# Insensitive Nitrogen-Rich Materials Incorporating the Nitroguanidyl Functionality

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**Abstract:** A new class of nitroguanidylfunctionalized nitrogen-rich materials derived from 1,3,5-triazine and 1,2,4,5tetrazine was synthesized through reactions between *N*-nitroso-*N'*-alkylguanidines and the hydrazine derivatives of 1,3,5-triazine or 1,2,4,5-tetrazine. These compounds were fully characterized using multinuclear NMR and IR spectroscopies, elemental analysis, and dif-

#### Introduction

The design and synthesis of new compounds known as highenergy density materials (HEDMs) has been the focus of our group for the past decade.<sup>[1-3]</sup> In the pursuit of new HEDMs, current interest not only focuses on the energetic properties of the target material (density, detonation velocity, and detonation pressure) but also concerns about the environment and safety issues of the material, including the "greenness" of explosion products, their toxicity to human health, and their sensitivity toward heat, shock, friction, and electrostatic discharge. With this background, considerable effort has been devoted to developing new-generation HEDMs with integrated properties including high density, good thermal stability, high detonation velocity and pressure, low sensitivity, environmentally benign explosion products, low cost, and ease of production in sizeable amounts. To date, numerous HEDMs with new structures have been designed and synthesized.<sup>[4,5]</sup> Unfortunately, for most developed HEDMs, it is very difficult to simultaneously meet the needs of all of the following criteria, that is, high density, high energy, low sensitivity to thermal shock and friction, and environmentally benign nature, to list a few. Therefore, the development of new environmentally benign HEDMs with excellent integrated performance must be one of the main goals in future energetic materials research.

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ferential scanning calorimetry (DSC). The heats of formation for all compounds were calculated with Gaussian 03 and then combined with experimen-

**Keywords:** nitrogen heterocycles • nitrogen-rich materials • nitroguanidyl functionality • sensitivity • tetrazine • triazine tal densities to determine the detonation pressures (*P*) and velocities ( $D_v$ ) of the energetic materials. Interestingly, some of the compounds exhibit an energetic performance (*P* and  $D_v$ ) comparable to that of RDX, thus holding promise for application as energetic materials.

High-nitrogen heterocycles represent a unique class of energetic molecules, which have recently attracted significant interest in the fields of energetic materials. For some highnitrogen heterocyclic molecules, such as triazole,<sup>[6]</sup> tetrazole,<sup>[7]</sup> triazine,<sup>[8]</sup> and tetrazine,<sup>[9]</sup> most of their energy derives from a combination of positive heats of formation and generation of large volumes of environmentally benign nitrogen gas under decomposition with a high order of energy release. Relative to traditional carbon-based energetic compounds such as TNT and TATB, the energetic materials derived from high-nitrogen heterocycles can offer some promising advantages, for example, relatively "greener" combustion products, higher enthalpy of formation, and/or higher energetic performance. Moreover, the high-nitrogen content of the energetic molecules usually means higher molecular densities, and the low hydrogen and carbon content makes the achievement of a good oxygen balance of these materials much easier. In this sense, the high-nitrogen heterocycles have been considered as very promising building blocks for the construction of ideal HEDMs, in which the 1,3,5-triazine and 1,2,4,5-tetrazine rings are among the typical examples due to their high-energy N-N and C-N bonds, as well as their intense ring strain. From the viewpoint of designing high-performance energetic materials, the most widely used strategy is to incorporate some energy-containing groups such as nitro, azido, azo, or N-oxide into the molecular backbone of the high-nitrogen heterocycles, in particular the 1,3,5-triazine or 1,2,4,5-tetrazine ring. By virtue of this strategy, several tetrazine- or triazine-derived energetic materials have been reported (Scheme 1).<sup>[10,11]</sup> For example, 3,6-diazido-1,2,4,5-tetrazine (1) displays a very high heat of formation (about 6709 kJ kg<sup>-1</sup>),<sup>[12]</sup> and 4,4'6,6'-tetraazido-2,2'-azo-1,3,5-triazine (2)<sup>[8b]</sup> has a heat of formation of  $6164 \text{ kJ kg}^{-1}$ (Scheme 1). Although these compounds are highly energetic



Scheme 1. Examples of some high-nitrogen compounds based on 1,2,4,5-tetrazine or 1,3,5-triazine.

due to their positive heats of formation, the characteristics of high sensitivity significantly limit their application potential for use on a large scale.

