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Energetic Nitrogen-Rich Salts of 1-(2-Hydroxyethyl)-5-nitriminotetrazole

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1-(2-Hydroxyethyl)-5-nitriminotetrazole (**2**) was formed by the reaction of 5-amino-1-(2-hydroxyethyl)tetrazole (**1**) and 100 % HNO_3. Compound **1** was obtained by alkylation of 5-amino-1*H*-tetrazole with 2-chloroethanol. Nitrogen-rich salts such as the ammonium (**3**), hydroxylammonium (**4**), guanidinium (**5**), aminoguanidinium (**6**), diaminoguanidinium (**7**), triaminoguanidinium (**8**), azidoformamidinium (**9**), and diaminouronium (**10**) 1-(2-hydroxyethyl)-5-nitriminotetrazolate were prepared by deprotonation or metathesis reactions. Compounds **3**–**10** were fully characterized by single-crystal X-ray diffraction (except for **9** and **10**), vibrational spectroscopy (IR and Raman), multinuclear NMR spectroscopy, elemental analysis, and differential scanning calorimetry (DSC) measurements. The heats of formation of **4**–**10** were calculated by the atomization method based on CBS-4M enthalpies. With these values and the X-ray densities, several detonation parameters such as the detonation pressure, velocity, energy, and temperature were computed using the EXPLO5 code. In addition their sensitivities towards impact, friction, and electrical discharge were tested using a BAM drophammer, a friction tester, and a small-scale electrical discharge device.

Introduction

The design of new energetic materials[1] often involves nitrogen-rich heterocycles, such as triazoles and tetrazoles. Tetrazole derivatives have the outstanding property of often combining high nitrogen contents and a highly positive heat of formation with acceptable thermal stability and sensitivities owing to their aromatic ring systems. The thermal stability of tetrazole compounds can usually be increased by deprotonation and salt formation. Deprotonation also positively influences the sensitivity. Another way to control sensitivity and performance is the introduction of functional side chains at the nitrogen and/or carbon atoms. Great performances have been accomplished with tetrazoles comprising nitrogen and oxygen-containing functional groups, such as nitro groups ($R–NO_2$),[2] nitrate esters ($R–ONO_2$),[3] and nitramine functionalities ($R–NHNO_2$).[4] In addition, the formation of tetrazolium salts with oxygen-rich counter-anions such as NO_3^-[5,6] or $N(NO_2)_2^-$[7,8] are in the focus of research because they have balanced oxygen contents. In particular, 5-nitriminotetrazoles, which can be obtained by facile synthetic routes,[9] and 1-substituted 5-nitriminotetrazoles, such as 1-methyl-5-nitriminotetrazole and 1-ethyl-5-nitriminotetrazole, have been known for some time.[10] Moreover, various *N*-alkylations of 5-aminotetrazoles, which involve different alkylation reagents such as methyl iodide, dimethyl- and diethyl sulfate, and chloroethanol are known.[11] Here we report on different salts of 1-(2-hydroxyethyl)-5-nitriminotetrazole (**2**), which is one of the products obtained by nitration of 5-amino-1-(2-hydroxyethyl)tetrazole (**1**).[12] The hydroxy group is able to participate in hydrogen bonds and can therefore increase stability. This can be seen by comparing these compounds with their *O*-nitrated analogues, which show much lower decomposition temperatures.[13]

Results and Discussion

Synthesis

5-Amino-1-(2-hydroxyethyl)tetrazole (**1**) was synthesized from the reaction of the sodium salt of 5-amino-1*H*-tetrazole with 2-chloroethanol in aqueous solution under reflux conditions. 5-Amino-2-(2-hydroxyethyl)tetrazole can also be isolated from this reaction.[12] 1-(2-Hydroxyethyl)-5-nitriminotetrazole (**2**) is obtained by treating **1** with a stoichiometric amount of fuming nitric acid. Using an excess of nitric acid yields the *O*-nitrated species 1-(2-nitratoethyl)-5-nitriminotetrazole. Eight nitrogen-rich salts of **2** were synthesized, which are the ammonium (**3**), hydroxylammonium (**4**), guanidinium (**5**), aminoguanidinium (**6**), diaminoguanidinium (**7**), triaminoguanidinium (**8**), azidoformamidinium (**9**), and diaminouronium (**10**) salt.

The syntheses of the nitrogen-rich salts of **2** are either based on Brønsted acid–base chemistry or metathesis reactions. In the case of **3**, **4**, **8**, and **10**, the free acid **2** was deprotonated by the free bases in aqueous solution. Although diaminourea, ammonia, and hydroxylamine are available as their free bases, triaminoguanidine was prepared by the reaction of a suspension of triaminoguanidin-

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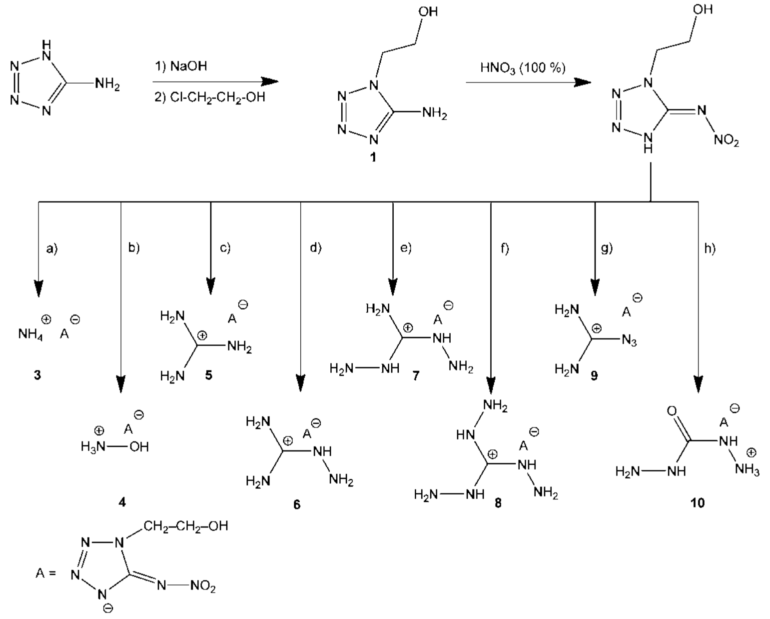

