



Synthesis of Novel Energetic N-(1-Carboxymethyl-1*H*-tetrazole-5-yl)-hydrazinium Salts

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Abstract: Synthesis of materials with acceptable performance and low sensitivity to physical stimuli is one of the overall goals of energetic materials. The creation of networks of hydrogen bonds affords good stability to the trigger bonds. In this respect azole-based ionic high-energy materials (especially aminotetrazoles) and other nitrogen-rich compounds have strong hydrogen bonds. Significant stability, insensitivity to a physical stimulus and also good performance are thus created. In this study salts derived from N-(1-carboxymethyl-1*H*-tetrazole-5-yl)-hydrazinium chloride were synthesized. Anion exchange of the chlorine with nitrate, 5-aminotetrazolate, (5-amino-tetrazole-1-yl)-acetate and (5-nitriminotetrazole-1-yl)-acetate was performed, with precipitation of AgCl. All of the products were characterized using ¹H NMR, ¹³C NMR, FTIR spectroscopy, differential scanning calorimetry (DSC), impact sensitivity and UV-Vis spectroscopy. Among the advantages of this study are the use of methods and available equipment and low-risk solvents during the reaction and the formation of minimum by-products.

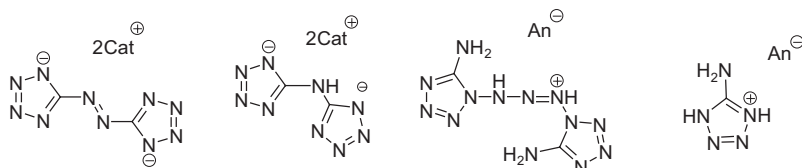
Keywords: aminotetrazole, hydrazinium salts, nitriminotetrazole, nitrogen-rich salts, nitrogen salt formation

1 Introduction

Nitrogen-rich compounds based on C/N heteroaromatic rings with high nitrogen content are at the forefront of high-energy materials research [1-3]. After decades of work in the preparation of energetic materials with high performance and low sensitivity, there are still concerns in this area. The desirable features for energetic

compounds include positive heat of formation, high density, high pressure and detonation velocity, high thermal stability and low sensitivity to external forces such as vibration, impact, shock, and friction [4-7].

In recent years, energetic nitrogen-rich compounds have been highly regarded. Triazole, tetrazole, and pyrazine compounds are highly regarded in this group. Unlike high-energy compounds with carbon backbones or pressure cages, after combustion, large volumes C, CO₂ and large amounts of N₂ gas are released that from the standpoint of the environment and green chemistry are very important and desirable. The stability of energetic ionic compounds can also be upgraded with selected cations. So the exploration of energetic salts with the correct choice of cations and anions, because of their widespread use in explosives, propellants and pyrotechnics, has received wide attention. They have high positive heat of formation, higher stability and also, often, a higher density, than the analogous nonionic types. Frequently changing the anionic and cationic components, can readily adjust their properties [8-11] (Scheme 1).



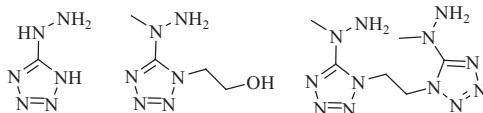
Scheme 1. Examples of some recent advances in energetic aminotetrazole salts

During the preparation of free tetrazole from its derivatives, the heterocyclic ring displayed remarkable stability in the presence of acids, alkalis, and oxidizing and reducing agents. The tetrazole ring is thermodynamically stable, as demonstrated by the fact that it is recovered unchanged after long periods of boiling and heating. Because of the high nitrogen content, its compounds may be of high density, releasing considerable energy and gases upon decomposition/explosion. This gives rise to the superior explosive properties of many tetrazole derivatives. The physical and explosive properties of tetrazole derivatives are rather easily modified by the replacement of substituents on the tetrazole ring with various functional groups [12-16].

