

## Azole-Based Energetic Salts

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### 1. INTRODUCTION

Energetic materials include explosives, propellants, and pyrotechnics that are used for a variety of military purposes and civilian applications.<sup>1–3</sup> An explosive is defined as a material that on initiation undergoes a chemical reaction liberating a large amount of heat and so

exerting a high pressure on its surroundings. Explosives may be classified as primary and secondary explosives: the former are very sensitive and low-performing compounds,<sup>4,5</sup> which are commonly used to initiate a more powerful and less sensitive secondary explosive.<sup>6</sup> Propellants differ from explosives in that they do not detonate but rather combust and thus are substances or mixtures of substances that burn rapidly or deflagrate in a closed chamber releasing a significant volume of gas at a rate to produce high temperatures and pressure, which are sufficient to raise pressure and provide propulsive force (or impulse) to accelerate and move (propel) an object (such as rockets, projectiles, or missiles).<sup>7–9</sup> Pyrotechnics are materials capable of undergoing self-contained and self-sustained exothermic chemical reactions for the production of an audiovisual effect (explosion, fire, light, heat, smoke, sound, or gas emission).<sup>10–13</sup> However, while the purpose of explosives and propellants is the transfer of chemical energy in the molecular to macroscopic kinetic energy, the purpose of pyrotechnic substances and mixtures is to use chemical energy in the molecular to generate defined visual and acoustic effects.<sup>14</sup>

Many new energetic materials have emerged recently in order to meet the challenging requirements to improve the performance of existing products. The key requirements include tailored performance, insensitivity, stability, vulnerability, and environmental safety.<sup>2,13,15–17</sup> The development and testing of energetic materials is an exciting and challenging area of chemistry, from applied as well as fundamental aspects. Considering the many applications of non-nuclear energetic materials as explosives or propellants, it is important to discover new representatives with significant advantages over compounds currently used not only for military but also for civilian purposes. A new generation energetic material has to meet a variety of standards to become widely accepted. In addition to performance properties, the desired criteria are (i) insensitivity toward destructive stimuli, such as electrostatic discharge, heat, friction, and impact, to ensure safe handling procedures and enhance controllability of kinetic energy release and (ii) low solubility in water and hydrolytic stability for environmental reasons, as well as longevity and compatibility questions and other criteria addressing high-priority ecological toxicity requirements.<sup>1,2,13</sup>

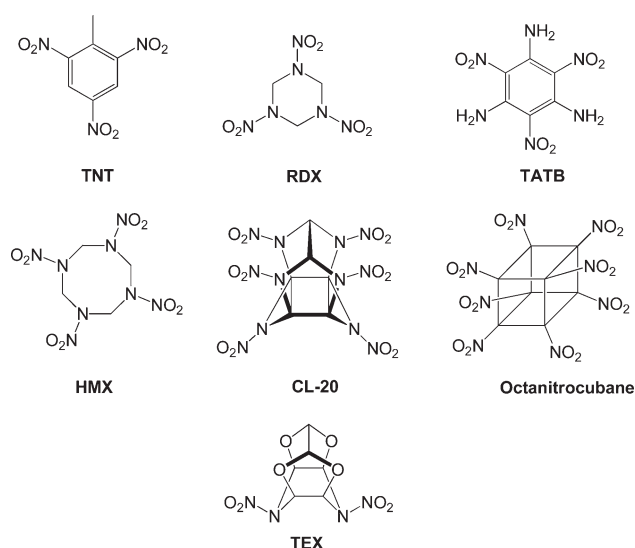
Modern weaponry relies on energetic materials to explode or propel, but the usefulness of these materials is not limited to the military. They are also used in various ignitors and ignition systems, as well as for different purposes, such as blasting, mining, and other civil engineering. Automotive safety relies on a number of pyrotechnics and propellants to deploy airbags and seatbelt tensioners. These materials store relatively large amounts of energy in a compact and readily deliverable form.

An energetic material is a compound or a mixture of compounds that, when subjected controllably to friction, impact, spark, or shock, undergoes rapid, heat-producing decomposition. Creating a

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Scheme 1. Structures of TNT, RDX, TATB, HMX, CL-20, Octanitrocubane, and TEX

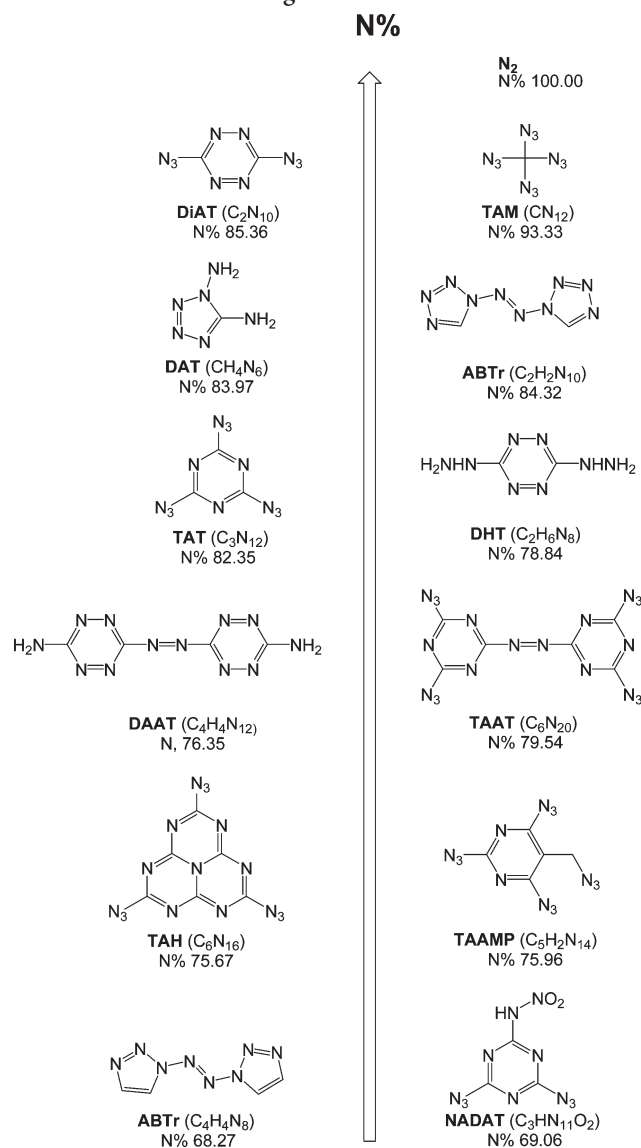


monomolecular energetic material is a central process to acquiring materials, such as 2,4,6-trinitrotoluene (TNT), in which each molecule contains an oxidizing component and a fuel component. The performance of an energetic material depends mainly on its oxygen balance (composition), density, and heat of formation, of which the latter two are governed to some extent by the molecular structure. Counteracting the correlation of high performance with high sensitivity is the use of systems which form extensive hydrogen-bonded networks in the solid state; these hydrogen-bonded networks enhance the stabilization of the material substantially.<sup>18</sup>

High-energy density materials (HEDMs) are materials used for energy storage and as propellants and explosives.<sup>15,19</sup> HEDMs refers to energetic molecules that store and release their energy only through making and breaking of chemical bonds. The primary uses of such HEDMs are as secondary explosives and in propellant applications. Their performance strongly depends on stoichiometry.<sup>20</sup> The key properties for HEDMs include the C/H/N ratio, oxygen balance, density, heat of formation, sensitivity (impact/friction/shock/electrostatic discharge), thermal and hydrolytic stability, detonability, environmental acceptability. Some of these may be contradictory, which makes attaining better HEDMs while concomitantly maintaining satisfactory physical properties is an extremely challenging goal. Traditional hydrogen, oxygen, nitrogen and carbon substances within this class of compounds are TNT,<sup>21–25</sup> 1,3,5,7-tetranitro-1,3,5,7-tetrazocine (HMX),<sup>26–32</sup> 1,3,5-trinitro-1,3,5-triazine (RDX),<sup>33–37</sup> triaminotritrobenzene (TATB),<sup>38–45</sup> 2,4,6,8,10,12-hexanitro-2,4,6,8,10,12-hexaazaisowurtzitane (CL-20),<sup>46–50</sup> octanitrocubane,<sup>51,52</sup> and 4,10-dinitro-4,10-diaza-2,6,8,12-tetraoxaisowurtzitane (TEX)<sup>53,54</sup> (Scheme 1). Unfortunately, most of these nitro explosives are strongly polluting. The release of explosive compounds to the environment often results in contamination of surface and ground waters, soils, and sediments.<sup>55,56</sup>

High nitrogen energetic materials are another area of advanced HEDMs aimed at future defense and space sector needs. Nitrogen-rich compounds gain their energy from high heats of formation and not by intramolecular oxidation of a C backbone such as found for conventional explosives including TNT or pentaerythritol tetranitrate (PETN).<sup>57</sup> They are also of interest as ligands in coordination chemistry.<sup>58–60</sup> Some of them have

Scheme 2. Selected Nitrogen-Rich Molecules

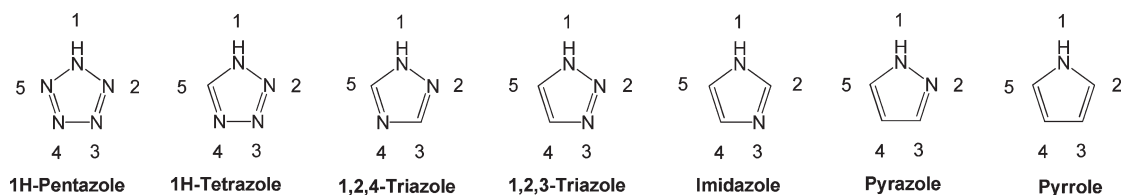


interesting optical properties,<sup>61–63</sup> and some can even be used as precursors of functional materials.<sup>64,65</sup>

High nitrogen content materials have a large number of N–N and C–N bonds and therefore exhibit large positive heats of formation. These materials often show remarkable insensitivity toward electrostatic discharge, friction, and impact. Triazoles, tetrazines, and triazines are the nitrogen rich organic compounds currently in use for energetic applications. 4,4'-Azobis(1,2,4-triazole),<sup>66</sup> 6-nitroamino-2,4-diazido[1,3,5]triazine (NADAT),<sup>67</sup> 2,5,8-tri(azido)-s-heptazine (TAH),<sup>68,69</sup> 2,4,6-triazido-5-(azidomethyl)-pyrimidine (TAAMP),<sup>70</sup> 3,3'-azobis(6-amino-1,2,4,5-tetrazine (DAAT),<sup>71</sup> 4,4',6,6'-tetra(azido)azo-1,3,5-triazine (TAAT),<sup>72,73</sup> 2,4,6-tri(azido)-1,3,5-triazine (TAT),<sup>69</sup> 3,6-dihydrazino-1,2,4,5-tetrazine (DHT),<sup>69,74,75</sup> 1,5-diamino-tetrazole (DAT),<sup>76–78</sup> 1,1'-azobis(tetrazole) (ABTe),<sup>79</sup> 3,6-di(azido)-1,2,4,5-tetrazine (DiAT),<sup>69,75</sup> and tetraazidomethane (TAM)<sup>80</sup> are recent typical examples of nitrogen compounds used as energetic materials (Scheme 2).

The low percentages of C and H in these compounds have triple positive effects: (i) enhance density; (ii) allow a good oxygen

Scheme 3. Structural Formulae of Unsubstituted Neutral Azoles (Only Includes Nitrogen)



balance to be achieved easily; and (iii) produce a larger number of moles of gaseous products per gram of the high-energy material.<sup>2</sup>

The high-energy content of HEDMs stems from the presence of adjacent nitrogen atoms poised to form nitrogen gas ( $N_2$ ). Nitrogen is unique among all other elements of the periodic table in that the bond energy per two-electron bond increases from a single over a double to a triple bond, resulting in dinitrogen being more stable than any other nitrogen species.<sup>81</sup> The decomposition of these compounds results predominantly in the generation of dinitrogen which makes them very promising candidates for applications requiring environmentally friendly, highly energetic materials. Generation of nitrogen gas as a decomposition product of energetic materials is desired to avoid environmental risk. Nitrogen-rich HEDMs are quite different from classical explosives (such as TNT, RDX, and HMX) (Scheme 1). They derive most of their energy from their high positive heats of formation<sup>83</sup> while the latter gain their energy from oxidation of the carbon backbone. However, HEDMs such as TEX, octanitrocubane, or CL-20 obtain their energy from their substantial cage strain. Such transformations are accompanied with an enormous energy release due to the wide difference in the average bond energies of  $N-N$  (160 kJ/mol) and  $N=N$  (418 kJ/mol) compared to that of  $N\equiv N$  (954 kJ/mol).<sup>2</sup> These compounds derive most of their energy from a high heat of formation ( $\Delta H_f$ ), a quantity strongly coupled to the nitrogen content of a molecule. This large thermodynamic driving force for molecular nitrogen production also explains the inherent instability of many nitrogen-rich compounds.

The interest in HEDMs has increased in recent years. With inspiration drawn from modern science, the design and synthesis of novel energetic materials are evolving to develop a class of materials that integrate the desirable characteristics of high-energy density and rapid energy release along with high stability. The challenge, in part, in designing energetic materials lies in the necessity to improve their safety, reliability, and load bearing capability. Some of the key factors driving the requirement for a candidate for chemical energetic materials include: (a) improved performance in terms of increased specific impulse and density, (b) high thermal stability, low detonability, and reduced sensitivity to external stimuli, such as impact, friction, shock, and electrostatic discharge, and (c) clean low molecular weight gases as the combustion products and mitigation of environmental and toxicological hazards (and the resulting costs) associated with currently used propellants. The search for promising high-energy materials during the past decade has led to the discovery of a vast number of compounds that combine a high nitrogen content with high heats of formation and good stabilities.<sup>83</sup>

Studying structure property relationships and using computer codes to predict the energetic properties based on molecular structure, has greatly enhanced the development of new energetic materials with better performance. Over the past decade, energetic heterocyclic compounds have attracted considerable interest.<sup>13,16,84–92</sup> Higher energetic performance has always been

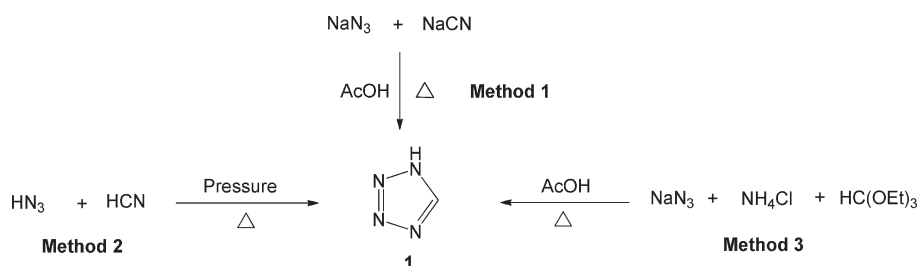
a primary requirement for research and development of explosives and propellants; however, these types of materials often exhibit poorer thermal stability and higher sensitivity to thermal shock, friction, and electrostatic discharge, and vice versa. In principle, a combination of these positive properties is desirable. The performance of an energetic compound is a function of its density, oxygen balance, and heat of formation. Density is one of the most important factors because the detonation pressure is dependent on the square of the density and the detonation velocity is proportional to the density based on an empirical equation proposed by Kamlet.<sup>93–95</sup>

Energetic salts which are among the most recent and exciting developments of HEDMs, continue to attract considerable work. Attractive sources of novel energetic materials include a wide range of neutral molecules and salts. The syntheses of new heterocyclic-based energetic salts appeared a decade ago. They inherited the novel physical and chemical properties of ionic liquids and salts which render them useful for many purposes, such as environmentally benign (“green”) solvents, catalysts, electrolytes, energetic materials, etc. Chemists are interested in ionic liquids and salts as potential replacements for currently used monopropellants such as hydrazine, which is carcinogenic, is highly toxic, and has relatively modest performance characteristics.<sup>16</sup>

These materials that are salt-based often possess advantages over nonionic molecules since they tend to exhibit very low vapor pressures essentially eliminating the risk of exposure through inhalation. They have high positive heats of formation, and high thermal stabilities, and those ionic compounds often have higher densities than their atomically similar nonionic analogues. In addition, their properties can be carefully tuned via the choice of the component ions, and they are readily optimized and improved through the judicious combination of different cations and anions, as well as by independent modification of cationic and anionic components. These processes significantly increase the number of energetic compounds available. Such novel properties suggest energetic organic compounds for a variety of unique applications, including gas generators, smoke-free pyrotechnic fuels, solid fuels in micropropulsion systems, fire extinguishers on board military aircraft, effective precursors for carbon nitride nanomaterials, and carbon nanospheres.

Nitrogen-containing heterocycles are one of the sources of energetic salts. Some of the primary requirements of an energetic compound for practical application include readily available starting materials in addition to a safe and simple synthetic route. Azoles comprise a class of five-membered heterocyclic ring compounds containing at least one other noncarbon atom, either nitrogen, sulfur, or oxygen. The parent compounds are aromatic and have two double bonds (Scheme 3). Major advances in the chemistry of pyrazoles, imidazoles, triazoles, tetrazoles, and related fused heterocyclic derivatives have occurred.<sup>96–99</sup> These azoles are also widely found as core structures in a large variety of compounds that possess important agrochemical and pharmaceutical activities;<sup>100–104</sup> the ability of these heterocyclic nuclei

Scheme 4. Synthesis of 1H-Tetrazole



to serve both as biomimetics and reactive pharmacophores encourages their role in numerous drugs,<sup>105–110</sup> and they play a major role in coordination chemistry.<sup>111–115</sup> However, these aspects of their broad synthetic value are beyond the scope of this review. The reader is encouraged to peruse refs 96–115.

The enthalpies of formation of azoles are dependent on their ring structures. They can be adjusted by substitution of the hydrogen atoms with various energetic functional groups. These groups can significantly adjust the physical properties (density, oxygen balance, thermal stability, enthalpy of formation, sensitivity or melting point, etc.) of the azoles and eventually result in a better exothermicity of the combustion and detonation processes of the molecules.<sup>116</sup> Much attention has been focused on azoles, in particular tetrazole, triazole, imidazole, pyrazole, etc., as the core of energetic compounds. These substituted azoles paired with the energetic anions form new energetic salts. They are the most popular five-membered heterocycles for designing new energetic salts and ionic liquids. Modification of those five-membered heterocycles with different groups to design new energetic salts and ionic liquids has developed recently.<sup>5</sup> The salts combine several advantages such as smokeless combustion, high heats of formation, high propulsive power, and high specific impulse ( $I_{sp}$ ), when they are serving as explosives, propellants, or pyrotechnics. Various energetic cations or anions derived from tetrazole, triazole, and imidazole, in which each cation or anion pairs with a family of its counterparts through metathetical or protonation reactions have been well-documented.

Usually the chemical properties of those new salts have been determined [(IR and Raman, and multinuclear NMR ( $^1\text{H}$ ,  $^{13}\text{C}$ ,  $^{15}\text{N}$ ) spectroscopy, differential scanning calorimetry (DSC) and mass spectrometry] along with the determination of their energetic characteristics. In addition, the crystal structures of some of the compounds have been studied as available. The heats of formation have been calculated by computational studies or by the experimental data from heats of combustion (from bomb calorimetry). Several detonation properties, such as detonation pressure ( $P$ ), detonation velocity ( $D$ ), and specific impulse ( $I_{sp}$ ), were obtained using either EXPLOS<sup>117–123</sup> or CHEETAH software.<sup>124–126</sup>

Sensitivities were tested using a BAM drop hammer, as well as a BAM friction tester and an electrical spark device. With respect to developing new high explosives, many of the salts which have shown the most promising values were successfully tested to determine the sensitiveness of a substance to the effect of intense heat under high confinement in a Koenen test.<sup>127,128</sup>

In subsequent sections, these substances and their derivatives are considered in more detail. Despite significant theoretical and practical interest in many of these materials, they have often been investigated incompletely, and frequently trustworthy information is only marginal. It should be remembered that highly energetic salts always represent some danger and working with them demands extensive

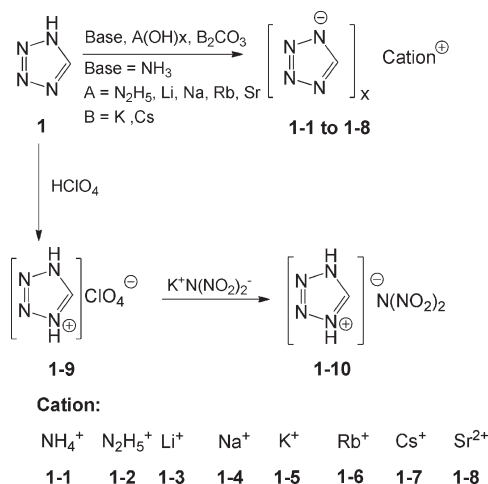
care and accuracy, as well as good knowledge in the field of chemistry and broad experience in working with sensitive unstable materials.

Through the efforts of scientists in this area, more interesting energetic salts or ionic liquids have been designed and synthesized. This brief account covers the new families of azole-based energetic salts from 2007 through 2010. Those energetic azole-based salts exhibit suitable characteristics in order to be classified as new highly energetic members of the well-known class of ionic salts and liquids. Recent developments in the design, synthesis, and the available property data [density, melting point ( $T_m$ ), decomposition temperature ( $T_d$ ), glass transition temperature ( $T_g$ ), heat of formation (HOF), detonation pressure ( $P$ ), detonation velocity ( $D$ ), impact sensitivity (IS), friction sensitivity (FS), electrostatic discharge (ESD) sensitivity, specific impulse ( $I_{sp}$ , impulse per unit weight-on-earth of propellant in seconds), etc.] of the most recent energetic ionic liquids and salts, and their potential applications as new explosives, propellants, or pyrotechnics are provided.

## 2. TETRAZOLE-BASED ENERGETIC SALTS

Tetrazoles are an important core of energetic materials because of the practical and theoretical significance of these unique compounds and the diversity of their properties. The tetrazole ring is comprised of four nitrogen atoms and one carbon atom. During the preparation of free tetrazole from its derivatives, the heterocyclic ring displayed remarkable stability in the presence of acids, alkalis, oxidizing agents, 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.<sup>129–133</sup> Upon elimination of a proton from the NH moiety of tetrazole, the highly aromatic tetrazolate anion is formed. Because of the flat structure of the tetrazole ring and its 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.<sup>129–133</sup> 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. The combination of interesting energetic properties and unusual chemical structures has attracted numerous researchers to this unique class of compounds. Tetrazole compounds usually have high heats of formation because of the nitrogen–nitrogen bonds, ring strain, and high density. The introduction of the tetrazole ring has allowed the preparation of high-performing explosives. Many tetrazole-based explosives can be employed as primary explosives, sensitizers, or components of electric ignitors.<sup>129–133</sup> Those energetic materials have proven to be unique because of their good performance



Scheme 5. Syntheses of Salts from 1*H*-Tetrazole

(high nitrogen content, high density, good thermal stability, and low sensitivity).<sup>18</sup>

Recently in publications devoted to high-energy substances, considerable interest in tetrazole derivatives has surfaced which is partially because tailoring can lead to primary explosives with unique properties. Energetic salts based on tetrazoles show the desirable properties of high N-atom content and thermal stability arising from its aromatic characteristics.

### 2.1. 1*H*-Tetrazole Salts<sup>134–138</sup>

1*H*-Tetrazole can be synthesized using various routes (Scheme 4).<sup>134</sup> The dipolar cycloaddition between HN<sub>3</sub> and HCN (method 2)<sup>135</sup> or NaN<sub>3</sub> and NaCN (method 1)<sup>136</sup> can only be reached by the use of pressure, catalysts or long reaction times because of the HOMO and LUMO energies of these compounds.<sup>134</sup> The most straightforward method for the synthesis of 1*H*-tetrazole (**1**, **TZ**) is the reaction of sodium azide with ammonium chloride and orthoethyl formate in glacial acetic acid (method 3).<sup>134</sup>

Crystalline 1*H*-tetrazole is very sensitive to impact (<4 J) but not to friction. This substance can be easily deprotonated using common bases such as ammonia, hydrazine, or the alkali and alkaline earth metal hydroxides or carbonates forming the corresponding tetrazolate salts of **1–1** to **1–9**.<sup>134–138</sup> 1*H*-Tetrazolium dinitramide (**1–10**) was synthesized by reacting potassium dinitramide with 1*H*-tetrazolium perchlorate (**1–9**)<sup>137</sup> (Scheme 5). The physical properties of these tetrazole salts are listed in Table 1.

Most tetrazolate salts are highly endothermic compounds (Table 1). Some of the tetrazolates (**1–1**, **1–2**, **1–3**, **1–5**, **1–6**, and **1–7**) and the tetrazolium salt (**1–10**) exhibit positive heats of formation ranging between 76 and 367 kJ/mol.<sup>134,137</sup> Compound **1–10** has the highest value at 367 kJ/mol.<sup>137</sup> Safety testing includes impact and friction sensitivity tests of the tetrazole-containing salts. On the sensitive side are the tetrazolate (**1**) and tetrazolium dinitramide (**1–10**) salts with impact sensitivities of <4 and 2 J, respectively.<sup>134,137</sup> Compared with the commonly used explosives (TNT, HMX, RDX and TATB in Table 1), these salts are more sensitive than RDX. In contrast the (substituted) guanidinium salts (**4–8**) have sensitivities much lower than those of RDX and HMX. However, the tetrazolium metal salts (**1–1** to **1–8**) are insensitive.

The salts **1–6** and **1–7** exhibit densities greater than 2 g/cm<sup>3</sup> because of the presence of the monovalent heavy metal cations.<sup>134</sup>

None of the salts melts before decomposing at high temperatures (Table 1). The most thermally stable derivatives of **1** are the strontium salt **1–8** and lithium salt **1–3** where decomposition occurred at 335 and 380 °C, respectively.<sup>134,138</sup> The lowest decomposition temperature is shown by **1–10** at 130 °C.<sup>137</sup> The number of calculated detonation pressure values for tetrazolate salts are limited. Only **1** and its ammonium and hydrazinium salts are available which lie in the range between 16.4 and 21.1 GPa.<sup>134</sup> Detonation velocities are found between 7546 and 8271 m/s (comparable to TATB 8114 m/s).<sup>134,139</sup> Since **1–1** and **1–2** show low densities in comparison with other tetrazoles, they are unspectacular with regard to high explosive properties. It was also shown that the **1–8** pellet groups burned brightly, with an intense red flame and its respective color purity exceeded the control value. Salt **1–8** yielded some broken pellets, suggesting that a higher consolidation force is necessary.<sup>138</sup> Compounds **1–3** and **1–8** have been suggested as smokeless red colorants in novel pyrotechnic compositions.<sup>134</sup>

### 2.2. 5-Amino-tetrazole Salts<sup>140–152</sup>

5-Aminotetrazole (**5-AT**, **2**), a simple, commercially available, nitrogen-rich (82%) compound, has also been utilized as a precursor of energetic salts (alkali metal salts and nitration products). Compound **2** is obtained by the diazotation of aminoguanidine with nitrous acid (Scheme 6, method 1)<sup>148</sup> or by the reaction of hydrazoic acid with dicyandiamide (Scheme 6, method 2).<sup>149</sup> Use of method 1 forms azidoformamidinium nitrate (starting from aminoguanidinium nitrate) which, after deprotonation, cyclizes to **2**. In method 2, dicyandiamide depolymerizes to cyanamide, which then reacts with hydrazoic acid to give **2**.<sup>150</sup> Both methods give good results and yield **2** in a sufficiently pure state for any potential use. Method 1 is rapid and safe but the yield is low (about 75%), while method 2 is slow and the reactant, hydrazoic acid, is highly toxic, dangerous, and explosive but gives higher overall yield and better product quality.

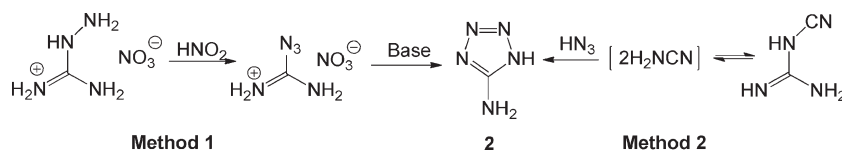
Compound **2** is a weak acid (p*K*<sub>a</sub> ≈ 6).<sup>151</sup> It has most often been employed as a cation precursor in energetic salts because it behaves as a weak base with strong inorganic acids (p*K*<sub>a</sub> ≤ 0) under normal conditions<sup>151,152</sup> which can be protonated by perchloric,<sup>153,154</sup> nitric,<sup>155,156</sup> sulfuric,<sup>157</sup> picric,<sup>139,158</sup> and hydrohalic acids (HX, X = Cl, Br, I).<sup>159</sup> Protonation of **2** with picric acid formed 5-AT picrate (**2–1**).<sup>158</sup> Halide salts of **2** (**2–2** to **2–4**) were synthesized by protonation with HX (X = Cl, Br, I) in an alcoholic solution (methanol or ethanol) according to Scheme 7 to yield hydrated 5-AT halide salts. Compounds **2–2** to **2–4** can be used to synthesize energetic materials by metathesis reactions. They are useful intermediates as transfer reagents of the CH<sub>4</sub>N<sub>5</sub> cation to form energetic materials.<sup>151</sup>

Protonation of **2** with a large excess of perchloric acid or nitric acid rendered the corresponding perchlorate salt (**2–5**)<sup>151</sup> or nitrate salt (**2–6**).<sup>155,156,160,161</sup> Because of the slow separation of **2–5** from the reaction mixture, it was more conveniently prepared by metathesis of **2–3** with anhydrous silver perchlorate in alcoholic solution (Scheme 7). Using a smaller excess of perchloric acid (1.35 equiv) resulted in the formation of an interesting adduct between **2–5** and **2** (**2–7**) (Scheme 8). The metathesis reaction between the **2–5** and potassium dinitramide gave **2–8**. The complexes of disilver 5-amino-1*H*-tetrazolium perchlorate (**2–9**) and nitrate (**2–10**) were prepared by treating **2** with the corresponding silver salt and acid (Scheme 8).

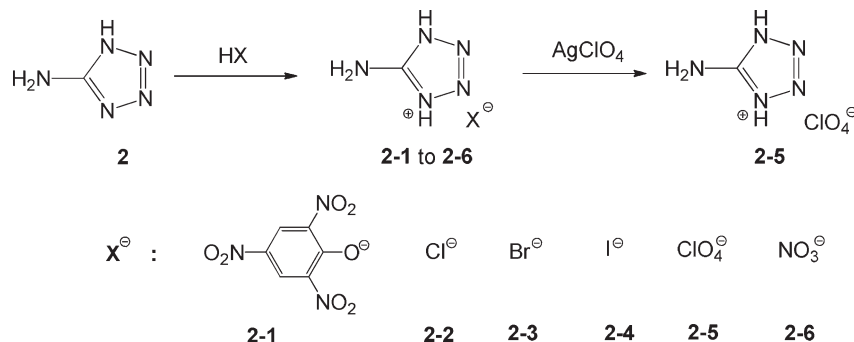
Table 1. Properties of 1*H*-Tetrazole and Its Salts

salt	density (g/cm <sup>3</sup> )	<i>T</i> <sub>d</sub> (°C)	Δ <i>H</i> <sub>f</sub> <sup>o</sup> (kJ/mol)	<i>P</i> (GPa)	<i>D</i> (m/s)	IS (J)	FS (N)	ref
1	1.53	188	237	21.0	7813	<4	>360	134
1-1	1.34	216	154	21.1	8276	>100	>360	134
1-2	1.39	232	145	16.4	7546	>100	>360	134
1-3	1.47	380	76			>100	>360	134
1-4	1.75	303	−291			>100	>360	134
1-5	1.77	308	174			>100	>360	134
1-6	2.37	240	150			>100	>360	134
1-7	3.12	305	144			>100	>360	134
1-8	1.88	335	−1293			>100	>360	134, 138
1-9	2.02							137
1-10	1.82	130	367	36.5	9215	2	28	137
TNT	1.65	295	−67	19.5	6881	15		139
TATB	1.93	~360	−154	31.2	8114	50		139
RDX	1.82	230	93	35.2	8977	7.4		139
HMX	1.91	287	105	39.6	9320	7.4		139

Scheme 6. Synthesis of 5-Aminotetrazole



Scheme 7. Syntheses of 5-Aminotetrazolium Salts (Part 1)

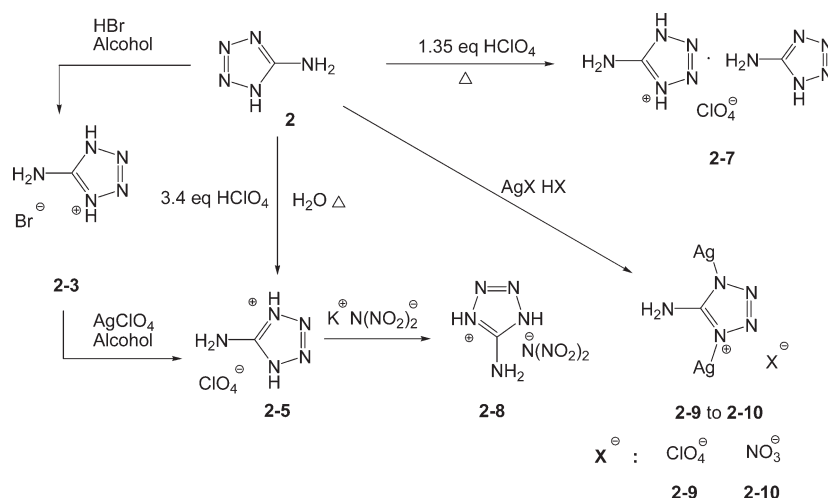


The combination of the nitrogen-rich 5-At moiety with typical energetic anions (e.g.,  $\text{ClO}_4^-$ ,  $\text{NO}_3^-$ , picrate) yields compounds with interesting energetic properties. Compound 2-5 can be regarded as a primary explosive in view of its high sensitivity values comparable to commonly used initiators (e.g., lead diazide), whereas 2-7 has a surprisingly low sensitivity comparable to secondary explosives (e.g., TNT). This is attributed to packing effects caused by the particularly extensive hydrogen-bonding found in the crystal of 2-7. Attempts to synthesize the energetically interesting 2 adduct of 5-amino-1*H*-tetrazolium nitrate (2-6)<sup>161</sup> either by boiling 2 with its nitrate salt or by reaction of 2 with different amounts of nitric acid resulted in recovery of the starting materials.