Scheme 1. Synthesis of nitrogen-rich salts of **2** under different reaction conditions: a) aqueous NH_3, 50 °C, 5 min; b) aqueous hydroxylamine (50% w/w), 50 °C, 5 min; c) guanidinium carbonate, H_2O, reflux, 5 min; d) aminoguanidinium bicarbonate, H_2O, reflux, 5 min; e) 1. $AgNO_3$, H_2O, room temp., 5 min; 2. diaminoguanidinium iodide, H_2O, 30 °C, 30 min; f) triaminoguanidine (free base), 40 °C, 5 min; g) 1. $AgNO_3$, H_2O, room temp., 5 min; 2. azidoformamidinium chloride, H_2O, 30 °C, 30 min; h) diaminourea, 50 °C, 5 min.

ium chloride with 1 equiv. of sodium hydroxide in water under N_2. Triaminoguanidine separates from the reaction mixture as a white solid upon addition of DMF and, after it was isolated in a Schlenk frit, it was kept under N_2 (Scheme 1).

The preparation of triaminoguanidine as a free base facilitated the synthesis of triaminoguanidinium salts as it eliminated the need of hydrazinolysis reactions of the corresponding aminoguanidinium salts or metathesis reactions involving silver nitrate. However, for the preparation of **7** and **9**, a metathesis reaction using silver nitrate in the first step and the corresponding nitrogen-rich halide in a second step remains indispensable as diaminoguanidine or azidoformamidine are still unknown as free bases. Salts **5** and **6** were prepared by reacting **2** with the corresponding carbonate, where carbon dioxide is expelled from the reaction mixture during a short period of heating in aqueous medium.

Molecular Structures

To determine the molecular structures of **3**–**8** in the crystalline state an Oxford Xcalibur3 diffractometer with a Spellman generator (voltage 50 kV, current 40 mA) and a KappaCCD detector was used. The data collection and reduction were performed using the CRYSALISPRO software.[14] The structures were solved with SIR-92[15] or SHELXS-97,[16] refined with SHELXL-97,[17] and finally checked using the PLATON software[18] integrated in the WINGX software suite.[19] The non-hydrogen atoms were refined anisotropically and the hydrogen atoms were located and freely refined. The absorptions were corrected by a SCALE3 ABSPACK multiscan method.[20] Selected data and parameters of the X-ray determinations are given in Tables 1 and 2.

The structure of **2**, which crystallizes in the space group $P\bar{1}$ with a density of 1.733 $g\,cm^{-3}$ has recently been determined by our group.[14]

The following ionic compounds contain the 1-(2-hydroxyethyl)-5-nitriminotetrazolate anion. Although showing different arrangements of the hydroxyethyl substituent, the bond lengths of the anion are very similar in all structures. A comparison can be found in Table 2.

Compound **3** crystallizes in the chiral monoclinic space group $P2_1$ with two molecules in the unit cell and a density of 1.617 $g\,cm^{-3}$. The molecular structure is shown in Figure 1. The structure of the anion is similar to that observed for neutral **2**. The nitriminotetrazole part is nearly planar, which can be seen by the C1–N5–N6–O1 torsion angle of –1.8(4)°. The structure of **3** is stabilized by various H-bonds involving the ammonium cation, which are shown in Figure 2.

Compound **4** crystallizes in the monoclinic space group $P2_1/n$ (Figure 3). Its density of 1.614 $g\,cm^{-3}$ is equal to that of the ammonium salt. Usually, hydroxylammonium tetrazolates show a significantly higher density (ca. 0.1 $g\,cm^{-3}$) than their ammonium homologues.[21] All *N*- and *O*-bonded hydrogen atoms participate in strong hydrogen bonds, e.g. N7–H7a···O3^{i}: 0.92(2), 1.82(2), 2.725(2) Å, 169(2)°; N7–H7b···N4^{ii}: 0.98(2), 1.95(2), 2.892(2) Å, 160(2)°; N7–H7c···O1^{iii}: 0.97(2), 2.07(2), 2.977(3) Å, 155.3(19)°; O4–H4···N3^{iv}: 0.81(2), 2.01(2), 2.818(2) Å, 170(2)°; O3–H3···O2^{v}: 0.89(3), 1.99(3), 2.848(2) Å, 162(3)°; symmetry codes: (i) x, 1 + y, z; (ii) –0.5 + x, 1.5 – y, –0.5 + z; (iii) 0.5–x, –0.5 + y, 0.5 – z; (iv) –0.5 + x, 0.5 – y, –0.5 + z; (v) x, –1 + y, z.

Table 1. X-ray data and parameters for **3**–**8**.

