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Energetic Materials

Bis(nitroamino-1,2,4-triazolates): *N*-Bridging Strategy Toward Insensitive Energetic Materials**

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Abstract: *Modern energetic motifs for military and civilian applications are most often evaluated using various criteria, for example, energetic properties, production costs, and safety issues. Given this background, the design of energetic materials requires a deep understanding of both detonation performance and molecular stability. Here a new family of energetic bis(nitroamino-1,2,4-triazolates), which exhibit good thermal stabilities, excellent detonation properties, and low sensitivities, has been designed. Furthermore, two hydroxylammonium bis(azolates) with pyrazole and tetrazole backbones were synthesized, and they exhibit energetic properties analogous to the triazoles. This work highlights the application potential of N-bridged bis(azolates) as promising energetic materials.*

As a significant branch of material science, energetic materials, including explosives, propellants, and pyrotechnics, continue to be an intensively investigated area of the utmost importance. Since nitroglycerin has been used successfully as an explosive, the development of energetic ingredients has contributed greatly not only to military applications, but also to the solution of many civilian engineering problems whose aim is to expedite laborious processes.[1] Traditional investigations of energetics mainly focus on enhancing detonation performance to achieve more powerful materials. However, driven by growing environmental and safety concerns, considerable research interest tends to be directed more to productive processes that result in low pollution and various properties, for example, insensitivity toward impact and friction, high densities and heats of formation, and environmentally benign degradation and decomposition products.[2] In this new situation, the advancement of energetic materials faces diverse challenges to reach high energetic performance in combination with meeting environmental and safety requirements.

In general, compounds functionalized with energetic groups (NO_2, $NHNO_2$, N_3, N=N, etc.) typically possess high densities and heats of formation. However, in most cases, the assembly of numerous explosophores in one molecule gives rise to a dramatic decrease in thermal and impact stability. For example, some traditional explosives, such as RDX (1,3,5-trinitrotriazacyclohexane)[3] and HMX (cyclo-1,3,5,7-tetramethylenene-2,4,6,8-tetranitramine),[4] exhibit good detonation properties arising from polynitroamino groups, yet they are sensitive to mechanical stimuli. Given this background, nitrogen-rich azoles are expected to be a promising alternative for the construction of advanced energetic materials. Combined with high nitrogen content and high heats of formation, most azole-based compounds feature good densities and detonation properties.[5] Moreover, the nitrogen atoms of azole rings are capable of further functionalization, for example, *N*-amination,[6] *N*-hydroxylation,[7] and *N*-alkylation,[8] thereby contributing to diverse strategies of designing energetic materials.

Recently, our group has been interested in developing *N*-substituted nitrogen-rich compounds and exploring their energetic applications. A new family of alkyl- and alkoxy-bridged nitroiminotetrazoles was designed and synthesized by a straightforward method involving the concise formation of tetrazoles through cycloaddition of cyanogen azide with primary amines, followed by nitration with 100% HNO_3.[9] Among them, *N*-ethylene-bridged bis(5-nitroiminotetrazole) is the best representative with a high density and excellent detonation velocity and pressure comparable to RDX and HMX. In comparison, *N*-alkoxy-bridged derivatives are featured with enhanced oxygen balance and improved detonation properties, but with reduced stabilities. Furthermore, when reacted with nitrogen-rich bases, they are capable of giving rise to varying energetic salts, thus expanding their applications.[10]

After we had investigated the merits of an *N*-bridging strategy and demonstrated the promising energetic properties, we paid further attention to production costs and safety concerns. For example, a modified method to prepare *N*-ethylene-bridged bis(5-nitroiminotetrazole) has been reported, which constitutes a concise synthesis without using cyanogen bromide. However, the practical application may be impeded by low reaction yield and selectivity.[11] In our continuing efforts to develop practical bridged energetic materials, we now report a new family of ethylene-bridged bis(nitramino-1,2,4-triazolates) formed from 3-amino-5-nitro-1,2,4-triazole and dibromoethane. Compared to bis(nitroiminotetrazolates), this contribution has several advantages, for example, low-cost reagents, as well as good reaction yields and high reaction selectivity. More importantly, most ionic derivatives of these triazolates have low impact and friction sensitivities, but retain desirable density and detonation properties.

