Explosives

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From *N*-Nitro to *N*-Nitroamino: Preparation of High-Performance Energetic Materials by Introducing Nitrogen-Containing Ions

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Abstract: *In the design of energetic materials, high energetic performance and good molecular stability are two main goals. Energetic functionalization which strives for maximum energy often results in unstable chemical bonds and causes safety problems in practical production and storage operations. In this work, N-nitro- and N-nitroamino-functionalized mono- and bis(1,2,4-triazoles) were synthesized and characterized by infrared, and multinuclear NMR spectra, and elemental analyses. The N-nitroamino-functionalization strategy was employed for bis(imidazole), leading to high density compound* ***14*** *(2.007 g cm^{-3} at 100 K; 1.94 g cm^{-3} at room temperature) and energetic salt* ***15****. While N-nitro-functionalized products are thermally unstable and highly moisture sensitive, N-nitroamino-functionalized energetic salts, which are comprised of additional nitrogen-containing ions, exhibit good density, moderate to excellent structural stabilities, and high performance.*

Energetic materials play a pivotal role in both military and civilian fields, e.g., aerospace propellants, mining engineering, and pyrotechnic technology. With increasingly variable application demands for high energy density materials (HEDMs), energetic performance and molecular stability become two key criteria in evaluating overall properties.[1] At the molecular level, most typical HEDMs are composed of organic frameworks and oxidizing moieties, such as 2,4,6-trinitrotoluene (TNT)[2] and triaminotrinitro benzene (TATB).[3] Heterocyclic chemistry supports the development of energetic materials in the design of versatile nitrogen-rich backbones.[4] In comparison with carbocyclic analogues, heterocycle-based HEDMs feature high heats of formation, and good thermal stability, as well as enhanced detonation performance arising from tremendous energy storage in nitrogen-rich backbones.[5]

While nitrogen-rich heterocycles have become the core motif in the search for new HEDMs, their compatibility with other energetic functionalized groups is receiving increased attention.[6] Diversified energetic functionalized groups, e.g., nitro, nitroamino, azido, azo, azoxy, trinitromethyl, and trinitroethylamino groups are incorporated with nitrogen-rich backbones to tailor the energetic properties.[7] Among these, the nitro group is considered to be one of the superior energetic functionalities because of the favorable balance between stability and performance. In comparison, nitroamino and azido functionalities tend to increase the density and detonation properties; however, their molecular stabilities associated with thermal behavior, and impact and friction sensitivity are not competitive with their nitro-functionalized analogues.[8]

Here, our synthetic interest focuses on the various nitro- and nitroamino-functionalized mono and bis(1,2,4-triazoles) (Scheme 1). In spite of the good calculated performance for **2** and **7**, the high moisture sensitivity and low thermal stability result in both being unstable when stored at room temperature. Interestingly, the *N*-nitroamino-functionalized compounds (**4** and **10**) are more stable thermally and the neat compounds can be stored for an extended period. The ionic derivatives of **4** and **10** show enhanced molecular stability and excellent detonation properties. Compared to *N*-nitro-functionalized compounds (**2** and **7**), further introduction of nitrogen-containing ions acts as an energetic buffer to stabilize greatly the nitrogen-rich frameworks, and retain high energetic performance. Additionally, introduction of the *N*-nitroamino functionality into bis(imidazoles) also gives rise to new analogues **14** and **15** which have promising energetic performance.

