



4-Amino-3-hydrazino-1,2,4-triazole: a Precursor for the Preparation of Divalent Energetic Materials

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Abstract: 4-Amino-3-hydrazino-1,2,4-triazole (AHT) was developed as a divalent cation. The multivalent structure can be used to increase the number of nitrogen-rich heterocycles, thereby increasing the heat of formation and improving the detonation performance. Herein we report on a family of divalent energetic salts, which exhibit excellent properties, *viz.* acceptable density, good detonation performance, and desirable thermal and impact stabilities. The structural features of the salts were further determined by single-crystal X-ray diffraction. In addition, the detonation properties calculated for these energetic salts identified them as competitively energetic compounds.

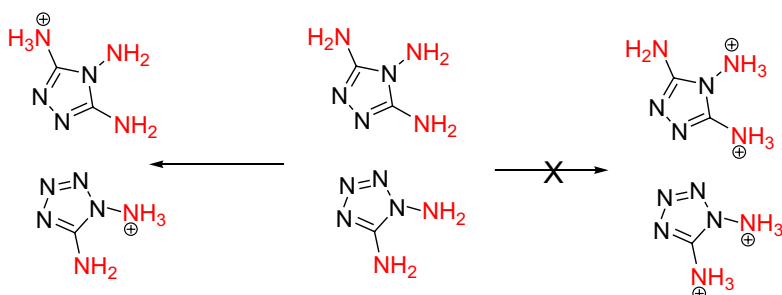
Keywords: energetic materials, detonation performance, nitrogen heterocycle

1 Introduction

Nitrogen-rich energetic salts are of great interest because their properties can be changed by careful choice of the component ions [1-5]. By combining the appropriate backbones with suitable functional groups, the energetic properties can be tuned and improved [6-8]. Nitrogenous heterocycles, such as triazole [9-11], tetrazole [12, 13], triazine [14, 15], and tetrazine [16, 17], provide good backbones for the discovery of new energetic compounds. Such heterocycles are often modified by functional groups such as $-\text{NH}_2$ and $-\text{NH}-\text{NH}_2$ to act as cations.

The incorporation of hydrazino groups increases the heat of formation of the entire molecule and the density, and also lowers the sensitivity [12]. Amino groups are often incorporated intoazole heterocycles because their derivatives

are easily protonated [3, 18, 19]. These traditions have led to many chemical advances. Various energetic cations derived from amino-substituted triazoles and tetrazoles, in which each cation pairs with a member of a family of nitrogen-rich anions to form new energetic salts, have been well documented [20-23]. However, despite the number of basic groups (such as amino groups) introduced into the azole ring, the compounds were protonated only to form monovalent cations (Scheme 1) [24-30].



Scheme 1. Azoles substituted with two or three amino groups were protonated only as monovalent cations

A divalent cation can pair with two oxygen-enriched anions, which are useful in increasing the density and improving the detonation performance [31]. However, to the best of our knowledge, research on divalent cations is lacking. The introduction of two oxygen-enriched anions into energetic salts will increase the oxygen balance and the density of the entire molecule. Furthermore, the multivalent structure can increase the number of nitrogen-rich heterocycles, thereby increasing the heat of formation and improving the detonation performance. Both amino and hydrazino groups behave as electron-withdrawing groups in these heterocycles while forming energetic salts. Hence, the incorporation of both amino and hydrazino groups into a heterocyclic ring enables it to be protonated to form a divalent cation.

Because of the protonation of the groups $-\text{NH}_2$ and $-\text{NH}-\text{NH}_2$, 4-amino-3-hydrazino-1,2,4-triazole (AHT) may be protonated by strong mineral acids such as HNO_3 [32]. Although AHT has been reported in some literature [33, 34], no systematic reports on the physical properties of the structures were given for the compounds. The effect of functional groups such as $-\text{NH}_2$ and $-\text{NH}-\text{NH}_2$ on the triazole moiety, and the divalent cationic characteristics of the 1,2,4-triazole backbone, are also unknown.

