



Energetic Nitrogen-rich Salts

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Abstract: Energetic salts as a unique class of energetic materials have recently been investigated widely, since they possess advantages over their atomically similar nonionic analogues – they tend to exhibit lower vapor pressures, higher densities and better thermal stabilities. Furthermore, these salts are readily improved upon by the appropriate combination of different cations and anions. Over the last twenty years, our group has continued to synthesize and study novel ionic energetic materials. Here, we have summarized all of the series of nitrogen-rich energetic salts. This review gives an overview of the various studies dealing with synthetic aspects and some of the physicochemical properties of ionic compounds that are based on ammonia, guanidine, semicarbazide, carbonylhydrazide, tetrazine, tetrazole, triazole and imidazole. In addition, their potential applications in the fields of explosives and propellants are discussed. We hope these investigations will be helpful in providing a wider insight for future research in the area of energetic salts.

Keywords: energetic salts, synthesis, characterization, crystal structure, review

1 Introduction

During recent decades, considerable progress has been achieved in the development of modern high energy density materials (HEDM), of which energetic nitrogen-rich salts are among the most exciting developments [1]. The salt-based materials often possess advantages over their atomically similar nonionic analogues, since they tend to exhibit lower vapor pressures, higher densities and higher thermal stabilities [2]. Furthermore, the large number of N-N

and C-N bonds in the so called “nitrogen-rich” ionic compounds directly results in high heats of formation. At the same time, their low carbon and hydrogen contents give them a good oxygen balance [3]. It is known that nitrogen-rich compounds possess many advantages compared to traditional explosives such as TNT, HMX and RDX; most of their energy derives from a combination of positive heats of formation rather than oxidation of the carbon backbone in traditional explosives. The large number of hydrogen-bonding networks (especially between amino and nitro groups) in ionic energetic materials are known to confer stability and relative insensitivities to physical stimuli, as well as good performance [4].

Most importantly, these nitrogen-rich salts are environmentally friendly (green materials), because a high proportion of the decomposition products of these compounds will be dinitrogen. Chemists are greatly interested in these “green” materials as potential alternatives to the currently used explosives and propellants, such as RDX, which has been identified as toxic and possibly carcinogenic [5]. In addition, the properties of these salts are readily optimized and improved by the appropriate combination of different cations and anions, as well as a result of independent modification of the ionic components [6]. Considerable efforts has been made in the design and synthesis of energetic nitrogen-rich salts, with higher performance and enhanced insensitivity, by choosing appropriate ions, especially in the work of Klapötke’s group in Germany and Shreeve’s group in the United States, which are leading the development of energetic ionic salts [7].

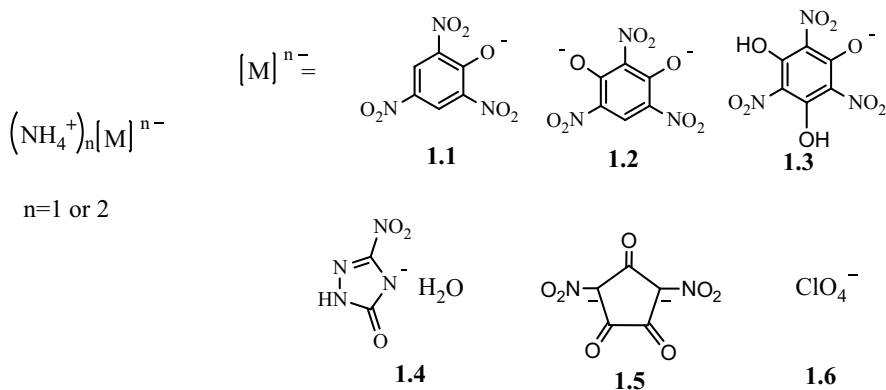
Our group, which has a continuing interest in the area of ionic materials, was prompted to research in this area, and our results over the last twenty years are reviewed here. This review gives an overview of our various studies, dealing with synthetic aspects and some of the physicochemical properties of ionic materials. The potential applications of these ionic compounds as explosives and propellants are also discussed.

2 Ammonium-based Salts

The ammonium ion (chemical formula: NH_4^+) has a tetrahedral structure, its chemical properties are similar to those of metal ions and it is readily formed by reaction of ammonia with acidic substances.

The reactions of ammonia with energetic acids yield ammonium salts. Thus ammonium salts with picric acid (**1.1**), 2,4,6-trinitroresorcinol (**1.2**), trinitrophenol (**1.3**), 3-nitro-1,2,4-triazol-5-one (**1.4**, as the monohydrate),

3,5-dinitrocyclopentane-1,2,4-trione (**1.5**) [8] have been reported. Ammonium perchlorate is another energetic salt (**1.6**), synthesized by reacting ammonia with concentrated perchloric acid [9], and its molecular structure was the first to be reported (Scheme 1). All of the salts were characterized by elemental analysis, DSC (differential scanning calorimetry) and single-crystal X-ray diffraction (Figure 1). These salts are energetic and stable at moderate temperatures, within the range 220-250 °C. The structural study of **1.1**, **1.3**, **1.6** showed significant hydrogen bonding between the ammonium cation and the deprotonated benzene rings or perchlorate anions, which contributes to their relatively high densities, 1.91, 1.994, and 1.952 g·cm⁻³, respectively. By contrast, crystal water will decrease the density of a compound such **1.4** (1.65 g·cm⁻³) [8e]. The enthalpy of formation of **1.1**, which was calculated using the Gaussian 03 program, was 49.03 kJ·mol⁻¹, and showed promising calculated performance values (P = 27.02 GPa, D = 7.92 km·s⁻¹), compared to TNT (P = 19.5 GPa, D = 6.89 km·s⁻¹) [8d].