N-Nitro- and *N*-nitroamino-functionalized monocyclic 1,2,4-triazoles (**2**–**5**) were prepared from 3-nitro-1*H*-1,2,4-triazole (**1**).[9] Since *N*,*N'*-dinitro-functionalized bi(1,2,4-triazole) (**7**) was highly unstable, our research interest was then focused on *N*,*N'*-dinitroamino-functionalized bi(1,2,4-triazole) (**10**). Employing modified amination conditions with *O*-tosylhydroxylamine, 5,5'-dinitro-2*H*,2'*H*-3,3'-bi(1,2,4-triazole)-2,2'-diamine (**9**) was prepared from the ammonium salt, **8**. (Scheme 2) Nitration of **9** occurred using mixed acid (sulfuric acid and fuming nitric acid) and **10** was obtained by filtration. Unlike the highly moisture-sensitive *N*,*N'*-dinitro analogue **7**, *N*,*N'*-dinitroamino-functionalized bi(1,2,4-triazole), **10**, exhibited unexpected hydrolytic stability. Reactions of **10** with two equimolar amounts of nitrogen-rich bases in ethanol or aqueous solution resulted in energetic salts (**11a**–**11f**) in nearly quantitative yields. To prepare the triaminoguanidium salt (**11g**), an alternative synthesis was used via a dipotassium intermediate, **12**, with triaminoguanidium hydrochloride.

To examine the superiority of the *N*-nitroamino functionality, bis(imidazole) was chosen as a backbone to construct new high-density heterocycles. The nitration reaction of diamino compound **13** in mixed acid at low temperature (−15 to −10 °C) yielded **14** in excellent yield. The following metathesis reactions with hydroxylammonium chloride gave rise to dihydroxylammonium salt **15**. The structures of the *N*-

