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# A Comparative Study on Insensitive Energetic Derivatives of 5-(1,2,4-Triazol-*C*-yl)-tetrazoles and their 1-Hydroxy-tetrazole Analogues

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**Abstract.** The synthesis and characterization of selected nitrogen-rich salts based on 5-(1,2,4-triazol-*C*-yl)tetrazoles and their 1-hydroxy-tetrazole analogues is presented. The combination with guanidinium, triaminoguanidinium, and hydroxylammonium cations leads to enhanced performance and sensitivities. The main focus of this work is on the energetic properties of those ionic derivatives in comparison to the neutral compounds. Additionally, the positive influence of the

### Introduction

In the last decades, research in the field of energetic materials faced a profound change. Numerous studies raised awareness of the toxicity of widely-used substances like TNT, RDX, and HMX and their degradation products towards humans and the environment.<sup>[1]</sup> Additionally, modern safety requirements of the armed forces<sup>[2]</sup> cause a growing demand for material less vulnerable to stimuli like shock, heat, and bullet impact. Research around the globe focuses strongly on compounds based on nitrogen-rich heterocycles, since those liberate mostly molecular nitrogen as innoxious product of combustion or explosion. Furthermore, attractive energetic properties due to substantial ring strain and highly positive heats of formation attract notice to the research of environmentally friendly highpower energetic materials.<sup>[3]</sup> Recent studies on C-C connected heterocycles like bistriazoles and bistetrazoles revealed excellent characteristics regarding stability and detonation properties.<sup>[3a,4]</sup> The connection via C–C bond of a triazole ring with its opportunity to introduce a large variety of energetic moieties and a tetrazole or a N-hydroxy-tetrazole ring implying a large energy content leads to energetic materials with tunable properties.<sup>[5]</sup> Due to the fact that nitrogen-rich salts of energetic compounds show an increased stability compared to the uncharged compounds, we present the treatment of energetic triazole compounds with several nitrogen-rich bases to form

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introduction of *N*-oxides in energetic materials is shown. Structural characterization was accomplished by means of Raman, IR, and multinuclear NMR spectroscopy. The standard enthalpies of formation were calculated for selected compounds at the CBS-4M level of theory, the detonation parameters were calculated using the EXPLO5.05 program. Additionally, thermal stability was measured via DSC and sensitivities against impact, friction, and electrostatic discharge were determined.

the corresponding salts. Cations like guanidinium, triaminoguanidinium or hydroxylammonium not only increase the overall nitrogen content and thus the heat of formation, but also improve the performance characteristics.<sup>[4a,6]</sup>.

The focus of this study is on the synthesis and full characterization of energetic salts of 5-(1,2,4-triazol-C-yl)tetrazoles (1, 2) and their 1-hydroxy-tetrazole analogues (3, 4). The energetic performance and sensitivity data of the ionic compounds are presented and compared to the neutral precursors. Additionally, the positive influence of the introduction of *N*-oxides in energetic materials is shown.

# **Results and Discussion**

#### **Synthesis**

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All four neutral 5-(1,2,4-triazol-C-yl)tetrazoles (1, 2) and 5-(1,2,4-triazol-C-yl)tetrazol-1-oles (3, 4) were synthesized as published recently starting from 5-amino-1*H*-1,2,4-triazole-3carbonitrile.<sup>[5]</sup> In the case of compounds 1 and 2, first of all the tetrazole ring was built up by a cycloaddition with sodium azide, followed by introduction of the energetic moieties via Sandmeyer reaction or nitration with nitric acid (Scheme 1).<sup>[5a]</sup>



Scheme 1. Synthesis of NTT (1) and NATT (2).

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A different approach was used for the synthesis of compounds **3** and **4**. The energetic moieties were primarily introduced by modification of the amine group of 5-amino-1*H*-1,2,4-triazole-3-carbonitrile. Multiple reaction steps including the formation of an amidoxime, chlorination, chlorine to azide exchange and finally cyclization lead to the 1-hydroxy-tetrazole compounds **3** and **4** (Scheme 2).<sup>[5b]</sup>



Scheme 2. Synthesis of 5-(3-nitro-1H-1,2,4-triazol-5-yl)tetrazol-1-ol (NTTO) (3) and 5-(5-nitrimino-1,4H-1,2,4-triazol-3-yl)tetrazol-1-ol (NATTO) (4).

Preparation of the corresponding salts of compounds 1–4 was accomplished by diluting the neutral compound in ethanol and addition of two equivalents of the corresponding organic base (Scheme 3). This step benefits from the very poor solubility of the ionic target molecules, contrary to the neutral ones, which dissolve readily in ethanol. Precipitation of the desired ionic compounds occurred almost quantitative and led to high purities.

#### Multinuclear NMR Spectroscopy

All compounds were investigated using <sup>1</sup>H, <sup>13</sup>C, and <sup>14</sup>N NMR spectroscopy. The <sup>13</sup>C{<sup>1</sup>H}-spectra show three signals for the carbon atoms in the expected range, deprotonation with nitrogen-rich bases shifts the signals of all carbon atoms to lower field in comparison to the uncharged compounds. The signal of the carbon atom next to the energetic moiety is shifted furthest downfield for all compounds in the range of 157.3 ppm (**2c**) and 165.9 ppm (**3b**).

The signal of the bridging carbon of the triazole ring can be observed in the range of 151.4 ppm (**2a**) to 157.3 ppm (**1c**) and the corresponding signal of the tetrazole carbon atom is located in the range of 148.4 ppm (**2a**) to 156.4 ppm (**1c**) for the triazolyl-tetrazole compounds. In the case of the tetrazole-1 *N*-oxide compounds, all signals of the bridging carbon atoms are shifted to higher field. The signal of the triazole ring can be observed in the range of 147.8 ppm (**4a**) to 152.8 ppm (**3c**) and the corresponding signal of the tetrazole carbon atom is located in the range of 137.7 ppm (**4c**) to 139.2 ppm (**3a**). The <sup>14</sup>N{<sup>1</sup>H}</sup> NMR spectra of all compounds show a broad signal for the nitro group between -10 ppm and -25 ppm. Based on comparable ionic compounds, <sup>[4a,6]</sup> the proton signals of all cations can be found in the expected range.

Due to the insufficient solubility of compound 2a-c and 4a-c,  $^{15}N{^{1}H}$  NMR spectra were recorded for compounds 1c and 3c, as illustrated in Figure 1. The assignments are based on

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Scheme 3. Synthetic route to the nitrogen-rich salts derived from 1–4 using the corresponding nitrogen-rich bases (hydroxylamine, guanidi-nium carbonate, triaminoguanidine).

comparison with similar molecules and additional theoretical calculations using Gaussian 09 (MPW1PW91/aug-ccpVDZ).<sup>[7]</sup> The signals of the triazole nitrogen atoms as well as the nitro group can be found in both cases in the expected range very similar to the recently published 3,3'-dinitro-5,5'bistriazolate anion.<sup>[8]</sup> Two well resolved resonances are observed in the <sup>15</sup>N NMR spectrum of the tetrazolate compound **1c** at -7.3 (N5/6), and -67.6 ppm (N4/7), which is in good agreement with the resonances of the 5,5'-bistetrazolate anion (-3.0, -66.0).<sup>[3a]</sup> The tetrazole-*N*-oxide ring of compound **3c** shows four well resolved resonances. The signals can be observed at shifts of -82.4 (N4), -20.2 (N5), -17.0 (N6), and -54.0 ppm (N7), comparable with the signals of the similar 5,5'-bistetrazole-1,1'-diolate anion.<sup>[9]</sup>

#### Single Crystal X-ray Structure Analysis

All compounds were recrystallized from water, which mainly led to the formation of microcrystalline material not suitable for X-ray analysis. Only crystals of compounds **3b** were appropriate and the crystal structure is discussed in the following. The bond lengths and torsion angles within the azole rings are all in the range of formal C–N and N–N single and double bonds (C–N: 1.47 Å, 1.22 Å; N–N: 1.48 Å, 1.20 Å).<sup>[10]</sup> The C<sub>3</sub>–N<sub>5</sub>–N<sub>6</sub> angle of the *N*-oxide anion has an value of 108.7(1)° as compared to 109.9(2)° for the neutral compound **3**. As expected the N5–O3 bond length is shortened to 1.317(2) Å upon deprotonation [1.345(2) Å in **3**]. The tor-





**Figure 1.** <sup>15</sup>N{<sup>1</sup>H}NMR spectra of compounds **1c** (bottom) and **3c** (top) recorded in [D<sub>6</sub>]DMSO. The *x* axis represents the chemical shift  $\delta$  in ppm.

sion angle between both heterocycles and the one of the nitro group is very small  $[2.7(2)^{\circ} \text{ and } 0.8(2)^{\circ}]$ , which leads to a nearly planar assembly. Compound **3b** crystallizes as a monohydrate in the monoclinic space group  $P2_1/n$  with a density of 1.639 g·cm<sup>-3</sup>, the formula unit is shown in Figure 2.