Scheme 1. Salts based on ammonia.

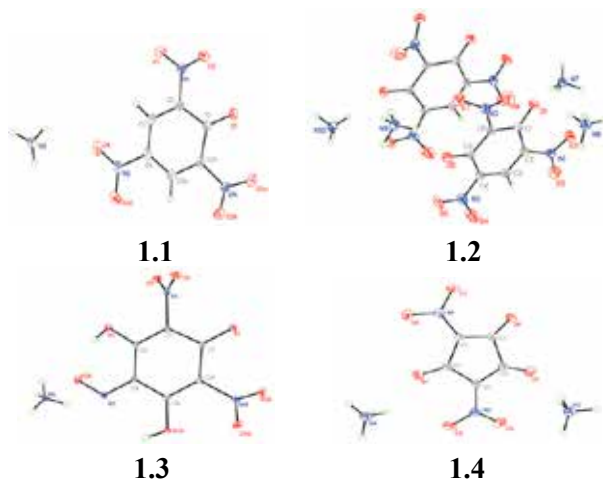
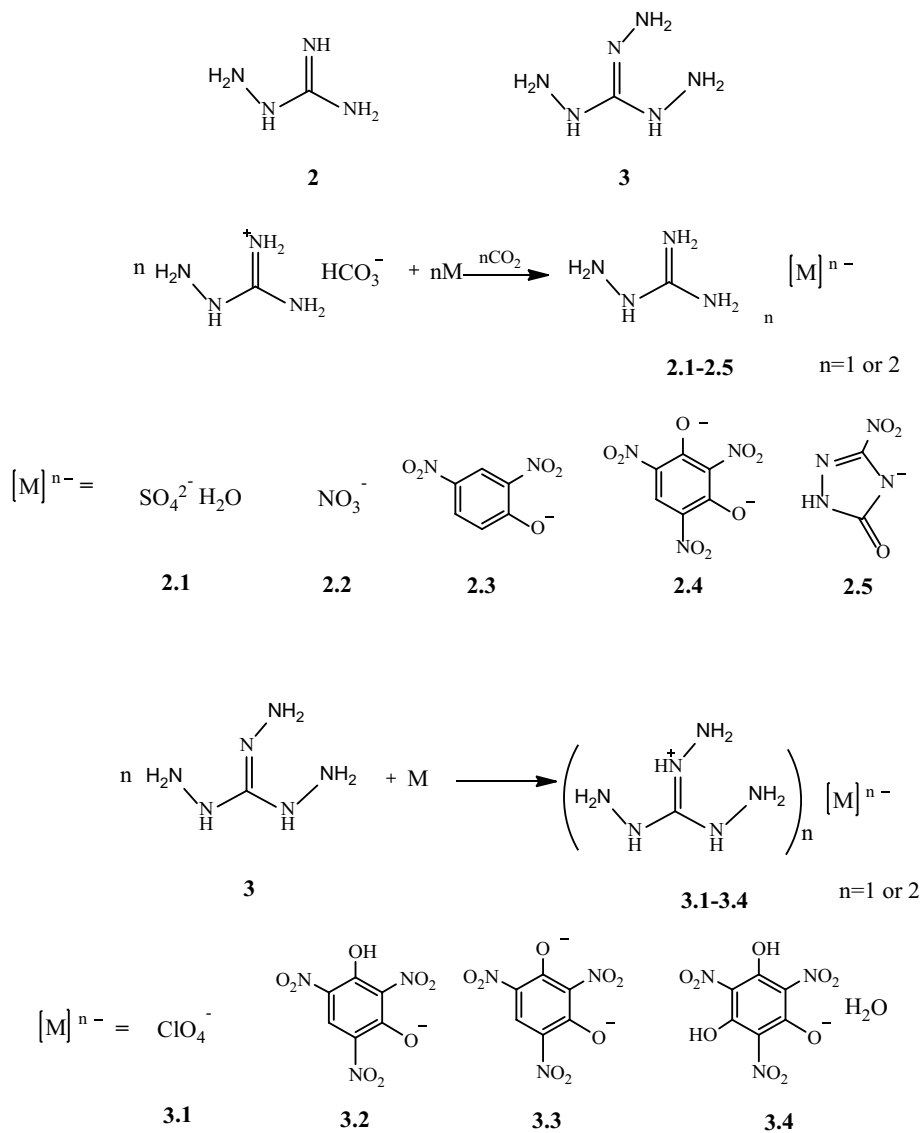


Figure 1. Selected crystal structures of ammonium salts.

3 Guanidine-based Salts

Aminoguanidine (**2**) (N% = 75.7%) and triaminoguanidine (**3**) (N% = 80.7%) are widely studied due to their high-nitrogen content on the one hand and low toxicity levels on the other. The neutral structures of **2** and **3** are unstable and they are easily protonated under acidic conditions to become cations. The delocalized electrons in these cations form a large π bond, conferring more stable [10].

Aminoguanidine (**2**) and triaminoguanidine (**3**) salts with mono- or dianions (**2.1** to **2.5**, **3.1** to **3.4**, respectively) were synthesized by the reaction of the stoichiometric amounts of aminoguanidinium bicarbonate or neutral triaminoguanidine with the free-acids (Scheme 2) [11]. The nitrogen-rich salts of **2** and **3** (Figure 2) generally have a positive enthalpy of formation; the molecular structures have high nitrogen contents, and the carbon and hydrogen contents are low, making them easier to achieve oxygen balance; a large amount of gas is released during explosion or burning and almost no residue is left. In addition, they showed low sensitivity towards to friction and impact stimuli, indicating that they can be used as components in gas generating agents or in propellant compositions to improve the combustion characteristics of the propellant. From calculations, **2.5** has potential to be a gassing agent in airbags, due to it relatively high nitrogen content (N% > 50%), high density ($d = 1.698 \text{ g}\cdot\text{cm}^{-3}$), and good stability [12].