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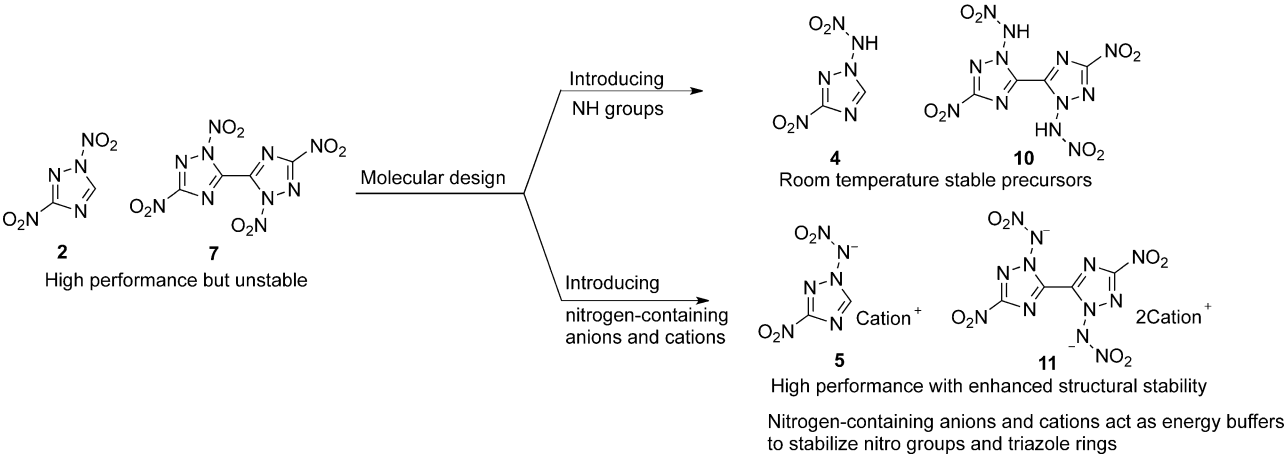
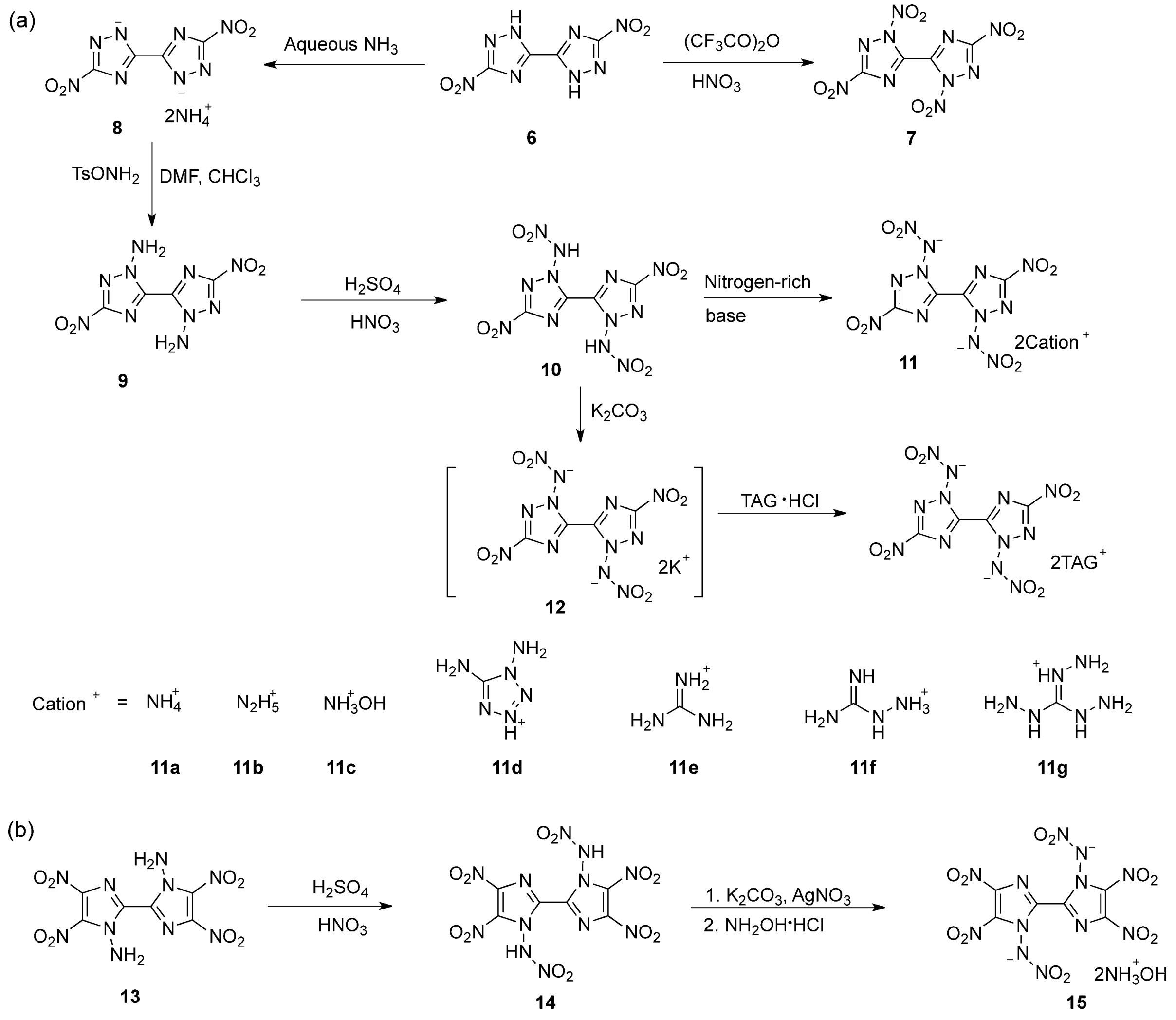


Scheme 1. *N*-Nitro- and *N*-nitroamino-functionalized 1,2,4-triazoles.