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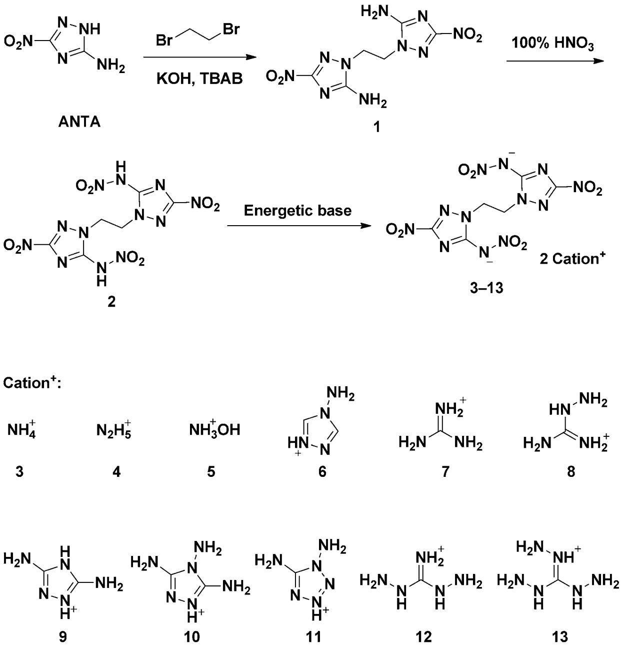
In our initial study, various substituted nitrotriazoles, including 3,5-dinitro-1,2,4-triazole, 5-bromo-3-nitro-1,2,4-triazole, and 3-amino-5-nitro-1,2,4-triazole, were used to test the coupling reaction establishing the ethylene bridge. While amino-substituted nitrotriazoles were converted to the desired ethylene-bridged product, the other two reactions resulted in the *N*-vinyl triazole as the main product. Using tetraethylammonium bromide(TEAB) as a phase-transfer catalyst and KOH as the base, the reaction of 3-amino-5-nitro-1,2,4-triazole with dibromoethane formed 1,1′-(ethane-1,2-diyl)-bis(3-nitro-1H-1,2,4-triazol-5-amine) (**1**) in good yield and high purity (Scheme 1). The formation of the *N*-ethylene bridge showed good selectivity and only a trace amount of an isomer was observed. However, this isomer has been isolated and characterized (see the Supporting Information). When treated with 100 % nitric acid, **1** was readily converted to the corresponding nitramine product **2**. Consequently, a series of nitrogen-rich salts (**3**–**13**) were prepared by using **2** as an acid to react with energetic bases. Energetic salt **11** was formed with an anion/cation ratio of 1:1, even when excess 1,5-diaminotetrazole was used. Interestingly, nitramine **2** reacted directly with tri- and diaminoguanidine hydrochloride without the presence of a base, leading to **12** and **13**, respectively. All compounds were fully characterized by NMR and IR spectroscopy, thermal stability, density, impact sensitivity, and elemental analyses. Structural confirmation of **3**, **5**, and **9** was obtained from single-crystal X-ray diffraction analyses. The structures of compounds **5**·4 H_2O and **9** are shown in Figure 1 (**3**·2 H_2O can be found in the Supporting Information).[12]



Scheme 1. Synthesis of bis(nitroamino-1,2,4-triazolates).

In the IR spectra, characteristic absorption bands range from 1300 cm^{-1} to 1600 cm^{-1}, which were attributed to the nitro and nitroamino groups. The other intense absorption bands at 3100–3450 cm^{-1} were assigned to N–H bonds of the energetic cations. ^{1}H NMR spectra of compound **1** show a single resonance assignable to the ethylene group at $\delta = 4.39$ ppm. For nitroamino compound **2**, the corresponding resonance was at a slightly lower field of $\delta = 4.63$ ppm. In the ^{13}C NMR spectra of energetic salts **3**–**13**, except for three signals ($\delta \approx 160$, 157, and 46 ppm) associated with the anion, the other signals are assigned to the energetic cations.

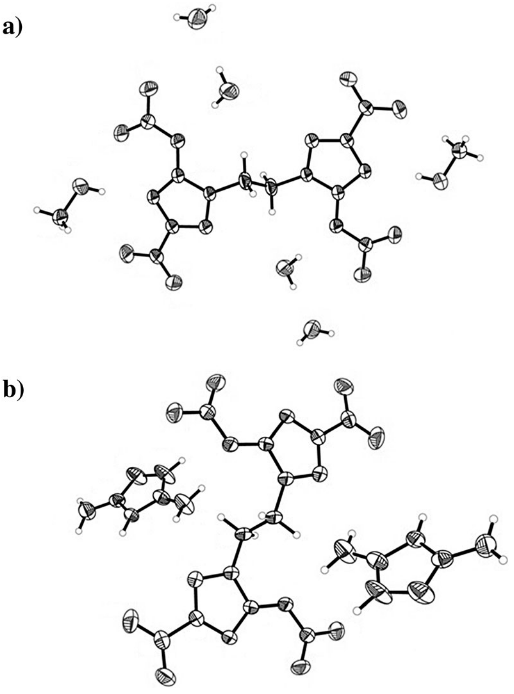


Figure 1. Single-crystal X-ray structures of **5**·4 H_2O (a) and **9** (b).