Scheme 2. Salts based on guanidine.

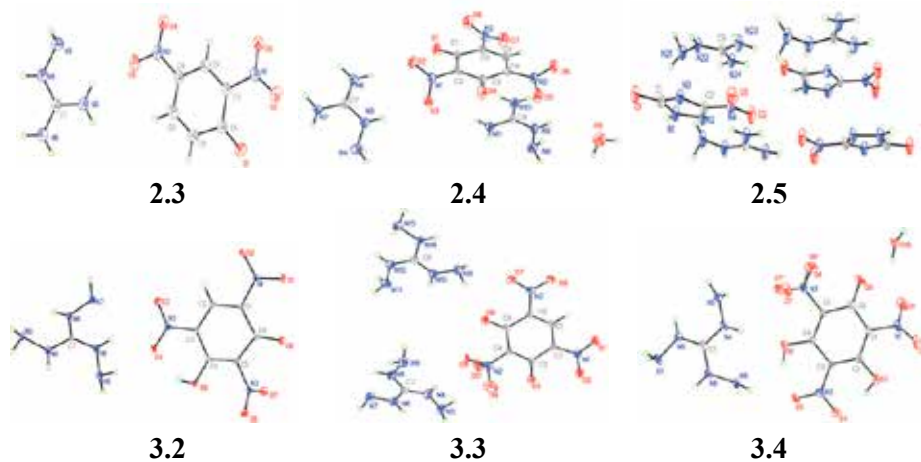


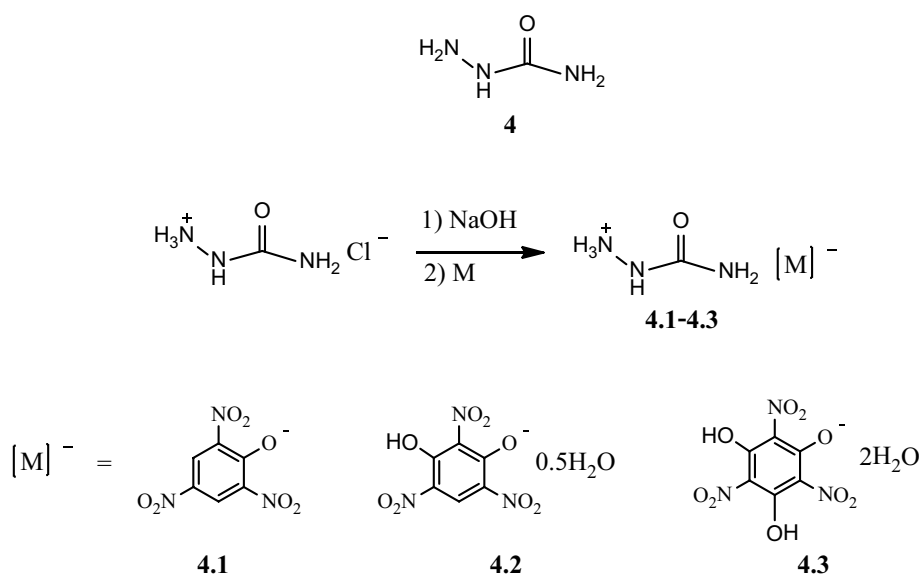
Figure 2. Selected crystal structures of guanidine salts.

4 Semicarbazide-based Salts

Semicarbazide (**4**) is an important intermediate in organic synthesis and is widely used in preparing pharmaceuticals, including nitrofurans (furazolidone, nitrofurazone, nitrofurantoin) and related compounds. Its molecule is rich in nitrogen atoms and consists of a hydrazine group, a carbonyl group and an amino group, which determine its lively chemical reactivity. The salts, consisting of the protonated semicarbazide cation paired with nitrophenol anions, were the first to be synthesized and determined by X-ray single crystal diffraction. Semicarbazide hydrochloride was reacted with sodium hydroxide until the pH reached about 8-9, and then reacted with an aqueous solution of the nitrophenol. This procedure gave excellent yields of the semicarbazide salts of picric acid (**4.1**), 2,4,6-trinitroresorcinol, as the hemihydrates (**4.2**), and 2,4,6-trinitrophenol as the dihydrate (**4.3**) [13].

Single-crystal X-ray analysis of these salts (Figure 3) indicated the existence of significant hydrogen bonding between the semicarbazide cations and the nitrophenol anions, to which their high density (range 1.768-1.835 g·cm⁻³) was attributed. These extensive hydrogen bonds also make an important stabilizing contribution to the ionic compounds. The calculated enthalpy of formation of **4.1** was -69.03 kJ·mol⁻¹. Using the Kamlet-Jacobs equations [14], the detonation velocity and detonation pressure of **5.1** were: $D = 7.94 \text{ km}\cdot\text{s}^{-1}$, $P = 27.86 \text{ GPa}$, significantly better than those of TNT, a traditional explosive. In addition, other

properties, such as being environmentally friendly, the energetic salt **4.1** has a wide range of prospective research and development areas. The TG-DTG and DSC analysis of **4.2** and **4.3** showed that they undergo a dehydration process and then decompose at a relatively high temperature (>178 °C), corresponding to a large weight loss on the TG-DTG curves, with further weight loss occurring continuously with heating; the products are essentially gases, with no final residue. The sensitivities of **5.2** and **5.3** are low, with no detonation being observed either in the drop hammer test (2 kg, 50 cm) or the friction sensitivity test (90°, 1.96 MPa) [13a, b].