Scheme 2. Synthesis of *N*-functionalized 1,2,4-triazoles and imidazoles.

functionalized 1,2,4-triazoles and imidazoles are supported by ^{1}H NMR, ^{13}C NMR, and IR spectroscopy, and elemental analysis. Compounds **9**, **10**, **11c** and **13** were further investigated by employing single-crystal X-ray crystallography that displays insight into structural features (Figure 1). The detailed data can be found in the Supporting Information.[10]

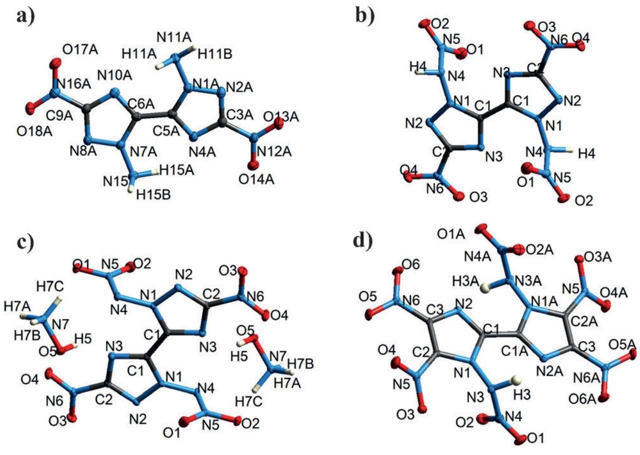


Figure 1. a) Single-crystal X-ray structures of a) **9**, b) **10**, c) **11c**, and d) **14**.

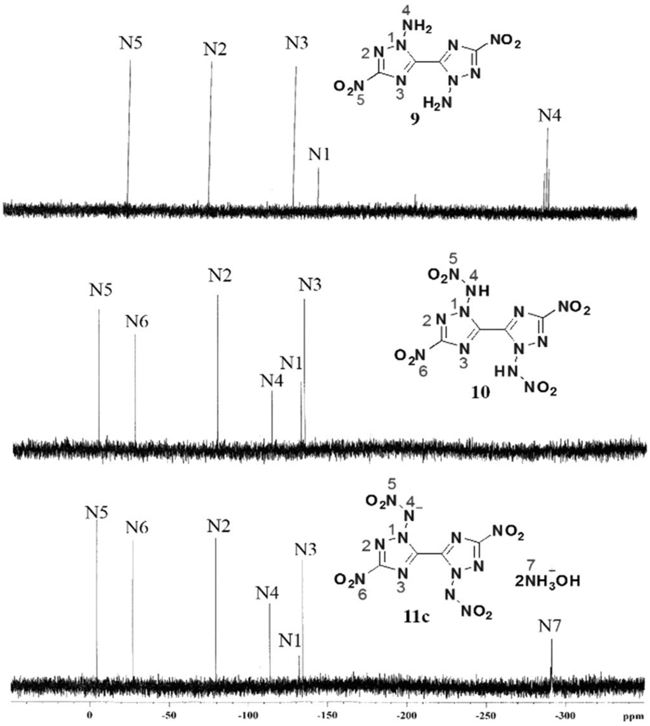


Figure 2. ^{15}N NMR spectra of **9**, **10**, and **11c**.

Compared to the highly unstable *N*, *N'*-dinitro-functionalized compound **7**, rational molecular design by introducing additional NH groups or nitrogen-containing anions and cations gives rise to more stable analogues, i.e., compound **10** and energetic salt **11c**. The difference in molecular stabilities can be attributed mainly to hydrogen bonding interactions in **10** and **11c**, while for **7** it is not possible to form strong hydrogen bonds due to the absence of active hydrogen. In the crystal structure of **10**, six intermolecular hydrogen bonds are found in each molecule. Among them, four hydrogen bonds are formed between NH groups and *C*-NO_2 groups (N4-4⋯O3 and N4-H4⋯O4) and two hydrogen bonds are formed between NH groups and the triazole ring (N4-H4⋯N3). In comparison, **11c** exhibits remarkably enhanced intramolecular and intermolecular interactions with 26 hydrogen bonds, most of which arise from the interactions between nitroamino anions and hydroxylammonium cations. In general, hydrogen bonds with an interatomic H⋯O distance less than 2.0 Å are classified as strong interactions. With respect to **11c**, the shortest hydrogen bond interaction was found at N7-H7B⋯O2 with an H⋯O distance of 1.811 Å.

