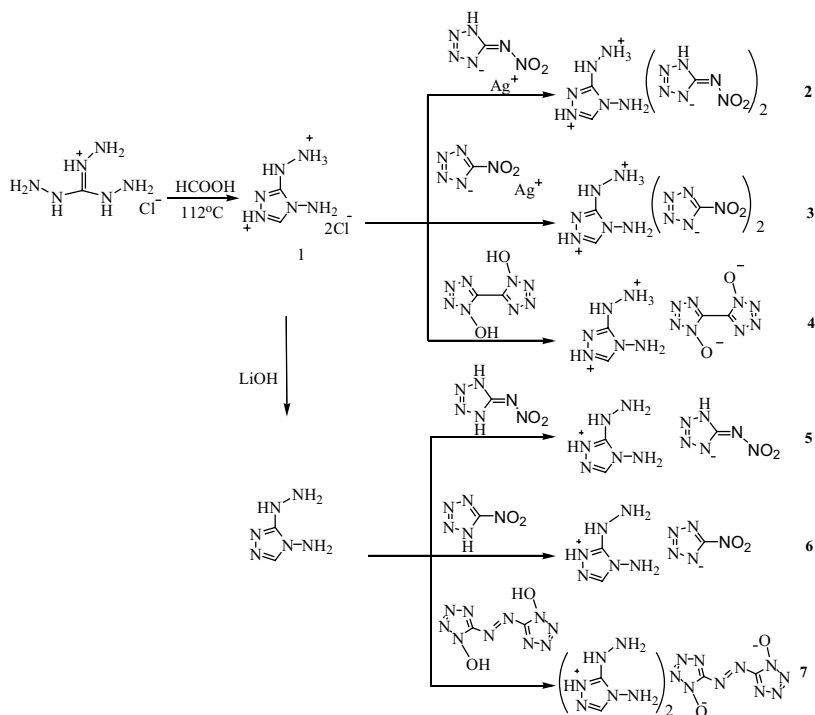
and oxygen-containing groups) [29-32]. In addition, the thermal stability is also enhanced through the formation of these hydrogen bonds. While the incorporation of amino groups is one of the simplest routes for increasing the nitrogen content, it in turn improves the properties (Scheme 2) [2, 33-36]. In our previous work, oxygen containing tetrazoles derived from 3,5-diamino-1,2,4-triazole (DATr) were prepared, and they show competitive properties [37, 38]. In the present paper, we report some oxygen-containing tetrazolate salts based on 3-hydrazino-4-amino-1,2,4-triazole (HATr). HATr possesses several of the merits mentioned above, and moreover, the incorporation of the hydrazine moiety into a heterocyclic ring will increase the heat of formation of the entire molecule [8]. These salts display potentially significant physical and energetic properties.

2 Results and Discussion

2.1 Synthesis

The synthetic pathways to all of the new energetic salts are shown in Scheme 3. 3-Hydrazinium-4-amino-1,2,4-1*H*-triazolium dichloride (HATr·2HCl, **1**) was synthesized according to a literature procedure [39]. The synthesis is based on the reaction of triamino-guanidinium chloride and formic acid in concentrated hydrochloric acid.

The nitrogen-rich salts of 3-hydrazino-4-amino-1,2,4-triazole (HATr) were synthesized by means of metathesis reactions or Brønsted acid-base reactions. Obviously, the metathesis reactions of the silver salts with halides is one of the most straightforward methods for the synthesis of energetic salts. The impetus for the reaction is the formation of silver halides, which have very low solubility in water and can thus be easily separated by simple filtration. Thus, the energetic salts **2** and **3** were readily synthesized by the metathesis reactions of **1** with two equivalents of the corresponding silver salts. Following the same method, salt **4** was obtained by straight reaction between 3-hydrazinium-4-amino-1*H*-1,2,4-triazolium dichloride and 1*H*,1'*H*-5,5'-bi-tetrazole-1,1'-diol dihydrate, since the salts of 1*H*,1'*H*-5,5'-bi-tetrazole-1,1'-diol also exhibit low solubility in water. Interestingly, the simple acid-base reaction of 3-hydrazino-4-amino-1,2,4-triazole with nitrogen-rich acids can only give rise to mono-protonated 3-hydrazino-4-amino-1,2,4-triazolium salts (**5-7**).