Scheme 3. Salts based on semicarbazide.

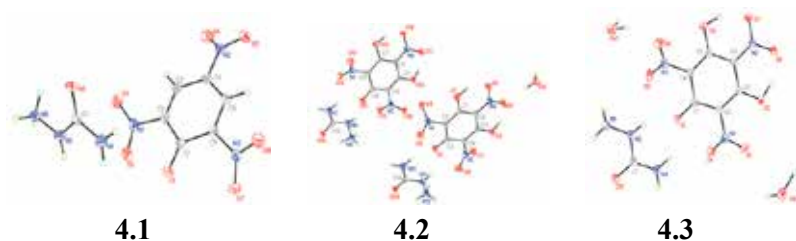
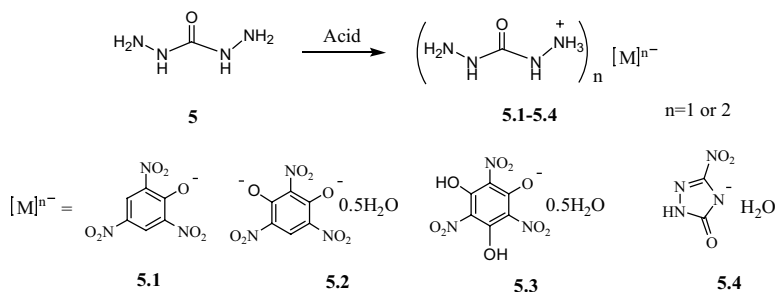


Figure 3. Selected crystal structures of semicarbazide salts.

5 Carbohydrazone-based Salts

Carbohydrazone (**5**) is a hydrazine derivative which has been used as a precursor of energetic materials or can be used directly for explosives and rocket propellant ingredients. Furthermore, carbohydrazone is an important nitrogen-rich ligand ($N = 62.18\%$) with non-bonded, lone pair electrons on the nitrogen atoms of the amino groups and the oxygen of the carbonyl group. Therefore, it is a widely used ligand in coordination compounds. In addition, compound **5** is readily soluble in water either at room temperature or at reflux, the aqueous solution is alkaline, whilst it is insoluble in alcohol, ether, chloroform and benzene. It is a relatively weak base, and therefore can be protonated by strong acids, offering an alternative synthetic pathway for the synthesis of energetic salts **5-1** to **5-4** (Scheme 4) [16].

The enthalpy of formation of **5.1** was positive [16a], $45.60 \text{ kJ}\cdot\text{mol}^{-1}$, and its calculated detonation velocity and detonation pressure were $8.06 \text{ km}\cdot\text{s}^{-1}$ and 28.64 GPa , respectively. The crystal density of **5.1-5.4** were reported to be in the range $1.651\text{-}2.008 \text{ g}\cdot\text{cm}^{-3}$ (**5.3**) (Figure 4) [16]. When salt **5.3** was heated over the temperature range $40\text{-}500 \text{ }^\circ\text{C}$ at a heating rate of $10 \text{ }^\circ\text{C}\cdot\text{min}^{-1}$, almost no residue was left. In DSC studies, **5.3** exhibited an endotherm at $140 \text{ }^\circ\text{C}$, and a major exotherm between $164\text{-}232 \text{ }^\circ\text{C}$. Since the long chain of the carbohydrazone cation extends the molecular space, it exhibited less sensitivity to mechanical stimuli. Due to its high nitrogen content ($N\% > 30\%$) and with no crystal water, **5.1** can be used as a gas-generating agent in airbag systems.



Scheme 4. Salts based on carbohydrazone.