In the ^{1}H NMR spectra of N-amino compounds **9**, signals of NH_2 groups bonded to triazole rings were found at 7.51 ppm. The ^{13}C NMR chemical shifts of the triazole ring in dinitroamine **10** and its ionic derivatives (**11a**–**11g**) appear at 158 and 140 ppm. In the infrared spectrum of the diamino compound **9**, two characteristic absorption bands at 3333 and 3300 cm^{-1} can be attributed to *N*-amino groups, whereas absorption bands for nitro groups were observed at 1310–1600 cm^{-1}.

As seen in Figure 2, the ^{15}N NMR spectra of diamine **9**, dinitroamine **10**, and hydroxylammonium salt, **11c**, are shown measured in [D$_6$]-DMSO. The ^{15}N{H} NMR spectrum of **9** shows five signals at $\delta = -28.23$ (N5), −79.38 (N2), −132.78 (N3), −148.51 (N1), −292.47 ppm (N4). In comparison, dinitramine **10** shows an additional signal at $\delta = -4.31$ ppm arising from the nitroamino group. The triazole anion of **11c** exhibits chemical shifts similar to the molecular compound, **10;** the only difference is the signal of N1 which becomes weaker due to the deprotonation of the nitroamine.

The thermal stabilities of *N*-nitro/*N*-nitroamino-functionalized triazoles were determined using differential scanning calorimetrical (DSC) measurements. As shown in Table 1, diamino compound **9** exhibits the highest thermal stability at 271 °C. Although *N,N'*-dinitroamino compounds **10** and **14** decompose at 116 °C and 121 °C, respectively, their ionic derivatives (**11a**–**11g** and **15**) have enhanced thermal stabilities ranging between 135 °C and 252 °C. Among them, the ammonium salt **11a** and the guanidinium salt **11e** with decomposition temperatures of 223 °C and 252 °C, respectively, are superior to RDX (T_d, 205 °C). As a significant evaluation criterion, density determines the detonation performance of HEDMs. These new *N*-functionalized 1,2,4-triazole and imidazoles exhibit good to excellent densities, ranging from 1.72 to 1.94 $g\,cm^{-3}$. In addition to density, heats of formation also play a pivotal role in high-performance energetic materials; the computation was performed by using the Gaussian03 (Revision D.01) suite of programs.[11] As can be seen in Table 1, all of the 1,2,4-triazoles and imidazoles are endothermic with positive heats of formation. In general, energetic materials functionalized with multiple nitro groups tend to exhibit lower heats of formation. However, **9** exhibits a higher heat of formation than that of precursor **6** since *N*-functionalization results in additional N−N bonds (**6**, 1.34 $kJ\,g^{-1}$; **9**, 1.71 $kJ\,g^{-1}$). With a high nitrogen 1,5-diaminotetrazolium cation, **11d** has the most positive enthalpy of formation, 3.07 $kJ\,g^{-1}$, due to the large number of N−N and N=N bonds.

For HEDMs, the evaluation of energetic performance depends, to a great extent, on the detonation velocity (v_D) and detonation pressure (P). Based on experimental densities and

Table 1: Physical properties of *N*-functionalized 1,2,4-triazoles and imidazoles.

Compd.	T_d[a] [°C]	*d*[b] [g cm^{-3}]	ΔH_f[c] [kJ mol^{-1}/kJ g^{-1}]	*P*[d] [GPa]	ν_D[e] [m s^{-1}]	IS[f] [J]	FS[g] [N]	OB[h] [%]
9	271	1.83 (1.86[j])	439.5/1.72	31.8	8677	40	360	−12.5
10	121	1.88 (1.92[j])	591.7/1.71	38.2	9243	3	40	13.9
11a	223	1.77	434.9/1.15	33.1	8769	10	120	0
11b	170	1.81	746.9/1.82	36.4	9170	7	120	−3.90
11c	166	1.86 (1.89[j])	535.6/1.30	39.1	9330	8	120	7.77
11d	160	1.79	1667.9/3.07	35.5	9131	5	80	−8.79
11e	252	1.74	431.5/0.93	28.4	8456	40	360	−13.8
11f	197	1.72	680.3/1.38	28.9	8570	40	360	−16.2
11g	200	1.73	1123.9/2.03	31.3	8927	10	160	−20.2
14	116	1.94 (2.01[j])	481.1/1.11	40.1	9350	3	40	18.4
15	135	1.85	449.0/0.90	38.2	9169	6	80	12.8
RDX[k]	205	1.81	80.0/0.36	34.9	8748	7	120	0
HMX[k]	280	1.90	104.8/0.36	39.5	9320	7	120	0

