

Nitrogen-Rich Heterocycles

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Abstract Many advantages accrue from nitrogen-rich heterocyclic compounds compared to traditional molecular energetic compounds. Utilization of heterocyclic nitrogen-containing cations and anions in energetic salts gives rise to lower vapor pressures, higher heats of formation and higher densities. Additionally, smaller amounts of hydrogen and carbon contribute to a better oxygen balance than normally is found with their carbocyclic analogues. Nitrogen-rich compounds are promising high energetic materials that may be more acceptable than their alternatives for both industrial and military uses since a higher percentage of their decomposition products will be dinitrogen.

Keywords Nitrogen rich · Energetic · Heterocycles · Heat of formation · Density · Thermochemistry

1 Introduction

Energetic materials store relatively large amounts of available energy that is compact and readily deliverable. Explosives are employed when very rapid rates of energy application and high pressures are essential, for example to produce high intensity shock waves in air, water, rock, and water such as in mining, road construction, and other civil engineering purposes; in shaped charges and many specialty devices requiring high rates of energy transmission; and for initiation of detonation phenomena. However, wherever a readily controllable source of energy is required for periods of time ranging from milliseconds in guns to seconds in rockets, propellants which evolve gases are employed as a working fluid for propelling projectiles and rockets, driving turbines, operating pumps, and starting engines. For industrial purposes, more than 90% of the energetic compositions used are based on ammonium nitrate [1, 2]. The single-component explosives most commonly employed for military compositions are RDX, HMX, TNT, nitrocellulose, and nitroglycerin [1–16].

Research programs worldwide endeavor to discover high-energy density materials (HEDM) with high performance and/or enhanced insensitivity with respect to thermal shock, friction, and electrostatic discharge. These modern HEDMs derive most of their energy either from: (i) their very high positive heats of formation; or (ii) oxidation of the carbon backbone, as with traditional energetic materials [17, 18]. The first group of energetic materials is exemplified by modern nitro-compounds, such as: CL-20 (2,4,6,8,10,12-(hexanitro-hexaaza) cyclododecane), TNAZ (1,3,3-trinitroazetidine), FOX-7 (1,1-diamino-2,2-dinitroethene), hepta- and octanitrocubanes (having high densities and energies utilizing substantial cage strain), 3,3'-azobis (6-amino-1,2,4,5-tetrazine), and tetrazole azide. TNT (trinitrotoluene), RDX (1,3,5-trinitro-1,3,5-triazacyclohexane), and HMX (1,3,5,7-tetranitro-1,3,5,7 tetraazacyclooctane) are found in the second group [19–23].

High-nitrogen compounds form a unique class of energetic materials whose energy is derived from their very high heats of formation directly attributable to the large number of inherently energetic N–N and C–N bonds rather than from the overall heats of combustion [24]. Heterocyclic-based molecular compounds have most often been utilized in energetic roles due to higher heats of formation, density, and oxygen balance than those of their carbocyclic analogues. In the cases where heterocyclic rings (containing amino, nitro, or azide substituents) are paired with nitrate, perchlorate, dinitramide, or picrate anions, highly energetic salts are formed. With the ex-

ception of perchlorate, these salts are more environmentally acceptable since a higher percentage of their decomposition products is dinitrogen. Another area of expanding interest is based on high energy salts in which both the cation and the anion are high-nitrogen species. All of these energetic salts possess advantages over non-ionic molecules due to lower vapor pressures and higher densities. While the use of high nitrogen compounds is likely to be limited because of cost, the main advantages of such compounds would be for low flame temperature (low gun barrel corrosion), tactical missiles, and low signature among others.

Over the past several years a relatively large number of publications describing energetic nitrogen-rich salts have appeared. This review which covers this chemistry from January 1999 through late 2006 is timely and arises because of our continuing involvement in this subject. By covering the current advances in this rapidly growing field, the review should be of great interest to the scientific community.

2

Triazolium-Based Heterocycles

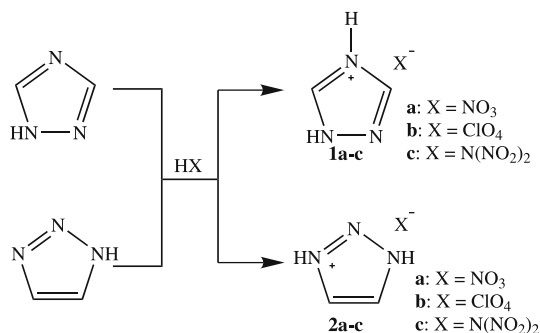
Triazoles are five-membered aromatic heterocycles that contain three nitrogen atoms located at the 1,2,3 or 1,2,4 positions in the ring. A large number of ionic compounds that contain a triazole derivative are described as energetic materials.

2.1

1,2,3- and 1,2,4-Triazolium Heterocycles

1,2,3-triazole and 1,2,4-triazole have positive heats of formation of 272 kJ/mol and 109 kJ/mol, respectively [25, 26]. The salts comprised of the protonated heterocyclic cations paired with perchlorate, nitrate, or dinitramide anions were initially synthesized [27–29]. Reactions of 1,2,4-triazole or its 1,2,3-isomer with concentrated nitric, perchloric, or dinitramidic acid gave excellent yields of 1,2,4- or 1,2,3-triazolium nitrate (**1a**) or (**2a**), perchlorate (**1b**) or (**2b**), and dinitramide (**1c**) or (**2c**), respectively (Scheme 1). All the salts were characterized by Raman, IR, and NMR spectroscopy, density determination, elemental analysis, DSC (differential scanning calorimetry), TGA (thermogravimetric analysis), and initial safety testing. The melting points of 1,2,3-triazolium salts are lower than their 1,2,4-triazolium analogues (Table 1). Some of these salts (**1b–c**, **2a–c**) have melting points < 100 °C and thus fall into the ionic liquid class.

These salts are energetic and are stable at moderate temperatures, with the two perchlorate salts the most thermally stable, followed by the nitrates, and the dinitramides the least. A single crystal X-ray diffraction study of **1b**

**Scheme 1****Table 1** Yields, thermal characteristics, and densities of 1,2,4- and 1,2,3-triazolium salts

Compound	Yield (%)	Anion	T _m °C	T _d °C	Density (calc.) g/cm ³	ΔH_f° kJ/mol
1a	99	NO ₃ ⁻	137	182	1.64 (1.55)	- 42.7
1b	93	ClO ₄ ⁻	89	285	1.96 (1.75)	- 1.3
1c	93	N(NO ₂) ₂ ⁻	75	120	1.66 (1.64)	149.9
2a	99	NO ₃ ⁻	68	125	1.57 (1.55)	42.9
2b	85	ClO ₄ ⁻	73	200	1.79 (1.77)	90.4
2c	99	N(NO ₂) ₂ ⁻	61	80	1.66 (1.64)	228.2

T_m, melting point, T_d, thermal degradation temperature, ΔH_f° standard heat of formation (calculated by Gaussian 03)

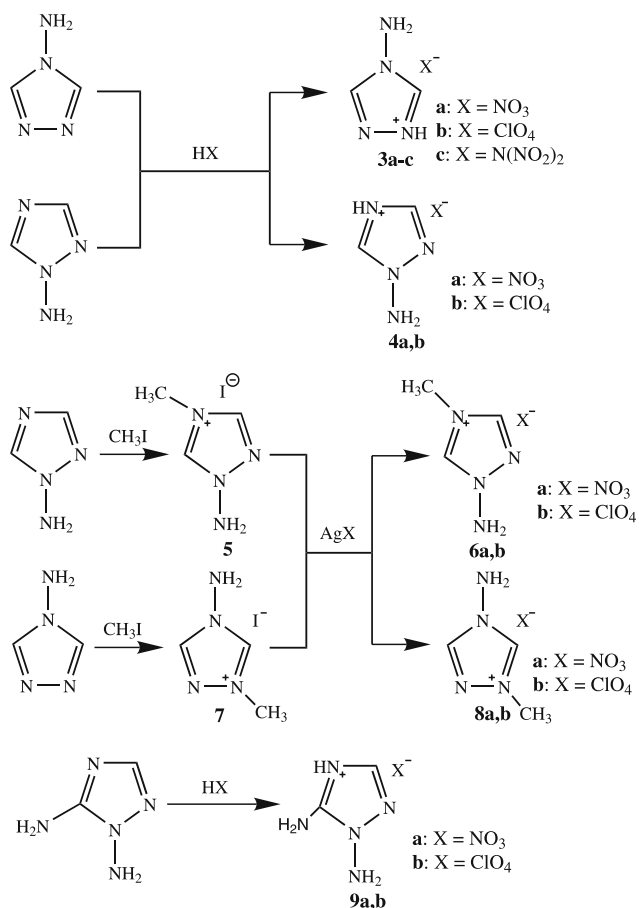
showed that significant hydrogen bonding exists between the perchlorate anion and the protonated 1,2,4-triazolium ring, which likely contributes to its relatively high density. Interestingly, the 1,2,3-triazolium salts are in general less dense, which suggests less efficient packing in the crystal.

2.2

Triazolium Heterocycles Containing Amino Substituents

Incorporation of amino groups into a heterocyclic triazole ring is one of the simplest routes to enhance thermal stability [8]. The N-amino group behaves as an electron-withdrawing group in these high-nitrogen heterocycles that, when paired with perchlorate, nitrate, or dinitramide anions, form energetic salts. 4-Amino-1,2,4-triazolium nitrate (**3a**), perchlorate (**3b**), and dinitramide (**3c**) are formed by the reaction of 4-amino-1,2,4-triazole with the concentrated acids, HNO₃, HClO₄, and HN(NO₂)₂, respectively, under reaction conditions analogous to those utilized for (**1a-c**) and (**2a-c**) [27–29].

1-Amino-1,2,4-triazole with concentrated HNO_3 and HClO_4 led to the formation of the corresponding salts (**4a**) and (**4b**) in excellent yields (Scheme 2) [30]. Iodomethane with 1-amino-1,2,4-triazole gave a quaternary salt (**5**) that underwent metathesis with AgNO_3 and AgClO_4 to give high yields of the corresponding nitrate (**6a**) and perchlorate (**6b**) salts, respectively. Similarly when 1-methyl-4-amino-1,2,4-triazolium iodide (**7**) was metathesized with AgNO_3 and AgClO_4 , the salts, 1-methyl-4-amino-1,2,4-triazolium nitrate (**8a**) and 1-methyl-4-amino-1,2,4-triazolium perchlorate (**8b**), were formed [31]. The syntheses of 1,5-diamino-1,2,4-triazolium nitrate (**9a**) and 1,5-diamino-1,2,4-triazolium perchlorate (**9b**) were also reported (Scheme 2) [30]. Characterization by elemental analysis, and vibrational, multinuclear NMR, and mass spectra confirmed these structures. Single crystal X-ray structural analysis of 1-methyl-4-amino-1,2,4-triazolium per-



Scheme 2

chlorate (**8b**) showed the existence of significant hydrogen bonding between the perchlorate anion and the amino group, and that methylation had indeed occurred at N-1. Physical and thermal characteristics of these salts are tabulated in Table 2 [31].

In Table 2 certain interesting facts regarding thermal characteristics of the compounds are shown. For example, the position of the methyl group on the ring does not impact the melting points of 1-amino-4-methyl-1,2,4-triazolium nitrate (**6a**) ($T_g - 62^\circ\text{C}$) and 1-methyl-4-amino-1,2,4-triazolium nitrate (**8a**) ($T_g - 60^\circ\text{C}$). The analogous perchlorate salts (**6b**) and (**8b**) melt at 91°C and 86°C , respectively. However, the nitrate salts, 1-amino-1,2,4-triazolium nitrate (**3a**) (m.p. 69°C) and 4-amino-1,2,4-triazolium nitrate (**4a**) (m.p. 121°C), are considerably higher melting than their methyl-substituted analogs. Apparently the opportunity for hydrogen bonding, as well as modified packing effects and reduced lattice energies, is markedly reduced in the methylated salts. Thermal degradation temperatures for both perchlorate and nitrate salts are increased when a methyl group is present in the ring. Introduction of a second amino functionality causes the melting point (**4b** vs. **9b**) to increase and the enthalpy of formation to become more positive, but appears to have essentially little impact on other properties. The standard molar enthalpies of formation for perchlorate salts are invariably higher than those of nitrates (Table 2).

The synthesis and characterization of a series of nitrate salts, **10a-d**, based on 1-alkyl-4-amino-1,2,4-triazolium cations (alkyl = methyldecyl, isopropyl,

Table 2 Density and thermal characteristics of amino-1,2,4-triazolium salts

Compound	Anion	Tm ^a °C	Td ^a °C	Density (calc.) g/cm ³	ΔH_f° ^c kJ/mol
3a	NO ₃ ⁻	69	180	1.60 (1.58)	77.1
3b	ClO ₄ ⁻	84	210	1.81 (1.78)	117.2
3c	N(NO ₂) ₂ ⁻	20	146	- (1.66)	273.6
4a	NO ₃ ⁻	121	149	1.69 (1.75)	72.8
4b	ClO ₄ ⁻	91	235	1.80 (1.92)	126.6
6a	NO ₃ ⁻	- 62	217	1.51 (1.60)	45.7
6b	ClO ₄ ⁻	91	235	1.66 (1.77)	91.3
8a	NO ₃ ⁻	- 60	221	1.55 (1.60)	57.6
8b	ClO ₄ ⁻	86	259	1.80 (1.92)	106.9
9a	NO ₃ ⁻	159	149	1.65 (1.76)	196.2
9b	ClO ₄ ⁻	138	-	1.83 (1.93)	240.9

^a melting point

^b thermal degradation temperature

^c standard heat of formation (calculated by Gaussian 03)

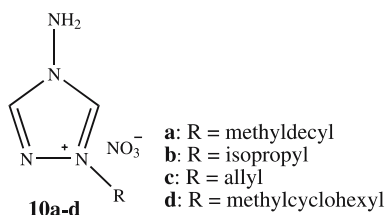


Fig. 1 1-Alkyl-4-amino-1,2,4-triazolium nitrates

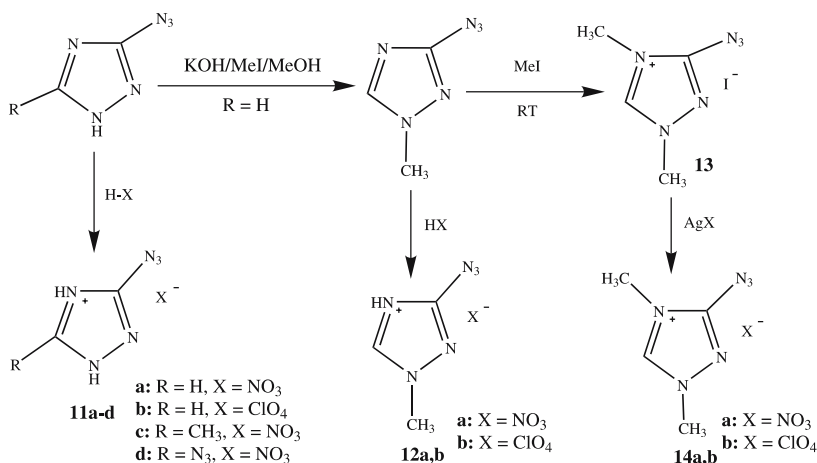
allyl, and methylcyclopropyl) have been reported (Fig. 1) [32–34]. Single crystal X-ray diffraction studies of 1-isopropyl-4-amino-1,2,4-triazolium nitrate (**10b**) (triclinic, $P\bar{1}$ symmetry) and 1-methylcyclohexyl-4-amino-1,2,4-triazolium nitrate (**10d**) (monoclinic, $P2_1/n$ symmetry) indicated that in both cations, the amino group is twisted and does not saddle the triazole ring in a symmetric fashion. This most likely arises from the extensive hydrogen bonding within the crystal structure which, however, does not affect the bond distances in the structures in a significant manner [32–34]. 1-Amino-3-substituted-1,2,3-triazolium salts have been examined [34].

2.3

Triazolium Heterocycles Containing Azido Substituents

Substitution of the hydrogen atoms of azoles by various nitrogen-containing energetic functional groups occurs in a straightforward manner. When endothermic moieties, such as the azido group, are incorporated into azoles, the heats of formation of the azoles are increased [31, 35, 36]. For example, the standard enthalpy of formation for 3-azido-1,2,4-triazole ($\Delta H_f = +458$ kJ/mol) is approximately four times larger than that of 1-H-1,2,4-triazole [36]. These azido-substituted azoles, when paired with nitrate, perchlorate, or azolate, e.g., 4,5-dinitro-imidazolate or 5-nitrotetrazolate anions, formed energetic salts [31, 37].

Quaternization of various nitrogen-containing energetic salts based on azido-1,2,4-triazoles (Scheme 3) [31] occurred readily in good yields with concentrated nitric or perchloric acid in methanol to give 3-azido-1,2,4-triazolium nitrate (**11a**), 3-azido-1,2,4-triazolium perchlorate (**11b**), 5-methyl-3-azido-1,2,4-triazolium nitrate (**11c**), and 3,5-diazido-1,2,4-triazolium nitrate (**11d**). Under similar reaction conditions, 1-methyl-3-azido-1,2,4-triazole reacted with concentrated nitric and perchloric acids to give 1-methyl-3-azido-1,2,4-triazolium nitrate (**12a**), and 1-methyl-3-azido-1,2,4-triazolium perchlorate (**12b**), respectively. A quaternary salt (**13**) formed when iodomethane was reacted with 1-methyl-3-azido-1,2,4-triazole. Subsequent metathetical reactions with AgNO_3 and AgClO_4 led to 1,4-dimethyl-3-azido-1,2,4-triazolium nitrate (**14a**) and 1,4-dimethyl-3-azido-1,2,4-triazolium perchlorate (**14b**), respectively.