Due to the planarity of both cation and anion, the crystal structure of **3b** is built up by planes that are kept together by a strong network of hydrogen bonds. A shown in Figure 3, each NTTO<sup>2–</sup> anion is surrounded by five guanidinium cations via strong hydrogen bonds towards the atoms of the azole rings and the oxygen O1 of the nitro group (Table 1). It is remarkable to note that all accessible nitrogen atoms (and the *N*-oxide O3) act as acceptor for hydrogen bonds, which is merely possible due to the several N–H groups of the surrounding guanidinium cations. All contacts lie well within the sum of van der Waals radii  $[r_w(O) + r_w(N) = 3.07 \text{ Å}, r_w(N) + r_w(N) = 3.20 \text{ Å}]^{[11]}$  with a *D*-*A* length between 2.801(2) Å and 3.199(2) Å. Most of the hydrogen bonds are strongly directed with *D*–H-*A* angles between 155(2)° and 175(2)°. In addition,



**Figure 2.** Molecular structure of guanidinium 5-(3-nitro-1,2,4-triazolate-5-yl)tetrazol-1-olate (**3b**). Thermal ellipsoids are set to 50% probability.

the oxygen atom O1 is involved in a electrostatic interaction with the  $\pi$  electrons of the overlying tetrazole ring, which supports the stacking of the layers.



**Figure 3.** Formation of planes in the crystal structure of **3b**. Thermal ellipsoids are set to 50% probability. Symmetry codes: (*i*) 1/2-x, 1/2+y, 1/2-z; (*ii*) x, -1+y, z; (*iii*) 1-x, -y, -z; (*iv*) 1/2+x, 1/2-y, -1/2+z; (v) 1-x, 1-y, -z.

# Theoretical Calculations, Performance Characteristics, and Stabilities

The heats of formation of all compounds were calculated on the CBS-4M level of theory using the atomization energy method and utilizing experimental data (for further details and results refer to the Supporting Information). All compounds show highly endothermic enthalpies of formation in the range of 234 kJ·mol<sup>-1</sup> (**1b**) to 1009 kJ·mol<sup>-1</sup> (**4c**), all by far outperforming RDX (70 kJ·mol<sup>-1</sup>).

In order to estimate the detonation performances of the prepared compounds selected key parameters were calculated with EXPLO5 (version 5.05)<sup>[20]</sup> and compared to RDX. The calculated detonation parameters using experimentally deter-

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Table 1. Hydrogen bonds present in 3b.								
D–H•••A	<i>d</i> (D–H) /Å	<i>d</i> (H•••A) /Å	<i>d</i> ( <i>D</i> – <i>A</i> ) /Å	< (D–H•••A) /°				
O4 <sup>i</sup> –H4b····N2	0.87(2)	2.06(2)	2.916(2)	169(2)				
N9 <sup>ii</sup> –H9a····O4	0.86 (2)	1.98(2)	2.801(2)	158(2)				
N9 <sup>iv</sup> –H9b····N3	0.85(2)	2.10(2)	2.920(2)	165(2)				
N10 <sup>iv</sup> -H10a-N8	0.90(2)	2.20(2)	3.095(2)	175(2)				
N11-H11a····N6	0.86 (2)	2.32(2)	3.175(2)	173(2)				
N11 <sup>ii</sup> -H11b····O4	0.86(2)	2.32(2)	3.053(2)	143(1)				
N12 <sup>i</sup> -H12a····O3	0.86(2)	2.10(2)	2.814(2)	140 (2)				
N12 <sup>v</sup> -H12b····N7	0.86(2)	2.40(2)	3.199(2)	155(2)				
N13 <sup>i</sup> -H13aN1	0.89(2)	2.16(2)	3.040(2)	170(2)				
N13 <sup>i</sup> -H13b····N2	0.89(2)	2.32(2)	3.152(2)	154(2)				
N14 <sup>iii</sup> –H14a•••O1	0.87(2)	2.19(2)	3.044(2)	164(2)				
N14 <sup>v</sup> -H14b····N7	0.87(2)	2.37(2)	3.172(2)	154(2)				

Symmetry operators: (i) 1/2-x, 1/2+y, 1/2-z; (ii) x, -1+y, z; (iii) 1-x, -y, -z; (iv) 1/2+x, 1/2-y, -1/2+z; (v) 1-x, 1-y, -z.

mined densities (gas pycnometry at 25  $^{\circ}$ C with dried compounds) and calculated heats of formation are summarized in Table 2 and Table 3.

### Sensitivity

Regarding the precursor compounds NATT (2) and NATTO (4), both show very high sensitivity towards impact, friction, and electrostatic discharge. One of the key aspects of this study was the synthesis of ionic derivatives that are safer to handle, while being at least equally energetic. In the case of compounds 2a-c, the sensitivity towards impact is reduced from 1 J to 40 J and the sensitivity towards friction could be lowered to 160 N (2a), 324 N (2b) and 360 N (2c). Compounds 4a-c also show lower sensitivity values [8 J (4a), 40 J (4b), 10 J (4c)] in comparison to the neutral compound 4, however the low sensitivities of the corresponding compounds bearing no *N*-oxide are only reached for compound 4b.

Figure 1 shows the thermal decomposition of the ionic derivatives  $2\mathbf{a}-\mathbf{c}$  (solid lines) and  $4\mathbf{a}-\mathbf{c}$  (dashed lines).

As expected, the thermal stability of all ionic compounds mostly depends on the cation, however the ionic *N*-oxide compounds (**4a**–**c**) all show a lower decomposition temperature in comparison to compounds **2a–c** as it is expected for *N*-hydroxy azoles.<sup>[12]</sup> With a decomposition temperature of 238 °C (**2b**) and 212 °C (**4b**), only the guanidinium salts show a higher onset temperature compared to RDX (Figure 4).

The sensitivity of the neutral NTT (1) and NTTO (3) towards external stimuli could also be further decreased by deprotonating with organic bases. All compounds (except 3a) show an impact sensitivity of 40 J and friction sensitivity of 360 N. As shown in Figure 3, the guanidinium salt (3b) shows a remarkably high decomposition temperature (296 °C) in comparison to the neutral compound 1, whereas compound 3c starts to decompose at 190 °C and 3a at 182 °C.

Again, the ionic *N*-oxide compounds (3a-c) show lower decomposition temperatures in comparison to compounds 1a-c, only the guanidinium salt **3b** exceeds 200 °C with a thermal stability of 269 °C (Figure 5).



**Figure 4.** DSC plots of ionic derivatives  $2\mathbf{a}-\mathbf{c}$  (solid lines) and  $4\mathbf{a}-\mathbf{c}$  (dashed lines). DSC plots were recorded with a heating rate of 5 K·min<sup>-1</sup>.

#### Performance

The results of theoretical calculations regarding performance are summarized in Table 2 and Table 3. In general, the triazol-C-yl-tetrazoles show lower performance values in comparison to their 1-hydroxy-tetrazole analogues. As expected, the additional oxygen atom generally leads to increased energetic properties due to a higher density and an even greater energy output.<sup>[12b,14]</sup> In comparison to the ionic derivatives of compounds 1 and 2, a marked performance increase is seen. The detonation velocities of the hydroxyl ammonium salts **3a** and **4a** are increased by about 500 ms<sup>-1</sup>. For the guanidinium salts **3b** and **4b**, the influence of the additional oxygen is slightly lower; however, the detonation velocity is still increased by about 270 m·s<sup>-1</sup>. The introduction of the *N*-oxide Date: 01-08-13 17:21:45

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Figure 5. DSC plots of ionic derivatives 1a-c (solid lines) and 3a-c (dashed lines). DSC plots were recorded with a heating rate of 5 K·min<sup>-1</sup>.

also positively influences other detonation parameters like the detonation pressure or the energy of explosion (increased by approximately  $500 \text{ kJ} \cdot \text{kg}^{-1}$ ).