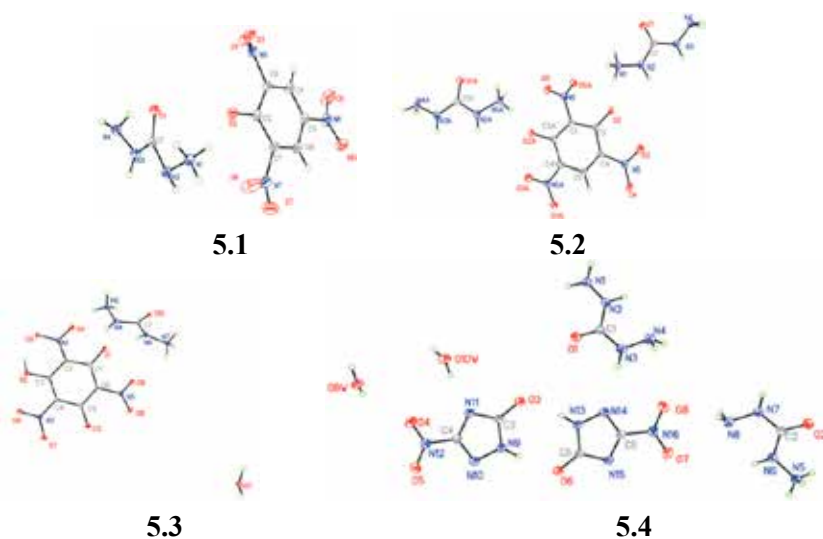


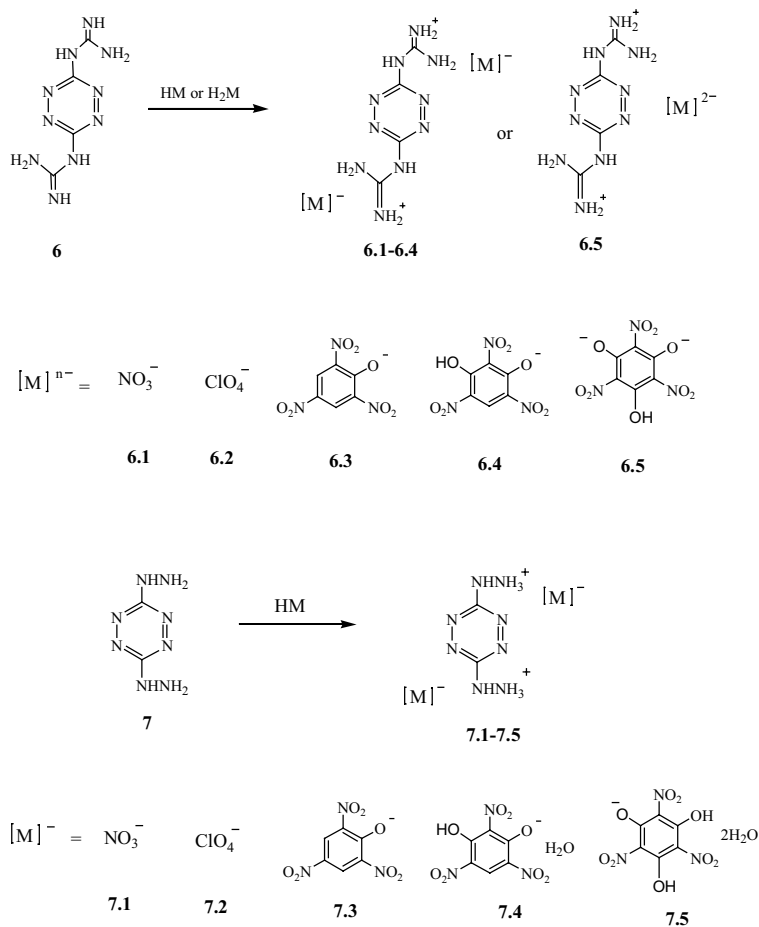
Figure 4. Selected crystal structures of carbonylhydrazide salts.

6 Tetrazine-based Salts

There has been worldwide interest in the study of tetrazine derivatives because of their high reactivity for aromatic compounds, high enthalpy of formation and high theoretical density, and can meet the fundamental requirements of green energetic materials. The 1,2,4,5-tetrazine (*s*-tetrazine) ring system is electroactive and has a high electron affinity [17].

The synthesis and properties of various ionic *s*-tetrazine energetic materials such as **6.1-6.5** and **7.1-7.5** have been reported (Scheme 5). Energetic salts **6.1-6.5** and **7.1-7.5** were synthesized by reaction of nitric acid, perchloric acid and nitrophenols with 3,6-diguanidino-*s*-tetrazine and 3,6-dihydrazino-*s*-tetrazine [18]. All of the salts were well-characterized, and the X-ray crystal structures of **6.2** and **7.1**, **7.2**, **7.5** were also determined (Figure 5). The crystal densities were 1.977, 1.840, 2.031 and 1.859 g·cm⁻³, respectively. The calculated enthalpies of formation of **7.2-7.5** were positive, whereas that of **7.1** was -572.5 kJ·mol⁻¹. The detonation velocities and detonation pressures of **6.2** ($D = 8.31 \text{ km}\cdot\text{s}^{-1}$, $P = 32.6 \text{ GPa}$) and **7.5** ($D = 8.63 \text{ km}\cdot\text{s}^{-1}$, $P = 34.04 \text{ GPa}$) were reported. When these salts were heated over the temperature range 40-600 °C at a heating rate of 10 °C·min⁻¹, all of the salts left no residue. In DSC studies, the hydrated salts **7.4** and **7.5** began to decompose after the loss of the lattice water molecules, while the other salts decomposed directly without melting. Salts **6.3** and **6.4** exhibited

an exotherm at 210 °C, while salts **7.1-7.3** and **6.5** exhibited lower exotherms (94.7-190 °C), and salt **6.2** showed the highest exotherm, 255.7 °C. The salts **6.3-6.5** were insensitive to shock, friction or flame. Detonation was not observed in either the drop hammer test or friction, flame sensitivity tests. However, **7.1-7.5** and **6.2** show relatively high sensitivity towards frictional stimulation, and **7.1, 7.2,** and **7.4** also have a high impact sensitivity.



Scheme 5. Salts based on tetrazines.

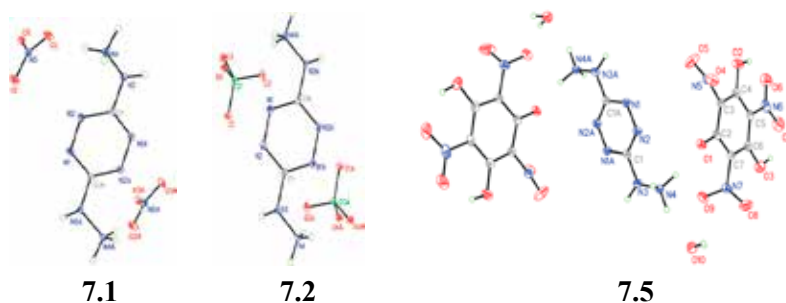


Figure 5. Selected crystal structures of tetrazine salts.