Scheme 3

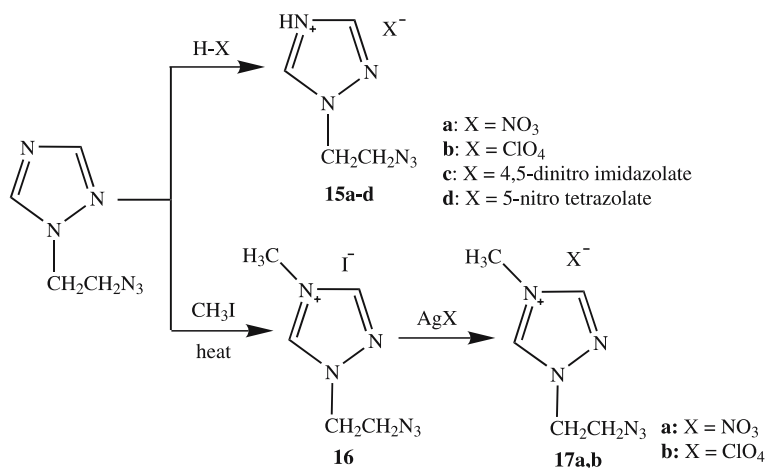
These azido triazolium salts were characterized by elemental analysis, IR, ¹H and ¹³C NMR, and mass spectra, and DSC studies. Examination of the crystal structures of **11a** and **14a** illustrated the influence of significant hydrogen bonding between the nitrate anion and the protonated 1,2,4-triazole ring for **11a**. This accounts for its higher density, 1.76 g/cm³ and m.p. 147 °C, compared with that of **14a** (*d* = 1.58 g/cm³, m.p. 98 °C), in which the presence of the methyl group on the triazole ring reduced the opportunity for hydrogen bonding (Table 3).

The chemistry of energetic salts and ionic liquids containing azidoethyl-substituted triazolium rings was examined [37]. Reaction of 1-(2-azidoethyl)-1,2,4-triazole with nitric acid, perchloric acid, 4,5-dinitroimidazole, and 5-nitrotetrazole gave 1-(2-azidoethyl)-1,2,4-triazolium nitrate (**15a**), 1-(2-azidoethyl)-1,2,4-triazolium perchlorate (**15b**), 1-(2-azidoethyl)-1,2,4-triazolium 4,5-dinitroimidazolates (**15c**), and 1-(2-azidoethyl)-1,2,4-triazolium 5-nitrotetrazolate (**15d**) salts in > 97% yield (Scheme 4). 1-(2-Azidoethyl)-1,2,4-triazole was also reacted with iodomethane to form 1-(2-azidoethyl)-4-methyl-1,2,4-triazolium iodide (**16**), which upon metathesis with the silver salts of nitric and perchloric acids formed 1-(2-azidoethyl)-4-methyl-1,2,4-triazolium nitrate (**17a**), and 1-(2-azidoethyl)-4-methyl-1,2,4-triazolium perchlorate (**17b**), respectively, in very good yields. The melting points of all these salts were found to be lower than 100 °C, and most of them are liquids at room temperature. The standard heats of formation for the perchlorate salts are more positive than those of the nitrate analogues. Most of these salts showed good thermal stability, moderate densities, and positive heats of formation (Table 3).

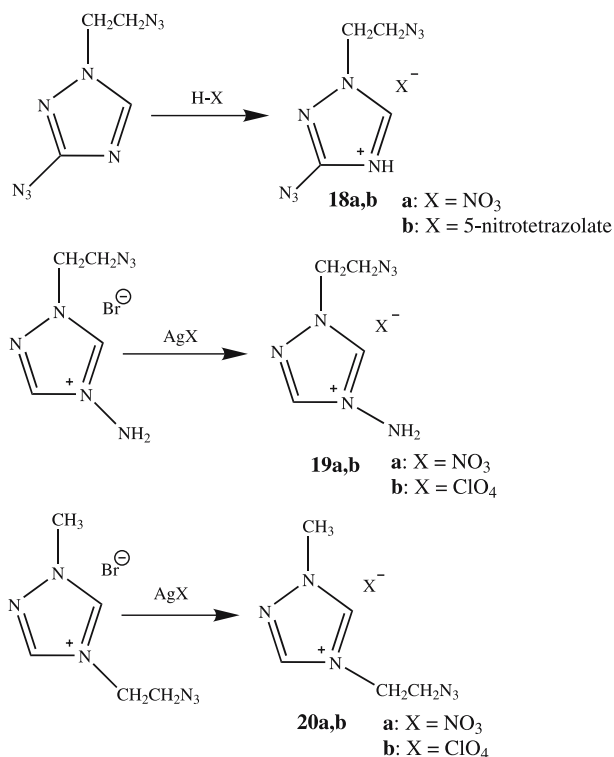
Reactions of 1-(2-azidoethyl)-3-azido-1,2,4-triazole with concentrated nitric acid and 5-nitrotetrazole gave 1-(2-azidoethyl)-3-azido-1,2,4-triazolium

Table 3 Density and thermal data of azido and azidoethyl-1,2,4-triazolium salts

Compound	Anion	Tm ^a °C	Td ^b °C	Density (calc.) g/cm ³	ΔH_f° ^c kJ/mol
11a	NO ₃ ⁻	147	174	1.76 (1.80)	326.3
11b	ClO ₄ ⁻	123	154	–	–
11c	NO ₃ ⁻	118	136	1.61 (1.68)	301.4
11d	NO ₃ ⁻	97	136	–	712.5
12a	NO ₃ ⁻	66	139	1.63 (1.66)	301.4
12b	ClO ₄ ⁻	55	187	1.66 (1.80)	353.2
14a	NO ₃ ⁻	98	129	– (1.58)	279.2
14b	ClO ₄ ⁻	68	147	–	–
15a	NO ₃ ⁻	99	170	1.60 (–)	287.5
15b	ClO ₄ ⁻	– 56	150	1.61 (–)	338.7
15c	4,5-dinitro imidazolate	85	140	1.62 (–)	538.6
15d	5-nitro tetrazolate	– 42	164	1.51 (–)	744.4
17a	NO ₃ ⁻	– 57	119	1.49 (–)	274.4
17b	ClO ₄ ⁻	– 52	192	1.60 (–)	315.5
18a	NO ₃ ⁻	– 54	142	1.58 (–)	651.5
18b	5-nitro tetrazolate	– 46	141	1.52 (–)	1098.9
19a	NO ₃ ⁻	70	153	1.57 (–)	405.2
19b	ClO ₄ ⁻	– 46	218	1.63 (–)	450.6
20a	NO ₃ ⁻	– 56	143	1.45 (–)	283.3
20b	ClO ₄ ⁻	63	152	1.59 (–)	321.8

^a melting point^b thermal degradation temperature^c standard heat of formation (calculated by Gaussian 03)**Scheme 4**

nitrate (**18a**) and 1-(2-azidoethyl)-3-azido-1,2,4-triazolium 5-nitro tetrazolate (**18b**). Metathesis of 1-(2-azidoethyl)-4-amino-1,2,4-triazolium bromide and 1-methyl-4-(2-azidoethyl)-1,2,4-triazolium bromide with AgNO_3 and AgClO_4 gave good yields of 1-(2-azidoethyl)-4-amino-1,2,4-triazolium nitrate (**19a**), 1-(2-azidoethyl)-4-amino-1,2,4-triazolium perchlorate (**19b**), 1-methyl-4-(2-azidoethyl)-1,2,4-triazolium nitrate (**20a**), and 1-ethyl-(2-azidoethyl)-1,2,4-triazolium perchlorate (**20b**) (Scheme 5) [37].



Scheme 5

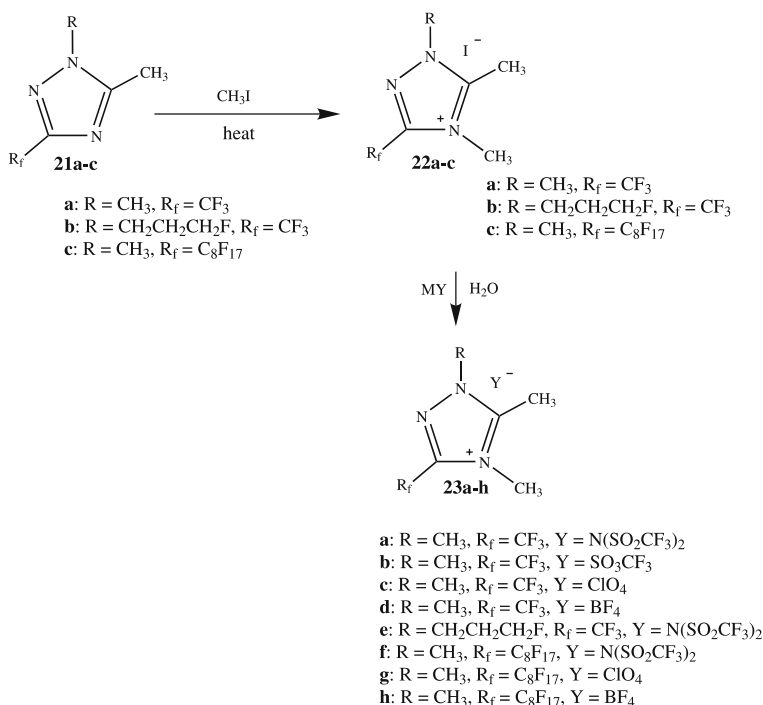
Density and thermal characteristics of azido- and azidoethyl-containing triazolium derivatives are summarized in Table 3. The data show that the position of a substituent group on the triazolium ring played an important role, e.g., T_g (-57°C) for 1-(2-azidoethyl)-4-methyl-1,2,4-triazolium nitrate (**17a**) and 1-methyl-4-(2-azidoethyl)-1,2,4-triazolium nitrate (**20a**) ($T_g - 56^\circ\text{C}$) are essentially the same, but their decomposition temperatures (**17a**, T_d , 119°C ; **20a**, T_d , 143°C) differ markedly [37]. For the analogous perchlorate salts, the melting points and thermal degradation temperatures are T_g , -52°C and T_d , 192°C for **17b**, and T_m , 63°C and T_d , 152°C for **20b**, respectively.

Density and enthalpy of formation are important characteristics of energetic salts and are governed by their molecular structures. As is shown in Table 3, in general, the densities for the salts having perchlorate as anions are higher than those of the analogous nitrates. Comparing the standard molar enthalpy (ΔH_f°) of the salts, when perchlorate is used as an anion, the positive heats of formation are higher than those of the corresponding nitrates. Considering **15a** to **15d**, the impact of the anion on heat of formation of 1-(2-azidoethyl) 1,2,4-triazolium salts decreases in the order 5-nitro-tetrazolate > 4,5-dinitro-imidazolate > perchlorate > nitrate.

2.4

Triazolium Heterocycles Containing Fluoroalkyl Substituents

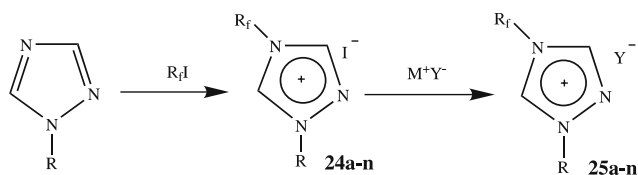
Substituents at carbon atoms of 1,2,4-triazoles was efficiently achieved by designing triazoles with the required substituents in place [38, 39]. Through this process various fluoroalkyl-substituted 1,2,4-triazolium salts were obtained [40], first via reaction of 1,3,5-substituted triazoles (**21a-c**) with iodomethane to form quaternary salts (**22a-c**), which when metathesized with various metal salts resulted in ionic liquids and energetic salts (**23a-h**) (Scheme 6). The yields of products are usually excellent.



Scheme 6

Characterization of these salts was achieved by elemental analyses, IR, multinuclear NMR, and GC mass spectra. The bis(trifluoromethanesulfonyl)-amide salts (**23a,e,f**) are insoluble in water, which helped in purification. The solubilities of these salts in organic solvents increase with increasing dielectric constant of the solvent. Their melting points decrease in the order $\text{SO}_3\text{CF}_3^- > \text{BF}_4^- > \text{ClO}_4^- > \text{N}(\text{SO}_2\text{CF}_3)_2^-$ [40], which is attributable to the nature of the diffuse charge on the latter anion. Salts with larger cations have lower melting points due to less efficient packing in the solid phase.

Reactions of 1-alkyl-1,2,4-triazoles with polyfluoroalkyl halides resulted in quaternization of the triazole ring at N-4 to yield **24a-n** (Scheme 7). Metathe-



Comp.	R	R _f	Y	T _m (°C) ^a	T (°C) ^b
25a	CH ₃	(CH ₂) ₂ CF ₃	N(SO ₂ CF ₃) ₂	-58 (Tg)	376
25b	(CH ₂) ₃ CH ₃	(CH ₂) ₂ CF ₃	N(SO ₂ CF ₃) ₂	-67 (Tg)	395
25c	(CH ₂) ₆ CH ₃	(CH ₂) ₂ CF ₃	N(SO ₂ CF ₃) ₂	-67 (Tg)	402
25d	(CH ₂) ₉ CH ₃	(CH ₂) ₂ CF ₃	N(SO ₂ CF ₃) ₂	-68 (Tg)	400
25e	(CH ₂) ₃ CH ₃	(CH ₂) ₂ (CF ₂) ₃ CF ₃	N(SO ₂ CF ₃) ₂	69	394
25f	(CH ₂) ₆ CH ₃	(CH ₂) ₂ (CF ₂) ₃ CF ₃	N(SO ₂ CF ₃) ₂	55	396
25g	(CH ₂) ₉ CH ₃	(CH ₂) ₂ (CF ₂) ₃ CF ₃	N(SO ₂ CF ₃) ₂	53	396
25h	CH ₃	(CH ₂) ₂ (CF ₂) ₅ CF ₃	N(SO ₂ CF ₃) ₂	62	381
25i	(CH ₂) ₃ CH ₃	(CH ₂) ₂ (CF ₂) ₅ CF ₃	N(SO ₂ CF ₃) ₂	53	396
25j	(CH ₂) ₆ CH ₃	(CH ₂) ₂ (CF ₂) ₅ CF ₃	N(SO ₂ CF ₃) ₂	22	405
25k	(CH ₂) ₃ CH ₃	(CH ₂) ₂ (CF ₂) ₃ CF ₃	PF ₆	296	357
25l	(CH ₂) ₆ CH ₃	(CH ₂) ₂ (CF ₂) ₃ CF ₃	PF ₆	298	354
25m	(CH ₂) ₃ CH ₃	(CH ₂) ₂ (CF ₂) ₅ CF ₃	PF ₆	289	361
25n	(CH ₂) ₃ CH ₃	(CH ₂) ₂ (CF ₂) ₃ CF ₃	SO ₃ CF ₃	173	391

^a Phase transition temperature. ^b Thermal degradation.

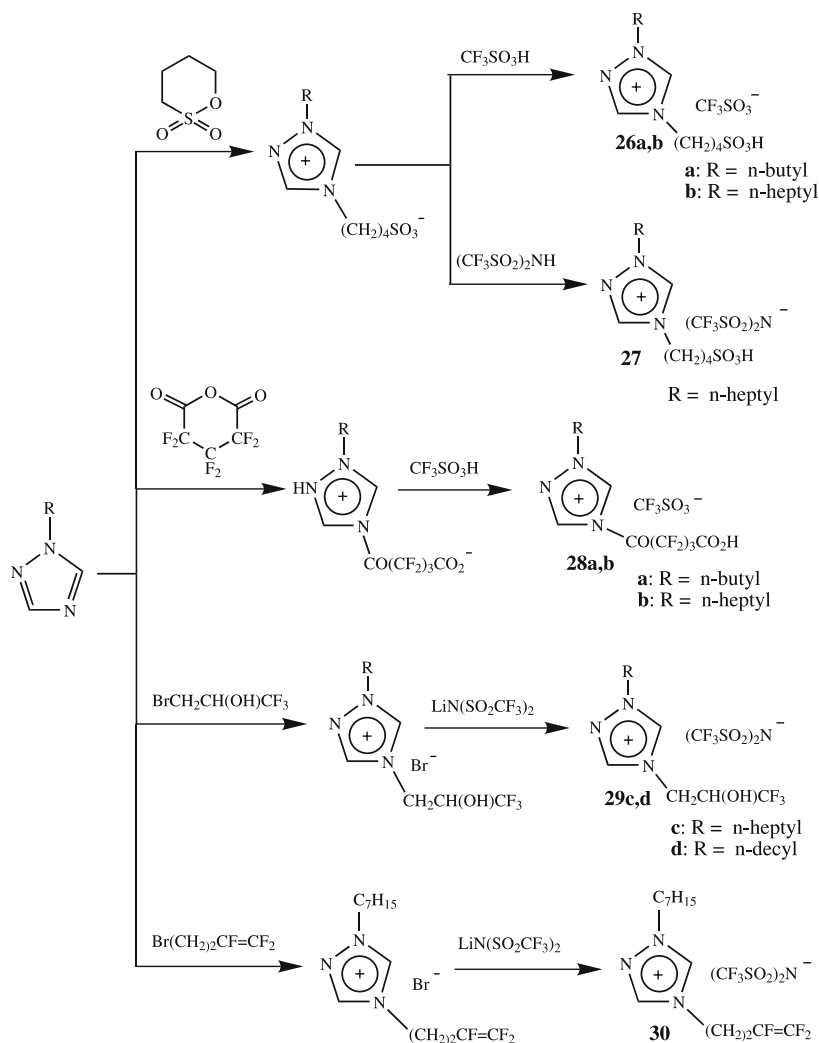
Scheme 7

sis of **24a–n** with various metal salts gave excellent yields of salts which include the bis(trifluoromethanesulfonyl)amide salts of 1-methyl-4-(3,3,3-trifluoropropyl)-1,2,4-triazolium (**25a**), 1-butyl-4-(3,3,3-trifluoropropyl)-1,2,4-triazolium (**25b**), 1-heptyl-4-(3,3,3-trifluoropropyl)-1,2,4-triazolium (**25c**), 1-decyl-4-(3,3,3-trifluoropropyl)-1,2,4-triazolium (**25d**), 1-butyl-4-(1*H*,1*H*,2*H*,2*H*-perfluorohexyl)-1,2,4-triazolium (**25e**), 1-heptyl-4-(1*H*,1*H*,2*H*,2*H*-perfluorohexyl)-1,2,4-triazolium (**25f**), 1-decyl-4-(1*H*,1*H*,2*H*,2*H*-perfluorohexyl)-1,2,4-triazolium (**25g**), 1-methyl-4-(1*H*,1*H*,2*H*,2*H*-perfluorooctyl)-1,2,4-triazolium (**25h**), 1-butyl-4-(1*H*,1*H*,2*H*,2*H*-perfluorooctyl)-1,2,4-triazolium (**25i**), 1-heptyl-4-(1*H*,1*H*,2*H*,2*H*-perfluorooctyl)-1,2,4-triazolium (**25j**); the hexafluorophosphate salts of 1-butyl-4-(1*H*,1*H*,2*H*,2*H*-perfluorohexyl)-1,2,4-triazolium (**25k**), 1-heptyl-4-(1*H*,1*H*,2*H*,2*H*-perfluorohexyl)-1,2,4-triazolium (**25l**), 1-butyl-4-(1*H*,1*H*,2*H*,2*H*-perfluorooctyl)-1,2,4-triazolium (**25m**); and the trifluoromethane-sulfonate salt of 1-butyl-4-(1*H*,1*H*,2*H*,2*H*-perfluorohexyl)-1,2,4-triazolium (**25n**) (Scheme 7) [41, 42]. Salts containing longer alkyl and polyfluoroalkyl substituents have lower melting points because of the less efficient packing in the solid. The densities were found to be higher with elongation of the fluoroalkyl substituent and with higher fluorine concentration. Cations with bulkier alkyl groups resulted in salts of lower density.