^{15}N NMR spectra are particularly useful for nitrogen-rich compounds. The spectroscopic data for the new nitroamino compound **2** and its energetic derivatives were measured and a few selected spectra are shown in Figure 2. The ^{15}N{H} NMR spectrum of **2** shows six signals at $\delta = -26.50$ (N4), −26.54 (N6), −92.47 (N2), −147.97 (N3), −175.86 (N1), −183.61 (N5) ppm. In contrast, the nitrogen signals of its corresponding anions in **3**–**13** shift slightly to lower field, which are found at $\delta \approx -15$ (N4), −24 (N6), −99 (N2), −152 (N3), −160 (N1), −187 (N5). Also, the amino groups of the other energetic cations appear ranging from −280 to −360 ppm, in which the ammonium cation is found at the highest field ($\delta = -359.24$ ppm).

The thermal stability of these new compounds was determined by differential scanning calorimetry (DSC). Ethylene-bridged bis(aminotriazole) **1** exhibits a rather high decomposition temperature at 307 °C. Although nitraminotriazole **2** decomposes at low temperature (107 °C), its ionic derivatives have enhanced thermal stabilities ranging from 163 to 250 °C. Among them, the triaminoguanidinium salt **13** has a better thermal stability than the other ionic derivatives, which most likely can be attributed to extensive hydrogen bonding. Densities of all compounds were measured with a gas pycnometer and found in the range between 1.64 and 1.84 $g\,cm^{-3}$. Acyclic guanidinium derivatives (**7**, **8**, **12**, and **13**)

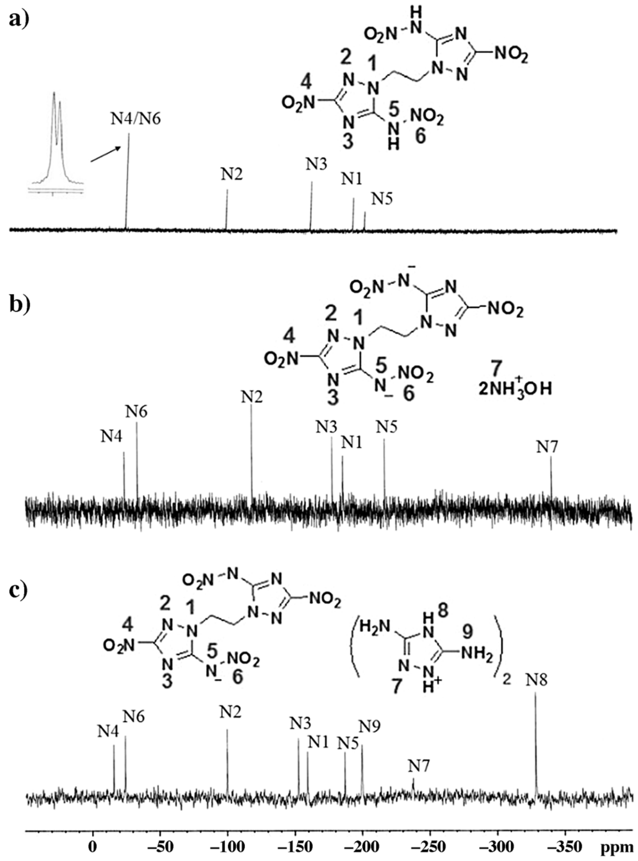


Figure 2. ^{15}N NMR spectra of **2** (a), **5** (b), and **9** (c).

have relatively low densities, whereas the other heterocycle-based compounds (e.g., **9**–**11**) exhibited higher densities.

The heats of formation (ΔH_f) of these compounds were calculated using the Gaussian 03 (Revision D.01) suite of programs.[14] Neutral compounds **1** and **2** were calculated based on the gas-phase enthalpies and the sublimation enthalpies, while ionic derivatives (**3**–**13**) were calculated based on the values of cation, anion, and lattice energy. The heats of formation range from 0.52 to 1.87 kJ g^{-1}, in which **6** has the highest at 1.87 kJ g^{-1}. With the data on density and heat of formation in hand, detonation velocities and pressures of all compounds were calculated with EXPLO5 (version 6.01). The detonation velocities lie within the range from 8008 to 8966 m s^{-1}, most of which outperform TATB (8144 m s^{-1}) and are comparable to RDX (8977 m s^{-1}). Similarly, these compounds have favorable detonation pressures as well, falling between 23.7 and 35.4 GPa vis-à-vis 35.2 GPa for RDX.