Researchers have replaced salts with conventional, high-energy compounds that are toxic and sensitive to various types of stimuli [17]. It is important to note that these compounds can be used in cases such as gas generators, pyrotechnics, smokeless fuels, solid-fuel micro-propulsion systems, fire suppression systems on military aircraft, precursors for nanomaterials, carbon nitride and carbon nanospheres [18, 19]. Also, there is considerable interest in the medicinal and biological

applications of tetrazoles, including 5-aminotetrazoles, due to their reported anti-allergic and anti-asthmatic antiviral and anti-inflammatory, anti-neoplastic, and cognition disorder activities [20]. Tetrazoles are also applied as ligands in coordination chemistry [21], as explosives and rocket propellants. Another important application of tetrazoles is in the preparation of dyes and pigments; they tend to show a good compromise between performance and sensitivity [22].

Theoretical studies have shown that the incorporation of hydrazino groups into a heterocyclic ring increases the heat of formation of the entire molecule. In addition the $-NH-NH_2$ structure can increase the intra- and inter-molecular hydrogen bonds, which are useful in increasing the density and lowering the sensitivity. Moreover, the hydrazino group also increases the overall molecular nitrogen content. Recent modelling and testing have shown that the presence of high concentrations of nitrogen containing species in the combustion products of propellants can reduce gun barrel erosion by promoting the formation of iron nitride rather than iron carbide on the interior surface of the barrel. The hydrazine moiety is also widely used as a propellant component. Thus, new hydrazine-substituted azoles may be compatible with traditional energetic materials [8] (Scheme 2).



Scheme 2. Examples of some recent advances in energetic salts containing hydrazine groups

Our interest in the study of aminotetrazole derivatives prompted us to develop simple, and efficient procedures for the synthesis of the *N*-(1-carboxymethyl-1*H*-tetrazole-5-yl)-hydrazinium based salts, with high nitrogen and energy content.

2 Materials and Methods

Caution: Although we experienced no difficulties in handling these materials, with such high positive heats of formation they could be unstable. Therefore, manipulations must be carried out in a hood behind a safety shield. Eye protection and leather gloves must be worn. Extreme caution should be exercised at all times during the synthesis, characterization, and handling of any of these materials, and mechanical actions involving scratching or scraping must be avoided.

2.1 Instruments and analysis

All reagents and solvents used in this study were commercially available and were purchased from commercial supplier Merck. All materials were commercially available and used as received. All melting points were determined in open capillaries with a Gallenkamp instrument. UV-Visible spectrophotometry was determined with a Rey Leigh UV-2601, Beijiny Beifun-Ruili Analytical instrument (Group) Co. Ltd. IR spectra were recorded by using KBr pellets for solids on a Nicolet 800 spectrometer. ^1H spectra were recorded on a Bruker (Avance DRX) spectrometer operating at 250 MHz, 300 MHz, and 500 MHz and ^{13}C NMR spectra were recorded on a Bruker (Avance DRX) spectrometer operating at 75 MHz, 100 MHz, and 125.71 MHz, using D_2O and $[\text{D}_6]\text{DMSO}$ as the locking solvent unless otherwise stated. ^1H and ^{13}C NMR chemical shifts are reported in ppm relative to TMS. DSC measurements were carried out using a Shimadzu instrument with a DSC-50 module. Thermal transitions were determined at a scan rate of $10\text{ }^\circ\text{C}\cdot\text{min}^{-1}$ and under a nitrogen atmosphere. The sensitivities towards impact and friction were measured by BAM methods.

2.2 Preparation of 5-aminotetrazole monohydrate [30]

Dicyandiamide (three times recrystallized, 5000 mg, 5.95 mmol), sodium azide (7470 mg, 11.9 mmol), boric acid (11000 mg, 17.8 mmol) and water (100 mL) were added to a round-bottom flask equipped with a condenser and a magnetic stirring bar, and allowed to reflux for 24 h. After completion of the reaction, hydrochloric acid (37%, about 12 mL) was added and the pH was adjusted to 2-3. The mixture was then cooled in a refrigerator ($4\text{ }^\circ\text{C}$) for 18 h and white crystals deposited. The solid was filtered off and washed three times with water ($3\times 10\text{ mL}$) and dried at $60\text{ }^\circ\text{C}$ for 5 h. The product (45.8 g, 68% yield) was obtained as white crystals; m.p. $201\text{--}205\text{ }^\circ\text{C}$; IR: (N–H) 3485, 3384, 3274, 3199 vs, 1642, 1450, (N–N=N–) 1299, 1155 m, 1058 $\text{s}\cdot\text{cm}^{-1}$; ^{13}C NMR (125 MHz, $[\text{D}_6]\text{DMSO}$): 156.91 (–C–NH₂) ppm.