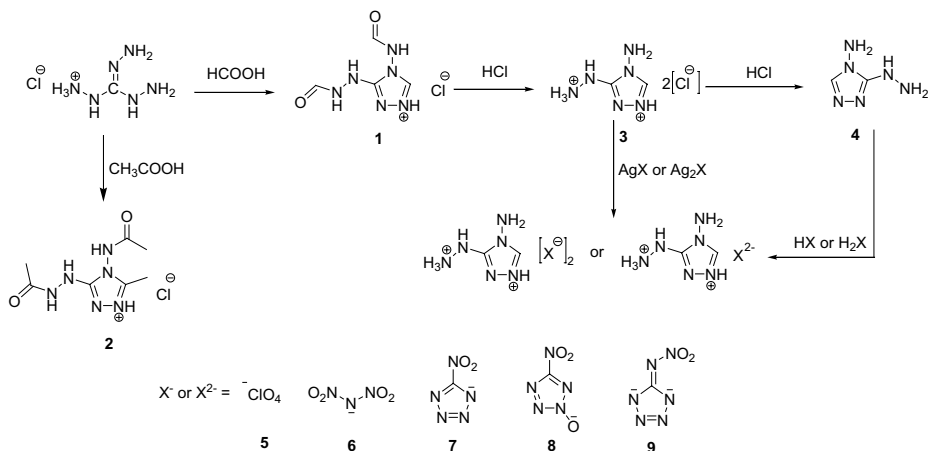
Herein, we report the synthesis of a series of AHT-based energetic salts, as well as their significant physical and energetic properties. By comparing these

new compounds with their analogous monovalent salts, we clearly demonstrate the capability of divalent cations to form high-performance energetic compounds.

2 Results and Discussion

2.1 Synthesis

Guanidine hydrochloride was refluxed in 3 equiv. of hydrazine hydrate at 110 °C for 2 h, to yield triaminoguanidine hydrochloride (TAG•HCl) [35-37]. Refluxing TAG•HCl in formic acid and removal of the solvent produced a viscous residue, from which a moderate yield of 4-formamido-3-formylhydrazino-triazole hydrochloride **1** was isolated. **1** was then hydrolyzed by hydrochloric acid and water (1:1 ratio) to form 4-amino-3-hydrazino-1,2,4-triazolium dihydrochloride **3**.



Scheme 2. Synthesis of the 4-amino-3-hydrazino-1,2,4-triazolium based salts

Five energetic salts **5-9** based on oxygen-rich anions and the AHT cation were then synthesized (Scheme 2). Such salts would be expected to have relatively high oxygen contents. Compounds **5-9** were readily synthesized from **3** in methanol or water by anion exchange with silver perchlorate, silver dinitramide, silver 5-nitrotetrazolate, silver 5-nitrotetrazolate-2*N*-oxide, and silver 5-nitroiminotetrazolate, respectively. By treating **3** with a stoichiometric amount of NaHCO₃, 4-amino-3-hydrazino-1,2,4-triazole (AHT, **4**) was isolated. Compounds **5-9** can also be prepared by treating AHT with the corresponding acid.

2.2 X-ray crystallography

The crystal structures of **5**•1.5H₂O and **7** were determined by single-crystal X-ray diffraction. The structures of **5**•1.5H₂O and **7** are shown in Figures 1 and 2, respectively. Compound **5**•1.5H₂O crystallized in a triclinic crystal system (space group *P*-1). The C1–N3, C1–N2, N1–N2, C2–N1, and C2–N3 bond lengths were 1.297 Å, 1.356 Å, 1.374 Å, 1.295 Å, and 1.338 Å, respectively. The bond lengths of C1–N4 and N3–N6 were 1.369 Å and 1.396 Å, respectively, and are in the expected range. The amino unit [torsion angles N6–N3–C2–N1 179.887(501)°, N6–N3–C1–N2 –178.798(450)°] and the 1,2,4-triazole ring were approximately in the same plane. However, with torsion angles of –30.54 for N5–N4–C1–N2, and 23.37 for N5–N4–C1–N3, the hydrazino group bonded to the 1,2,4-triazole ring is considerably twisted out of the ring plane.