[a] Decomposition temperature (onset). [b] Density measured by gas pycnometer (25 °C). [c] Heat of formation. [d] Detonation pressure (calculated with Explo5 v6.01). [e] Detonation velocity (calculated with Explo5 v6.01). [f] Impact sensitivity. [g] Friction sensitivity. [h] Oxygen balance (based on CO) for $C_aH_bO_cN_d$, $1600(c-a-b/2)/M_W$, M_W = molecular weight. [j] Crystal density. [k] RDX = 1,3,5-trinitroperhydro-1,3,5-triazine; HMX = octahydro-1,3,5,7-tetranitro-1,3,5,7-tetrazocine.

calculated heats of formation, detonation properties were calculated using Explo5 v 6.01.[12] Calculated detonation pressures and velocities of resulting compounds fall in the ranges from 28.4 GPa to 40.1 GPa, and from 8456 m s^{-1} to 9350 m s^{-1}, respectively, which are comparable to those of RDX (*P*, 34.9 GPa, ν_D, 8748 m s^{-1}). Among them, the detonation parameters of **14** (*d*, 1.94 g cm^{-3}, *P*, 40.1 GPa, ν_D, 9350 m s^{-1}) are even superior to high explosive HMX (*d*, 1.90 g cm^{-3}, *P*, 39.5 GPa, ν_D, 9320 m s^{-1}). The impact sensitivity of diamino compound **9** is 40 J. As is the case for many nitroamine compounds, **10** and **14** are relatively sensitive to impact (IS, 3 J); however, the ionic derivatives (**11a**–**11g**, and **15**) possess enhanced stabilities, with impact sensitivities ranging from 5 J to 40 J. A similar trend is found in friction sensitivity tests, where it can be seen that while **10** and **14** are friction sensitive (40 N), **11a**–**11d**, **11g**, and **15** are relatively less friction sensitive (FS, 80–160 J), and **9**, **11e**, and **11f** are friction insensitive (FS, 360 J). Additionally, oxygen balances (OB) of these compounds fall between −20.2 to 18.4 %. The positive OB values (7.77–18.4) and good densities (1.85–1.94 g cm^{-3}) of several compounds (**10**, **11c**, **14**, and **15**) suggest their potential use as high dense energetic oxidizers.

N-Nitro and *N*-nitroamino functionalities were investigated in search of high-performance energetic materials. Based on the comparative experimental properties and computational analysis, it is shown that introduction of additional nitrogen-containing ions in energetic salts (**11a**–**11g** and **15**) stabilizes the azole moieties and nitro groups via multiple hydrogen-bond interactions. Compound **10** and **14** exhibit high density and superior detonation performance with relative low stabilities. Here the energetic salt **11c** has excellent detonation properties with acceptable sensitivities, which are comparable to those of the high explosives RDX and HMX. In comparison with the fact that most nitro-functionalized compounds are more stable than their corresponding nitroamino-functionalized compounds, this comparative investigation illustrates an interesting case and provides a promising strategy in designing high-performance energetic materials.

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[9] See the Supporting Information.

[10] CCDC 1058145 (**9**), 1058144 (**10**), 1404848 (**11c**), and 1404847 (1**4**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre.

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