In our continuing effort to seek new energetic materials, here we present our attempts at designing and synthesizing a series of high-nitrogen triazine- or tetrazine-derived compounds through the strategy of incorporating an energetic nitroguanidyl group into the backbone of the 1,3,5-triazine or 1,2,4,5-tetrazine ring. For these new compounds, the high nitrogen content of both the nitroguanidyl group and the molecular backbone (i.e., 1,2,4,5-tetrazine or 1,3,5-triazine ring) is expected to contribute higher crystal density, higher heats of formation, and environmentally benign decomposition products (N<sub>2</sub>), and thereby to result in an excellent detonation performance. Meanwhile, some significant characteristics of the triazine or tetrazine ring, for instance, the high thermal stability as well as the low sensitivity toward heat, shock, friction, and electrostatic discharge, are expected to endow the target materials with excellent safety properties.

## **Results and Discussion**

It is known that *N*-nitroso-*N*'-alkylguanidines can readily react with alkylamines to eliminate the nitrosamino group and form nitroguanidyl-functionalized alkylamines.<sup>[13]</sup> Thus, we began our synthesis of *N*-methyl-*N*-nitroso-*N*'-nitroguanidine (**4**), which can provide a nitroguanidyl group. The commercially available nitroguanidine was first reacted with methylamine to form methyl-*N*'-nitroguanidine in good yield (84%) and then was nitrosated by sodium nitrite in the presence of 70% nitric acid to yield **4**.<sup>[13]</sup> The aqueous solutions of hydrazine derivatives of 1,3,5-tetrazine-based compounds can react at or below room temperature with **4** to yield the nitroguanidyl-functionalized 1,3,5-tetrazine-derived products (**5–7**) in good yields (Scheme 2).

With three nitroguanidyl-functionalized triazine derivatives in hand, we turned our attention to the preparation of nitroguanidyl-functionalized 1,2,4,5-tetrazine derivatives. At room temperature, the aqueous suspension of hydrazine derivatives of 1,2,4,5-tetrazine can react with **4** to give the nitroguanidyl-functionalized tetrazine compound **8** in high yield (Scheme 3). Moreover, for the purpose of comparison, two acyclic carbonyl-bridged nitroguanidyl derivatives (**9**– **10**) were also synthesized using the same synthetic methodology (Scheme 3). Note that the attempts of reactions between the amino derivatives of 1,3,5-triazine (e.g., 2,4,6-triamino-1,3,5-triazine) or the amino derivatives of 1,2,4,5-tetra-



Scheme 2. Synthesis of nitroguanidyl-functionalized triazine derivatives 5–7.



Scheme 3. Synthesis of nitroguanidyl-functionalized tetrazine derivative 8 and acyclic carbonyl-bridged nitroguanidyl derivatives 9–10.

zine (e.g., 3,6-diamino-1,2,4,5-tetrazine) and **4** did not result in the corresponding nitroguanidyl-functionalized derivatives, probably due to the decreased reactivity of the amino group relative to the hydrazine group.

The structures of the six new compounds **5–10** are supported by IR, <sup>1</sup>H NMR, <sup>13</sup>C NMR, and <sup>15</sup>N NMR spectroscopic data as well as elemental analysis. In the <sup>1</sup>H NMR spectra, the hydrogen resonances of the -NH-NH- groups, which are attached to the nitroguanidyl group, appeared at low field (8.0–10.5 ppm). In the <sup>13</sup>C NMR spectra, due to the strong electron-withdrawing effect of the nitroguanidyl group was always observed as a weak peak in the range of 161–162 ppm. The <sup>15</sup>N NMR spectra of some of the new com-

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[D<sub>6</sub>]DMSO solvent, and chemical shifts are given with respect to CH<sub>3</sub>NO<sub>2</sub> as external standard. The <sup>15</sup>N NMR spectra of compounds 5 and 6 are given in Figure 1. The strong signals assigned to the nitro groups (N1)

measured in

were

at

-12.22 ppm for **5** and **6**, respectively. The signal of the N2

atom, which is directly attached

to the nitro group, can be as-

signed to the resonances at the

(-144.24 ppm and -144.14 ppm

lowest

-12.25

and

field

pounds

appear

second

For energetic materials, thermal stability and density are two of the most important properties. In this work, except for the compound 6 ( $T_d = 195 \,^{\circ}$ C), the decomposition temperature  $(T_d)$  of all other nitroguanidyl-functionalized compounds is higher than 200°C (Table 1), thus indicating that these compounds are promising energetic materials that exhibit good thermal stability. Of these, 5 has the highest thermal stability,  $T_d = 260$  °C, which is higher than that of RDX (230 °C). The densities of these new nitroguanidyl-functionalized compounds ranged between 1.66 and 1.81 g cm<sup>-1</sup>, of which **8** exhibits the highest density at  $1.81 \text{ g cm}^{-3}$ , which is very close to that of RDX ( $1.82 \text{ g cm}^{-3}$ ).