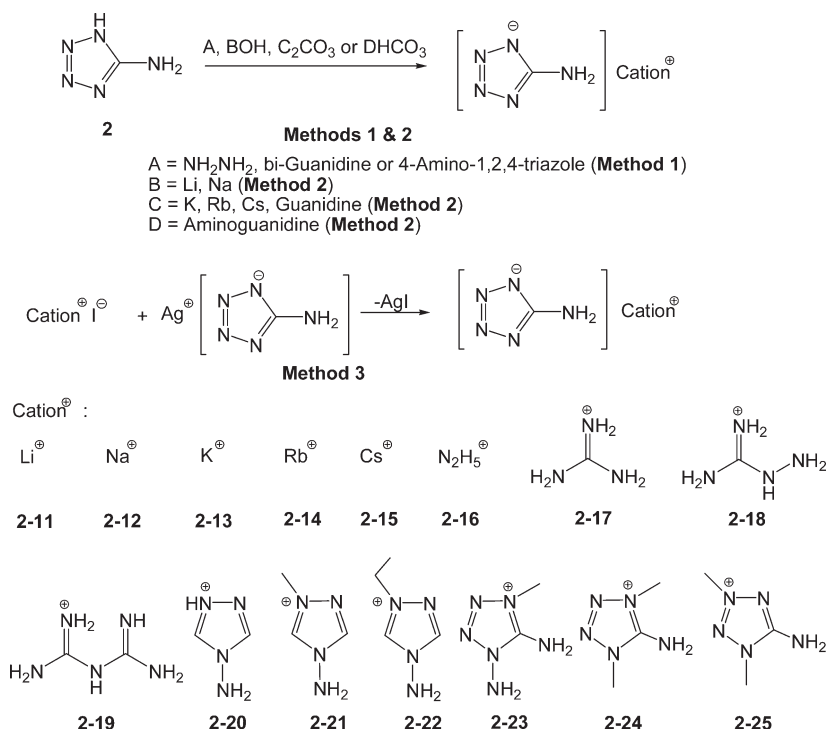
Compound 2 also behaves as a weak acid and can be used to obtain nitrogen-rich energetic salts and ionic liquids. The AT anionic salts and ionic liquids were prepared by using three different methodologies (Scheme 9). Compound 2 can be easily

deprotonated in aqueous solution using strong bases (hydrazine, biguanidine,  $\text{LiOH}$ , and  $\text{NaOH}$ , method 1).<sup>150</sup> Salts 2-11, 2-12, 2-16, 2-19, and 2-20 were synthesized by using this methodology. The reaction of guanidinium,  $\text{K}^+$ ,  $\text{Rb}^+$  and  $\text{Cs}^+$  carbonates and aminoguanidine bicarbonate with 2 resulted in 2-13, 2-14, 2-15, 2-17, and 2-18, respectively, with concomitant release of carbon dioxide (method 2);<sup>150</sup> 2-21 to 2-25 were prepared from AgAT (silver 5-aminotetrazolate was prepared in situ from commercially available 5-aminotetrazole by reaction with sodium hydroxide and precipitation by adding a solution of silver nitrate in water)<sup>143</sup> and the corresponding iodide salts (method 3).<sup>152</sup> Alkali metal salts of 2 are common intermediates in the synthesis of alkylated aminotetrazoles and their derivatives and can also be used as coloring agents in modern pyrotechnics, due to their high nitrogen content. They show no sensitivity toward friction (>360 N) or impact (>50 J).<sup>140,151</sup> Their thermal behavior is characterized by defined melting points and thermal

Scheme 8. Syntheses of 5-Aminotetrazolium Salts (Part 2)



Scheme 9. Syntheses of 5-Aminotetrazolate Salts

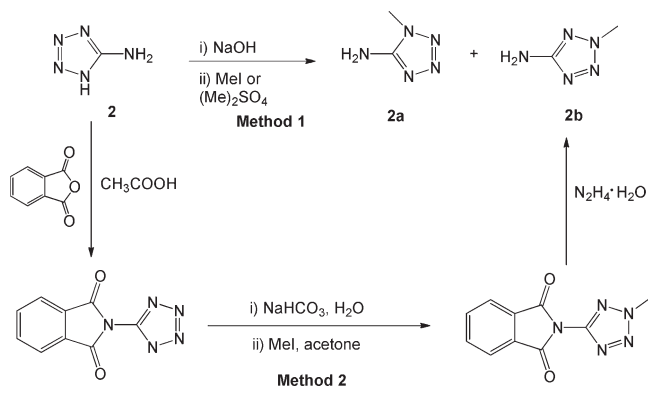


decompositions above 350 °C.<sup>152</sup> Compounds 2-11 to 2-15 are, in spite of their high nitrogen content, nonenergetic materials with characteristic flame colors, are safe to handle showing a low impact sensitivity of more than 75 J (except for 2-11), and are insensitive toward friction and impact.<sup>137,150,152</sup>

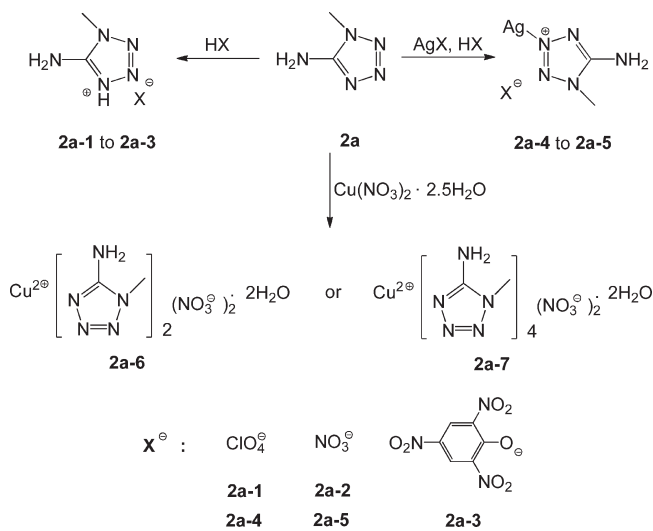
5-Aminotetrazole (2) is an especially valuable intermediate in the synthesis of tetrazole compounds because of its varied reactions and its ease of preparation. 5-Amino-1-methyltetrazole (major isomer, 2a) and 5-amino-2-methyltetrazole (minor isomer, 2b) can be obtained by methylation of the sodium salt of 5-aminotetrazole with dimethyl sulfate or MeI (Scheme 10, method 1).<sup>140,141,162,163</sup>

A new method involving the deactivation of the amino group in 5-aminotetrazole by protection with phthalic anhydride to form *N*-(1*H*-tetrazol-5-yl)phthalimide was described. The latter can be selectively methylated with methyl iodide or dimethyl sulfate to form exclusively *N*-(2-methyltetrazol-5-yl) phthalimide followed by deprotection to give 5-amino-2-methyltetrazole (2b) in an improved overall yield (Scheme 10, method 2).<sup>152</sup> The introduction of methyl groups helps to reduce the sensitivity of the compounds while concomitantly increasing their thermal stability at the cost of performance and makes interesting compounds accessible. Compound 2a or 2b react with strong acids (either perchloric or nitric acid) to generate the

Scheme 10. Methylation of 5-Aminotetrazole



Scheme 11. Syntheses of 1-Methyl-5-aminotetrazolium Salts

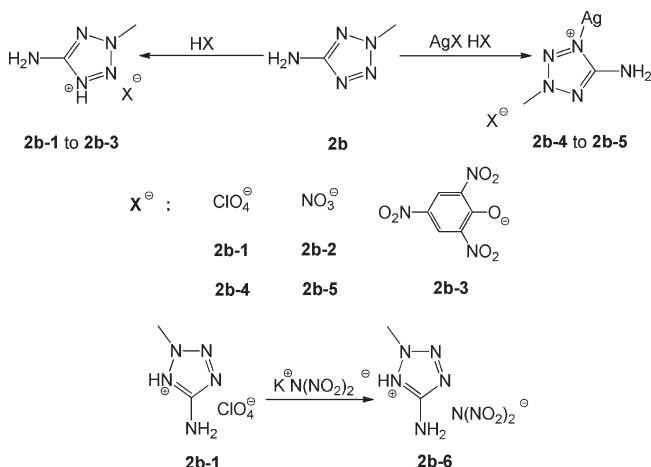


corresponding energetic salts **2a-1–2a-3** and **2b-1–2b-3** (Scheme 11).<sup>140,141,147</sup> The complexes of disilver 5-amino-1-H-tetrazolium perchlorate (**2-9**) and nitrate (**2-10**) have high impact sensitivity. Compounds **2a** and **2b** are used to tune the high sensitivity of these compounds, which were treated either with  $\text{AgNO}_3$  or  $\text{AgClO}_4$  in the corresponding acid (i.e., nitric or perchloric acid) to prepare a new family of silver salts with methylated tetrazole ligands (**2a-4**, **2a-5**, **2b-4** and **2b-5**) (Schemes 11 and 12).<sup>141</sup> The copper compounds, diaquacopper(II) di(1-methyl-5-aminotetrazole) nitrate (**2a-6**), and diaquacopper(II) tetra(1-methyl-5-aminotetrazole) nitrate (**2a-7**) were synthesized by the reaction of copper(II) nitrate with different ratios of reactants.<sup>138</sup>

Strong acids can easily protonate **2a** and **2b**, yielding nitrate (**2a-2**, **2b-2**), perchlorate (**2a-1**, **2b-1**) and picrate (**2a-3**, **2b-3**) (Schemes 11 and 12). Through metathesis reactions, the dinitramide salt of **2b-6** can be synthesized (Scheme 12).<sup>141</sup>

Energetic ionic materials based on aminotetrazoles are also known to form strong hydrogen-bonding networks and thus show remarkable stability and considerable insensitivity to physical stimuli, while providing good performance. In addition, known aminotetrazole salts are mainly composed of nitrogen and thus have large positive heats of formation as well as high

Scheme 12. Syntheses of 2-Methyl-5-aminotetrazolium salts



densities comparable to or greater than those of widely used neutral, covalent, organic molecular explosives. The salts only have slight negative oxygen balances when an oxygen-rich counteranion (nitrate, dinitramide, and perchlorate) is used. Furthermore, energetic ionic materials tend to exhibit lower vapor pressures than similar neutral nonionic analogues, essentially eliminating the risk of exposure through inhalation. Given these properties, aminotetrazole-based compounds have long been of interest as potential energetic materials.<sup>144</sup>

Methylation of **2a** and **2b** with methyl iodide or  $\text{Me}_2\text{SO}_4$  resulted in regioselective methylation to yield iodide salts with isomeric 1,4-dimethyl-5-aminotetrazolium and 1,3-dimethyl-5-aminotetrazolium cations.<sup>163</sup> They were used as precursors for building new energetic salts of 5-imino-1,3-dimethyltetrazole and 5-imino-1,4-dimethyltetrazole with perchlorate (**2c-1**, **2d-1**), nitrate (**2c-2**, **2d-2**), azide (**2c-3**, **2d-3**), dinitramide (**2c-4**, **2d-4**), and picrate (**2c-5**, **2d-5**) anions. The general method (illustrated in Schemes 13 and 14)<sup>140,144,145,147</sup> involves a metathesis reaction of iodide and silver salts which were used as “energetic anion transfer reagents”.

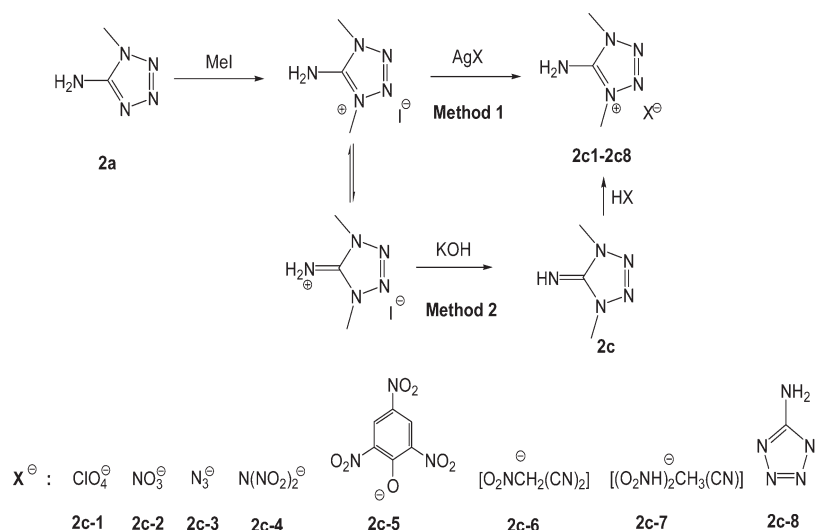
The free-base 1,4-dimethyl-5-iminotetrazole (**2c**) was also synthesized in yields >85% by deprotonation of the iodide salt using potassium hydroxide in alcohol.<sup>147</sup> This allows for a safer alternative method for large scale synthesis of the reported 1,4-dimethyl-5-aminotetrazolium salts (Scheme 13).<sup>143</sup> Compound **2c** is readily soluble in water, alcohol, acetone, or acetonitrile either at room temperature or at reflux but insoluble in diethyl ether or chloroform.<sup>143</sup> It is a relatively strong base, which can be protonated by mild acids and offers an alternative synthetic pathway to the synthesis of energetic salts **2c-1** to **2c-8**, which does not make use of highly sensitive silver salts, for example,  $\text{AgN}_3$  or  $\text{AgN}(\text{NO}_2)_2$ , and therefore, provides a safer large scale procedure for the synthesis of tetrazolium salts.<sup>164,165</sup>

The high nitrogen content, high thermal stability, low sensitivity, and relatively high detonation parameters of derivatives of **2c-1–2c-8** and **2d-1–2d-5** make them prospective candidates as a new class of insensitive, environmentally friendly energetic materials.<sup>140,144,145,147</sup>

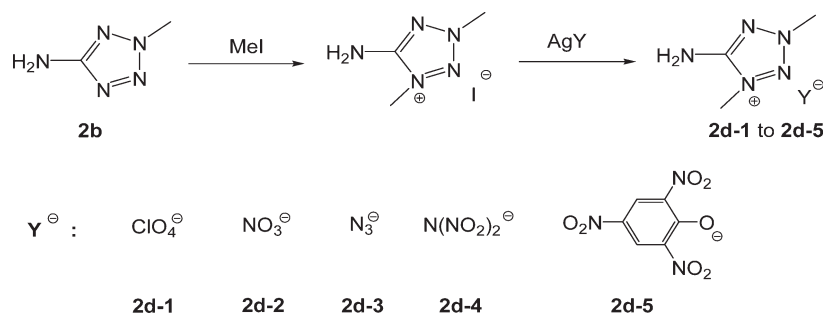
Unexpectedly, salts that contain the asymmetric 5-amino-1,3-dimethyltetrazolium cation have higher densities than analogous compounds which contain the isomeric 5-amino-1,4-dimethyltetrazolium cation, even though the former has lower symmetry.<sup>144</sup> This is because of the secondary interactions of the cation



Scheme 13. Syntheses of 1,4-Dimethyl-5-aminotetrazolium Salts



Scheme 14. Syntheses of 1,3-Dimethyl-5-aminotetrazolium Salts



and anion in the salt and is reflected in the better detonation properties of the new compounds that represent a new class of nitrogen-rich, high-performing materials with low impact sensitivities and good potential for energetic applications.<sup>144</sup>

Alkylation of 5-aminotetrazole (**2**) with 2-chloroethanol leads to a mixture of the N-1 (**2e(a)**) and N-2 (**2e(b)**) isomers of (2-hydroxyethyl)-5-aminotetrazole (Scheme 15).<sup>166</sup> Treatment of 1-(2-hydroxyethyl)-5-aminotetrazole (**2e(b)**) with  $\text{SOCl}_2$  gave 1-(2-chloroethyl)-5-aminotetrazole (**2f**).<sup>167</sup> 1-(2-Azidoethyl)-5-aminotetrazole (**2g**) was generated by the reaction of **2f** with sodium azide. The protonation of **2e** and **2g** with dilute nitric acid led to 1-(2-hydroxyethyl)-5-aminotetrazolium nitrate (**2e-1**) and 1-(2-azidoethyl)-5-aminotetrazolium nitrate (**2g-1**), respectively. Similarly, protonation of **2g** with perchloric acid led to 1-(2-azidoethyl)-5-aminotetrazolium perchlorate monohydrate (**2g-2**) (Scheme 15).<sup>146,168</sup>

All of the 5-amino-tetrazole derivatives and their salts are shown in Table 2. Most of them are highly endothermic compounds. Their heats of formation range between  $-1136$  (**2-12**) and  $732$  (**2b-1**) kJ/mol.<sup>141,144,150</sup> Standard BAM Fall-hammer techniques were used to measure their impact sensitivities.<sup>141,143,162</sup> Impact sensitivities range from those of the relatively insensitive **2-1**–**2-4**, **2-24**, **2-25**, **2a-3**, **2b-3**, **2d-5**, **2e-1** ( $>40$  J) to the very sensitive compounds **2-5**, **2-8**, **2-9**, **2a-1**, **2b-1**, and **2b-5** ( $\sim 1$ – $2$  J).<sup>141,142,147</sup> Thermal stabilities studies by DSC

show that 5-imino-tetrazole derivatives and their salts decompose between  $145$  (**2c-7**) and  $319$  °C (**2-9**).<sup>141,147</sup> The most thermally stable derivatives of **2** are the aminoguanidinium salts **2-9** and **2c-2** where decomposition occurred at  $319$  and  $315$  °C, respectively (Table 2).<sup>141,147</sup> The calculated detonation pressures ( $P$ ) lie in the range between  $13.3$  (**2e**) and  $38.4$  (**2-8**) GPa (comparable to RDX,  $35.2$  GPa). Detonation velocities are between  $6876$  (**2c-5**) and  $9429$  (**2-8**) m/s (comparable to RDX  $8977$  m/s and HMX  $9320$  m/s).<sup>13,139,140</sup> Safety testing (impact, friction, and electrostatic discharge sensitivity tests) for most salts was carried out. Comparing the impact sensitivities, **2-5** ( $1.5$  J), **2-8** ( $2$  J), **2-9** ( $2$  J), **2a-1** ( $3$  J), **2b-1** ( $1$  J), **2b-4** ( $5$  J), **2b-5** ( $2$  J), **2c-2** ( $5.5$  J), **2c-4** ( $5$  J), **2d-1** ( $3.5$  J), and **2g-2** ( $5$  J) are more sensitive than HMX and RDX.<sup>139,141,142,144,146,147</sup> Other salts have sensitivities much lower than that of RDX, ranging from  $10$  to greater than  $100$  J. Such sensitivities are desired for safe explosives used in insensitive munitions (IMS). The calculated energetic performance of **2g** shows that it represents a nitrogen-rich fuel for propellant charges.<sup>146</sup> A simple smoke test method was used to test the combustion behavior of the copper(II) compounds **2a-6** and **2a-7**. Copper complexes **2a-6** and **2a-7** show a green flame, with **2a-6** being less intense than **2a-7**. They offer the opportunity to substitute for the toxic barium salts in pyrotechnic applications.<sup>138</sup>

The attractive properties summarized above combine with reasonably high hydrolytic and thermal stabilities to make them

Scheme 15. Syntheses of 1-Alkyl-5-aminotetrazolium Salts

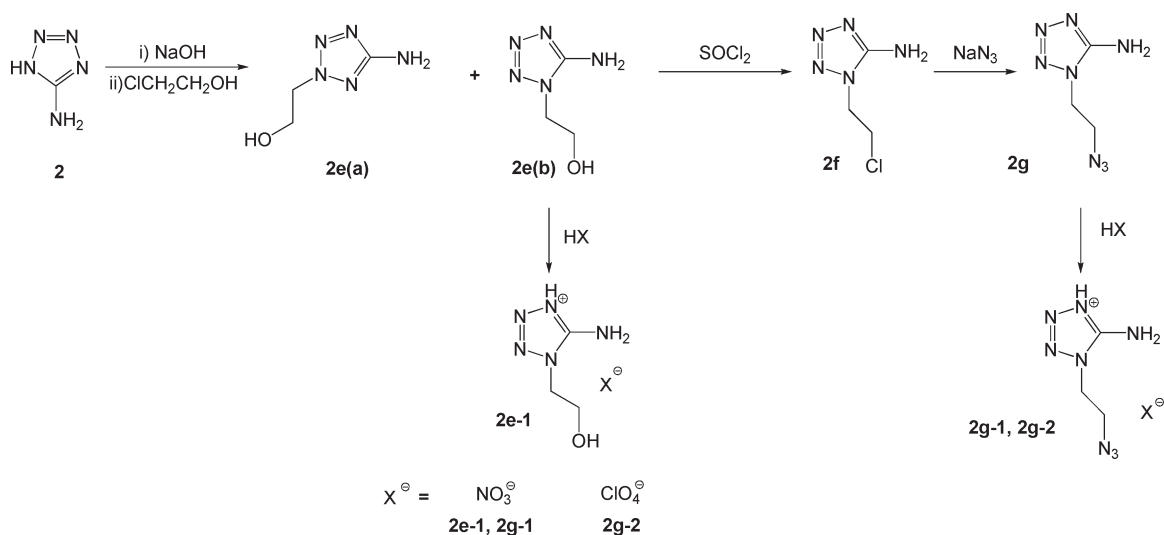


Table 2. Properties of 5-Amino-Tetrazoles Derivatives and Their Salts

compound	density (g/cm <sup>3</sup> )	T <sub>m</sub> (°C)	T <sub>d</sub> (°C)	ΔH <sub>f</sub> <sup>o</sup> (kJ/mol) <sup>a</sup>	ESD (±) <sup>b</sup>	P (GPa)	D (m/s)	thermal shock	IS (J)	friction (N)	ref
2-1	1.66	148	>175	−129 (9) [200]	—	25.6 [30.1]	7795 [8308]	burns rapidly	>40	>360	140
2-2	2.09	100 (−H <sub>2</sub> O)	175	—	—	—	—	—	>40	>360	151
2-3	2.36	110 (−H <sub>2</sub> O)	195	—	—	—	—	—	>40	>360	151
2-4	1.92	110 (−H <sub>2</sub> O), 178	182	—	—	—	—	—	>40	>360	151
2-5	—	176	180	—	0.1	—	—	explodes	1.5	8	142
											141
2-6	1.87	—	173	—	—	—	—	deflagrates	>30	>360	141
2-7	1.86	169	170	—	0.4	—	—	deflagrates	22	260	142
2-8	—	—	117	329	0.75	38.4	9429	—	2	20	137
2-9	—	—	319	—	+	—	—	explodes	2	<5	141
2-10	1.74	—	298	—	+	—	—	explodes	15	18	141
2-11	1.55	196	—	−399	—	—	—	—	>75	—	150
2-12	1.96	306	—	−1136	—	—	—	—	—	—	150
2-13	2.47	263	—	−202	—	—	—	—	—	—	150
2-14	2.84	238	—	−26	—	—	—	—	—	—	150
2-15	1.48 (1.55)	223	—	3	—	—	—	—	—	—	150
2-16	1.54 (1.46)	125	164	384	24.8	—	8786	—	—	—	152
2-17	1.51 (1.49)	126	220	205	19.4	—	8055	—	—	—	152
2-18	1.41 (1.44)	96	211	302	20.1	—	8149	—	—	—	152
2-19	1.62 (1.55)	141	207	307	16.3	—	7529	—	—	—	152
2-20	1.46 (1.49)	114	217	565	23.3	—	8360	—	—	—	152
2-21	1.39 (1.44)	(−24)	174	546	18.9	—	7334	—	—	—	152
2-22	1.57 (1.56)	(−38)	171	523	16.4	—	7397	—	—	—	152
2-23	1.53	171	190	655	23.2	—	8385	—	—	—	152
2-24	1.77	168	230	392 (15) [531]	20.0 [22.5]	7875 [8260]	burns	>40	>360	143	
2-25	1.65	127	242	456 (20) [596]	22.1 [24.0]	8217 [8456]	burns	>40	>360	143	
2a-1	1.72	125	245	—	+	—	—	explodes	3	10	141
											147
2a-2	—	162	178	—	—	25.6	8100	burns	>30	>360	141
											147
2a-3	—	175	270	−171 (48) [171]	—	21.2 [24.5]	7343 [7755]	burns	>40	>360	140
2a-4	1.84	102 (−H <sub>2</sub> O), 154	252	—	—	—	—	deflagrates	<5	120–360	141

Table 2. Continued

compound	density (g/cm <sup>3</sup> )	T <sub>m</sub> (°C)	T <sub>d</sub> (°C)	ΔH <sub>f</sub> <sup>o</sup> (kJ/mol) <sup>a</sup>	ESD (±) <sup>b</sup>	P (GPa)	D (m/s)	thermal shock	IS (J)	friction (N)	ref
2a-5	1.62	182	226		—			deflagrates	10	100–360	141
2b-1	1.71	125	196	732 (32) [532]	+			explodes	1	6	141
											144
2b-2		123	161	131 (15) [110]	—	25.9 [25.5]	8150 [8109]	burns	>30	>360	141
											144
2b-3		161	242	−180(26) [152]	—	20.4 [24.2]	7213 [7722]	burns	>40	>360	140
2b-4	1.67	286	289		+			deflagrates	2	<5	141
2b-5	1.52	none	259		—			deflagrates	20	100–360	141
2b-6	1.51 (1.53)	—	148	296	0.8	29.0	8548	—	5	64	137
2c-1	1.57	225	315	—	—			deflagrates	5.5	96	147
2c-2	1.64	181	270	—	—	20.2	7500	burns	>30	>360	147
2c-2	1.41 (1.45)	178	206	63							145
2c-3	1.56 (1.55)	186	>250	—	—	21.7	8200	burns	>30	>360	147
2c-4	1.63	120	174	—	—	21.2	7500	deflagrates	5	360	147
2c-5	1.57	210	269	−216 (45) [142]	—	17.8 [21.2]	6876 [7384]	burns	>40	>360	140
2c-6	1.48	94	260	443	—			—	—		145
2c-7	1.58	—	145	281	—			—	—		145
2d-1	1.64	132	285	535 (36) [518]	+				3.5	24	144
2d-2	1.50	150	199	67 (26) [87]	—	22.6 [22.7]	7850 [7864]	burns	>30	>360	144
2d-3	1.6	171	282	544 (24) [536]	—	23.5 [23.2]	8436 [8393]	deflagrates	>30	>360	144
2d-4	1.55	58	168	205 (33) [300]	—	23.7 [25.3]	7869 [8097]	deflagrates	15	>360	144
2d-5	1.50	180	278	−229 (34) [122]	—	17.6 [20.4]	6846 [7252]	burns	>40	>360	140
2e(b)	1.66	160	—	−105		13.3	6645		>100	>360	146
2e-1	1.66	—	160	11		23.3	7784		>50	>360	146
2f		150	—	143	—				>100	>360	146
2g		130	—	413 [550]		19.1 [21.8]	7619 [8043]		10	360	146
2g-1		—	148	457		27.1	8329		7	160	146
2g-2		—	172	—	—				5	120	146

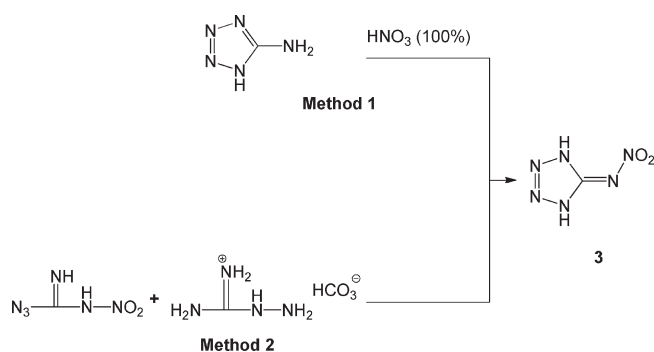
<sup>a</sup> Uncertainties are given in parentheses; calculated values are given in square brackets. <sup>b</sup> Rough sensitivity to electrostatic discharge: +, sensitive; −, insensitive.

prospective candidates for future applications as high-explosive compounds, gas generators, or components of propellants or propellant charges.

### 2.3. 5-Nitroimino-tetrazole Salts

5-Nitroimino-tetrazoles (3),<sup>169–178</sup> which are five-membered aromatic heterocycles with a nitroimine functional group, are one interesting approach in the development of new energetic materials. Because they are inexpensive and easy to manufacture via various routes, nitroiminotetrazoles (3) have been long known. There are three main synthesis routes: (1) protonation of 2 using warm concentrated HNO<sub>3</sub> to form 5-aminotetrazole nitrate (2-6)<sup>156,167,169</sup> (Scheme 16, method 1); (2) cyclization of nitroguanilyazide (also known as nitroazidoformamidine)<sup>167</sup> (Scheme 16, method 2); and (3) the most recent method of syntheses for 5-nitroiminotetrazole (3), 1-methyl-5-nitroiminotetrazole (3a), 2-methyl-5-nitroaminotetrazole (3b), 1-(2-hydroxyethyl)-5-nitroiminotetrazole (3c) and 1-(2-chloroethyl)-5-nitroiminotetrazole (3d) based on one-step nitration of functional derivatives of 5-amino-1H-tetrazole (2) with HNO<sub>3</sub> (100%) (Schemes 17 and 18).<sup>118,171,172,175</sup> Synthesis and characterization of various guanidinium nitroimino-tetrazolate salts, which can be prepared from silver nitroimino-tetrazolate by metathesis, have been reported as HEDMs.<sup>179</sup>

### Scheme 16. Synthesis of 5-Nitroiminotetrazole



The reactions of 5-nitroiminotetrazole (3) with heterocyclic bases yield 5-nitroimino-1H-tetrazolate monohydrate salts with 1-methyl-5-aminotetrazolium (3-1), 4-amino-1,2,4-triazolium (3-7), 5-nitroimino-1H-tetrazolate (3-8), 5-amino-tetrazolium, 1,2,4-triazolium (3-9), 1-propyl-1,2,4-triazolium (3-10), and 3-azido-1,2,4-triazolium (3-11) cations (Schemes 19–23).<sup>172</sup> However, when 3 was reacted with 2-methyl-5-aminotetrazole (2b), no protonation was observed; rather cocrystallization of 5-nitraminotetrazole and 2-methyl-5-aminotetrazole (3-2)

occurred which indicates that **2b** is the weaker base and is therefore more difficult to protonate.<sup>179,180</sup> Guanidine and aminoguanidine salts with mono- or dianions or 5-nitroimino-1,2,3,4-tetrazolate (**3-3** to **3-6**) were synthesized by the reaction of **3** with stoichiometric amounts of guanidine carbonate or aminoguanidine bicarbonate (Scheme 20). Compound **3** was deprotonated using potassium hydroxide to form the corresponding potassium salt, which was transformed into silver 1-methyl-5-nitriminotetrazolate by reaction with AgNO<sub>3</sub> in aqueous solution (Scheme 21). Guanidinium (**3a-1**), 1-amino-guanidinium (**3a-2**), 1,3-diaminoguanidinium (**3a-3**), 1,3,5-triaminoguanidinium (**3a-4**), and azidoformamidinium (**3a-5**) 1-methyl-5-nitriminotetrazolate were prepared by metathesis reactions driven by the precipitation of AgCl. An alternative synthesis method is the reaction of guanidinium perchlorates and potassium 1-methyl-5-nitroiminotetrazolate. This route eliminates the use of the light sensitive silver salt. Compounds **3a-1** to **3a-5** can be recrystallized from water/ethanol mixtures resulting in colorless crystals.<sup>177</sup>

2-Methyl-5-nitraminotetrazole can be easily deprotonated in aqueous solution using alkali hydroxides forming the corresponding alkali salts in nearly quantitative yields. These form the silver salt by the reaction with AgNO<sub>3</sub> in aqueous solutions (Scheme 22).<sup>118</sup> The nitrogen-rich 2-methyl-5-nitraminotetrazolate salts, such as guanidinium (**3b-6**), 1-amino-guanidinium (**3b-7**), 1,3-diamino-guanidinium (**3b-8**), 1,3,5-triamino-guanidinium (**3b-9**), azidoformamidinium (**3b-10**), hydrazinium (**3b-11**), diaminouronium 2-methyl-5-nitraminotetrazolate (**3b-12**), as well as an urea adduct (**3b-13**), can easily be obtained via Brønsted acid–base reactions using the guanidinium carbonates or metathesis reactions using silver 2-methyl-5-nitraminotetra-

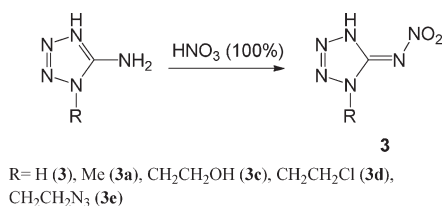
zolate and the guanidinium chlorides in aqueous solution with high yields and good purity.<sup>118</sup> The triaminoguanidinium salt **5** was synthesized via the hydrazinolysis of the aminoguanidinium salt **3b-7**.<sup>118</sup> In addition, the sensitivities toward impact, friction, and electrical discharge were tested using the BAM drop hammer, BAM friction tester, as well as a small scale electrical discharge device. Although the salts are energetic materials with high nitrogen content, they show good stabilities toward friction, impact and thermolysis (Table 3). The performance of diaminouronium 2-methyl-5-nitraminotetrazolate (**3b-12**) qualifies it for further investigations concerning military applications.<sup>118</sup>

Nitration of the amino group in aminotetrazole leads to enhanced energetic character as well as higher sensitivity compared to aminotetrazole and improves the oxygen balance. The methyl group lowers the sensitivity compared to the nonmethylated 5-nitroiminotetrazole.<sup>175</sup> The potassium salt of 1-methyl-5-nitroiminotetrazole, prepared by deprotonation using potassium hydroxide, was transformed into silver 1-methyl-5-nitroiminotetrazolate by reaction with silver nitrate.<sup>179</sup> The strontium 5-nitriminotetrazolate dihydrate (**3-12**), strontium bis(1-hydro-5-nitriminotetrazolate) tetrahydrate (**3-13**), strontium bis(1-methyl-5-nitriminotetrazolate) monohydrate (**3a-6**), and strontium bis(2-methyl-5-nitraminotetrazolate)·*x*H<sub>2</sub>O (*x* = 2–4) (**3b-1**) were synthesized by the reactions of strontium hydroxide octahydrate and **3**, **3a**, and **3b**, respectively.<sup>173</sup> The copper complexes **3-14**–**3-16** (Scheme 20), **3a-7**–**3a-9** (Scheme 21), and **3b-2**–**3b-5** (Scheme 22) were synthesized by combination of either aqueous copper nitrate trihydrate or aqueous copper chloride solutions with **3**, **3a**, and **3b**.<sup>170</sup>

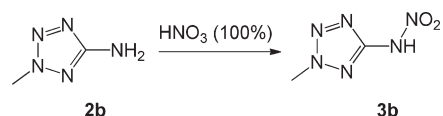
Nitration of **2e**, **2f**, and **2g** yields 1-(2-hydroxyethyl)-5-nitriminotetrazole (**3c**), 1-(2-chloroethyl)-5-nitriminotetrazole (**3d**), and 1-(2-azidoethyl)-5-nitriminotetrazole (**3e**). The coordination of **3c**, **3d**, and **3e** with copper nitrate trihydrate, gave copper complexes trans[diaquabis{1-(2-hydroxyethyl)-5-nitriminotetrazolato- $\kappa^2 N^4, O^5$ }-copper(II)}] (**3c-1**), trans[diaquabis{1-(2-chloroethyl)-5-nitriminotetrazolato- $\kappa^2 N^4, O^5$ }-copper(II)}] dihydrate (**3d-4**), and [diaquabis{1-(2-azidoethyl)-5-nitriminotetrazolato- $\kappa^2 N^4, O^5$ }-copper(II)}] (**3e-1**) (Scheme 23).<sup>146</sup>

Physical properties of the nitroiminotetrazole derivatives and their salts are given in Table 3. They are highly endothermic compounds. The enthalpies of all compounds are positive ranging between 22 (**3a**·H<sub>2</sub>O) and 694 (**3-11**) kJ/mol.<sup>172,180</sup> However, their thermal stabilities are marginal. Differential scanning calorimetry (DSC) studies show that decomposition of the nitroiminotetrazolates occurs between 69.0 (**3-10**) and 243.6 (**3-5**) °C with the majority decomposing ~120 °C (**3**, **3-1**, **3a**, **3b**, and **3d**). Impact sensitivities range from those of the

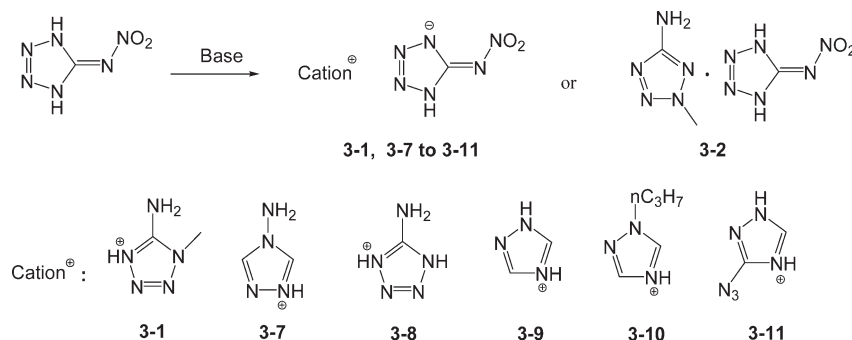
Scheme 17. Synthesis of 1-Alkylated-5-nitroiminotetrazole



Scheme 18. Synthesis of 2-Methyl-5-nitriminotetrazole

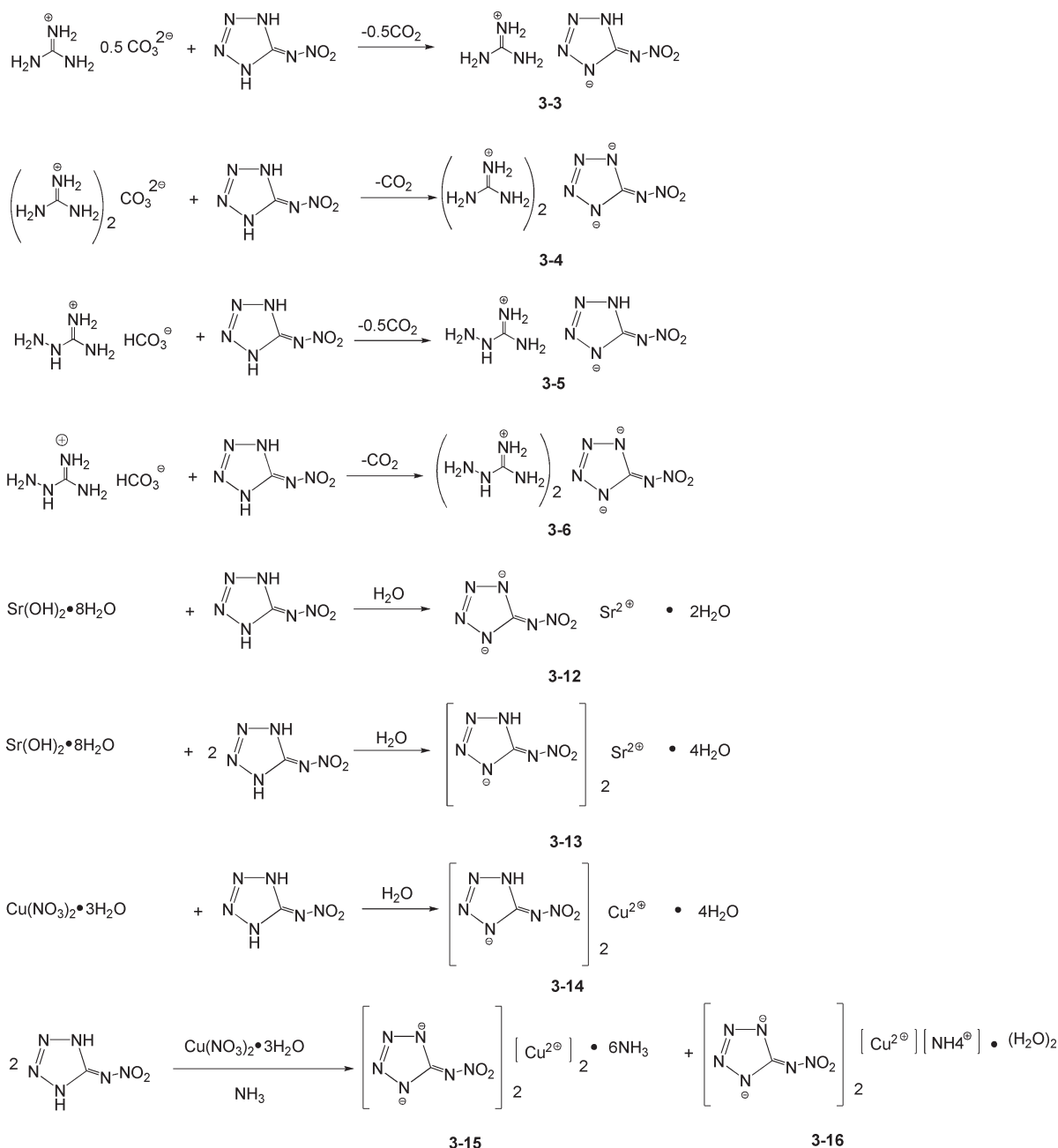


Scheme 19. Syntheses of 5-Nitriminotetrazolate Salts (Part 1)





Scheme 20. Syntheses of 5-Nitriminetetrazolate Salts (Part 2)