Salt **7** crystallizes in a monoclinic crystal system (space group *P*2 (1)/*c*) (Figure 2a), and has a calculated density of 1.789 g·cm⁻³ (296(2) K). The main changes observed are for the N6 and N10 nitrogen atoms, which undergo protonation in 4-amino-3-hydrazino-1,2,4-triazole. Protonation results in a lengthening of the N6–N7 distance (1.433 Å), which is longer than an N–N single bond (1.398 Å). The hydrazino and amino units lie in the plane of the triazole ring (torsion angles N10–N9–C2–N8 –175.86°, N11–N8–C2–N7 176.71°).

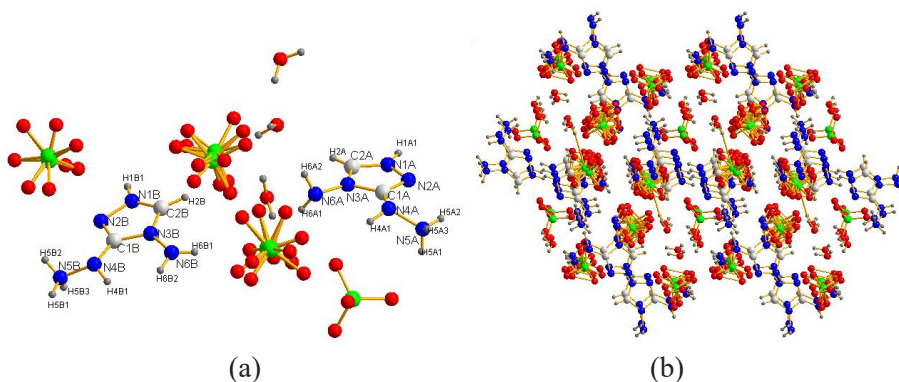


Figure 1. (a) View of the molecular unit of **5**•1.5H₂O; (b) Unit cell packing of **5**•1.5H₂O (4-Amino-3-hydrazino-1,2,4-triazolium diperchlorate hydrate)

As can be seen from Figure 1b, and Figure 2b, there are many hydrogen bonds between the cations and the anions of salts **5**•1.5H₂O and **7**, such as in **5**•1.5H₂O: (N(6a)–H(6a2)..O(4z), 2.408; N(6a)–H(6a2)..O(4a), 2.665; O(7)–

H(7b)..C(1), 2.71; O(7)–H(7b)..O(4), 1.85; and so forth. Figure 2 shows that the proton of the 1,2,4-triazole ring of **7** forms a strong hydrogen bond with the nitrotetrazole anion: [N(11d)–H(10c)..O(1d), 2.521(378); N(11d)–H(10c)..N(1d), 1.898(378); N(6a)–H(6a)..C(3a), 1.903(425); N(6a)–H(6a)..N(4a), 2.001(493); N(10b)–H(10f)..N(1c), 1.8426 (431).

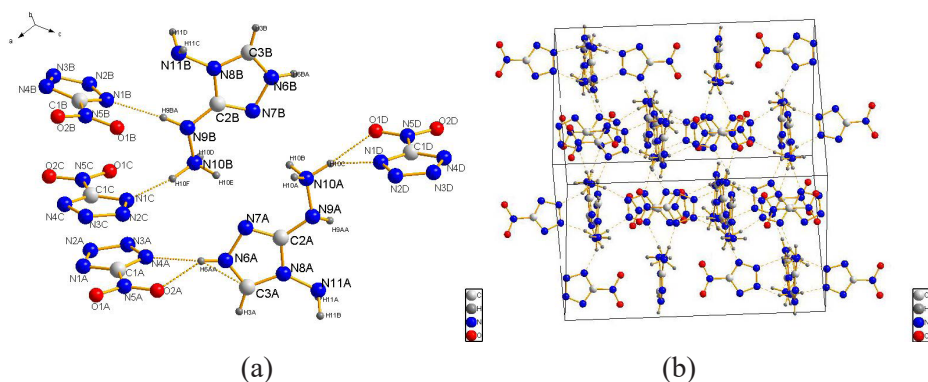


Figure 2. (a) View of the molecular unit of **7**; (b) Unit cell packing of **7** (4-Amino-3-hydrazino-1,2,4-triazolium di-5-nitrotetrazolate)

2.3 Physicochemical properties

The AHT salts have acceptable thermal stability with decomposition temperatures ranging from 126.7 °C (**6**) to 173.9 °C (**9**). Except for **6**, which melts at 85.6 °C, the other salts decompose without melting. Except for **9**, all of the salts show two exothermic peaks, which result from the secondary decomposition of the salts.