Scheme 3. Synthesis of compound **1** and its salts **2-7**

2.2 X-ray crystal structures

Suitable single crystals of compounds **2-7** were selected for X-ray crystal structure determination. The data and parameters of the measurements and refinements are collected in the S.I. (Table S1). Here, only three examples of the crystal structures are discussed, since they exhibit interesting properties from a crystallographic point of view.

A reactant stoichiometry of 1:2 in the di(5-nitrimino-tetrazolate) salt **2** was obtained, as its diprotonated 3-hydrazinium-4-amino-1H-1,2,4-triazolium salt with the inclusion of one molecule of crystal water per molecular unit. Compound **2**· H_2O crystallizes in the orthorhombic space group $Pbcn$, with eight molecules in the unit cell and a density of $1.755 \text{ g}\cdot\text{cm}^{-3}$. As shown in Figure 1, the asymmetric unit contains one crystallographically independent HATr^{2+} cation, and two 5-nitrimino-tetrazolate anions, in which proton transfers from the nitramino groups of 5-nitramino-tetrazole to the triazole ring (N1) and hydrazine (N6) of HATr were confirmed. The geometry of the 3-hydrazinium-4-amino-1H-1,2,4-triazolium di-cation is very similar in compounds **2-4**. The C-N

bond lengths in the triazolite ring vary between 1.303(4)–1.370(4) Å, which are between C–N single bonds (1.47 Å) and C=N double bonds (1.22 Å), suggesting that some multiple bond character is present [40]. A similar trend was observed for the N1–N2 bond. These findings indicate conjugation of the positive charge throughout the aromatic rings. The torsion angle N4–N3–C1–N2 was $-179.2(3)^\circ$, illustrating that the amino group and the triazole ring are almost in the same plane. In contrast to this, the hydrazino unit (angle: 10.0°) is a little bent out of the ring plane. The packing structure of **2**, built up by several hydrogen bonds, and depicted in Figure 2 is viewed along the b axis. Such extensive hydrogen-bonding interactions between cations and anions form a complex 3D network.