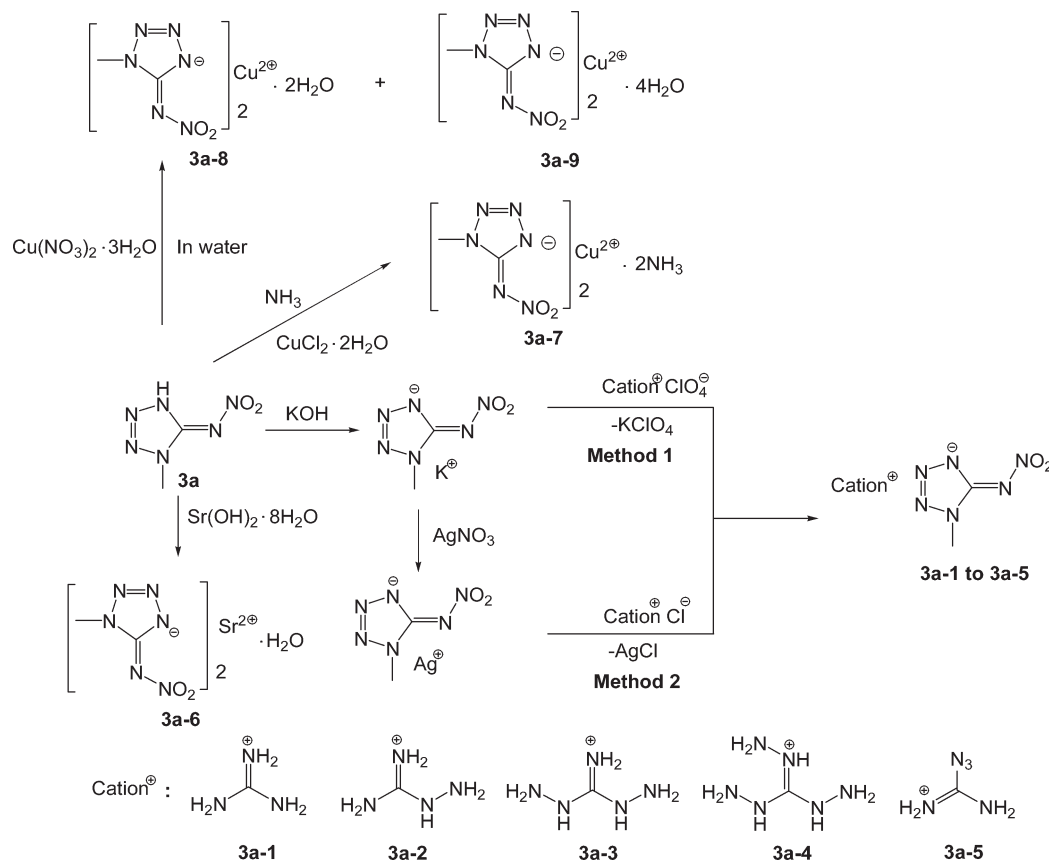


relatively nonsensitive **3a-1**, **3d-1**, and **3d-2** ( $>40$  J) to the very sensitive compounds **3-2** and **3e** ( $<2$  J).<sup>146,179,180</sup> The calculated detonation pressures of aminotetrazolate salts lie in the range between 18.1 (**3-5**) and 39.4 (**3**) GPa (comparable to RDX, 35.17 GPa). Detonation velocities are found between  $D = 7617$  (**3-5**) and  $D = 9450$ <sup>180</sup> or  $9173$ <sup>179</sup> (**3**) m/s (comparable to HMX  $D = 9320$  m/s and RDX  $D = 8977$  m/s).<sup>139</sup>

The color performance of copper complexes **3c-1**, **3d-3**, and **3e-1** was tested for application as coloring agents in “green” pyrotechnics. Complexes **3c-1** and **3e-1** show a brilliant green flame, and complex **3d-3** gives a bright blue flame. The combustion of these complexes is almost smokeless, which makes them promising coloring agents in modern pyrotechnic compositions.<sup>146</sup> Salt **3a-6** burned with an intense bright red flame and its color purity

exceeded the control value.<sup>138</sup> The color performance of copper complexes **3-14–3-16**, **3a-3a-9**, and **3b-2–3b-5** was also tested.<sup>138</sup> For the latter copper-tetrazole complexes, sensitivity tests show that the values range from “very sensitive” and therefore comparable to primary explosives, to “insensitive” depending on the amount of coordinated water or ammonia. Flame colors were intensely green. Burning is also nearly smokeless and free of carbon residues. This suggests especially **3-15**, **3-16**, and **3a-7**, as well as **3b-4** and **3b-5**, as promising candidates for green colorants in modern smokeless pyrotechnic compositions.<sup>170</sup> The nitroiminotetrazole salts are highly endothermic compounds which could make them of interest for future applications as environmentally friendly and high-performing energetic materials.<sup>181,182</sup>

Scheme 21. Syntheses of 1-Methyl-5-nitriminotetrazolate Salts



#### 2.4. 5-Nitro-tetrazole Salts

5-Amino-1H-tetrazole (**2**) was diazotated with nitrous acid (generated in situ) in the presence of copper(II) sulfate to give the copper 5-nitrotetrazolate salt (**4-1**).<sup>183</sup> Sodium 5-nitrotetrazolate (**4-4**) was obtained by digesting the highly insoluble copper salt with sodium hydroxide.<sup>184</sup> After removal of the black copper(II) oxide by filtration, the basic solution was treated in situ with acid and then reacted with ammonia to precipitate ammonium 5-nitrotetrazolate (**4-2**).<sup>185</sup>

Neutral compounds **4** (Scheme 24), **4a**, and **4b** can be easily detonated by impact (<2 J) and with their high detonation velocities and excellent combined oxygen and nitrogen contents offer more powerful and environmentally friendly alternatives to commonly used primary explosives in initiating devices.<sup>186</sup> Each of the compounds shows a highly exothermic decomposition peak (DSC). Unfortunately **4** is hygroscopic, which limits its applications.<sup>186</sup> Furthermore **4**, **4a**, and **4b** are too unstable thermally for use as conventional high explosives.<sup>186</sup> Compound **4-2** was subsequently deprotonated with a suitable metal hydroxide or carbonate in alcoholic or aqueous solution, with concomitant formation of ammonia or carbon dioxide, to yield the desired 5-nitrotetrazolate salts **4-3** to **4-11** (Scheme 24).<sup>184</sup> Alkali metal salts with the energetic 5-nitrotetrazolate anion showed good thermal stabilities up to  $\geq 200^\circ\text{C}$  (Table 4).<sup>18</sup>

Standard sensitivity tests indicate that the salts with the harder lithium and sodium cations have lower sensitivity toward shock and friction mainly because that they contain crystal water.<sup>184</sup> Whereas the remainder of the salts form anhydrous

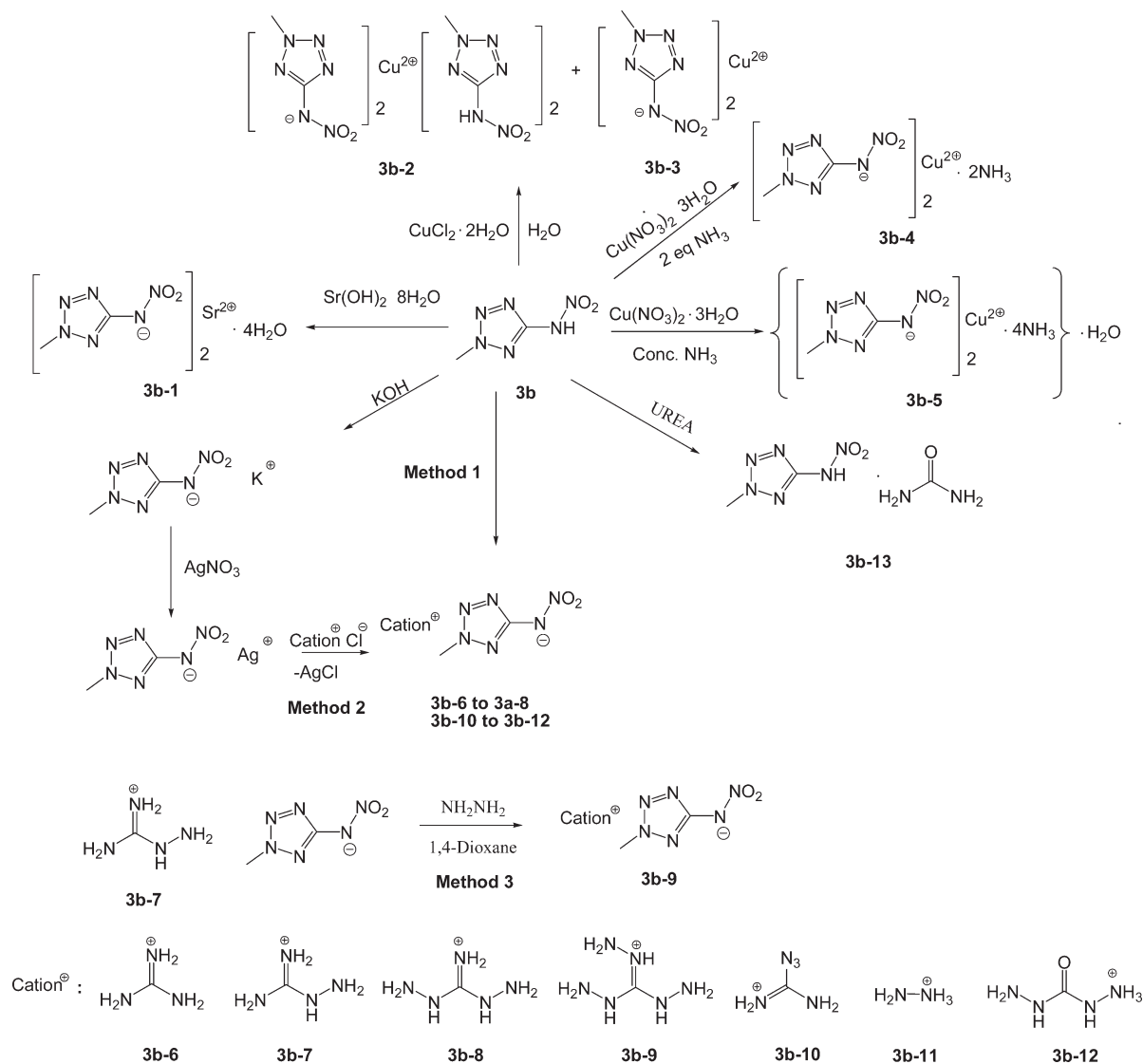
species and thus show increased sensitivities but are devoid of a toxic metal, such as lead, making them of interest as prospective replacements for commonly used primary explosives.<sup>184</sup>

All alkaline earth metal salts contain water of crystallization which is reflected in the lower sensitivity of these compounds toward shock and friction compared to anhydrous alkali metal salts containing the same anion. They have potential use as energetic materials.<sup>185,187</sup> Compound **4-4** has been used as a stand-alone energetic material and as an additive in explosive and propellants mixtures.<sup>183</sup>

Silver 5-nitrotetrazolate (**4-12**) was prepared by precipitation as a white, highly sensitive powder from the sodium salt (**4-4**) with silver nitrate in water.<sup>184</sup> In addition, salts with metal cations, a new family (ammonium, **4-2**; hydrazinium, **4-13**; guanidinium, **4-14**; aminoguanidinium, **4-15**; diaminoguanidinium, **4-16**; and triaminoguanidinium, **4-17**) of simple, nitrogen-rich energetic salts based on 5-nitro-2H-tetrazole (HNT), were also synthesized (Scheme 25).<sup>185,188</sup>

Initially, the compounds **4-13** to **4-17** were prepared by metathesis of **4-12** with the corresponding bromide or iodide salts as shown in Scheme 25 (method 1).<sup>187</sup> But the syntheses of energetic salts for study using **4-12** as the 5-nitrotetrazole transfer reagent were unsuitable since silver 5-nitrotetrazolate is extremely sensitive to impact, friction, and electrostatic discharge; only small amounts should be prepared. In addition, silver salts tend to be reduced by aminated guanidines and hydrazines to elemental silver leading to substantial decomposition of hydrazine and amino-, diamino-, and triaminoguanidine moieties during the reaction.

Scheme 22. Syntheses of 2-Methyl-5-nitriminotetrazolate Salts



Therefore, **4-2** was used successfully as a starting material to synthesize **4-13** to **4-17** (Scheme 25, method 2).<sup>187</sup> This method is suitable for scale-up and, with the exception of the sensitive explosive materials, **4-13** and **4-17**, products have been obtained on at least a ~5 g scale. Compound **4** has found use in reaction with azolium bases, such as 5-aminotriazole and substituted tetrazoles to form 5-aminotetrazolate salts, **4-18** to **4-21** (Scheme 26).<sup>172,189</sup> Specific impulse values represent the impulse (change in momentum) per unit amount of propellant used.  $I_{sp}$  is an important property for the characterization of propellants.<sup>51</sup> Unfortunately few values have been reported for these materials; however,  $I_{sp}$  values (>240 s) of **4-20** and **4-21** (246.0 and 249.2 s) may make them attractive for propellant applications.<sup>172</sup>

All of these salts show good thermal stabilities (most of the salts have decomposition temperatures above 180 °C). Their densities are slightly lower than those desired for new high performance energetic materials (1.8–2.0 g/cm<sup>3</sup>) but are nonetheless in the range of currently used explosives (1.6–1.8 g/cm<sup>3</sup>) (Table 4).

Although silver 5-nitrotetrazolate (**4-12**) and copper(II) 5-nitrotetrazolate·5-nitrotetrazole·dihydrate (**4-1**) could be used as 5-nitrotetrazolate sources and they are useful reagents for the synthesis of 5-nitrotetrazolate salts, the extremely high sensitivity of both materials makes the transfer of the 5-nitrotetrazolate anion hazardous and not suitable for scale-up.<sup>183</sup> To minimize the hazards involved from the transfer of the 5-nitrotetrazolate anion and to scale up the synthesis of 5-nitrotetrazolate salts suitable for industrial application, the two compounds were stabilized by coordination with a chelating ligand. Silver (ethylenediamine) 5-nitrotetrazolate (**4-22**) and bis(ethylenediamine)-copper(II) 5-nitrotetrazolate (**4-23**) were synthesized in high yields (Scheme 7).<sup>183</sup>

Compounds **4-22** and **4-23** are synthesized as safer 5-nitrotetrazolate anion transfer reagents, and the potential of **4-22** for the synthesis of tetrazolium salts is exemplified (Scheme 28).<sup>183</sup> In addition, a copper complex, triamminecopper(II) 5-nitrotetrazolate (**4-24**) with ammonia ligands containing the 5-nitrotetrazolate anion, was synthesized (Scheme 27) and can be easily initiated by impact and by laser induction.<sup>183</sup> It offers a safer and

Scheme 23. Syntheses of 1-Alkyl-5-nitriminotetrazole and Their Salts

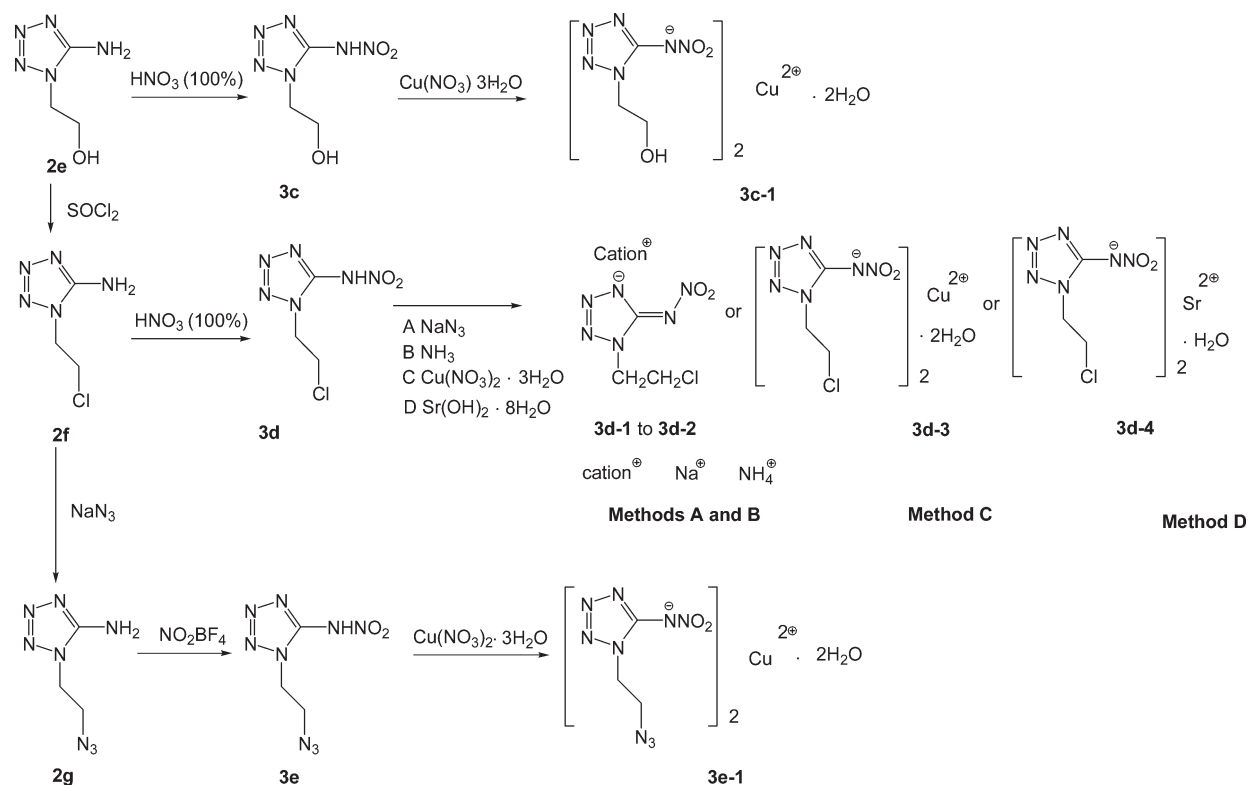


Table 3. Properties of Substituted Nitroiminotetrazoles and Their Salts

compound	density (g/cm <sup>3</sup> )	T <sub>m</sub> (°C)	T <sub>d</sub> (°C)	ΔH <sub>f</sub> <sup>o</sup> (kJ/mol) <sup>a</sup>	PP (GPa)	D (m/s)	IS (J)	FS (N)	ESD (+/−) <sup>b</sup> (J)	I <sub>sp</sub> (s)	ref
3 <sup>c</sup>	1.87		122	264	36.3	9173	1.5	8	—		175
				322	39.4	9450			0.19		180
3 · H <sub>2</sub> O	1.81		122	54	32.3	8849	9	140	0.38		180
3-1	1.59		139	122	20.8	7619	3	144	1.5		180
3-2	1.66		159	444	24.7	8093	2	72	0.46		180
3-3	1.61		228	74	22.1	8069				192.3	171
3-4	1.5		244	87	18.1	7617				187.0	171
3-5	1.64		227	168	25	8479				200.9	171
3-6	1.55		216	329	22.6	8312				204.3	171
3-7	1.72	143	184	441	27	8506				218.9	172
3-8	1.63	165	165	488	25.5	8276				229.0	172
3-9	1.74	177	177	328	26	8334				208.7	172
3-10	1.48	69	122								172
3-11	1.68	89	135	694	25.9	8230				233.5	172
3-12	2.42	230	351				30	>360	1.0		173
3-13	2.20	163	227				20	288	0.4		173
3-14	2.06						30	>360			170
3-15	2.01						>50	>360			170
3-16	2.01						>40	>360			170
3a <sup>c</sup>	1.76		125	260	29.5	8433	12.5	160	—		175
				287	29.9	8464			0.28		180
3a · H <sub>2</sub> O	1.64		125	22	23.9	7894	19	320	0.35		180
3a-1	1.55		210	155	20.6	7747	40	>360			179
3a-2	1.57		216	257	22.7	8062	10	>360			179
3a-3	1.61		208	352	26.1	8559	7.5	>360			179

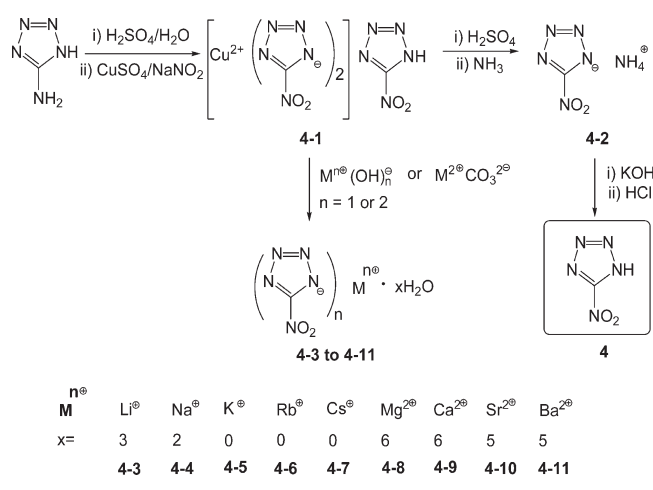


Table 3. Continued

compound	density (g/cm <sup>3</sup> )	T <sub>m</sub> (°C)	T <sub>d</sub> (°C)	ΔH <sub>f</sub> <sup>0</sup> /kJ/mol <sup>a</sup>	PP (GPa)	D (m/s)	IS (J)	FS (N)	ESD (+/−) <sup>b</sup> (J)	I <sub>sp</sub> (s)	ref
3a-4	1.57		210	569	27.3	8770	6	240			179
3a-5	1.61		165	405	23.0	7910	4	160			179
3a-6	2.19	—	350				40	>360	0.9		173
3a-7	1.85						15	>360			170
3b	1.67		122	380	28.9	8434	3.0	145			175
3b-1	1.83	165	230				>50	>360	0.01		173
3b-2	1.86						2	30			170
3b-3	2.07						1	18			170
3b-4	1.86						20	300			170
3b-5	1.72						40	30			170
3b-6	1.63	176	212	255	25.0	8300	30	192	0.2		118
3b-7	1.61	146	210	366	26.0	8495	6	120	0.2		118
3b-8	1.57	138	203	479	26.2	8603	10	160	0.16		118
3b-9	1.57	143	188	587	27.7	8827	6	120	0.18		118
3b-10	1.57	114	148	687	25.8	8290	3	72	0.2		118
3b-11		73	208				7	120	0.1		118
3b-12	1.73	131	195	345	30.7	8864	5	168	0.5		118
3b-13	1.59	—	158	120	22.4	7806	10	288	0.2		118
3c	1.73		138	201	28.0	8254	6	55			146
3c-1	1.82		245	—	—	—	>50	—			146
3d	1.72		130	278	—	—	28	>360			146
3d-1	1.86		184	—	—	—	>50	>360			146
3d-2	1.64		196	—	—	—	>50	>360			146
3d-3	1.87		233	—	—	—	>50				146
3d-4	2.03		208		0.75	—	>10	>360			138
3e·H <sub>2</sub> O	1.78		128	165	34.1	8943	25	360			146
3e	1.67		140	[629]	[27.5]	[8320]	2	80			146
3e-1	1.78		205	—	—	—	25	300			146

<sup>a</sup> Calculated values (from electronic energies) are given in brackets. <sup>b</sup> Rough sensitivity to electrostatic discharge: +, sensitive; −, insensitive. <sup>c</sup> Different values for the properties of the compound were reported in different references.

### Scheme 24. Syntheses of 5-Nitrotetrazolate Salts (Part 1)



more environmentally friendly alternative to commonly used compounds (e.g., lead azide) and has potential as a more environmentally friendly primary explosive.<sup>183</sup>

Compounds 2a and 2b were treated as with 2 to obtain the methylated nitrotetrazolates. Diazotization with 2 equiv of

sodium nitrite in the presence of a non-nucleophilic acid (e.g., sulfuric acid) yields 1-methyl-5-nitrotetrazole (4a) and 2-methyl-5-nitrotetrazole (4b) as crystalline compounds (Scheme 29).<sup>186</sup>

Salt 4-4 was selectively alkylated with bromoacetonitrile to yield 5-nitrotetrazol-2-ylacetone nitrile (4c) (Scheme 30). The 1,3-dipolar cycloaddition of azide ion to 4c yielded 5-(5-nitrotetrazol-2-ylmethyl)tetrazole monohydrate (4d), which was subsequently reacted with a stoichiometric amount of a suitable alkali metal base (bicarbonate or carbonate) or nitrogen base resulting in energetic salts with Li<sup>+</sup> (4d-1), Na<sup>+</sup> (4d-2), K<sup>+</sup> (4d-3), Rb<sup>+</sup> (4d-4), Cs<sup>+</sup> (4d-5), ammonium (4d-6), guanidinium (4d-7), and aminoguanidinium (4d-8) cations.<sup>188</sup>

The HOF/CH<sub>3</sub>CN complex is easily prepared from diluted fluorine and aqueous acetonitrile and is one of the powerful oxygen transfer reagents which was found to have many applications in organic reactions.<sup>193–204</sup> Tetrazole N-oxides could be synthesized by using the powerful oxygen transfer reagent HOF/CH<sub>3</sub>CN in rapid and high yield reactions.<sup>205</sup> It is found that HOF/CH<sub>3</sub>CN is able to transfer oxygen atoms to the 1- or 2-substituted 5-alkyl or aryl tetrazole ring and resulting in the corresponding N-oxides 4a to 4d (Scheme 31). This novel route features mild conditions and high yields. X-ray structure analysis and <sup>15</sup>N NMR experiments indicate that the preferred position for the incorporation of the oxygen is on the N-3 atom

Table 4. Properties of Substituted Nitrotetrazoles and Their Salts

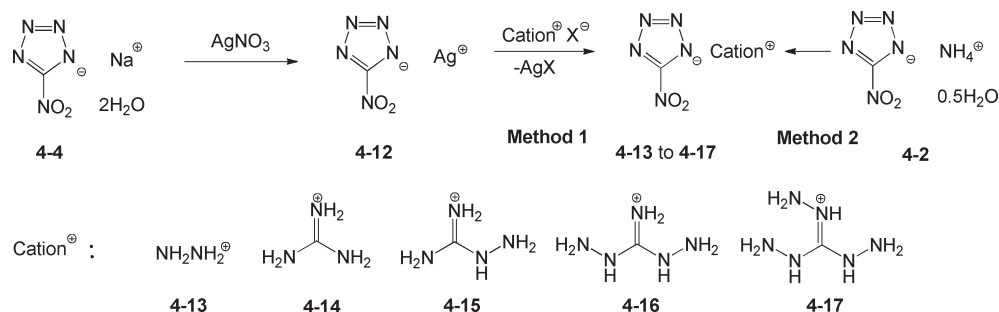
compound	density (g/cm <sup>3</sup> )	$T_m$ (°C)	$T_d$ (°C)	$\Delta H_f^\circ$ (kJ/mol) <sup>a</sup>	$P$ (GPa)	$D$ (m/s)	IS (J)	FS (N)	ESD (+/-) <sup>b</sup> (J)	thermal shock	ref
4	1.90	98	130	281	39.0	9457	<1	<5	—	deflagrates	186
4a	1.67	75	150	247	26.2	8109	1	40	0.20	combusts	186
4b	1.63	45	155	278	25.7	8085	2	82	0.50	combusts	186
4-1		—	230				<3	<5	+	explodes	183
4-2		—H <sub>2</sub> O	210		23.9	7950	<1.5	<96		deflagrates	185, 188
4-3	1.61	69 (—H <sub>2</sub> O)	270	610 (55)			25	324			184
4-4	1.73	75 (—H <sub>2</sub> O)	200	360 (65)			>30	~360			184
4-5	2.03	168	195	—			10	<5			184
4-6	2.49	146	192				5	<5			184
4-7	2.99	158	194				10	<5			184
4-8		119 (—H <sub>2</sub> O)	195				≥40	240			185
4-9		120 (—H <sub>2</sub> O)	180				35	84			185
4-10		104 (—H <sub>2</sub> O)	210				15	48			185
4-11		129 (—H <sub>2</sub> O)	235				2.5–5	<20			185
4-12		—	273				<1	<5	+	explodes	183
4-2	1.64	207, 68 (—H <sub>2</sub> O)	217	—70 (20) [51.6]	22.5	7740	4	120	—	explodes	187
4-13	1.72	135	188	180 (90) [343.7]	30.1	8750	2	16	+	explodes	187
4-14	1.64	212	217	—10 (30) [191]	20.1	7500	>30	>360	—	burns	187
4-15	1.66	147	211	160 (20) [308]	24.7	8190	30	360	—	deflagrates	187
4-16	1.60	108	216	300 (40) [437]	24.4	8230	4	360	—	deflagrates	187
4-17	1.60	96	191	390 (40) [602]	26	8480	2	48	—	explodes	187
4-17a	1.60	63, 95 (—H <sub>2</sub> O)	191	120 (40) [353]	20.7	7680	>30	>360	—	deflagrates	187
4-18	1.63	151	197	409	22.6	7865					172
4-19	1.38	—55 ( $T_g$ )	131								172
4-20	1.75	159	163	571	31.4	8843					172
4-21	1.71	128	161	651	30.7	8844					172
4-22			212				>40	<240		explodes	183
4-23			225				<7	<252		explodes	183
4-24			245				<2	<18		explodes	183
4c	1.75	118	210	496	29.5	8356	<7	<18		burns	188
4d·H <sub>2</sub> O	1.80	99 (—H <sub>2</sub> O), 167 (mp)	214	298	28.7	8341	<8	120–360		deflagrates	188
4d	1.80	168	214	550	30.2	8688	<2	<180		deflagrates	188
4d-1		81 (—H <sub>2</sub> O)	180				<4	<5			190
4d-2		125 (—H <sub>2</sub> O)	192				<6	<12			190
4d-3		89 (—H <sub>2</sub> O)	184				<8	<30			190
4d-4		102 (—H <sub>2</sub> O)	170				<6	<5			190
4d-5		100 (—H <sub>2</sub> O), 183 (mp)	186				<15	<60			190
4d-6·H <sub>2</sub> O	1.60	83 (—H <sub>2</sub> O)	206	128	21.3	7658	>30	>360		deflagrates	188
4d-6	1.60	—	208	383	22.8	7861	<20	<300		deflagrates	188
4d-7	1.64	191	196	567	24.3	8066	>30	>360		deflagrates	188
4d-8	1.63	128	201	616	25.0	8202	>30	>360		deflagrates	188
4e	1.70	—	120	309	40.4	9447	—	—	—		191
4e-1	1.69	—	173	152	32.2	8885	7	120	0.25		191
4e-2	1.64	—	157	219	39.0	9499	4	60	0.05		191
4e-3		—	211	137	26.6	8201	>40	252	0.20		191
4e-4		—	185	256	28.5	8514	20	112	0.20		191
4e-6		—	174	361	29.2	8686	40	120	0.20		191
4e-7		—	153	472	29.4	8768	25	72	0.20		191

<sup>a</sup>Uncertainties are given in parentheses, calculated values are given in square brackets. <sup>b</sup>Rough sensitivity to electrostatic discharge: +, sensitive; —, insensitive.

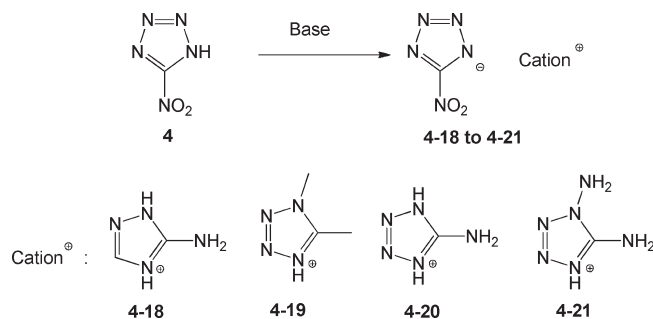
(Scheme 31).<sup>205</sup> Considering the commercial availability of premixed gases of fluorine and nitrogen, this method of

transferring oxygen may become a method of choice for many cases where the alternatives are not sufficiently potent.<sup>205</sup>

Scheme 25. Syntheses of 5-Nitrotetrazolate Salts (Part 2)



Scheme 26. Syntheses of 5-Nitrotetrazolate Salts (Part 3)



Ammonium nitrotetrazolate-2*N*-oxide (**4e-1**) is synthesized by the oxidation of ammonium 5-nitrotetrazolate hemihydrate in a saturated Oxone solution at 40 °C (Scheme 32).<sup>191,192</sup> After acidification of the reaction liquors, separation of the free acid nitrotetrazole-2*N*-oxide (**4e**) was possible.<sup>191</sup> Salts **4e-1**, **4e-3**, and **4e-4** with nitrotetrazolate-2*N*-oxide anion were prepared from the ammonium salt by simple acid–base chemistry and metathesis reactions with either acid or amino guanidinium bicarbonate while salts **4e-6** and **4e-7** were prepared from the silver salt **4e-5** and aqueous diaminoguanidinium iodide or triaminoguanidinium chloride (Scheme 32). Hydroxylammonium salt (**4e-2**) was prepared by metathesis with the ammonium salt (**4e-1**).<sup>191</sup>

Salt **4e-7** has the lowest decomposition temperature at 153 °C and guanidinium salt (**4e-3**) has the highest at 211 °C.<sup>191</sup> The substituted guanidinium salts of **4e** show that an increased number of amino substituents on the guanidinium cation leads to decreased thermal stability. Large liquid ranges are seen for salts **4e-6** and **4e-7**, making them potential melt-cast explosives. It is worth noting that unlike silver nitrotetrazolate (**21**), the silver salt (**4e-5**) is not a sensitive primary explosive and can be safely handled.<sup>191</sup> Ammonium (**4e-1**), diamino-guanidinium (**4e-6**), and triaminoguanidinium (**4e-7**) salts of nitrotetrazolate-2*N*-oxide have detonation properties (detonation velocity and pressure) similar to those of RDX, making them potential green replacements for RDX.<sup>191</sup>

The impact sensitivities of ammonium (**4e-1**) and hydroxylammonium (**4e-2**) salts are 4 and 7 J, respectively,<sup>191</sup> which are more sensitive than that of RDX. However, the substituted guanidinium salts (**4e-3**, **4e-4**, **4e-6**, and **4e-7**) have impact sensitivities much safer than that of RDX, ranging from 20 to greater than 40 J.<sup>191</sup> Such sensitivities are desired for safe explosives used in insensitive munitions. In all cases, with the exception of the aminoguanidinium salt (**4e-4**), the salts of nitro-

tetrazolate-2*N*-oxide are less sensitive than the corresponding nitrotetrazolate salts.

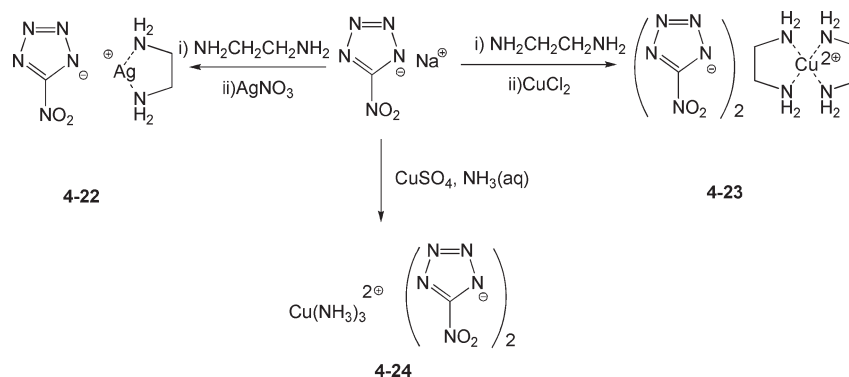
The physicochemical properties of all 5-nitrotetrazole derivative salts are given in Table 4. The thermal behavior of the nitrotetrazole salts was investigated by DSC. The neutral molecule 5-nitrotetrazole (**4**) shows the lowest decomposition temperature at 130 °C.<sup>186</sup> All the salts have higher thermal stabilities.<sup>172,183–187</sup> The highest decomposition temperature is shown by the silver salt (**4-12**) at 273 °C,<sup>183</sup> but it is quite sensitive to impact and friction. Lithium 5-nitrotetrazolate (**4-3**) has the second highest decomposition temperature at 270 °C; it is insensitive to impact (25 J) and friction (324 N).<sup>184</sup>

Most nitrotetrazolate salts have positive heats of formation. The two with the highest values are **4d-8** (617 kJ/mol) and **4-3** (610 kJ/mol).<sup>184</sup> Calculated detonation parameters show that the free acid **4**, **4e**, and the hydroxylammonium salt of the latter (**4e-2**) have detonation characteristics which outperform HMX. Salts **4e-1**, **4e-6**, and **4e-7** show detonation properties (detonation velocity and pressure) similar to those of RDX, making both of these compounds potential green replacements for RDX. The impact, friction, and electrostatic discharge sensitivity tests show salts **4e-1** and **4e-2** have impact sensitivities of 7 and 4 J,<sup>191</sup> respectively. These are slightly more sensitive than and comparable to RDX, respectively. In contrast, the substituted guanidinium salt **4e-6** has an impact sensitivity much safer than that of RDX.