2.3 Preparation of 1-carboxymethyl-5-aminotetrazole [31]

In chloroacetic acid (500 mg, 5.28 mmol), 5-aminotetrazole monohydrate (450 mg, 5.28 mmol), and sodium hydroxide (590 mg, 10.57 mmol) in water (10 mL) were added to a round-bottom flask equipped with a condenser and a magnetic stirring bar and was refluxed for 20 h. After cooling the mixture was made strongly acidic with concentrated hydrochloric acid. After cooling overnight a precipitate had separated to give the product (0.28 g, 45.41% yield) as white crystals; m.p. $210\text{--}213\text{ }^\circ\text{C}$; IR: (N–H and O–H) 3388, 3315, 3270, 3205 vs, 3010 (–CH₂), 2976 m, (–C=O) 1697 vs, 1638, 1586, 1496, (N–N=N–)

1259 $\text{s}\cdot\text{cm}^{-1}$; ^{13}C NMR (75 MHz, $[\text{D}_6]\text{DMSO}$): 168.80 ($-\text{C}=\text{O}$), 156.01 ($-\text{C}-\text{NH}_2$), 46.62 ($-\text{CH}_2$) ppm.

2.4 Preparation of (5-nitriminotetrazole-1-yl)-acetic acid

NH_4NO_3 (600 mg, 7.5 mmol) was dissolved in H_2SO_4 (98%, 6 mL) in a beaker equipped with a magnetic stirring bar. The solution was cooled to $0-4^\circ\text{C}$ and (5-amino-tetrazole-1-yl)-acetic acid (0.60 mg, 0.0041 mmol) was added in small portions to the nitration mixture. The reaction mixture was stirred for 7-8 h at $0-4^\circ\text{C}$. After completion of the reaction, the mixture was poured onto crushed ice. The aqueous mixture was extracted with EtOAc (3×10 mL). The combined organic extracts were dried (MgSO_4) and the solvent was evaporated to give the product (0.28 g, 57% yield) as white crystals; m.p. $160-163^\circ\text{C}$; IR: ($\text{N}-\text{H}$ and $\text{O}-\text{H}$) 3544, 3467 vs, ($-\text{CH}_2$) 3016, 2968 vs, ($-\text{C}=\text{O}$) 1736 vs, 1634, 1582, 1486, ($-\text{NO}_2$) 1403 s, 1338, 1308 vs, ($\text{N}-\text{N}=\text{N}-$) 1224 vs cm^{-1} ; ^{13}C NMR (75 MHz, $[\text{D}_6]\text{DMSO}$): 167.73 (vs, $-\text{C}=\text{O}$), 151.14 ($-\text{C}-\text{NNO}_2$), 48.27 ($-\text{CH}_2$) ppm.

2.5 General procedure for the preparation of silver salts

5-Aminotetrazole, (5-aminotetrazol-1-yl)-acetic acid, and (5-nitriminotetrazol-1-yl)-acetic acid (1-2 equiv) were treated separately with sodium hydroxide (1.1-2.1 equiv) in water in a round-bottom flask equipped with a magnetic stirring bar and heated at $50-60^\circ\text{C}$ under air. The mixture was vigorously stirred under these reaction conditions and the reaction was complete after 1 h. After completion of the reaction, silver nitrate (1-2 equiv) was dissolved in deionized water in a beaker equipped with a magnetic stirring bar and the solution of the sodium salt was added in the dark. The silver salt precipitated immediately as a white powder. The suspension was stirred for 2 h at ambient temperature. The product was filtered off and dried.