A high-yield, efficient procedure to synthesize functionalized alkyl/fluoroalkyl-containing triazolium quaternary salts and triazolium ionic liquids led to triazolium cations that contained covalently bound anionic sites, such as, fluorocarboxy, sulfonate, fluorohomoallylic, and fluoroalkanol groups [43, 44]. These were converted by metathetical reactions with fluorine-containing anions to low-melting salts (**26a,b**, **27**, **28a,b**, **29c,d**, **30**) (Scheme 8) [43]. These functionalized triazolium salts exhibit many characteristics associated with excellent ionic liquids with respect to stability in air and water, and when heated. All are liquids at 25 °C.

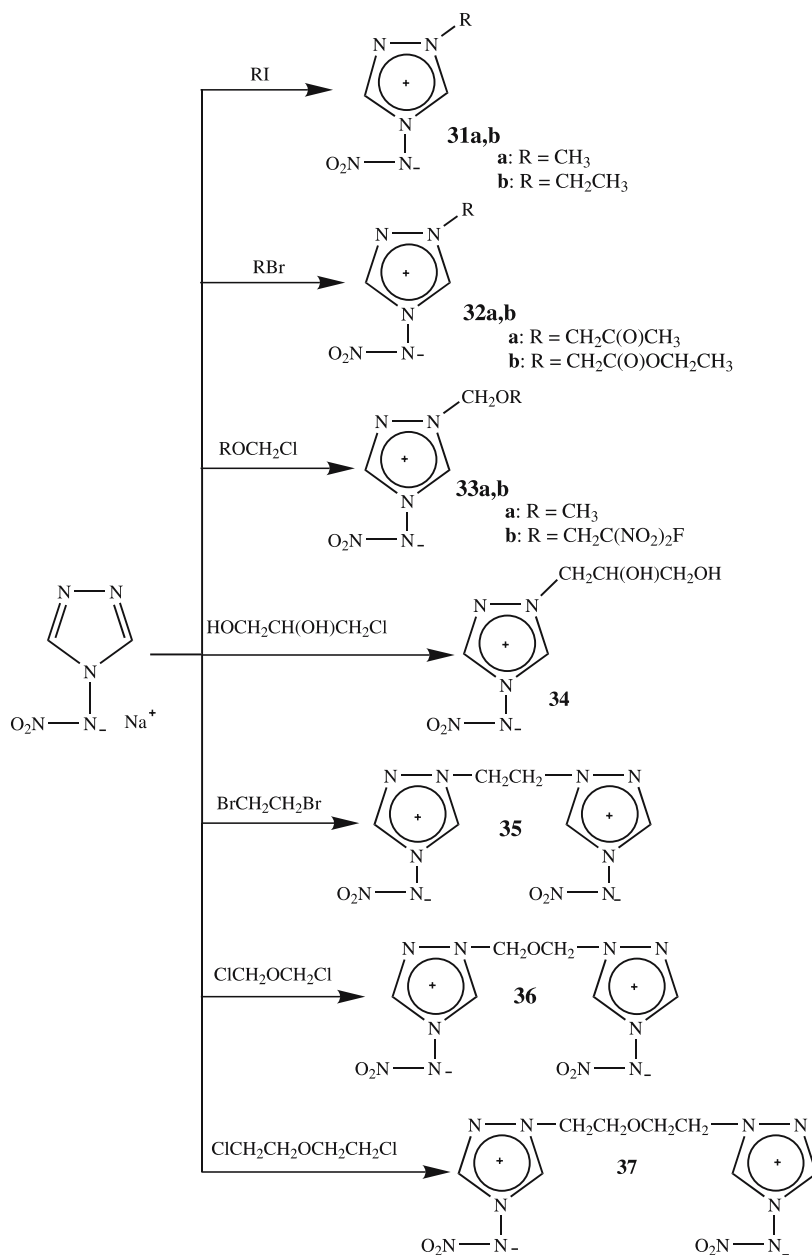
A synthetic route to 1-alkyl-1,2,4-triazolium 4-nitroimides was developed based on alkylation of the metal salts of 4-nitramino-1,2,4-triazole with halo- and dihaloalkanes (Scheme 9) [44]. These salts are 1-methyl-1,2,4-triazolium 4-nitroimide (**31a**), 1-ethyl-1,2,4-triazolium 4-nitroimide (**31b**), 1-(2-oxapropyl)-1,2,4-triazolium 4-nitroimide (**32a**), 1-ethoxycarbonylmethyl-1,2,4-triazolium 4-nitroimide (**32b**), 1-methoxymethyl-1,2,4-triazolium 4-nitroimide (**33a**), 1-(4-fluoro-4,4-dinitro-2-oxabutyl)-1,2,4-triazolium 4-nitroimide (**33b**), 1-(2,3-dihydroxypropyl)-1,2,4-triazolium 4-nitroimide (**34**), bis(nitroimido-1,2,4-triazolium-1-yl)ethane (**35**), 1,3-bis(4-nitroimido-1,2,4-triazolium-1-yl)-2-oxapropane (**36**), and 1,3-bis(4-nitroimido-1,2,4-triazolium-1-yl)-3-oxapentane (**37**).

These salts are solid and were characterized by IR, NMR and elemental analysis. In the IR spectra the characteristic absorption bands due to an N-nitroimido group bonded to a heterocycle are observed at 1280–1300 and 1390–1415 cm^{-1} . The nitramino group that would have shown absorption bands at 1550–1620 cm^{-1} is absent. In the ^1H NMR spectra, the signals



Scheme 8

for the protons of the triazole ring are nonequivalent and are shifted down-field relative to the signals for the protons in the starting material which is evidence that supports the imide structure. This conclusion is supported by the ^{13}C NMR data. However, no thermal or physical properties were reported.



Scheme 9

2.5

1,2,4-Triazolium Azolate Heterocycles

Lithium dicyano-1,2,3-triazolate was reported as a useful electrolyte (**38**) [45]. 1-Butyl-3-methylimidazolium 3,5-dinitro-1,2,4-triazolate (**39**) (Fig. 2) (m.p. 32 °C, T_d 239 °C) resulted from the metathesis of 1-butyl-3-methylimidazolium halide with potassium 3,5-dinitro-1,2,4-triazolate [46–49]. However, no energetic characterization was carried out for this material. Some novel ionic liquids made up of azolium cations and anions were also reported. These salts are: 1-ethyl-3-methylimidazolium 1,2,4-triazolate (**40**) (T_g – 76 °C, T_d 207 °C, η 60.2 cP at 25 °C) and tetrazolate (**41**) (T_g – 89 °C, η 42.5 cP at 25 °C) (Fig. 2). Both **40** and **41** were prepared by the coupling reactions of 1-ethyl-3-methylimidazolium hydroxide with triazole or tetrazole, respectively [50].

On the basis of the fact that both 4,5-dinitro-imidazole and 5-nitro-tetrazole are strong NH acids ($pK_a = 0.8$ for 5-nitro-tetrazole) [51], energetic salts with various 1,2,4 triazolium derivatives as cations and 4,5-dinitro-imidazolate and 5-nitrotetrazolate anions were obtained [52]. 4,5-Dinitro-imidazole and 5-nitro-tetrazole were reacted with various N-4-substituted derivatives of 1,2,4-triazoles to produce energetic ionic salts including: 1,2,4-triazolium 4,5-dinitro-imidazolate (**42a**), 1-methyl-1,2,4-triazolium 4,5-dinitro-imidazolate (**42b**), 3-azido-1,2,4-triazolium 4,5-dinitro-imidazolate (**42c**), 1-methyl-3-azido-1,2,4-triazolium 4,5-dinitro-imidazolate (**42d**), 1,2,4-triazolium 5-nitro-tetrazolate (**43a**), 1-methyl-1,2,4-triazolium 5-nitrotetrazolate (**43b**), 3-azido-1,2,4-triazolium 5-nitro-tetrazolate (**43c**), and 1-methyl-3-azido-1,2,4-triazolium 5-nitro-tetrazolate (**43d**) (Scheme 10), as well as 4-amino-1,2,4-triazolium 4,5-dinitro-imidazolate (**42e**) and 4-amino-1,2,4-triazolium 5-nitro-tetrazolate (**43e**).

Densities and thermochemical characteristics of the azolium azolates are given in Table 4. When 5-nitro-tetrazolate was used as the anion, the melting points of the compounds were lower than those of the corresponding

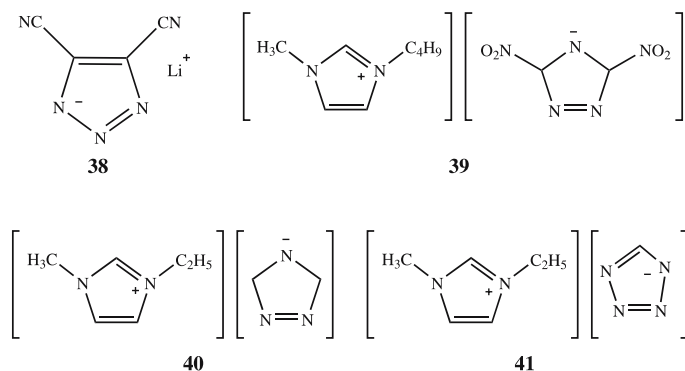
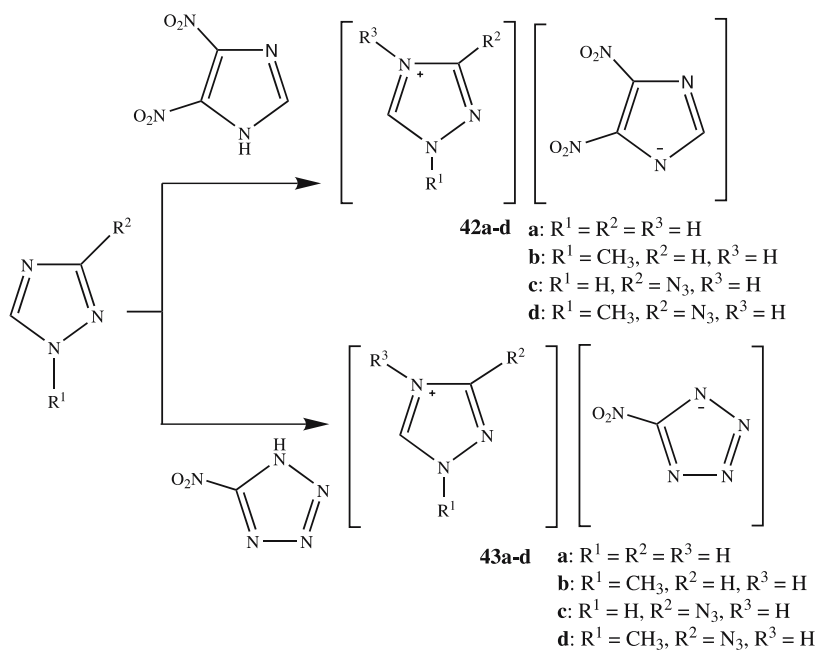


Fig. 2 Ionic salts containing azole ions



Scheme 10

Table 4 Density and thermal characteristics of triazolium azolate salts

Compound	Anion	Tm ^a °C	Td ^b °C	α^c %	Density (calc.) g/cm ³	$\Delta H_f^{\circ c}$ kJ/mol
42a	4,5-dinitroimidazolate	156	165	32	1.73	232.1
42b	4,5-dinitroimidazolate	102	150	25	1.66	200.6
42c	4,5-dinitroimidazolate	92	158	33	1.70	593.5
42d	4,5-dinitroimidazolate	80	145	26	1.60	560.5
42e	4,5-dinitroimidazolate	137	149	30	1.65	348.7
43a	5-nitrotetrazolate	137	183	25	1.53	436.2
43b	5-nitrotetrazolate	62	163	18	1.52	402.7
43c	5-nitrotetrazolate	-35	161	26	1.53	800.9
43d	5-nitrotetrazolate	-38	141	19	1.45	768.5
43e	5-nitrotetrazolate	102	190	23	1.58	545.2

^a melting point^b thermal degradation temperature^c oxygen coefficient^d standard heat of formation (calculated by Gaussian 03)

4,5-dinitro-imidazolates, while the thermal decomposition temperatures were higher. The opportunity for hydrogen bonding, in addition to modified packing effects and reduced lattice energies, with the anion is reduced in methyl-substituted compounds, resulting in lower melting points. The densities exceed 1.45 g/cm^3 for all the compounds. Energetic salts that incorporate the nitro group substantially improve the oxygen balance of the corresponding compounds and eventually result in higher heats of combustion and detonation processes. The oxygen coefficients (α) [53] for the new salts are between 0.18 and 0.33 (Table 4) and are within the range reported for known energetic compounds [54].

3

Tetrazolium-Based Heterocycles

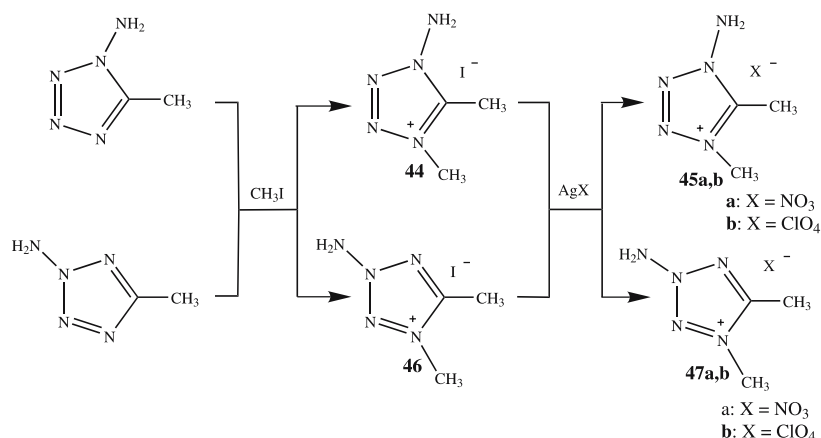
Tetrazoles are unsaturated five-membered heterocycles that contain four nitrogen atoms in the ring. The enthalpies of energetic chemical systems are governed by their molecular structure. Moving from imidazole (ΔH_f° , + 58.5 kJ/mol) to 1,2,4-triazole (ΔH_f° , + 109.0 kJ/mol) to tetrazole (ΔH_f° , + 237.2 kJ/mol) [35], there is an increasing positive trend in heats of formation. Since the generation of molecular nitrogen as an end-product of propulsion or explosion is highly desired in order to avoid environmental pollution and health risks, as well as to reduce detectible plume signatures, compounds containing a backbone of directly linked nitrogen atoms (caterated nitrogen) are of great interest.

3.1

Tetrazolium Heterocycles Containing Amino and Azido Substituents

Aminotetrazoles have a high nitrogen content and, despite their large positive enthalpies of formation [55], are thermally stable [56]. They are, therefore, prospective high energy materials. The synthesis of various tetrazolium salts containing amino substituents on the ring via reactions of 1-amino-5-methyl tetrazole, and 2-amino-5-methyl tetrazole with iodomethane resulted in quaternary salts (**44**) and (**46**). Metathesis with AgNO_3 or AgClO_4 formed 1-amino-4,5-dimethyltetrazolium nitrate (**45a**) or perchlorate (**45b**), and 2-amino-4,5-dimethyltetrazolium nitrate (**47a**) or perchlorate (**47b**) in high yields (Scheme 11) [30, 31]. Elemental analyses, and IR, multinuclear NMR, and mass spectral analyses support the syntheses (Table 5).

A high yield synthesis of 5-amino-tetrazolium nitrate (**48**) is obtained from the reaction of 5-amino-tetrazole with nitric acid (Scheme 12) [57]. Its characterization was accomplished through IR, Raman, and multinuclear (^1H , ^{13}C , ^{15}N) NMR spectroscopy, and DSC. Bomb calorimetry, sensitivity measurements, and ab initio calculations were also performed. From the combined



Scheme 11

Table 5 Densities and thermal characteristics of substituted amino, aminomethyl, and polymethyl tetrazolium salts

Compound	Anion	Tm ^a °C	Td ^b °C	Density (calc.) g/cm ³	ΔH_f^c kJ/mol
45a	NO ₃ ⁻	-59	170	1.50 (1.55)	141.1
45b	ClO ₄ ⁻	51	182	1.81 (1.78)	183.8
47a	NO ₃ ⁻	94	173	- (1.55)	132.0
47b	ClO ₄ ⁻	140	238	1.65 (1.71)	179.5
50a	NO ₃ ⁻	121	181	1.51 ^d	174.6 ^e
50b	N(NO ₂) ₂ ⁻	85	184	1.72 ^d	385.6 ^e
50c	N ₃ ⁻	135	137	1.42 ^d	676.6 ^e

^a melting point

^b thermal degradation temperature

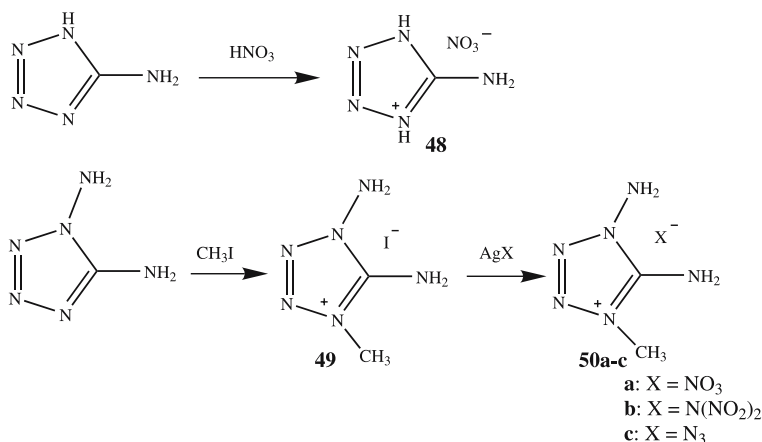
^c standard heat of formation (calculated by Gaussian 03)

^d X-ray (calc)

^e [59]

experimental and theoretical calculations, **48** is predicted to be a powerful and promising explosive with a good oxygen balance and low sensitivity.