To obtain the optimized structures and frequency analyses of the new compounds 5-10, density functional theory calculations were performed at the level of Becke three-parameter Lee-Yang-Parr (B3LYP) parameters up to the 6-31G+ (d,p) basis sets using Gaussian 03. All of the optimized

Table 1. Physical properties of nitroguanidine-functionalized energetic compounds.

Compd	Mw	N %	$T_{\rm d}^{\rm [a]}$	$ ho^{ ext{bl}}$	$\Delta H_{ m f}^{[c]}$	$\Delta H_{ m f}^{[c]}$	$D_v^{[d]}$	$P^{[e]}$	IS <sup>[f]</sup>	FS <sup>[g]</sup>	OB <sup>[h]</sup>
	$[gmol^{-1}]$	[wt %]	[°C]	[g cm <sup>-3</sup> ]	$[kJ mol^{-1}]$	$[kJ g^{-1}]$	$[m s^{-1}]$	[GPa]	[J]	[N]	[%]
5	228.17	61.39	260	1.70	172.4	0.76	7672	22.2	> 40	360	-42.1
6	432.28	58.32	195	1.74	577.8	1.34	8378	28.7	> 40	360	-22.2
7	656.42	59.75	201	1.71	597.7	0.91	7812	23.9	> 40	360	-24.4
8	316.20	62.02	201	1.81	733.1	2.32	8884	33.7	32	120	-20.2
9	264.16	53.02	206	1.66	107.7	0.41	8138	26.5	> 40	360	-12.1
10	322.20	52.17	200	1.75	7.0	0.02	8263	27.9	> 40	360	-14.9
RDX	222.12	37.84	230	1.82	92.6	0.42	8977	35.2	7.4	120	0
HMX	296.16	37.84	287	1.91	104.8	0.35	9320	39.6	7.4	120	0

[a] Thermal decomposition temperature under nitrogen gas (determined by the DSC exothermal peak, 5°Cmin<sup>-1</sup>). [b] Density measured by a gas pycnometer (25°C). [c] Heat of formation calculated with Gaussian 03. [d] Detonation velocity calculated with EXPLO 5.05. [e] Detonation pressure calculated with EXPLO 5.05. [f] Impact sensitivity measured by BAM drop hammer; [g] Friction sensitivity measured by a BAM friction tester. [h] Oxygen balance (%) for  $C_aH_bN_cO_d$ : OB (%) = 1600×(d-a-b/2)/Mw (based on carbon monoxide).

for 5 and 6, respectively) due to the presence of the nitro group. Next, the resonance signals in the range of -200 to -207 ppm are assigned to the nitrogen signal from the triazine ring (N6 and N7 of 5, and N6 of 6), probably due to the more electron-deficient character of the nitrogen atom in the triazine ring than the nitrogen atoms in the -NH- groups and the -NH<sub>2</sub> groups. For 5, the assignment of the resonance peaks of N6 and N7 can be further determined by the relative abundance of the resonance signal since there are two N6 atoms and only one N7 atom in the triazine ring. The nitrogen signal of the amino groups that are attached to the triazine ring or from the nitroguanidyl group can be assigned to the resonances at the highest field (ranging from -295 to -298 ppm) due to the electronrich nature, while the N4 and N5 signals from the -NH-NHgroups are observed at a relatively lower field than the signals of -NH2 groups. However, it is difficult to distinguish further assignments between N4 and N5 signals. It should be pointed out that the <sup>15</sup>N NMR analysis of nitroguanidylfunctionalized tetrazine derivatives is difficult to achieve, mainly due to poor solubility in most deuterated solvents (even in  $[D_6]DMSO$ ).

structures were characterized to be true local energy minima on the energy potential surface (ESP) without imaginary frequencies. The electrostatic potential (ESP) of the three energetic compounds 6-8 was computed at the optimized structure at the B3LYP/6-31G + (d,p) level of theory. Figure 2 shows the ESP for the 0.001 electron/bohr<sup>3</sup> isosurface of the electron density evaluated at the B3LYP level of theory. It has recently been reported by Politzer, Murray et al.,<sup>[14]</sup> and extensively used by Rice et al.,<sup>[15]</sup> that the patterns of the computed ESP on the surface of molecules in general can be related to the sensitivity of the bulk material. According to Politzer's theory,<sup>[14]</sup> the impact sensitivity of an energetic compound can be expressed as a function of the extent of this anomalous reversal of the strengths of the positive and negative surface potentials. From the ESP of compounds 6-8, the regions of positive potential and negative potential are difficult to differentiate by the color, that is, no atypical imbalance related to the impact sensitivities can be observed between stronger positive regions and weaker negative ones. This is in good accord with the experimental results of relatively high impact sensitivity and friction sensi-



Figure 2. Optimized structures and electrostatic potential surfaces of compounds **6–8** (B3LYP/6-31G+(d,p), 0.001 electron/bohr<sup>3</sup> isosurface, energy values -0.2 to +0.1 H). The red and blue regions of the ruler (from top to bottom) indicate regions of more negative and positive charges, respectively.