2.6 Preparation of N-(1-carboxymethyl-1H-tetrazole-5-yl)-hydrazinium chloride (2)

(5-Amino-tetrazole-1-yl)-acetic acid (200 mg, 0.70 mmol) was dissolved in NaOH (15%, 1 mL) in a round-bottom flask equipped with a magnetic stirring bar, and potassium permanganate (200 mg, 0.70 mmol) in H_2O (1 mL) was added dropwise at 50°C . The dark green reaction mixture was stirred at 50°C (30 min). Ethanol (0.2 mL) was added and the thick, brown slurry was refluxed for 2 h. The still hot mixture was filtered and the solid was washed with boiling water as long as the filtrate was still yellow. Hydrochloric acid (37%, 2-3 mL) was added dropwise to the yellow filtrate solution and a large quantity of bubbles was generated; the yellow solution became pale. The mixture was stirred for 30 min

and then warmed slowly to 50 °C. After stirring for an additional 30 min, until no more bubbles were generated, the solution was concentrated under vacuum to produce an orange-yellow mixture. This mixture was mixed with methanol and the inorganic salt was removed by filtration. After filtering, the solvent was removed under reduced pressure to give the product (0.04 g, 18% yield) as orange crystals; IR: (N–H and O–H) 3396, 3331, 3144 vs, (–CH₂) 3008 m, (–C=O) 1700 m, 1628, 1403, (N–N=N–) 1273 m, (–Cl) 825, 666 m, cm⁻¹; ¹³C NMR (75 MHz, D₂O): 172.33 (–C=O), 156.39 (–C–NH), 54.25 (–CH₂); UV/VIS (H₂O): λ_{max} (lg ε): 310-313 nm.

2.7 Preparation of N-(1-carboxymethyl-1*H*-tetrazole-5-yl)-hydrazinium nitrate (3)

A solution of AgNO₃ (100 mg, 0.60 mmol) in distilled water (1.5 mL) was added dropwise, in the dark, to the solution of compound 2 (100 mg, 0.60 mmol) in deionized water (1.5 mL) with stirring. After 2-3 h the precipitate was filtered off and rinsed with distilled water (4 mL). The filtrate plus washings was concentrated by rotary evaporation to give the product (0.10 g, 88% yield) as yellow crystals; IR: (N–H and O–H) 3396, 3329, 3140 vs, (–CH₂) 3008 m, (–C=O) 1700 w, 1628, 1494, (–NO₂) 1383 vs, (N–N=N–) 1280 m, cm⁻¹; UV/VIS (H₂O): λ_{max} (lg ε): 293-296 nm.

2.8 Preparation of N-(1-carboxymethyl-1*H*-tetrazole-5-yl)-hydrazinium-(5-nitrimino-tetrazole-1-yl)-acetate (4)

A mixture of compound 2 (50 mg, 0.20 mmol) in deionized water (1.5 mL) and silver (5-nitroimino-tetrazole-1-yl)-acetate (300 mg, 0.1 mmol) in distilled water (1.5 mL) was stirred in the dark at room temperature. The precipitate was filtered off and rinsed with distilled water (5 mL). The clear filtrate was evaporated to dryness under reduced pressure to obtain the product (42 mg, 85% yield) as white crystals; IR: (N–H and O–H) 3396, 3329, 3256, 3138 vs, (–CH₂) 3008 m, (–C=O) 1734 w, 1628, 1586, 1403, (–NO₂) 1403 s, 1389, 1360 m (N–N=N–) 1269 w, cm⁻¹; ¹³C NMR (125 MHz, D₂O): 172.08 (–COOH), 171.93 (–COO), 170.15 (–C–NNO₂), 156.00 (–C–NH–NH₃), 55.52 (–CH₂COO), 50.24 (–CH₂COOH) ppm; UV/VIS (H₂O): λ_{max} (lg ε): 280-283 nm.

2.9 Preparation of N-(1-carboxymethyl-1*H*-tetrazole-5-yl)-hydrazinium 5-aminotetrazolate (5)

Compound (5) was synthesized by mixing silver 5-aminotetrazolate (300 mg, 1.50 mmol) with a solution of compound (2) (100 mg, 0.6 mmol) in deionized water (1.5 mL) in the dark. After stirring for 2-3 h a white precipitate had separated

and, after filtering, the solvent was removed under reduced pressure to give the product (0.10 g, 80% yield) as white crystals; IR: (N–H and O–H) 3396, 3331, 3154 vs, (–CH₂) 3008 m, (–C=O) 1700 w, 1628, 1403, (N–N=N–) 1269 w, cm⁻¹; ¹³C NMR (125 MHz, [D₆]DMSO): 171.96 (–C=O), 155.61 (–C–NHNH₃), 148.47 (–C–NH₂), 55.27 (–CH₂), ppm; UV/VIS (H₂O): λ_{max} (lg ε): 379–381 nm.