The syntheses of 1,5-diamino-4-methyltetrazolium salts via quaternization, e.g., of 1,5-diamino-1*H*-tetrazole with iodomethane, gave 1,5-diamino-4-methyl-tetrazolium iodide (**49**) in 86% yield [58–63]. Subsequent metathesis of **49** with silver nitrate, silver dinitramide, or silver azide led to 1,5-diamino-4-methyl-tetrazolium nitrate (**50a**), 1,5-diamino-4-methyltetrazolium dinitramide (**50b**), or 1,5-diamino-4-methyltetrazolium azide (**50c**) in good yields. Most of these salts exhibited good thermal stability. Salt **50b** as



Scheme 12

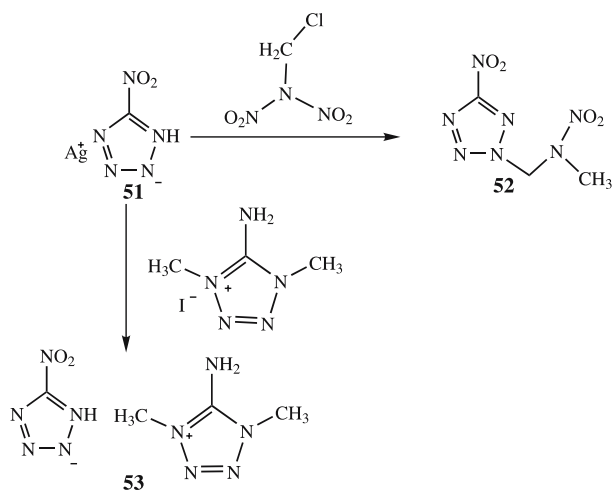
well as **45a**, **45b**, and **47a** melt at < 100 °C which qualifies them as energetic ionic liquids.

These salts were characterized by IR, Raman and NMR spectroscopy, mass spectrometry, elemental analysis, X-ray, and initial safety testing (impact and friction sensitivity). Low impact sensitivities were demonstrated. Densities and thermochemical characteristics of substituted amino, amino-methyl, and polymethyl tetrazolium salts are summarized in Table 5. All of these new salts exhibit thermal stabilities > 170 °C based on *DSC/TGA* studies (except the azide). The densities of 1-amino-4,5-dimethyl tetrazolium perchlorate (**45b**) and 1-methyl-4,5-diamino tetrazolium dinitramide (**50b**) are markedly higher than the others.

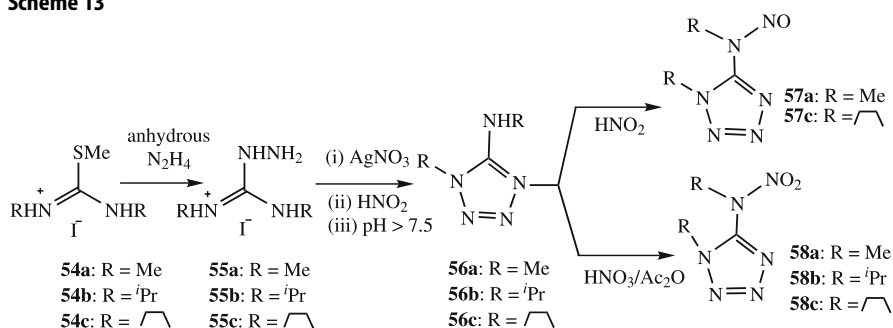
Synthesis and characterization of 1-nitrotetrazolato-2-nitro-2-azapropene (**52**) and 1,4-dimethyl-5-aminotetrazolium 5-nitrotetrazolate (**53**) are reported in high yields (Scheme 13). Compounds **52** and **53** are white powders and were characterized by single crystal X-ray analysis. Compound **52** explodes when thrown in a flame. Both **52** and **53** have low impact sensitivity [64, 65].

Nitrogen-rich energetic heterocycles, N-nitroso- (**57a,c**) and N-nitramino-tetrazole (**58a-c**) were synthesized from the corresponding aminotetrazoles (**56a-c**) by the direct nitration with acetic anhydride/HNO₃ (Scheme 14). The conversion of **57a,c** with peroxytrifluoroacetic acid yielded the corresponding nitraamines in high yields (**58a**: 82%, **58c**: 80%). Compounds **56a,c**, **57a,c**, **58a-c** were characterized by single crystal X-ray analysis. The calculated heats of formation for **58a** and **58c** were found to be positive (11.7 and 357.0 kJ mol⁻¹, respectively) and the calculated detonation velocity of 5988 ms⁻¹ (**58a**) is similar to the values of TNT and nitroglycerin [66].

The chemistry of 5-azidotetrazole, 5-azido-1-phenyltetrazole, and tetrazolypentazole has been reported. The 5-pentazolyl and 5-azido derivatives

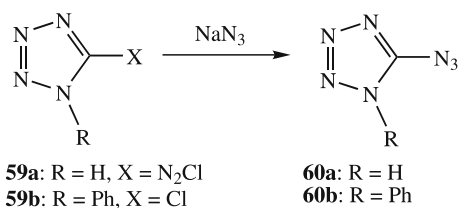


Scheme 13



Scheme 14

(60a,b) of tetrazole include large amounts of nitrogen at 90.6 and 88.3 weight percent. While the pentazole compound decomposes at low temperature, 5-azido tetrazole is stable at room temperature but extremely sensitive (and should be synthesized in only small amounts). 5-Azido-1-phenyl tetrazole (60b) is found to be stable and characterized by single crystal X-ray analysis (Scheme 15) [63, 67].

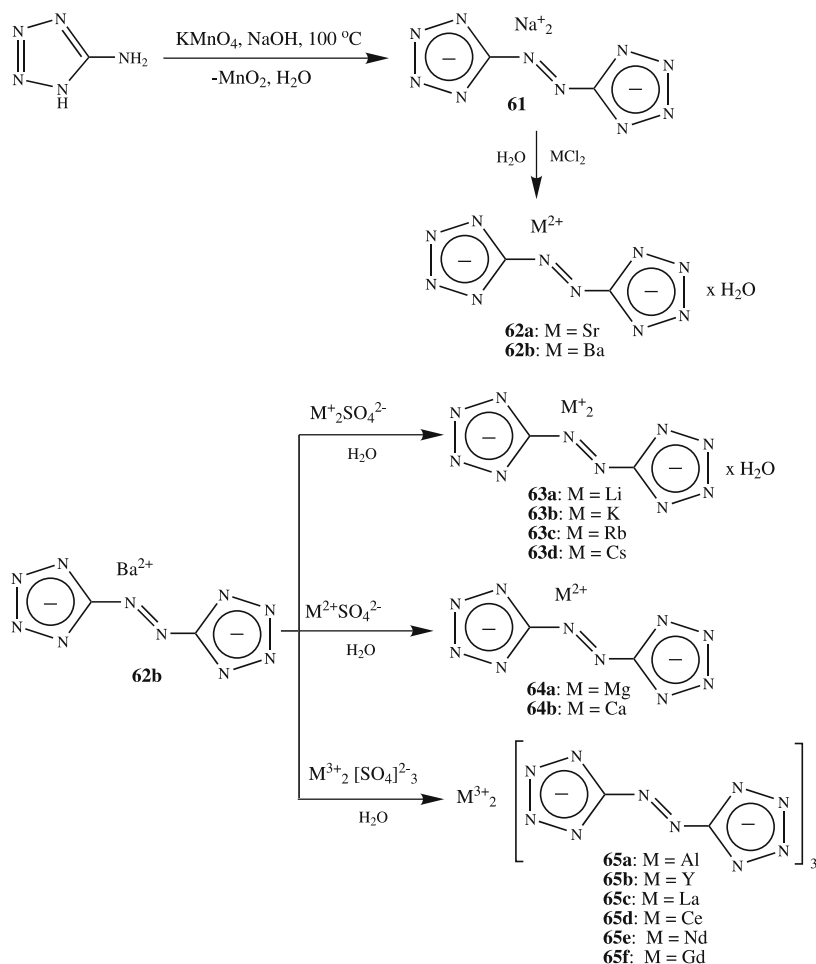


Scheme 15

3.2

Tetrazolium Heterocycles Containing 5,5'-Azotetrazolate Anions

In the 1890s, Thiele first prepared sodium 5,5'-azotetrazolate (**61**) from oxidation of 5-amino-tetrazole with potassium permanganate [68–71]. Reaction of strontium and barium chlorides with an aqueous solution of **61** gave strontium 5,5'-azotetrazolate (**62a**) and barium 5,5'-azotetrazolate (**62b**), respectively [72]. Both salts were insoluble in water. Barium 5,5'-azotetrazolate (**62b**), was used with various metal sulfates to produce the corresponding 5,5'-azotetrazolate salts (**63a–d**, **64a,b**, and **65a–f**), in water (Scheme 16). These metal salts often contain water of crystallization, and loss of water has been observed during storage. Upon loss of water, the sensitivity



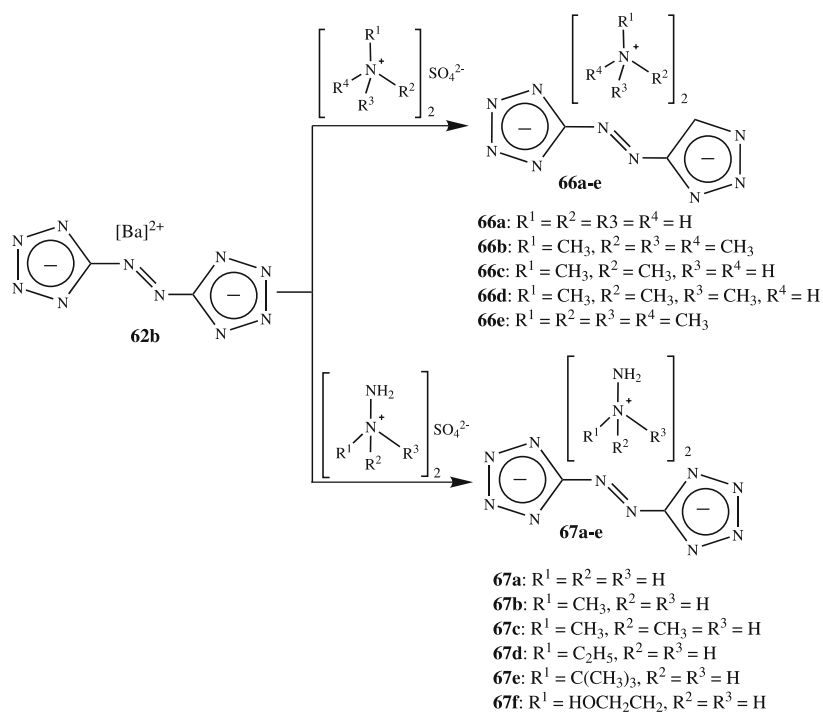
Scheme 16

of the compounds to shock and friction increased drastically. The salts were characterized by IR, Raman, and NMR spectroscopy, and their thermal properties were studied by DSC and TGA. X-ray crystal studies on sodium 5,5'-azotetrazolate pentahydrate (**61**), barium 5,5'-azotetrazolate pentahydrate (**62b**), lithium 5,5'-azotetrazolate hexahydrate (**63a**), rubidium 5,5'-azotetrazolate dihydrate (**63c**), calcium 5,5'-azotetrazolate octahydrate (**64b**), yttrium 5,5'-azotetrazolate docosahydrate (**65b**), and gadolinium 5,5'-azotetrazolate hydrate (**65f**) show that the water molecules were either in the coordination sphere of the cation or bound by hydrogen bonds. The azotetrazolate ion is not connected to the harder cations such as calcium or yttrium, and the salt decomposed in water, due to its acidity, to form tetrazolhydrazine with concomitant evolution of nitrogen. The free acid 5,5'-azotetrazolate, synthesized from the sodium salt with HBF_4 , was decomposed within seconds at room temperature but could be retained at -30°C .

Salts of 5,5'-azotetrazolate with protonated nitrogen bases (e.g., ammonium guanidinium and triaminoguanidinium) are unique gas-generating agents producing little smoke or residue, which may lead to a variety of applications, including gas generators and explosives [73, 74]. Salts of the 5,5'-azotetrazolate dianion with various methylated ammonium (**66a-e**) and hydrazinium (**67a-d,f**) cations were obtained from the reactions of barium 5,5'-azotetrazolate (**62b**) with appropriate ammonium and hydrazinium sulfates [73-78]. However, N,N,N-trimethylhydrazinium 5,5'-azotetrazolate, $[(\text{CH}_3)_3\text{N-NH}_2]_2^+ [\text{N}_4\text{C-N=N-CN}_4]^{2-}$ (**67e**) was obtained by the metathesis of trimethylhydrazinium iodide and silver 5,5'-azotetrazolate (Scheme 17).

Other 5,5'-azotetrazolates reported include salts that contain cations such as: bis(hexahydropyridazinium) (**67g**), bis[N-amino-1-azonia-cyclohexane] (**67h**), bis[ethylene-dihydrazinium (+1)] (**67i**), ethylenedihydrazinium (+2) (**67j**), bis[N-amino-*N',N'*-dimethyl-guanidinium] (**67k**), diguanidinium (**67l**), bis(triaminoguanidinium) (**67m**), and bis(azidoformamidinium) (**67n**) (Fig. 3) [76, 79]. These salts were characterized by IR, Raman, and NMR spectroscopy, and elemental analyses; X-ray crystal structures of **66a,c,e**, **67a,e,j**, and **67l** were determined.

The salts were insensitive to shock, friction, or electric discharge ($\sim 20\text{ kV}$). Detonation was not observed in either the drop hammer test (5 kg, 50 cm) or when the salts were ground forcefully in a mortar. None of these salts melts, but rather decomposes at specific temperatures with rapid gas evolution. Above the decomposition point, explosion occurred upon rapid heating to give nitrogen gas as the main product, especially if the compound was compressed before heating. The decomposition temperature decreased for salts with NH^+ functions as the number of methyl groups increased. The hydrazine salts also produced large amounts of hydrogen, which decreased with the increasing number of methyl groups. The ammonium compounds (**66a-c**) produced only small amounts of hydrogen, whereas none was detected for **66d,e** [76]. The formation of methane was observed for all salts.



Scheme 17

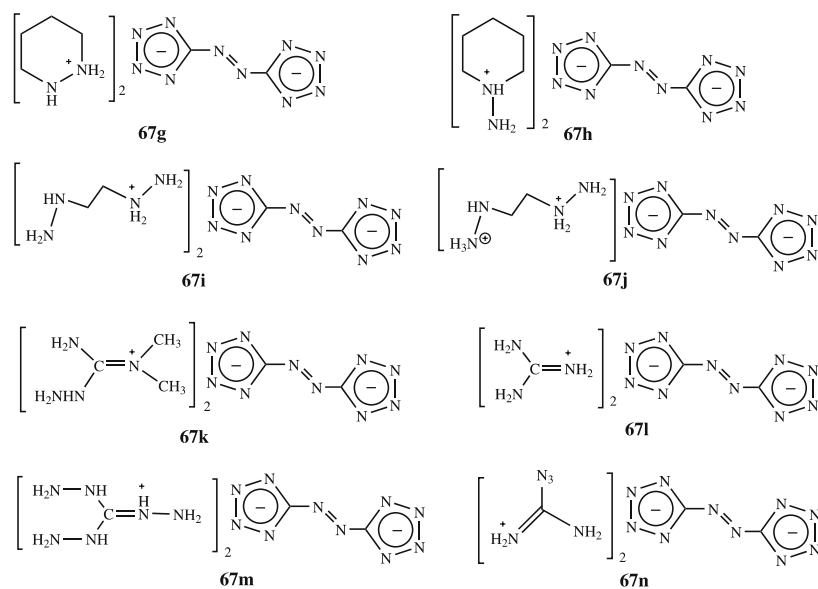
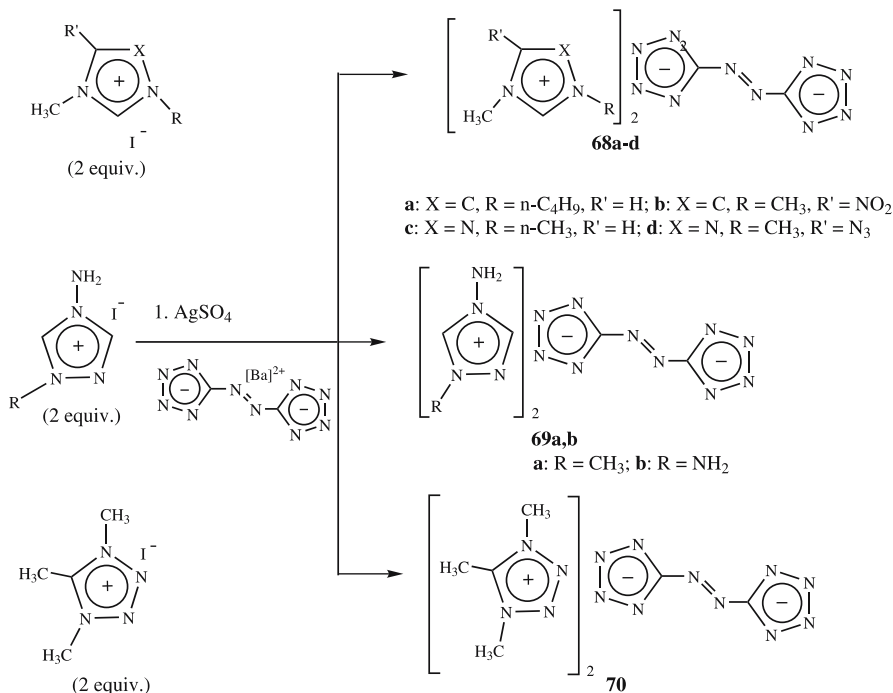


Fig. 3 Salts of 5,5'-azotetrazolate dianions with hydrazinium derivative cations

Heats of formation of hydrazinium [75], ammonium 5,5'-azotetrazolates [79], and guanidinium [24, 80], were measured as $\Delta H_f^\circ = + 858$, $+ 443$, and $+ 410 \text{ kJ mol}^{-1}$, respectively. In order to compare these properties with azotetrazolates that contain heterocyclic cations, imidazolium, triazolium, and tetrazolium derivatives were synthesized and characterized (Scheme 18) [81]. Surprisingly, while most azotetrazolates exhibit melting points in excess of 160°C , [bis(1-butyl-3-methyl-imidazolium)] 5,5'-azotetrazolate (**68a**) was a liquid at 25°C with a melting point of 3°C , similar to its 3,5-dinitrotetrazolate analog [46].