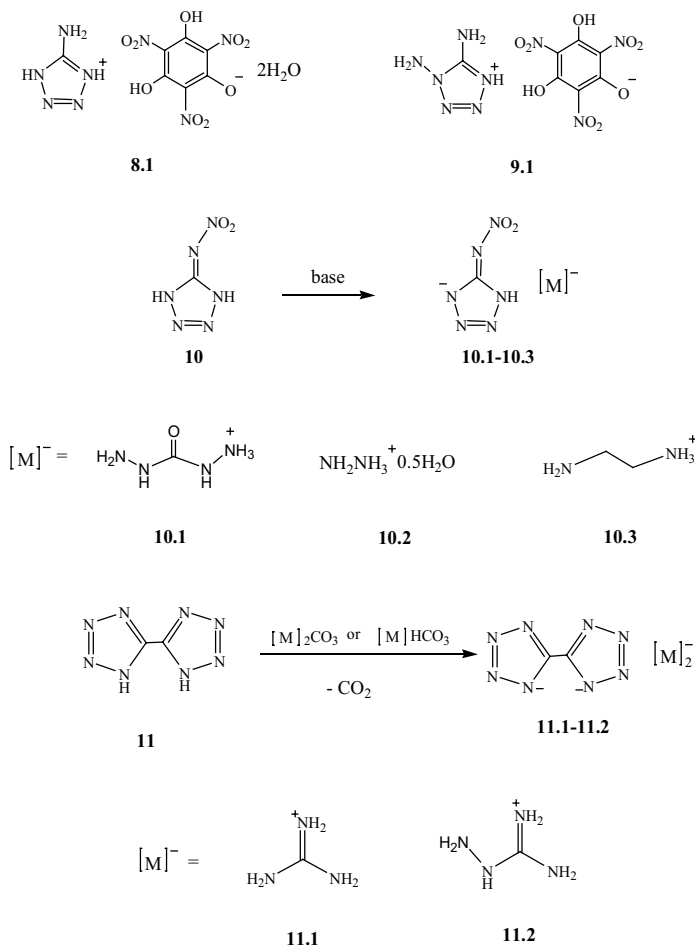
7 Tetrazole-based Salts

Tetrazoles are five-membered ring heterocycles which possess aromatic reactivity. Heterocyclic compounds that contain a large percentage of nitrogen atoms normally have high heats of formation; the heat of formation of tetrazole is $+237.2 \text{ kJ} \cdot \text{mol}^{-1}$ [19]. Tetrazole and its derivatives have a high nitrogen content and better detonation capabilities, and are one of the most important sources of high-nitrogen energetic materials. Due to the environmentally friendly nitrogen gas being the major product of combustion, tetrazoles are of great interest. Since tetrazole compounds can be not only cations but also anions, this greatly enriches the types of energetic salts for discovering desirable detonation performance, and as a precursor of ionic energetic materials, attracts more and more attention.

Aminotetrazoles have a high nitrogen content and large positive enthalpies. they are prospective materials for the generation of gases as blowing agents and solid propellants. The synthesis of tetrazolium salts containing amino substituents on the ring by reaction of 5-aminotetrazole (**8**) or 1,5-diaminotetrazole (**9**) with 2,4,6-trinitro-1,3,5-trihydroxybenzene, resulted in the quaternary salts **8.1** and **9.1** respectively. Proof of synthesis was supported by elemental analysis, IR spectroscopy and single crystal X-ray diffraction (Figure 6) [20].

By taking advantage of the fact that 5-nitraminotetrazole (**10**) is a strong NH acid, energetic salts (**10.1-10.3**) with various nitrogen-rich compounds as cations and **10** as the anion were obtained [21]. Single crystal X-ray diffraction studies of **10.1** illustrated the influence of significant hydrogen bonding between the carbohydrazide cation and the deprotonated tetrazole ring. This hydrogen bonding accounts for the high density ($1.815 \text{ g} \cdot \text{cm}^{-3}$) and melting point ($>170 \text{ }^\circ\text{C}$). A thermal study of **10.3** showed good thermal stability (decomposition before melting, and an endothermic process with a peak temperature of $249.3 \text{ }^\circ\text{C}$).

Sensitivity testing of the 5-nitraminotetrazolate salts indicated surprisingly low sensitivities both to flame and impact. However, **10.1** and **10.2** showed high sensitivity to friction, with initiation rates of 92% and 80%, respectively [21].



Scheme 6. Salts based on tetrazoles.

The high nitrogen salts **11.1** and **11.2** of bitetrazole (**11**) were synthesized by the reaction of stoichiometric amounts of guanidine carbonate or aminoguanidine bicarbonate with the free-acid, bitetrazole (Scheme 6) [22]. Both salts were investigated by means of DSC-TGA, elemental analysis, IR, 1H and ^{13}C NMR and MS methods. According to the DSC-TGA study, these salts show great thermal stability, the melting temperatures being 319 °C and 252 °C, respectively.

The sensitivities of neutral bitetrazole are higher than those of the bitetrazolate salts in which the presence of nitrogen-rich cations increases the opportunity for hydrogen bonding. Since these salts have a high nitrogen content ($N\% > 75\%$) with no crystal water, and produce little smoke or residue, they can be used as components of gas-generating agents.