	3	**4**	**5**	**6**	**7**	**8**
Empirical formula	$C_3H_9N_7O_3$	$C_3H_9N_7O_4$	$C_4H_{11}N_9O_3$	$C_4H_{12}N_{10}O_3$	$C_4H_{14}N_{11}O_{3.5}$	$C_4H_{14}N_{12}O_4$
FW [g mol^{-1}]	191.17	207.17	233.22	248.24	544.52	278.27
Crystal system	monoclinic	monoclinic	monoclinic	orthorhombic	triclinic	monoclinic
Space group	$P2_1$	$P2_1/n$	$P2_1/n$	$Pbca$	$P\bar{1}$	$P2_1/n$
Color and habit	colorless needle	colorless rod	colorless rod	colorless block	colorless rod	colorless rod
Size [mm]	0.07 × 0.09 × 0.24	0.10 × 0.13 × 0.24	0.18 × 0.26 × 0.28	0.14 × 0.21 × 0.23	0.14 × 0.20 × 0.21	0.10 × 0.15 × 0.25
a [Å]	7.7187(11)	9.6947(15)	11.5414(5)	12.3825(5)	7.0028(5)	11.8798(5)
b [Å]	5.3085(6)	5.3571(8)	5.1839(3)	7.0555(4)	11.5518(8)	6.9453(4)
c [Å]	10.1444(16)	16.597(2)	16.3739(7)	23.8917(10)	14.9190(9)	14.0032(6)
α [°]	90	90	90	90	89.254(5)	90
β [°]	109.216(16)	98.427(13)	103.149(4)	90	76.494(5)	100.430(4)
γ [°]	90	90	90	90	76.641(6)	90
V [Å^3]	392.51(10)	852.7(2)	953.96(8)	2087.29(17)	1140.67(14)	1136.30(10)
Z	2	4	4	8	2	4
$\rho_{\text{calcd.}}$ [g cm^{-3}]	1.617	1.614	1.624	1.580	1.585	1.627
μ [mm^{-1}]	0.140	0.144	0.137	0.133	0.135	0.136
F(000)	200	432	488	1040	572	584
λMo-K_α [Å]	0.71073	0.71073	0.71073	0.71073	0.71073	0.71073
T [K]	173	173	173	173	173	173
θ min., max. [°]	4.3, 33.7	4.3, 26.0	4.3, 26.0	4.4, 26.0	4.2, 26.0	4.2, 26.5
Dataset	–11:11; –8:7; –8:15	–11:8; –6:6; –20:20	–14:14; –4:6; –20:19	–15:11; –8:2; –17:29	–8:8; –14:14; –18:18	–14:13; –8:8; –17:17
Reflections collected	3189	4196	3471	5344	11636	5047
Indep. reflections	1542	1672	1867	2047	4466	2342
R_{int}	0.082	0.037	0.020	0.031	0.043	0.026
Observed reflections	562	995	1285	1411	2561	1639
Parameters	154	163	189	202	446	228
R_1 (obsd.)[a]	0.0440	0.0367	0.0305	0.0340	0.0335	0.0344
wR_2 (all data)[b]	0.0466	0.0834	0.0649	0.0757	0.0571	0.0789
S[c]	0.62	0.84	0.88	0.86	0.76	0.91
Resid. density [e/Å^3]	–0.20, 0.22	–0.19, 0.27	–0.20, 0.19	–0.26, 0.19	–0.22, 0.18	–0.20, 0.30
Device type	Oxford Xcalibur3 (CCD)					
Solution	SIR-92	SIR-92	SHELXS-97	SHELXS-97	SHELXS-97	SHELXS-97
Refinement	SHELXL-97					
Absorption correction	multiscan					

[a] $R_1 = \Sigma \lVert F_o \rvert - \lvert F_c \rVert / \Sigma \lvert F_o \rvert$. [b] $wR_2 = [\Sigma[w(F_o^2 - F_c^2)^2]/\Sigma[w(F_o)^2]]^{1/2}$; $w = [\sigma_c^2(F_o^2) + (xP)^2 + yP]^{-1}$ and $P = (F_o^2 + 2F_c^2)/3$. [c] $S = [\Sigma\{w(F_o^2 - F_c^2)^2\}/(n - p)]^{1/2}$ (n = number of reflections; p = total number of parameters).

Table 2. Anion bond lengths [Å] in the structures of **3**–**8**.

	3	**4**	**5**	**6**	**7**	**8**
O1–N6	1.263(3)	1.2612(18)	1.2500(14)	1.2416(16)	1.2568(17)	1.2566(16)
O2–N6	1.263(3)	1.260(2)	1.2616(15)	1.2654(15)	1.2593(17)	1.2446(17)
N1–N2	1.354(3)	1.345(2)	1.3491(17)	1.3501(16)	1.3495(18)	1.3492(17)
N1–C1	1.340(4)	1.351(2)	1.3538(17)	1.3521(17)	1.3493(19)	1.353(2)
N1–C2	1.484(4)	1.468(2)	1.4619(17)	1.4676(19)	1.469(2)	1.466(2)
N2–N3	1.308(4)	1.297(2)	1.2944(16)	1.2908(17)	1.2970(18)	1.2942(18)
N3–N4	1.374(3)	1.366(2)	1.3710(17)	1.3638(17)	1.3736(18)	1.3599(18)
N4–C1	1.346(4)	1.336(2)	1.3269(17)	1.3234(19)	1.330(2)	1.3374(19)
N5–N6	1.315(4)	1.308(2)	1.3185(16)	1.3232(16)	1.3171(18)	1.3268(19)
N5–C1	1.380(4)	1.365(2)	1.3739(18)	1.3760(18)	1.374(2)	1.3637(18)
C2–C3	1.516(5)	1.506(3)	1.516(2)	1.510(2)	1.510(3)	1.523(3)
O3–C3	1.433(4)	1.396(3)	1.4216(19)	1.427(2)	1.417(2)	1.414(2)

All guanidinium derivatives investigated in this work crystallize in common space groups (**5**, **8**: monoclinic $P2_1/n$, **6**: orthorhombic $Pbca$, **7**: triclinic $P\bar{1}$). Interestingly, **5** (1.624 g cm^{-3}) and **8** (1.618 g cm^{-3}) have slightly higher densities compared to **6** (1.580 g cm^{-3}) and **7** (1.585 g cm^{-3}). All of the cations show structures that are in agreement with those found in the corresponding guanidinium series of 2-methyl-5-nitriminotetrazolates.[22] The molecular structure of **5** is shown in Figure 4. The nitro group is slightly twisted out of the tetrazole ring plane [angle N4–C1–N6–O1: 4.4(2)°]. The structure of **5** is dominated by a strong hydrogen bonded network involving all guanidinium protons as well the hydroxyl hydrogen atom.