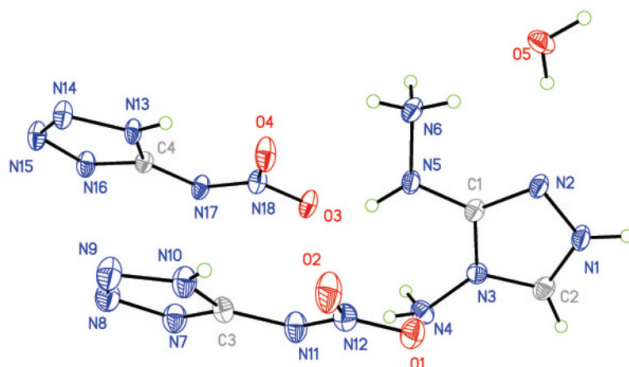


Figure 1. Thermal ellipsoid plot 30% and labelling scheme for salt **2**·H₂O

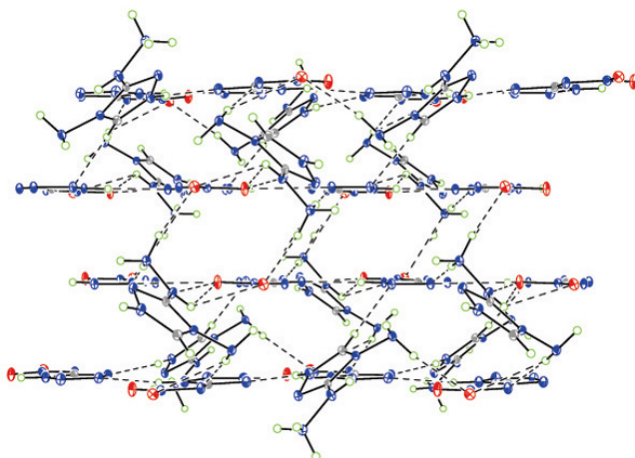


Figure 2. Packing diagram of **2** viewed down the b axis

The energetic compound 3-hydrazino-4-amino-2*H*-1,2,4-triazolium 1*H*-5-nitrimino-tetrazolate monohydrate (**5**·**H₂O**) crystallizes from water in the monoclinic space group *P2(1)/n*, with four molecules per unit cell and a density of 1.661 g·cm⁻³ at 296 K. The density of compound **5**·**H₂O** is lower than that of compound **2**·**H₂O**, due to the lack of one 1*H*-5-nitrimino-tetrazolate that is an ionic attractive force, although the structure is stabilized by strong hydrogen bonds. As shown in Figure 3, the asymmetric unit contains one crystallographically independent HATr cation, and one 5-nitrimino-tetrazolate anion, in which proton transfer from the nitramino group of 5-nitramino-tetrazole to the N2 (N8 in the label) of HATr was confirmed. The torsion angle of N10–N9–C2–N7 was –174.8°, larger than that of the cation in compound **2**, illustrating that the amino group is a little bent out of the ring plane. The NH–NH₂ group is a little twisted out of the triazole ring plane (4.4°), but the angle was decreased from that of compound **2**. The structure is also dominated by several intermolecular strong hydrogen bonds (Figure 4).

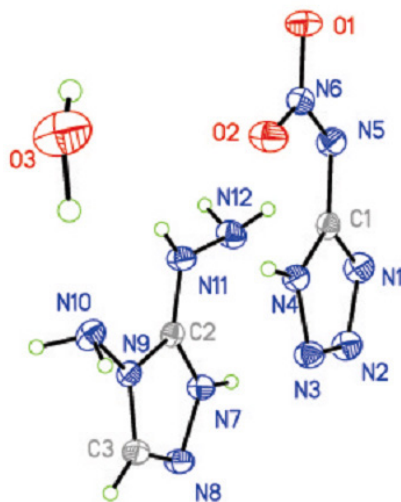


Figure 3. Thermal ellipsoid plot 30% and labelling scheme for salt **5**·**H₂O**

The unit cell of **7** crystallizes in the monoclinic space group *P2(1)/c*. By including two molecular moieties in the unit cell, the calculated density is 1.684 g·cm⁻³ at 296 K (Figure 5). The main change observed is the N2 (N4 and N4A in the label) nitrogen atoms, which undergoes protonation in HATr. The angle of the tetrazole rings in 1*H*,1'*H*-5,5'-azotetrazole-1,1'-diolate anion

was 0.1° , making the azo ring system completely planar. The torsion angle of $N10-N9-C2-N7$ was -175.8° , illustrating that the amino group is a little bent out of the ring plane. The angle between the $NH-NH_2$ group and the triazole was 0.4° . The angles of the ring system and the bond lengths behave in the same way as described for the cation of compound **5**. As seen in the Figure 6, a complex 3D network was also formed due to extensive hydrogen bonding between the cations and the anions.