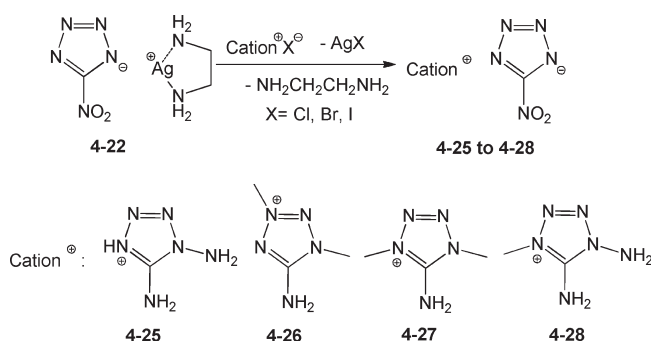
## 2.5. 1,5-Diamino-tetrazole Salts

Four synthetic methods for the preparation of 1,5-diaminotetrazole (**5**) have been described in the literature.<sup>77</sup> Through the reaction of 5-aminotetrazole (**2**) as the sodium salt with hydroxylamine-*O*-sulfonic acid (HOSA), **5** is formed as well as the 2,5-diamino-2*H*-tetrazole isomer **5a** (Scheme 33, method 1).<sup>77</sup> Compound **5** was also prepared by treatment of thiosemicarbazide with lead(II) oxide and sodium azide (Scheme 33, method 2).<sup>189</sup> In 1984, further investigation into its synthesis and properties gave **5** in 59% yield.<sup>117</sup> Later it was synthesized by using aminoguanidinium chloride and HNO<sub>2</sub>. The reaction solution was carefully adjusted to pH 8 to deprotonate the amino-substituted azido guanyl chloride intermediate, which cyclized to form **5** in 58% yield (Scheme 33, method 3).<sup>132,206</sup> However, a further report appearing in the same year recommended special caution in this synthesis of **5** stating that it was pure following ethanol extraction. A very shock sensitive alkali metal salt of tetrazolyl azide<sup>207</sup> produced by double diazotization of diaminoguanidine with HNO<sub>2</sub> often was observed as a byproduct at this step. Most current methods can be applied efficiently to bis(1,5-diaminotetrazole) derivatives

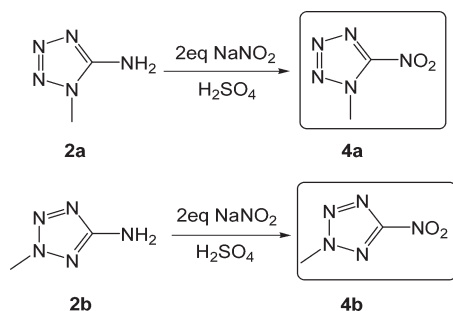
Scheme 27. Syntheses of 5-Nitrotetrazolate Salts (Part 4)



Scheme 28. Syntheses of 5-Nitrotetrazolate Salts (Part 5)



Scheme 29. Synthesis of Methyl 5-Nitrotetrazole



(Scheme 33, method 4).<sup>208</sup> Reactions of dihydrazines with 5–6 equivalents of cyanogen bromide and an excess of sodium azide led to diaminotetrazoles **5** and **5b–5e** in good yields.<sup>78</sup> Compound **5** was protonated by strong acids such as nitric acid and perchloric acid which resulted in the nitrate (**5-1**) and perchlorate (**5-2**) derivatives (Scheme 34).<sup>207,209</sup> Compound **5** can be methylated by methyl iodide in acetonitrile resulting in 1,5-diamino-4-methyltetrazolium iodide (**5f**).<sup>210</sup> The metathesis reactions of **5f** with various silver salts gave energetic salts **5f-1** to **5f-6** containing the 1,5-diamino-4-methyltetrazolium cation.<sup>210</sup>

The energetic compound, 1,5-diamino-1*H*-tetrazol-4-ium dinitramide (**5-3**), was synthesized by the reaction of potassium dinitramide with **5-2** (Scheme 35).<sup>210</sup> Both compounds have detonation properties comparable to RDX; they are potential valuable ingredients in high explosive compositions.

A safer synthesis of 1,5-diamino-4-methyltetrazolium 5-nitrotetrazolate (**5f-4**), suitable for scale-up, was introduced involving the reaction of 1-amino-5-imino-4-methyltetrazole free base with ammonium 5-nitrotetrazolate (Scheme 36)<sup>209</sup> that avoids use of the highly sensitive silver 5-nitrotetrazolate (**4-12**).<sup>57</sup>

A summary of physicochemical properties of 1,5-diamino-tetrazole derivatives and their salts can be found in Table 5. Nearly all of the compounds (except **5f-4**) exhibit positive heats of formation ranging from 42 kJ/mol (**5f-1**) to 550 kJ/mol (**5f-5**), and middle to high densities ranging from 1.44 g/cm<sup>3</sup> (**5b** and **5c**) to 1.77 g/cm<sup>3</sup> (**5-3**).<sup>209,210</sup> Salts **5-3** and **5f-3** show the lowest decomposition temperatures of 135 and 137 °C, respectively;<sup>209,210</sup> the highest is shown by **5f-2** at 184 °C.<sup>210</sup> Calculated detonation properties (detonation velocity and pressure) indicate that **5-3** is similar to RDX.<sup>139,210</sup> However, its low decomposition temperature likely will preclude its application. Compound **5f-4** represents a new high-nitrogen material (67.2% N) with remarkably low impact (>30 J) and friction sensitivity (>360 N),<sup>210</sup> and similar performance to common explosives such as TNT and nitroguanidine making **5f-4** of likely interest in propellant charge formulations or, in combination with a suitable oxidizer, as a solid propellant.<sup>209</sup>

## 2.6. 5-Nitroguanidyltetrazole Salts<sup>211</sup>

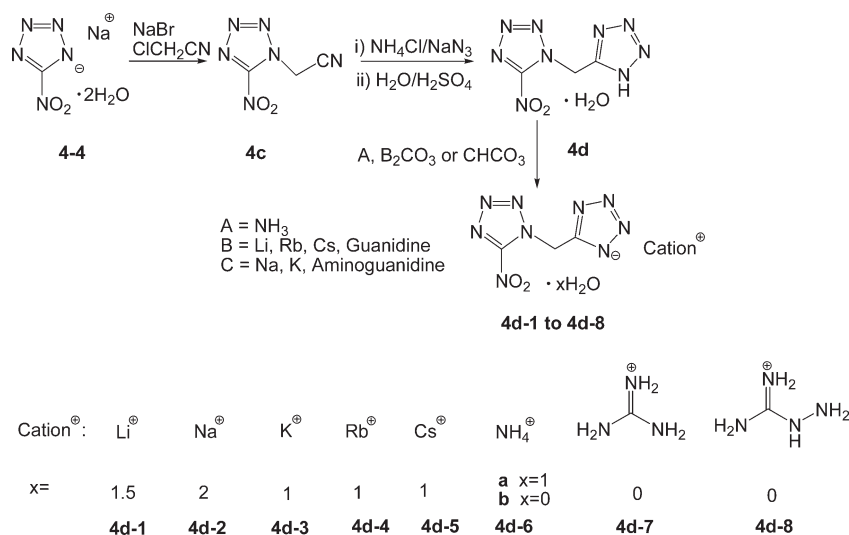
5-Nitroguanidyltetrazole (**6**) was easily synthesized by the nitration of 2-methyl-2-thiopseudouronium sulfate, followed by reaction with 5-aminotetrazole (Scheme 37).<sup>211</sup> The treatment of **6** with a half equivalent of Ba(OH)<sub>2</sub> in water gave the barium salt which when reacted with sulfate salts, formed in situ by reaction of halide salts and Ag<sub>2</sub>SO<sub>4</sub>, gave rise to the corresponding energetic salts **6-1** to **6-10**.<sup>211</sup> The synthetic pathway to the salts is depicted in Scheme 37. The 5-nitroguanidyltetrazolate anion combines the properties of the nitroguanidyl fragment with the tetrazolate backbone and forms extensive intramolecular hydrogen bonds. Their salts show excellent thermal stabilities and high positive heats of formation.<sup>211</sup>

A summary of the physicochemical properties of 5-nitroguanidyltetrazolate salts is given in Table 6.

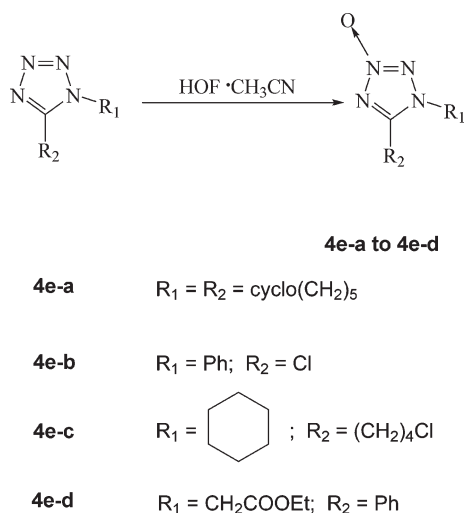
All salts are highly endothermic compounds, and all of the compounds exhibit positive heats of formation ranging between 47 (**6-5**) and 659 kJ/mol (**6-10**).<sup>211</sup> With the exception of **6-7**, the densities of the salts fall in the range of currently used explosives (1.6–1.8 g/cm<sup>3</sup>).<sup>211</sup> All salts decomposed between 157 (**6-10**) and 221 °C (**6-5**) and have specific impulse values ranging between 173.3 (**6-5**) and 245.0 s (**6-6**).<sup>211</sup> The calculated



Scheme 30. Syntheses of 5-(5-Nitrotetrazol-2-ylmethyl)tetrazolate Salts



Scheme 31. Syntheses of 1- or 2-Substituted 5-Alkyl or Aryl Tetrazole N-Oxides



detonation pressures (*P*) salts lie in the range between  $P > 21.4$  and  $P > 33.7$  GPa (comparable to RDX);<sup>211</sup> detonation velocities lie between  $D > 7357$  and  $D < 9469$  m/s (HMX 9320 m/s) and higher than those of the conventionally used TNT.<sup>139,211</sup> Some salts display energetic performances comparable to those of TATB, RDX, and HMX. Salt **6-4** shows detonation properties (detonation velocity and pressure) similar to those of HMX and salts **6-3** and **6-6** similar to those of RDX, which would suggest them to be potential green replacements for RDX and HMX; unfortunately, their thermal stabilities tend to rule out this use.<sup>211</sup>

## 2.7. 4-Amino-3-(5-tetrazolyl)furazan Salts<sup>212</sup>

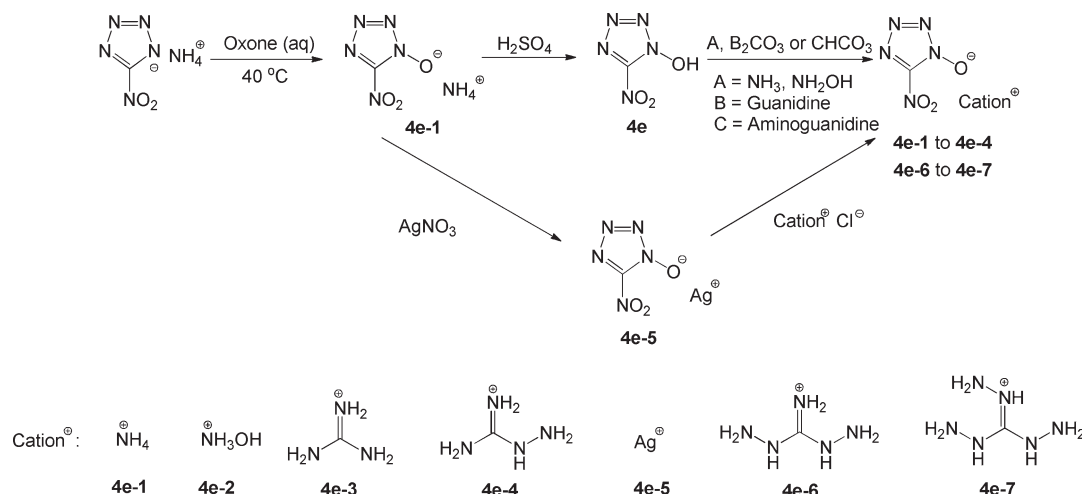
4-Amino-3-(5-tetrazolyl)furazan (**7**) was synthesized in a straightforward manner from the reaction of malononitrile, sodium nitrite, and hydroxylamine,<sup>162</sup> followed by oxidation with PbO<sub>2</sub>, and cycloaddition with NaN<sub>3</sub> (Scheme 38).<sup>141,163</sup> Direct reactions of **7** with ammonia and 1-methylimidazole

resulted in the formation of salts **7-1** and **7-10**, respectively. Energetic salts **7-2** to **7-7** were readily synthesized by metathesis reactions of the 4-amino-3-(5-tetrazolyl)furazan barium salt formed in situ with corresponding sulfate salts. Reactions of the latter barium salt with an equivalent amount of dicationic carbonic dihydrazidinium sulfate or biguanidinium sulfate gave rise to the monocationic salts **7-8** and **7-9**, respectively, which were confirmed by elemental analysis and the crystal structure of **7-9**. With similar protocols, the heterocycle-based energetic salts **7-11**–**7-13** were prepared through one-pot reactions of iodide salts, Ag<sub>2</sub>SO<sub>4</sub>, **7**, and Ba(OH)<sub>2</sub>.<sup>212</sup> All of the salts possess high positive heats of formation and most of them exhibit better thermal stability than their 5-nitrotetrazolate and 5-nitraminotetrazolate analogues as well as other furazan-based salts.

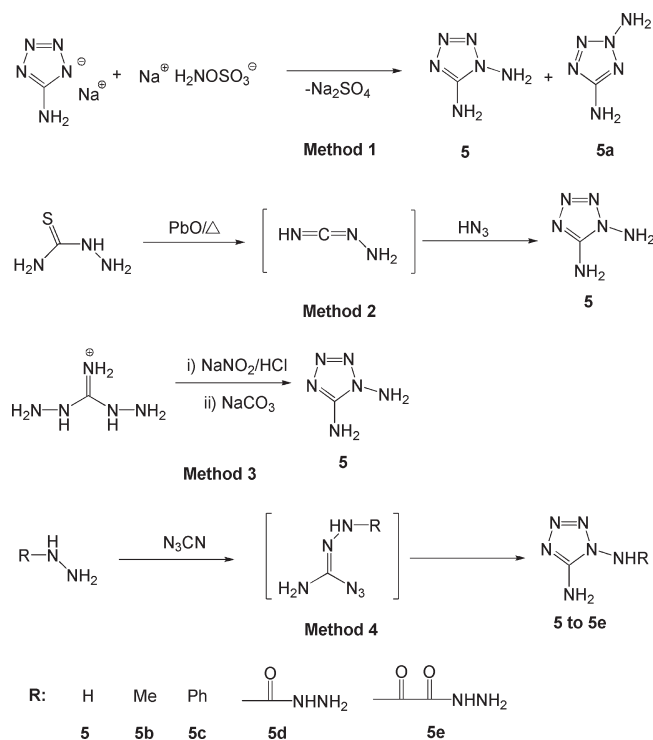
Furazan-functionalized tetrazolate-based energetic salts combine the properties of a furazan fragment and a tetrazolate backbone. They exhibit excellent thermal stabilities and high positive heats of formation. A summary of physicochemical properties of 4-amino-3-(5-tetrazolyl)furazan salts is presented in Table 7. The salts decomposed between 170 (**7-12**) and 289 °C (**7-1**).<sup>212</sup> All salts are highly endothermic compounds; they exhibit positive heats of formation ranging between 177 (**7-7**) and 730 kJ/mol (**7-13**), which are higher than their 5-nitrotetrazolate, 5-nitraminotetrazolate, and 5-aminotetrazolate analogues. All compounds have specific impulse values ranging between 182.3 (**7-7**) and 219.5 s (**7-6**).<sup>212</sup> Calculated detonation parameters show that most of the salts have detonation properties (detonation velocity and pressure) similar to those of TNT.<sup>139,212</sup> Salt **7-8** has the highest detonation parameters but these are lower than those of RDX.<sup>139,212</sup> Despite lower oxygen balance and lower density, the calculated detonation velocity and pressure of some salts are comparable to those of conventional explosive TNT. All of the 4-amino-3-(5-tetrazolyl)furazan salts can be classified as insensitive materials.<sup>212</sup>

## 2.8. 5-Dinitromethyltetrazole Salts

Mono- and dianionic 5-dinitromethyltetrazolate salts were prepared by the reaction of 5-dinitromethyltetrazole and various azoles and amines using stoichiometric amounts (1:1 or 1:2 mol ratio) of reactants.<sup>213,214</sup> The salts exhibit good detonation and thermodynamic properties that make them competitive

Scheme 32. Synthesis of Nitrotetrazolate-2*N*-oxide Salts

Scheme 33. Syntheses of Diamino-4-methyltetrazole and Their Derivatives



with some common energetic materials. Three methods are available: (1) 5-dinitromethyltetrazole (8) was prepared from cyanoacetic acid through a four-step process (Scheme 39, method 1).<sup>140,215–219</sup> Compound 8 could also be prepared from 5-(trinitromethyl)-1*H*-tetrazole (Scheme 39, method 2).<sup>220</sup> A third more convenient method is via condensation of 1,1-diamino-2,2-dinitroethylene with hydrazine hydrate followed by sodium nitrite-mediated heterocyclization of the intermediate amidrazone hydrazinium salt.<sup>221</sup> This method avoids the intermediate isolation of the explosive amidrazone itself (Scheme 39, method 3).<sup>221</sup> Many derivatives of 8 have been prepared as are shown in Scheme 40.

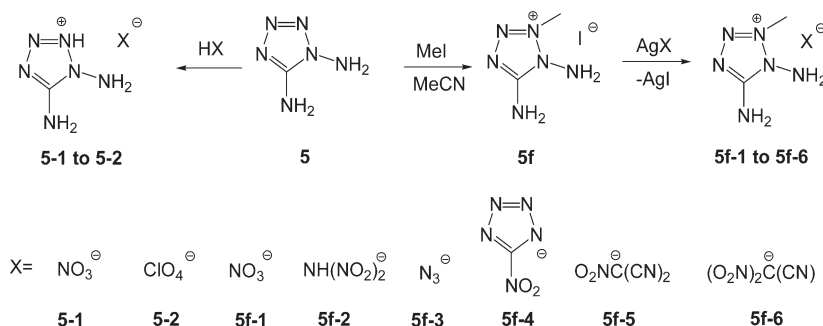
All salts have low to middle decomposition temperatures ranging from 84.5 (8-14) to 193.4 °C (8-15);<sup>213</sup> all exhibit positive heats of formation ranging between 10 (8-19) and 670 (8) kJ/mol. Salts 8-11 and 8-14 show detonation properties (detonation velocity and pressure) similar to those of RDX suggesting them to be potential green replacements for RDX.<sup>139,213</sup> Unfortunately their thermal stabilities are insufficient for this role. The neutral molecule 8 shows similar detonation properties to those of HMX, but low impact and friction sensitivities limit its application. Some of the new salts of 5-dinitromethyltetrazole (8) exhibits attractive physical properties (Table 8).

Most of the salts have good specific impulse values ranging between 191.9 (8-24) and 237.7 s (8-23). The heat of formation of the 5-dinitromethyltetrazolate dianion (228.7 kJ mol<sup>-1</sup>) is considerably more positive than that of the 5-dinitromethyltetrazolate monoanion at 70.0 kJ mol<sup>-1</sup>, giving rise to salts with common cations which have higher heats of formation. The lattice energies of the dianionic salts are about 2.5 times larger than the monoanionic salts because of their greater molecular masses and lower densities, which cause a concomitant decrease in the heats of formation. The decreased hydrogen bond interactions in the asymmetric 5-dinitromethyltetrazolate dianion structure causes it to be less dense than that of the monoanionic analogue; however, calculated detonation properties are comparable to explosives, such as TNT, NTO, TNAZ, and ADN.<sup>213,214</sup>

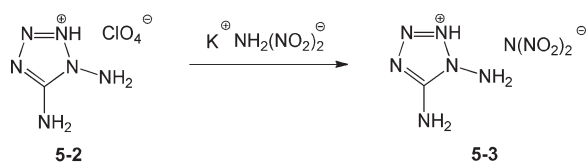
## 2.9. Tetrazole-5-Carboxylic Acid-Based Salts<sup>222,223</sup>

In contrast to the nitro group of nitrotetrazolate, the carboxylic moiety of tetrazole-5-carboxylic acid can form stable frameworks of intermolecular interactions and thus are then able to bind metal ions in mono-, bi-, or multidentate types of coordination.<sup>222</sup> Moreover, the two different points of coordination (the carboxylate moiety and tetrazolate moiety) can lead to interesting materials with new properties.<sup>223</sup>

Tetrazole-5-carboxylic acid were prepared in two different ways (Scheme 41).<sup>223</sup> The first method was the synthesis of ethyl 1*H*-tetrazole-5-carboxylate which was converted into the corresponding disodium salt of tetrazole-5-carboxylic acid (9-1).<sup>222</sup> Then the solution was acidified and the desired metal nitrate was added (Scheme 41, method 1).<sup>222</sup> The second pathway was to

Scheme 34. Synthesis of 1,5-Diamino-1*H*-tetrazol-4-ium and 1,5-Diamino-4-methyltetrazolium Salts

Scheme 35. Synthesis of 1,5-Diamino-tetrazolium Dinitramide



generate directly the dipotassium salt of the tetrazole-5-carboxylic acid (**9-2**) by the reaction of ethyl cyanofornate with sodium azide.<sup>223</sup>

Salts **9-1** and **9-2** were converted into the desired strontium (**9-3**), barium (**9-4**), copper (**9-5**), manganese (**9-6**), and silver (**9-7**) salts.<sup>223</sup> The analysis of the thermal stability by DSC-measurements revealed that **9-7** was the most thermally unstable compound with a point of decomposition at 200 °C. Compounds **9-3**, **9-4**, **9-5**, and **9-6** decompose at 337, 366, 254, and 386 °C, respectively.<sup>223</sup> Compounds **9-3**, **9-4**, and **9-7** are not sensitive toward friction and impact. In case of the transition metal salts, **9-5** is sensitive toward friction at >288 N, whereas **9-6** at >324 N is slightly more stable.<sup>223</sup> Neither compound is sensitive toward impact. The flame coloration of the salts **9-3** (red), **9-4** (pale green), and **9-5** (green) renders them promising components for pyrotechnic applications.<sup>223</sup> They are slightly soluble in water and lack toxic moieties (nitro groups, azides) or anions (perchlorate), which makes them ecologically interesting substitutes for toxic pyrotechnic compositions.<sup>223</sup>

## 2.10. Bistetrazole or Bridged Bistetrazole Salts

5,5'-Bis(tetrazole) monohydrate (**10a**) was synthesized by the reaction of sodium dicyanamide with sodium azide under acid-catalyzed conditions (Scheme 42).<sup>63</sup> It has a high heat of formation of 531.7 kJ/mol.<sup>224</sup> Its *N,N,N',N'*-tetraaminopiperazinium 5,5'-bistetrazolate salt **10a-2** was prepared through metathesis reaction and has suitable properties.<sup>225</sup> Interestingly, the metathesis reactions of barium 5-(tetrazole-5-yl)tetrazolate with doubly charged cations of biguanidine and biaminourea salts gave carbonic hydrazylhydrazidinium 5-(tetrazole-5-yl)tetrazolate (**10a-5**) and guanylguanidinium 5-(tetrazole-5-yl)tetrazolate (**10a-6**) instead of the expected 5,5'-bistetrazolate salts of **10a-3** and **10a-4**.<sup>226</sup>

In Table 9 is a summary of physicochemical properties of 5,5'-bistetrazolate and 5-(tetrazole-5-yl)tetrazolate salts. The compounds exhibit positive heats of formation >550 kJ/mol.<sup>225,226</sup> Salt **10a-6** has the highest decomposition temperature at 251 °C.<sup>226</sup> These salts have moderate densities that range

between 1.50 g/cm<sup>3</sup> (**10a-2** and **10a-6**) to 1.68 g/cm<sup>3</sup> (**10a-5**).<sup>225,226</sup> Calculated detonation properties (detonation velocity and pressure) show that those for **10a-5** are similar to those of TATB.

The first synthesis of 5,5'-bis(1*H*-tetrazolyl)amine (Bta) (**10b**) by the cyclization reaction of sodium dicyanamide and sodium azide in the ratio of 1:2 resulted in the monohydrate by refluxing sodium dicyanamide, sodium azide, and trimethylammonium chloride in water (Scheme 43).<sup>227,228</sup>

Dehydration of the monohydrate at elevated temperature and reduced pressure gave the anhydrous compound (Scheme 43, method 1). Currently, there are three synthesis procedures for **10b**: (1) the in situ reaction of hydrazoic acid (prepared from sodium azide and a weak acid like trimethylammonium chloride, boric acid, or ammonium chloride) with sodium dicyanamide;<sup>229</sup> (2) the reaction of sodium dicyanamide with sodium azide in the presence of a catalyst like zinc chloride, bromide or perchlorate, followed by an acidic workup (Scheme 43, method 2);<sup>230</sup> and (3) the reaction of 5-amino-tetrazole with cyanogen bromide under base-catalyzed conditions forming the 5-cyanaminotetrazolide anion followed by a subsequent cycloaddition of hydrazoic acid under acidic conditions (Scheme 43, method 3).<sup>228,230</sup>

Through metathesis reactions or direct neutralization, **10b** salts **10b-1** to **10b-20** were synthesized (Scheme 44).<sup>231–235</sup> The copper compound diammine bis(tetrazolato)amine copper(II) (**10b-21**) was synthesized by the reaction of **10b** with Cu(II) chloride in ammonia solution.<sup>138</sup> Syntheses of Bta salts provide a new and straightforward approach to highly energetic materials. In Table 10, it can be seen that all 5,5'-bis(1*H*-tetrazolyl)amine salts have positive heats of formation ranging between 356 (**10b-1**) and 1293 (**10b-3**) kJ/mol.<sup>231</sup> The experimental densities range from 1.51 (**10b-7**) to 1.75 g/cm<sup>3</sup> (**10b-19**). Impact sensitivity data are not available for these salts.<sup>226,231</sup> Thermal stabilities of these energetic salts were studied with differential scanning calorimetry (DSC). All salts decomposed between 165 (**10b-7**) and 269 °C (**10b-10**).<sup>226,231</sup> The calculated detonation pressures lie in the range between  $P > 17.5$  (**10b-4**) and  $P < 34.9$  GPa (**10b-2**), comparable to RDX 35.2 GPa.<sup>139,231</sup> Detonation velocities lie between  $D > 7636$  (**10b-4**) and  $D < 9926$  m/s (**10b-2**) comparable to HMX 9320 m/s. Copper(II) bistetrazolylamine (**10b-21**) offers the opportunity to substitute for toxic barium salts in pyrotechnic applications.<sup>9</sup> These properties coupled with rather high thermal stabilities and densities make these high-nitrogen materials attractive candidates for energetic applications.<sup>231–234</sup>

Metathesis reactions of sodium 5,5'-azobistetrazolate pentahydrate or barium 5,5'-azobistetrazolate with different iodide or

Scheme 36. Synthesis of 1,5-Diamino-4-methyltetrazolium 5-Nitrotetrazolate

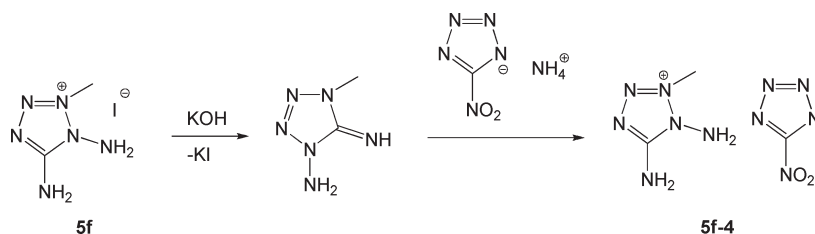
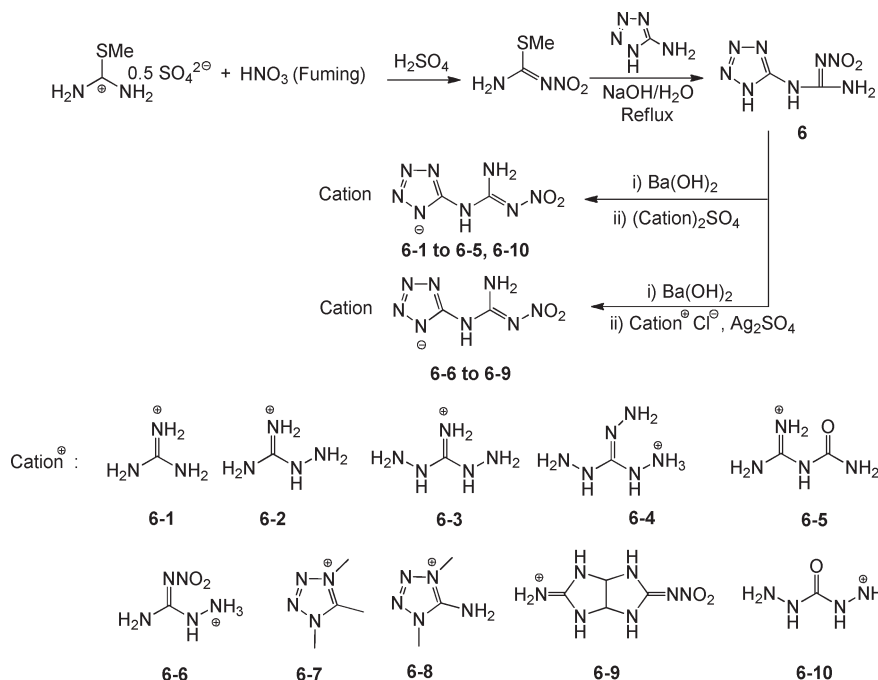


Table 5. Properties of Substituted 1,5-Diamino-Tetrazole Derivatives and Their Salts

compound	density (g/cm <sup>3</sup> ) <sup>a</sup>	T <sub>m</sub> (°C)	T <sub>d</sub> (°C)	ΔH <sub>f</sub> <sup>o</sup> (kJ/mol)	P (GPa) <sup>a</sup>	D (m/s) <sup>a</sup>	IS (J)	friction (N)	thermal Shock	ref
5-3	1.77	—	135	409	36.0	9306		0.67		209
5b	1.65	—	223	639	24.1	8255	25			78
5c	1.65	—	232	499	21.2	7767	25			78
5d	1.63	—	215	523	21.5	7886	25			78
5e	1.62	—	209	1289	25.0	8331	1.5			78
5f-1	1.51	121	181	42	19.9 [23.4]	7482 [7682]	>40	120	deflagrates	210
5f-2	1.72	85	184	92	28.9 [33.6]	8470 [8827]	7	24	explodes	210
5f-3	1.42	135	137	162	21.8 [20.8]	8224 [7405]	15	192	deflagrates	210
5f-4	1.55	190	191	−24	13.9 [15.5]	6539 [6109]	30	>360	deflagrates	210
5f-5	1.48 [1.52]	72	176	550						145
5f-6	1.64 [1.62]	116	182	388						145

<sup>a</sup> Calculated values are given in brackets.

Scheme 37. Syntheses of 5-Nitroguanidyltetrazolate Salts



sulfate salts in water led to the formation of the corresponding 5,5'-azobistetrazolate salts (10c-1 to 10c-29). 5,5'-Azobistetrazolates (10c-11 to 10c-21) could also be synthesized from 5-hydrazine bistetrazole (10d) because of its sensitivity to oxidation (Scheme 45).<sup>233</sup>

In addition to the above-mentioned 5,5'-azobistetrazolate salts, the complete series of the lanthanoid (Ce, Pr, Nd, Sm, Eu, Gd, Ce, Pr, Nd, Sm, Eu, and Gd) compounds with the 5,5'-azobistetrazolate anion obtained directly from the lanthanoid nitrate and sodium 5,5'-azobistetrazolate have been synthesized

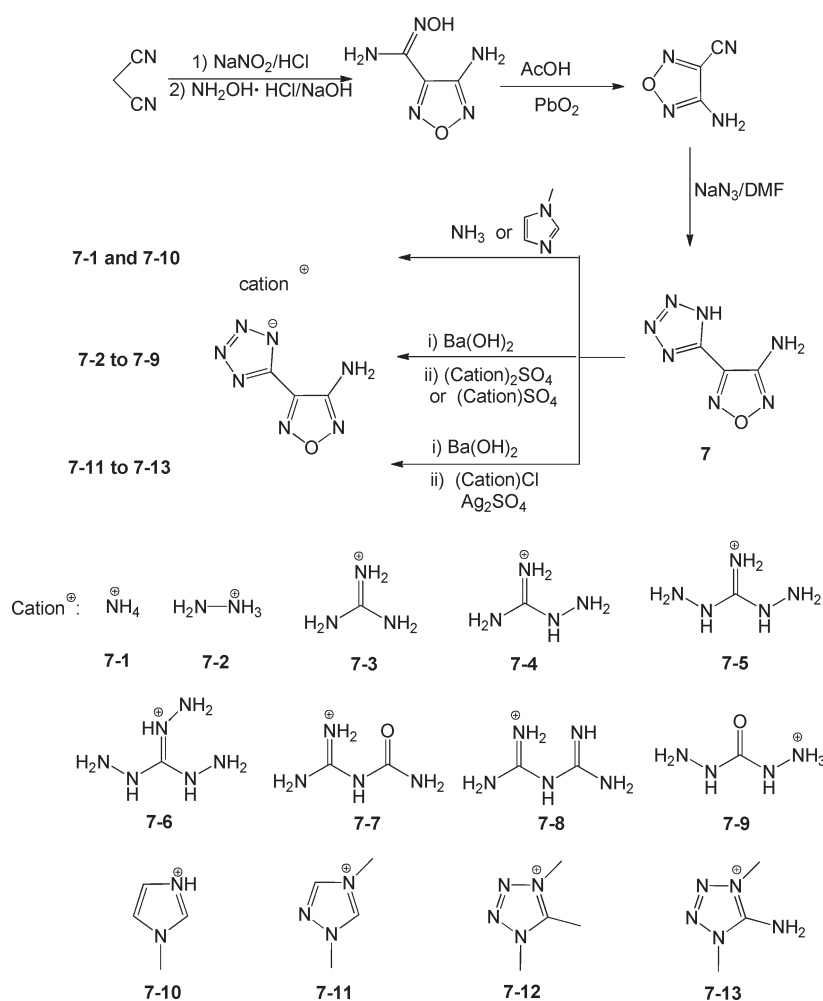


Table 6. Properties of 5-Nitroguanidyltetrazolate Salts<sup>211</sup>

salt	density (g/cm <sup>3</sup> )	T <sub>m</sub> (°C)	T <sub>d</sub> (°C)	ΔH <sub>f</sub> <sup>o</sup> (kJ/mol)	P (GPa)	D (m/s)	I <sub>sp</sub> (s)
6-1	1.60 <sup>a</sup> [1.63]		210	253	22.5	8108	191.3
6-2	1.66	211	217	350	26.2	8643	199.7
6-3	1.71		206	455	30.0	9122	208.2
6-4	1.72 [1.74]	175	185	562	33.0	9469	221.7
6-5	1.65		221	47	21.4	7943	173.3
6-6	1.72 [1.77]		171	557	33.7	9171	245.0
6-7	1.52	132	174	555	19.8	7357	205.3
6-8	1.61		158	590	22.7	8065	210.4
6-9	1.70 [1.73]	155	271	527	25.9	8380	212.7
6-10	1.66 [1.69]	dec	157	659	27.7	8627	219.9

<sup>a</sup> Calculated values are given in brackets.

Scheme 38. Synthesis of 4-Amino-3-(5-tetrazolyl)furazan Salts



and characterized.<sup>236</sup> Of all these compounds, the La salt always forms with a lower H<sub>2</sub>O content.<sup>57,236,237</sup>

In Table 11 a summary of physicochemical properties of salts that contain the azobistetrazolate anion is given. They decompose between 142 (10c-3) and 239 °C (10c-23).<sup>232,234</sup> All salts exhibit positive heats of formation ranging between 483 (10c-25) and 1852 kJ/mol (10c-7).<sup>232,235</sup> Calculated detonation parameters show that the majority of the salts have similar detonation properties

(detonation velocity and pressure) to those of TNT and can be classified as insensitive materials (10c-24 to 10c-29).<sup>18,83,225,235</sup>

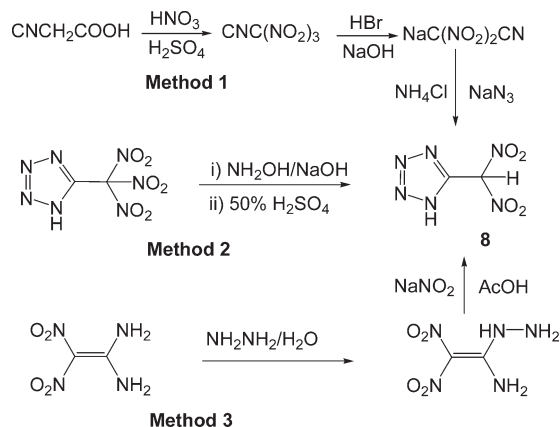
Many 5,5'-azobistetrazolate salts have found practical applications:<sup>83</sup> (1) the guanidinium, triaminoguanidinium, and hydrazinium salts in gas generators for fire extinguishing systems or airbags; (2) heavy metal salts of 5,5'-azobistetrazolate (e.g., [Pb(OH)]<sup>+</sup>) as initiators;<sup>150</sup> (3) 1,1'-dimethyl- 5,5'-azotetrazole as an additive in solid rocket propellants, etc; (4) 10c-2 did

Table 7. Properties of 4-amino-3-(5-tetrazolyl)furanan salts<sup>212</sup>

salt	density (g/cm <sup>3</sup> ) <sup>a</sup>	T <sub>m</sub> (°C)	T <sub>d</sub> (°C)	ΔH <sub>f</sub> <sup>o</sup> (kJ/mol)	P (GPa)	D (m/s)	I <sub>sp</sub> (s)
7-1	1.62	278	289	412	22.9	8075	214.6
7-2	1.60	161	197	561	24.8	8338	229.7
7-3	1.50	181	262	394	18.5	7640	194.2
7-4	1.55	189	257	490	20.4	7747	203.4
7-5	1.54	149	228	600	21.6	7932	212.5
7-6	1.62	207	216	704	25.4	8544	219.5
7-7	1.64 [1.68]	211	213	177	19.9	7732	182.3
7-8	1.77	225	251	441	25.9	8673	188.2
7-9	1.68	162	199	484	25.7	8466	213.0
7-10	1.45	125	262	515	15.8	7063	195.0
7-11	1.46 [1.47]	55	204	597	17.5	7372	203.1
7-12	1.44	109	170	695	17.6	7412	208.1
7-13	1.51	205	212	730	19.7	7338	212.6

<sup>a</sup> Calculated values are given in brackets.