The molecular structure of **6** is shown in Figure 5. The packing of **6** can be described as a wavelike layer structure along the ac plane. A view of the layers, illustrating the intense hydrogen bond network is shown in Figure 6.

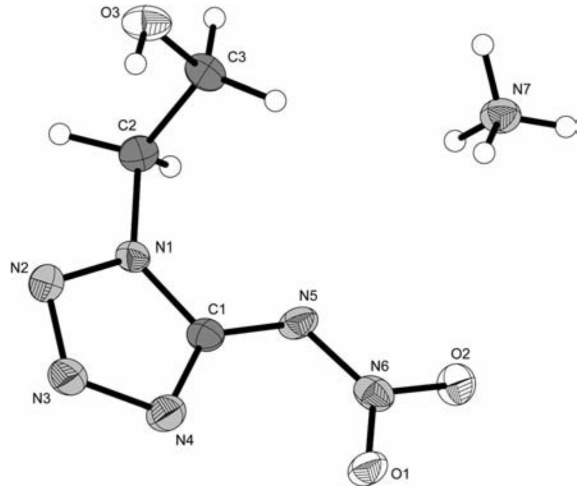

Figure 1. Molecular structure of **3**. Hydrogen atoms shown as spheres of arbitrary radius and ellipsoids are drawn at 50% probability.

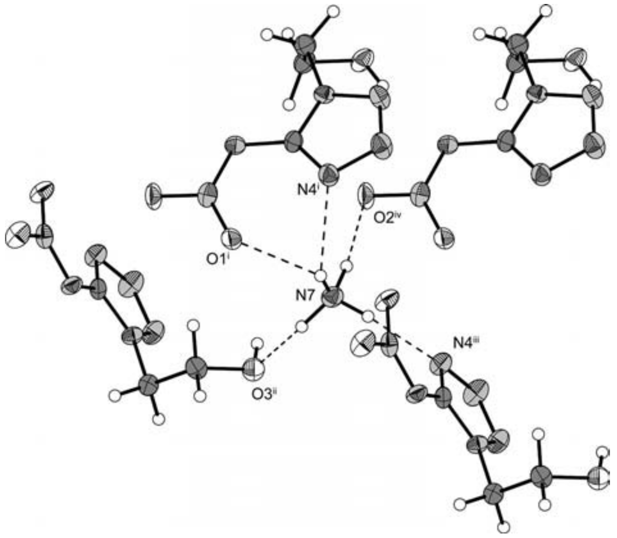

Figure 2. Hydrogen bonding of one ammonium cation in the structure of **3**. Hydrogen bond lengths [Å] and angles: N7–H7a···O1$^{\text{i}}$ 0.83(4), 2.30(4), 2.959(4), 136(4)°; N7–H7C···N4$^{\text{i}}$ 0.83(4), 2.52(4), 3.227(5), 144(4)°; N7–H7b···O3$^{\text{ii}}$ 1.05(4), 1.85(4), 2.874(4), 164(3); N7–H7d···N4$^{\text{iii}}$ 0.95(4), 2.08(4), 3.018(4), 172(4); N7–H7a···O2$^{\text{iv}}$ 1.00(4), 1.96(4), 2.954(4), 169(3); symmetry codes: (i) 1 – *x*, –0.5 + *y*, 1 – *z*; (ii) *x*, –1 + *y*, *z*; (iii) 1 + *x*, *y*, *z*; (iv) 1 – *x*, 0.5 + *y*, 1 – *z*.

Crystalline **7** could only be obtained as its hemihydrate. The molecular structure is depicted in Figure 7.

In contrast to the structure of related triaminoguanidinium 1-(2-nitratoethyl)-5-nitriminotetrazolate,[13] crystals of which were obtained as its monohydrate, **8** solidified without inclusion of crystal water. The molecular structure of **8** is shown in Figure 8.

The packing of **8** is built by alternating columns along the *c* axis, which is shown in Figure 9. A strong hydrogen bond network can be found within the columns. Alternating moieties consisting of two hydrazinium cations as well as dimeric tetrazolate units are connected by strong classical N–H···N and N–H···O hydrogen bonds.

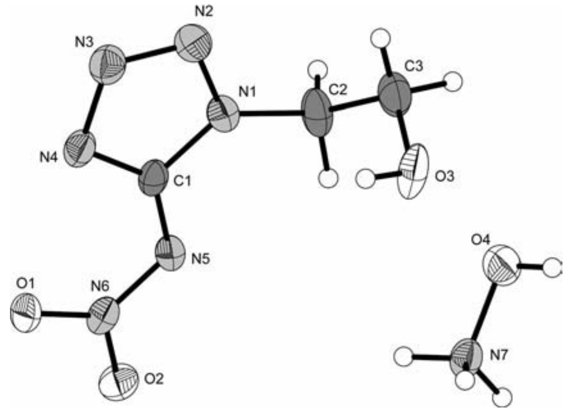

Figure 3. Molecular structure of **4**. Hydrogen atoms shown as spheres of arbitrary radius and thermal displacements set at 50% probability.