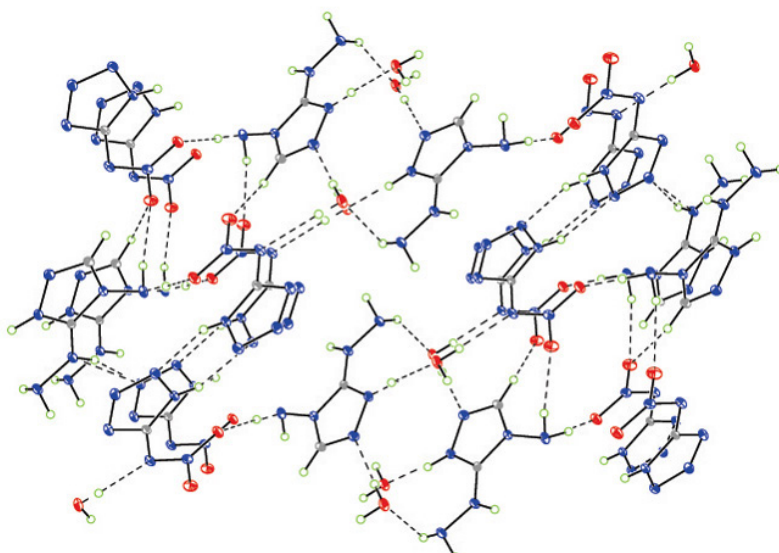


Figure 4. Packing diagram of **5** viewed down the *b* axis

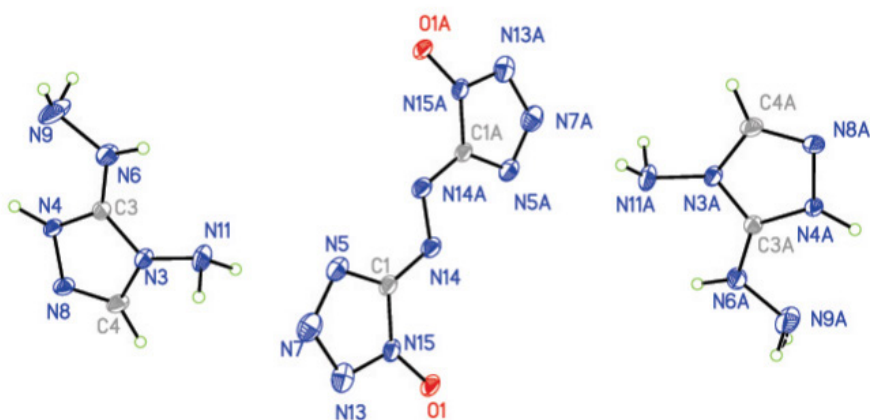


Figure 5. Thermal ellipsoid plot 30% and labelling scheme for salt **7**

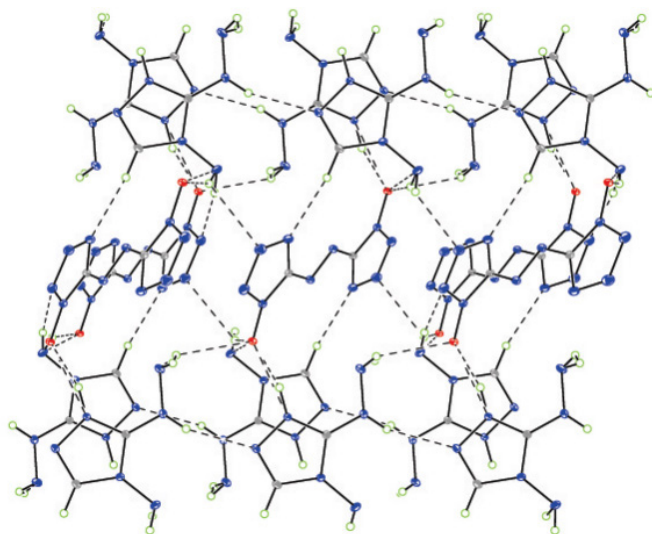


Figure 6. Packing diagram of **7** viewed down the *b* axis

The crystal structures of compounds **3**, **4** and **6** were also determined and are presented in the S.I.

2.3 Theoretical computation

All electronic structure calculations were carried out using the Gaussian 03 program package [41]. The geometric optimization of protonated HATr was carried out using B3-LYP functional with 6-311+G** basis set and single-point energies were calculated at the MP2/6-311++G** level of theory [42]. The optimized structures were characterized to be true local energy minima on the potential energy surfaces without imaginary frequencies.

In order to illustrate the protonated sites of HATr, three possible tautomers of mono-protonated HATr (**a-c**) and three possible tautomers of doubly-protonated HATr (**d-f**) were constructed. The optimized molecular structures of these various protonated HATr species and their relative energy values are gathered in Figure 7.