The measured densities of the AHT salts ranged from 1.789 g·cm⁻³ to 2.168 g·cm⁻³ (Table 1). Salt **5** possesses the highest density of 2.168 g·cm⁻³, exceeding that of the other perchlorate salts, (*e.g.*, 1,2,4-triazolium perchlorate, 1.96 g·cm⁻³ [38]; 4-amino-1,2,4-triazolium perchlorate, 1.81 g·cm⁻³ [39]; 5-aminotetrazolium perchlorate, 1.92 g·cm⁻³ [40]; tetrazolium perchlorate, 2.021 g·cm⁻³ [38], *etc.*). The physical densities of the AHT salts are higher than those of the corresponding 4-amino-1,2,4-triazolium salts, *e.g.*, 4-amino-1,2,4-triazolium nitrate: 1.60 g·cm⁻³ [39], 4-amino-3-hydrazino-1,2,4-triazolium dinitrate: 1.811 g·cm⁻³ [32]. This result shows that the introduction of an extra oxygen-enriched anion can sharply increase the density. This increase may be attributed to the higher oxygen content of the anions.

It may be seen from Table 1 that most of these multivalent energetic salts exhibit positive heats of formation, salt **7** showing the highest value of 2.12 kJ·g⁻¹ (RDX: 0.38 kJ·g⁻¹; HMX: 0.36 kJ·g⁻¹). Of the energetic salts considered, salt **7**

has the highest molar enthalpy of formation of $730.1 \text{ kJ}\cdot\text{mol}^{-1}$. The calculated heat of formation of AHT is $2033.5 \text{ kJ}\cdot\text{mol}^{-1}$.

The salts containing double anions have higher densities and higher heats of formation than those with a single anion. As seen in Figure 3, the compounds in which AHT is paired with two oxygen-enriched anions possess higher densities and heats of formation. The introduction of an extra dinitramide to AHT increased the density and the heat of formation of the entire molecule by $0.05 \text{ g}\cdot\text{cm}^{-3}$ and $331.7 \text{ kJ}\cdot\text{mol}^{-1}$, respectively.

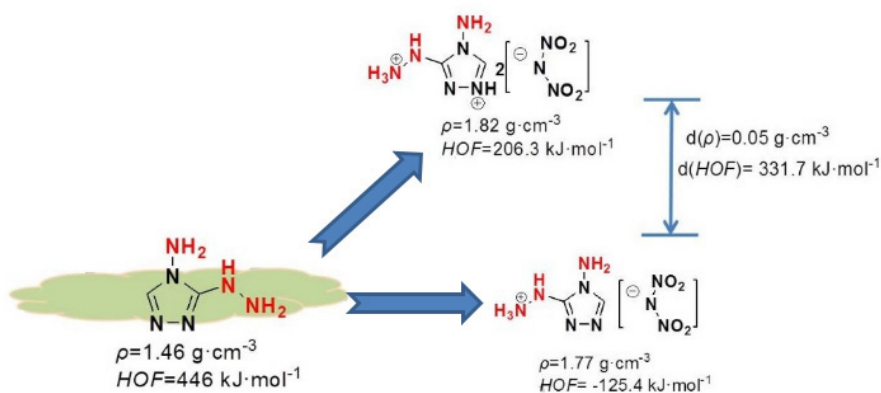


Figure 3. A comparison between 4-amino-3-hydrazino-1,2,4-triazolium based monovalent and divalent energetic salts

The AHT-based compounds have moderate nitrogen content, some of them exceeding 50% and reaching as high as 69%. Most of the salts considered in this study exhibit a good oxygen balance. In particular, the oxygen balance of compounds **5** and **6** are 10.2% and 9.8%, respectively. Compound **9** has a significant negative oxygen balance of -32.8% , since it possess a single anion.