## Scheme 39. Synthesis of 5-Dinitromethyltetrazole



indeed meet the criteria for being nitrogen-rich and has proven to be very desirable ingredients in erosion-reduced gun propellants;<sup>137</sup> (5) copper salt (**10c-22**) may be a potential “green” energetic material as a gas generator or additive in solid rockets as low-smoke propellant ingredients.<sup>234</sup>

The properties of 5,5′-azobistetrazolate salts make them attractive for further study as a new class of high performing, insensitive, environmentally more benign and also thermally stable energetic materials. In particular, the good thermal stability in combination with high nitrogen content and detonation parameters comparable to RDX make the compounds suitable candidates for further study as new low-pollution HEDMs.<sup>83</sup>

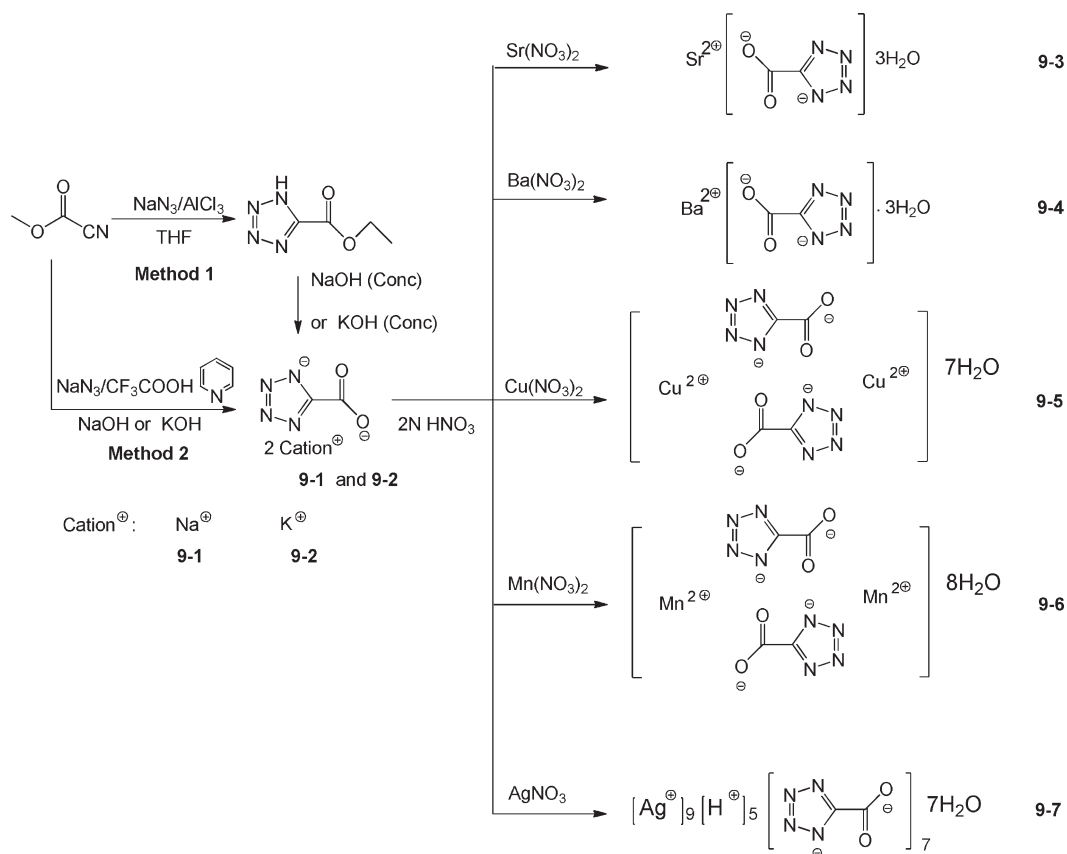
5,5-Hydrazine-1,2-diylbis(1*H*-tetrazole) (HBT, **10d**) was synthesized in high yield from inexpensive starting materials and fully characterized, including X-ray structure determination.<sup>18,233</sup> It was synthesized by the reduction of sodium 5,5-azobistetrazolate pentahydrate (**10c-1**) with magnesia powder.<sup>233</sup> After acid workup, a white, powdery precipitate of 5,5-hydrazine-1,2-diylbis(1*H*-tetrazole) (HBT, **10d**) formed (Scheme 46).<sup>18</sup> Straightforward preparations of energetic salts which contain the nitrogen-rich 5,5′-hydrazinebistetrazolate anion [(C<sub>2</sub>H<sub>2</sub>N<sub>10</sub>)<sup>2-</sup>] and alkali metals (Li<sup>+</sup>, **10d-1**; Na<sup>+</sup>, **10d-2**; K<sup>+</sup>, **10d-3**; Rb<sup>+</sup>, **10d-4**; and Cs<sup>+</sup>, **10d-5**) are given by reaction of the free acid **10d** and a suitable alkali hydroxide or carbonate salt (Scheme 47).<sup>238</sup>

Compound **10d** was boiled with an alkaline earth metal hydroxide in aqueous solution to give the corresponding salts **10d-6** to **10d-9**.<sup>239</sup> The reactions of **10d** with N-bases yield energetic N-rich salts based on the 5,5′-(hydrazine-1,2-diyl)bis[1*H*-tetrazol-1-ide] anion with ammonium (**10d-10**), hydrazinium (**10d-11**), guanidinium (**10d-12**), and aminoguanidinium (**10d-13**) cations.<sup>240</sup> Compound **10d** is a prospective candidate for applications in gas generators, propellants, or solid rockets as a low-smoke propellant ingredient. The moderate friction-sensitivity value of **10d** (108 N) could be reduced by forming several N-rich salts with ammonium, hydrazinium, and guanidinium cations (compounds **10d-10** to **10d-13**). The salts **10d-10** to **10d-13** have high detonation parameters, and are yet insensitive materials, suggesting potential for application as environmentally friendly, highly energetic materials.<sup>240</sup>

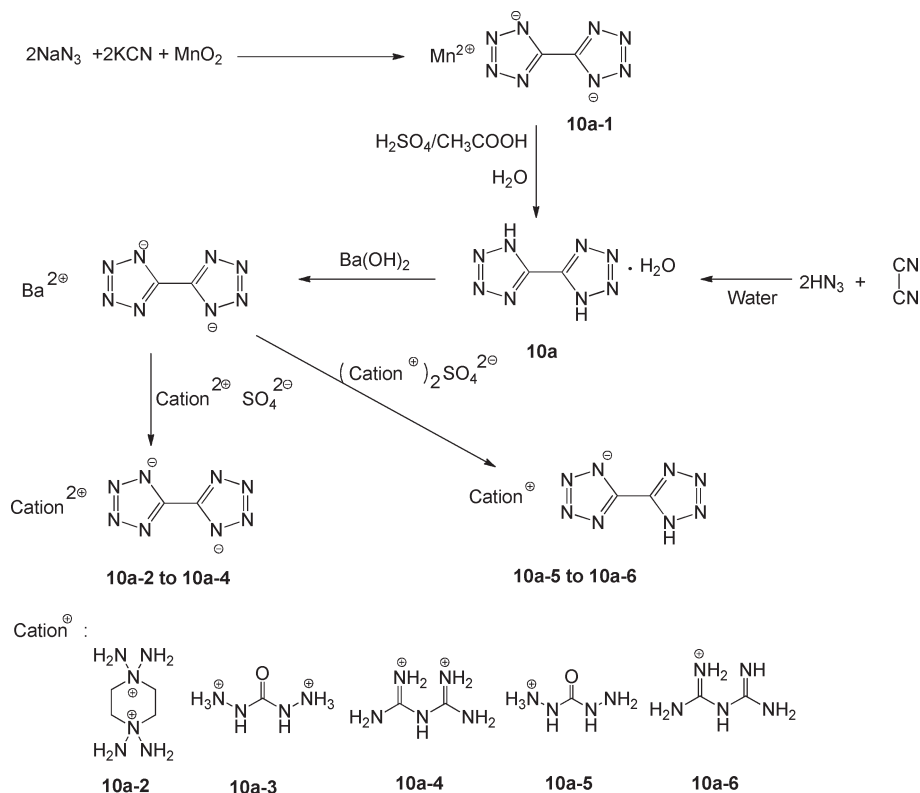
The free acid, **10d**, was stable in air for extended periods of time and it proved to be very safe to handle (impact sensitivity >30 J, and friction sensitivity 108 N).<sup>18,233</sup> The compound is an insensitive nitrogen-rich material (83.3%) with a detonation velocity (8523 m/s) and detonation pressure (27.7 GPa) similar to TATB and shows good thermal stability (>200 °C).<sup>18,233</sup> The high nitrogen content and high thermal stability of the salts make them interesting as more environmentally friendly pyrotechnic ingredients than commonly used materials, for example, Sr-(ClO<sub>4</sub>)<sub>2</sub>.<sup>238</sup> The advantage of the sensitivity to oxidation of the salts of HBT suggests a new synthesis of the already known nitrogen-rich ammonium azotetrazolate (**10d-10**) and hydrazinium azotetrazolate (**10d-11**), as well as the alkali and alkaline-earth azotetrazolates (**10d-1** to **10d-9**), which would then avoid the hazard of handling the highly sensitive barium azotetrazolate as the starting material.<sup>233</sup> The use of insensitive **10d** instead of the barium salt makes the synthesis much safer and applicable for scaling up.<sup>233</sup> The high performance of **10d** causes it to meet nearly all of the criteria for new energetic materials which suggests further study as a prospective gas generator, additive in solid rockets as low-smoke propellant ingredients or in propellant charges.<sup>18,240</sup>

In Table 12 is shown that most of 5,5-hydrazine-1,2-diylbis(1*H*-tetrazole) salts (**10d-2**, **10d-4** to **10d-13**) exhibit positive heats of formation ranging between 80 and 1530 kJ/mol. The known sensitivity data show these materials are not sensitive to impact and friction. Thermal stabilities of the compounds were studied using differential scanning calorimetry (DSC); all **10d**



Scheme 41. Syntheses of 1*H*-Tetrazole-5-carboxylate Salts

Scheme 42. Syntheses of 5,5'-Bistetrazolate Salts



Bis(tetrazolylaminotetrazine) (**10e**) was first synthesized and characterized at the Los Alamos National Laboratory.<sup>241</sup> The salient features of **10e** are low impact sensitivity, nonexplosive, nonpyrotechnic, and an inflammable solid that decomposes rapidly without flame and produces nitrogen gas as the main combustion product.<sup>242</sup> 3,6-Bis-5-ylamino-tetrazolate-1,2,4,5-tetrazine (**10e**) was obtained by the reaction of 3,6-dichloro-1,2,4,5-tetrazine and 2 equiv of the sodium salt of 5-aminotetrazole (method 1 in Scheme 48) since the 3,6-dichloro-1,2,4,5-tetrazine is a powerful electrophile being similar in reactivity to picryl fluoride. Compound **10e** could also be obtained by the nucleophilic substitution of the 3,5-dimethylpyrazole leaving group of compound 3,6-bis(3,5-dimethylpyrazol-1-yl)-1,2,4,5-tetrazine by 5-aminotetrazole in hot sulfolane (method 2 in Scheme 48).<sup>242–246</sup>

Guanidinium 3,6-bis-5-ylamino-tetrazolate-1,2,4,5-tetrazine (**10e-1**) was obtained by the reaction of guanidine carbonate and **10e** in water.<sup>225</sup> The 3,6-bis-5-ylamino-tetrazolate-1,2,4,5-tetrazine anion has a high heat of formation (965.0 kJ mol<sup>-1</sup>),<sup>225</sup> which is much higher than those for the 5,5'-bistetrazolate (594.9 kJ mol<sup>-1</sup>), iminobis(5-tetrazolate) (630.0 kJ mol<sup>-1</sup>), and 5,5'-azobistetrazolate (774.0 kJ mol<sup>-1</sup>) anions.<sup>225</sup> This places it among the anions with the highest heats of formation. As a result, the heats of formation of guanidine salts decrease in the order: 3,6-bis-5-ylamino-tetrazolate-1,2,4,5-tetrazine (**10e-1**, 1346.2 kJ mol<sup>-1</sup>) > guanidine 5,5-azobistetrazolate (**10c-1**, 486.5 kJ mol<sup>-1</sup>) > guanidine iminobis(5-tetrazolate) (**10b-4**, 465.5 kJ mol<sup>-1</sup>) > guanidine 5,5-hydrazine-1,2-diylbis(1H-tetrazole) (**10d-12**, 352.0 kJ mol<sup>-1</sup>).<sup>240</sup> Compound **10e-1** also has good thermal stabilities (decomposes at 285.2 °C), but its low density (1.47 g/cm<sup>3</sup>) gives rise to mediocre detonation properties ( $P = 20.5$  GPa,  $D = 7673$  m/s,  $I_{sp} = 221.9$ s) (Table 13).<sup>225</sup> This is typical of all of these salts.

**Table 9.** Properties of 5,5'-bistetrazolate and 5-(Tetrazole-5-yl)-tetrazolate Salts

salt	density (g/cm <sup>3</sup> )	$T_m$ (°C)	$T_d$ (°C)	$\Delta H_f^\circ$ (kJ/mol)	$P$ (GPa)	$D$ (m/s)	ref
<b>10a-2</b>	1.50		209	565.9			225
<b>10a-5</b>	1.68	200	224	589.2	27.2	8749	226
<b>10a-6</b>	1.60		251	558.8	20.4	7906	226

The reaction of cyanogen azide, which was generated in situ, with different dihydrazines was applied to the synthesis of bis(1,5-diaminotetrazole) derivatives **10f** to **10i** (Scheme 49).<sup>78,247</sup>

The preparation of disubstituted 5-aminotetrazole compounds by a convenient method is based on the reaction of cyanogen azide with primary amines.<sup>181</sup> The nitration of these aminotetrazoles with 100% nitric acid without a solvent gives disubstituted nitroiminotetrazole derivatives **10j** and **10k** (Scheme 50).<sup>181</sup> Similarly, the reaction of ethylenebis(oxyamine) and cyanogen azide resulted in the preparation of the 1,1'-ethylenebis(oxy)bis(5-aminotetrazole). Upon treating it with 100% HNO<sub>3</sub>, the corresponding highly energetic oxy-nitroimino-tetrazole **10l** was prepared in good yield.<sup>182</sup>

Carbonyl or oxalyl-bridged diaminotetrazole led to energetic salts **10f-1**, **10f-2**, **10g-1**, and **10g-2** with excess aqueous ammonia or hydrazine hydrate.<sup>247</sup> Guanidium salts **10f-3** to **10f-6** and **10g-3** to **10g-6** were prepared by metathesis reactions of barium diaminotetrazolate with guanidine, aminoguanidine, diaminoguanidine, or triaminoguanidine sulfate in good yields (Scheme 51).<sup>247</sup>

The calculated detonation pressures of the carbonyl- or oxalyl-bridged diaminotetrazole energetic salts lie in the range between  $P = 19.5$  and  $P = 25.5$  GPa (comparable to TNT = 19.5 GPa).<sup>247</sup> Detonation velocities fall between  $D = 7815$  and  $D = 8707$  m/s (comparable to TNT = 6900, ADN = 8681, and TATB = 8630 m/s) (Table 13).<sup>139,247</sup> Furthermore, these new high nitrogen energetic salts exhibit remarkably low impact sensitivities (>40 J).<sup>247</sup>

The bridged bis(nitroiminotetrazole) **10j** and **10k** react easily with a variety of nitrogen bases and yield salts (**10j-1** to **10j-6** and **10k-1** to **10k-4**) with ethylene- and propylene-bridged bis(nitroiminotetrazolates) (Scheme 52).<sup>181,182</sup> Also, shown in Scheme 52, are the syntheses of the diaminoguanidinium (**10j-7**) and triaminoguanidinium (**10j-8**) ethylene-bridged bis(nitroiminotetrazolates).<sup>248</sup> Two energetic salts, **10j-7** and **10j-8**, were synthesized using the silver salt of **10j** which was obtained by metathesis of the salt of **10j** and silver nitrate, with the corresponding chloride salts.<sup>248</sup>

The energetic salts **10l-1** to **10l-4** were generally obtained by acid–base reactions between **10l** and energetic bases in aqueous solutions (Scheme 53).<sup>248</sup> Also shown are the syntheses of the diaminoguanidinium (**10l-5**) and triaminoguanidinium (**10l-6**) oxy-nitroimino-tetrazolate salts.<sup>83</sup> Two energetic salts, **10l-5** and **10l-6**, were synthesized using the silver salt of **10l**, which was

**Scheme 43.** Syntheses of 5,5'-Bis(1H-tetrazolyl)amine

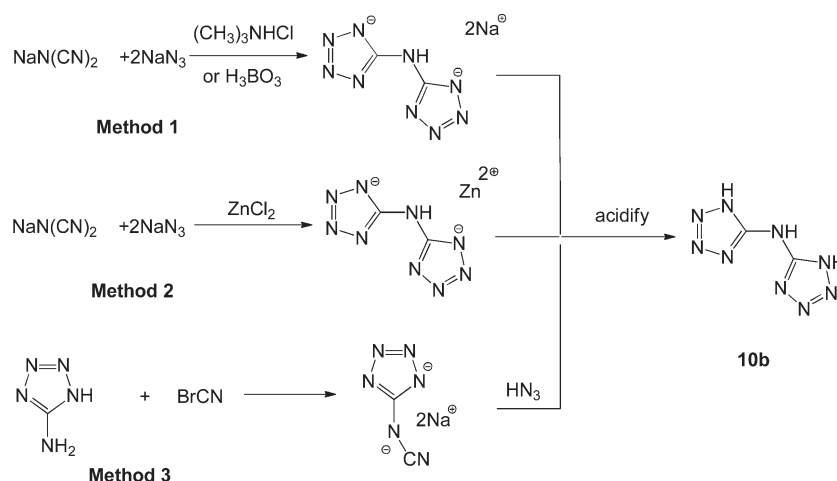






Table 10. Properties of 5,5'-Bis(1*H*-tetrazolyl)amine Salts

salt	density (g/cm <sup>3</sup> ) <sup>a</sup>	T <sub>m</sub> (°C)	T <sub>d</sub> (°C)	ΔH <sub>f</sub> <sup>o</sup> (kJ/mol)	P (GPa)	D (m/s)	ref
10b-1	1.56 [1.60]	142	230	356	21.6	8309	231
10b-2	1.72 [1.63]	216	235	671	34.9	9926	231
10b-3	1.71 [1.64]		244	1293	29.3	9009	231
10b-4	1.52 [1.49]	259	260	465	17.5	7636	231
10b-5	1.59 [1.53]	192	218	678	22.9	8486	231
10b-6	1.55 [1.57]	159	196	939	23.6	8560	231
10b-7	1.51 [1.60]	164	165	1195	23.9	8572	231
10b-8	1.58 [1.52]	170	180	1208	20.3	7814	231
10b-9	1.59		183	598	20.1	8125	225
10b-10	1.66		269	594	28.1	8936	226
10b-11	1.66	248	249	750	30.7	9257	226
10b-12	1.62	263	268	565	23.2	8343	226
10b-13	1.64	210	234	669	25.7	8696	226
10b-14	1.55	205	213	793	24.0	8413	226
10b-15	1.58	211	213	900	26.3	8748	226
10b-16	1.63	227	231	374	19.4	7677	226
10b-17	1.64		201	1003	24.7	8401	226
10b-18	1.58	257	258	920	21.3	7860	226
10b-19	1.75	187	189	672	33.6	9487	226
10b-20	1.69	257	258	635	25.1	8645	226
10b-21	1.99		281				138

<sup>a</sup> Calculated values are given in square brackets.

5-azidotetrazolate, which was protonated using dilute hydrochloric acid. The product 5-azido-1*H*-tetrazole (**10x**) was isolated (Scheme S5, method 1).<sup>250</sup> The synthesis of **10x** can also be achieved by the diazotation of 5-amino-1*H*-tetrazole (Scheme S5, method 2) with isoamyl nitrite/HCl mixture (HNO<sub>2</sub>) yielded the tetrazolyldiazonium salt [CHN<sub>4</sub>–N<sub>2</sub>]<sup>+</sup>[Cl]<sup>–</sup> as an intermediate which was then converted into the 5-azidotetrazole (**1**) by treatment with sodium azide<sup>251</sup> or by the reaction (Scheme S5, method 3) of 5-hydrazino-1*H*-tetrazole with one equivalent NaNO<sub>2</sub> and HCl in aqueous solutions.<sup>250</sup> The advice against attempting this synthesis (Scheme S5, method 2) is based on the formation of highly explosive tetrazole diazonium intermediates.<sup>250</sup> The reaction (Scheme S5, method 4) of diaminoguanidinium salts with two equivalents of HNO<sub>2</sub><sup>252</sup> also ends in the formation of **10x**, which is also obtained as a byproduct in an advanced synthesis of 1,5-diaminotetrazole<sup>76</sup> by using only one equivalent of HNO<sub>2</sub>.<sup>253</sup> A quite uncommon reaction (Scheme S5, method 5) is the alkaline degradation of the primary explosive tetracene using Ba(OH)<sub>2</sub>.<sup>250,254,255</sup>

The salts, hydrazinium (**10x-1**), ammonium (**10x-2**), amino-guanidinium (**10x-3**), guanidinium (**10x-4**), lithium (**10x-5**), sodium (**10x-6**), potassium (**10x-7**), cesium (**10x-8**), and calcium (**10x-9**) azidotetrazolate were prepared by deprotonation of 5-azido-1*H*-tetrazole (**10x**) using common bases like ammonia, hydrazine, or alkali, as well as alkaline earth metal salts.<sup>256</sup> The substitution of the secondary amine in the piperidine ring did not occur in the reaction of cyanogen azide with the highly hindered 4-amino-2,2,6,6-tetramethylpiperidine. However, the piperidinium azidotetrazolate salt, **10x-10** was obtained (Scheme S5).<sup>249</sup>

5-Azidotetrazolate salts are extremely sensitive and highly energetic compounds (Table 15), which should be assigned to the class of primary explosives and only be handled with appropriate precautions.<sup>250</sup> The sensitivities are higher than those of neutral 5-azidotetrazole and depend on the hydrogen

bonding network.<sup>250</sup> The metal salts (K<sup>+</sup>, Rb<sup>+</sup>, Cs<sup>+</sup>), which contain no water molecules are highest in sensitivity and explode even in concentrated aqueous solutions.<sup>256</sup> Crystal structure studies show that the geometry of the anion is in agreement with that of **10x**. Vibrational and NMR spectroscopy are valuable methods to identify 5-azidotetrazolate salts. The heats of formation, as well as several detonation parameters of the nitrogen-rich compounds hydrazinium (**10x-1**), ammonium (**10x-2**), and aminoguanidinium (**10x-4**) 5-azidotetrazolates, were determined by computational study. Results show that the compounds **10x-1**, **10x-2**, and **10x-4** are highly endothermic and have good detonation values as well as specific impulses when combusted with suitable oxidizers. The decomposition temperatures lie in the range 135 to 160 °C, and they are probably too sensitive for practical applications.<sup>256</sup>

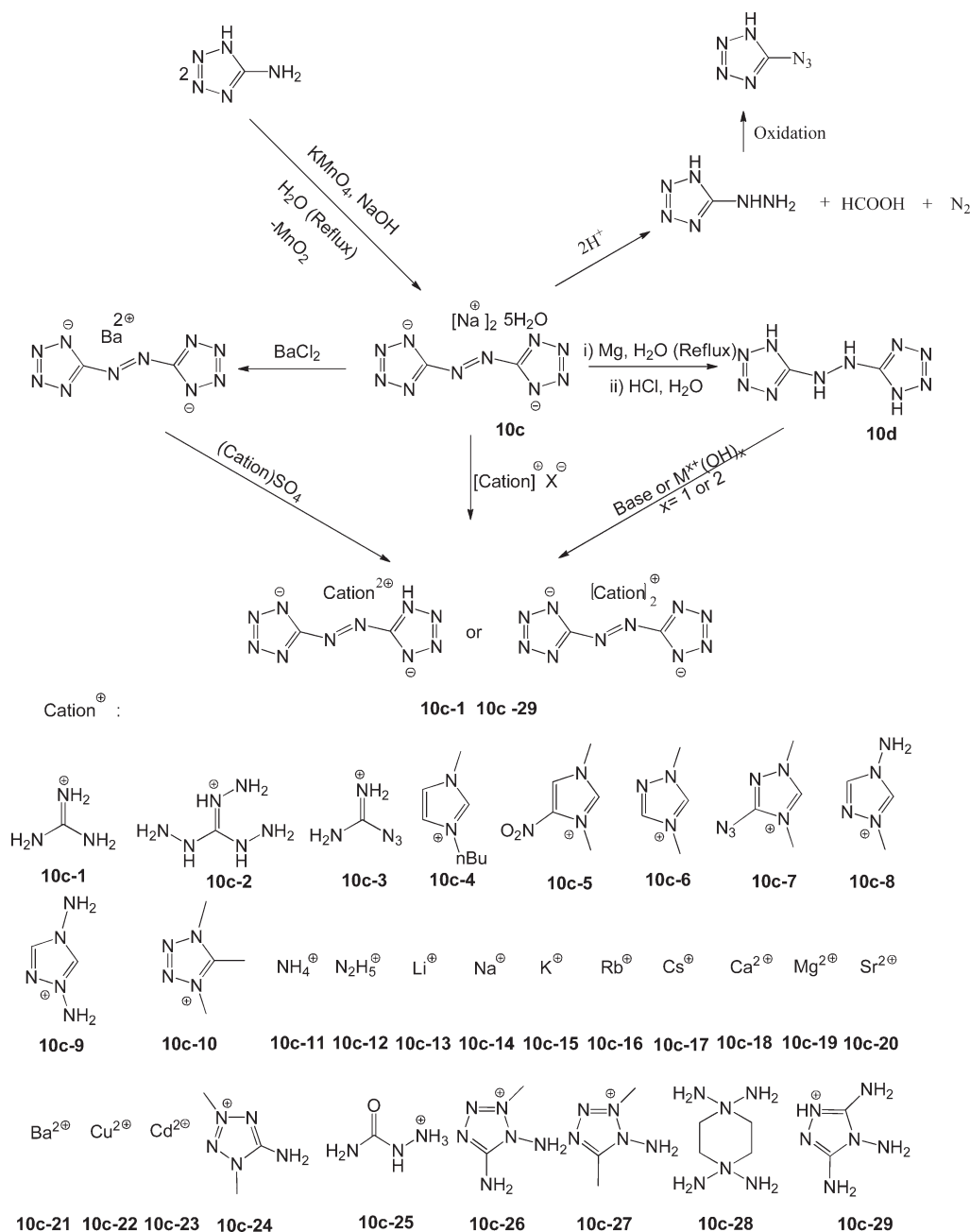
### 3. TRIAZOLE-BASED ENERGETIC SALTS

Triazoles are nitrogen-containing five-membered heterocycles either one of a pair of isomeric chemical compounds with molecular formula C<sub>2</sub>H<sub>3</sub>N<sub>3</sub>; two isomers are 1,2,3-triazole and 1,2,4-triazole. Substituted 1,2,3-triazoles can be prepared through the azide alkyne Huisgen cycloaddition in which an azide and an alkyne undergo a 1,3-dipolar cycloaddition reaction.<sup>257–262</sup> It is a surprisingly stable structure compared to other organic compounds with three contiguous nitrogen atoms. 1,2,4-Triazoles are obtained using the Einhorn–Brunner or the Pellizzari reaction.<sup>263,264</sup> Calculations show that 1,2,3-triazole has a higher positive heat of formation (in gas phase: 268 kJ/mol) than 1,2,4-triazole (in gas phase: 194 kJ/mol). A large number of triazole derivatives have been used to produce energetic salts.

#### 3.1. 3,4,5-Triamino-1,2,4-triazole Salts

3,4,5-Triamino-1,2,4-triazole (guanazine, **11**) can be synthesized by heating dimethylcyanamide with hydrazine hydrate

Scheme 45. Syntheses of 5,5'-Azobistetrazolate Salts



under reflux (method 1) or by the reaction of method 2.<sup>263–266</sup> Compound **11** has a high nitrogen content (73.6%), which, in protonated form, makes it attractive for the potential formation of nitrogen-rich energetic salts (Scheme 56). The amino groups of **11** will give rise to the formation of significant hydrogen-bonded networks, which will result in salts with high densities. The specific structure of **11** makes it a reasonable starting material to synthesize ionic energetic compounds.<sup>267–269</sup> Direct neutralization of 3,4,5-triamino-1,2,4-triazole (**11**) leads to the energetic salts **11-1** to **11-8** (Scheme 57).<sup>266–268</sup> Guanazinium salts have mid range densities from 1.63 (**11-5**) to 1.78 g/cm<sup>3</sup> (**11-6**).<sup>267</sup> The calculated detonation pressures (P) for the guanazinium salts **11** fall in the range of 24.3 (**11-5**) to 30.3 GPa (**11-6**), and the detonation velocities (D) are distributed

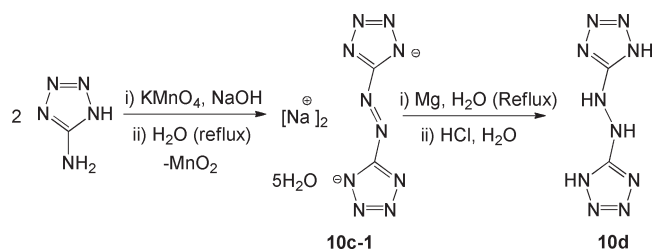
from 8055 (**11-7**) to 9048 ms<sup>−1</sup> (**11-6**) (Table 16). Their denotation data are lower than the corresponding values for RDX but most of them are superior to TNT. In addition, DSC analysis shows that the decomposition temperatures of most the guanazinium salts were >200 °C (except **11-3**).<sup>140,266,268</sup> These guanazinium salts have calculated heats of formation between 229 (**11-7**) and 1047 kJ mol<sup>−1</sup> (**11-3**).<sup>140,266,268</sup> The guanazinium salts may be of interest as potential energetic materials with low impact sensitivity. It is possible to methylate **11** readily with MeI to yield methylguanazinium iodide (**11a-1**) which is a suitable starting material for the synthesis of guanazinium salts of energetic interest.<sup>266–268</sup> Salts that contain the novel methylguanazinium cation with energetic anions were synthesized by metathetical reactions yielding a family of new heterocycle-based

Table 11. Properties of Azobistetrazolate Salts

salt	density (g/cm <sup>3</sup> )	<i>T</i> <sub>m</sub> (°C)	<i>T</i> <sub>d</sub> (°C)	$\Delta H_f^\circ$ (kJ/mol) <sup>a</sup>	<i>P</i> (GPa) <sup>a</sup>	<i>D</i> (m/s) <sup>a</sup>	IS (J)	FS (N)	thermal shock	ref
10c-1	1.54	262		487						232
10c-2	1.60		209	1171						232
10c-3	1.62		142							232
10c-4	1.26	3		897						232
10c-5	1.54	145		1094						232
10c-6	1.42	182		1136						232
10c-7	1.55	155		1852						232
10c-8	1.57	180		1130						232
10c-9	1.59	189		1620						232
10c-10	1.46			1335						232
10c-22	2.10		217				<3			234
10c-23	2.59		239				<3			234
10c-24	1.41		193	1363 (35) [1846]	19.0 [21.5]	7667 [8089]	>40	>360	deflagrates	235
10c-246H <sub>2</sub> O	1.40	~119 (–H <sub>2</sub> O)	194	1612 (30) [1848]	25.1 [25.8]	8585 [8685]	>40	>360	deflagrates	235
10c-25	1.61	121	145	483 (24) [1053]	23.4 [29.7]	8125 [8886]	>40	>360	burns	235
10c-252H <sub>2</sub> O	1.64	127, ~96 (–H <sub>2</sub> O)	160	–257 (21) [1052]	20.0 [32.8]	7694 [9258]	>40	>360	burns	235
10c-262H <sub>2</sub> O	1.44		197	1157	20.2	7820	>30	>360	deflagrates	83
10c-26	1.43		193	1491	20	7803	>30	>360	explodes	83
10c-272H <sub>2</sub> O	1.55		183	947	22.4	8090	>30	>360	deflagrates	83
10c-27	1.43		170	1617	21.1	7977	>30	>360	deflagrates	83
10c-28	1.59		193	759	20.7	8127				225
10c-29	1.71		212	524	19.9	7683	>30	>360		18

<sup>a</sup>Uncertainties are given in parentheses, calculated values are given in square brackets.

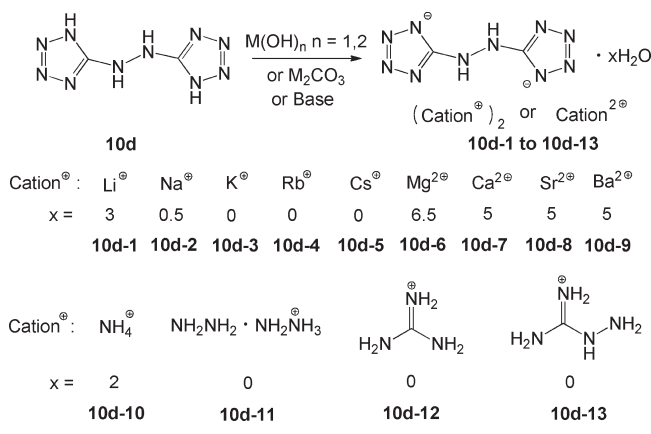
Scheme 46. Synthesis of 5,5'-Hydrazine-1,2-diylbis-(1H-tetrazole)



salts (Scheme 57, **11a-1** to **11a-8**). For the methylguanazinium salts, the presence of nitrate and perchlorate anions enhances the decomposition points of the compounds (Table 16), whereas the 5-nitrotetrazolate (**11a-6**) and dinitramide (**11a-7**) salts have lower thermal stabilities.<sup>266</sup> With the exception of **11a-4**, all materials exhibit excellent thermal stabilities (>310 °C).<sup>266</sup> All methylguanazinium salts have moderate densities >1.4 g cm<sup>–3</sup>, which are, in general, in the range of currently used explosives (1.4–1.8 g cm<sup>–3</sup>) and have excellent combined oxygen and nitrogen balances which are interesting from an environmental point of view.<sup>140,266,268–270</sup> Additionally, all methylguanazinium salts can be classified as insensitive or having low sensitivity to classical stimuli.

The preliminary sensitivity testing of the methylguanazinium salts indicates surprisingly low sensitivities to both friction and impact.<sup>266</sup> The highest friction and impact sensitivities were found for the perchlorate (**11a-4**, 220 N) and the dinitramide (**11a-7**, 20 J) salts, respectively.<sup>266</sup>

Scheme 47. Syntheses of 5,5'-(Hydrazine-1,2-diyl)bis-[1H-tetrazol-1-ide] Salts



In addition, DSC analysis was used to assess the thermal stabilities of the compounds which were found to be >200 °C with concomitant decomposition, whereas **11a-6**·H<sub>2</sub>O and **11a-7** have clearly defined melting points at 162 and 129 °C, respectively, with decomposition occurring ~30 °C above the melting point.<sup>266</sup> These compounds have calculated heats of formation between –167.9 (**11a-8**) and 1792.6 kJ mol<sup>–1</sup> (**11a-5**) with calculated detonation velocities between 7162 (**11a-8**) and 8922 m/s (**11a-5**·H<sub>2</sub>O), making them of interest as new highly energetic materials with low sensitivity.<sup>270–272</sup> Selective nitrosation of **11** produces the 3-nitrosamino-4,5-diamino-1,2,4-triazole (nitrosoguanazine, **11b**).<sup>269</sup> Treating **11b** with NaOH or

Table 12. Properties of 5,5-Hydrazine-1,2-diylbis(1H-tetrazole) and Its Salts

compound	density (g/cm <sup>3</sup> )	<i>T</i> <sub>m</sub> (°C)	<i>T</i> <sub>d</sub> (°C)	$\Delta H_f^{2a}$ (kJ/mol)	<i>P</i> <sup>a</sup> (GPa)	<i>D</i> (m/s)	IS (J)	friction (N)	thermal shock	ref
10d	1.84	207	208	414	27.7	8523	>30	>108		18, 233
10d-1	1.66	216	324	−120 (100)			>30	>360		238
10d-2		262	300	80 (90)			~30	>360		238
10d-3			236	−370 (160)			~30	>360		238
10d-4	2.69		230	345 (110)			~30	>360		238
10d-5	3.10		240	280 (80)			~30	>360		238
10d-6	1.68	142, 158 (−H <sub>2</sub> O)	220, 250	955 (70)			>30	>360	deflagrates	239
10d-7	1.90	140, 160 (−H <sub>2</sub> O)	220, 260	1530 (70)			>30	>360	deflagrates	239
10d-8	2.09	150, 185 (−H <sub>2</sub> O)	276	1140 (100)			>30	>360	deflagrates	239
10d-9	2.21	128, 154 (−H <sub>2</sub> O)	260	895 (70)			>30	>360	deflagrates	239
10d-10 <sup>[b]</sup>	1.62		196	438 (19) [104]	31.3 [39.4]	9423 [10330]	>30	>360	deflagrates	240
10d-11	1.60	154	182	706 (14) [164]	29.0 [38.5]	9272 [10341]	>30	>360	deflagrates	240
10d-12	1.60		214	352 (20) [101]	19.9 [29.2]	7914 [9159]	>30	>360	deflagrates	240
10d-13	1.62	142	194	623 (295) [197]	24.6 [33.1]	8630 [9666]	>30	>360	deflagrates	240

<sup>a</sup>Uncertainties are given in parentheses, calculated values are given in square brackets.