2.10 Preparation of N-(1-carboxymethyl-1H-tetrazole-5-yl)-hydrazinium-(5-amino-tetrazole-1-yl)-acetate (6)

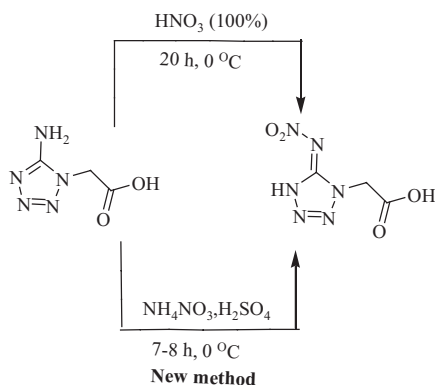
A mixture of compound (2) (80 mg, 0.41 mmol) in deionized water (1.5 mL) and silver (5-amino-tetrazole-1-yl)-acetate (300 mg, 1.20 mmol) in deionized water (1.5 mL) was stirred at room temperature for 3–4 h in the dark. The precipitate was then filtered off and the filtrate was concentrated under vacuum by rotary evaporation to give the product (0.10 g, 80% yield) as white crystals; IR: (N–H and O–H) 3396, 3329, 3256, 3138 vs, (–CH₂) 3008 m, (–C=O) 1683 w, 1628, 1586, 1403, (N–N=N–) 1271 w, cm⁻¹; ¹³C NMR (100 MHz, D₂O): 171.98 (–COOH), 165.96 (–COO), 155.69 (–C–NHNH₃), 148.11 (–C–NH₂), 55.27 (–CH₂COOH), 30.08 (–CH₂COO); UV/VIS (H₂O): λ_{max} (lg ε): 347–350 nm.

3 Results and Discussion

Nitro compounds have long been the focal point of useful energetic compounds [23–25]. The energy from traditional nitro compounds results primarily from the combustion of the carbon backbone, which consumes the oxygen provided by the nitro groups. The presence of nitro groups tends to decrease the heat of formation but contributes markedly to the overall energy performance. The search for new and improved energetic materials, suitable for use as explosives, propellants, or pyrotechnics, is a continuing challenge. The synthesis of energetic salts as a special class of highly energetic materials has received increased interest over the past decade. The present search for energetic salts is directed mainly towards the modification of cations or the synthesis of organic anions. The further development of energetic salts requires new anions that exhibit high safety, performance, density, and stability [23].

Nitration of the amino group in aminotetrazoles leads to enhanced energetic character as well as higher sensitivity compared to the aminotetrazoles themselves and improves the oxygen balance. The methyl group lowers the sensitivity compared to the non-methylated 5-nitriminotetrazole [26]. 5-Nitriminotetrazoles, which can be prepared from 5-aminotetrazole and 100% nitric acid, as high nitrogen compounds are good candidates for high explosives because they combine both

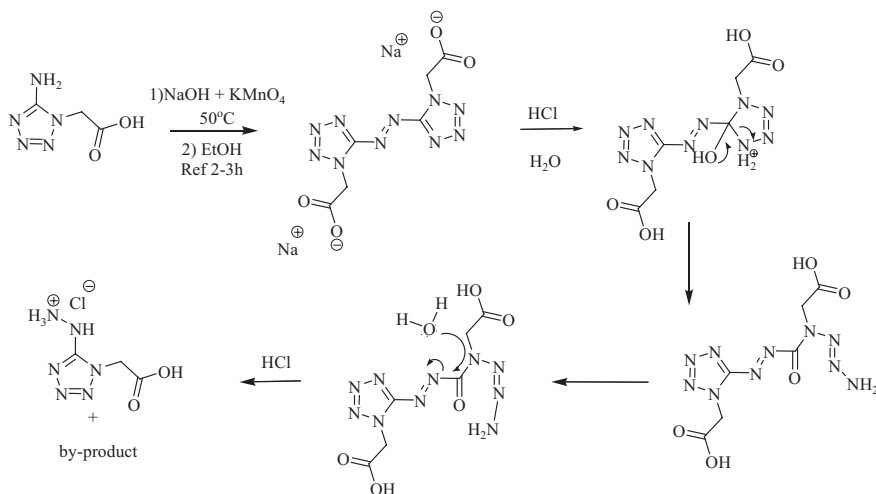
the strongly oxidizing nitrimino-group and the energetic nitrogen-rich backbone in a single molecule [27]. In the present study this substance was synthesized using a mild and inexpensive reaction (Scheme 3) and (5-nitriminotetrazole-1-yl)-acetate was exchanged with chlorine in two compounds.