tivity of these three compounds (Table 1). The heats of formation of **5–10** were calculated with Gaussian 03 by using the method of isodesmic reactions (Scheme 4). From Table 1, the nitroguanidyl-functionalized tetrazine compound (**8**) exhibited very high positive heats of formation (2.32 kJ g<sup>-1</sup>). In comparison with most of the nitroguanidylfunctionalized tetrazine or triazine derivatives (**6–8**), the heats of formation of the carbonyl-bridged nitroguanidyl derivatives (**9–10**) are much lower (i.e., 0.41 kJ g<sup>-1</sup> and 0.02 kJ g<sup>-1</sup>, respectively), likely due to the absence of a high ring strain energy deriving from the triazine or tetrazine rings.

By using the calculated heats of formation and the experimentally measured densities, the detonation pressures (*P*) and velocities ( $D_{\nu}$ ) of **5–10** were calculated based on traditional Chapman–Jouget thermodynamic detonation theory using EXPLO 5.05 (Table 1). For these new nitroguanidylfunctionalized compounds, the calculated detonation velocities lie in the range between 7672 and 8884 m s<sup>-1</sup>, most of which are remarkably higher than that of TATB (8114 m s<sup>-1</sup>). Among them, **8** exhibits the highest detonation velocity ( $8884 \text{ m s}^{-1}$ ), which is comparable to that of RDX (8977 m s<sup>-1</sup>). The detonation pressures range between 22.9 and 33.7 GPa, in which the highest P value of 8 (33.7 GPa) is slightly lower than that of RDX (35.2 GPa). More importantly, most of these new energetic compounds exhibited low sensitivities toward impact and friction, that is, the IS values are >40 J and the FS values are 360 N, further highlighting their likely application potential. Among them, compound 8 has an IS value of 32 J and an FS value of 120 N, respectively. The oxygen balance (OB) is the index of the deficiency or excess of oxygen in a compound required to convert all carbon atoms into carbon monoxide and all hydrogen atoms into water. In this work, for a compound with the molecular formula of CaHbNcOd, the oxygen balance is calculated as follows: OB  $(\%) = 1600 \times (d-a-b/2)/$ Mw (Table 1). Unfortunately, the six new energetic compounds exhibited negative OB values ranging from -12.1 % to -42.1%, mainly due to the relatively higher carbon and hydrogen content in the molecules.

#### Conclusions

In summary, a new class of nitroguanidyl-functionalized triazine and tetrazine derivatives has been synthesized and fully characterized. All the nitrogen-rich compounds derived from 1,3,5-triazine and 1,2,4,5-tetrazine showed good thermal stabilities and low impact sensitivities. Of these, **8** exhibited an energetic performance comparable to that of RDX (i.e., 33.7 GPa for *P* and 8884 m s<sup>-1</sup> for  $D_{\nu}$  for **8** versus 35.2 GPa for *P* and 8977 m s<sup>-1</sup> for  $D_{\nu}$  for RDX, respectively). In addition to the energetic properties, all the energetic materials are impact-insensitive, further highlighting their application potentials as new-generation insensitive energetic materials.

## **Experimental Section**

#### Safety Precautions

Although none of the compounds described herein has exploded or detonated in the course of this research, these materials should be handled with extreme care using the best safety practices. Manipulation must be carried out in a hood behind a safety shield. Leather gloves must be worn.

#### General Methods

<sup>1</sup>H, <sup>13</sup>C, and <sup>15</sup>N NMR spectra were recorded on 300 MHz (Bruker AVANCE 300) and 500 MHz (Bruker AVANCE 500) nuclear magnetic resonance spectrometers operating at 300.13, 75.48, and 50.69 MHz, respectively, by using [D<sub>6</sub>]DMSO as the solvent and locking solvent unless otherwise stated. Chemical shifts in <sup>1</sup>H and <sup>13</sup>C NMR spectra are reported relative to Me<sub>4</sub>Si and those in <sup>15</sup>N NMR spectra relative to MeNO<sub>2</sub>. The decomposition temperatures were determined by a differential scanning calorimeter (TA Instruments, model Q 10) at a scan rate of 5°C min<sup>-1</sup>. Samples were placed in a 40 µL hermetically sealed aluminum pan with a pinhole at the top of the pan. IR spectra were recorded using KBr pellets on a BIORAD model 3000 FTS spectrometer. Densities of the compounds were determined at room temperature by employing a Micromeritics AccuPyc 1330 gas pycnometer. Elemental analyses were carried



Scheme 4. Isodesmic reactions for compounds 5-10.

out using an Exeter CE-440 elemental analyzer. Impact and friction sensitivity measurements were made using a standard BAM drop hammer and a BAM friction tester.