From Figure 7, the energy value of conformation **a** is much higher than the other conformations (**b**, **c**) of mono-protonated HATr. Theoretically, two conformations **b** and **c** may exist since the energy differences between them are quite small, although only **b** was found in this work (salts: **2-4**). Regarding the doubly-protonated HATr (**d-f**), the energy differences between the three conformers are very large, **f** is the most stable tautomer because it has the lowest energy, which agrees with the experimental results (salts: **5-7**).

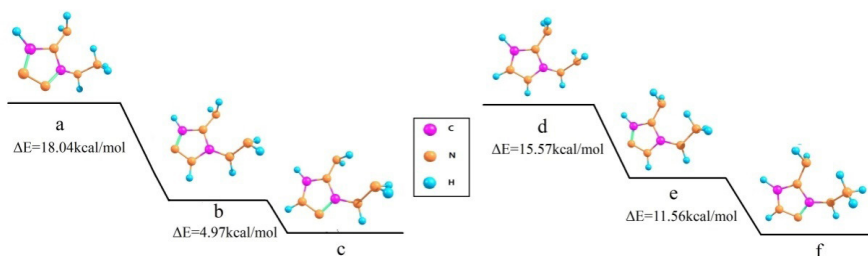


Figure 7. The studied protonated HATr species and their relative energy values

2.4 Physical properties of the energetic compounds

Thermal stability is a key concern in evaluating potential applications of energetic materials. All of the new compounds (**2-7**) were examined using differential scanning calorimetry (DSC) at a heating rate of $5\text{ }^{\circ}\text{C}\cdot\text{min}^{-1}$, and exhibited decomposition onset temperatures between $152\text{-}237\text{ }^{\circ}\text{C}$. The thermal stability of salt **4** is superior to RDX ($205\text{ }^{\circ}\text{C}$) with a measured decomposition onset temperature of $237\text{ }^{\circ}\text{C}$ (Table 1).

High heats of formation is a promising advantage of nitrogen-rich compounds. Computations were performed using the Gaussian 03 suite of programs to obtain values of the heats of formation (see S.I.) [43-46]. The mono-protonated HATr cation has a positive heat of formation of $745.9\text{ kJ}\cdot\text{mol}^{-1}$, whereas its di-protonated HATr cation possesses a higher value of $1808.6\text{ kJ}\cdot\text{mol}^{-1}$. The heats of formation for all of these energetic salts (**2-7**) are higher than the currently used explosives TNT ($-67.0\text{ kJ}\cdot\text{mol}^{-1}$) and RDX ($80\text{ kJ}\cdot\text{mol}^{-1}$).

Based on the values of the density and heats of formation, the detonation pressures (P), and detonation velocities (D) were calculated using the Kamlet-Jacobs equations [47]. The calculated detonation pressures and detonation velocities lie in the ranges $19.4\text{-}28.6\text{ GPa}$, and $6720\text{-}8039\text{ m}\cdot\text{s}^{-1}$, respectively, which are comparable to or greater than those of TNT (19.5 GPa , $6881\text{ m}\cdot\text{s}^{-1}$). Of the salts with similar anions, the HATr²⁺ salts gave higher values for the detonation parameters than the HATr⁺ salts.

In addition to the heats of formation and detonation properties, the sensitivities were measured by standard procedures, and are listed in Table 2. The salts **2-7** show varying sensitivities, ranging from sensitive to less sensitive (IS, $4\text{-}25\text{ J}$; FS, $42\text{-}108\text{ N}$). Of the salts with similar anions, double protonation of HATr leads to increased sensitivity values towards impact and friction. Compounds **2** and **3** are both very sensitive with regard to impact (IS: 4 J , 4 J ; FS: 42 N , 80 N , respectively), while **5** and **6** display much lower sensitivity toward impact (IS: 8 J , 11.5 J ; FS: 96 N , 96 N , respectively).