Scheme 18

Although the quaternized salts of 1,4 dimethyl-3-azido triazolium (**68d**), bis(1,4-diamino-1,2,4-triazolium) (**69b**), and 1,4,5-trimethyl tetrazolium (**70**) 5,5'-azotetrazolate have lower nitrogen content than the bis(triaminoguanidinium) derivative, their heats of formation are much higher at $+ 1852.4$, $+ 1620.0$, and $+ 1334.8 \text{ kJ/mol}$, respectively, with densities of ~ 1.46 – 1.59 g cm^{-3} (Table 6). The structure of **69a**, determined by single crystal X-ray analysis, shows that the unit cell was packed as a layered structure with hydrogen bonds and an interlayer distance of 3.04 \AA [82–87]. In contrast to the metal azotetrazolates [72], none of these salts (except **70**) was solvated. Compounds (**68b–70**) decomposed violently upon melting. Microwave of **69a**

Table 6 Densities and thermal characteristics of azotetrazolate derivatives

Compound	T _m ^a °C	Density (calc.) g/cm ³	ΔH _f ^{o b} kJ/mol
67l	262	1.54	486.5
67m	209 ^c	1.60	1171.2
67n	142 ^c	1.62	–
68a	3	1.26	896.9
68b	145	1.54	1094.2
68c	182	1.42	1136.2
68d	155	1.55	1852.4
69a	180	1.57	1129.5
69b	–	1.59	1620.0
70	189	1.46	1334.8

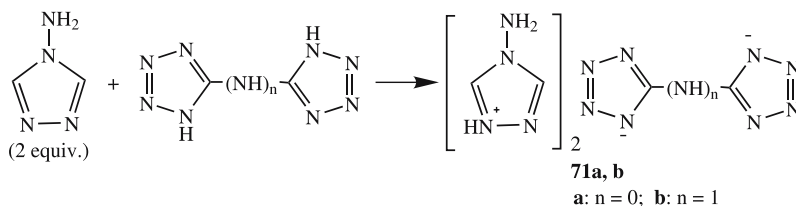
^a melting point^b standard heat of formation (calculated by Gaussian 03)^c thermal decomposition temperature

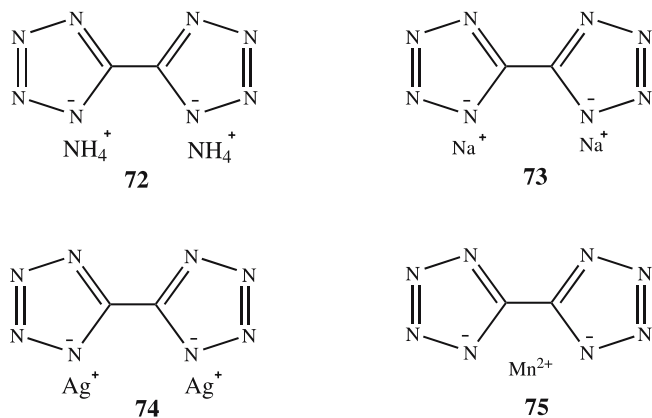
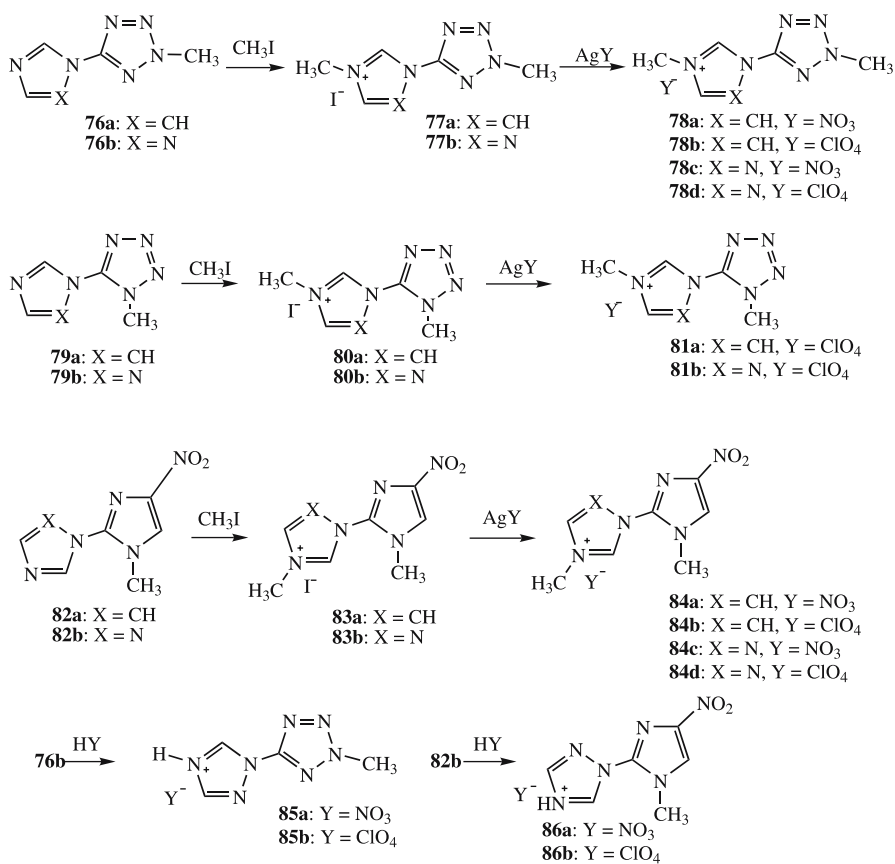
at 200 °C caused a violent decomposition leading to the formation of a carbon black powder. With the exception of **69b**, which spontaneously evolved nitrogen gas, most of the salts were stable at room temperature for at least two months.

3.3

Bistetrazolate Heterocycles

Although there are several reports of 5,5'-bistetrazolate [82–87] and imino-bis(5-tetrazolate) [88–90] salts, most are described in the patent literature. Some processes have been developed for preparing various 5,5'-tetrazolate salts, which were very useful as slightly toxic and easy to handle gas-generating agents for air bags and as high molecular weight foaming agents. In methanol at reflux, bistriazole or iminobis(5-tetrazole) readily quaternized 4-amino-1,2,4-triazole to prepare [bis(4-amino-triazolium)] 5,5'-bistetrazolate (**71a**) or [bis(4-amino-triazolium)] iminobis(5-tetrazolate) (**71b**) (Scheme 19) [81].

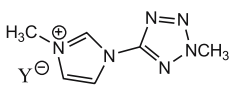
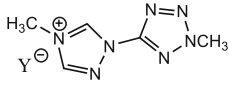
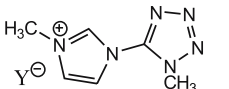
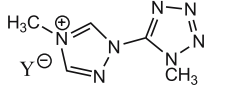
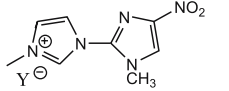
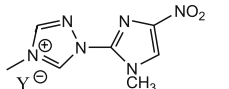
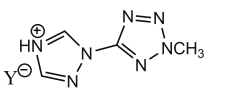
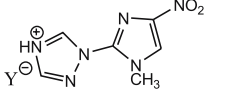
**Scheme 19**

**Fig. 4** 5,5'-bistetrazolate salts**Scheme 20**

The diammonium (72), disodium (73), disilver (74), and manganese(II) (75) 5,5' bistetrazolates are also known (Fig. 4) [82–87]. Chemistry of copper complexes with bis(tetrazolyl)amine has been also studied and some of them are of interest as additives in pyrotechnics and ammonium perchlorate-based propellants [86].

The chemistry of various nitrogen-rich energetic bicyclic azolium salts has been described. The thermally stable bicyclic azolium salts (78a–d, 81a–b, 84a–d, 85a,b, 86a,b) with densities ranging between 1.52–1.67 g/cm³, were prepared by quaternization with nitric acid or perchloric acid or

Table 7 The structures and properties of bicyclic azolium salts

Compound	Y	No	T _m ^a °C	T _d ^b °C	<i>d</i> g/cm ³	Δ _f H _m ^c kJ/mol
	NO ₃	78a	79	175	1.519(1.531)	–
	ClO ₄	78b	110	283	1.631(1.653)	–
	NO ₃	78c	151	151	1.515(1.574)	310.8
	ClO ₄	78d	141	293	1.639(1.695)	357.7
	ClO ₄	81a	159	295	1.648(1.653)	–
	ClO ₄	81b	152	240	1.645(1.695)	412.3
	NO ₃	84a	125	190	1.581(1.574)	–
	ClO ₄	84b	169	289	1.641(1.678)	–
	NO ₃	84c	–	145	1.566(1.612)	–
	ClO ₄	84d	227	282	1.652(1.716)	–
	NO ₃	85a	154	166	1.565(1.644)	341.8
	ClO ₄	85b	128	229	1.648(1.773)	385.5
	NO ₃	86a	153	165	1.617(1.676)	209.9
	ClO ₄	86b	–	175	1.674(1.784)	345.6

^a melting point

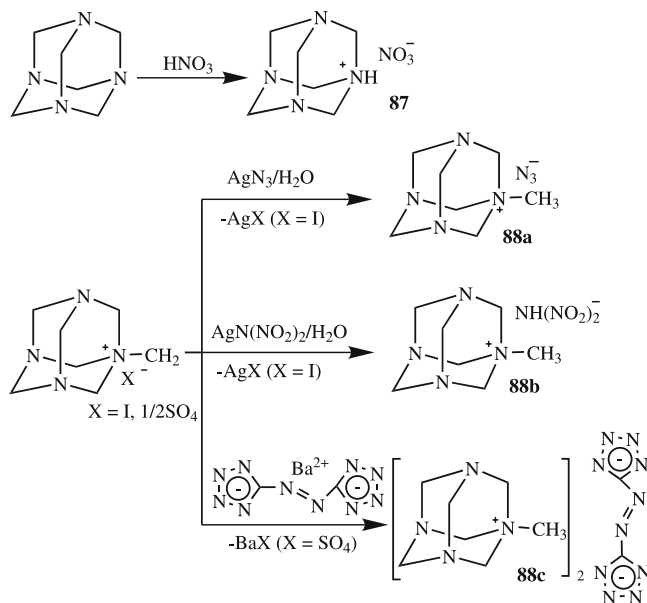
^b thermal decomposition temperature

^c standard heat of formation (calculated by Gaussian 03)

iodomethane followed by metathesis reactions with silver nitrate and silver perchlorate (Scheme 20, Table 7). The structures of **81b** and **86b** were confirmed by single-crystal X-ray analysis [91].

4 Urotropinium-Based Heterocycles

The chemistry of high-energy density materials (HEDM) containing only C, H, N, and O atoms is of great interest. Urotropine, a nitrogen-rich cage molecule, when paired with energetic anions, formed energetic salts. The initial preparation of urotropinium salts was carried out in the 1950s [92], and subsequently the syntheses of a variety of them were reported [93]. Urotropinium nitrate (**87**) [colorless crystals, m.p. 157–161 °C (dec.), density (from X-ray) 1.47 g/cm³] was prepared by the reaction of urotropine with nitric acid. N-methylurotropinium azide (**88a**) [white solid, m.p. 165–170 °C (dec.), density 1.4 g/cm³], N-methylurotropinium dinitramide (**88b**) [white solid, m.p. 121–124 °C (dec.), density 1.46 g/cm³], and N-methylurotropinium azotetrazolate (**88c**) [yellow crystals, m.p. 181–184 °C (dec.), density 1.46 g/cm³] were prepared from either the corresponding iodide or sulfate (Scheme 21). Because of the high sensitivity and explosive nature of anhydrous silver azide, an alternative route for **88a** using sodium azide with N,N-dimethylurotropinium diiodide was utilized [94]. All the salts

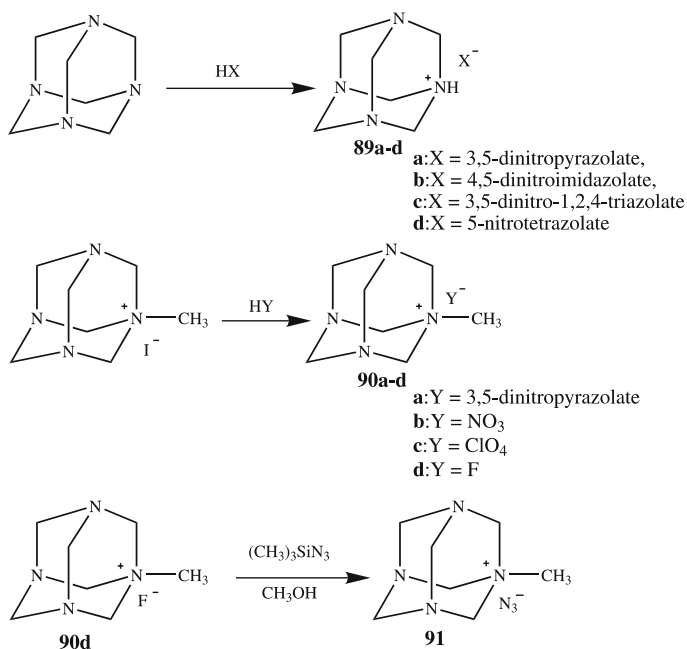


Scheme 21

were handled easily, were insensitive to air or light, and were soluble in polar organic solvents. They were characterized by analytical and spectroscopic (IR, Raman, ^1H , ^{13}C , ^{14}N NMR) methods, and X-ray diffraction techniques.

The X-ray crystal structure of **87** (monoclinic, space group $P2_1/C$) consisted of a urotropinium cation linked to a planar nitrate group via hydrogen bridges. The structures of **88a–c** showed separation of anions and cations without contact. The azide ion in **88a** (monoclinic, space group $P2_1/m$) is linear; the dinitramide ion in **88b** (monoclinic, space group $P2_1$) is asymmetric; and the azotetrazolate anion in **88c** (monoclinic, space group C_2/m) is planar [93].

The syntheses of urotropinium and N-methylurotropinium salts were extended to include several other energetic organic and inorganic anions, such as 3,5-dinitro-pyrazolate, 4,5-dinitro-imidazolate, 3,5-dinitro-1,2,4-triazolate, 5-nitro-tetrazolate, perchlorate, nitrate, and azide [94]. In methanol solution, urotropine was found to react readily with 3,5-dinitro-pyrazole, 4,5-dinitro-imidazole, 3,5-dinitro-1,2,4-triazole, and 5-nitro-tetrazole to form urotropinium 3,5-dinitro-pyrazolate (**89a**), 4,5-dinitro-imidazolate (**89b**), 3,5-dinitro-1,2,4-triazolate (**89c**), and 5-nitro-tetrazolate (**89d**). Reaction of silver salts of 3,5-dinitro-1,2,4-triazole, nitric, perchloric, and hydrofluoric acid with N-methylurotropinium iodide led to N-methylurotropinium 3,5-dinitro-1,2,4-triazolate (**90a**), nitrate (**90b**), perchlorate (**90c**), and fluoride (**90d**)



Scheme 22

Table 8 Phase transition, decomposition temperature, density, nitrogen content (N), oxygen coefficient (α), and thermochemical results for urotropinium salts at 298.2 K

Compound	T _m ^a °C	T _d ^b °C	Density (calc) g/cm ³	N ^c %	α %	ΔH_f° ^e kJ/mol
89a	180	184	1.56	37.6	16	299.0
89b	183	183	1.41	37.6	16	254.6
89c	177	182	1.72	42.1	18	268.7
89d	166	169	1.48	49.4	10	435.3
90a	170	202	1.45	40.2	16	250.7
90b	194	196	1.42	32.2	14	- 30.6
90c	200	205	1.47	22.0	-	14.5
91	165	176	1.35	49.7	0	468.8

^a melting point;^b thermal decomposition temperature;^c nitrogen content;^d oxygen coefficient;^e standard heat of formation (calculated by Gaussian 03)

salts. N-methylurotropinium azide (**91**) is made by the reaction of **90d** with (CH₃)₃SiN₃ (Scheme 22, Table 8) [94]. The structure of **90b** was confirmed by single crystal X-ray analysis.

5 Tetrazine-Based Heterocycles

There has been considerable interest in the study of the reactivity and properties of various tetrazine derivatives. The 1,2,4,5-tetrazine ring system is electroactive and has a high electron affinity. Tetrazines possess high positive heats of formation and large crystal densities—properties important in energetic materials applications. Additionally, they seem to be insensitive to destructive stimuli such as friction, impact, and electrostatic discharge.

The synthesis and properties of various ionic 1,2,4,5-tetrazine explosives and energetic materials including 3,6-diguanidino-1,2,4,5-tetrazine diperchlorate (**92a**), 3,6-diguanidino-1,2,4,5-tetrazine dinitrate (**92b**), 3,6-diguanidino-1,2,4,5-tetrazine-1,4-di-N-oxide diperchlorate (**93a**), 3,6-diguanidino-1,2,4,5-tetrazine-1,4-di-N-oxide dinitrate (**93b**), disilver 3,6-bis-nitroguanyl tetrazine (**94**), bistriamino-guanidinium 3,6-bis-nitro-guanyl tetrazine (**95**), 3,6-dihydrazino-1,2,4,5-tetrazine diperchlorate (**96a**), 3,6-dihydrazino-1,2,4,5-tetrazine dinitrate (**96b**), 3,6-dihydrazino-1,2,4,5-tetrazine bis-(dinitramide) (**96c**), and 3,6-dihydrazino-1,2,4,5-tetrazine bis-dinitroimidazolate (**97**) were reported (Fig. 5) [95–98].