Of all described compounds, the triaminoguanidinium salt **3c** and the hydroxylamonium salt **4a** exhibit the best calculated performance values regarding the detonation parameters, sensitivities, and thermal stability. Compound **4a** displays the best performance with a calculated detonation velocity of 9014 m·s<sup>-1</sup>, a detonation pressure of 348 kbar and a decomposition temperature of 179 °C. The triaminoguanidinium compound exhibits energetic properties in the range of RDX with 8728 m·s<sup>-1</sup>, a detonation pressure of 299 kbar and a decompo-

sition temperature of 181 °C, along with a very high nitrogen content of 68.9 %.

Although lower performance values ( $v_{det} = 7974 \text{ m} \cdot \text{s}^{-1}$  and 7970 m·s<sup>-1</sup>) were calculated for the guanidinium salts **3b** and **4b**, these compounds displays the highest decomposition temperatures of 269 °C and 212 °C together with an insensitivity towards friction and impact.

The most interesting compounds regarding the energetic properties are the hydroxylammonium and triaminoguanidinium compounds (**4a** and **3c**). Those compounds exhibit decomposition temperatures slightly below 200 °C and performance values in the range of RDX [8728 m·s<sup>-1</sup> (**3c**)] or even well above [9014 m·s<sup>-1</sup> (**4a**)].

# Conclusions

By reacting the nitro- and nitrimino triazolyl-tetrazole compounds (1, 2) and their 1-hydroxy-tetrazole analogues (3, 4)with nitrogen-rich organic bases, twelve ionic nitrogen rich energetic materials were synthesized and fully characterized by means of vibrational and NMR spectroscopy as well as sensitivity towards impact and friction. Their thermal behavior was investigated with differential scanning calorimetry and their energetic properties calculated theoretically. The ionic Noxide compounds (3a-c, 4a-c) show lower decomposition temperature in comparison to the compounds bearing no Noxide, however the stability is mainly influenced by the corresponding cation. Most of the compounds show reduced sensitivities in comparison to their neutral precursors, especially the ionic compounds based on NATT (2a-c) and NATTO (4a-c) are much safer to handle, since the stability towards friction and impact was considerably increased.

Regarding the detonation properties, the performance is mostly affected by the cation. The guanidinium salts always show the lowest detonation velocities, the hydroxylammonium

Table 2. Physico-chemical properties of compounds 1 and 3 and their corresponding ionic derivatives (a-c) in comparison to hexogen (RDX).

	1 (NTT)	3 (NTTO)	1a	1b	1c	3a	3b	3c	RDX <sup>n)</sup>
Formula	C <sub>3</sub> H <sub>2</sub> N <sub>8</sub> O <sub>2</sub>	C <sub>3</sub> H <sub>2</sub> N <sub>8</sub> O <sub>3</sub>	C <sub>3</sub> H <sub>8</sub> N <sub>10</sub> O <sub>4</sub>	C <sub>5</sub> H <sub>12</sub> N <sub>14</sub> O <sub>2</sub>	C <sub>5</sub> H <sub>18</sub> N <sub>20</sub> O <sub>2</sub>	C <sub>3</sub> H <sub>8</sub> N <sub>10</sub> O <sub>5</sub>	C <sub>5</sub> H <sub>12</sub> N <sub>14</sub> O <sub>3</sub>	C <sub>5</sub> H <sub>18</sub> N <sub>20</sub> O <sub>3</sub>	C <sub>3</sub> H <sub>6</sub> N <sub>6</sub> O <sub>6</sub>
Molecular mass /g·mol <sup>-1</sup>	182.1	198.10	248.16	300.24	390.33	264.15	316.24	406.32	222.12
Impact sensitivitya) /J	25	35	40	40	40	8	40	10	7
Friction sensitivity <sup>b)</sup> /N	288	360	360	>360	>360	360	360	360	120
ESD test /J	0.85	0.13	0.15	0.6	0.4	0.2	0.5	0.35	
N <sup>c)</sup> /%	61.5	56.6	56.44	65.3	71.8	53.0	62.0	68.9	37.8
$\Omega^{ m d)}$ /%	-43.9	-32.3	-38.7	-74.6	-69.7	-30.3	-65.8	-63.0	-21.6
$T_{\rm dec}$ . <sup>e)</sup> /°C	211	152	182	296	190	175	269	181	210
$\rho^{\text{f}}/\text{g}\cdot\text{cm}^{-3}$	1.70	1.86	1.78	1.71	1.68	1.81	1.72	1.70	1.82
$\Delta_f H_{\rm m}^{\circ g)}$ /kJ·mol <sup>-1</sup>	518	446	316	234	958	356	260	977	70
$\Delta_f U^{\circ h} / kJ \cdot kg^{-1}$	2430	2335	1385	896	2582	1456	936	2529	417
EXPLO5 (V5.05) values:									
$-\Delta_E U^{\circ i}$ /kJ kg <sup>-1</sup>	4730	5407	5201	2866	4285	5750	3471	4688	6128
$T_{\rm E}^{\rm j)}/{\rm K}$	3833	4217	3651	2259	2830	3939	2593	3073	4207
$p_{C-J}^{k}$ /kbar	254	337	291	219	290	352	244	299	349
$V_{\rm Det}$ . <sup>1)</sup> /m•s <sup>-1</sup>	7919	8655	8473	7682	8644	8996	7974	8728	8749
Gas vol. m) /L·kg-1	682	677	808	773	826	799	781	831	740

a) BAM drophammer, grain size  $(75-150 \,\mu\text{m})$ . b) BAM friction tester, grain size  $(75-150 \,\mu\text{m})$ . c) Nitrogen content. d) Oxygen balance. e) Temperature of decomposition by DSC ( $\beta = 5 \,^{\circ}\text{C}$ , onset values). f) Densities based on gas-pycnometer measurements of anhydrous compounds at 25  $\,^{\circ}\text{C}$ . g) Molar enthalpy of formation. h) Energy of formation. i) Energy of explosion. j) Explosion temperature. k) Detonation pressure. l) Detonation velocity. m) Assuming only gaseous products. n) Values based on Ref. [13].

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Table 3. Physico-chem	cal properties of compour	ds 2 and 4 and their corre	sponding ionic derivatives	(a-c) in coi	mparison to hexogen (	RDX).
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•	1 1	-		-					
	<b>2</b> (NATT)	4 (NATTO)	2a	2b	2c	<b>4</b> a	4b	4c	RDX <sup>n)</sup>
Formula	C <sub>3</sub> H <sub>3</sub> N <sub>9</sub> O <sub>2</sub>	C <sub>3</sub> H <sub>3</sub> N <sub>9</sub> O <sub>3</sub>	C3H9N11O4	C <sub>5</sub> H <sub>13</sub> N <sub>15</sub> O <sub>2</sub>	C <sub>5</sub> H <sub>19</sub> N <sub>21</sub> O <sub>2</sub>	C <sub>3</sub> H <sub>9</sub> N <sub>11</sub> O <sub>5</sub>	C <sub>5</sub> H <sub>13</sub> N <sub>15</sub> O <sub>3</sub>	C <sub>5</sub> H <sub>19</sub> N <sub>21</sub> O <sub>3</sub>	C <sub>3</sub> H <sub>6</sub> N <sub>6</sub> O <sub>6</sub>
Molecular mass /g·mol <sup>-1</sup>	197.1	213.11	263.2	315.26	405.34	279.17	331.25	421.34	222.12
Impact sensitivitya) /J	<1	< 1	40	40	40	8	40	10	7
Friction sensitivity <sup>b)</sup> /N	18	60	160	>360	324	288	360	288	120
ESD-test /J	0.07	0.13	0.15	0.6	0.2	0.1	0.8	0.3	_
N <sup>c)</sup> /%	64.0	59.2	58.5	66.6	72.6	55.2	63.4	69.8	37.8
$\Omega^{ m d)}$ /%	-44.6	-33.8	-38.7	-74.6	-69.7	-31.5	-65.2	-62.6	-21.6
$T_{\rm dec}$ , e)/°C	215	116	194	238	191	179	212	186	210
$\rho^{\rm f}/{\rm g}\cdot{\rm cm}^{-3}$	1.70	1.85	1.75	1.68	1.66	1.79	1.70	1.67	1.82
$\Delta_f H_{\rm m}^{\circ g)}$ /kJ·mol <sup>-1</sup>	576	515	354	261	978	418	304	1009	70
$\Delta_f U^{\circ h} / kJ \cdot kg^{-1}$	2549	2502	1458	946	2542	1607	1033	2521	417
EXPLO5 (V5.05) values:									
$-\Delta_E U^{\circ i}$ /kJ kg <sup>-1</sup>	4804	5470	5273	2915	4246	5769	3495	4643	6128
$T_{\rm E}^{\rm j)}/{\rm K}$	3781	4126	3684	2281	2814	3898	2600	3033	4207
$p_{C-I}^{(k)}$ /kbar	262	342	293	221	289	348	242	288	349
$V_{\text{Det}}$ . <sup>1)</sup> /m·s <sup>-1</sup>	8062	8776	8500	7709	8628	9014	7970	8628	8749
Gas vol. m)/L·kg <sup>-1</sup>	712	708	807	773	827	818	791	836	740