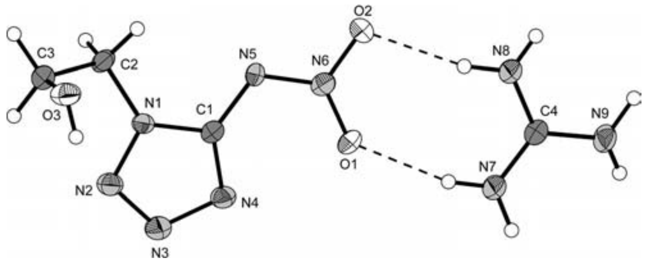

Figure 4. Molecular structure of **5**. Hydrogen atoms shown as spheres of arbitrary radius and thermal displacements set at 50% probability.

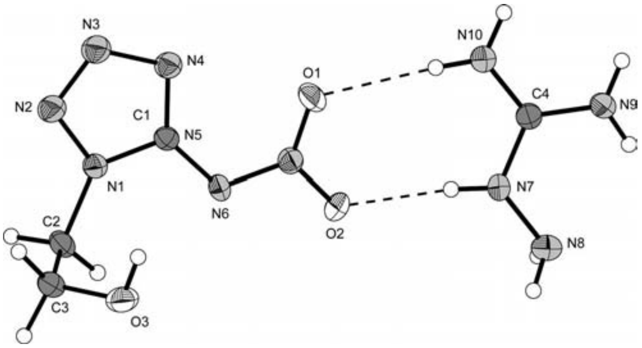

Figure 5. Molecular structure of **6**. Hydrogen atoms shown as spheres of arbitrary radius and thermal displacements set at 50% probability.

NMR Spectroscopy

Compounds **3**–**10** were investigated by ^{1}H and ^{13}C NMR spectroscopy. Tetramethylsilane (^{1}H, ^{13}C) was used as standard. The spectra were recorded in [D$_6$]DMSO (for **3**–**7**, **9**, **10**) and D$_2$O (for **8**).

The tetrazole carbon atom signals are located in a range from 156.2–157.6 ppm, which is about 7 ppm downfield shifted compared to **2** and can be traced back to the deprotonation of the tetrazole ring system. In contrast, deproton-

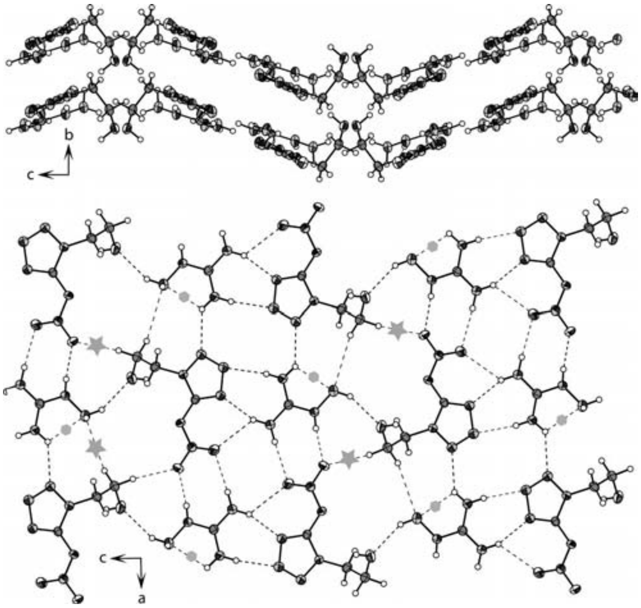

Figure 6. Hydrogen bond network stabilizing the wavelike layer structure of **6**. Nonclassical C–H···O hydrogen bonds are marked with an asterisk, intramolecular hydrogen bonds with a hexagon.

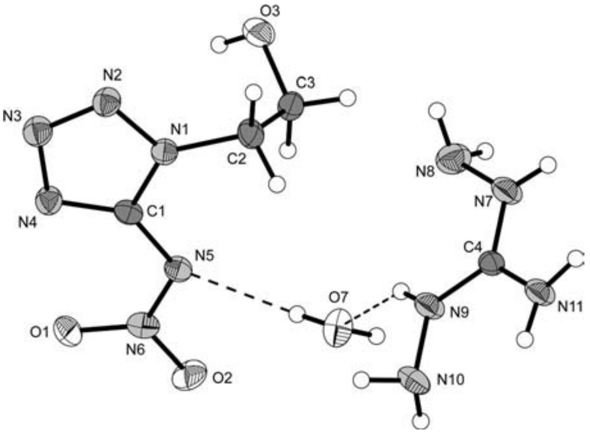

Figure 7. Molecular structure of **7**. Hydrogen atoms shown as spheres of arbitrary radius and thermal displacements set at 50% probability.

ation of the ring system does have a particular impact on the chemical shifts of the carbon atom signals of the aliphatic side chain. The signals are found at 58.1–59.2 ppm and 48.3–50.4 ppm, respectively, however, a final assignment to the hydroxyl- and tetrazole ring-connected methylene moiety remains unclear. The values are very close to those found for **2** (58.1 and 50.4 ppm). Looking at the proton chemical shifts of the anion, there is an indication for the final assignment of the signals, which is the signal of the guanidinium salt at 3.67 ppm; it can be identified as a doublet of triplets due to ^3J coupling between the methylene protons and the neighboring hydroxy group. Therefore, the signals located at chemical shifts of 4.03–4.25 ppm can be assigned to the tetrazole-connected methylene unit, whereas the signals shifted to 3.65–3.85 ppm arise from the hydroxyl-connected methylene unit. Again, the shifts are not strongly affected by the deprotonation of the tetrazole ring, which can be stated after comparison to the values for **2** (4.22 and 3.77 ppm). The carbon and proton chemical shifts of the cations are very similar to those found in literature for nitrogen-rich salts of other nitriminotetrazolate compounds.[13,22]