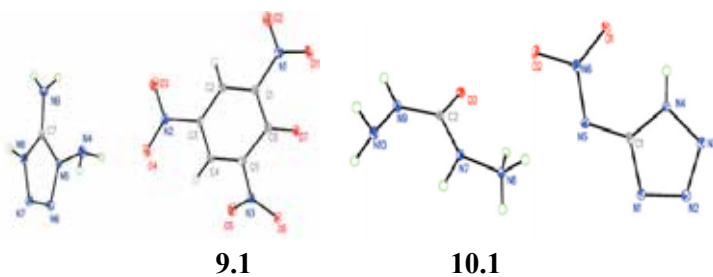


Figure 6. Selected crystal structures of tetrazole salts.

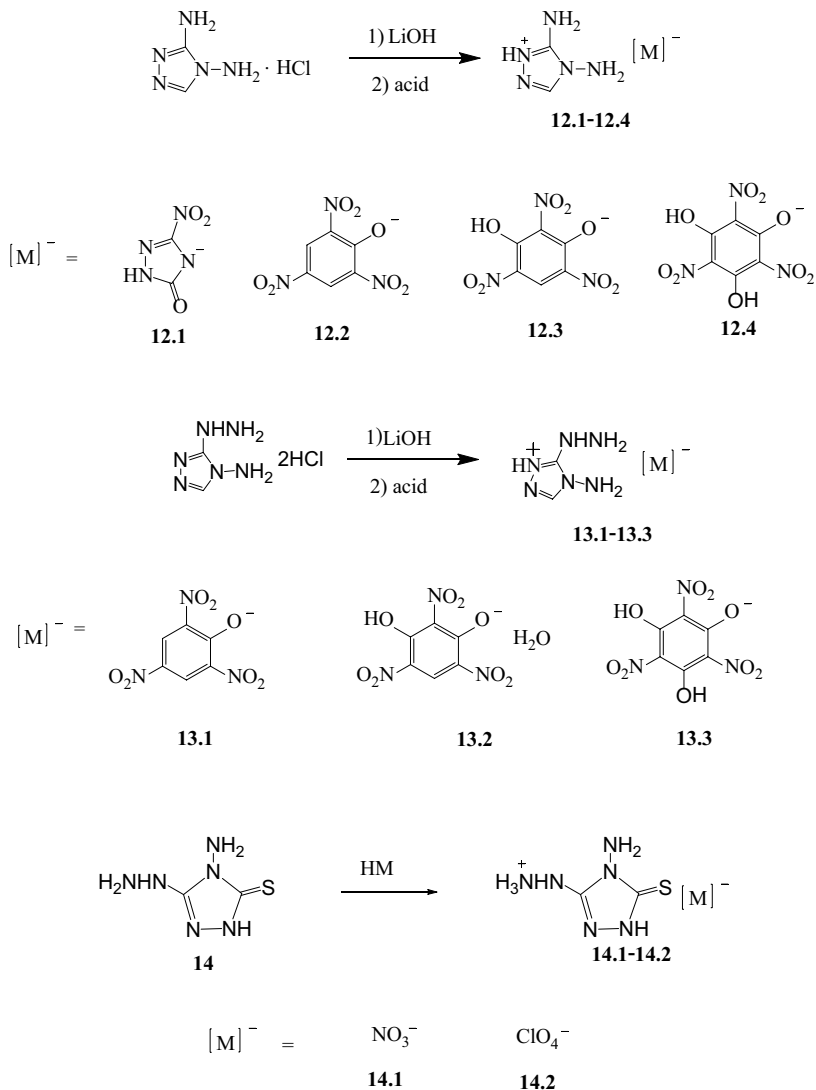
8 Triazole-based Salts

Triazoles are five-membered ring heterocycles that contain three nitrogen atoms. As important high nitrogen compounds, triazoles are easy to complex with ions and have the ability to form hydrogen bonds, so triazoles are of great interest in the present context [23].

The incorporation of $-NH_2$ groups on the triazole ring is one of the simplest routes to enhance thermal stability [24], and the incorporation of $-NH-NH_2$ groups onto a heterocyclic ring will increase the heat of formation. In addition, the $-NH_2$ and $-NH-NH_2$ moieties can increase the intra- and intermolecular hydrogen bonding, resulting in salts with high densities and low sensitivities [25].

Compounds 3,4-diamino-1,2,4-triazole (**12**) and 3-hydrazino-4-amino-1,2,4-triazole (**13**) have high nitrogen contents ($N\% > 70\%$), which, in the protonated form, make them attractive for the potential formation of nitrogen-rich ionic energetic compounds. Compounds **12** and **13** have been obtained by reacting lithium hydroxide with their corresponding hydrochloride salts, then reaction with nitrophenols or NTO leads to the energetic salts **12.1-12.4** and **13.1-13.3** respectively (Scheme 7) [26]. Direct neutralization of 4-amino-3-mercapto-5-hydrazinotriazole (**14**) leads to energetic salts **14.1** and **14.2**. These salts are stable at moderate temperatures, with the salt **12.1** ($231.1\text{ }^\circ\text{C}$) being the most thermally stable and the salt **14.1** ($149.7\text{ }^\circ\text{C}$) being the least. Their energies of combustion were measured in a Parr 1104 oxygen bomb calorimeter under O_2 .

The values showed that all of these salts release a large amount of energy during combustion, with **13.1** (11.5 MJ·kg⁻¹) possessing the largest combustion energy, compared with the energies of combustion of RDX, HMX and TNT which were 9.60, 9.44-9.88 and 15.22 MJ·kg⁻¹, respectively [27]. The salts of **12** and **13** were insensitive to flame and impact, however **12.1** and **13.3** showed a relatively high sensitivity to friction.



Scheme 7. Salts based on triazoles.