The detonation pressures (P) and detonation velocities (D) of the resulting AHT salts were calculated using the EXPLO5 program (version 6.01). The calculated P and D values of the salts fall in the range $25.6\text{--}40.9 \text{ GPa}$ and $8170\text{--}9592 \text{ m}\cdot\text{s}^{-1}$, respectively. Salt **6** possesses the best detonation performance, with a P of 40.9 GPa and a D of $9592 \text{ m}\cdot\text{s}^{-1}$. Because of the high density and good oxygen balance, the detonation parameters of compounds **5** ($P = 40.5 \text{ GPa}$, $D = 9147 \text{ m}\cdot\text{s}^{-1}$) and **8** ($P = 34.4 \text{ GPa}$, $D = 9029 \text{ m}\cdot\text{s}^{-1}$) are superior to those of RDX. The salts containing double anions show better detonation properties than the 1,2,4-triazole based salts with a single anion. The marked increase in performance proves the advantage of introducing the extra oxygen-enriched anion.

Impact sensitivity measurements were performed using the Brucceton method on a type 12 tooling. Salts **7** and **8** with impact sensitivities of 4.5 J and 4.0 J, respectively, are highly sensitive explosives. Salt **6** is sensitive with an impact sensitivity of 6.9 J, suggesting that it can be a primary explosive. Based on the relatively high detonation properties, good thermal stabilities and reasonable impact sensitivities, the multivalent AHT based energetic salts show potential for use as energetic materials.

Table 1. The physicochemical properties of related energetic salts compared with RDX and HMX

Salt	T_d ¹	T_{sd} ²	d_c/d_m ⁴	ΔH_L° ⁵	$\Delta H_f^\circ/\Delta H_f^\circ$ ⁷	P ⁸	D ⁹	IS ¹⁰
5	163.8	302.6	2.07/2.168	1640.0	-268.7/-0.85	40.5	9147	10.9
6	126.7	266.5	1.82/1.892	1570.4	206.3/0.63	40.9	9592	6.9
7	164.9	231.4	1.72/1.789	1529.0	730.1/2.12	31.0	8831	4.5
8	173.4	252.3	1.76/1.821	1504.4	710.5/1.89	34.4	9029	4.0
9	173.9	-	1.69/1.795	2045.5	374.0/1.53	28.5	8765	21.3
RDX ¹¹	204.1	230	1.82	-	83.8/0.38	35.2	8977	7.4
HMX ¹¹	276	287	1.91	-	105/0.361	39.6	9320	7.4

¹ Decomposition temperature [°C]; ² Secondary decomposition temperature [°C]; ³ Calculated density [$\text{g}\cdot\text{cm}^{-3}$]; ⁴ Measured density [$\text{g}\cdot\text{cm}^{-3}$] using ULTRAPYC 1200, Automatic Density Analyzer; ⁵ Lattice energy [$\text{kJ}\cdot\text{mol}^{-1}$]; ⁶ Molar enthalpy of formation of salt [$\text{kJ}\cdot\text{mol}^{-1}$];

⁷ Enthalpy of formation of ionic salts per gram [$\text{kJ}\cdot\text{g}^{-1}$]; ⁸ Detonation pressure [GPa]; ⁹ Detonation velocity [$\text{m}\cdot\text{s}^{-1}$]; ¹⁰ Impact sensitivity [J]; ¹¹ Data from Ref. [41].

3 Conclusions

In this article, we have prepared and fully characterized a new family of energetic salts based on AHT divalent cations. These salts are thermally stable between 126.7-173.9 °C. The structures of **5**·1.5H₂O, and **7** were confirmed by single-crystal X-ray diffraction. The densities of the AHT salts fall within the range 1.795 $\text{g}\cdot\text{cm}^{-3}$ (**9**) to 2.168 $\text{g}\cdot\text{cm}^{-3}$ (**5**). Most of the salts have reasonable impact sensitivities (4-30 J). Based on the EXPLO5 v6.01 calculations, all of these salts exhibit relatively high detonation performances. We may safely conclude that the divalent cation, paired with two oxygen-enriched anions, will increase the heat of formation of the entire molecule and the density, in addition to improving the detonation performance. The amino and hydrazino groups were proven to be good moieties for developing new energetic divalent cations. Studies on other divalent cations are currently underway.