Scheme 48. Synthesis of Guanidinium 3,6-Bis-5-ylamino-tetrazolate-1,2,4,5-tetrazine

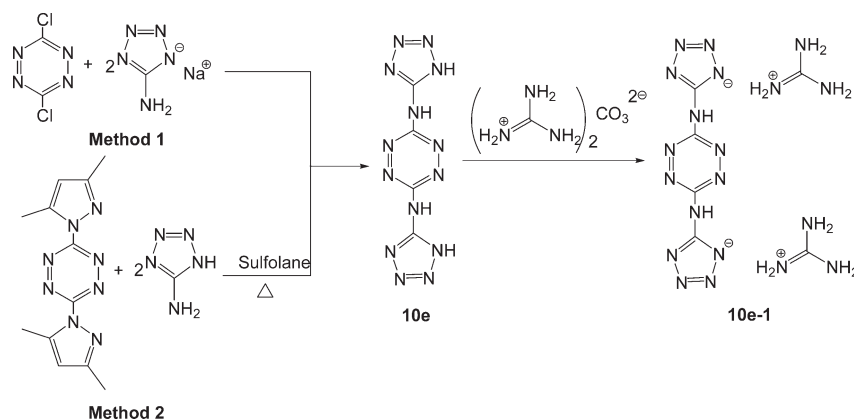


Table 13. Properties of Bridged Bis(1,5-diaminotetrazoles) and Their Salts

salt	density (g/cm <sup>3</sup> )	<i>T</i> <sub>m</sub> (°C)	<i>T</i> <sub>d</sub> (°C)	$\Delta H_f^o$ (kJ/mol)	<i>P</i> (GPa)	<i>D</i> (m/s)	IS (J)	ref
10e-1	1.47		285	1346	20.5	7673		225
10f	1.65		223	555	24.1	8255	25	247
10f-1	1.54	151		513	21.3	7939	>40	247
10f-2	1.57	92		662	24.0	8340	>40	247
10f-3	1.65	197		464	23.0	8297	>40	247
10f-4	1.68	201		569	25.5	8658	>40	247
10f-5	1.61	178		681	24.1	8446	>40	247
10f-6	1.5		207	796	21.6	8017	>40	247
10g	1.65		232	415	21.2	7767	25	247
10g-1	1.58	121	226	271	20.6	7893	>40	247
10g-2	1.63	181		589	26.0	8667	>40	247
10g-3	1.61	98	189	262	19.5	7815	>40	247
10g-4	1.62	194		495	22.2	8218	>40	247
10g-5	1.66	207		720	25.3	8707	>40	247
10g-6	1.56	156		979	23.8	8403	>40	247
10h	1.63		215	523	21.5	7886	25	78
10i	1.62		209	1289	25.0	8331	1.5	78



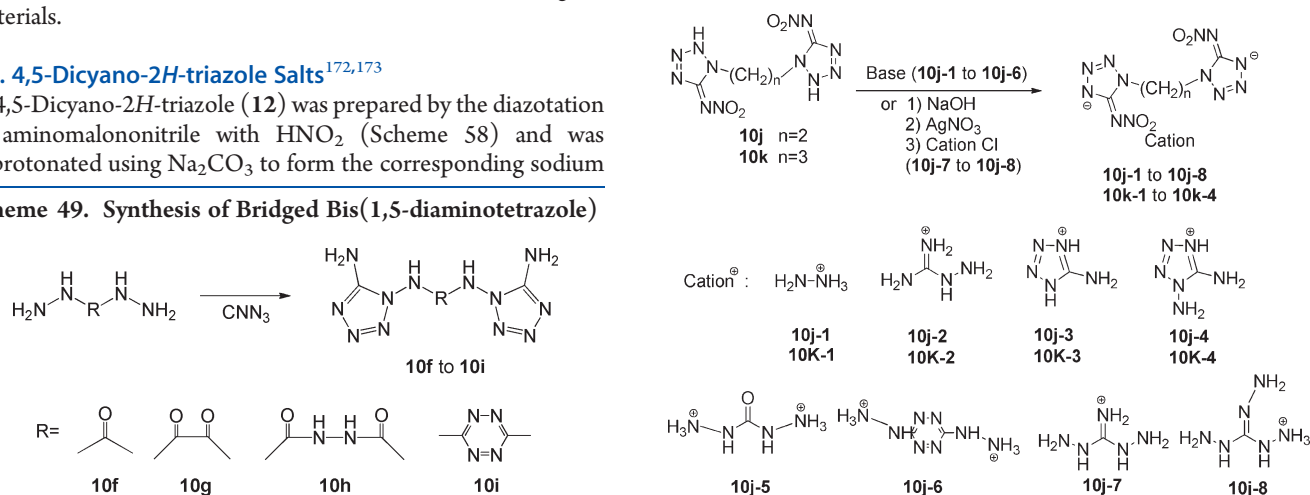
KOH in water gives the respective salts, **11b-1** and **11b-2**.<sup>269</sup> Crystal structures of **11b-1** and **11b-2** confirm that nitrosation of **11** has occurred on C–NH<sub>2</sub> rather than on N–NH<sub>2</sub>.<sup>269</sup> DSC study shows that the salts **11b-1** and **11b-2** have high thermal stabilities.<sup>269</sup> The reaction of copper(II) nitrate with **11b-1** or **11b-2** in water forms nitrosoguanazine anion–Cu(II) complex **11b-3**, which contains three Cu(II) cations, three nitrosoguanazine anions, and hydroxide, along with two nitrate ions and two water molecules. Compound **11b** can be easily converted to **11c** by heating in H<sub>2</sub>O or H<sub>2</sub>O/HOAc (Scheme 57).<sup>269</sup> Guanazine derivatives **11b** and **11c** contain multiple reactive amine groups which should be of interest as intermediates for energetic materials.

### 3.2. 4,5-Dicyano-2H-triazole Salts<sup>172,173</sup>

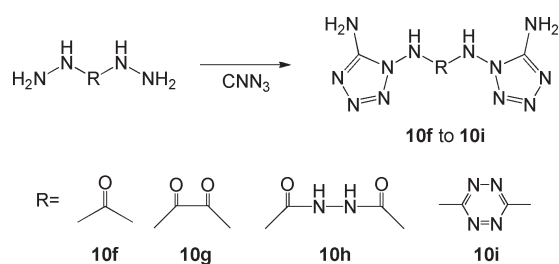
4,5-Dicyano-2H-triazole (**12**) was prepared by the diazotation of aminomalononitrile with HNO<sub>2</sub> (Scheme 58) and was deprotonated using Na<sub>2</sub>CO<sub>3</sub> to form the corresponding sodium

salt of the 4,5-dicyano-1,2,3-triazolate anion (**12-1**) as a monohydrate.<sup>92</sup> Reaction of **12-1** with AgNO<sub>3</sub> gave silver 4,5-dicyano-1,2,3-triazolate (**12-2**), which was used to prepare the ammonium (**12-3**), hydrazinium (**12-4**), guanidinium (**12-5**), aminoguanidinium (**12-6**), diaminoguanidinium (**12-7**), and triaminoguanidinium (**12-8**) salts of the 4,5-dicyano-1,2,3-triazolate anion in metathetical reactions from the corresponding ammonium and guanidinium halides.<sup>273</sup>

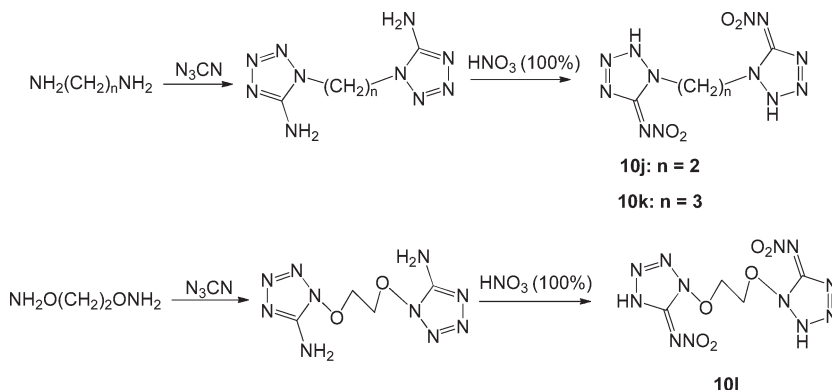
### Scheme 52. Syntheses of Bridged Bis(nitroiminotetrazolate) Salts (Part 1)



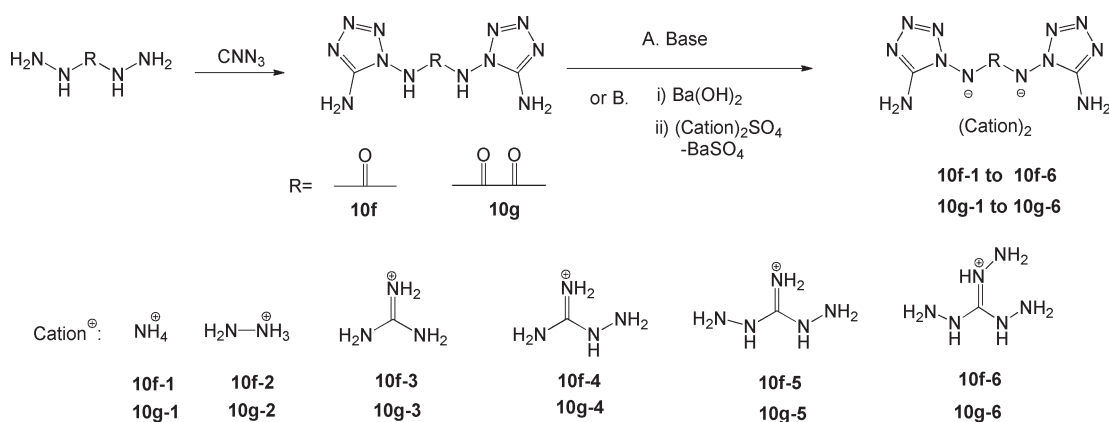
### Scheme 49. Synthesis of Bridged Bis(1,5-diaminotetrazole)



### Scheme 50. Syntheses of Disubstituted Nitroiminotetrazoles



### Scheme 51. Syntheses of Carbonyl or Oxalyl-Bridged Diaminotetrazolate Salts



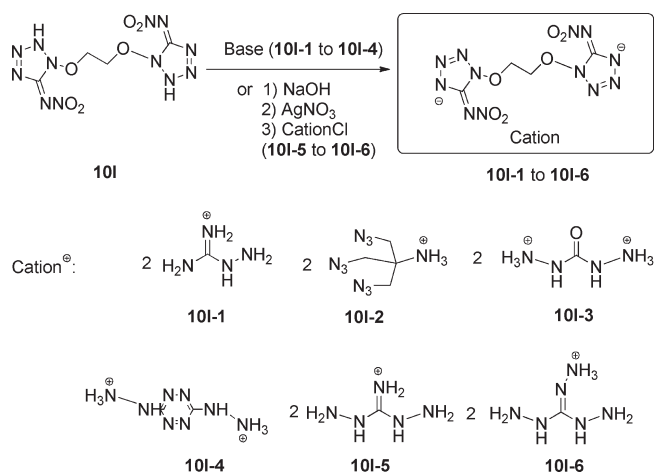
All 4,5-dicyano-2*H*-triazolate salts were found to be impact (>30 J) and friction insensitive (>360 N) (Table 17). Salt **12-5** shows the highest thermal decomposition temperature at 241 °C; the lowest is shown by salt **12-6** at 219 °C.<sup>172</sup>

All the salts have positive heats of formation ranging from 398 to 795 kJ/mol.<sup>172</sup> Because of the limited detonation abilities of compounds **12**, **12-5**, **12-6**, and **12-7**, based on the low velocity of detonation and the low detonation pressure, the only compound of potential use as an energetic material is **12-8** with a detonation velocity and detonation temperature similar to TNT, making it a potential green replacement for TNT.

### 3.3. Polyamino-1-guanyl-triazole Salts<sup>274</sup>

A series of new energetic salts based on the polyamino-1-guanyl-triazole cation was synthesized (Scheme 59). Their properties were modified by varying the guanyl substituents or the amino substituents on the triazole ring.<sup>274</sup> Synthetic routes to

**Scheme 53. Syntheses of Bridged Bis(nitroiminotetrazolate) Salts (Part 2)**



energetic 3-amino-1-guanyl-triazole, 3,5-diamino-1-guanyl-triazole, 3-amino-*N*-amidino-1-guanyl-triazole, and 3,5-diamino-*N*-amidino-1-guanyl triazole dinitramide salts, **13-1** to **13-4**, are depicted in Scheme 59.<sup>274</sup>

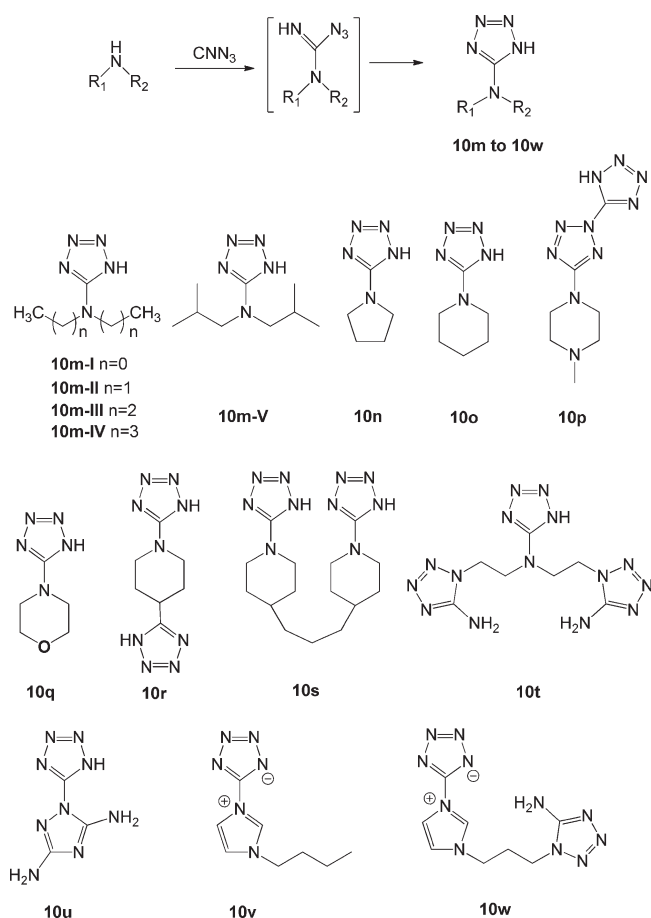
3-Amino-1-guanyl-1,2,4-triazole hydrochloride, and 3,5-diamino-1-guanyl-1,2,4-triazole hydrochloride were synthesized by the reaction of amino and diamino-substituted 1,2,4-triazole hydrochlorides with cyanamide, respectively.<sup>274</sup> When 3-amino-triazole was reacted with cyanoguanidine in a similar manner, 5-amino-*N*-amidino-1-guanyl-1,2,4-triazole hydrochloride was obtained. A possible mechanism is that 3-amino-1,2,4-triazole hydrochloride undergoes a 1,3-shift followed by reaction with cyanoguanidine. In a previous report,<sup>274</sup> when 3-amino-1,2,4-triazole was reacted with alkyl isothiocyanates, a similar 1,3-shift addition product, 5-amino-1-[alkylamino(thiocarbonyl)]-1*H*-1,2,4-triazole, was found.

3,5-Diamino-*N*-amidino-1-guanyl-1,2,4-triazole hydrochloride was formed in an analogous manner when **13-2** was reacted with cyanoguanidine. Subsequent metathetical reactions with a solution of silver dinitramide gave energetic salts, **13-1**–**13-4**. Physical characteristics and some key properties of these energetic materials, including density, heat of formation, decomposition temperature, and detonation velocity and pressure, are given in Table 18.

The thermal stabilities of these salts, ranging from 175 to 197 °C, for **13-1**–**13-4** are superior to that of ADN (145 °C) by nearly 30 °C.<sup>274</sup> In general, the new salts with 3-amino-triazole as cation are thermally less stable, compared to the analogous 3,5-diamino-triazole cation salts, for example, **13-1** and **13-2**, that decompose at 188.1 and 196.8 °C, respectively.<sup>274</sup> The stabilities of the salts were influenced by the substituent present; changing from guanyl to *N*-amidino-guanyl gives rise to a decrease in thermal stability, that is, **13-2** at 196.8 °C and **13-4** at 183.2 °C.<sup>274</sup> 3,5-Diamino-1-guanyl-triazole dinitramide **13-2** has the highest decomposition temperature, which likely arises from extensive hydrogen bonding interactions between the four amino groups

**Table 14. Properties of Disubstituted Nitroiminotetrazole and Their Salts**

salt	density (g/cm <sup>3</sup> )	<i>T</i> <sub>m</sub> (°C)	<i>T</i> <sub>d</sub> (°C)	Δ <i>H</i> <sub>f</sub> <sup>o</sup> (kJ/mol)	<i>P</i> (GPa)	<i>D</i> (m/s)	IS (J)	ref
<b>10j</b>	1.86		194	1038	38.2	9329	10	181
<b>10j-1</b>	1.73	223		1067	35.3	9478	10	181
<b>10j-2</b>	1.61		255	993	26.3	8531	10	181
<b>10j-3</b>	1.69		196	1611	29.6	8756	15	181
<b>10j-4</b>	1.70	174		1768	31.2	8990	10	181
<b>10j-5</b>	1.72		203	1094	32.0	8957	10	181
<b>10j-6</b>	1.82		203	1231	34.3	9303	15	181
<b>10j-7</b>	1.58		220	1233	26.5	8568	7	248
<b>10j-8</b>	1.60	132	195	1458	28.6	8860	>40	248
<b>10k</b>	1.66		173	1032	28.1	8374	10	181
<b>10k-1</b>	1.62	123		1055	29.3	8846	15	181
<b>10k-2</b>	1.56	220		959	23.8	8209	15	181
<b>10k-3</b>	1.63		203	1578	26.5	8409	15	181
<b>10k-4</b>	1.66	157		1728	28.8	8742	10	181
<b>10l-1</b>	1.60		200	1029	26.8	8472	6	248
<b>10l-2</b>	1.60		151	2944	26.6	8377	<1	248
<b>10l-3</b>	1.70		130,146	1134	32.2	8789	6	248
<b>10l-4</b>	1.78		147	1270	33.3	9030	2	248
<b>10l-5</b>	1.68	160	164	1254	28.7	8741	5	248
<b>10l-6</b>	1.61	95 (−H <sub>2</sub> O) 160	162	1487	29.4	8840	4	248

**Scheme 54. Reactions of Secondary Amines, Triazoles, and Imidazoles with Cyanogen Azide**

of the cation and four oxygen atoms of the dinitramide. The heats of formation for **13-1**–**13-4** fall between 149 and 218 kJ/mol.<sup>274</sup> *N*-Amidino-1-guanyl-triazole dinitramide salts have higher heats of formation than those of the 1-guanyl-triazole dinitramides, for example, **13-3** and **13-4**, ( $\Delta H_f = 218$ , and 172 kJ/mol) and **13-1** and **13-2** ( $\Delta H_f = 186$ , and 149 kJ/mol), respectively.<sup>274</sup> These values are also more positive than the calculated heat of formation for ADN (−123 kJ/mol).<sup>274</sup> Calculation of detonation properties values shows that **13-2** has the highest detonation pressure ( $P = 31.0$  GPa) and velocity ( $D = 8775$  m/s).<sup>274</sup> All of the salts have reasonable specific impulse values ranging between 204.0 (**13-4**) and 227.7 s (**13-1**).<sup>274</sup> In general, the new salts with 3-amino-1-guanyl-triazole as cation have lower detonation properties, compared to the analogous 3,5-diamino-1-guanyl-triazole cation salts, for example, **13-1** and **13-2** at  $P = 29.9$  GPa,  $vD = 8568$  m/s and  $P = 31.0$  GPa,  $vD = 8775$  m/s, respectively.<sup>274</sup> Longer guanyl substituents result in lower detonation properties, for example, changing the guanyl to *N*-amidino-guanyl, the detonation pressure decreases, for example, **13-4**,  $P = 28.5$  GPa,  $vD = 8651$  m/s; **13-2**,  $P = 31.0$  GPa,  $vD = 8775$  m/s.<sup>274</sup> Salt **13-2** has detonation properties similar to those of RDX.

### 3.4. Nitroamino-triazole Salts<sup>171,275</sup>

3-Nitroamino-1,2,4-triazole (**14a**), 4-nitroamino-1,2,4-triazole (**14b**) and 1-nitroamino-1,2,3-triazole (**14c**), which contain five catenated nitrogen atoms, were synthesized through nitration of the neutral aminotriazoles (Scheme 60).

The neutral compounds **14b** and **14c** displayed good detonation properties. A variety of new energetic salts based on the 3-nitroamino-1,2,4-triazolate (**14a-1** and **14a-2**) (Scheme 61),<sup>171</sup> 4-nitroamino-1,2,4-triazolate (**14b-1** to **14b-9**) and 1-nitroamino-1,2,3-triazolate (**14c-1** to **14c-7**) anions were synthesized (Scheme 62).<sup>275</sup>

In Table 19 is a summary of physicochemical properties of the nitroamino-triazoles and their salts. Relative to the parent compounds, **14a**, **14b**, and **14c**, the thermal stabilities of these salts were improved remarkably.<sup>275</sup> All the salts of 4-nitroamino-1,2,4-triazole (**14b**) and 1-nitroamino-1,2,3-triazole (**14c**) show higher decomposition temperatures than the neutral molecules **14b** and **14c**.<sup>275</sup> Salt **14c-4** has the lowest decomposition temperature at 147 °C; the highest decomposition temperature is shown by the salt **14a-1** at 251.8 °C.<sup>275</sup> Comparison of the salts of 3-nitroamino-1,2,4-triazolate, 1-nitroamino-1,2,3-triazolate and 4-nitroamino-1,2,4-triazolate with the same cations shows that while the 1,2,4-triazolates in general have higher decomposition temperatures, the 1,2,3-analogues invariably have higher heats of formation. The densities of the pairs of salts do not vary more than 0.1 g cm<sup>−3</sup>; however, these small differences are reflected clearly in the detonation pressures. All the salts have positive heats of formation ranging from 6 (**14b-5**) to 888 (**14c-3**) kJ/mol.<sup>275</sup> Theoretical calculations show all the salts have relatively high positive molar enthalpies of formation and moderate detonation properties. Compounds **14b** and **14c** show detonation properties (detonation velocity and pressure) similar to those of RDX which suggests that these compounds may be potential green replacements for RDX; however, the properties of their salts are not as attractive as those of their neutral precursors, which likely precludes their application.

### 3.5. Bis[3-(5-nitroimino-1,2,4-triazole)] Salts<sup>139,276–278</sup>

Bis[3-(5-nitroimino-1,2,4-triazole)] ( $H_2BNT$ , **15**) is an interesting molecule for design of energetic salts because its mono-anionic salt shows promising thermal stability (200 °C) and poor solubility in organic solvents, water, and acids.<sup>276,277</sup> On the basis of the symmetric nature of **15**, a much easier and more straightforward method for its synthesis was developed (Scheme 63).

The condensation of aminoguanidine hydrochloride with inexpensive oxalic acid and subsequent cyclization gave rise to bis[3-(5-amino-1,2,4-triazolyl)],<sup>278</sup> which when nitrated with concentrated nitric acid and sulfuric acid gave **15**. The sodium salt of bis[3-(5-nitroimino-1,2,4-triazole)] (**15-1**) was obtained by adding aqueous NaOH to a hot aqueous solution of **15** (pH ~10).<sup>139</sup> Salt **15-1** is soluble in hot water. Metathesis reactions of **15-1** with monocationic halides in hot water resulted in the formation of corresponding energetic salts **15-2** to **15-12**.<sup>139</sup> The treatment of **15-1** with excess of dicationic sulfates gave rise to **15-11** and **15-12** in high yield and purity. As shown in Table 20, all of the salts exhibit excellent thermal stabilities.

The decomposition temperatures, which fall in the range 198–290 °C, are higher than that of  $H_2BNT$  (165 °C) and comparable to those of RDX (230 °C) and HMX (287 °C).<sup>139</sup> The densities of **15-2**–**15-12**, which are between 1.63 and 1.95 g/cm<sup>3</sup>, are higher than those of the reported 3-nitroamino-1,2,4-triazole analogues.<sup>171,279</sup> It should be noted that the densities of commonly used explosives such as TNT, TATB, RDX, and HMX are in this range. Interestingly, the densities of **15-2** and **15-11** fall close to new high performance energetic materials (1.8–2.0 g/cm<sup>3</sup>).<sup>139</sup> The density of **15-11** (1.95 g/cm<sup>3</sup>) is the highest of the reported energetic salts.<sup>139</sup> Salts **15-4** to **15-12**

Scheme 55. Syntheses of 5-Azidotetrazolate Salts

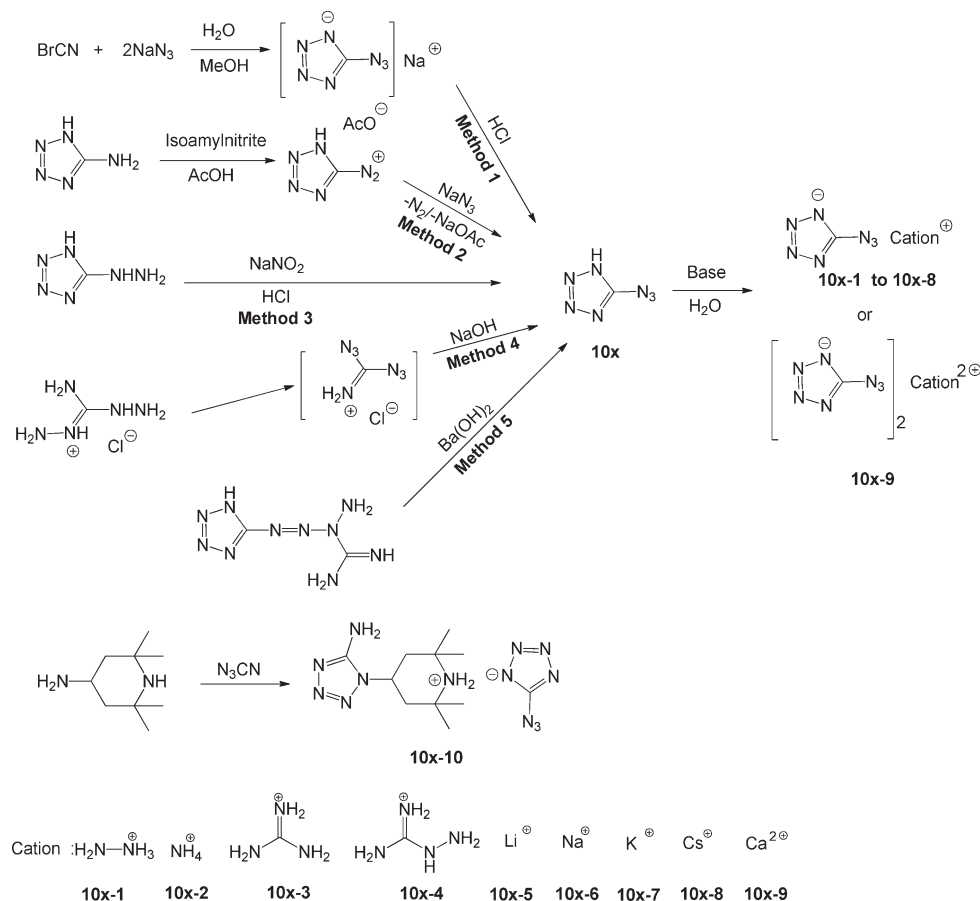


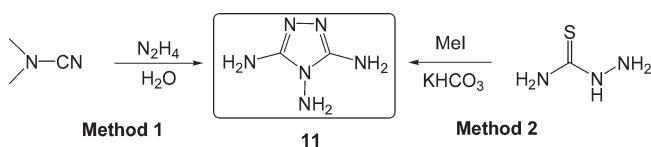
Table 15. Properties of 5-Azidotetrazolate Salts

salt	density (g/cm <sup>3</sup> )	$T_d$ (°C)	$\Delta H_f^\circ$ (kJ/mol)	$P$ (GPa)	$D$ (m/s)	ESD (mJ)	IS (J)	FS (N)	ref
10x-1	1.57	136	703	30.6	9231	5	<1	5	256
10x-2	1.61	157	544	28.7	8917	10	<1	5	256
10x-4	1.52	159	642	24.1	8424	40	1	7	256

possess much lower impact sensitivities than RDX and HMX (7.4 J), which suggests that they can serve as potential alternatives for safer energetic materials to replace RDX. The impact sensitivities of 15-5, 15-6, 15-9, and 15-10 are greater than 40 J, so they can be classified as insensitive materials.

All of the salts exhibit positive heats of formation falling in the range 0.14–1.91 kJ/g. In addition, they have good specific impulse values ranging between 191.3 (15-5) and 240.0 s (15-3).<sup>139</sup> The calculated detonation pressures of 15-2 to 15-11, which lie between 24.3–36.0 GPa, are higher than that of TNT (19.53 GPa) and are comparable to those of TATB (31.15 GPa) and RDX (35.2 GPa).<sup>139</sup> Detonation velocities ( $\nu_D$ ) were found from 8267–9407 m/s; they are higher than those of TNT (6881 m/s) and TATB (8114 m/s) and compare favorably with those of RDX (8977 m/s) and HMX (9320 m/s).<sup>139</sup> The promising performance suggests potential applications of BNT<sup>2-</sup> salts as ingredients in explosives and propellants. This is especially the case for 15-2, 15-3, and 15-11, as their energetic performance values

Scheme 56. Synthesis of 3,4,5-Triamino-1,2,4-triazole



are very similar and even superior to those of RDX, which indicates that they may serve as a series of promising alternatives to RDX.

### 3.6. Triazole-Based Liquid Azide Ionic Liquids

Ionic liquid azides from azidoethyl-, alkyl-, and alkenyl-substituted derivatives of 1,2,4- and 1,2,3-amino-triazoles were prepared through metathesis reactions (Scheme 64). The salts possess melting points below 100 °C (Table 21). The unique character of these ionic liquid azides is based upon the fact that they are not simple protonated salts like the previously reported substituted hydrazinium azides.<sup>280</sup> The presence of quaternary nitrogen confers both thermal stability and negligible volatility. This work demonstrated that true room-temperature ionic liquid azides can be obtained. The azide anion did not cause the compounds to become too sensitive to be handled safely and an alternative preparative route has been described avoiding silver azide. This would seem to indicate that these new, less volatile, less sensitive, liquid azides may hold great potential as energetic materials.<sup>280</sup>



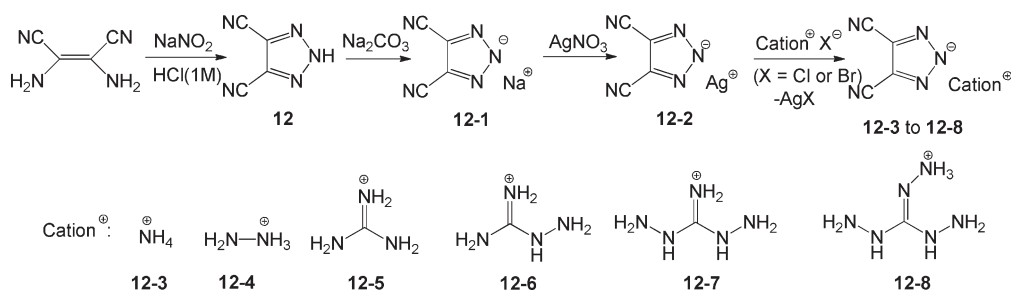


Table 16. Properties of 1,2,4-Triazolium Salts

compound	density (g/cm <sup>3</sup> ) <sup>a</sup>	T <sub>m</sub> (°C)	T <sub>d</sub> (°C)	ΔH <sub>f</sub> <sup>o</sup> (kJ/mol)	P (GPa)	D (m/s)	IS (J)	FS (N)	thermal shock	ref
11-2 <sup>a, b</sup>	1.75		269	−120 (45) [130]	22.5 [25.0]	7495 [7808]	>40	>360	burns rapidly	140
11-3	1.68[1.68]		191	1047	25.2	8280	25			268
11-4	1.71[1.63]		219	495	27.0	8646	>40			268
11-5	1.63[1.63]	170	257	871	24.3	8399	>40			268
11-6	1.78[1.69]		231	359	30.3	9048	>40			268
11-7	1.71[1.76]	196	242	229	25.8	8055				268
11-8	1.64[1.65]	103	209	633	24.8	8323	>40			268
11a-2	1.40	212	215	531	27.5	8719	>40	320	deflagrates	266
11a-3	1.67	258	261	64	25.8	8270	>40	>360	burns	266
11a-4	1.67	247	310	498			25	220	deflagrates	266
11a-5·H <sub>2</sub> O	1.58		201	1793	28.6	8922	>40	>360	deflagrates	266
11a-5 <sup>b</sup>	~1.58			1793	27.7	8834				266
	1.71		212	524	19.9	7683	>30	>360		270
11a-6·H <sub>2</sub> O	1.58	162	196	519	25.6	8330	>40	>360	burns	266
11a-6	~1.58			519	23.9	8117				266
1a-17	1.66	129	160	276	27.7	8383	20	360	deflagrates	266
11a-8	1.69	207	250	−168 (21) [99]	19.8 [22.1]	7162 [7486]	>40	>360	burns	140
11b-1		131	259							269
11b-2			228							269
11b-3			218							269
11c			175							269
11c-1			172							269

<sup>a</sup>Uncertainties are given in parentheses, calculated values are given in square brackets. <sup>b</sup>Different values for the properties of the compound were reported in different references.

Scheme 58. Syntheses of 4,5-Dicyano-1,2,3-triazolate Salts

Table 17. Properties of 4,5-Dicyano-2H-triazole and Its Salts<sup>172</sup>

salt	density (g/cm <sup>3</sup> )	T <sub>m</sub> (°C)	T <sub>d</sub> (°C)	ΔH <sub>f</sub> <sup>o</sup> (kJ/mol)	P (GPa)	D (m/s)
12	1.55	149	221	473	14.3	6377
12-5	1.42	135	241	398	13.0	6466
12-6	1.45	108	219	518	15.9	7054
12-7	1.43	124	228	631	17.1	7307
12-8	1.48	169	227	795	21.0	7919

reduction process.<sup>287</sup> Halide-free, efficient syntheses of azolium azolates (1,3-dimethylimidazolium 4,5-dinitroimidazolate and 1,3-dimethylimidazolium 4-nitro-1,2,3-triazolate) were realized by reaction of 1,3-dimethylimidazolium-2-carboxylate with

neutral azoles via a one-pot synthesis with an easily removed byproduct (CO<sub>2(g)</sub>) (Scheme 66).<sup>288</sup> The method avoids halide and metal impurities. It was developed to prepare eutectic mixtures of the salts and the eutectic point compositions of mixtures of these salts could be determined readily.<sup>288</sup>

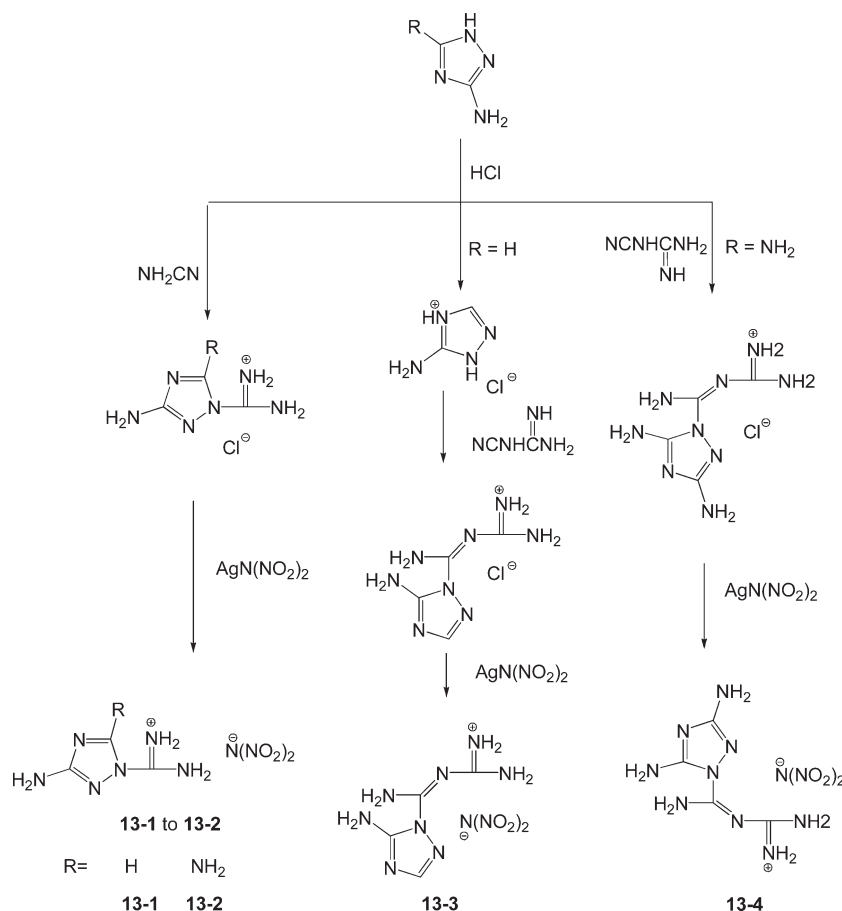
In the following section, several new energetic salts with the pyrazole or imidazole group in the structure are described.