Table 1. Properties of salts **2-7** compared with TNT and RDX

Salt	T_d^g [°C]	d^b [g·cm ⁻³]	OB ^d	ΔH_L^e [kJ·mol ⁻¹]	ΔH_f^g cation [kJ·mol ⁻¹]	ΔH_f^g anion [kJ·mol ⁻¹]	ΔH_f^h [kJ·mol ⁻¹]	P^i [GPa]	D^j [m·s ⁻¹]	IS ^k [J]	FS ^l [N]	ESD ^m [J]
2	152	1.755(1.795)	-38.5	1542.3	1808.6	176.1	618.5	28.6	8039	4	42	1.0
3	160	1.711	-41.6	1527.2	1808.6	112.8	507.0	25.3	7665	4	80	1.8
4	237	1.722	-56.3	1993.2	1808.6	587.7	403.0	22.4	7206	17.5	108	3.2
5	164	1.661(1.710) ^c	-52.5	487.8	745.9	176.1	434.2	24.6	7565	11.5	96	2.2
6	167	1.657	-52.4	491.9	745.9	112.8	366.8	19.4	6720	8	96	2.8
7	167	1.683 ^c	-63.9	1152.3	745.9	768.7	1108.2	24.4	7577	25	60	1.0
TNT [48]	295	1.65	-18.6	-	-	-	95.3	19.5	6881	15	353	0.4
RDX [49]	205	1.82	0	-	-	-	83.8	34.9	8748	7.4	120	0.2

^a Decomposition temperature (onset). ^b Densities obtained from X-ray measurements at 298 K, values in parentheses were corrected by subtracting the volume of a water molecule [V(H₂O) = 25 Å³] [50]. ^c Recalculated from low-temperature X-ray densities ($d_{298K} = d_T / (1 + \alpha_V(298 - T))$; $\alpha_V = 1.5 \times 10^{-4} \text{ K}^{-1}$). ^d Oxygen balance (OB). ^e Lattice energy. ^f Molar enthalpy of the formation of cation. ^g Molar enthalpy of the formation of anion. ^h Molar enthalpy of the formation of salt. ⁱ Detonation pressure. ^j Detonation velocity. ^k Friction sensitivity. ^l Friction sensitivity. ^m Electrostatic discharge.

3 Conclusions

Nitrogen-rich energetic salts using HATr as a singly or doubly charged cation and a series of oxygen-containing tetrazoles as anions were synthesized in high yields. The series of salts were well characterized by single-crystal X-ray diffraction, and the results show that their structures are dominated by an extensive hydrogen bonded network due to amino groups, hydrazo groups and oxygen atoms in the molecules. It was also found that the introduction of hydrazino groups into heterocyclic rings increases the heat of formation. In addition, the detonation performance of the energetic salts identified them as competitively energetic compounds, and in some cases close to those of RDX.

4 Experimental

4.1 General methods

Reagents and solvents were purchased from Sinopharm Chemical Reagent Co., Ltd and were used as received. Differential scanning calorimetry (DSC) was examined on a model Pyris-1 differential scanning calorimeter at a scan rate of $5\text{ }^{\circ}\text{C}\cdot\text{min}^{-1}$. IR spectra were measured with a Bruker Equinox 55. The heats of formation of the ionic derivatives were obtained by using the method of isodesmic reactions. Computations were carried out using the Gaussian 03 suite of programs [47]. Geometric optimization and frequency analyses were carried out using B3LYP/6-311+G** level, and single energy points were calculated at the MP2/6-311++G** level of theory [42].

4.2 Crystal structure determination

The crystal structures of **2-7** were determined by single-crystal X-ray diffraction. The data were collected on a Rigaku Saturn724+ CCD diffractometer or Bruker SMART by using Mo K_{α} radiation. The structure was refined by using full-matrix least-squares on F^2 with the SHELXTL refinement package [51, 52]. All non-hydrogen atoms were refined with the atoms' anisotropic thermal parameters. Hydrogen atoms were found from residual density maps and refined with riding model isotropic thermal parameters. Crystallographic data and the structure refinement results for compounds **2-7** are summarized in S.I. (Table S1).

3-Hydrazinium-4-amino-1*H*-1,2,4-triazolium di-chloride (**1**) was synthesized according to a literature method [39].