#### Preparation of N-Methyl-N'-nitroguanidine (4)

First, N-methyl-N'-nitroguanidine was synthesized according to previously reported methods.<sup>[13]</sup> An alkaline solution of nitroguanidine (0.1 mol, 10.4 g) in 30 mL of water containing KOH (0.215 mol, 12 g) was prepared. The solution was heated to 40 °C to dissolve the nitroguanidine and then methylamine hydrochloride (0.2 mol, 13.5 g) was added with stirring. The temperature was increased to 59°C and maintained at 59-61 °C for 30 min. The resulting clear solution was cooled in an ice-water bath to 5-6 °C. The white precipitate was filtered off, washed with cold water (30 mL), and dried in air to yield N-methyl-N'-nitroguanidine (10.0 g, 84.7 %) as a white solid (m.p. 151-154 °C). Then, N-methyl-N'-nitroguanidine (0.085 mol, 10.0 g) was dissolved in H<sub>2</sub>O (100 mL) by the addition of 30 mL 70% HNO3. The resulting solution was cooled in an ice bath and NaNO2 (0.18 mol, 12.4 g) dissolved in water (20 mL) was added over a period of 5 min. The mixture was stirred for 30 min, and then the resulting precipitate was filtered and washed with cold water to afford 4 (8.75 g) as a yellow crystalline product (m.p. 112-113°C). The structure of 4 was confirmed by <sup>1</sup>H NMR spectroscopic analysis, which is agreement with the reported data.[14]

#### Synthesis of 5

2,4-Diamino-6-chloro-1,3,5-triazine was readily synthesized according to a method previously reported.[16] 2,4-Diamino-6-hydrazinyl-1,3,5-triazine was also obtained by a reported method.<sup>[17]</sup> Hydrazine hydrate (4.32 g, 4.2 mL, 86.4 mmol) was added dropwise to a suspension of 2,4-diamino-6chloro-1,3,5-triazine (2.5 g, 17.7 mmol) in water (20 mL). The mixture was stirred overnight at 85°C. The white solid was filtered off, washed with water (300 mL), and dried under high vacuum to afford pure 2,4-diamino-6hydrazinyl-1,3,5-triazine (72%, 1.80 g). The synthesis of 5 is as follows: Nmethyl-N-nitroso-N'-nitroguanidine (4, 0.34 g, 2.2 mmol) was added to an aqueous solution (25 mL) of 2,4-diamino-6-hydrazinyl-1,3,5-triazine (0.282 g, 2 mmol) at room temperature. The mixture was stirred at room temperature for 18 h. After completion of the reaction, the resulting precipitate was filtered off, washed with cold water (10 mL), and dried to give 5 as a pale yellow powder (83%, 0.38 g).  $T_d =$ 260 °C; IR (KBr):  $\tilde{v} = 3351, 3231, 3099,$ 1656, 1545, 1487, 1368, 1318, 1242, 1067, 1028, 807, 638, 519,  $426 \text{ cm}^{-1}$ ; <sup>1</sup>H NMR:  $\delta = 9.68$  (s, 1 H, -NH-), 8.49 (s, 2H, -NH<sub>2</sub>), 8.08 (s, 1H, -NH-), 6.41 ppm (s, 4H, -NH<sub>2</sub>); <sup>13</sup>C NMR:  $\delta =$ 167.7, 167.2, 161.5 ppm; elemental analysis (%) calcd for C<sub>4</sub>H<sub>8</sub>N<sub>10</sub>O<sub>2</sub> (228.17): C 21.06, H 3.53, N 61.39; found: C 21.00, H 3.61, N 60.15.

#### Synthesis of 6

Pure 2,4,6-trihydrazinyl-1,3,5-triazine was readily synthesized according to a method previously reported.<sup>[18]</sup> The synthesis of **6** is as follows: *N*-methyl-

*N*-nitroso-*N*'-nitroguanidine (**4**) (0.51 g, 3.3 mmol) was added to an aqueous solution (50 mL) of 2,4,6-trihydrazinyl-1,3,5-triazine (0.171 g, 1 mmol) at room temperature. The mixture was stirred at room temperature for 18 h. After completion of the reaction, the resulting precipitate was filtered off, washed with cold water (50 mL), and dried to give **6** as a pale yellow powder (78%, 0.34 g).  $T_d$ =195°C; IR (KBr):  $\tilde{\nu}$ =3416, 3309, 3241, 2932, 1642, 1584, 1539, 1429, 1384, 1294, 1053, 955, 812, 710, 612, 470 cm<sup>-1</sup>; <sup>1</sup>H NMR:  $\delta$ =9.80 (s, 1 H, -NH-), 9.33 (s, 1 H, -NH\_-), 8.56 (s, 1 H, -NH-), 8.15 ppm (s, 1 H, -NH); <sup>13</sup>C NMR:  $\delta$ =167.9, 161.4 ppm; elemental analysis (%) calcd for C<sub>6</sub>H<sub>12</sub>N<sub>18</sub>O<sub>6</sub> (432.28): C 16.67, H 2.80, N 58.32; found: C 17.08, H 3.35, N 57.12.