#### 4.1. 2,4,5-Trinitroimidazole-Based Energetic Salts

Recently, 2,4,5-trinitroimidazole (TNI, 18) was synthesized by the nitration of 2,4-dinitroimidazole (Scheme 67, method 1)<sup>289</sup> or of 2,4,5-triiodoimidazole (Scheme 67, method 2).<sup>290,291</sup>

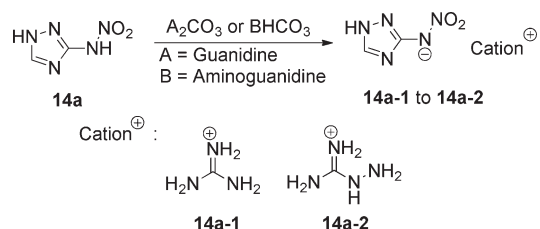
The energetic salts formed with 2,4,5-trinitroimidazolate as the anion were synthesized (Scheme 68) and fully characterized. The introduction of TNI provides a new, straightforward approach to highly energetic salts that exhibit acceptable physical properties,

Scheme 59. Syntheses of Salts with the Polyamino-1-guanyl-triazole Cation

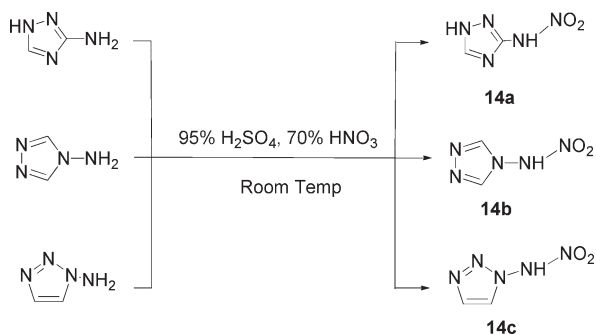
Table 18. Properties of Polyamino-guanyl-1,2,4-triazole and Its Salts<sup>274</sup>

salt	density ( $\text{g}/\text{cm}^3$ )	$T_d$ ( $^\circ\text{C}$ )	$\Delta H_f^\circ$ ( $\text{kJ}/\text{mol}$ )	$P$ (GPa)	$D$ (m/s)	$I_{\text{sp}}$ (s)
13-1	1.76	188.1	186	29.9	8568	227.7
13-2	1.78	196.8	149	31.0	8775	219.3
13-3	1.66	174.7	218	23.9	8040	209.9
13-4	1.76	183.2	172	28.5	8651	204.0

Scheme 61. Syntheses of 3-Nitroamino-1,2,4-triazolate Salts



Scheme 60. Syntheses of Nitroamino-triazoles

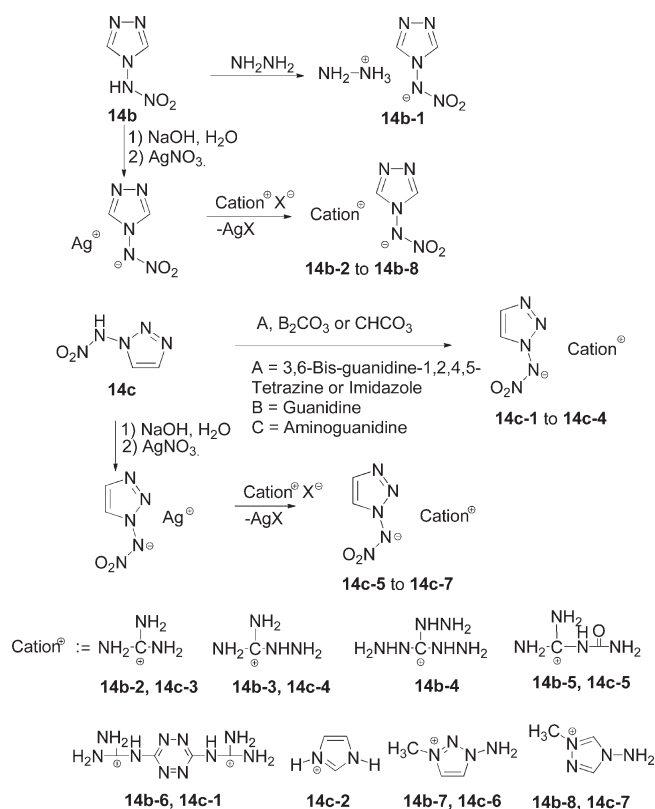


such as relatively high densities ( $>1.75 \text{ g}/\text{cm}^3$ ) and thermal stabilities ( $T_d > 198.1 \text{ }^\circ\text{C}$ ).<sup>291</sup> Theoretical and empirical

calculations show that all the salts have relatively high positive molar enthalpies of formation. In Table 22 the physicochemical properties of trinitroimidazolate salts are summarized. The standard enthalpies of formation for the TNI salts range from  $\Delta H_f^\circ = -60$  (18-3) to  $616 \text{ kJ}/\text{mol}$  (18-2) with experimentally determined densities  $>1.70 \text{ g}/\text{cm}^3$ .<sup>291</sup> The highest density of any salt is  $1.86 \text{ g}/\text{cm}^3$  (18-2).<sup>291</sup> Thermal stabilities of these energetic salts were studied with DSC. All nitroimino-tetrazolates decomposed between  $198.1$  (18-2) and  $270.1 \text{ }^\circ\text{C}$  (18-1).<sup>291</sup> The calculated detonation pressures of these salts lie in the range between  $P = 23.8$  and  $P = 34.1 \text{ GPa}$  (comparable to  $\text{RDX} = 35.2 \text{ GPa}$ ).<sup>139,291</sup> Detonation velocities lie between  $D = 7691$  and  $D = 8695 \text{ m/s}$  (comparable to  $\text{RDX} = 8977 \text{ m/s}$ ).<sup>139,291</sup> All of the TNI compounds show calculated detonation velocities and detonation pressures comparable to those of explosives such as

TATB and RDX. In addition, all of these salts have rather high specific-impulse values with the highest value at 254.8 s, which suggests energetic materials applications as propellants.<sup>291</sup> These properties coupled with rather high thermal and hydrolytic stabilities make these TNI energetic salts attractive candidates for energetic applications.<sup>291</sup>

**Scheme 62.** Syntheses of 4-Nitroamino-1,2,4-triazolate and 1-Nitroamino-1,2,3-triazolate Salts



#### 4.1.1. Azole-Based Hypergolic Energetic Salts<sup>292–301</sup>

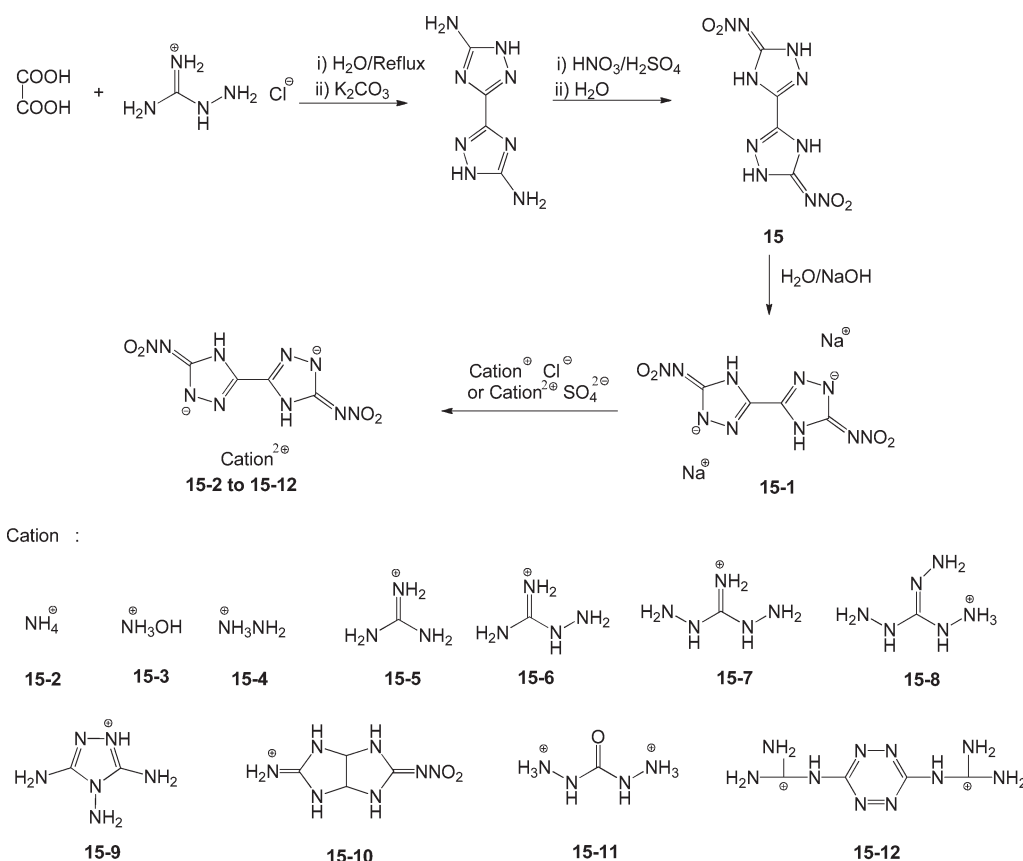
Hypergolic fuels are special propellants, which consist of a fuel and an oxidizer. They can ignite spontaneously upon contact without an additional ignition source to bring about combustion. In traditional hypergolic systems, the common fuels of choice are hydrazine, monomethylhydrazine (MMH), and *N,N*-dimethylhydrazine (UDMH) with oxidizing agents. Unfortunately, hydrazine and its derivatives are acutely toxic and carcinogenic substances and have high vapor pressures. Therefore alternative nontoxic liquid hypergolic fuels that have low vapor pressures and high energy densities are necessary.

Hydrazinium azide was discovered more than a century ago.<sup>302</sup> According to the modern definition of ionic liquids (a salt with a melting point below 100 °C), it could be regarded as an ionic liquid since its melting point is 75 °C. It is interesting to note that a propellant-containing hydrazinium azide was test-fired and spontaneous ignition was achieved upon contact with inhibited, red-fuming nitric acid (IRFNA).<sup>303</sup> It is the first reported hypergolic ignition of an ionic liquid and consequently ionic liquids have been considered possible candidates in bipropellant applications. In 2008, several imidazolium-based ionic liquid azides with saturated and unsaturated side chains, salts **19-1** to **19-11**, in Scheme 69, were prepared and some of their physical and structural properties were investigated (Table 23). The reactivity of the ionic liquid azides with commonly used oxidizers such as IRFNA and  $\text{N}_2\text{O}_4$  was studied.<sup>299</sup> It was demonstrated successfully that both the cation and anion in ionic liquid azides will react with the oxidizer. However, the initial heat release during these reactions did not result in hypergolic ignition of the material under the tested conditions.<sup>299</sup> Although the ignition tests carried out with these ionic liquids azides did not reveal any hypergolic properties, the violent nature of their reactions was sufficiently encouraging to justify the expectation that variations in test conditions and ionic liquids could lead to practical ionic liquids hypergol.<sup>293</sup> In their following work, the authors found that dicyanamide salts with 1-allyl-3-methyl-imidazolium, 1-(3-butenyl)-3-methyl-imidazolium, 1-propargyl-3-methyl-imidazolium, 1-methyl-4-amino-1,2,4-triazolium, 1-butyl-3-methyl-imidazolium,

**Table 19.** Properties of Energetic Salts Based on Nitroamino-triazoles

salt	density (g/cm <sup>3</sup> )	<i>T</i> <sub>m</sub> (°C)	<i>T</i> <sub>d</sub> (°C)	$\Delta H_f^\circ$ (kJ/mol)	<i>P</i> (GPa)	<i>D</i> (m/s)	<i>I</i> <sub>sp</sub> (s)	ref
<b>14b</b>	1.82	172	180	340	33.4	8793		275
<b>14c</b>	1.80		105	367	33.0	8743		275
<b>14a-1</b>	1.55		252	50	18.2	7465	187.1	171
<b>14a-2</b>	1.58		226	158	20.8	7920	198.0	171
<b>14b-1</b>	1.66	135	194	372	29.7	8868		275
<b>14b-2</b>	1.48	184	240	205	19.7	7700		275
<b>14b-3</b>	1.50	138	220	309	22.0	8011		275
<b>14b-4</b>	1.55	167	200	532	24.4	8366		275
<b>14b-5</b>	1.60		205	6	18.8	7501		275
<b>14b-6</b>	1.58		211	790	20.2	7506		275
<b>14b-7</b>	1.47	−33	206	627	20.0	7663		275
<b>14b-8</b>	1.54	138	213	553	21.4	7487		275
<b>14c-1</b>	1.51	189	230	257	20.4	7587		275
<b>14c-2</b>	1.50	71	187	368	20.9	7783		275
<b>14c-3</b>	1.62		226	888	21.2	7765		275
<b>14c-4</b>	1.51	86	147	408	18.6	7403		275
<b>14c-5</b>	1.54	142	162	65	19.3	7282		275
<b>14c-6</b>	1.43	−45	195	684	19.2	7532		275
<b>14c-7</b>	1.63	92	192	600	22.7	7957		275

Scheme 63. Synthesis of Bis[3-(5-nitroimino-1,2,4-triazole)] Salts

Table 20. Properties of Energetic Salts of Bis[3-(5-nitroimino-1,2,4-triazole)]<sup>139</sup>

salt	$d^a$ (g/cm <sup>3</sup> ) <sup>a</sup>	$T_m$ (°C)	$T_d$ (°C)	$\Delta H_f^\circ$ (kJ/mol)	$P$ (GPa)	$D$ (m/s)	IS (J)	$I_{sp}$ (s)
15-2	1.83 [1.89]		217	106	34.9	9407		200.8
15-3	1.78		218	276	32.4	8856		240.0
15-4	1.63		220	516	26.2	8455	11	227.1
15-5	1.70 [1.77]		265	163	26.6	8634	>40	191.3
15-6	1.71	242	248	398	26.3	8603	>40	202.3
15-7	1.68		235	640	27.0	8701	31	212.6
15-8	1.64	237	244	885	27.0	8705	23	221.9
15-9	1.75 [1.78]	178	198	809	28.3	8792	>40	207.8
15-10	1.80		281	837	27.3	8474	>40	212.3
15-11	1.95	162	222	47	36.0	9399	38	194.7
15-12	1.80		290	320	24.3	8267	32	182.8

<sup>a</sup> Calculated values are given in brackets.

1-butyl-1-methylpyrrolidinium, and *n*-butyl-3-methylpyridinium, were shown to be hypergolic with N<sub>2</sub>O<sub>4</sub> or WFNA.<sup>293</sup> It appears that the key to hypergolicity in these systems is the dicyanamide anion.<sup>298</sup>

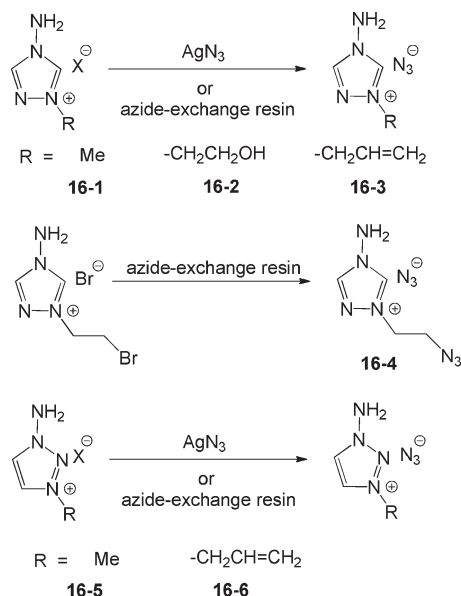
With the discovery of these ionic liquid hypergols, a new path for transitioning these materials into bipropellant applications seemed clear. It is expected that these systems can now be fine-tuned for energy content, performance, and desirable physical properties and that they could replace state-of-the-art, highly toxic hydrazine, and its derivatives.<sup>291–301</sup>

Then a series of new hypergolic reactions were reported with a variety of cations (2,2-dimethyltriazanium) and anions.<sup>292–301</sup> Since this review focuses on azole-based energetic salts, only this type of hypergolic energetic salt is reported here. For more details, see the recent review “Ionic Liquids as Hypergolic Fluids” which has been accepted by *Angew. Chem.*<sup>301</sup> These salts (19–21 to 19–21) were synthesized in a straightforward manner through metathesis reactions (Scheme 70).<sup>293,294,297</sup>

In Table 23, the physicochemical properties of the ionic liquids with substituted imidazolium, and triazolium cations

(19-12 to 19-21) are summarized. They exhibit desirable physicochemical properties, such as low melting points and good thermal stabilities; they are impact insensitive materials.<sup>103f</sup> They were shown to be promising candidates as hypergolic ionic liquids through combustion tests with 100% HNO<sub>3</sub>.<sup>301</sup> These ionic liquids are the brightest hope to date to be the next class of hypergolic materials to replace hydrazine and its derivatives in hypergolic propellant systems.

**Scheme 64. Syntheses of Triazole-Based Liquid Azide Ionic Liquids**



**Table 21. Properties of Energetic Salts of Triazole-Based Liquid Azide**<sup>280</sup>

salt	density (g/cm <sup>3</sup> )	<i>T</i> <sub>m</sub> (°C)	<i>T</i> <sub>d</sub> (°C)	Δ <i>H</i> <sub>f</sub> <sup>o</sup> (kJ/mol)	IS (J)	FS (N)
16-1		43	129	569	>20	>360
16-2		50	156	623	>20	>360
16-3	−50		129	389	17.6	353
16-4	−57		109	674	13.2	
16-5	−62		114	724	<6	
16-6			106	933	>15 <20	

#### 4.2. 3,4,5-Trinitropyrazole-Based Energetic Salts<sup>304,305</sup>

Direct nitration of 3,5-dinitropyrazole was found to be the route of choice to trinitropyrazole (TNP, **20**), which exhibits remarkable and unprecedented properties for a strong electron-deactivated aromatic heterocycle (Scheme 71, method 1).<sup>304</sup> Oxidation of aminodinitropyrazoles can also give **18** (Scheme 71, methods 2 and 3).<sup>304</sup> Compound **20** is not hygroscopic, is weakly acidic, and displays low sensitivity toward external stimuli and outstanding thermal and chemical stability compared to that of other all carbon-nitrated azoles. Beyond the scope of the nitroazole chemistry, **20** has the best thermal and chemical stability of any fully nitrated aromatic system (i.e., polynitroarylenes, furazans, furoxans).<sup>304</sup>

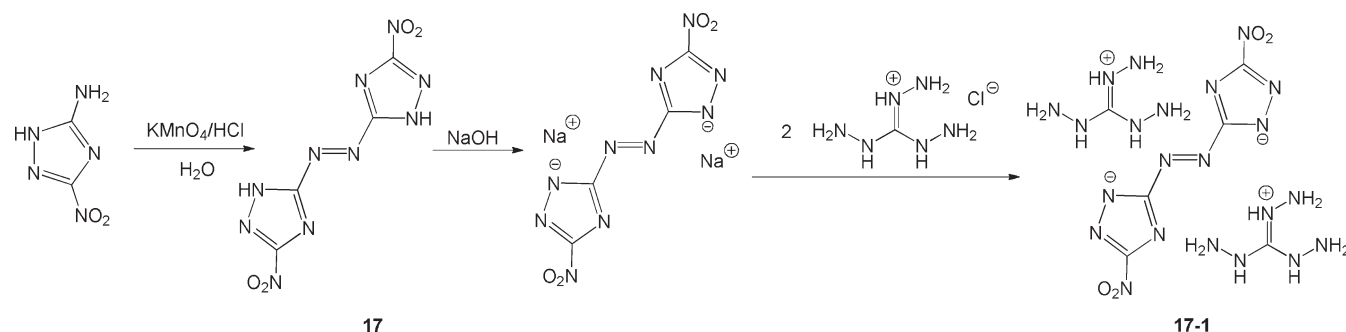
High-density energetic salts (**20-1** to **20-13**) that are comprised of nitrogen-rich cations and the 3,4,5-trinitropyrazolate anion were synthesized in high yield by neutralization or metathesis reactions (Scheme 72).<sup>305</sup> On the basis of the calculated heats of formation and measured densities, the detonation performances (pressure: 23.7–31.9 GPa; velocity: 7586–8543 m/s) of the 3,4,5-trinitropyrazolate salts are comparable to 1,3,5-triamino-2,4,6-trinitrobenzene (TATB, 31.2 GPa and 8114 m/s) (Table 24).<sup>305</sup>

Hammer tests show that the impact sensitivities of these salts are not less than 35 J, which places them in the insensitive class. Densities for the 3,4,5-trinitropyrazolate salts were found to fall in the range between 1.61 (**20-10**) and 1.77 g/cm<sup>3</sup> (**20-4**) (measured with a gas pycnometer), which places them in a class of relatively dense energetic materials.<sup>305</sup> The specific impulse values of the TNP salts range between 228.9 and 269.6 s suggesting application of these energetic materials as propellants.<sup>305</sup> Except for **20-1** (40 J) and **20-11** (35 J), the impact sensitivities of the 3,4,5-trinitropyrazolate salts are greater than 40 J.<sup>305</sup> Based on rather low impact sensitivities, high stabilities, and detonation properties, the 3,4,5-trinitropyrazolate salts have potential as energetic materials.

#### 4.3. 4-Amino-3, 5-dinitro-pyrazole-Based Energetic Salts<sup>306</sup>

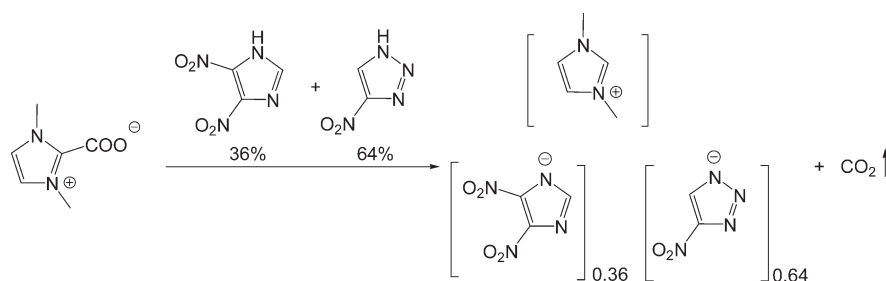
The synthesis of 4-amino-3, 5-dinitro-pyrazole (**19**) first resulted from the alkaline hydrolysis of 3,5-dinitro-4-(methoxycarbonyl) aminopyrazole reported in 1993 (Scheme 73 method 1)<sup>307</sup> and then improved later (Scheme 73 method 2).<sup>308</sup> Recently, the reaction of 3,4,5-trinitro-1*H*-pyrazole with ammonia under mild conditions underwent regioselective nucleophilic substitution of the 4-positioned nitro group to give **19** (Scheme 73 method 3). 4-Amino-3,5-dinitropyrazole (HANP, **21**) has a high crystal density of 1.90 g/cm<sup>3</sup>.<sup>306</sup> It is easily deprotonated to form 4-amino-3,5-dinitropyrazolate anion. Our group synthesized 15 nitrogen-rich 4-amino-3,5-dinitropyrazolate energetic salts in high yield by neutralization or metathesis reactions (Scheme 74).<sup>306</sup>

**Scheme 65. Preparation of Triaminoguanidinium 3,3'-Dinitro-5,5'-azo-1,2,4-triazole**

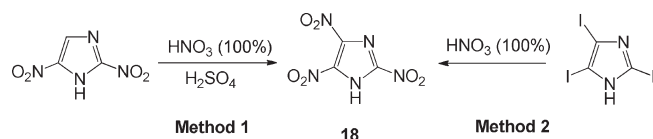




**Scheme 66.** One-Pot Synthesis of the Eutectic Mixture  $[1,3\text{-Dimethyl-imidazolium}][4,5\text{-dinitro-imidazolate}]_{0.36}[4\text{-nitro-triazolate}]_{0.64}$



**Scheme 67.** Synthesis of 2,4,5-Trinitroimidazole



The key properties of the resulting energetic salts are listed in Table 25. The salts exhibit much lower impact sensitivities ( $>60$  J), acceptable densities ( $1.54\text{--}1.84\text{ g cm}^3$ ) and good thermal stabilities ( $169\text{--}303\text{ }^\circ\text{C}$ ).<sup>306</sup> These compounds show detonation pressures ( $20.99\text{--}32.55\text{ GPa}$ ) and velocities ( $7712\text{--}8751\text{ m/s}$ ). The detonation properties of salts **21-9** ( $32.55\text{ GPa}$ ,  $8743\text{ m/s}$ ) and **21-11** ( $28.85\text{ GPa}$ ,  $8751\text{ m/s}$ ) are comparable to those of 1,3,5-triamino-2,4,6-trinitrobenzene (TATB,  $31.15\text{ GPa}$ ,  $8114\text{ m/s}$ ).<sup>306</sup>

## 5. STRUCTURES AND PROPERTIES OF ENERGETIC SALTS

Similar to other energetic materials, higher performance is the prime requirement in the field of research and development of energetic salts. The aim of developing energetic salts is to achieve higher performance for real applications. Compartmentalized molecular level design of new energetic salts based on pairing energetic cations and anions allows for producing energetic salts with diverse physicochemical properties. For instance, 31 azolate salts were synthesized by pairing diverse cations (tetraphenylphosphonium, ethyltriphenylphosphonium, *N*-phenyl pyridinium, 1-butyl-3-methylimidazolium, tetrabutyl, tetraethyl-, and tetramethylammonium) with azolate anions (5-nitrobenzimidazolate, 5-nitrobenzotriazolate, 3,5-dinitro-1,2,4-triazolate, 2,4-dinitroimidazolate, 4-nitro-1,2,3-triazolate, 4,5-dinitroimidazolate, 4,5-dicyanoimidazolate, 4-nitroimidazolate, and tetrazolate) (Scheme 75).<sup>309</sup>

These azolates are stable and favorable structure–property relationships were most often achieved when changing from 4- and 4,5-disubstituted anions to 3,5- and 2,4-disubstituted anions; 3,5-dinitro-1,2,4-triazolate was the most promising anion among all the anions in Scheme 75 based on its contributions to the entire set of target properties.<sup>309</sup> Electron-withdrawing groups, such as nitro or nitrile, destabilized substituents on both the aromatic core of cations and anions. The study allowed for the examination of the effects of both cation and anion on the physicochemical properties of ionic liquids.

The results show that both cations and anions contribute to the physicochemical properties of energetic salts, such as low melting point, high thermal stabilities, good oxygen balance, high nitrogen content, low impact and shock sensitivity, and high

solid-state density, etc. These properties represent the “effectiveness” of the energetic salts. However, these requirements are somewhat mutually exclusive.<sup>309</sup> Most often compounds with lower thermal stability and higher impact sensitivity exhibit better explosive performance and vice versa. Therefore, the most important object of design and synthesis of new energetic salts require them to exhibit good energy capability and optimal safety (reduced vulnerability, shock and impact insensitivity) relative to those in current use.<sup>310</sup>

Characterization of energetic salts include their physical properties, performance, and sensitivities which are based on a series of tests to evaluate their detonation and energy release behavior.<sup>1</sup> This consists of examining (1) the structure of the molecules and particularly the presence of well-known “explosophore” groups (such as the nitro and azide group) to calculate the oxygen balance (OB); (2) the thermal stability of the substance that can be evaluated by calorimetric methods; and (3) a series of tests that include determining density, melting point, and decomposition temperatures.<sup>310</sup>

The syntheses and testing of new energetic salts are costly in terms of time and money. All the new energetic salts require testing not only for their physicochemical properties but also for their toxicological and environmental impact. Taking into account the above considerations, developing simple theoretical and empirical methods are useful for predicting detonation performance or specific impulse, estimating chemical stability (such as sensitivity), and physical and thermodynamic properties of energetic materials. Different theoretical models can reduce costs and inherent danger of tests associated with synthesis, test and evaluation of the energetic salts and eliminate poor candidates for energetic salts before investing in synthesis thus minimizing the waste ensuing from experimental measurements.<sup>311</sup> They allow experimental researchers to expend resources only on those salts that show promise of enhanced performance, reduced sensitivity or reduced environmental hazard, and good physical and thermodynamic properties. In addition, they provide a considerable insight into the understanding of factors affecting the behavior of energetic salts and help the chemist to develop systematic and scientific formulations of appropriate futuristic target molecules with desired performance, sensitivity, and thermochemical properties. Finally, these methods should be cost-effective, environmentally desirable, and have time-saving capabilities.

The use of chemical structure as a means to predict physical properties and physicochemical properties has been the subject of intense research in recent years. The structure–property relationship studies have found wide applications in various research areas of chemistry as an efficient tool in the correlation

Scheme 68. Syntheses of 2,4,5-Trinitroimidazolate Salts

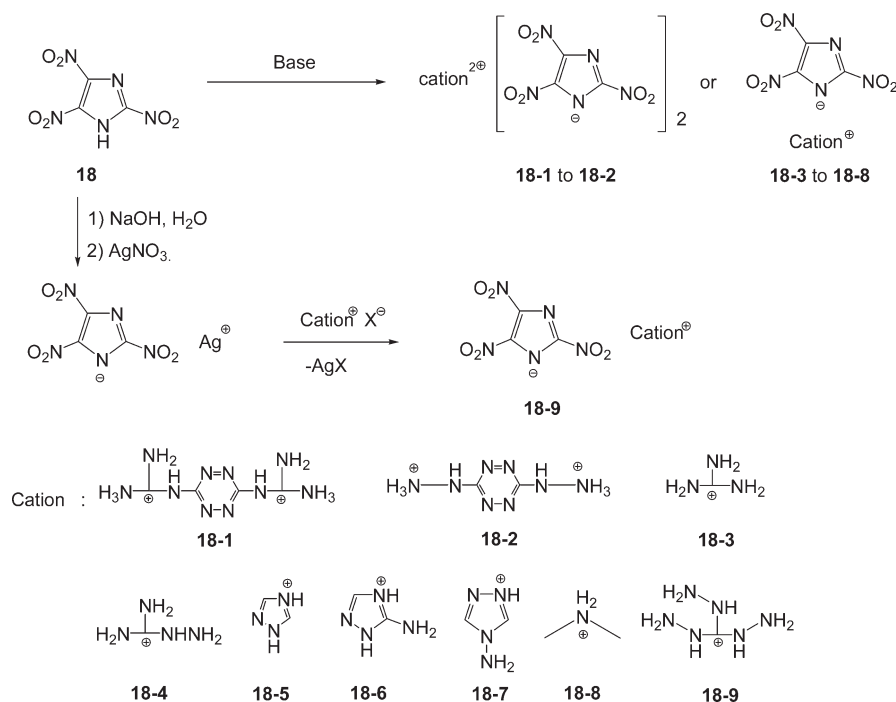


Table 22. Physical Properties of Trinitroimidazolate Salts

salt	density (g/cm <sup>3</sup> )	T <sub>m</sub> (°C)	T <sub>d</sub> (°C)	ΔH <sub>f</sub> <sup>∘</sup> (kJ/mol)	P (GPa)	D (m/s)	I <sub>sp</sub> (s)	ref
18-1	1.76		270.2	267	26.2	7979	220.2	291
18-2	1.86	127.0	198.1	616	34.1	8695	254.8	291
18-3	1.70	174.2	240.7	−51	25.0	7835	226.6	291
18-4	1.75	80.7	253.4	44	28.2	8197	232.4	291
18-5	1.76	146.4	220.5	209	26.8	7963	236.4	291
18-6	1.86		207.8	180	31.0	8416	229.1	291
18-7	1.85	182.1	238.9	310	31.5	8450	241.3	291
18-8	1.70			−54	23.8	7691	222.0	291
18-9	1.71	125.0	214.0	263	28.9	8441	243.2	292

and prediction of diverse physicochemical properties.<sup>312</sup> Most of the key properties of energetic materials such as density, energy, melting points, thermal stability, sensitivity, and toxicity could be predicted by the study of their structures.<sup>313</sup>

Two primary approaches that have been taken in the prediction of physicochemical parameters based on the structure of energetic materials are (1) group contribution methods and (2) quantitative structure–property/activity relationships (QSPR/QSAR). The group contribution methods are based on the numbers and types of molecular groups that form the compound and the interactions between next nearest neighbors in an attempt to address the existence of isomers and their influence on the properties of interest.<sup>314–318</sup> Quantitative structure–property/activity relationships connect physical or chemical properties to a set of molecular descriptors. QSPR and QSAR methodology is based on the development of a mathematical relation between a macroscopic property and the molecular structure for a particular set of similar compounds.<sup>319–324</sup> To date they have been devoted mainly to biological, and toxicological applications but their use to predict physicochemical properties is a growing interest.<sup>319</sup>

Significant efforts have been directed toward development of empirical and theoretical models that will predict various important properties of an energetic material.<sup>310,325–339</sup> Several authors use the concepts of QSPR and QSAR to calculate diverse properties of several energetic materials.<sup>330–339</sup> For energetic ionic liquids and salts, the following methods have commonly been applied: melting point,<sup>313</sup> density,<sup>340,341</sup> and heat of formation.<sup>284,342–346</sup>

Different models and computer codes are validated for the different properties of energetic salts and classes of energetic salts based on their chemical structures. These methods allow an estimate of potential performance or possible hazard for energetic materials and determine if further experimental investigations are needed to evaluate and screen explosive hazards of potentially energetic substances.<sup>337,347,348</sup>

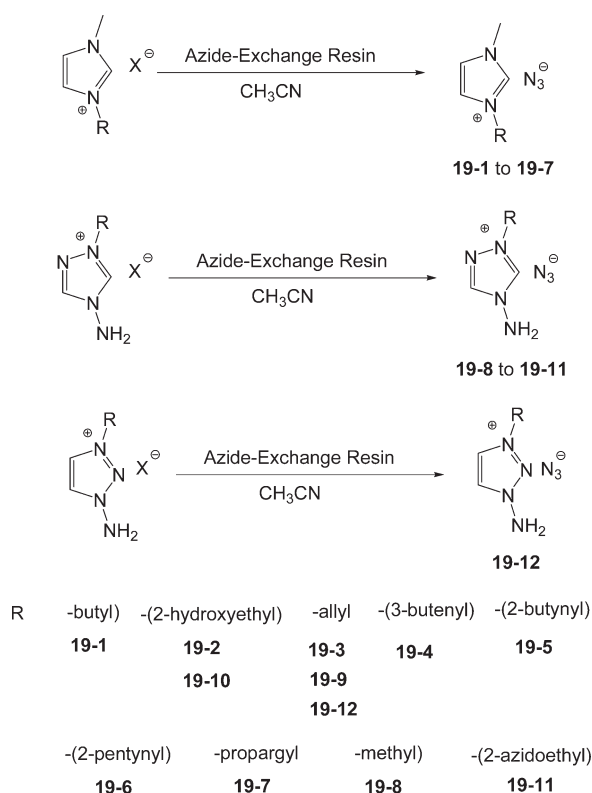
To assess potential performance of an energetic compound in explosive or propellant cases, the heat of formation and density are considered as key properties. These are the important detonation parameters that can be used as the energy available to do mechanical work and estimating potential damage to surroundings. They could be used by some software such as CHEETAH,<sup>124–126</sup> EXPLOS,<sup>117–123</sup> or various empirical methods<sup>348</sup> to calculate

explosive properties, such as detonation pressure, detonation velocity and specific impulse. In the following section, the recent research about the density, and heat of formation of azole-based energetic salts is discussed.

### 5.1. Density

Density is usually calculated from X-ray or empirical formula or determined experimentally by use of a pycnometer.<sup>349</sup> Among all the physical properties of energetic salts, density is crucial because the higher the density, the greater number of moles of an explosive

**Scheme 69. Syntheses of Liquid Azide Ionic Liquids**



that can be packed into a limited volume. The performance of an explosive is greatly sensitive to its crystalline density but is somewhat less sensitive to its heat of formation.<sup>350</sup> Different procedures such as group-contribution and quantum mechanical methods are employed to predict the density of energetic salts.<sup>340,351,352</sup>

QSPRs were first used for liquid densities as well as melting points of a new class of energetic ionic liquids.<sup>340</sup> On the basis of ab initio studies, the molecular geometries of the cations of the ionic liquids were optimized followed by the derivation of the density and melting point from molecular orbital, thermodynamic, and electrostatic descriptors. Good correlations with the experimental data were found. The correlation coefficients for melting point QSPRs (three-parameters) and for density QSPRs (one-parameter) exceed 0.9. The method can be used in the design of energetic salts. Derivation of melting point quantitative structure–property relationships (QSPRs) for energetic ionic liquids could therefore greatly aid in the molecular design of new compounds.<sup>340</sup>

Research on tabulating the volumes of a variety of mainly inorganic cations and anions was done earlier to predict lattice energy<sup>339</sup> recently encouraged us to develop a set of volume parameters for salts and room temperature ionic liquids for the eq 1 (where  $W$  is the molar weight of the energetic salt ( $\text{g mol}^{-1}$ );  $\rho$  is the density; and  $V$  is the molecular volume of the salt).<sup>341</sup>

$$\rho = W / (0.6022V) \quad (1)$$

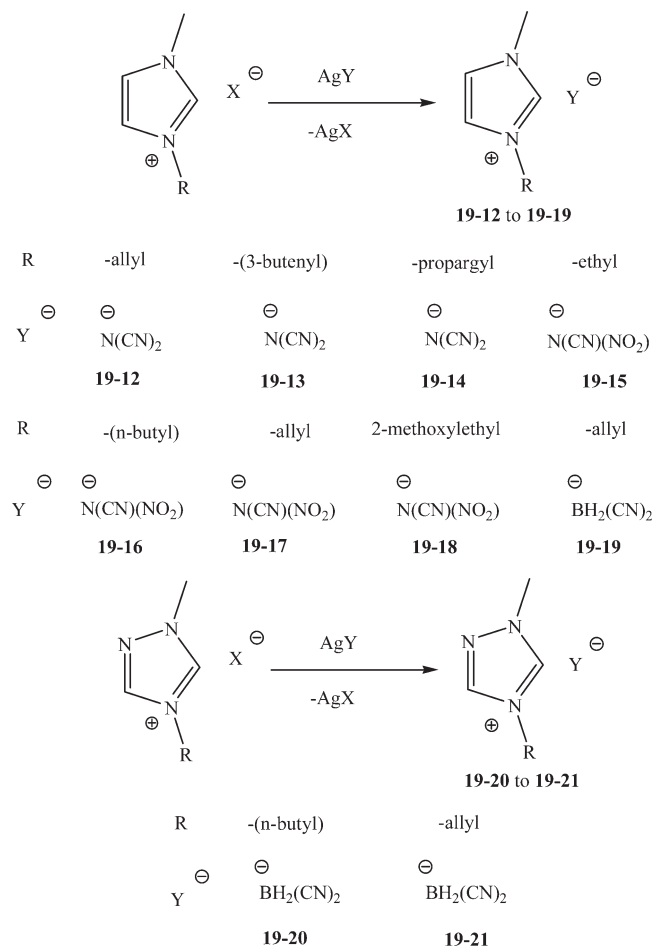
On the basis of this equation, the density of the most common imidazolium, pyridinium, pyrrolidinium, tetralkylammonium, and phosphonium-based room temperature ionic liquids at atmospheric pressure and room temperature can be predicted with a low mean absolute deviation from the experimental values. It proved to be a rapid and facile method of group additivity for estimation of density specifically for room-temperature ionic liquids and salts. To compensate for strong hydrogen bonding in energetic materials, we developed new volume parameters designated for neutral high-energy density materials, which gives a mean absolute deviation (MAD) of  $0.026 \text{ g} \cdot \text{cm}^{-3}$  and a mean relative absolute error of 1.5% for 261 explosives with an average density of  $1.803 \text{ g} \cdot \text{cm}^{-3}$ .<sup>338</sup>

**Table 23. Physical Properties of Azole-Based Hypergolic Salts**

salt	density ( $\text{g}/\text{cm}^3$ )	$T_g$ ( $^{\circ}\text{C}$ )	$T_m$ ( $^{\circ}\text{C}$ )	$T_d$ ( $^{\circ}\text{C}$ )	$\Delta H_f^{\circ}$ ( $\text{kJ}/\text{mol}$ )	ID <sup>a</sup> (ms)	$I_{sp}$ (s)	ref
19-1		−74	36	222	305			299
19-2		−3	36	214	167			299
19-3		−77	19	150	448			299
19-4		−57	45	188	423			299
19-5			66	115	598			299
19-6		−55	19	107	582			299
19-12		−85		207		42		293
19-13		−90		210		27		293
19-14		−61		144		110		293
19-15	1.18	−73		253		78	192.3	297
19-16	1.13	−90		256		81	186.4	297
19-17	1.11	−91		220		46	196.7	297
19-18	1.21	−82		266		65	187.0	297
19-19	0.99	<−80		266		8		292
19-20	0.99	<−80		220		32		292
19-21	1.03	<−80		217		6		292

<sup>a</sup> Oxidizer: White fuming nitric acid (WFNA, 100%  $\text{HNO}_3$ ).