a) BAM drophammer, grain size  $(75-150 \,\mu\text{m})$ . b) BAM friction tester, grain size  $(75-150 \,\mu\text{m})$ . c) Nitrogen content. d) Oxygen balance. e) Temperature of decomposition by DSC ( $\beta = 5 \,^{\circ}\text{C}$ , onset values). f) Densities based on gas-pycnometer measurements of anhydrous compounds at 25  $^{\circ}\text{C}$ . g) Molar enthalpy of formation. h) Energy of formation. i) Energy of explosion. j) Explosion temperature. k) Detonation pressure. l) Detonation velocity. m) Assuming only gaseous products. n) Values based on Ref. [13].

and triaminoguanidinium salts are basically in the same range. In general, the triazol-C-yl-tetrazoles show lower performance values in comparison to their 1-hydroxy-tetrazole analogues. The detonation velocities of the hydroxylammonium salts are increased by about  $500 \text{ m} \cdot \text{s}^{-1}$  due to the *N*-oxide. For the guanidinium salts, the influence of the additional oxygen is slightly lower; however the detonation velocity is still increased by about  $270 \text{ m} \cdot \text{s}^{-1}$ . The introduction of an *N*-oxide in tetrazole based energetic materials obviously positively influences the detonation parameters due to a higher density and an even greater energy output, however this advantage comes along with lower decomposition temperatures.

# **Experimental Section**

*Caution:* Although all presented nitroazoles are rather stable against outer stimuli, proper safety precautions should be taken when handling the dry materials. The neutral nitraminoazole is of high sensitivity and tends to explode under the influence of heat, impact, or friction. Lab personnel and the equipment should be properly grounded and protective equipment like earthed shoes, leather coat, Kevlar<sup>®</sup> gloves, ear protection, and face shield is recommended.

**General:** All chemical reagents and solvents were obtained from Sigma-Aldrich Inc. or Acros Organics (analytical grade) and were used as supplied without further purification. <sup>1</sup>H, <sup>13</sup>C{<sup>1</sup>H}, <sup>14</sup>N{<sup>1</sup>H} and NMR spectra were recorded with a JEOL Eclipse 400 instrument in  $[D_6]DMSO$  at 25 °C. The chemical shifts are given relative to tetramethylsilane (<sup>1</sup>H, <sup>13</sup>C) or nitro methane (<sup>14</sup>N) as external standards and coupling constants are given in Hertz (Hz). Infrared (IR) spectra were recorded with a Perkin-Elmer Spectrum BX FT-IR instrument equipped with an ATR unit at 25 °C. Transmittance values are qualitatively described as "very strong" (vs), "strong" (s), "medium" (m), "weak" (w), and "very weak" (vw). Raman spectra were recorded with a Bruker RAM II spectrometer equipped with a Nd:YAG laser (200 mW) operating at 1064 nm and a reflection angle of 180°. The intensities are reported as percentages of the most intense peak and are given in parentheses. Elemental analyses (CHNO) were performed

with a Netzsch Simultaneous Thermal Analyzer STA 429. Melting and decomposition points were determined by differential scanning calorimetry (Linseis PT 10 DSC, calibrated with standard pure indium and zinc). Measurements were performed at a heating rate of 5 K·min<sup>-1</sup> in closed aluminum sample pans with a 1  $\mu$ m hole in the lid for gas release to avoid an unsafe increase in pressure in a nitrogen flow of 20 mL·min<sup>-1</sup> with an empty identical aluminum sample pan as a reference.

For initial safety testing, the impact and friction sensitivities as well as the electrostatic sensitivities were determined. The impact sensitivity tests were carried out according to STANAG 4489,<sup>[15]</sup> modified according to WIWEB instruction 4-5.1.02<sup>[16]</sup> with a BAM<sup>[17]</sup> drop hammer. The friction sensitivity tests were carried out according to STANAG 4487<sup>[18]</sup> and modified according to WIWEB instruction 4-5.1.03<sup>[19]</sup> with the BAM<sup>[17]</sup> friction tester. The electrostatic sensitivity tests were accomplished according to STANAG 4490<sup>[20]</sup> with an electric spark testing device ESD 2010EN (OZM Research).

**Crystallographic Measurements:** The single-crystal X-ray diffraction data of **3b** was collected with an Oxford Xcalibur3 diffractometer equipped with a Spellman generator (voltage 50 kV, current 40 mA), Enhance molybdenum K<sub>a</sub> radiation source ( $\lambda = 71.073$  pm), Oxford Cryosystems Cryostream cooling unit, four circle kappa platform and a Sapphire CCD detector. Data collection and reduction was performed with CrysAlisPro.<sup>[21]</sup> The structure was solved with SIR97,<sup>[22]</sup> refined with SHELXL-97,<sup>[23]</sup> and checked with PLATON,<sup>[24]</sup> all integrated into the WinGX software suite.<sup>[25]</sup> The finalized CIF file was checked with checkCIF.<sup>[26]</sup> Intra- and intermolecular contacts were analyzed with Mercury.<sup>[27]</sup>

Crystallographic data (excluding structure factors) for the structure in this paper have been deposited with the Cambridge Crystallographic Data Centre, CCDC, 12 Union Road, Cambridge CB21EZ, UK. Copies of the data can be obtained free of charge on quoting the depository number CCDC-946356 (**3b**) (Fax: +44-1223-336-033; E-Mail: deposit@ccdc.cam.ac.uk, http://www.ccdc.cam.ac.uk).

The precursors 1 and 2 as well as 3 and 4 were synthesized according to literature.<sup>[5]</sup>

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Energetic Derivatives of 5-(1,2,4-Triazol-C-vl)-tetrazoles and their 1-Hydroxy-tetrazole Analogues