#### Synthesis of 7

Bis-(4,6-dihydrazino-[1,3,5]triazin-2-yl)-diazene was synthesized according to a method previously reported.<sup>[19]</sup> The synthesis of **7** is as follows: *N*-methyl-*N*-nitroso-*N*'-nitroguanidine (**4**, 4.2 mmol, 0.62 g) was added to an aqueous solution (50 mL) of bis-(4,6-dihydrazino-[1,3,5]triazin-2-yl)diazene (0.31 g, 1 mmol) at room temperature. The mixture was stirred at room temperature for 18 h. After completion of the reaction, the resulting precipitate was filtered off, washed with cold water (50 mL), and dried to give the **7** as a yellow powder (74%, 0.49 g).  $T_d$ =201°C; IR (KBr):  $\tilde{\nu}$ =3302, 1590, 1539, 1499, 1376, 1277, 1056, 812, 552, 474 cm<sup>-1</sup>; <sup>1</sup>H NMR:  $\delta$ =9.80 (s, 1H, -NH-), 9.33 (s, 1H, -NH\_), 8.56 (s, 1H, NH), 8.15 ppm (s, 1H, NH); <sup>13</sup>C NMR:  $\delta$ =167.5, 161.4 ppm; elemental analysis

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(%) calcd for  $C_{10}H_{16}N_{28}O_8$  (656.42): C 18.30, H 2.46, N 59.75; found: C 18.61, H 3.03, N 56.40.

#### Synthesis of 8

3,6-Dihydrazino-1,2,4,5-tetrazine (1 mmol) was synthesized according to a method previously reported.<sup>[20]</sup> The synthesis of **8** is as follows: *N*methyl-*N*-nitroso-*N*'-nitroguanidine (**4**) (0.34 g, 2.2 mmol) was added to an aqueous solution (50 mL) of 3,6-dihydrazino-1,2,4,5-tetrazine (0.142 g, 1 mmol) at room temperature. The mixture was stirred at room temperature for 18 h. After completion of the reaction, the resulting precipitate was filtered off, washed with cold water (50 mL), and dried to give **8** as an orange powder (86 %, 0.27 g).  $T_d$ =201°C; IR (KBr):  $\tilde{\nu}$ =3379, 3218, 1620, 1603, 1578, 1521, 1433, 1321, 1282, 1187, 1063, 1026, 949, 762, 570, 471 cm<sup>-1</sup>; <sup>1</sup>H NMR:  $\delta$ =10.10 (s, 1H, -NH-), 9.94 (s, 1H, -NH-), 8.62 (s, 1H, -NH-), 8.43 ppm (s, 1H, -NH-); <sup>13</sup>C NMR:  $\delta$ =162.2, 161.8 ppm; elemental analysis (%) calcd for C<sub>4</sub>H<sub>8</sub>N<sub>14</sub>O<sub>4</sub> (316.20): C 15.19, H 2.55, N 62.02; found: C 15.28, H 2.89, N 62.74.

#### Synthesis of 9

*N*-Methyl-*N*-nitroso-*N*'-nitroguanidine (**4**, 0.34 g, 2.2 mmol) was added to an aqueous solution (50 mL) of carbohydrazide (0.09 g, 1 mmol) at room temperature. The mixture was stirred at room temperature for 18 h. After completion of the reaction, the resulting precipitate was filtered off, washed with cold water (50 mL), and dried to give **9** as a white powder (69 %, 0.18 g).  $T_d$ =206 °C; IR (KBr):  $\tilde{\nu}$ =3389, 3290, 3229, 3131, 1649, 1562, 1427, 1364, 1297, 1246, 1177, 1090, 1055, 957, 773, 680, 565, 473 cm<sup>-1</sup>; <sup>1</sup>H NMR:  $\delta$ =9.58 (s, 1H, -NH-), 8.94 (s, 1H, -NH-), 8.67 (s, 1H, NH), 8.15 ppm (s, 1H, NH); <sup>13</sup>C NMR:  $\delta$ =161.6, 156.7 ppm; elemental analysis (%) calcd for C<sub>3</sub>H<sub>8</sub>N<sub>10</sub>O<sub>5</sub> (264.16): C 13.64, H 3.05, N 53.02; found: C 13.43, H 3.02, N 51.52.