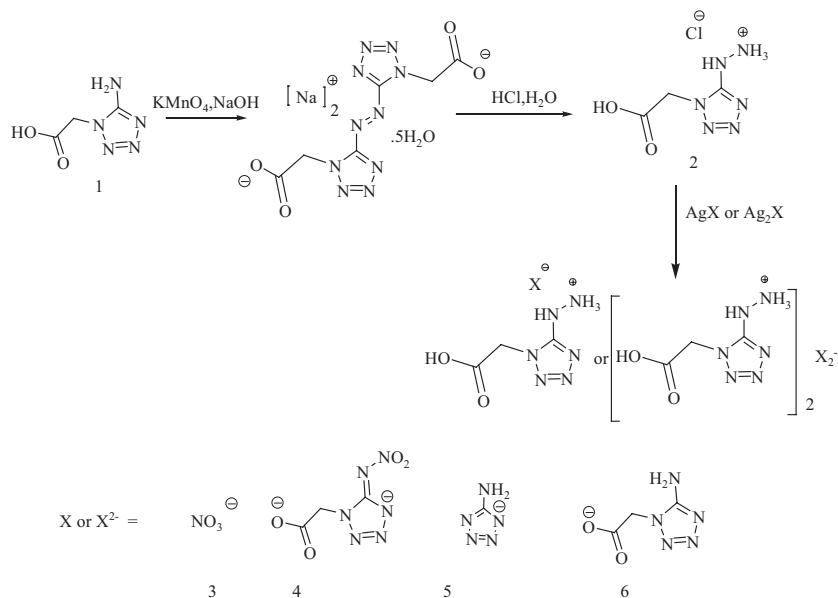
Scheme 3. Synthetic pathway for 5-nitriminotetrazoles

Commercially available, inexpensive (5-amino-tetrazole-1-yl)-acetic acid was oxidized by potassium permanganate in sodium hydroxide solution, yielding sodium (5,5'-azotetrazol-1-yl)-acetate pentahydrate (Na_2ZTA), which was isolated. Na_2ZTA was then dissolved in distilled water and reacted with an excess of dilute hydrochloric acid; subsequently, the solvent was removed under vacuum to produce a yellow-orange mixture. This mixture was then washed with absolute methanol to produce N-(1-carboxymethyl-1*H*-tetrazole-5-yl)-hydrazinium chloride (2) (Scheme 4). As shown in Scheme 5, a family of energetic salts based on nitrogen-rich anions and the N-(1-carboxymethyl-1*H*-tetrazole-5-yl)-hydrazinium chloride (HTZA) cation were prepared. Such salts would be expected to possess a high nitrogen and a relatively high oxygen content. The combination of the nitrogen-rich cation (HTZA) with an oxygen-rich anion forms a class of energetic materials whose energy is derived from their very high positive heats of formation (directly attributed to the large number of inherently energetic N–N, N–O, and N–C bonds) as well as the combustion of the carbon atoms. Compounds 3–6 were readily synthesized by anion exchange of silver nitrate, silver 5-aminotetrazolate, silver (5-amino-tetrazole-1-yl)-acetate and silver (5-nitriminotetrazole-1-yl)-acetate with N-(1-carboxymethyl-1*H*-tetrazole-5-yl)-hydrazinium chloride in H_2O . The structures of the compounds were confirmed by ^1H and ^{13}C NMR, IR and UV-Vis spectroscopy. In the ^{13}C NMR spectra, two weak signals (*ca.* 156–172 ppm) and one strong signal

(ca. 54-55 ppm) were assigned to the cation, and these chemical shifts changed a little due to interactions between the cations and anions.