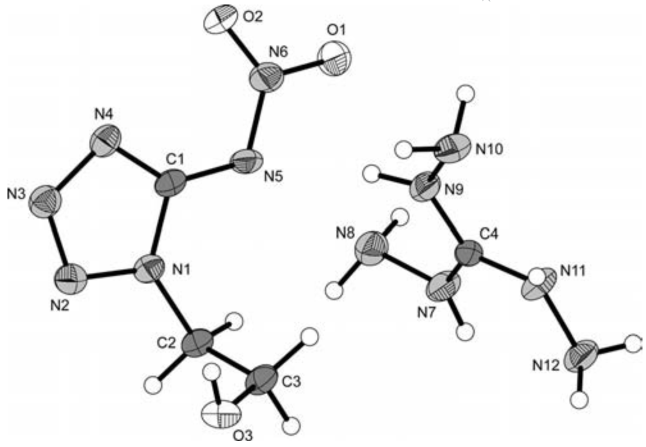

Figure 8. Molecular structure of **8**. Hydrogen atoms shown as spheres of arbitrary radius and thermal displacements set at 50% probability.

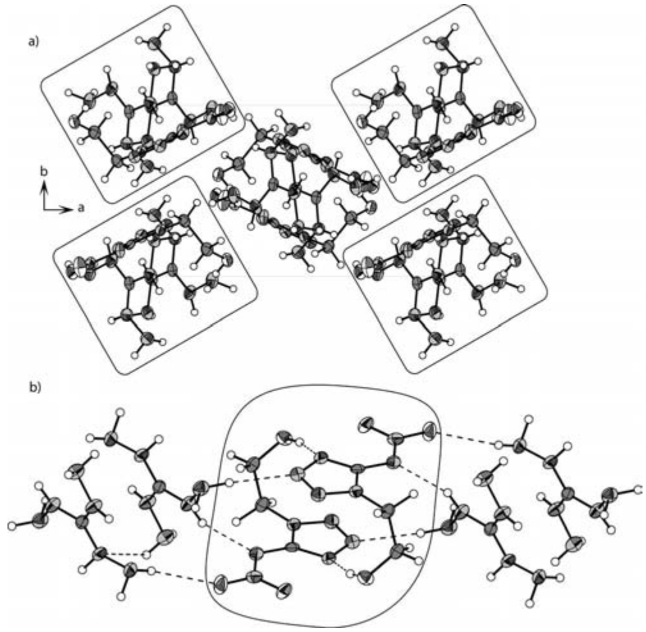

Figure 9. Packing of crystalline **8**. a) View along the columns parallel to the *c* axis; b) hydrogen bonds and dimer formation (marked) within the columns.

Sensitivities and Thermal Stability

Impact sensitivity tests were carried out according to STANAG 4489[23] modified instruction[24] using a BAM (German Bundesanstalt für Materialforschung) drophammer.[25] The friction sensitivity tests were carried out

Table 3. Energetic properties and detonation parameters of **2**–**10**.

	2	**3**	**4**	**5**	**6**	**7**	**8**	**9**	**10**
Formula	$C_3H_6N_6O_3$	$C_3H_9N_7O_3$	$C_3H_9N_7O_4$	$C_4H_{11}N_9O_3$	$C_4H_{12}N_{10}O_3$	$C_4H_{14}N_{11}O_{3.5}$	$C_4H_{14}N_{12}O_4$	$C_4H_9N_{11}O_3$	$C_4H_{12}N_{10}O_4$
FW [g mol^{-1}]	174.14	191.17	207.17	233.22	248.24	272.12	278.27	259.09	264.10
IS [J][a]	6	10	15	>40	10	>40	18	9	40
FS [N][b]	55	144	160	240	192	144	>360	120	288
ESD test [J][c]	–	0.15	0.50	0.25	0.15	0.20	0.80	0.15	0.60
N [%][d]	48.27	51.29	47.33	54.06	56.43	56.60	60.41	59.45	53.01
Ω [%][e]	–55.13	–62.77	–50.20	–72.04	–70.90	–67.58	–69.00	–58.64	–60.55
$T_{dec.}$ [°C][f]	138	205	178	225	225	208	215	154	191
Density [g cm^{-3}][g]	1.73	1.617	1.614	1.624	1.580	1.585	1.627	1.6 (est.)	1.6 (est.)
$\Delta_f H_m°$ [kJ mol^{-1}][h]	110	85	148	47	158	148	370	470	133
$\Delta_f U°$[kJ kg^{-1}][i]	739	569	831	322	759	675	1460	1924	626
	Detonation parameters calculated by *EXPLO5.04*								
$-\Delta_E U°$ [kJ kg^{-1}][j]	4827	4541	5497	3699	3984	3319	4428	4839	4459
T_E [K][k]	3314	2989	3542	2601	2714	2558	2869	3357	2986
p_{C-J} [kbar][l]	275	246	268	223	222	202	260	240	238
D [m s^{-1}][m]	8270	8074	8298	7775	7805	7488	8304	7989	7974
Gas vol. [L kg^{-1}][n]	768	823	828	803	816	812	836	780	822