3-Hydrazinium-4-amino-1*H*-1,2,4-triazolium di(5-nitramino-tetrazolate) (2)

A mixture of compound **1** (0.347 g, 2 mmol) and silver 5-nitramino-tetrazolate (0.83 g, 2.4 mmol) in methanol (15 mL) was stirred at room temperature for 3 h. The precipitate was then filtered off and the solvent was removed under reduced pressure to produce a colourless solid product in 82% yield (0.40 g). The crystals of **2**·H₂O were grown from water. IR (KBr): $\nu = 3372(\text{vs}), 3303(\text{vs}), 1715(\text{m}), 1674(\text{m}), 1529(\text{vs}), 1428(\text{s}), 1332(\text{w}), 1303(\text{w}), 1212(\text{m}), 1060(\text{w}), 957(\text{m}), 862(\text{m}) \text{ cm}^{-1}$. MS(ESI+): $m/z = 115.05 [\text{C}_2\text{H}_7\text{N}_6^+]$; MS(ESI-): $m/z = 128.95 [\text{CHN}_6\text{O}_2^-]$. C₄H₁₀N₁₈O₄ (374.24): calcd. C 12.84, H 2.69, N 67.37; found C 12.81, H 2.66, N 67.42.

3-Hydrazinium-4-amino-1*H*-1,2,4-triazolium di(5-nitro-tetrazolate) (3)

Silver 5-nitro-tetrazolate (1.332 g, 6 mmol) was added to a solution of compound **1** (0.468 g, 2.5 mmol) dissolved in methanol (30 mL). The solution was stirred for 4 h, and then filtered. The clear filtrate was evaporated to dryness under reduced pressure to produce a colourless solid product in 78% yield (0.448 g); m.p.: 141.9 °C. IR (KBr): $\nu = 3334(\text{vs}), 3147(\text{vs}), 1726(\text{w}), 1666(\text{vs}), 1544(\text{vs}), 1463(\text{m}), 1448(\text{s}), 1318(\text{m}), 1195(\text{m}), 953(\text{w}), 838(\text{s}) \text{ cm}^{-1}$. MS(ESI+): $m/z = 114.95 [\text{C}_2\text{H}_7\text{N}_6^+]$; MS(ESI-): $m/z = 113.90 [\text{CN}_5\text{O}_2^-]$. C₄H₈N₁₆O₄ (344.21): calcd. C 13.96, H 2.34, N 65.11; found C 13.93, H 2.37, N 65.15.

3-Hydrazinium-4-amino-1*H*-1,2,4-triazolium 1*H*,1'*H*-5,5'-bi-tetrazole-1,1'-diolate (4)

1*H*,1'*H*-5,5'-Bi-tetrazole-1,1'-diol (1.03 g, 5 mmol) was dissolved in a few milliliters of water, and compound **1** (0.936 g, 5 mmol) was added to the clear solution. The mixture was briefly heated to 70 °C and then filtered. After cooling to room temperature, **4** precipitated from the filtrate as small crystalline colourless needles in 82% yield (1.16 g). IR (KBr): $\nu = 3266(\text{vs}), 3142(\text{vs}), 2927(\text{m}), 1926(\text{w}), 1664(\text{vs}), 1554(\text{s}), 1421(\text{vs}), 1418(\text{s}), 1354(\text{m}), 1255(\text{s}), 1176(\text{m}), 1101(\text{m}), 999(\text{w}) \text{ cm}^{-1}$. MS(ESI+): $m/z = 115.10 [\text{C}_2\text{H}_7\text{N}_6^+]$; MS(ESI-): $m/z = 169.00 [\text{C}_2\text{HN}_8\text{O}_2^-]$. C₄H₈N₁₄O₂ (284.20): calcd. C 16.90, H 2.84, N 69.00; found C 16.93, H 2.81, N 69.04.