Hydroxylammonium 5-(5-Nitro-1,2,4-triazolate-3-yl)-tetrazolate (1a): 5-(5-Nitro-1,2,4-triazol-3-yl)-tetrazole (NTT, 1) (0.5 g, 2.7 mmol) was diluted in EtOH (25 mL) and hydroxylamine (50 wt% in water, 0.32 mL, 5.5 mmol) was added. The precipitate was filtered off and washed with EtOH and Et<sub>2</sub>O to yield **3a** (0.51 g, 2.0 mmol, 74%) as slightly yellow powder. <sup>1</sup>H NMR ([D<sub>6</sub>]DMSO):  $\delta = 9.43$  (s, 3 H, NH<sub>3</sub>-OH). <sup>13</sup>C NMR ([D<sub>6</sub>]DMSO):  $\delta = 164.7, 153.5, 153.3.$ <sup>14</sup>N NMR ([D<sub>6</sub>]DMSO):  $\delta = -18$  (NO<sub>2</sub>) ppm. IR:  $\tilde{v} = 3624$  (w), 3562 (w), 3016 (m), 2699 (s), 1643 (m), 1617 (m), 1513 (s), 1480 (m), 1469 (vs), 1407 (s), 1393 (vs), 1321 (m), 1308 (s), 1292 (m), 1284 (m), 1252 (s), 1236 (s), 1191 (m), 1144 (m), 1114 (m), 1102 (s), 1047 (w), 1011 (m), 1011 (m), 1001 (s), 842 (s), 777 (s), 764 (s), 730 (m), 716 (m), 655 (m) cm<sup>-1</sup>. **Raman** (200 mW):  $\tilde{v}$  (rel. int.) = 1583(95), 1522(5), 1513(4), 1473(9), 1410(45), 1399(49), 1323(35), 1293(8), 1285(16), 1194(7), 1145(5), 1115(100), 1105(22), 1087(11), 1047(9), 1040(11), 1006(13), 847(12), 778(4), 765(4), 395(6), 343(5) cm<sup>-1</sup>. Elemental analysis (C3H8N10O4): calcd. C 14.25, H 3.25, N 56.44%; found: C 14.68, H 3.44, N 52.38%. MS: m/z (FAB<sup>-</sup>): 181.0 [C<sub>3</sub>HN<sub>8</sub>O<sub>2</sub><sup>-</sup>]; (FAB<sup>+</sup>): 34.1 [NH<sub>4</sub>OH<sup>+</sup>]. **DSC** (onset, 5 K·min<sup>-1</sup>): T<sub>Dec</sub>: 190 °C. Sensitivities (grain size:  $< 100 \,\mu\text{m}$ ): FS:  $> 360 \,\text{N}$ , IS: 40, ESD: 0.15 J.

Guanidinium 5-(5-Nitro-1,2,4-triazolate-3-yl)-tetrazolate (1b): 5-(5-Nitro-1,2,4-triazol-3-yl)-tetrazole (NTT, 1) (0.5 g, 2.7 mmol) was diluted in EtOH (20 mL). A solution of guanidinium carbonate (0.49 g, 2.7 mmol) in water (5 mL) was added, the mixture was refluxed for 15 min, and subsequently cooled to room temperature. The precipitate was filtered off and washed with EtOH and Et<sub>2</sub>O to yield **3b** (0.75 g, 2.5 mmol, 91%) as yellow powder. <sup>1</sup>H NMR ([D<sub>6</sub>]DMSO):  $\delta = 7.46$ (s, 6 H, NH<sub>2</sub>, G<sup>+</sup>). <sup>13</sup>C NMR ([D<sub>6</sub>]DMSO):  $\delta$  = 165.6, 158.8, 156.3, 155.9. <sup>14</sup>N NMR ([D<sub>6</sub>]DMSO):  $\delta = -25$  (NO<sub>2</sub>) ppm. IR:  $\tilde{v} = 3428$  (m), 3343 (m), 3084 (m), 1680 (s), 1653 (s), 1635 (s), 1582 (m), 1503 (m), 1465 (s), 1398 (s), 1377 (vs), 1302 (s), 1276 (m), 1187 (m), 1148 (m), 1141 (m), 1091 (s), 1035 (w), 1010 (w), 1002 (m), 838 (m), 781 (w), 775 (w), 775 (w), 716 (w), 657 (w) cm<sup>-1</sup>. Raman (200 mW):  $\tilde{\nu}$  (rel. int.) = 1585(76), 1556(7), 1520(6), 1471(7), 1399(50), 1391(66), 1310(33), 1278(39), 1190(2), 1105(100), 1094(79), 1061(4), 1043(10), 1037(10), 1013(19), 841(14), 778(3), 765(2), 536(10), 507(2), 474(2), 394(3) cm<sup>-1</sup>. Elemental analysis (C<sub>5</sub>H<sub>12</sub>N<sub>14</sub>O<sub>2</sub>): calcd. C 20.00, H 4.03, N 65.31%; found C 20.60, H 4.13, N 62.96%. MS: m/z(FAB<sup>+</sup>): 60.0 [CH<sub>6</sub>N<sub>3</sub><sup>+</sup>]; (FAB<sup>-</sup>): 181.1 [C<sub>3</sub>HN<sub>8</sub>O<sub>2</sub><sup>-</sup>]; DSC (onset, 5 K·min<sup>-1</sup>):  $T_{\text{Dec}}$ : 286 °C. Sensitivities (grain size: < 100 µm): FS: > 360 N, IS: 40 J, ESD: 0.6 J.

Triaminoguanidinium 5-(5-Nitro-1,2,4-triazolate-3-yl)-tetrazolate (1c): Triaminoguanidine (0.57 g, 5.5 mmol) was added to a solution of 5-(5-nitro-1,2,4-triazol-3-yl)-tetrazole (NTT, 1) (500 mg, 2.746 mmol) in ethanol (20 mL) and the mixture was refluxed for 15 min. After cooling to room temperature, the precipitate was collected by filtration, washed with EtOH and Et<sub>2</sub>O to yield 3c (0.98 g, 2.5 mmol, 91%) as yellow powder. <sup>1</sup>H NMR ([D<sub>6</sub>]DMSO):  $\delta = 8.79$ (s, 3 H, NH, TAG<sup>+</sup>), 4.61 (s, 6 H, NH<sub>2</sub>, TAG<sup>+</sup>). <sup>13</sup>C NMR  $([D_6]DMSO): \delta = 165.6, 159.3, 157.3, 156.4.$ <sup>14</sup>N NMR  $([D_6]DMSO):$  $\delta = -14 (NO_2)$ . <sup>15</sup>N NMR ([D<sub>6</sub>]DMSO):  $\delta = -7.3 (N5/6), -19.2 (N8),$ -57.8 (N1), -59.0 (N2), -67.6 (N4/7), -146.2 (N3), -288.3 (TAG+, NH), -328.8 (TAG<sup>+</sup>, NH<sub>2</sub>) ppm. IR:  $\tilde{v}$  = 3367 (m), 3299 (m), 3155 (m), 1685 (vs), 1671 (vs), 1601 (w), 1509 (s), 1462 (m), 1380 (s), 1336 (m), 1293 (m), 1264 (m), 1219 (w), 1194 (w), 1141 (s), 1083 (s), 1013 (m), 994 (s), 936 (s), 834 (m), 721 (m), 662 (w), 641 (m), 641 (m) cm<sup>-1</sup>. **Raman** (200 mW):  $\tilde{v}$  (rel. int.) = 1574(81), 1559(30), 1513(4), 1464(9), 1393(32), 1379(79), 1305(32), 1277(20), 1265(24), 1193(3), 1096(99), 1087(95), 1038(8), 1031(11), 996(2), 885(8), 836(10), 781(4), 640(2), 405(5) cm<sup>-1</sup>. Elemental analysis

(C<sub>5</sub>H<sub>18</sub>N<sub>20</sub>O<sub>2</sub>): calcd. C 15.39, H 4.65, N 71.77%; found: C 17.55, H 4.25, N 71.58%. MS: *m/z* (FAB<sup>+</sup>): 105.1 [CH<sub>9</sub>N<sub>6</sub><sup>+</sup>], (FAB<sup>-</sup>): 181.1  $[C_3HN_8O_2^-]$ ; **DSC** (onset, 5 K·min<sup>-1</sup>):  $T_{Dec}$ : 192 °C. Sensitivities (grain size:  $< 100 \,\mu\text{m}$ ): FS:  $> 360 \,\text{N}$ , IS: 40 J, ESD: 0.4 J.