[a] Impact sensitivity (BAM drophammer,[25] 1 of 6). [b] Friction sensitivity (BAM friction tester,[25] 1 of 6). [c] Electrostatic discharge device (OZM).[29] [d] Nitrogen content. [e] Oxygen balance. [f] Decomposition temperature from DSC (β = 5 °C). [g] From X-ray diffraction. [h] Calculated (CBS-4M) heat of formation. [i] Energy of formation. [j] Energy of explosion. [k] Explosion temperature. [l] Detonation pressure. [m] Detonation velocity. [n] Assuming only gaseous products.

according to STANAG 4487[26] modified instructions[27] using a BAM friction tester. The classification of the tested compounds results from the "UN Recommendations on the Transport of Dangerous Goods".[28] Additionally all compounds were tested for sensitivity towards electrical discharge using an Electric Spark Tester ESD 2010 EN.[29] DSC measurements to determine the melt and decomposition temperatures of **2**–**10** (on about 1.5 mg of each energetic material) were performed in covered Al-containers containing a hole in the lid and a nitrogen flow of 20 mL per minute with a Linseis PT 10 DSC[30] calibrated with standard pure indium and zinc at a heating rate of 5 °C min^{-1}.

Compared to their 1-(2-nitratoethyl)-substituted sister compounds,[13] the nitrogen-rich salts of 1-(2-hydroxyethyl)-substituted nitriminotetrazole show excellent thermal stabilities: their decomposition points are above 200 °C with only a few exceptions [**4** (178 °C), **9**, and **10**]. It is a known feature of azidoformamidinium salts that, based on the azido moiety, these compounds decompose at lower temperatures than other nitrogen-rich salts.[22] Due to the hydroxyethyl substituent, which is located in the 1-position at the tetrazole ring, the thermal stability is increased with respect to unsubstituted nitriminotetrazolates. Not only the thermal stability, but also the sensitivities of the compounds are influenced in a positive manner by hydroxyethyl substitution of the aromatic ring system. Most sensitive, as expected, is **9** with an impact sensitivity of 9 J and a friction sensitivity of 120 N, which is still in the range of commonly used secondary explosives such as RDX (7.5 J, 120 N). The best performing salts, **4** and **8**, show sensitivities that are far below the values found for RDX (**4**: 15 J, 160 N; **8**: 18 J, >360 N). The sensitivities of the remaining compounds are spread over a range between the discussed compounds and range from insensitive towards impact (>40 J for **5** and **7**) to sensitive towards impact (10 J for **3** and **6**). The insensitivity of **7** towards impact can be explained by the crystal water included in the structure. The same reasons mentioned for the impact sensitivities apply to the friction sensitivities (144 N for **3** and **7** to 288 N for **10**). Apart from **8**, all compounds are classified as sensitive towards friction. A trend, which has been observed for other nitrogen-rich ionic compounds,[22] is the relative insensitivity of **5** (>40 J, 240N). All values for impact and friction sensitivity as well as the sensitivities towards electrical discharge and the decomposition temperatures are summarized in Table 3.

Heat of Formation

Heats of formation were computed theoretically. All calculations were carried out using the Gaussian G09 program package.[31] The enthalpies (*H*) and free energies (*G*) were calculated using the complete basis set (CBS) method of Petersson and coworkers in order to obtain very accurate energies. The CBS models use the known asymptotic convergence of pair natural orbital expressions to extrapolate using a finite basis set to the estimated complete basis set limit. CBS-4 begins with a HF/3-21G(d) geometry optimization; the zero point energy is computed at the same level. It then uses a large basis set SCF calculation as a base energy, and a MP2/6-31+G calculation with a CBS extrapolation to correct the energy through second order. A MP4(SDQ)/6-31+(d,p) calculation was used to approximate higher order contributions. In this study we applied the modified CBS-4M method (M referring to the use of minimal population localization), which is a reparametrized version of the original CBS-4 method and includes some additional empirical corrections.[32] The enthalpies of the gas phase species M (Table 4) were computed according to the atomization energy method [Equation (1)][33] described in the literature.[34]

$$\Delta_f H^\circ_{(g,M,298)} = H_{(\text{molecule},298)} - \Sigma H^\circ_{(\text{atoms},298)} + \Sigma \Delta_f H^\circ_{(\text{atoms},298)} \quad (1)$$

Table 4. CBS-4M calculation results and molecular volumes taken from X-ray structures.

M	$-H^{298}$/a.u.	$\Delta_f H^\circ$(g,M)/kcal mol^{-1}	V_M/nm^3
2	671.089203	41.5	
2 anion	670.586386	–9.5	174.0
NH_4^+	56.796608	151.9	
NH_4O^+	131.863249	177.9	
G^+	205.453192	136.6	
AG^+	260.701802	160.4	
DAG^+	315.949896	184.5	
TAG^+	371.197775	208.8	
AF^+	313.533549	234.9	88.5[a]
DAU^+	335.795706	155.6	78.7[b]
3		142.4	196.3
4		168.4	213.2
5		127.1	238.5
6		150.9	260.9
7 (H_2O)[a]		146.2	285.0
8		199.3	284.1
9		225.4	162.5
10		146.1	252.6

[a] Recalculated from the X-ray structure of azidoformamidinium nitrate. [b] Recalculated from the X-ray structure of diaminouronium nitrate.

Using calculated heats of sublimation for **2** by Trouton's Rule[35] and lattice enthalpies for the ionic compounds, the gas phase enthalpies of formation (Table 4) were converted into the solid state (standard conditions) enthalpy of formation $\Delta_f H_m^\circ$ (Table 3). Lattice energies (U_L) and lattice enthalpies (ΔH_L) were calculated from the corresponding molecular volumes according to Jenkin's equations.[36]

Lastly, the molar standard enthalpies of formation (ΔH_m) were used to calculate the molar solid state energies of formation (ΔU_m) according to Equation (2) (Table 4).

$$\Delta U_m = \Delta H_m - \Delta n\ RT \quad (2)$$

where Δn is the change of mol of gaseous components.