#### Synthesis of 10

*N*-Methyl-*N*-nitroso-*N*'-nitroguanidine (**4**, 0.34 g, 2.2 mmol) was added to an aqueous solution (50 mL) of 1,2-bis(hydrazinocarbonyl)hydrazine (0.148 g, 1 mmol) at room temperature. The mixture was stirred at room temperature for 18 h. After completion of the reaction, the resulting precipitate was filtered off, washed with cold water (50 mL), and dried to give **10** as a white powder (71%, 0.23 g).  $T_d$ =200°C; IR (KBr):  $\tilde{\nu}$ =3397, 3322, 3237, 1638, 1583, 1526, 1414, 1332, 1274, 1242, 1141, 1055, 1089, 781, 744, 624, 582, 469 cm<sup>-1</sup>; <sup>1</sup>H NMR:  $\delta$ =9.61 (s, 1H, -NH-), 8.97 (s, 1H, -NH-), 8.76 (s, 1H, -NH-), 8.53 (s, 1H, NH), 7.85 ppm (s, 1H, NH); <sup>13</sup>C NMR:  $\delta$ =161.7, 157.5 ppm; elemental analysis (%) calcd for C<sub>4</sub>H<sub>10</sub>N<sub>12</sub>O<sub>6</sub> (322.2): C 14.91, H 3.13, N 52.17; found: C 14.92, H 3.35, N 50.27.

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- a) H. Gao, J. M. Shreeve, Chem. Rev. 2011, 111, 7377-7436; b) R. P. Singh, R. D. Verma, D. T. Meshri, J. M. Shreeve, Angew. Chem. 2006, 118, 3664-3682; Angew. Chem. Int. Ed. 2006, 45, 3584-3601; c) Y.-H. Joo, J. M. Shreeve, Angew. Chem. 2009, 121, 572-575; Angew. Chem. Int. Ed. 2009, 48, 564-567; d) Y.-H. Joo, J. M. Shreeve, Angew. Chem. 2010, 122, 7478-7481; Angew. Chem. Int. Ed. 2010, 49, 7320-7323.
- [2] a) Y.-H. Joo, B. Twamley, J. M. Shreeve, *Chem. Eur. J.* 2009, *15*, 9097–9104; b) Y.-H. Joo, B. Twamley, S. Garg, J. M. Shreeve, *Angew. Chem.* 2008, *120*, 6332–6335; *Angew. Chem. Int. Ed.* 2008, 47, 6236–6239; c) H. Xue, H. Gao, B. Twamley, J. M. Shreeve, *Chem. Mater.* 2007, *19*, 1731–1739; d) V. Thottempudi, J. M. Shreeve, *J. Am. Chem. Soc.* 2011, *133*, 19982–19992.
- [3] a) Y.-H. Joo, J. M. Shreeve, J. Am. Chem. Soc. 2010, 132, 15081– 15090; b) R. Wang, H. Xu, Y. Guo, R. Sa, J. M. Shreeve, J. Am.

*Chem. Soc.* **2010**, *132*, 11904–11905; c) S. Garg, H. Gao, Y.-H. Joo, D. A. Parrish, Y. Huang, J. M. Shreeve, *J. Am. Chem. Soc.* **2010**, *132*, 8888–8890; d) V. Thottempudi, H. Gao, J. M. Shreeve, *J. Am. Chem. Soc.* **2011**, *133*, 6464–6471.