4 Experimental

Caution: Although we experienced no difficulties in handling these materials, the high positive heats of formation can render the compounds unstable.

4-Amino-3-hydrazino-1,2,4-triazolium dihydrochloride (3): Triaminoguanidine hydrochloride (TAG·HCl) (2.81 g, 20 mmol) was added to formic acid (b.p. 100.8 °C, 15 mL). The mixture was stirred and refluxed at 100-110 °C for 2 h. The excess volatile formic acid was removed under partial vacuum to recover a viscous, resinous residue. 4-Formamido-3-formylhydrazino-1,2,4-triazole hydrochloride (**1**) was isolated from this residue in moderate yield. The viscous residue was dissolved and stirred vigorously in dilute hydrochloric acid at 80 °C. As the reaction progressed, white crystals of 4-amino-3-hydrazino-1,2,4-triazolium dihydrochloride (**3**) precipitated. The product was filtered off and washed with several aliquots (50 mL total) of ice-water. The product was dried under high vacuum, and resulted in a good yield (2.28 g, 61%) of **3**. MS m/z (ESI⁺): 115.07, [C₂H₇N₆]⁺; elemental analysis (%) calc. for C₂H₈N₆Cl₂ (MW = 187.03 g·mol⁻¹): C, 12.83; H, 4.28; N, 44.92; found C, 12.80; H, 4.19; N, 45.12; IR (KBr): 3328, 3141, 2954, 2689, 1661, 1536, 1505, 1421, 1348, 1316, 1272, 1228, 1194, 1184, 1150, 1071, 1060, 1030, 951, 880, 772, 713, 663, 606, 558 cm⁻¹; ¹H NMR (D₂O) δ: 9.63, 9.19, 8.84, 7.63 ppm; ¹³C NMR (D₂O) δ: 154.28, 141.25 ppm; Impact sensitivity: >40 J.

4-Amino-3-hydrazino-1,2,4-triazole (4): Compound **3** (1.87 g, 10 mmol) was dissolved in distilled water (30 mL). While stirring, sodium bicarbonate (10 wt.%, 16.8 mL) was added dropwise. The colorless solution turned purple. The mixture was stirred for 60 min, and the solvent was then evaporated in vacuo to produce a purple mixture. The mixture was recrystallized from methanol and dried in air to produce a purple solid, **4** (yield 78%, 0.91 g). MS m/z (ESI⁺): 115.0 [C₂H₇N₆]⁺; elemental analysis (%) calc. for C₂H₆N₆ (MW = 114.11 g·mol⁻¹): C 21.05, H 5.26, N 73.68; found C 19.98, H 3.36, N 72.91; IR (KBr): 3319, 3151, 3028, 2846, 2655, 1620, 1585, 1520, 1464, 1253, 1202, 1056, 1028, 921, 854, 748, 653 cm⁻¹; ¹H NMR (D₂O) δ: 8.72, 8.36, 6.24 ppm; ¹³C NMR (D₂O) δ: 155.52, 144.32 ppm.

General procedure for the preparation of the energetic salts 5-9

To obtain energetic salts **5-9**, solutions of silver perchlorate, silver dinitramide, silver 5-nitrotetrazolate, and silver 5-nitrotetrazolate-2N-oxide (10 mmol) in distilled water (20 mL), or silver 5-nitroiminotetrazolate (5 mmol) in distilled water (10 mL), respectively, were added dropwise to a solution of compound **3** (0.935 g, 5 mmol) in distilled water (20 mL). After stirring at room temperature for 1 h, the precipitate was filtered off and rinsed with distilled water

(10 mL). The solvent (filtrate) was evaporated in a vacuum, the residue was recrystallized from methanol and dried in air to give the target product.