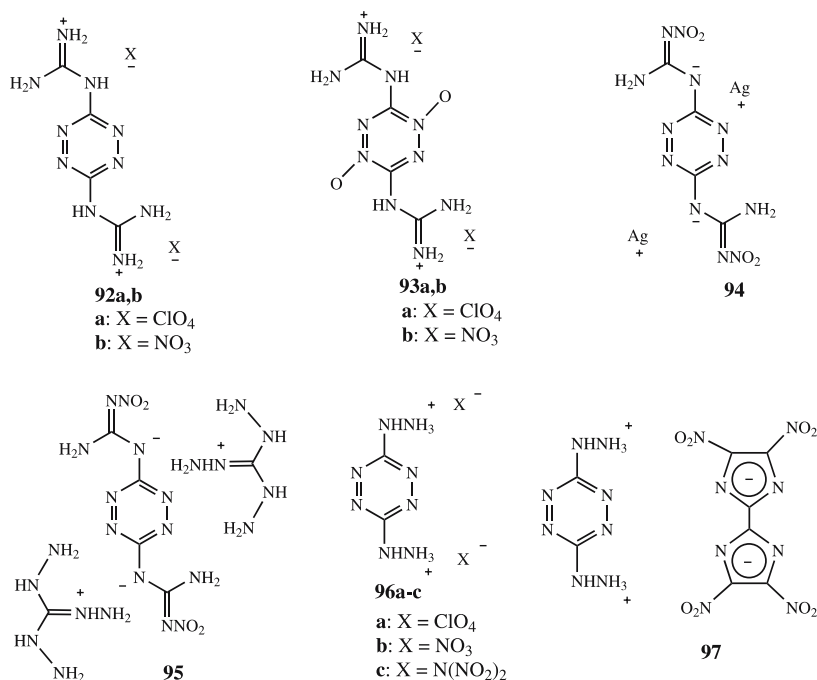


Fig. 5 Tetrazine-based energetic salts

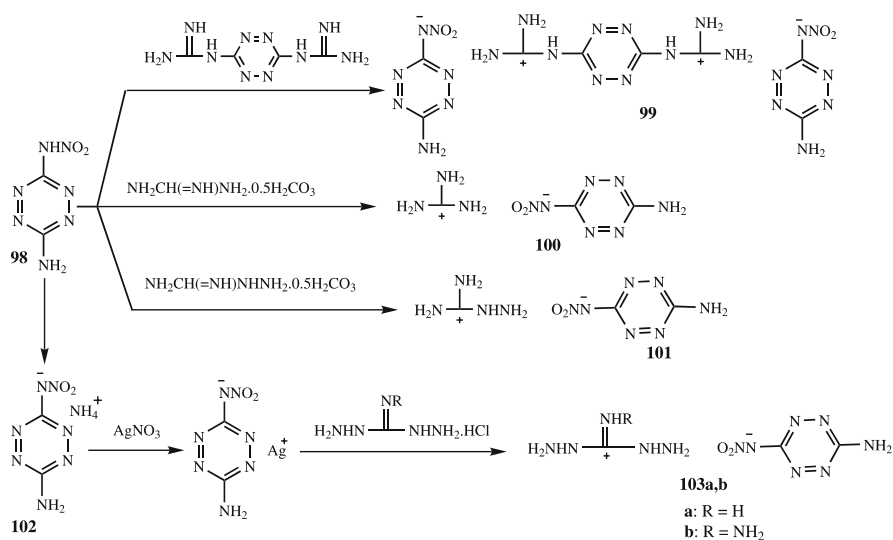
Energetic salts **92a,b**, **93a,b**, and **96a,b** were synthesized by the reaction of nitric acid and perchloric acid with 3,6-diguanidino-1,2,4,5-tetrazine, 3,6-diguanidino-1,2,4,5-tetrazine-1,4-di-N-oxide, and 3,6-dihydrazino-1,2,4,5-tetrazine, respectively, whereas **96c** was made by the reaction of dinitramide with 3,6-dihydrazino-1,2,4,5-tetrazine.

Synthesis of **94** and **95** involved the reaction of the disodium salt of 3,6-bis-nitroguanyl tetrazine with AgNO₃ and triaminoguanidinium hydrochloride, respectively.

Poly-rho tests, which are single shot experiments to determine detonation velocity as a function of density, were performed on **92a,b**. When **92a** is formulated with 5 weight percent of Kel-F 800 binder, a maximum pellet density of 1.79 g/cm³ was obtained. At this density, the detonation velocity measured was 8.07 km/s. The dinitrate derivative (**92b**) was formulated with 3 weight percent Estane binder and 3 weight percent nitro-plasticizer. At a maximum pellet density of 1.60 g/cm³, a detonation velocity of 7.31 km/s was obtained. Salt **93b** was found to be unstable based on DSC analysis, whereas salt **93a** showed improved thermal stability but less than **93a** [95]. The crystal density of **95** was reported to be 1.61 g/cm³, and the heat of formation was 300 ± 2 kcal/mol [97]. The densities of **96a-c**, **97** are reported to be in the range of 1.80 to 1.96 g/cm³ [96]. When these salts were heated

over the temperature range 40–500 °C at a scan rate of 20 °C/min, **96a–c** left no residue, whereas **97** left an orange powder. In DSC studies, **96a**, **96c** exhibited their major exotherm between 152 and 164 °C, respectively. Salt **96b** exhibited an exotherm at 190 °C, which is about 30 °C higher than **96a**, **96c**. Salt **97** showed the highest exotherm at 220 °C [96]. All tetrazine-based salts seem to have interesting explosive performance and extraordinary combustion properties [95–98].

The synthesis and properties of several high-nitrogen materials with 3-amino-6-nitroamino-tetrazine (ANAT) as the anion are reported (Scheme 23). These salts (**99**, **100**, **103a,b**) provide a new and easy approach to highly energetic salts. All these salts are relatively dense ($> 1.55 \text{ g/cm}^3$) and exhibit good thermal stability ($T_d > 148 \text{ °C}$). The calculated detonation velocities and detonation pressures are comparable to those of explosives such as Tetryl, PETN, TATB, and RDX. A combination of theoretical and empirical calculations shows that all these salts have high molar enthalpies of formation (Table 9) [99].

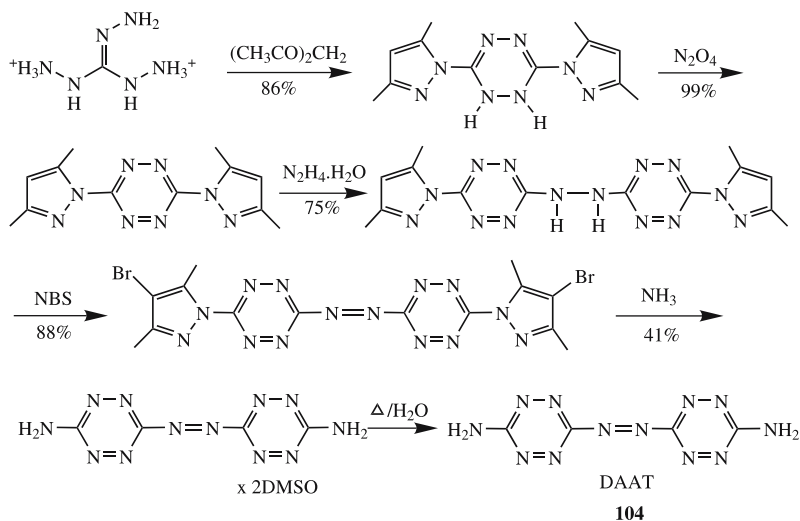


Scheme 23

The synthesis of 3,3'-azobis(6-amino-1,2,4,5-tetrazine) (DAAT) (**104**) is reported in a 20% yield after six reaction steps (Scheme 24). DAAT is a high nitrogen energetic material with remarkable thermal stability and insensitivity against friction and impact. DAAT decomposes at relatively high temperatures ($> 250 \text{ °C}$) releasing a very large amount of heat. A high nitrogen content of 70% in combustion with a low oxygen balance of -72.67% and a high heat of formation of $+1035 \text{ kJ/mol}$ measured by combustion calorimetry are some of the promising properties of DAAT which

Table 9 Structure and properties of energetic salts with ANAT anion

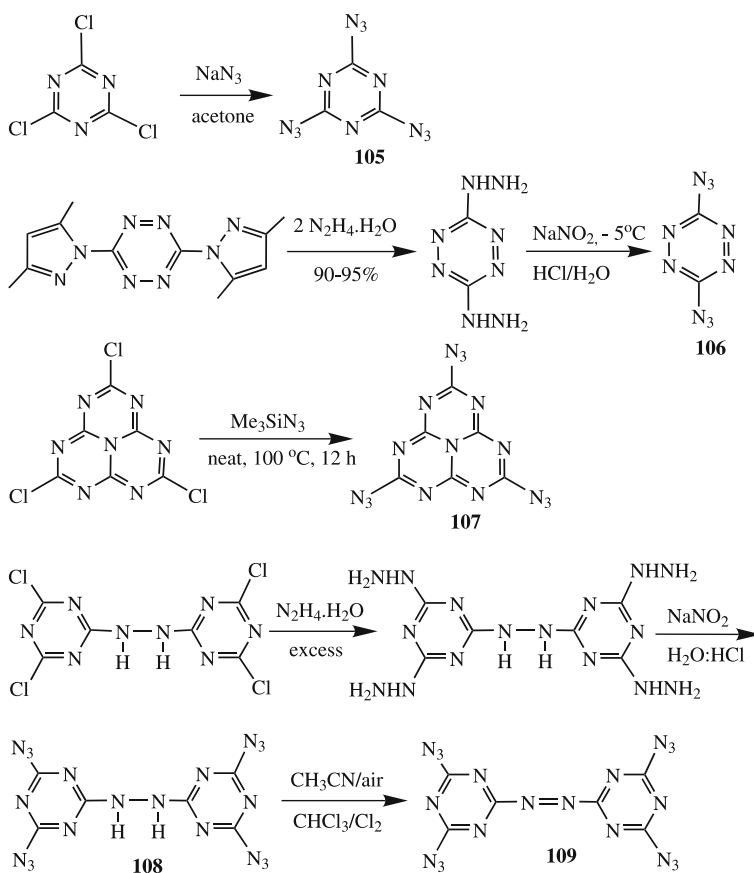
Compound	Td ^a °C	Density g/cm ³	ΔH _m ^{o b} kJ/mol
98	164.0	1.82	441.0 ^c
99	232.3	1.56	1088.8
100	248.1	1.62	340.7
101	205.4	1.71	443.2
102	174.0	1.63	370.0
103a	147.7	1.56	564.2
103b	163.5	1.59	671.5

^a thermal degradation temperature^b standard heat of formation (calculated by Gaussian 03)^c calculated heat of formation in the gas phase**Scheme 24**

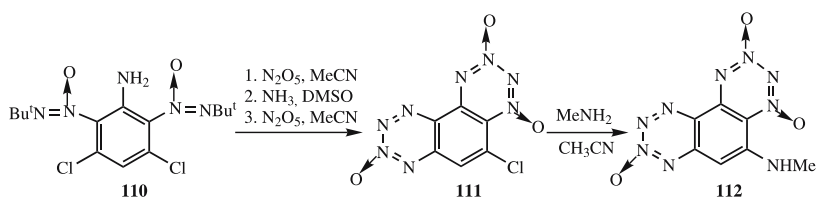
make it interesting as a new energetic component. The density of DAAT is 1.76 g/cm³ [100, 101].

The synthesis, characterization, and energetic properties of various heterocycles containing azide groups are reported. Compound **105** is prepared by the reaction of cyanuric chloride with sodium azide. The preparation of **106** utilizes the conversion of a pyrazole derivative by reaction with hydrazine to form the hydrazo intermediate which is subsequently reacted with NaNO₂. 2,5,8-Trichloro-*s*-heptazine is converted quantitatively into 2,5,8-triazido-*s*-heptazine (**107**) with trimethylsilyl azide. The nucleophilic reaction of hydrazine with 4,4',6,6'-tetra(chloro)hydrazo-1,3,5-triazine

gave 4,4',6,6'-tetra(hydrazine)hydrazo-1,3,5-triazine which when diazotized gave **108**. Reaction of **108** with $\text{CHCl}_3/\text{Cl}_2$ in acetonitrile led to the formation of **109** (Scheme 25) [102–106]. The novel heterocyclic system with the phenanthrene-type skeleton **111**, in which the benzene ring is annulated with 1,2,3,4-tetrazene-1,3-di-N-oxide rings, is of considerable interest in the context of the high-nitrogen system stability and from a heteroaromaticity stand point. The step-by-step synthetic approach to this system involves treatment of **110** with N_2O_5 resulting in the first 1,2,3,4-tetrazene 1,3-dioxane ring. Subsequent repeated treatment with N_2O_5 led to the formation of the second 1,2,3,4-tetrazene 1,3-dioxane ring (Scheme 26). The structure of **111** was confirmed by ^{13}C and ^{14}N NMR spectral studies. Compound **111** was also converted to **112** by the reaction with methylamine. Compound **111** begins to melt with decomposition at 140°C , and above 210°C ; compound **112** begins to decompose without melting [107].



Scheme 25



Scheme 26

6 Azetidinium-Based Heterocycles

Azetidinium-based explosives, such as 1, 3, 3-trinitroazetidinium [108, 109] demonstrate excellent performance partly because of the high strain associated with the four-membered ring. The basicity ($pK_b = 6.5$) of 3,3'-dinitroazetidinium [110] allowed the preparation of a variety of solid energetic 3,3'-dinitroazetidinium salts with high oxygen-balance [107], including 3,3'-dinitroazetidinium nitrate (**113a**), 3,3'-dinitroazetidinium 2,4-dinitroimidazolate (**113b**), 3,3'-dinitroazetidinium dinitramide (**113c**), 3,3'-dinitroazetidinium 5-nitro-1,2,4-triazol-3-onate (**113d**), 3,3'-dinitroazetidinium 3,5-dinitro-1,2,4-triazolate (**113e**), and 3,3'-dinitro-1-isopropylazetidinium dinitramide (**114**) (Fig. 6). These salts were synthesized in 82–95% yields, either by mixing the free base 3,3'-dinitroazetidinium with the appropriate acid or by metathesis of 3,3'-dinitroazetidinium trifluoromethanesulfonate [110] with ammonium salts of the acid. They were characterized by elemental analyses, IR, and ^{13}C NMR. Densities and thermal characteristics are tabulated in Table 10. All the salts were subjected to small-scale thermal and sensitivity tests [111].

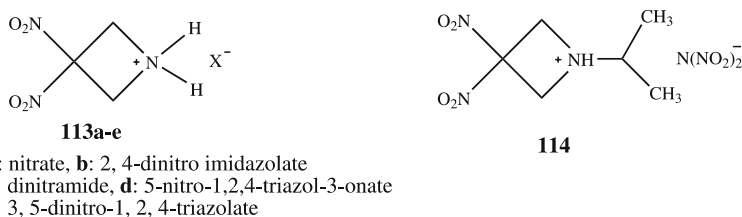


Fig. 6 Azetidinium-based energetic salts

The single crystal X-ray structures of 3,3'-dinitroazetidinium dinitramide (**113c**) (orthorhombic, space group $C_{mc}2_1$) and 1-isopropyl-3,3'-dinitroazetidinium dinitramide (**114**) (orthorhombic, space group $Pbca$) were also reported [112]. The latter was formed when an attempt to crystallize 3,3'-dinitroazetidinium nitrate from acetone was being made. X-ray structures have confirmed that the conformation adopted by the dinitramide ions in **113c** is quite different from the bend, twist, and torsion angles for the

Table 10 Densities and thermochemical properties of azetidinium salts

Compound	Density g/cm ³	T _m ^a °C	ΔH_f° ^b kJ/mol
113a	1.76	142	- 260 ± 8
113b	1.65	151	- 75 ± 50
113c	1.79	139	- 34 ± 16
113d	1.76	161	- 201 ± 4
113e	1.70	148	+ 84 ± 8
114	1.78	154	+ 21 ± 63 ^c

^a melting point^b [111] ^c [112]

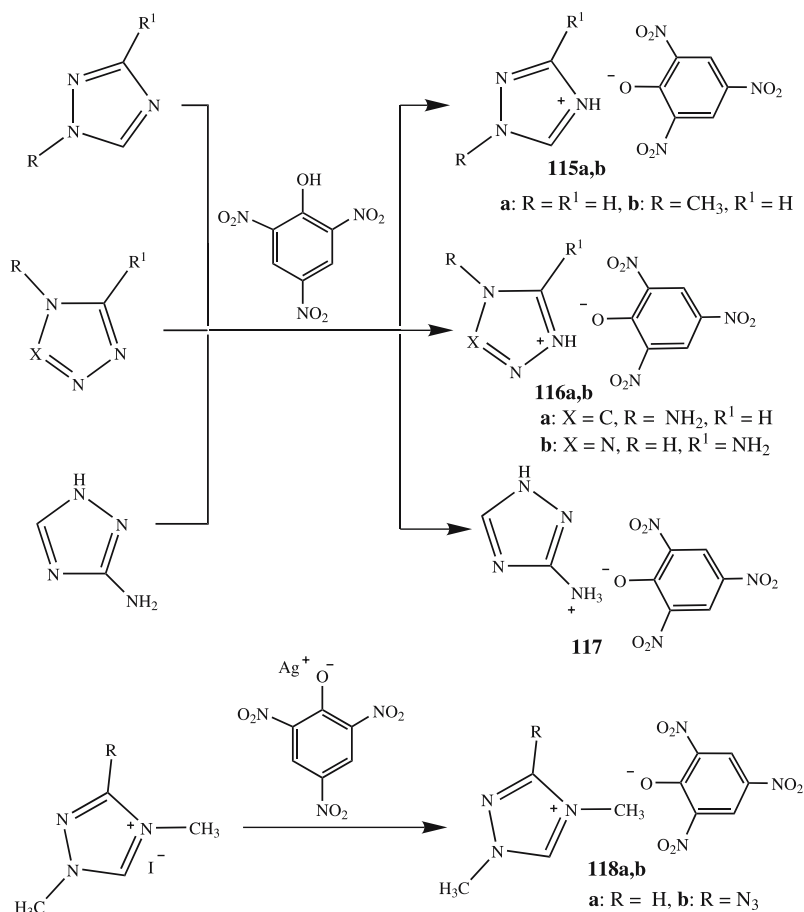
dinitramide ion in **114**. The possible reason for these dramatic differences in the conformations observed for **113c** and **114** is claimed to be due to the different symmetries for this ion found in the two structures, as well as the absence of hydrogen bonding interaction in **114** [112]. Dehydration of 3,3-dinitroazetidinium nitrate with acetic anhydride provided an alternate route for the synthesis of 1,3,3-trinitroazetidine [111]. The synthesis and characterization of ¹⁵N-labeled isomers of 3,3-dinitroazetidinium nitrate were also reported [113].