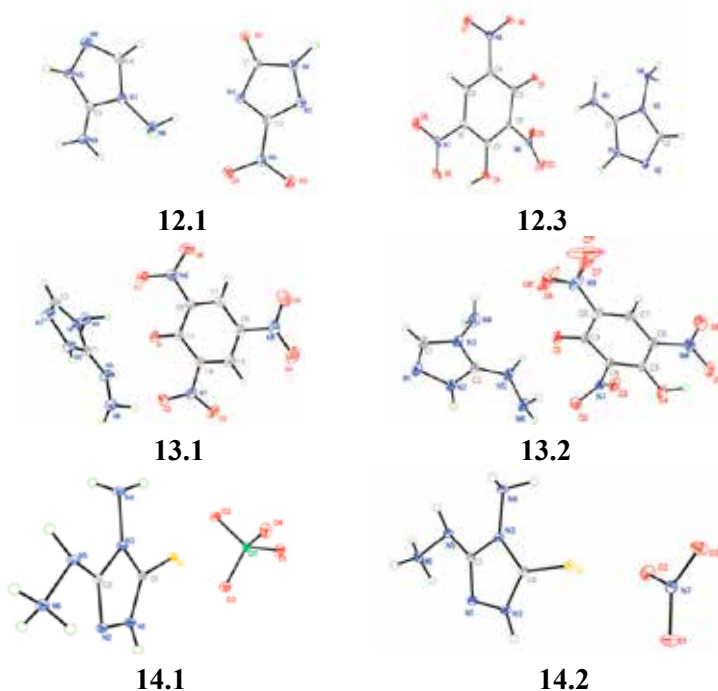


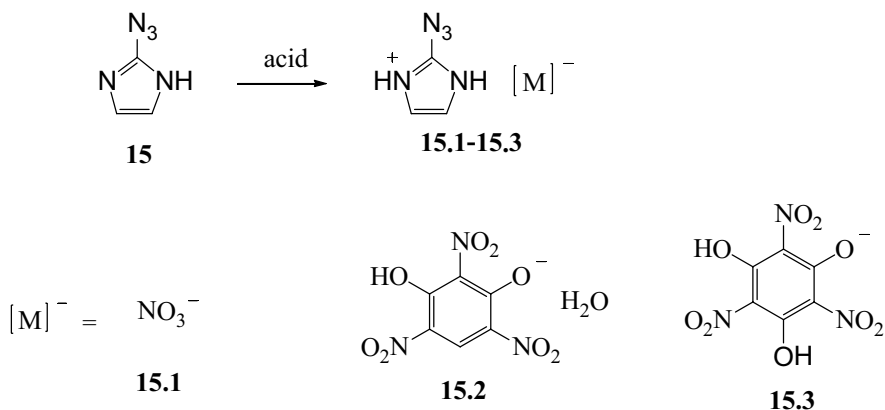
Figure 7. Selected crystal structures of triazole salts.

9 Imidazole-based Salts

Imidazole (IMI) is a five membered ring heterocyclic compound containing three carbon atoms and two nitrogen atoms [28]. Imidazole and its derivatives are widely used in energetic materials, agriculture, medicine and other fields. Heterocycles are often modified with the azido functional group, which can not only increase the overall nitrogen content but also rapidly increase the energy level [23, 29].

Three energetic salts **15.1-15.3** have been prepared directly by reacting 2-azidoimidazole (**15**) with HNO_3 , 2,4,6-trinitroresorcinol and trinitrophenol (Scheme 8) [29a]. The compounds were characterized by elemental analysis, IR spectra, DSC, TG-DTG studies and their crystal structures were reported (Figure 8). The salts decomposed before melting, and the thermal decomposition temperatures ranged from 109.2 °C (**15.1**) to 149.2 °C (**15.3**). According to the TG-DTG studies, **15.1** showed a main mass loss (80.2%) at 100~125 °C, followed by a slow mass loss, with no residue remaining; whereas

15.2 showed three medium mass losses. Surprisingly, the experimental sensitivity results showed that this series of salts was insensitive to impact and friction and had a certain degree of flame sensitivity, indicating that these salts are a class of non-sensitive nitrogen-rich ionic compounds. Salt **15.1** has potential as a component in pyrotechnic and gas-generating agents due to its low sensitivity and its combustion products being gases.



Scheme 8. Ionic salts based on 2-azidoimidazole.

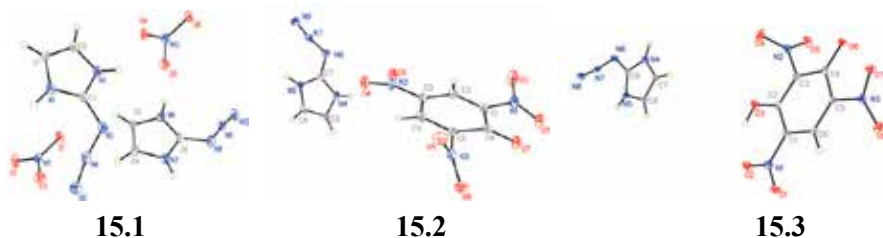


Figure 8. Selected crystal structures of imidazole salts.

10 Conclusions

Since nitrogen-rich energetic salts show high density, good thermal stability and environmentally friendly features, the design and synthesis of nitrogen-rich salts are an important direction for the development of energetic ionic compounds. Currently, synthesis research of such ionic compounds is still at the laboratory stage. In order to make these nitrogen-containing compounds applicable in propellants, pyrotechnic agents and other fields, an in-depth study of the synthetic

methods is required. The well-defined ionic salts will replace cast TNT, RDX explosives and other propellants.

Acknowledgements

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11 References

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