4-Amino-3-hydrazino-1,2,4-triazolium diperchlorate (5): Yield: 94%, colorless transparent crystals. MS m/z (ESI⁺): 115.1 [C₂H₇N₆]⁺; elemental analysis (%) calc. for C₂H₈N₆Cl₂O₈ (MW = 315.03 g·mol⁻¹): C 7.62, H 2.54, N 26.67; found C 7.66, H 2.60, N 26.10; IR (KBr): 3346, 3155, 2951, 1642, 1531, 1389, 1291, 1259, 1048, 927, 724, 616 cm⁻¹; ¹H NMR (D₂O) δ: 9.08, 8.21 ppm; ¹³C NMR (D₂O) δ: 153.35, 143.30 ppm.

4-Amino-3-hydrazino-1,2,4-triazolium bis-dinitramide (6): Yield: 90%, white solid. MS m/z (ESI⁺): 115.1 [C₂H₇N₆]⁺; elemental analysis (%) calc. for C₂H₈N₁₂O₈ (MW = 328.16 g·mol⁻¹): C 7.32, H 2.44, N 51.22; found C 7.29, H 2.52, N 51.04; IR (KBr): 3402, 3343, 3126, 1679, 1532, 1461, 1191, 1081, 983, 825, 769, 722, 578, 488 cm⁻¹; ¹H NMR (D₂O) δ: 8.99, 7.57 ppm; ¹³C NMR (D₂O) δ: 152.89, 142.87 ppm.

4-Amino-3-hydrazino-1,2,4-triazolium di-5-nitrotetrazolate (7): Yield: 93%, pale yellow solid. MS m/z (ESI⁺): 115.06 [C₂H₇N₆]⁺; m/z (ESI⁻): 114.0 [CN₅O₂]⁻; elemental analysis (%) calc. for C₄H₈N₁₆O₄ (MW = 344.21 g·mol⁻¹): C 13.95, H 2.33, N 65.12; found C 14.06, H 2.42, N 64.81; IR(KBr): 3344, 3036, 2775, 2597, 1998, 1705, 1639, 1596, 1527, 1506, 1430, 1311, 1211, 1084, 1056, 939, 912, 853, 707, 608 cm⁻¹; ¹H NMR (D₂O) δ: 9.43, 8.18, 7.75 ppm; ¹³C NMR (D₂O) δ: 167.43, 153.88, 142.05 ppm.

4-Amino-3-hydrazino-1,2,4-triazolium di-5-nitrotetrazolate-2N-oxide (8): Yield: 89%, white solid. MS m/z (ESI⁺): 115.07 [C₂H₇N₆]⁺; m/z (ESI⁻): 130.1 [CN₅O₃]⁻; elemental analysis (%) calc. for C₄H₈N₁₆O₆ (MW = 376.21 g·mol⁻¹): C 12.77, H 2.13, N 59.57; found C 12.89, H 2.40, N 58.81; IR(KBr) ν : 3347, 3167, 3026, 2734, 2891, 2787, 1725, 1673, 1542, 1491, 1346, 1284, 1255, 1153, 1105, 1062, 886, 873, 832, 757, 689, 642, 615 cm⁻¹; ¹H NMR (D₂O) δ: 9.52, 8.08, 7.87 ppm; ¹³C NMR (D₂O) δ: 169.26, 153.35, 143.23 ppm.

4-Amino-3-hydrazino-1,2,4-triazolium 5-nitroiminotetrazolate (9): Yield: 85%, white solid. MS m/z (ESI⁺): 115.1 [C₂H₇N₆]⁺; m/z (ESI⁻): 128.0 [CN₆O₂]⁻; elemental analysis (%) calc. for C₃H₈N₁₂O₂ (MW = 244.17 g·mol⁻¹): C 14.75, H 3.28, N 68.85; found C 14.82, H 3.52, N 66.92; IR(KBr): 3446, 3214, 3029, 1703, 1558, 1446, 1333, 1239, 1159, 1101, 1057, 1034, 1007, 843, 769, 741, 653 cm⁻¹; ¹H NMR (D₂O) δ: 8.29, 6.25 ppm; ¹³C NMR (D₂O) δ: 158.56, 153.79, 143.06 ppm.

Acknowledgments

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