7

Picrate-Based Heterocycles

While anhydrous picric acid is unstable, and its impact and friction sensitivities are higher than those of trinitrotoluene, many organic and inorganic picrates have been reported [9]. The picrate anion, when combined with high-nitrogen azolium cations, formed energetic salts with rather high positive heats of formation. By taking advantage of the acidic properties of picric acid, energetic salts containing picrate and dipicrate anions have been prepared [114]. Scheme 27 depicts synthetic routes to salts composed of azolium cations with monopicrate as the anion, including the following picrate salts: 1,2,4-triazolium (**115a**), 1-methyl-1,2,4-triazolium (**115b**), 4-amino-1,2,4-triazolium (**116a**), and 5-amino-tetrazolium (**116b**); and 1,2,4-triazolyl-3-ammonium (**117**), 1,4-dimethyl-1,2,4-triazolium (**118a**), and 1,4-dimethyl-3-azido-1,2,4-triazolium (**118b**). In Scheme 28 are shown the synthetic routes to the energetic bisazolium dipicrate salts. These dipicrate salts are 1,1'-methylenebisimidazolium (**119**), 1,1'-methylene bis(3-methylimidazolium) (**120a**), and 1,1'-methylene bis(4-methyltriazolium) (**120b**) [114].

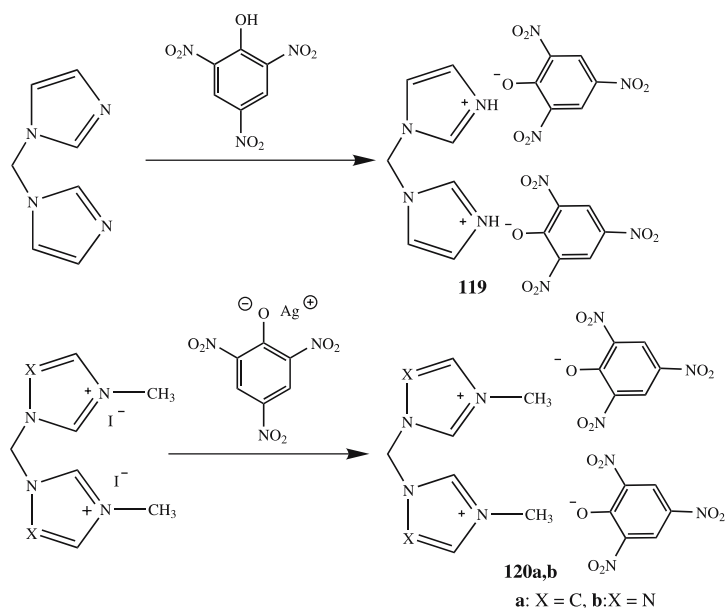
Triazolium or substituted triazolium picrates were first prepared via direct reaction of the triazole with picric acid in methanol or with silver picrate after



Scheme 27

quaternization with methyl iodide (Scheme 27). Bridged bis(imidazolium) or bis(tetrazolium)methane compounds were reacted with picric acid to form dipicrates, or they were quaternized and then metathesized to yield the desired salts. All of these salts were well-characterized, and X-ray crystal structures of **116a** and **116b** were also determined. Their physical characteristics and thermal properties along with those of other energetic materials which are included for comparison, are tabulated in Table 11.

Most of the picrates have good thermal stabilities and relatively high densities and oxygen balance. The bridged azolium picrates are thermally more stable than their monocationic picrate analogues. In general, the majority of these picrates were found to be more stable thermally than their nitrate analogues and less than the perchlorates. 5-Aminotetrazolium picrate (**116b**) was the densest of the picrate salts at 1.85 g/cm³ (calc. X-ray), which

**Scheme 28****Table 11** Physical characteristics and thermochemical data of picrate and dipicrate salts

Compound	Tm ^a °C	Td ^b °C	Density ^c g/cm ³	OB ^d %	ΔH_f° ^e kJ/mol
115a	169	196	1.77	-67	259.0
115b	91	185	1.72	-79	222.3
116a	197	228	1.64 ^f	-66	375.0
116b	147	214	1.85 ^f	-53	400.6
117	235	244	1.60	-66	275.2
118a	141	271	1.80	-91	189.5
118b	106	176	1.48	-78	557.1
119	215	283	1.52	-36	237.1
120a	184	313	1.63	-93	147.4
120b	216	242	1.67	-81	357.1
TAG-AT ^g	-	-	1.60	-73	1075
HMX	-	-	1.90	-21	75
Picric acid	-	-	1.77	-42	-213.6
RDX	-	-	-	-22	83.8

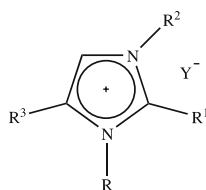
^a melting point;^b thermal decomposition temperature;^c gas pycnometer;^d oxygen balance = 1600 [(a+b/2-d)/FW for a compound with molecular formula CaHbNcOd];^e standard enthalpy of formation (calculated by Gaussian 03);^f X-ray (calc);^g triaminoguanidinium azotetrazolate

places it between picric acid (1.77 cm/g^3) and HMX (1.90 g/cm^3). Unexpectedly protonation in **116a** occurred at one of the ring-nitrogen atoms rather than on the N-amino group. However, in contrast, in the reaction of picric acid with the C-amino triazole, a high-melting ammonium salt (**117**) was formed.

8

Imidazolium-Based Heterocycles

Nitro- and azido-substituted imidazoles, when paired with nitrate or perchlorates, form solid energetic salts in excellent yields [31]. These salts are 1,3-dimethyl-5-nitroimidazolium perchlorate (**121a**), 1,3-dimethyl-5-nitroimidazolium nitrate (**121b**), 1,2,3-trimethyl-5-nitroimidazolium perchlorate (**121c**), 1,2,3-trimethyl-5-nitroimidazolium nitrate (**121d**), 1-ethyl-2,3-dimethyl-5-nitroimidazolium perchlorate (**121e**), 1-ethyl-2,3-dimethyl-5-nitroimidazolium nitrate (**121f**), 2-azidoimidazolium perchlorate (**121g**), and 2-azidoimidazolium nitrate (**121h**) (Fig. 7). Salts (**121a–f**) were made by the metathesis of the corresponding iodide salt with AgClO_4 and AgNO_3 , whereas **121g–h** are formed by the reactions of 2-azidoimidazole with HClO_4 and HNO_3 , respectively.



121a-h

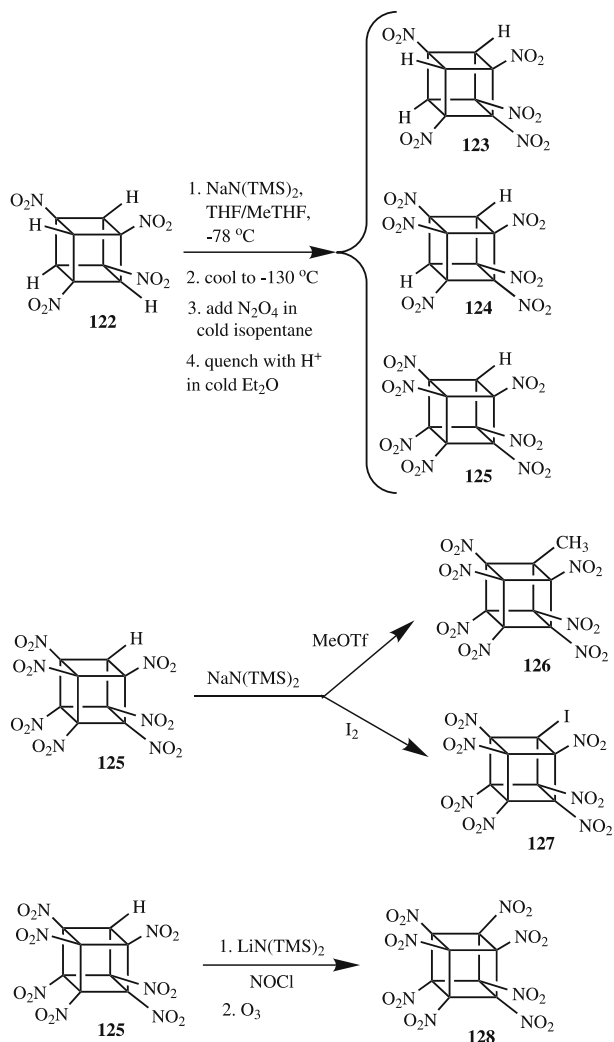
- a: $R = \text{CH}_3$, $R^1 = \text{H}$, $R^2 = \text{CH}_3$, $R^3 = \text{NO}_2$, $Y = \text{ClO}_4$
 b: $R = \text{CH}_3$, $R^1 = \text{H}$, $R^2 = \text{CH}_3$, $R^3 = \text{NO}_2$, $Y = \text{NO}_3$
 c: $R = \text{CH}_3$, $R^1 = \text{CH}_3$, $R^2 = \text{CH}_3$, $R^3 = \text{NO}_2$, $Y = \text{ClO}_4$
 d: $R = \text{CH}_3$, $R^1 = \text{CH}_3$, $R^2 = \text{CH}_3$, $R^3 = \text{NO}_2$, $Y = \text{NO}_3$
 e: $R = \text{C}_2\text{H}_5$, $R^1 = \text{CH}_3$, $R^2 = \text{CH}_3$, $R^3 = \text{NO}_2$, $Y = \text{ClO}_4$
 f: $R = \text{C}_2\text{H}_5$, $R^1 = \text{CH}_3$, $R^2 = \text{CH}_3$, $R^3 = \text{NO}_2$, $Y = \text{NO}_3$
 g: $R = \text{H}$, $R^1 = \text{N}_3$, $R^2 = \text{H}$, $R^3 = \text{H}$, $Y = \text{ClO}_4$
 h: $R = \text{H}$, $R^1 = \text{N}_3$, $R^2 = \text{H}$, $R^3 = \text{H}$, $Y = \text{NO}_3$

Fig. 7 Imidazolium-based energetic ionic salts

All these compounds are well-characterized solids. In general, the nitrate salts have lower melting points and thermal stabilities than the corresponding perchlorates. Energetic salts containing imidazolium triazolate or tetrazolate, and tetrazolium imidazolate are described in Sect. 2.5.

9 Nitrocubane-Based Heterocycles

Highly nitrated cubanes were predicted to be shock-insensitive, very dense, high-energy compounds with great potential as explosives and propellants. Various nitrocubanes, such as penta, hexa, hepta, and octa are reported in the literature. Applying Kamlett–Jacobs equations to octanitrocubane using predicted values for density ($1.9\text{--}2.2\text{ g cm}^{-3}$) and ΔH_f ($81\text{--}144\text{ Kcal mol}^{-1}$) led to calculated detonation velocities and pressures higher than that of



Scheme 29

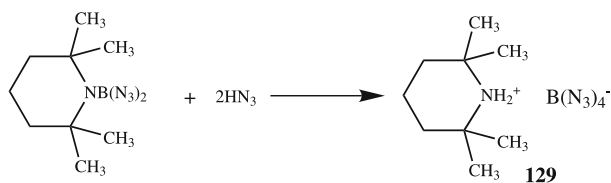
trinitrotoluene (TNT), 1,3,5,7-tetranitro-1,3,5,7 tetraazacyclooctane (HMX), and 2,4,6,8,10,12-hexanitrohexaazaisowurtzitane (CL-20). The chemistry of mono- to tetranitrocubanes had been reported earlier. Eaton et al. showed that the reaction of tetranitrocubane under different reaction conditions produced penta (123), hexa (124), and hepta (125) nitrocubanes in variable yields (Scheme 29). Alkali metal salts of 125 were prepared at low temperature in dichloromethane by reacting with $\text{NaN}(\text{TMS})_2$. When reacted with powerful electrophiles such as methyl triflate and iodine, methylheptanitrocubane (126) and iodoheptanitrocubane (127) were obtained in high yields. Octanitrocubane (128) is prepared by reacting 125 with $\text{LiN}(\text{TMS})_2$ and excess nitrosyl chloride at -78°C followed by ozonation.

Heptanitrocubane (125) is easily soluble in polar solvents, such as acetone, THF, and dichloromethane. Single crystal X-ray analysis of 125 has provided an accurate density at 21°C of 2.028 g cm^{-3} and showed many intermolecular contacts around each molecule. A solution of 125 in methanol turned yellow which may be due to the anion. Octanitrocubane (128) is a stable, white solid and somewhat soluble in hexane but readily soluble in polar organics. Characterization of 128 was based on single crystal X-ray analysis [115].

10

Miscellaneous

When 2,2,6,6-tetramethylpiperidino-boron diazide was reacted with HN_3 , the salt 2,2,6,6-tetramethylpiperidinium tetraazido-borate 129 resulted (Scheme 30) [116–119].



Scheme 30

Recently, the synthesis of a highly energetic, oxygen-balanced tetrazolium polynitratealuminate (130) was reported (Fig. 8) [120]. The material is hydrolytically unstable. A microwave-assisted synthesis of an organic heterocyclic azide (131) was reported in 88% yield (Scheme 31) [121].

Increasing the number of nitrogen atoms in heterocycles results in considerable gain in the standard enthalpy of formation in the resulting compounds. On the basis of this idea the synthesis and properties of cyclophosphazenes-containing azido and amino substituents on the phosphorus atoms were

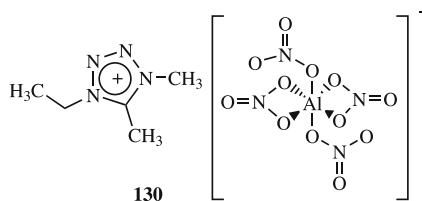
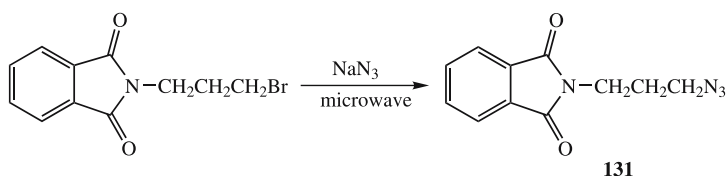
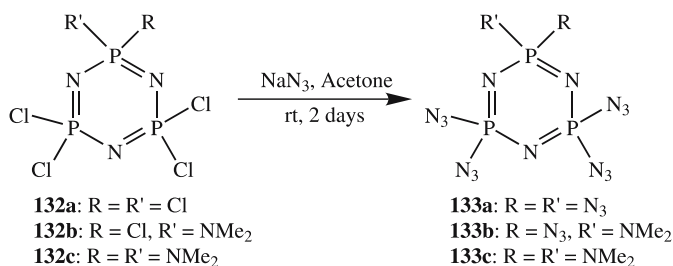


Fig. 8 Tetrazolium polynitratealuminate (**30**)



Scheme 31



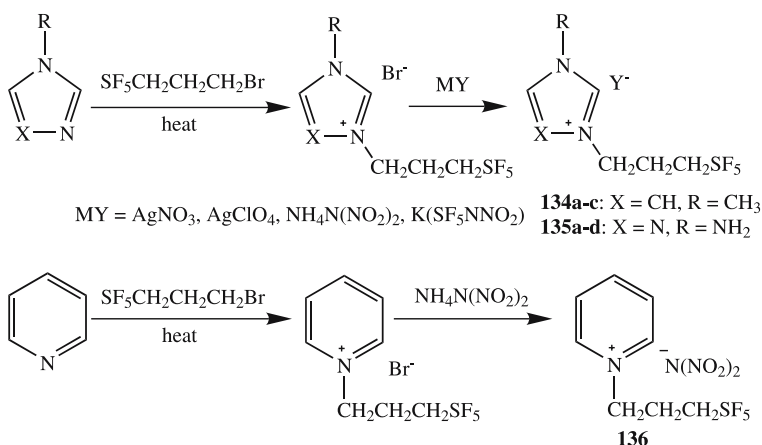
Scheme 32

studied. Reaction of **132a–c** with sodium azide in acetonitrile led to the formation of **133a–c** in very good yields (Scheme 32) [122, 123].

Compounds **133a** and **133b** are liquids, while **133c** is a solid at room temperature. Each was characterized by NMR, HRMS and IR spectroscopy. Compound **133a** is highly friction sensitive and is known to detonate. However, **133b** and **133c** are substantially more stable. The densities of **133b** and **133c** are 1.67 and 1.79 g/cm³, respectively [122, 123]. Compound **133a** has been recently fully characterized and its single crystal X-ray structure determined [123].

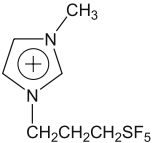
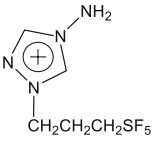
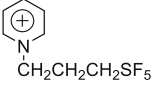
Energetic heterocyclic salts containing SF₅-propyl substituents on imidazole, 4-amino-1,2,4-triazole (**134a–c**, **135a–d**) and pyridine (**136**) moieties were synthesized (Scheme 33). These salts have moderate densities (> 1.4 g/cm³). The calculated heats of formation for dinitramide-containing salts are higher than perchlorate and nitrate salts (Table 12) [124].

Reduction of 2,4,6,8,10,12-hexanitro-2,4,6,8,10,12-hexaazaisowurtzitane (**137**) with stannous chloride dihydrate is reported to give a mixture of isomeric 2,4,6,8,10- and 2,4,6,8,12-pentanitro-2,4,6,8,10,12-hexaazaisowurt-



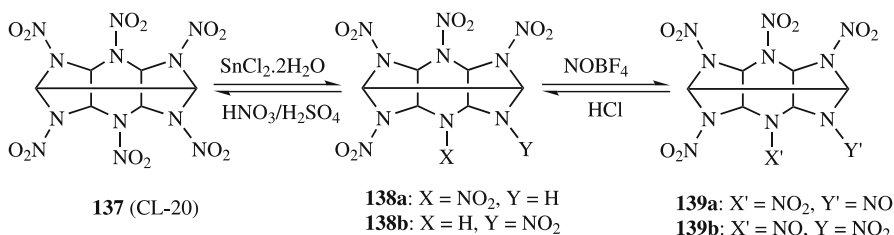
Scheme 33

Table 12 Structure and properties of SF₅-containing salts

Cation	Anion	No	Tm ^a °C	Td ^b °C	d ^d g/cm ³	Δ _f H _m ^{o d} kJ/mol
	NO ₃	134a	-33.7	172.3	1.54	-1030.9
	ClO ₄	134b	-68.0	247.1	1.46	-982.4
	[N(NO ₂) ₂]	134c	-50.7	201.7	1.52	864.0
	NO ₃	135a	58.6	145.8	1.43	-883.7
	ClO ₄	135b	50.7	242.7	1.41	-840.1
	[N(NO ₂) ₂]	135c	84.8	160.9	1.44	718.8
	[SF ₅ NNO ₂]	135d	-20.6	188.2	1.82	-1755.2
	[N(NO ₂) ₂]	136	11.0	182.3	1.47	-865.3

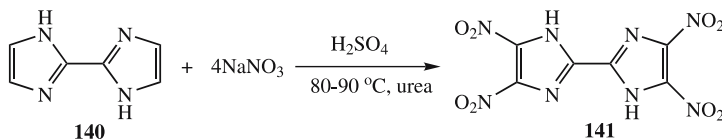
^a melting point^b thermal degradation temperature^c density, gas pycnometer^d standard heat of formation (calculated by Gaussian 03)

zitanes (**138a,b**). The ratio of products depends on the solvents used. Treatment of **138a,b** with NOBF₄ gave isomeric pentanitroso-2,4,6,8,10,12-hexaazaisowurtzitanes (**139a,b**) which can be converted into the starting NH materials by treating with HCl (Scheme 34) [125]. Isomeric pentani-

**Scheme 34**

trohexaazaisowurtzititanes (**138a,b**) are white powders which decompose at temperatures above 150 °C without melting. The nitroso derivatives (**139a,b**) are slightly yellowish powders, which decompose at temperatures below their melting points. Compound **138b** and **139b** are characterized by IR, NMR, and elemental analysis.