Scheme 4. Synthesis of N-(1-carboxymethyl-1H-tetrazole-5-yl)-hydrazinium chloride



Scheme 5. Synthesis of N-(1-carboxymethyl-1H-tetrazole-5-yl)-hydrazinium chloride and the N-(1-carboxymethyl-1H-tetrazole-5-yl)-hydrazinium based salts

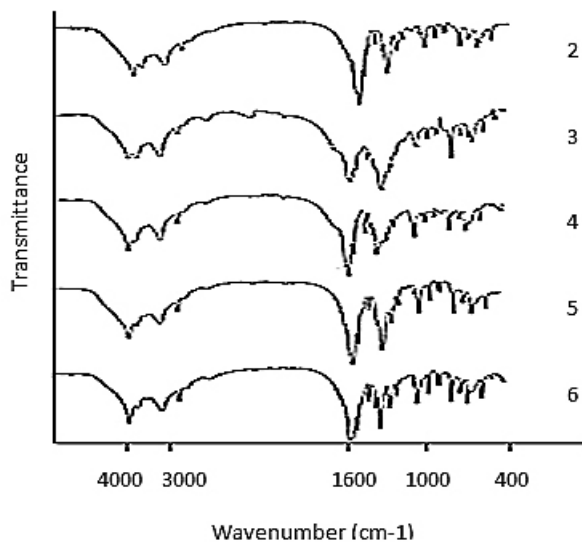


Figure 1. Panel plot of the IR spectra of the energetic salts derived from N-(1-carboxymethyl-1*H*-tetrazole-5-yl)-hydrazinium chloride

3.1 Vibrational spectroscopy

The FT-IR spectra of the synthesized compounds showed similar absorptions at 3000–3400 cm^{-1} (N–H), and 1600, 1400 (cm^{-1}) (heterocycle ring). The spectrum of 5-aminotetrazole is in perfect agreement with those reported in the literature [28, 29]. The spectrum of each compound showed characteristic bands of the relevant, energetic anion (nitrate, 5-aminotetrazolate, (5-aminotetrazole-1-yl)-acetate and (5-nitriminotetrazole-1-yl)-acetate) and a set of bands corresponding to the cation. The nitrate anion, NO_3^- , shows a strong (or very strong) IR absorption centered at 1300–1350 cm^{-1} (both 3 and 4; Figure 1). Other compounds, because of the similarity in their structures, did not exhibit significant NMR spectroscopy.

3.2 NMR Spectroscopy

In the ^{13}C NMR spectrum of salt 6, the methylene group in the anion occurs at higher field than in the cation because of the carboxylate adjacent to the methylene group is an electron donor and carboxylic group is an electron acceptor; furthermore for the ring carbon in salt 4, the ring carbon in the anion occurs at a higher field than in the cation because of the hydrazinium group adjacent to the ring carbon, an electron donor and the nitrimino group is an electron acceptor. The tetrazole carbon signal in 5 occurs upfield relative to

4 and 6 anionic compounds. The resonance peak for carbon connected to the hydrazine group is nearly overlapping in 2 and 3. The signal corresponding to the methylene group in 1-carboxymethyl-5-aminotetrazole at $\delta=46$ ppm is found at a higher field in salt 2 ($\delta=53$ ppm) and at a lower field in salt 6 ($\delta=30$ ppm).

3.3 Differential scanning calorimetry (DSC)

The thermal stabilities of the 5-hydrazinotetrazolium salts were determined by differential scanning calorimetric (DSC) measurements. The salts have good thermal stability, with decomposition temperatures ranging from 267.2 °C (5) to 351.3 °C (6). Compound 6 is more thermally stable than RDX and HMX. These differences indicate that the incorporation of hydrazino and carboxy groups into a tetrazole ring can enhance the thermal stability (Figure 2).