Hydroxylammonium 5-(5-Nitrimino-1,2,4-triazolate-3-yl)-tetrazolate (2a): Hydroxylamine (50 wt% in water, 0.26 mL, 4.5 mmol) was added to a solution of 5-(3-nitrimino-1,2,4-triazol-3-yl)-tetrazole (2) (0.5 g, 2.2 mmol) in ethanol (30 mL). The precipitate was collected by filtration and washed with EtOH and Et<sub>2</sub>O to yield 4a (0.30 g, 1.2 mmol, 54%) as slightly yellow solid. <sup>1</sup>H NMR ([D<sub>6</sub>]DMSO):  $\delta =$ 10.64 (s, 3 H, NH<sub>3</sub>OH). <sup>13</sup>C NMR ([D<sub>6</sub>]DMSO):  $\delta$  = 157.7, 151.4, 148.4. <sup>14</sup>N NMR ([D<sub>6</sub>]DMSO):  $\delta = -16$  (NO<sub>2</sub>) ppm. IR:  $\tilde{v} = 3187$  (w), 2938 (m), 2698 (m), 2691 (m), 1627 (w), 1573 (m), 1532 (m), 1512 (m), 1486 (m), 1450 (m), 1445 (m), 1417 (m), 1390 (m), 1370 (m), 1341 (s), 1333 (s), 1306 (m), 1263 (vs), 1239 (s), 1209 (s), 1185 (m), 1164 (m), 1137 (m), 1137 (m), 1114 (m), 1104 (s), 1091 (m), 1079 (m), 1060 (m), 1007 (m), 1000 (s), 969 (m), 879 (w), 850 (m), 832 (m), 777 (m), 761 (s), 746 (m), 732 (m), 720 (s), 693 (w) cm<sup>-1</sup>. Raman  $(200 \text{ mW}): \tilde{v} \text{ (rel. int.)} = 1629(91), 1597(94), 1568(68), 1531(28),$ 1512(16), 1487(19), 1426(5), 1381(6), 1371(6), 1263(7), 1212(5), 1187(6), 1167(4), 1144(22), 1115(31), 1081(13), 1063(8), 1040(7), 1028(28), 999(41), 881(5), 854(8), 756(16), 756(16), 748(12), 428(4), 329(4), 314(4), 235(4) cm<sup>-1</sup>. Elemental analysis (C<sub>3</sub>H<sub>9</sub>N<sub>11</sub>O<sub>4</sub>): calcd. C 13.69, H 3.45, N 58.54%; found: C 15.04, H 2.99, N 58.67%, MS: m/z (FAB<sup>+</sup>): 34.0 [NH<sub>4</sub>O<sup>+</sup>]; (FAB<sup>-</sup>): 196.1 [C<sub>3</sub>H<sub>2</sub>N<sub>9</sub>O<sub>2</sub><sup>-</sup>]; **DSC** (onset, 5 K·min<sup>-1</sup>):  $T_{\text{Dec}}$ : 194 °C. Sensitivities (grain size: < 100 µm): FS: 160 N, IS: 40, ESD: 0.15 J.

Guanidinium 5-(5-Nitrimino-1,2,4-triazolate-3-yl)-tetrazolate (2b): 5-(5-nitrimino-1,2,4-triazol-3-yl)-tetrazole (2) (0.5 g, 2.1 mmol) was dissolved in EtOH (30 mL). A solution of guanidinium carbonate (0.39 g, 2.2 mmol) in water (5 mL) was added, the mixture was refluxed for 15 min, and subsequently cooled to room temperature. The precipitate was collected by filtration and washed with EtOH and Et<sub>2</sub>O to yield **4b** (0.60 g, 1.9 mmol, 89%) as yellow powder. <sup>1</sup>H NMR  $([D_6]DMSO): \delta = 7.68 \text{ (s, 6 H, N}_{H_2}, G^+).$  <sup>13</sup>C NMR  $([D_6]DMSO): \delta$ = 158.3, 157.7, 155.2, 152.3. <sup>14</sup>N NMR ([D<sub>6</sub>]DMSO):  $\delta$  = -17 (NO<sub>2</sub>) ppm. IR:  $\tilde{v} = 3385$  (m), 1699 (m), 1665 (m), 1651 (s), 1637 (s), 1579 (w), 1516 (m), 1457 (m), 1399 (m), 1358 (m), 1333 (vs), 1280 (vs), 1236 (m), 1187 (m), 1136 (m), 1079 (s), 1039 (w), 1009 (w), 982 (m), 857 (w), 766 (m), 750 (w), 733 (m), 733 (m) cm<sup>-1</sup>. Raman (200 mW):  $\tilde{v}$  (rel. int.) = 1593(98), 1561(5), 1512(28), 1461(21), 1357(5), 1279(6), 1189(3), 1141(10), 1132(8), 1062(5), 1013(36), 860(4), 751(6), 550(5), 424(3), 321(3), 258(3) cm<sup>-1</sup>. Elemental analysis ( $C_5H_{13}N_{15}O_2$ ): calcd. C 19.05, H 4.16, N 66.64 %; found: C 19.50, H 4.14, N 64.67 %.  $\mbox{MS}{:}$ m/z (FAB<sup>+</sup>): 60.0 [CH<sub>6</sub>N<sub>3</sub><sup>+</sup>]; (FAB<sup>-</sup>): 196.1 [C<sub>3</sub>H<sub>2</sub>N<sub>9</sub>O<sub>2</sub><sup>-</sup>]; **DSC** (onset, 5 K·min<sup>-1</sup>):  $T_{\text{Dec}}$ : 238 °C. Sensitivities (grain size: < 100 µm): FS: > 360 N, IS: 40, ESD: 0.6 J.

Triaminoguanidinium 5-(5-Nitrimino-1,2,4-triazolate-3-yl)-tetrazolate (2c): Triaminoguanidine (380 mg, 3.65 mmol) was added to a solution of 5-(5-nitrimino-1,2,4-triazol-3-yl)-tetrazole (2) (360 mg, 1.83 mmol) in ethanol (30 mL). The mixture was refluxed for 20 min and cooled down to room temperature. The precipitate was collected by filtration and washed with EtOH and Et<sub>2</sub>O to yield 4c (0.69 g, 1.7 mmol, 93%) as colorless powder. <sup>1</sup>H NMR ([D<sub>6</sub>]DMSO):  $\delta$  = 12.80 (s, 1 H, H<sub>Triazole</sub>); 8.71 (s, 3 H, NH, TAG<sup>+</sup>); 4.57 (s, 6 H, NH<sub>2</sub>, TAG<sup>+</sup>). <sup>13</sup>C NMR ([D<sub>6</sub>]DMSO):  $\delta$  = 159.2 (TAG<sup>+</sup>), 157.3, 155.3, 153.0. <sup>14</sup>N NMR ([D<sub>6</sub>]DMSO):  $\delta = -17 (NO_2)$  ppm. IR:  $\tilde{v} = 1687$  (vs), 1624 (m), 1517 (s), 1464 (m), 1401 (m), 1353 (vs), 1272 (s), 1210 (m), 1179 (m), 1140 (s), 1061 (s), 1047 (s), 986 (vs), 958 (s), 857 (w), 778 (w), 763 (w), 731 (m), 716 (m), 634 (w) cm<sup>-1</sup>. **Raman** (200 mW):  $\tilde{v}$  (rel. int.) = 1587(100), 1518(55), 1466(17), 1402(10), 1359(14),

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1274(11), 1137(19), 1077(6), 1053(7), 1008(50), 859(5) cm<sup>-1</sup>. Elemental analysis (C<sub>5</sub>H<sub>19</sub>N<sub>21</sub>O<sub>2</sub>): calcd. C 14.28, H 4.72, N 72.57%; found: C 16.51, H 4.98, N 70.28%. **MS**: m/z (FAB<sup>+</sup>): 105.1 [CH<sub>9</sub>N<sub>6</sub><sup>+</sup>]; (FAB<sup>-</sup>): 196.1 [C<sub>3</sub>HN<sub>9</sub>O<sub>2</sub><sup>-</sup>]; **DSC** (onset, 5 K·min<sup>-1</sup>):  $T_{\text{Dec}}$ : 191 °C. **Sensitivities** (grain size: < 100 μm): FS: 324 N, IS: 40, ESD: 0.2 J.