A nitroimidazole explosive molecule (**141**) has been synthesized by treating 2,2'-bi-1*H*-imidazole (**140**) with an excess of sodium nitrate (Scheme 35). This compound may serve as an energetic filler for high explosive formulations. The sensitivity results of **141** varied from “more sensitive than RDX” to substantially “less sensitive than RDX” according to the purity and condition of the test sample [126].

**Scheme 35**

11

Summary and Outlook

Many advantages accrue from nitrogen-rich heterocyclic compounds compared to traditional molecular energetic compounds. Utilization of heterocyclic nitrogen-containing cations and anions in energetic salts gives rise to lower vapor pressures, higher heats of formation, and higher densities. Additionally, smaller amounts of hydrogen and carbon contribute to a better oxygen balance than normally is found with their carbocyclic analogues. Nitrogen-rich compounds are promising high energetic materials that may be more acceptable than their alternatives for both industrial and military uses since a higher percentage of their decomposition products will be dinitrogen.

References

1. Gregory CE (1984) Explosives for North American Engineers, vol 5. Trans Tech Publications, Clausthal-Zellerfeld, Germany
2. Davis TL (1943) The Chemistry of Powder and Explosives, vol 2. Wiley, New York
3. Cook MA (1958) The Science of High Explosives. Reinhold, New York
4. Akhavan J (2005) Explosives and Propellants. In: Seidel A (ed) Encyclopedia of Chemical Technology. Wiley, Hoboken, N.J.
5. Urbanski T (1964) Chemistry and Technology of Explosives, vol 3. Pergamon, Oxford
6. Bailey A, Murray SG (1989) Explosives, Propellant and Pyrotechnics. Brassey's, Oxford
7. Urbanski T (1984) Chemistry and Technology of Explosives, vol 4. Pergamon, Oxford, p 202
8. Agrawal JP (1998) Prog Energy Combust Sci 24:1–30
9. Singh G, Kapoor IPS, Mannan SM, Kaur J (2000) J Hazard Mater A79:1–18
10. Fried LE, Manaa MR, Pagoria PF, Simpson RL (2001) Ann Rev Mater Res 31:291–321
11. Singh RP, Verma RD, Meshri DT, Shreeve JM (2006) Angew Chem 45:3584–3601
12. Shlyapochnikov VA, Tafipolsky MA, Tokmakov IV, Baskir ES, Anikin OV, Strelenko YA, Luk'yanov OA, Tartakovskiy VA (2001) J Molec Struct 559:147–166
13. Pagoria PF, Lee GS, Mitchell AR, Schmidt RD (2002) Thermochim Acta 384:187–204
14. Lesnikovich AI, Ivashkevich OA, Levchik SV, Balabanovich AI, Gaponik PN, Kulak AA (2002) Thermochim Acta 388:233–251
15. Sikder AK, Sikder NJ (2004) J Hazard Mater A112:1–15
16. Bottaro J (2005) Ideas to Expand Thinking About New Energetic Materials. In: Shaw RW, Brill TB, Thompson DL (eds) Adv Ser Phys Chem, vol 16. World Scientific, Singapore, pp 473–501
17. Feuer H, Nielsen AT (1990) Nitro Compounds. VCH, New York
18. Nielsen AT (1995) Nitrocarbons. VCH, New York
19. Köhler J, Meyer R (1991) Explosivstoffe, 7th Ed. Wiley, Weinheim, Germany
20. Köhler J, Meyer R (1998) Explosivstoffe, 9th Ed. Wiley, Weinheim, Germany
21. Klapötke TM, Krumm B, Holl G, Kaiser M (2000) Energetic Materials: Modeling of Phenomena, Experimental Characterization, Environmental Engineering. Fraunhofer Institut, Karlsruhe, Germany
22. Simpson RL, Urtiew PA, Ornellas DL, Moody GL, Scribner KS, Hofman DM (1997) Propell Explos Pyrotech 22:249–255 and references cited therein
23. Krause HH (2005) New Energetic Materials. In: Teipal U (ed) Energetic Materials. Wiley, Weinheim, Germany
24. Hiskey MA, Chavez DE, Naud DL, Son SF, Berghout HL, Bolme CA (2000) Proc Int Pyrotech Semin 27:3–14
25. Pedley JB (1994) Thermochemical Data and Structure of Organic Compounds, vol I. Thermodynamic Research Center, College Station, TX
26. Jiminez P, Roux MV, Turrion CJ (1998) Chem Thermodyn 21:759–764
27. Drake GW, Hawkins T, Brand A, Hall L, McKay M, Vij A, Ismail I (2003) Propell Explos Pyrotech 28(4):174–180
28. Drake GW (2003) US Patent 6 509 473 B1
29. Schmidt MW, Gordon MS, Boatz JA (2005) J Phys Chem A 109:7285–7295
30. Xue H, Arritt SW, Twamley B, Shreeve JM (2004) Inorg Chem 43:7972–7977
31. Xue H, Gao Y, Twamley B, Shreeve JM (2005) Chem Mater 17:191–198

32. Drake GW, Hawkins T, Tollison K, Hall L, Vij A, Sobaski S (2005) In: Rogers RD, Seddon KR (eds) *Ionic Liquids-III A: Fundamentals, Progress, Challenges, and Opportunities*. ACS Symposium Series 902. ACS, Washington, DC, pp 259–302
33. Trohalaki S, Pachter R, Drake GW, Hawkins T (2005) *Energ Fuel* 19:279–284
34. Kaplan G, Drake G, Tollison K, Hall L, Hawkins T (2005) *J Heterocycl Chem* 42:19–27
35. Ostrovskii VA, Pevzner MS, Kofman TP, Tselinskii IV (1999) *Targets Heterocycl Syst* 3:467–526
36. Denault CC, Marx PC, Takimoto HH (1968) *J Chem Eng Data* 13:514–516
37. Xue H, Shreeve JM (2005) *Adv Mater* 17:2142–2146
38. Buscemi S, Pace A, Pibiri I, Vivona N, Spinelli D (2003) *J Org Chem* 68:605–608
39. Funabiki K, Noma N, Shibata K (1999) *J Chem Res Synop* pp 300–301, and references cited therein
40. Xue H, Twamley B, Shreeve JM (2004) *J Org Chem* 69:1397–1400
41. Mirzaei YR, Shreeve JM (2003) *Synthesis* 24–26
42. Mirzaei YR, Shreeve JM (2002) *J Org Chem* 67:9340–9345
43. Mirzaei YR, Xue H, Shreeve JM (2004) *Inorg Chem* 43:361–367
44. Shitov OP, Korolev VL, Bogdanov VS, Tartakovsky VA (2003) *Russ Chem Bull Int Ed* 52:695–699
45. Egashira M, Scrosati B, Armand M, Beranger S, Michot C (2003) *Electrochem Solid State Lett* 6(4):A71–A73
46. Katritzky A, Singh S, Kirichenko K, Holbrey JD, Smiglak M, Reichert MW, Rogers RD (2005) *Chem Commun* 868–870
47. Sitzmann MI (1978) *J Org Chem* 43:3389–3391
48. Kofman TP, Paketina EA (1997) *Russ J Org Chem (Eng Trans)* 33:1125–1132
49. Chernyshev VM, Zemlyakov ND, Il'in VB, Taranushich VA (2000) *Zh Prikl Khim* 73:791–793
50. Ogihara W, Yoshizawa M, Ohno H (2004) *Chem Lett* 33(8):1022–1023
51. Xue H, Gao Y, Twamley B, Shreeve JM (2005) *Inorg Chem* 44:5068–5072
52. Martin AR, Yallop HJ (1958) *Trans Faraday Soc* 54:257–267
53. Ostrovskii VA, Koldobskii GI, Shirokova NP, Poplavskii VS (1981) *Khim, Grterotsikl Soedin* 4:559–562
54. Krakovskii IM, MolChanova MS, Evtushenko AV, Shlyapochnikova VA (1998) *Russ Chem Bull* 47:1266–1273
55. Kozyro AA, Simirsky VV, Krasulin AP, Sevruk VM, Kabo GJ, Gopanik ML, Grigotiev YV (1990) *Zh Fiz Khim* 64:656–661
56. Gao A, Oyumi Y, Brill TB (1991) *Combust Flame* 83:345–352
57. von Denffer M, Klapötke TM, Kramer G, Spieß G, Welch JM, Heeb G (2005) *Propell Explos Pyrotech* 30:191–195
58. Klapötke TM, Mayer P, Schulz A, Weigand JJ (2005) *J Am Chem Soc* 127:2032–2033
59. Gálvez-Ruiz JC, Holl G, Karaghiosoff K, Klapötke TM, Löhnwitz K, Mayer P, Nöth H, Polborn K, Rohbogner CJ, Suter M, Weigand JJ (2005) *Inorg Chem* 44:4237–4253
60. Fisher G, Holl G, Klapötke TM, Weigand JJ (2005) *Thermochim Acta* 437:168–178
61. Geith J, Klapötke TM, Weigand J (2004) *Propell Explos Pyrotech* 29:3–8
62. Hammerl A, Klapötke TM, Nöth H, Warchhold M, Holl G (2003) *Propell Explos Pyrotech* 28:165–173
63. Hammerl A, Klapötke TM, Mayer P, Weigand JJ, Holl G (2005) *Propell Explos Pyrotech* 30:17–26
64. Klapötke TM, Mayer P, Verma V (2006) *Propell Explos Pyrotech* 31:263–268
65. Klapötke TM, Karaghiosoff K, Mayer P, Penger A, Welch JM (2006) *Propell Explos Pyrotech* 31:188–195

66. Karaghiosoff K, Klapötke TM, Mayer P, Piotrowski H, Polborn K, Willer RL, Weigand JJ (2006) *J Org Chem* 71:1295–1305
67. Hammerl A, Klapötke TM (2002) *Inorg Chem* 41:906–912
68. Thiele J (1892) *Liebigs Ann* 270:54–63
69. Thiele J, Marais JT (1893) *Justus Liebigs Ann Chem* 273:144–160
70. Thiele J (1893) *Ber Dtsch Chem Ges* 26:2645–2646
71. Thiele J (1898) *Justus Liebigs Ann Chem* 303:57–75
72. Hammerl A, Holl G, Klapötke TM, Mayer P, Noth H, Piotrowski H, Warchhold M (2002) *Eur J Inorg Chem* 834–845
73. Hiskey MA, Goldman N, Stine JR (1998) *J Energ Mater* 16:119–127
74. Peng Y, Wong C (1999) US Patent 5 877 300 CA 130:196656
75. Hammerl A, Klapötke TM, Nöth H, Warchhod M, Holl G, Kaiser M, Ticmanis U (2001) *Inorg Chem* 3570–3575
76. Hammerl A, Holl G, Kaiser M, Klapötke TM, Mayer P, Piotrowski H, Vogt M (2001) *Naturforschung* 847–856
77. Hammerl A, Holl G, Kaiser M, Klapötke TM, Mayer P, Nöth H, Piotrowski H, Suter M (2001) *Naturforschung* 857–870
78. Klapotke TM, Holl G (2001) *Green Chem* G75–G76
79. Hammerl A, Hiskey MA, Holl G, Klapötke TM, Polborn K, Stierstorfer J, Weigand J (2005) *Chem Mater* 17:3784–3793
80. Tappan BC, Ali AN, Son SF (2006) *Propell Explos Pyrotech* 31:163–168
81. Ye C, Xiao J-C, Twamley B, Shreeve JM (2005) *Chem Commun* 2750–2752
82. Hyoda S, Kita M, Sawada H, Nemugaki S, Otsuka S, Miyawaki Y, Ogawa T, Kubo Y (2000) US Patent 6040 453, CA: 132:207845
83. Hyoda S, Kita M, Sugino A, Ueta T, Sato K (2001) EU Patent 1 162 198, CA: 136:20077
84. Hyoda S, Kita M, Swada H, Nemugaki S, Ueta T, Satoh K, Otsuka S, Miyawaki Y, Taniguchi H (2000) EU Patent Appl, EP 1 016 662, CA: 133:74021
85. Torii S, Tsuyama M, Miyawaki Y, Kubo Y, Ogawa T (2000) *Jpn Kokai Tokkyo Koho, JP 2000281662*, CA 133:252440
86. Friedrich M, Gálvez-Ruiz JC, Klapötke TM, Mayer P, Weber P, Weigand JJ (2005) *Inorg Chem* 44:8044–8052
87. Hammerl A, Holl G, Kaiser M, Klapötke TM, Piotrowski H (2003) *Z Anorg Allg Chem* 629:2117–2121
88. Kita M, Ueda T (2004) *Jpn Kokai Tokkyo Koho, JP 2004067544*, CA 140:217643
89. Naud DL, Hiskey MA (2003) US Patent Appl Publ, 2003 060 634, CA:138:255236
90. Highsmith TK, Hajik RM, Wardle RB, Lund GK, Blau RJ (1995) US Patent 5 468 866
91. Gao Y, Ye C, Twamley B, Shreeve JM (2006) *Chem-Eur J* 12:9010
92. Foss ME, Hirst EL, Jones JKN, Springall HD, Thomas AT, Urbanski T (1950) *J Chem Soc* 624–628
93. Ang H-G, Fraenk W, Karaghiosoff K, Klapötke TM, Nöth H, Sprott J, Sutter M, Vogt M, Warchhold MZ (2002) *Z Anorg Allg Chem* 628:2901–2906
94. Xue H, Twamley B, Shreeve JM (2006) *Eur J Inorg Chem* 2959–2965
95. Chavez DE, Hiskey MA, Naud Di (2004) *Propell Explos Pyrotech* 29:209–215
96. Oxley JC, Smith JL, Chen H (2002) *Thermochim Acta* 91–99
97. Chavez DE, Hiskey MA, Gilardi RD (2004) *Org Lett* 6:2889–2891
98. Chavez DE, Tappan BC, Hiskey MA, Son SF, Harry H, Montoya D, Hagelberg S (2005) *Propell Explos Pyrotech* 30:412–417
99. Gao H, Wang R, Twamley B, Hiskey MA, Shreeve JM (2006) *Chem Commun* 4007–4009
100. Kerth J, Löbbbecke S (2002) *Propell Explos Pyrotech* 27:111–118

101. Chavez DE, Hiskey MA, Gilardi RD (2000) *Angew Chem Int Ed* 39:1791–1793
102. Huynh MHV, Hiskey MA, Chavez DE, Naud DL, Gilardi RD (2005) *J Am Chem Soc* 127:12537–12543
103. Huynh MHV, Hiskey MA, Archuleta JG, Roemer EL, Gilardi R, Chavez DE, Naud DL, Gilardi RD (2004) *Angew Chem Int Ed* 43:5658–5661
104. Miller DR, Swenson DC, Gillan EG (2004) *J Am Chem Soc* 126:5372–5373
105. Huynh MHV, Hiskey MA, Hartline EL, Montoya DP, Gilardi R (2004) *Angew Chem Int Ed* 43:4924–4928
106. Huynh MHV, Hiskey MA, Pollard CJ, Montoya DP, Hartline EL, Gilardi R (2004) *J Energ Mater* 22:217–229
107. Frumkin AE, Churakov AM, Strelenko YA, Kachala VV, Tartakovsky VA (1999) *Org Lett* 1:721–724
108. Archibald TG, Gilardi R, Baum K, George C (1990) *J Org Chem* 55:2920–2924
109. Coburn MD, Hiskey MA, Archibald TG (1997) *Waste Manag* 17:143–146
110. Hiskey MA, Coburn MD, Mitchell MA, Benicewicz BC (1992) *J Heterocycl Chem* 29:1855–1856
111. Hiskey MA, Stincipher MM, Brown JE (1993) *J Energ Mater* 11:157–165
112. Gilardi RD, Butcher RJ (1998) *J Chem Crystallogr* 28(3):163–169
113. Coburn MD, Hiskey MA, Oxley JC, Smith JL, Zheng W, Rogers E (1998) *J Energ Mater* 16(2):73–99
114. Jin C-M, Ye C, Piekarski C, Twamley B, Shreeve JM (2005) *Eur J Inorg Chem* 3760–3767
115. Zhang M-X, Eaton PE, Gilardi R (2000) *Angew Chem Int Ed* 39(2):404–401
116. Chung G, Schmidt MW, Gordon MS (2000) *J Phys Chem A* 104:5647–5650
117. Fau S, Bartlett RJ (2001) *J Phys Chem A* 105:4096–4106
118. Nguyen NT (2003) *Coordinat Chem Rev* 244:93–113
119. Christe KO, Dixon DA, McLemore D, Wilson WW, Sheehy JA, Boatz JA (2000) *J Fluor Chem* 101:151–153
120. Jones CB, Haiges R, Schroer T, Christe KO (2006) *Angew Chem Int Ed* 45:4981–4984
121. Ju Y, Kumar D, Verma RS (2006) *J Org Chem* 71:6697–6700
122. Muralidharan K, Omotowa BA, Twamley B, Piekarski C, Shreeve JM (2005) *Chem Commun* 5193–5195
123. Göbel M, Karaghiosoff K, Klapötke TM (2006) *Angew Chem Int Ed* 45:6037–6040
124. Gao H, Ye C, Winter RW, Gard GL, Sitzmann ME, Shreeve JM (2006) *Eur J Inorg Chem* 3221–3226
125. Lukyanov OA, Shykova NI (2004) *Russ Chem Bull Int Ed* 53:566–568
126. Gyeong S, Cho JR, Goh EM, Kim J-K (2005) *Propell Explos Pyrotech* 30:445–449