- [4] a) T. M. Klapötke, J. Stierstorfer, A. U. Wallek, *Chem. Mater.* 2008, 20, 4519–4530; b) T. M. Klapötke, C. Petermayer, D. G. Piercey, J. Stierstorfer, *J. Am. Chem. Soc.* 2012, *134*, 20827–20836; c) K. Banert, S. Richter, D. Schaarschmidt, H. Lang, *Angew. Chem.* 2013, 125, 3583–3586; *Angew. Chem. Int. Ed.* 2013, 52, 3499–3502.
- [5] a) Y. C. Li, C. Qi, S. H. Li, H. J. Zhang, C. H. Sun, Y. Z. Yu, S. P. Pang, J. Am. Chem. Soc. 2010, 132, 12172–12173; b) T. M. Klapötke, J. Stierstorfer, J. Am. Chem. Soc. 2009, 131, 1122–1134.
- [6] a) A. A. Dippold, T. M. Klapötke, *Chem. Eur. J.* 2012, *18*, 16742–16753; b) S. Garg, J. M. Shreeve, *J. Mater. Chem.* 2011, *21*, 4787–4795; c) G. H. Tao, B. Twamley, J. M. Shreeve, *J. Mater. Chem.* 2009, *19*, 5850–5854; d) C. Qi, S. Li, Y. Li, Y. Wang, X. Chen, S. Pang, *J. Mater. Chem.* 2011, *21*, 3221–3225.
- [7] a) T. Abe, Y.-H. Joo, G. Tao, B. Twamley, J. M. Shreeve, *Chem. Eur. J.* **2009**, *15*, 4102–4110; b) M-J. Crawford, T. M. Klapötke, F. A. Martin, C. M. Sabaté, M. Rusan, *Chem. Eur. J.* **2011**, *17*, 1683–1695; c) H. Gao, Y. Huang, C. Ye, B. Twamley, J. M. Shreeve, *Chem. Eur. J.* **2008**, *14*, 5596–5603.
- [8] a) Y. Huang, Y. Zhang, J. M. Shreeve, *Chem. Eur. J.* 2011, *17*, 1538–1546; b) M. V. Huynh, M. A. Hiskey, E. L. Hartline, D. P. Montoya, R. Gilardi, *Angew. Chem.* 2004, *116*, 5032–5036; *Angew. Chem. Int. Ed.* 2004, *43*, 4924–4928.
- [9] a) D. E. Chavez, M. A. Hiskey, R. D. Gilardi, Angew. Chem. 2000, 112, 1861–1863; Angew. Chem. Int. Ed. 2000, 39, 1791–1793; b) H. Gao, R. Wang, B. Twamley, M. A. Hiskey, J. M. Shreeve, Chem. Commun. 2006, 4007–4009; c) T. M. Klapötke, A. Preimesser, S. Schedlbauer, J. Stierstorfer, Cent. Eur. J. Energ. Mater. 2013, 10, 151–170.
- [10] a) T. M. Klapötke, F. A. Martin, J. Stierstorfer, Angew. Chem. 2011, 123, 4313–4316; Angew. Chem. Int. Ed. 2011, 50, 4227–4229; b) C. Ye, H. Gao, J. A. Boatz, G. W. Drake, B. Twamley, J. M. Shreeve, Angew. Chem. 2006, 118, 7420–7423; Angew. Chem. Int. Ed. 2006, 45, 7262–7265; c) M. A. Petrie, J. A. Sheehy, J. A. Boatz, G. Rasul, G. K. S. Prakash, G. A. Olah, K. O. Christe, J. Am. Chem. Soc. 1997, 119, 8802–8808.
- [11] a) D. E. Chavez, M. A. Hiskey, R. D. Gilardi, Org. Lett. 2004, 6, 2889–2891; b) D. E. Chavez, B. C. Tappan, M. A. Hiskey, S. F. Son, H. Harry, D. Montoya, S. Hagelberg, Propellants Explos. Pyrotech. 2005, 30, 412–417.
- [12] M. H. V. Huynh, M. A. Hiskey, D. E. Chavez, D. L. Naud, R. D. Gilardi, J. Am. Chem. Soc. 2005, 127, 12537–12543.
- [13] A. F. McKay, G. F. Wright, J. Am. Chem. Soc. 1947, 69, 3028-3030.
- [14] a) Computational Characterization of Energetic Materials. P. Politzer, J. S. Murray in Pauling's Legacy: Modern Modelling of the Chemical Bond (Eds.: Z. B. Maksic, W. J. Orville-Thomas), Theoretical and Computational Chemistry 6, Elsevier, New York, 1999, pp. 347–363; b) P. Politzer, J. S. Murray, J. M. Seminario, P. Lane, M. E. Grice, M. C. Concha, J. Mol. Struct. 2001, 573, 1–10; c) J. S. Murray, M. C. Concha, P. Politzer, Mol. Phys. 2009, 107, 89–97.
- [15] a) B. M. Rice, J. J. Hare, J. Phys. Chem. 2002, 106, 1770-1783; b) E. Gökçınar, T. M. Klapötke, M. P. Kramer, J. Phys. Chem. A 2010, 114, 8680-8686; c) Computational Aspects of Nitrogen-Rich HEDMs. B. M. Rice, E. F. C. Byrd, W. D. Mattson, In High Energy Density Materials (Ed.: T. M. Klapötke), Structure and Bonding 125, Springer, Berlin, 2007, pp. 153-194.
- [16] I. Hashiba, T. Tamura, H. Kousaka, U.S. Pat. 6878824 B2, 2005.
- [17] A. Baliani, G. J. Bueno, M. L. Stewart, V. Yardley, R. Brun, M. P. Barrett, I. H. Gilbert, J. Med. Chem. 2005, 48, 5570-5579.
- [18] Y. Fan, G. Li, Z. Li, H. Hou, H. Mao, J. Mol. Struct. 2004, 693, 217– 224.
- [19] J. C. Oxley, J. L. Smith, J. S. Moran, J. Energ. Mater. 2009, 27, 63-93.
- [20] D. E. Chavez, M. A. Hiskey, J. Heterocycl. Chem. 1998, 35, 1329– 1332.

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