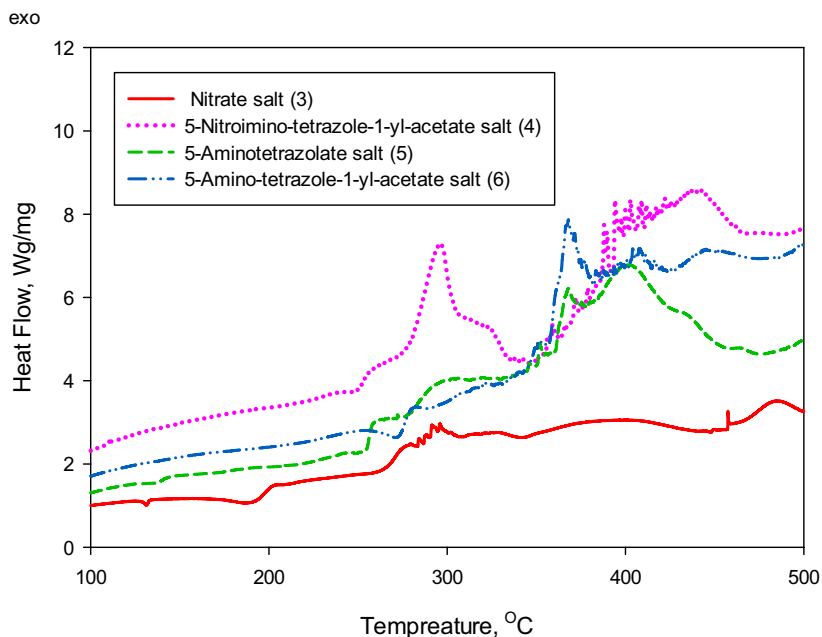


Figure 2. Panel plot of the DSCs of the energetic salts derived from N-(1-carboxymethyl-1*H*-tetrazole-5-yl)-hydrazinium chloride

3.4 Impact and friction sensitivity

The salt (5) exhibited a friction sensitivity of 324 N and is a highly sensitive explosive. However, the salts (3 and 4) are much less sensitive at 360 N, and the salt (6) is insensitive at more than 360 N, which is >238 N higher than that of HMX (Table 1).

The impact sensitivity of the hydrazinium salts in this study range from 8.4 N·m (5) to 10.5 N·m (6). The calculated impact sensitivity of the hydrazinium salts is higher than that of HMX and RDX (Table 1).

Table 1. The physicochemical properties of the energetic salts derived from N-(1-carboxymethyl-1H-tetrazole-5-yl)-hydrazinium chloride

Salt	Decomposition temperature [°C]	Oxygen balance [%]	Nitrogen content [%]	Friction sensitivity [N]	Impact sensitivity [N·m]
3	295.8	-32.6	44.3	360	9.5
4	296.2	-57.1	49.9	360	9.6
5	267.1	-69.1	63.3	324	8.4
6	351.3	-71.7	51.1	>360	10.5
RDX	230	-26.1	37.8	122	7.4
HMX	287	-21.6	37.8	122	7.4

4 Conclusions

A series of nitrogen-rich energetic salts based on HTZA by anion exchange of chlorine were prepared. The significant advantages of this methodology are high yields, simple methodology, simple work-up with no chromatographic separation, and the use of low-risk solvents during the reaction with minimum by-products. The use of water as the solvent suggests good prospects for the applicability of this process. Furthermore, the 5-nitriminotetrazoles, as high nitrogen compounds and good candidates for high explosives (because they combine both the strongly oxidizing nitrimino-group and the energetic nitrogen-rich backbone in a single molecule), with a simple and inexpensive method of synthesis, were fully characterized by DSC, NMR, IR, and UV-Vis spectroscopy. The resulting salts are thermally stable to 267-351 °C. The salts have reasonable friction sensitivities (324 N to >360 N) and salt 6 has the highest friction sensitivity at >360 N (friction: insensitive >360 N, less sensitive <360 N, 80 N < sensitive <360 N, very sensitive <80 N, extremely sensitive <10 N [32]). The HTZA salts have potential as energetic materials.

The hydrazino group, by increasing the nitrogen content and the hydrogen bond network, has been shown to be a useful moiety for developing new energetic cations. Studies on other hydrazino-substituted azole cations are currently ongoing.

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