Hydroxylamonium 5-(3-Nitro-1,2,4-1H-triazolate-5-yl)tetrazol-1olate (3a): Hydroxylamine (50 wt% in water, 0.3 mL, 5.0 mmol) was added to a solution of 5 (0.5 g, 2.5 mmol) in ethanol (50 mL) and stirred at 60 °C for 5 min. After cooling down to room temperature the precipitate was collected by filtration, washed with ethanol and diethyl ether, and dried in air to yield 3a as pale yellow powder. (0.54 g, 2.04 mmol, 81 %). <sup>1</sup>H NMR ([D<sub>6</sub>]DMSO):  $\delta$  = 9.76 (s, 3 H, NH<sub>3</sub>OH). <sup>13</sup>C NMR ([D<sub>6</sub>]DMSO):  $\delta$  = 165.6 (C-NO<sub>2</sub>), 150.9  $(C_{\text{triazole}})$ , 139.2  $(C_{\text{tetrazole}})$ . <sup>14</sup>N NMR ([D<sub>6</sub>]DMSO):  $\delta = -14$  (NO<sub>2</sub>) ppm. IR:  $\tilde{v} = 3204$  (w), 2953 (m), 2707 (m), 2703 (m), 1623 (w), 1540 (m), 1508 (m), 1478 (vs), 1422 (m), 1401 (m), 1352 (m), 1319 (m), 1306 (m), 1238 (m), 1220 (s), 1205 (vs), 1149 (m), 1049 (w), 1015 (m), 1000 (s), 839 (s), 758 (m), 715 (m), 715 (m), 658 (m)  $cm^{-1}$ . **Raman** (200 mW):  $\tilde{v}$  (rel. int.) = 1586(100), 1477(12), 1402(66), 1355(13), 1320(23), 1239(18), 1208(4), 1149(54), 1139(41), 1116(14), 1050(3), 1031(20), 1016(9), 845(4), 766(4), 753(8), 416(4), 378(3), 333(3), 271(3) cm<sup>-1</sup>. Elemental analysis (C<sub>3</sub>H<sub>2</sub>N<sub>8</sub>O<sub>3</sub>): calcd. C 13.64, H 3.05, N 53.02%; found C 14.79, H 3.17, N 54.79%. MS: m/z (FAB<sup>+</sup>): 34.2 [NH<sub>3</sub>OH<sup>+</sup>], *m*/*z* (FAB<sup>-</sup>): 197.1 [C<sub>3</sub>HN<sub>8</sub>O<sub>3</sub><sup>-</sup>]. Sensitivities (anhydrous, grain size  $< 100 \,\mu$ m): friction: 360 N; impact: 8 J. **DSC** (5 K·min<sup>-1</sup>):  $T_{dec.} = 175 \,^{\circ}C.$ 

Guanidinium 5-(3-Nitro-1,2,4-1H-triazolate-5-yl)tetrazol-1-olate (3b): A solution of guanidinium carbonate (0.45 g, 2.5 mmol) in water (5 mL) was added to a solution of 5 (0.5 g, 2.5 mmol) in ethanol (50 mL) and refluxed for 30 min. After cooling down to room temperature the precipitate was collected by filtration, washed with ethanol and diethyl ether, and dried in air to yield **3b** as yellow powder. (0.6 g, 1.9 mmol, 75 %). <sup>1</sup>H NMR ([D<sub>6</sub>]DMSO):  $\delta$  = 7.33 (s, 6 H, NH<sub>2</sub>, G<sup>+</sup>). <sup>13</sup>C NMR ([D<sub>6</sub>]DMSO):  $\delta = 165.9$  (C-NO<sub>2</sub>), 158.7 (C<sub>60</sub>), 151.9 ( $C_{\text{triazole}}$ ), 138.7 ( $C_{\text{tetrazole}}$ ). <sup>14</sup>N NMR ([D<sub>6</sub>]DMSO):  $\delta = -13.6$  (NO<sub>2</sub>) ppm. IR:  $\tilde{v} = 3478$  (m), 3423 (m), 3303 (m), 3116 (s), 1679 (s), 1648 (s), 1634 (s), 1580 (m), 1507 (m), 1468 (vs), 1390 (vs), 1352 (vs), 1304 (s), 1241 (s), 1213 (m), 1149 (m), 1075 (s), 993 (m), 840 (vs), 766 (s), 711 (m), 675 (s), 656 (vs), 656 (vs) cm<sup>-1</sup>. **Raman** (200 mW):  $\tilde{v}$  (rel. int.) = 1581(78), 1509(8), 1468(3), 1392(100), 1351(39), 1305(17), 1283(58), 1242(4), 1216(2), 1150(16), 1111(8), 1081(85), 1035(8), 1026(11), 1014(14), 842(9), 767(2), 755(4), 540(4), 494(2), 425(3), 318(2), 249(3), 249(3) cm<sup>-1</sup>. Elemental analysis ( $C_3H_2N_8O_3$ ): calcd. C 18.99, H 3.82, N 62.01 %; found: C 19.57, H 3.69, N 60.71 %. MS: m/z (FAB<sup>+</sup>): 60.0 [C<sub>6</sub>HN<sub>3</sub><sup>+</sup>], m/z (FAB<sup>-</sup>): 197.3 [C<sub>3</sub>HN<sub>8</sub>O<sub>3</sub><sup>-</sup>]. Sensitivities (anhydrous, grain size  $< 100 \,\mu$ m): friction: 360 N; impact: 40 J. **DSC** (5 K·min<sup>-1</sup>):  $T_{dec} = 269 \,^{\circ}\text{C}$ .

**Triaminoguanidinium 5-(3-Nitro-1,2,4–1H-triazolate-5-yl)tetrazol-1-olate (3c):** Triaminoguanidine (0.52 g, 5.0 mmol) was added to a solution of **5** (0.5 g, 2.5 mmol) in ethanol (50 mL) and the mixture was stirred at 40 °C for 30 min. After cooling down to room temperature the precipitate was collected by filtration, washed with ethanol and diethyl ether, and dried in air to yield **3c** as pale yellow powder. (0.67 g, 1.6 mmol, 66 %). <sup>1</sup>H NMR ([D<sub>6</sub>]DMSO):  $\delta$  = 8.7 (s, 3 H, NH, TAG<sup>+</sup>), 4.5 (s, 6 H, NH<sub>2</sub>, TAG<sup>+</sup>). <sup>13</sup>C NMR ([D<sub>6</sub>]DMSO):  $\delta$  = 166.3 (*C*–NO<sub>2</sub>), 159.7 (*C*<sub>TAG</sub>), 152.8 (*C*<sub>triazole</sub>), 138.9 (*C*<sub>tetrazole</sub>). <sup>14</sup>N NMR ([D<sub>6</sub>]DMSO):  $\delta$  = -17.0 (N6), -18.3 (N8), -20.2 (N5), -54.0 (N7), -57.0 (N1), -60.2 (N2), -82.4 (N4), -143.7 (N3), -289.4 (TAG<sup>+</sup>, NH), -329.8 (TAG<sup>+</sup>, NH<sub>2</sub>) ppm. **IR**:  $\tilde{v}$  = 3320 (m), 3175 (m), 1678 (s), 1662 (s), 1530 (m), 1465 (s), 1384 (s), 1343 (m), 1308 (s), 1191 (s), 1132 (s), 1100 (m), 987 (s), 956 (s), 953 (s), 907 (s), 904 (s), 877 (m), 839 (vs), 796 (m), 756 (s), 718 (m), 703 (m), 703 (m), 699 (s), 695 (s), 684 (s), 660 (s), 652 (s) cm<sup>-1</sup>. **Raman** (200 mW):  $\tilde{v}$  (rel. int.) = 3221(2), 1891(2), 1577(82), 1466(11), 1413(19), 1386(87), 1349(7), 1308(25), 1296(20), 1236(23), 1195(4), 1123(10), 1102(100), 1032(6), 1015(14), 883(3), 839(5), 759(4), 639(3), 502(2), 418(6), 370(3) cm<sup>-1</sup>. Elemental analysis (C<sub>3</sub>H<sub>2</sub>N<sub>8</sub>O<sub>3</sub>): calcd. C 14.45, H 4.47,N 68.94%; found: C 14.72, H 4.75, N 64.97%. **MS**: *m/z* (FAB<sup>+</sup>): 105.1 [CH<sub>9</sub>N3<sup>+</sup>], *m/z* (FAB<sup>-</sup>): 197.2 [C<sub>3</sub>HN<sub>8</sub>O<sub>3</sub><sup>-</sup>]. **Sensitivities** (anhydrous, grain size < 100 μm): friction: 360 N; impact: 10 J. **DSC** (5 K·min<sup>-1</sup>): *T*<sub>dec</sub>. = 181 °C.