Scheme 70. Syntheses of Hypergolic Ionic Liquids



This methodology was extended by allowing the estimation of densities of ionic liquids in wide ranges of temperatures (273.15–393.15 K) and pressures (0.10–100 MPa) through the use of our proposed parameter table.<sup>336</sup> Predicted densities of ionic liquids are in good agreement with available experimental literature values.

The group additivity method is based on summing-up the volume occupied by each atom or molecular fragment which is a simple procedure to estimate the density of energetic materials, but it cannot provide accurate density values because it does not consider the void between molecules accurately.

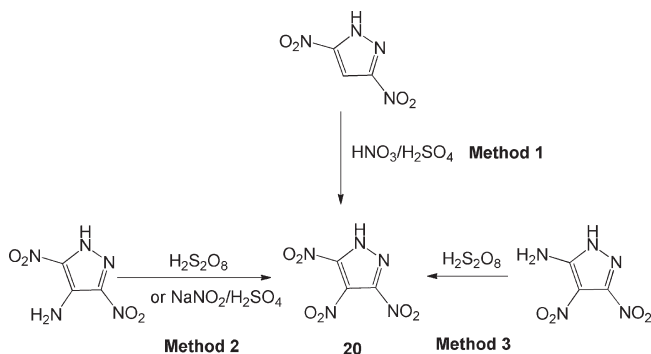
Equation 2, which reflects the intensities of the positive and negative potentials on the surfaces of the cations and anions, was recently developed.<sup>352</sup> In eq 2,  $A_s^+$  is the portion of the surface of the cation that has a positive electrostatic potential, and  $V_s^+$  is the average value of that potential;  $A_s^-$  and  $V_s^-$  are the analogous quantities for an anion.  $\alpha$ ,  $\beta$ ,  $\gamma$ , and  $\delta$  are coefficients.

$$\rho = \alpha(M/V_m) + \beta(V_s^+/A_s^+) + \gamma(V_s^-/A_s^-) + \delta \quad (2)$$

Equation 2 is a promising approach for the reliable prediction of ionic densities. For a database of 25 compounds the average absolute error is 0.033 g cm<sup>-3</sup> and the root-mean-square error is 0.040 g cm<sup>-3</sup>.

Two simple models were proposed to estimate the densities of salts: (1) a straightforward extension of a standard group contribution method and (2) a smarter approach based on

Scheme 71. Syntheses of 3,4,5-Trinitrotriazole



geometrical considerations. The group contribution method is a direct extension of the standard group contribution method, which is on the basis of charged group volumes derived from 1132 salts crystals from the Cambridge Structural Database (CSD).<sup>353</sup> Although such additive approaches have proved quite reliable, except for crystals characterized by low-density packing modes, the method has drawbacks: such as the dramatic increase in the number of parameters making further extension to new groups usually difficult, etc.

As a consequence, a new model based on atoms, rings, and hydrogen bonds was developed involving fewer parameters and taking into account the role of structural features on the crystal volume.<sup>353</sup> Use is made of atomic volumes and structural corrections associated respectively with rings and hydrogen bonds. The method results in 2.41% average absolute difference between the calculated density and the experimental density for 1519 salts. These systematically larger errors in density calculated for salts can be explained by the squeezing effect due to the strong coulomb interactions prevalent in ionic crystals, which might be difficult to describe with additive models. The method is useful to not only predict density at standard conditions but also to predict density at low temperature.<sup>353</sup> The ab initio crystal structure prediction is also a useful molecular simulation technique which uses a good quality model to describe intermolecular interactions among the atoms in crystals.<sup>354</sup>

A quantum mechanically based procedure (B3LYP density functional theory) can be used to predict the crystal density of ionic salts. In eq 3, the volume ( $V_m$ ) of the formula unit  $M_pX_q$  of an ionic crystal is simply the sum of the volumes of the ions contained in the formula unit

$$V_m = pV_{M^+} + qV_{X^-} \quad (3)$$

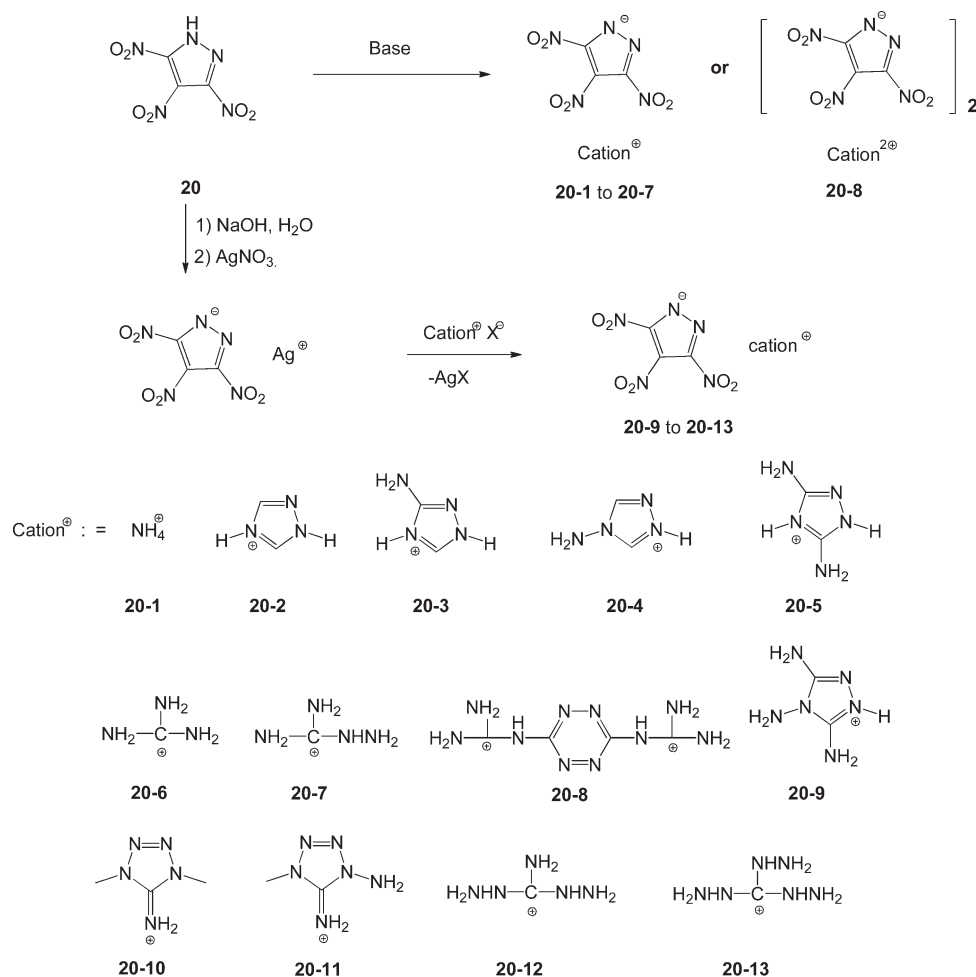
For the salts which contain hydrogen atoms, the authors use eq 4 to correct the volume of the salt

$$V_{(corrected)Opt} = V_{(uncorrected)Opt} - [0.6763 + 0.9418 \times (\text{no. of H atoms in the ion})] \quad (4)$$

The results indicate that, the root-mean-square (rms) deviation from experiment is within 5% (uncorrected) and 1.3% (corrected) for 71 ionic crystals.<sup>354</sup> The same methods were successfully used to predict substituted protonated and methylated tetrazole cation-containing salts.<sup>346</sup>

Although the quantum mechanically based procedure could be used to predict density of salts without a prior knowledge of their crystal structure, this approach has some limitations because it must be used by experts and takes much computational effort.

Scheme 72. Syntheses of 3,4,5-Trinitropyrazolate Salts

Table 24. Properties of Trinitropyrazolate Salts<sup>305</sup>

salt	density (g/cm <sup>3</sup> )	T <sub>m</sub> (°C)	T <sub>d</sub> (°C)	ΔH <sub>f</sub> <sup>o</sup> (kJ/mol)	P (GPa)	D (m/s)	IS (J)	I <sub>sp</sub> (s)
20-1	1.73		224	61	29.9	8461	40	263.0
20-2	1.69	158	167	299	25.6	7871	>40	245.0
20-3	1.71	171	171	274	26.0	7972	>40	237.9
20-4	1.77	168	168	401	31.9	8543	>40	269.6
20-5	1.76	188	196	236	27.7	8216	>40	230.2
20-6	1.66	163	235	28	24.7	7865	>40	235.6
20-7	1.69	136	222	134	26.9	8134	>40	240.9
20-8	1.68		243	452	24.3	7817	>40	228.9
20-9	1.76	206	206	355	28.8	8359	>40	236.5
20-10	1.61	166	219	375	23.7	7586	>40	230.5
20-11	1.64	120	167	460	25.2	7922	35	245.2
20-12	1.62	122	197	247	25.3	7983	>40	246.3
20-13	1.65	125	184	353	27.2	8236	>40	250.5

## 5.2. Heat of Formation

Heat of formation is another important physical property of energetic salts. It is a measure of energy content of an energetic material that can decompose, ignite, and explode by heat and impact. It is related directly to detonation parameters. Different approaches can be used to predict heats of formation of different classes of

energetic compounds which have been reviewed by some authors.<sup>339,355,356</sup> Although quantum mechanical and theoretical models can provide good results in prediction of gas phase heat of formation, often the standard state of the energetic salts of interest corresponds to the condensed phase. Thus, it is important to improve models for reliable prediction of condensed phase heats of formation

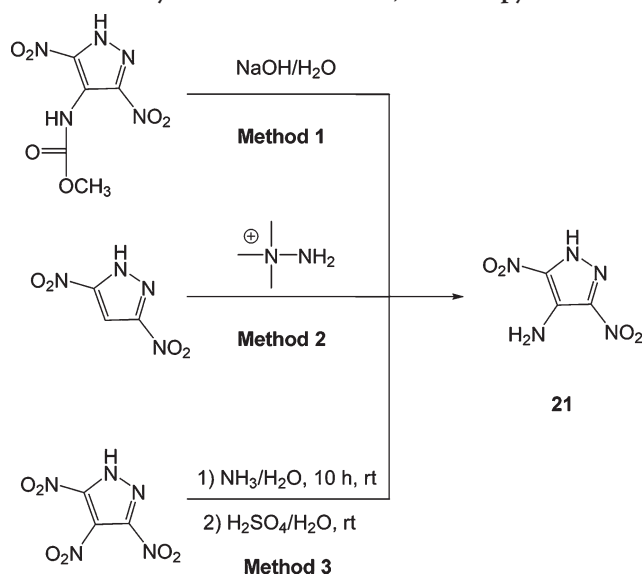


of energetic salts. Condensed phase heats of formation of energetic salts can be determined using the gas phase heat of formation and heat of phase transition (lattice energy) according to Hess's law of constant summation (Born–Haber energy cycle) (Scheme 76).<sup>345</sup>

On the basis of Scheme 76, the heat of formation of a salt can be simplified by the formula

$$\Delta H_f^\circ(\text{salt}, 298 \text{ K}) = \Delta H_f^\circ(\text{cation}, 298 \text{ K}) + \Delta H_f^\circ(\text{anion}, 298 \text{ K}) - \Delta H_L$$

Scheme 73. Syntheses of 4-Amino-3,5-dinitro-pyrazole



where  $\Delta H_L$  is the lattice energy of the salts, which could be predicted by the formula as<sup>339</sup>

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

where  $nM$  and  $nX$  depend on the nature of the ions  $M_p^+$  and  $X_q^-$ , respectively, and are equal to 3 for monatomic ions, 5 for linear polyatomic ions, and 6 for nonlinear polyatomic ions. The equation for lattice potential energy  $U_{\text{POT}}$  has the form

$$U_{\text{POT}}/\text{kJ mol}^{-1} = \gamma(\rho_m/M_m)^{1/3} + \delta$$

where  $\rho_m/\text{g cm}^{-3}$  is the density,  $M_m$  is the chemical formula mass of the ionic material, and values for  $\gamma$  and the coefficients  $\gamma/\text{kJ mol}^{-1} \text{ cm}$  and  $\delta/\text{kJ mol}^{-1}$  are taken from the literature.<sup>339</sup>

Systematic studies of the thermodynamics for forming a variety of imidazolium-based salts and ionic liquids have been carried out. DFT (B3LYP) and MP2 calculations are used in conjunction with an empirical approach based on molecular volumes to estimate the lattice enthalpies and entropies of various organic compounds. It has been applied to substituted imidazoles (precursors of ionic liquids or salts) and is a reliable method to predict the ability to synthesize a variety of salts including ones which are potentially HEDMs.<sup>344</sup> In addition to imidazolium salts, they extended their study to the heat of formation of triazolium and tetrazolium salts as well.<sup>343</sup> The heats of formation of substituted imidazole, 1,2,4-triazole, and tetrazole molecules and ions containing amino, azido, and nitro (including methyl) substituents are calculated using an isodesmic approach at the MP2/complete basis set level. On the basis of comparisons with experimental data for neutral analogues, the

Scheme 74. Syntheses of 4-Amino-3,5-dinitro-pyrazolate Salts

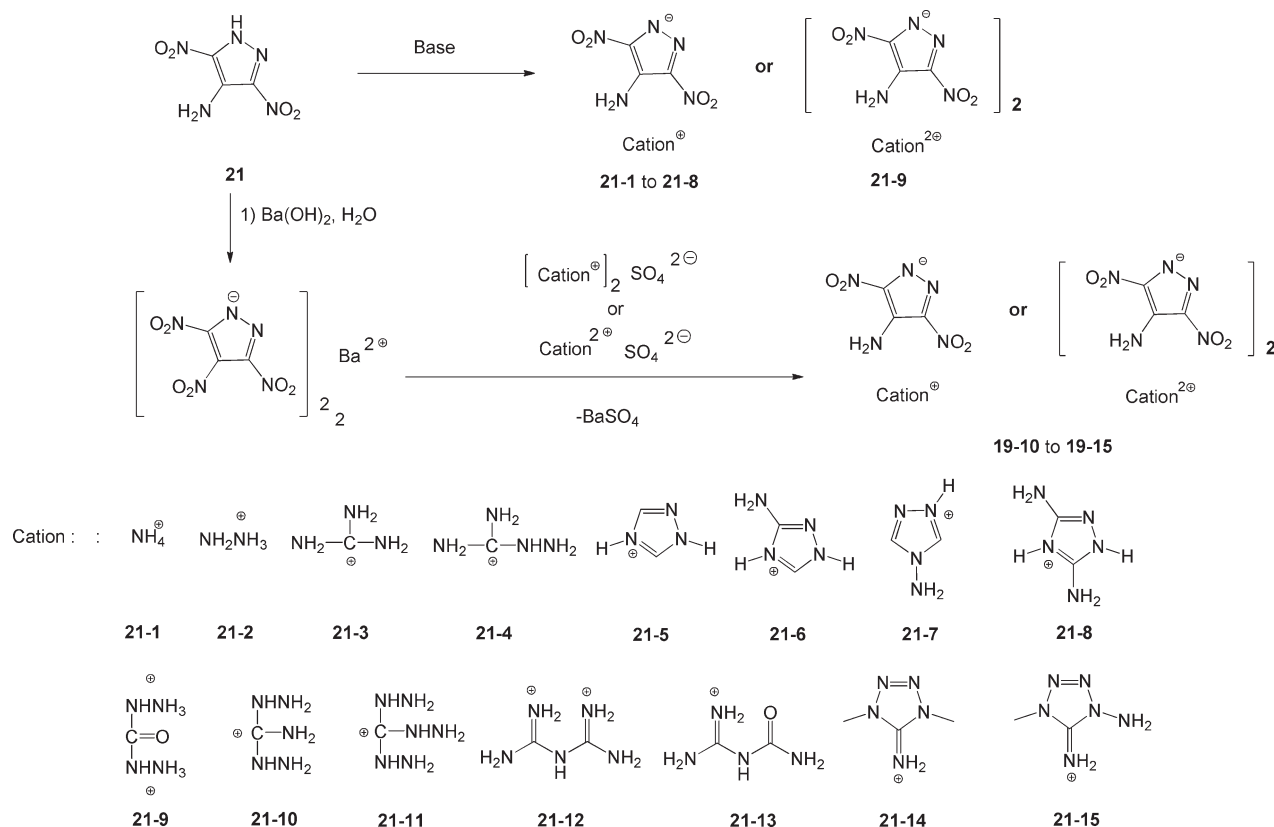
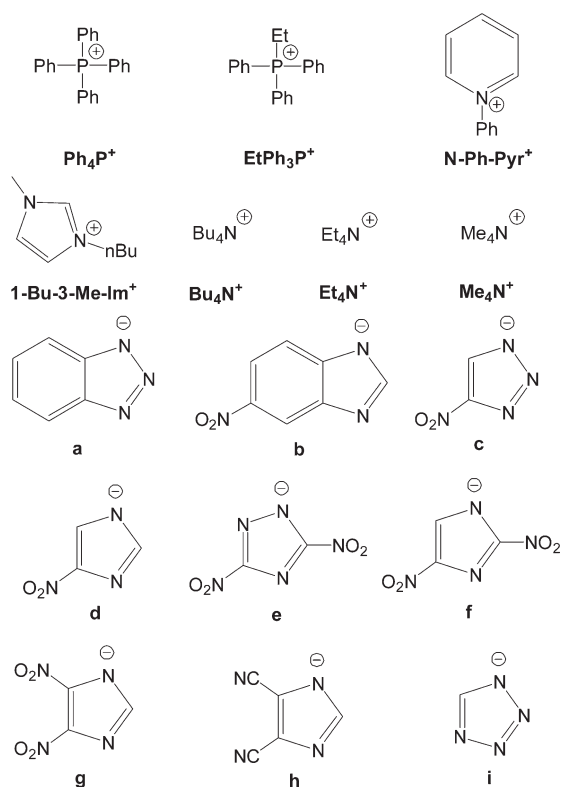


Table 25. Properties of 4-Amino-3,5-dinitro-pyrazolate Salts<sup>306</sup>

salt	density (g/cm <sup>3</sup> )	T <sub>m</sub> (°C)	T <sub>d</sub> (°C)	ΔH <sub>f</sub> <sup>o</sup> (kJ/mol)	P (GPa)	D (m/s)	I <sub>sp</sub> (s)
21-1	1.63		275	65	26.3	8139	230.9
21-2	1.64		221	223	26.4	8193	245.2
21-3	1.63		303	36	21.6	7717	205.5
21-4	1.69	223	223	140	25.2	8244	212.5
21-5	1.62		179	310	22.7	7444	221.9
21-6	1.67	257	257	284	22.4	7725	215.9
21-7	1.73	188	223	411	25.8	8123	228.2
21-8	1.79	270	270	241	27.1	8416	209.5
21-9	1.84	193	193	211	32.5	8743	230.6
21-10	1.67	201	201	251	28.9	8351	219.6
21-11	1.71		229	357	28.9	8751	225.6
21-12	1.72		169	100	24.2	7984	205.9
21-13	1.73	243	243	−166	23.1	7935	191.7
21-14	1.54	184	206	389	21.0	7712	218.4
21-15	1.60	173	173	471	22.4	7780	226.5

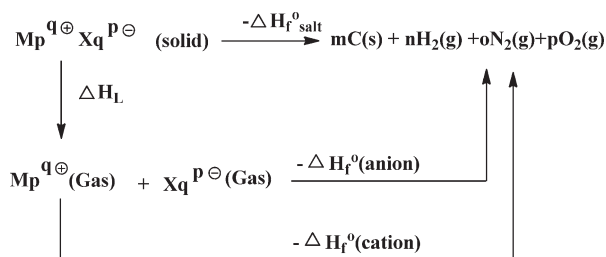
Scheme 75. Cation and Azolate Anion Combinations for Ionic Liquid



isodesmic reaction approach is accurate to <3 kcal/mol for the predicted cation and anion  $\Delta H_f^o$ . The  $\Delta H_f^o$  values of the energetic salts in the solid state are obtained. The results show that the substitution of functional groups on carbon versus nitrogen atoms of the heterocyclic cations has interesting stabilization and destabilization effects, respectively.

A computational approach to the prediction of the heats of formation of solid-state energetic salts from electronic structure and volume-based thermodynamics (VBT) calculations has been described. The predicted  $\Delta H_f^o$  values of the energetic salts are

Scheme 76. Born–Haber Cycle for the Formation of Energetic Salts



estimated to have error bars of 6–7 kcal/mol, on the basis of comparisons to established experimental  $\Delta H_f^o$  values of a subset of the salts studied. Based on a similar method, our group calculated heats of formation of 119 energetic salts.<sup>345</sup> Heats of formation of ions (cations and anions) and lattice energies were calculated separately based on Born–Haber energy cycles (Scheme 76). The method is straightforward and convenient and can be used to screen large numbers of energetic salts.<sup>345</sup>

Using similar methods, the effects of different substituents and energetic anions on the densities, heats of formation, energetic properties, and thermodynamics of formation for a series of energetic tetrazole salts were studied.<sup>346</sup> Results show that the functional groups, such as  $-\text{NO}_2$ ,  $-\text{NF}_2$ ,  $-\text{CN}$ ,  $-\text{N}_3$ , or  $-\text{NH}_2$ , are helpful in increasing the heats of formation of the tetrazolium salts. The  $-\text{NO}_2$  or  $-\text{NF}_2$  group is an effective substituent to increase the densities of substituted tetrazolium salts. Methylated tetrazole salts have lower heats of formation and density than that of protonated tetrazole salts. In addition, the  $-\text{NO}_2$ ,  $-\text{NF}_2$ , or  $-\text{N}_3$  group is an effective structural unit for enhancing the detonation performance for the substituted tetrazolium salts.<sup>346</sup>

The different methods to calculate solid phase heats of formation of ionic molecular crystals have been compared.<sup>342</sup> The G3MP2B3 method or an atom-equivalent method to predict gas phase heats of formation of the ionic components was used. Six methods to predict the lattice energies of the salts (three used extended lattice summations assuming the experimental crystal structures and an interaction potential composed of van der

Waals and Coulombic contributions) were utilized. The Coulombic terms employed three different quantum mechanically derived partial atomic charges (CHELPG, Mulliken, and RESP).<sup>342</sup>

The results show that the  $\Delta H_f$  values of 25 energetic molecular ionic salts generated using G3MP2B3  $\Delta H_f(g)$  were in better agreement with experimental values than those using the atom-equivalent method. For the entire set of compounds,  $\Delta H_f$  values calculated using extended lattice summations to generate the lattice enthalpies were in better agreement with experiment. The Jenkins/Gutowski models are convenient methods which require very modest computational resources (and can be

obtained quickly) and produce results that are approximately as accurate as those obtained using methods that explicitly calculate interatomic interactions in an ionic crystal (extended lattice summations). However, the Gutowski and Jenkins models have large potential errors for predicting lattice potential energies (errors for 1:1 molecular ionic crystals are 24–28 kcal/mol).<sup>342</sup>

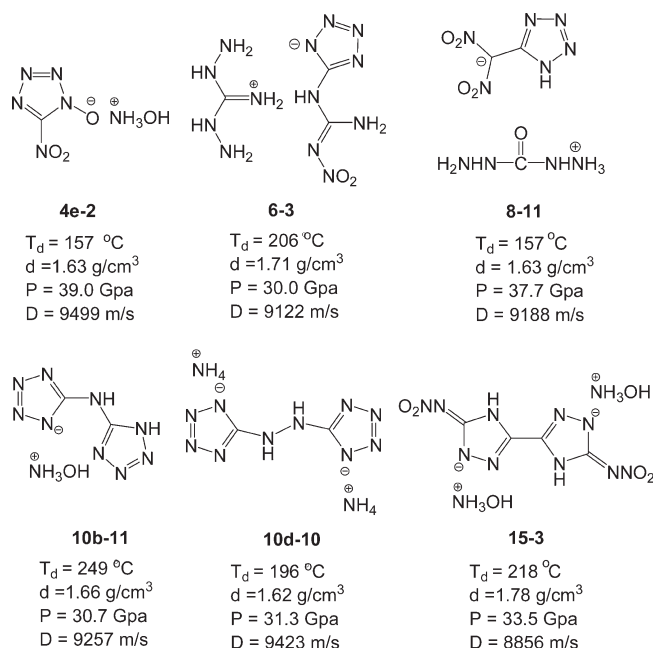
### 5.3. Are Energetic Salts Really That Green?

The idea of energetic ionic liquids (salts) came from ionic liquids. Because they have low vapor pressures under normal conditions,<sup>84</sup> they are considered to be “greener” energetic materials than the traditional materials. This kind of greenness is only limited to their one physical property; through the evaporation or sublimation to produce pollutants in the environment. But it is misinterpreted since the green energetic material should possess broader green properties including low toxicity and biodegradability. While most of the information about their physical, thermodynamic or detonation properties has been extended continuously, limited data with regard to the toxicity and ecotoxicity of energetic salts have been available. Similar to that of ionic liquids, the “green character” of energetic ionic liquids has usually been justified with their negligible vapor pressure, but even if ionic liquids do not evaporate and do not contribute to air pollution most of them are water-soluble and could enter the environment by this path (e.g., accidental spills, effluents). It should be noted that there have been many debates about ionic liquid greenness, the slight solubility of ionic liquids in water poses a potential risk to aquatic ecosystems, their low volatility can not completely eliminate potential environmental hazards and might pose serious threats to aquatic and terrestrial ecosystems.<sup>357–370</sup>

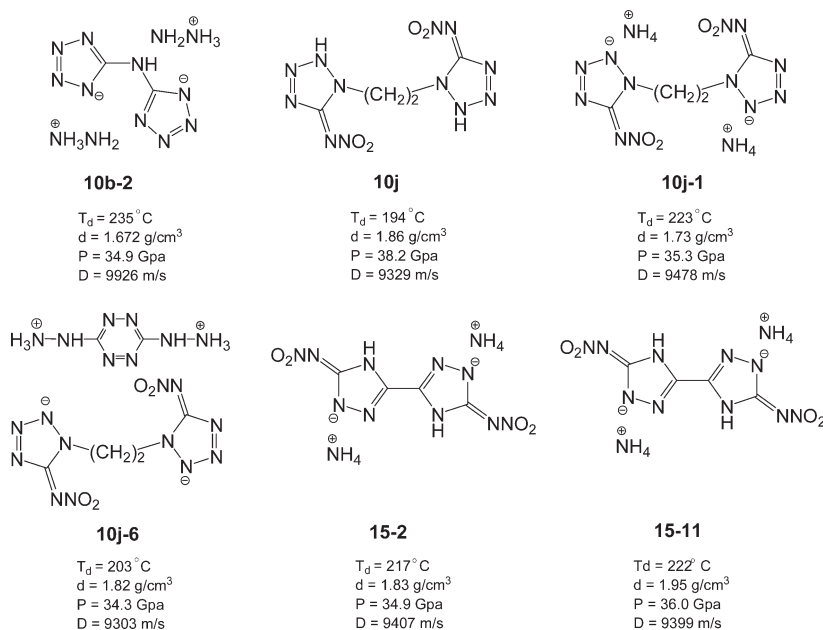
A considerable number of precursors to ionic liquids are toxic and environmentally hazardous. The studies of environmental impacts and toxicity of ionic liquids have shown that many of the commonly used ionic liquids are toxic in nature and their toxicities vary considerably across organisms and trophic levels.<sup>365–367,369,371</sup>

On the other hand, the energetic functional groups in energetic salts, such as nitro,<sup>372–376</sup> azide,<sup>377,378</sup> and cyano

**Scheme 77. Selected Energetic Azole-Based Salts As Candidates to Replace RDX**



**Scheme 78. Selected Energetic Azole and Their Salts As Candidates to Replace RDX**



groups<sup>379,380</sup> may have potential toxicity. In addition, the common explosives, such as TNT, HMX, and RDX, etc., and their degradation products have demonstrated toxic effects with symptoms of exposure that include methemoglobinemia, kidney trouble, jaundice, etc.<sup>56,82,381–383</sup> They can be toxic to a variety of biota and show a broad spectrum of toxicological behaviors ranging from mutagenic to carcinogenic activity.<sup>384–386</sup> Their long-term use has resulted in contamination by explosives at artillery and firing ranges and, in some cases, have become a major health hazard and environmental problems for both military and civilian personnel. In addition, the reductive transformation of the nitramine explosives (most are N-nitroso compounds from RDX, HMX, and CI-20, etc.) in the environment caused concerns among the general public because of potential carcinogenic effects. Proposed biodegradation mechanisms for cyclic nitramines include (a) formation of a nitramine free radical and loss of nitro functional groups, (b) reduction of nitro functional groups, (c) direct enzymatic cleavage, (d)  $\alpha$ -hydroxylation, or (e) hydride ion transfer. Pathway intermediates spontaneously decompose in water producing nitrite, nitrous oxide, formaldehyde, or formic acid as common end products.<sup>46</sup> Their N-nitroso metabolites have raised health concerns about human and environmental exposure. It has long been known that RDX exposure causes neurotoxicity, immunotoxicity, and an increased likelihood of cancer. The presence of those compounds in the environment may pose ecological risks and represent a significant remediation challenge.<sup>387</sup>

The principal problems associated with the use of the above-mentioned materials are the environmentally detrimental gases (i.e., NO<sub>x</sub> gases) formed upon decomposition and the fact that the performance of a material is often associated with high sensitivity to shock or friction, making handling of the compound troublesome. The Environmental Protection Agency has listed the cyclic nitramine RDX as a priority pollutant and HMX as a contaminant of concern.<sup>40</sup>

At this point, attention should be directed not only to the physical and detonation properties of the compounds, but also their biodegradability and toxicity. Considering that ionic liquids may not be green and based on the structures, most azole-based-energetic salts containing azide, cyano and nitroamine groups have potential toxicity. We can assume that the new azole-based energetic ionic liquids (salts) should not be touted as green chemicals simply because of their low volatility and the concomitant improvement in air quality. More information such as biodegradability and toxicity, etc., is needed to assess their potential impacts on the environment.

## 6. CONCLUSIONS AND FUTURE TRENDS

It is apparent that intensification in design and syntheses of modern HEDMs and most specifically in energetic salts is growing in interest among energetic materials researchers. This is not only because of the potential environmental impact if translated into applications to replace traditional energetic compounds, but also because it is attractive and challenging to achieve the molecular design of energetic materials that contain more energy, higher density, and better detonation properties.

It has been shown that modification of azoles with either a mono- or multifunctional energy group builds molecules which may be transformed into salts through neutralization or quaternization reactions combined with subsequent metathesis. In this

review, we used criteria that new HEDMs should meet to be considered possible replacements for commonly used energetic compounds such as RDX or HMX.<sup>18</sup> Ideally, new compounds should have detonation velocities ( $D$ ) greater than 8500 ms<sup>-1</sup> (RDX is 8977 ms<sup>-1</sup>)<sup>139</sup> and good thermal stabilities ( $T_d > 200$  °C); they should also be hydrolytically stable with shelf lives longer than 15 years, be compatible with binders or plasticizers, and be insensitive to impact ( $>7$  J) and friction ( $>120$  N) and have low (no) solubility in water. The decomposition products should be environmentally benign, and the yield for synthesis should be high and the associated cost low.<sup>18</sup> For the purpose of replacing traditional explosives, there are many salts collected in this review that could be used as promising candidates for pyrotechnics (1-3, 1-8, 2-11, 2-12, 2-13, 2-14, 2-15, 2a-6, 2a-7, 3c-1, 3d-3, 3e-1, 3-15, 3-16, 3a-7, 3b-4, 3b-5, 9-3, 9-4, 9-5, and 10b-21). In addition, some of the salts (2g, 3-5–3-11, 4-4, 4-18, 4-20, 4-21, 5f-4, 6-3, 6-4, 6-6–6-10, 7-1, 7-2, 7-4–7-6, 7-9, 7-11–7-13, 8-5, 8-10–8-15, 8-21, 8-23, 10c-2, 10c-22, 10d, 10e-1, 16-1–16-9, 17-1–17-10, 18-1–18-13) are potential propellants due to their good detonation properties and high  $I_{sp}$  values. Among all the collected azole-based salts in this review, while many salts have physical and detonation properties competitive with TNT or TATB, several compounds have similar or even better detonation properties compared to RDX (1-10, 5-3, 4e-2, 6-3, 6-6, 8-11, 10b-3, 10b-10, 10b-11, 10d-11, 15-3) and HMX (2-8, 4, 4e, 4e-2, 6-4, 8, 10b-2, 10b-19, 10d-10, 10j, 10j-1, 10j-6, 15-2, 15-11). When considering thermal stabilities and the sensitivities of the compounds, 4e-2, 6-3, 8-11, 10b-10, 10b-11, 10d-11, and 15-3 could be possible candidates to replace RDX (Scheme 77). Similarly, 10b-2, 10j, 10j-1, 10j-6, 15-2, and 15-11 may be possible candidates to replace HMX (Scheme 78). Among them, 19-1–19-21 provide a new path for transferring ionic liquids into bipropellant applications. The combination of different cations and anions can be used for fine-tuning the energy content, and thus the performance of the hypergolic ionic liquids.<sup>292–301</sup> These new hypergolic ionic liquids may provide a potential replacement for the highly toxic hydrazine and its derivatives.

This indicates that it is possible to have well-defined neutral molecules and their cations or anions for achieving energetic salts with good performance to replace traditional energetic materials. To accomplish that, it is important to start by understanding the relationship between molecular structure and energetic properties. Only through this knowledge will it be possible to rationalize the design of the molecule required and to try to synthesize the corresponding energetic salts. This is true regardless of whether or not the functional group or the ions selected for the modification of the salts will give high density, high energy, high nitrogen content, high thermal stability, or a combination thereof. Furthermore, and although it is not emphasized in the review, theoretical predictions (density, heat of formation, sensitivity parameters, thermal stability and detonation properties) will help to achieve better physical parameters, lessen expense, and reduce risk in experiments. The more reasonable procedure to search for energetic salts with the desired physicochemical properties may include three steps. The first step is the selection of possible cations and anions that may ensure the necessary properties of the target energetic. The second step is the estimation of properties for the selected energetic salts and selection of the most promising structures which may be the targets of a subsequent synthetic search. Third, only then should the syntheses of the target energetic salts and determination of their physical properties and detonation performance be undertaken.



The numerous publications on the synthesis and study of energetic salts in recent years reveal that this field is of major interest to the chemical community. We believe that working in this field is more satisfying if expertise from organic, inorganic, physical, and theoretical chemistry, materials science, nanoscience, toxicology, and engineering can be combined. If a symbiosis among the different disciplines is achieved, the reward will be not only to increase our fundamental knowledge of energetic materials but also to be able to transfer that knowledge into industrial applications. The use of eco friendly energetic salts can help to achieve a more sustainable chemical process, with a corresponding positive impact of chemistry on our society. Finally, it is the hope of the authors that this review will stimulate further work.

## 7. CAUTION

Readers are reminded that the information given in this review is intended to cover the progress of recent research on energetic azole salts. Most of the molecules (salts) collected in this review are nevertheless energetic materials that may be explosive under certain conditions. Their syntheses should be carried out by experienced personnel and handled with caution. In any case, carefully planned safety protocols and proper protective equipment, such as Kevlar gloves, ear protection, safety shoes and plastic spatulas, should be utilized at all times especially when working on a large scale (>1 g). The authors strongly suggest that the original references be consulted for detailed safety information.

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## DEDICATION

Dedicated to Professor Malcolm MacKenzie Renfrew on the occasion of his 101st birthday.

## GLOSSARY

$\Delta H_f^\circ$	standard heat of formation (kJ/mol)
HMX	1,3,5,7-tetranitro-1,3,5,7-tetrazocane
TNT	trinitrotoluene or 2-methyl-1,3,5-trinitrobenzene
RDX	1,3,5-trinitroperhydro-1,3,5-triazine
TATB	1,3,5-triamino-2,4,6-trinitrobenzene
$d$	density (g/cm <sup>3</sup> )
$T$	temperature (°C)
$T_m$	melting Point (°C)
$T_d$	decomposition temperature (°C)
$T_g$	glass transition temperature (°C)
$P$	detonation pressure (Gpa)
$D$	detonation velocity (m/s)
IS	impact sensitivity (J)
FS	friction sensitivity (N)
ESD	electrostatic discharge sensitivity (mJ)
$I_{sp}$	specific impulse (impulse per unit weight-on-earth of propellant in seconds), etc

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