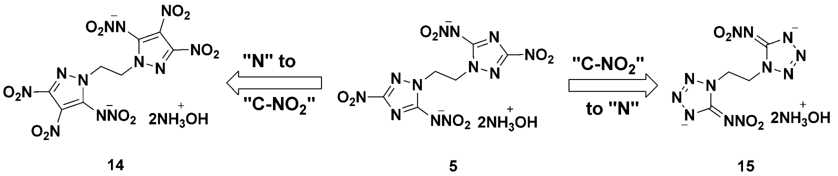
To further evaluate these energetic materials, impact sensitivities (IS) and friction sensitivities (FS) were measured by using a BAM Fallhammer apparatus and a BAM friction tester, respectively. While the amino-substituted compound **1** is impact insensitive (> 40 J), nitramine **2** has a reduced impact stability (10 J). Except for salts **4** and **5** (10 J), the other salts are less impact sensitive (35–40 J). Also, the same trend was found for friction sensitivities; **2** and **4** are of relatively high sensitivity (160 N) and the others are friction insensitive. Compared to *N*-alkyl and *N*-alkoxy-bridged bis(nitroiminotetrazoles),[10] most of the *N*-ethylene-bridged bis(nitroamino-1,2,4-triazolates) are less sensitive to mechanical stimuli.

As hydroxylammonium salt **5** exhibited good energetic performance, it was of interest to study other *N*-ethylene-bridged bis(azolates). Employing similar conditions, pyrazolate **14** was synthesized by coupling of 5-amino-3,4-dinitropyrazole and dibromoethane, followed by nitration with nitric acid and neutralization with hydroxylamine, which indicates the extensive scope of the *N*-bridging strategy. Additionally, the reaction of ethylene-bridged bis(nitroiminotetrazole) and hydroxylamine led to the bis(tetrazolate) **15** (see the Supporting Information). These two new compounds (**14** and **15**) were fully characterized and their properties listed in Table 1. When the "N" moiety is replaced by a "C-NO$_2$" moiety (Figure 3), pyrazolate **14** has an increased oxygen content and exhibits good energetic properties (*P*, 34.5 GPa, ν_D, 8744 m s^{-1}), which are slightly lower than those of **5**. By changing the "C-NO$_2$" moiety to an "N" moiety, the nitrogen content and detonation and pressure of tetrazolate **15** are

Table 1: Properties of the *N*-functionalized energetic compounds.

Comp.	T_d[a] [°C]	d[b] [g cm^{-3}]	ΔH_f[c] [kJ g^{-1}]	P[d] [GPa]	ν_D[e] [m s^{-1}]	IS[f] [J]	FS[g] [N]
1	307	1.72	1.11	24.5	8069	> 40	360
2	107	1.84	1.38	34.3	8816	10	160
3	196	1.75 (1.76)[h]	0.63	29.5	8554	35	360
4	195	1.73	1.32	30.1	8703	10	160
5	186	1.83 (1.87)[h]	0.81	35.4	8966	10	360
6	190	1.68	1.87	25.8	8177	> 40	360
7	212	1.67	0.52	23.7	8008	> 40	360
8	244	1.64	0.97	23.7	8036	> 40	360
9	193	1.74 (1.76)[h]	1.19	26.8	8373	> 40	360
10	244	1.70	1.56	25.5	8242	> 40	360
11	163	1.76	1.81	30.8	8618	> 40	360
12	203	1.68	1.34	26.5	8439	> 40	360
13	250	1.67	1.62	27.1	8528	> 40	360
14	140	1.80	0.67	34.5	8744	10	160
15	207	1.78	2.43	36.1	9366	15	120
TATB	324	1.93	−0.54	31.2	8144	50	360
RDX	205	1.80	0.42	35.2	8977	7.4	120

[a] Decomposition temperature. [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] Values in parentheses are derived from crystal densities at 293 K (densities of **3** and **5** were corrected according to Ref. [13])



14 **5** **15**

Figure 3. A study of various ethylene-bridged bisazolates.

higher than those of triazolate **5**. Additionally, while impact sensitivity tests show that pyrazolate **14** and tetrazolate **15** are similar to **5**, both **14** and **15** are more friction sensitive. Based on the properties of ethylene-bridged compounds with varying backbones, triazolate **5** competes well in both energetic performance and molecular stability. Moreover, compared to our previous study of bis(nitroiminotetrazolates),[10] this approach is featured with the obvious advantages of reagents of low cost and toxicity, thereby providing a promising route to design insensitive energetic materials.

In summary, bis(nitroaminotriazole) and its ionic derivatives have been characterized. Most of them possess good detonation properties and low insensitivity to impact and friction. Moreover, *N*-ethylene-bridged nitroamines (nitroimine) with different azole scaffolds, such as **14** and **15**, show competitive energetic properties similar to those of triazolate **5**. Additionally, this study highlights a general and practical approach to *N*-bridged bis(azolates), advancing their further application for preparing diversified energetic materials.

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Keywords: bis(1,2,4-triazolates) · detonation performance · energetic materials · polynitro compounds

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