3-Hydrazino-4-amino-2*H*-1,2,4-triazolium 1*H*-5-nitramino-tetrazolate (5)

3-Hydrazino-4-amino-1,2,4-triazole (0.57 g, 5 mmol) was dissolved in methanol (20 mL) and 5-nitramino-tetrazole (0.65 g, 5 mmol) was added. The mixture was heated and then filtered. The filtrate was completely evaporated, and a colourless solid was obtained in 83% yield (1.01 g). The crystals of **5**·H₂O

were grown from water. IR (KBr): $\nu = 3371(\text{vs}), 3244(\text{vs}), 3180(\text{vs}), 2664(\text{s}), 1714(\text{vs}), 1526(\text{m}), 1442(\text{s}), 1212(\text{m}), 1057(\text{m}), 956(\text{m}), 868(\text{w}) \text{ cm}^{-1}$. MS(ESI+): $m/z = 114.95 [\text{C}_2\text{H}_7\text{N}_6^+]$; MS(ESI-): $m/z = 129.00 [\text{CHN}_6\text{O}_2^-]$. $\text{C}_3\text{H}_8\text{N}_{12}\text{O}_2$ (244.17): calcd. C 14.76, H 3.30, N 68.84; found C 14.78, H 3.23, N 68.88.

3-Hydrazino-4-amino-2H-1,2,4-triazolium 5-nitro-tetrazolate (6)

3-Hydrazino-4-amino-1,2,4-triazole (0.57 g, 5 mmol) was dissolved in methanol (20 mL) and 5-nitro-tetrazole (0.575 g, 5 mmol) was added in one portion. The mixture was heated and then filtered. The filtrate was completely evaporated, and a colourless solid was obtained in 85% yield (0.97 g). Mp: 133.9 °C. IR (KBr): $\nu = 3371(\text{vs}), 3243(\text{vs}), 3033(\text{vs}), 1714(\text{w}), 1526(\text{vs}), 1442(\text{s}), 1328(\text{m}), 1213(\text{w}), 1057(\text{w}), 1021(\text{w}), 956(\text{m}), 868(\text{s}) \text{ cm}^{-1}$. MS(ESI+): 115.00 $[\text{C}_2\text{H}_7\text{N}_6^+]$; MS(ESI-): $m/z = 114.00[\text{CN}_5\text{O}_2^-]$. $\text{C}_3\text{H}_7\text{N}_{11}\text{O}_2$ (229.16): calcd. C 15.72, H 3.08, N 67.23; found C 15.75, H 3.12, N 67.26.

3-Hydrazino-4-amino-2H-1,2,4-triazolium 1H,1'H-5,5'-azotetrazole-1,1'-diolate (7)

3-Hydrazino-4-amino-1,2,4-triazole (0.57 g, 5 mmol) was dissolved in a few milliliters of water and 1H,1'H-5,5'-azotetrazole-1,1'-diol (0.45 g, 2.5 mmol) was added in one portion. The mixture was briefly heated to reflux and then filtered. After cooling to room temperature, **7** precipitated from the filtrate as small crystalline orange needles in 40% yield (0.31 g). IR (KBr): $\nu = 3349(\text{m}), 3251(\text{m}), 3051(\text{m}), 1712(\text{m}), 1659(\text{s}), 1552(\text{w}), 1474(\text{vs}), 1083(\text{w}), 939(\text{m}), 785(\text{vs}) \text{ cm}^{-1}$. MS(ESI+): 115.10 $[\text{C}_2\text{H}_9\text{N}_6^+]$; MS(ESI-): $m/z = 196.95[\text{C}_2\text{HN}_{10}\text{O}_2^-]$. $\text{C}_6\text{H}_{14}\text{N}_{22}\text{O}_2$ (426.32): calcd. C 16.90, H 3.31, N 72.28; found C 16.92, H 3.37, N 72.31.

Supporting Information

The data and parameters of the X-ray crystallographic measurements and refinements for all of the salts, several figures of the molecular structures and packing diagrams, as well as the methodology and details for the heats of formation, are included in the Supporting Information, available at <http://www.wydawnictwa.ipo.waw.pl/CEJEM/contents/2017/vol-14-number-1.html>

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