Hydroxylamonium 5-(5-Nitramino-1H-1,2,4-triazolate-3-yl) tetrazol-1-olate (4a): Hydroxylamine (50 wt% in water, 0.3 mL, 4.6 mmol) was added to a solution of 3 (0.5 g, 2.3 mmol) in ethanol (50 mL) and the mixture was stirred at 60 °C for 5 min. After cooling down to room temperature the precipitate was collected by filtration, washed with ethanol and diethyl ether, and dried in air to yield 4a as colorless powder (yield 0.52 g, 1.9 mmol, 80%). <sup>1</sup>H NMR ([D<sub>6</sub>]DMSO):  $\delta$  = 8.42 (s, 3 H, NH<sub>3</sub>OH<sup>+</sup>). <sup>13</sup>C NMR ([D<sub>6</sub>]DMSO):  $\delta$  = 158.1 (C–NHNO<sub>2</sub>), 147.8 (C<sub>triazole</sub>), 138.6 (C<sub>tetrazole</sub>). <sup>14</sup>N NMR ([D<sub>6</sub>]DMSO):  $\delta = -10$  (NO<sub>2</sub>) ppm. **IR**:  $\tilde{v} = 3464$  (s), 3366 (s), 3179 (s), 1644 (vs), 1523 (s), 1470 (vs), 1425 (s), 1405 (m), 1375 (s), 1344 (vs), 1273 (s), 1242 (s), 1209 (s), 1101 (s), 1085 (s), 1003 (s), 988 (s), 764 (s), 724 (vs) cm<sup>-1</sup>. **Raman** (200 mW):  $\tilde{v}$  (rel. int.) = 1606(97), 1600(100), 1539(20), 1491(15), 1481(20), 1386(12), 1359(6), 1319(3), 1252(9), 1152(21), 1138(17), 1085(3), 1030(25), 1017(34), 985(7), 876(7), 763(11), 755(10), 732(3), 600(3), 442(5), 303(2), 280(4), 280(4), 253(2) cm<sup>-1</sup>. Elemental analysis (C<sub>3</sub>H<sub>2</sub>N<sub>8</sub>O<sub>3</sub>): calcd. C 12.91, H 3.25, N 55.19%; found: C 13.19, H 3.33, N 53.72%. MS: m/z (FAB<sup>+</sup>): 34.1 [NH<sub>3</sub>OH<sup>+</sup>], *m/z* (FAB<sup>-</sup>): 212.1 [C<sub>3</sub>HN<sub>9</sub>O<sub>3</sub><sup>-</sup>]. Sensitivities (anhydrous, grain size  $< 100 \,\mu$ m): friction: 288 N; impact: 8 J. **DSC** (5 K·min<sup>-1</sup>):  $T_{dec.} = 179 \,^{\circ}C.$ 

Guanidinium 5-(5-Nitramino-1H-1,2,4-triazolate-3-yl)tetrazol-1olate (4b): A solution of guanidinium carbonate (0.42 g, 2.3 mmol) in water (5 mL) was added to a solution of 3 (0.5 g, 2.3 mmol) in ethanol (50 mL) and the mixture was refluxed for 30 min. After cooling down to room temperature the precipitate was collected by filtration, washed with ethanol and diethyl ether, and dried in air to yield 4b as colorless powder. (0.66 g, 2.0 mmol, 85 %). <sup>1</sup>H NMR ([D<sub>6</sub>]DMSO):  $\delta$  = 7.23 (s, 6 H, NH<sub>2</sub>, G<sup>+</sup>). <sup>13</sup>C NMR ([D<sub>6</sub>]DMSO):  $\delta$  = 158.6 (C, G<sup>+</sup>), 157.9 (C-NHNO<sub>2</sub>), 148.8 ( $C_{\text{triazole}}$ ), 138.1 ( $C_{\text{tetrazole}}$ ). <sup>14</sup>N NMR ([D<sub>6</sub>]DMSO):  $\delta$ = -11 (NO<sub>2</sub>) ppm. **IR**:  $\tilde{v}$  = 3548 (vw), 3456 (m), 3370 (m), 3179 (m), 3116 (m), 1681 (m), 1642 (vs), 1587 (w), 1523 (m), 1468 (s), 1425 (m), 1382 (s), 1369 (s), 1345 (vs), 1259 (m), 1243 (s), 1210 (m), 1159 (m), 1100 (m), 1084 (s), 1010 (m), 987 (s), 863 (w), 863 (w), 764 (s), 746 (m), 723 (s), 677 (m) cm<sup>-1</sup>. Raman (200 mW):  $\tilde{v}$  (rel. int.) = 3217(2), 1594(100), 1524(34), 1474(21), 1425(5), 1413(4), 1406(4), 1371(19), 1349(6), 1262(3), 1247(4), 1213(5), 1161(8), 1134(7), 1087(3), 1023(52), 1011(34), 988(3), 865(5), 773(6), 748(8), 539(7), 451(5), 451(5), 442(8), 273(4), 247(3) cm<sup>-1</sup>. Elemental analysis (C3H2N8O3): calcd. C 18.13, H 3.96, N 63.43%; found: C 17.80, H 4.17, N 59.31 %. MS: /z (FAB<sup>+</sup>): 60.1 [CH<sub>6</sub>N<sub>3</sub><sup>+</sup>], m/z (FAB<sup>-</sup>): 212.1  $[C_3HN_9O_3^{-}].$  Sensitivities (anhydrous, grain size  $<100~\mu m$ ): friction: 360 N; impact: 40 J. **DSC** (5 K·min<sup>-1</sup>):  $T_{dec} = 212 \text{ °C}$ .

**Triaminoguanidinium 5-(5-Nitramino-1H-1,2,4-triazolate-3-yl)tetrazol-1-olate (4c):** Triaminoguanidine (0.49 g, 4.6 mmol) was added to a solution of **5** (0.5 g, 2.3 mmol) in ethanol (50 mL) and the mixture was stirred at 40 °C for 30 min. After cooling down to room temperature the precipitate was collected by filtration, washed with ethanol and diethyl ether, and dried in air to yield **4c** as colorless powder (yield 0.83 g, 2.0 mmol, 84%). <sup>1</sup>**H NMR** ([D<sub>6</sub>]DMSO):  $\delta$  = 8.59 (s, 3 H, N*H*, TAG<sup>+</sup>), 4.36 (s, 6 H, N*H*<sub>2</sub>, TAG<sup>+</sup>). <sup>13</sup>**C NMR** ([D<sub>6</sub>]DMSO):  $\delta$  = 159.6

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(C<sub>TAG</sub>), 158.1 (*C*–NHNO<sub>2</sub>), 148.7 (*C*<sub>triazole</sub>), 137.7 (*C*<sub>tetrazole</sub>). <sup>14</sup>N NMR ([D<sub>6</sub>]DMSO):  $\delta = -10$  (*N*O<sub>2</sub>) ppm. IR:  $\tilde{\nu} = 3320$  (m), 3207 (s), 1685 (vs), 1524 (m), 1468 (s), 1328 (vs), 1237 (m), 1198 (m), 1133 (s), 1076 (m), 980 (s), 967 (s), 856 (m), 768 (s), 728 (m) cm<sup>-1</sup>. Raman (200 mW):  $\tilde{\nu}$  (rel. int.) = 3321(6), 3236(9), 1682(5), 1592(100), 1524(46), 1469(22), 1370(13), 1236(4), 1187(3), 1140(13), 1084(2), 1009(37), 883(13), 865(9), 749(10), 638(4), 417(6), 270(6) cm<sup>-1</sup>. Elemental analysis (C<sub>3</sub>H<sub>2</sub>N<sub>8</sub>O<sub>3</sub>): calcd. C 14.25, H 4.55, N 69.81%; found: C 13.82, H 4.78, N 64.78%. MS: *m/z* (FAB<sup>+</sup>): 105.0 [CH<sub>9</sub>N<sub>6</sub><sup>+</sup>], *m/z* (FAB<sup>-</sup>): 212.1 ([C<sub>3</sub>HN<sub>9</sub>O<sub>3</sub><sup>-</sup>]). Sensitivities (anhydrous, grain size < 100 µm): friction: 288 N; impact: 10 J. DSC (5 K·min<sup>-1</sup>): *T*<sub>dec</sub>. = 186 °C.

**Supporting Information** (see footnote on the first page of this article): Heats of formation, CBS-4M calculation results. Literature values for atomic heats of formation. Molecular volumes, lattice energies and lattice enthalpies.

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