The compound with the highest heat of formation is **9** (470 kJ mol^{-1}) followed by **8** (370 kJ mol^{-1}). The decrease in enthalpy due to water inclusion can be clearly seen by the low value of **7** (148 kJ mol^{-1}). Except for **3** (85 kJ mol^{-1}) and **5** (47 kJ mol^{-1}), all deprotonated nitrogen-rich salts formed are more endothermic than **2** (110 kJ mol^{-1}).

Detonation Parameters

The detonation parameters were calculated using the program EXPLO5 V5.04.[37] The program is based on the steady-state model of equilibrium detonation and uses Becker–Kistiakowsky–Wilson's equation of state (BKW E.O.S) for gaseous detonation products and Cowan–Fickett E.O.S. for solid carbon. The calculation of the equilibrium composition of the detonation products is performed by applying modified White, Johnson, and Dantzig's free energy minimization technique. The program is designed to enable the calculation of detonation parameters at the CJ point. The BKW equation in the following form was used with the BKWN set of parameters (α, β, κ, θ) where X_i is the mol fraction of the i^{th} gaseous product and k_i is the molar covolume of the i^{th} gaseous product:

$$pV/RT = 1 + xe^{\beta x}$$

$$x = (\kappa \Sigma X_i k_i)/[V(T + \theta)]^\alpha$$

$$\alpha = 0.5,\ \beta = 0.96,\ \kappa = 17.56,\ \theta = 4950$$

The calculations were performed using the maximum densities according to the crystal structures. The calculated detonation parameters of **9** and **10** are based on estimated densities of 1.60 g cm^{-3}. For comparison, several commonly used explosives were also calculated with the EXPLO5.04 code. The most important criteria of high explosives are the detonation velocity $V_{Det.}$ (TNT: 7253, HNS: 7436, PETN: 8320, RDX: 8747 m s^{-1}), the detonation pressure p_{CJ} (TNT: 216, HNS: 242, PETN: 320, RDX: 348 kbar) and the energy of explosion $\Delta_E U_m^\circ$ (TNT: –5227, HNS: –5476, PETN: –6190, RDX: –6125 kJ kg^{-1}). In terms of detonation velocity, **3**–**10** hardly reached the level of commonly used secondary explosives such as RDX. Most of the compounds reached calculated detonation velocities of 7700 to 8300 m s^{-1} and are therefore comparable to HNS, a thermally stable polynitrobenzene, and PETN, an aliphatic polynitrate ester, with **8** and **4** being the best performing compounds. A reason for the comparably low detonation velocities and detonation pressures is the highly negative oxygen balance of –50% to –72% arising from the ethyl side chain attached to the tetrazole ring. On the other hand, the tetrazole derivatives are thermally stabilized by the side chain and also show lower sensitivities against impact and friction compared to unsubstituted nitriminotetrazolates.

Conclusions

Several nitrogen-rich salts of 1-(2-hydroxyethyl)-5-nitriminotetrazole (**2**) were synthesized by deprotonation of the free acid **2** or metathesis reactions involving the silver salt of **2** and the corresponding nitrogen rich halides.

The salts **3**–**8** were characterized by single-crystal X-ray diffraction. They crystallize in the mono- and triclinic space groups $P2_1$ (**3**), $P2_1/n$ (**4**, **5**, **8**), $Pbca$ (**6**), and $P\bar{1}$ (**7**) with densities between 1.580 and 1.627 g cm^{-3}.

Compared to other nitrogen-rich nitriminotetrazolates, the compounds investigated show excellent thermal stabilities up to 225 °C. The impact and friction sensitivities of the nitrogen-rich salts were determined. They are classified as insensitive (**5**, **7**) or sensitive (**3**, **4**, **6**, **8**, **9**, **10**) towards impact and insensitive (**8**) or sensitive (**3**–**7**, **9**, **10**) towards friction.

Based on the crystal densities and CBS-4M enthalpies, several detonation parameters were calculated. Salts **4** and **8** show the highest values regarding the detonation velocity (**4**: 8298 m s^{-1}, **8**: 8304 m s^{-1}) and the detonation pressure (**4**: 268 kbar, **8**: 260 kbar). They are able to compete with commonly used TNT, however, the performance data for RDX are not reached.

Experimental Section

General: All reagents and solvents were used as received (Sigma–Aldrich, Fluka, Acros Organics) if not stated otherwise. Melting and decomposition points were measured with a Linseis PT10 DSC using a heating rate of 5 °C min^{-1}, which were checked with a Büchi melting point B-450 apparatus. ^{1}H, ^{13}C, and ^{15}N NMR spectra were measured with a JEOL instrument. All chemical shifts are quoted in ppm relative to TMS (^{1}H, ^{13}C) or nitromethane (^{14}N, ^{15}N). IR spectra were measured with a Perkin–Elmer Spektrum One FTIR instrument. Raman spectra were measured with a Perkin-Elmer Spektrum 2000R NIR FT-Raman instrument equipped with a Nd:YAG laser (1064 nm). Elemental analyses were performed with a Netsch STA 429 simultaneous thermal analyzer. Sensitivity data were determined using a BAM drophammer and a BAM friction tester. The electrostatic sensitivity tests were carried out using an Electric Spark Tester ESD 2010 EN (OZM Research) operating with the "Winspark 1.15" software package.

CAUTION! *1-(2-Hydroxyethyl)-5-nitriminotetrazole* (**2**) *and its salts* **3**–**10** *are all energetic compounds with sensitivity to various stimuli. Although we encountered no issues in the handling of these materials, proper protective measures (face shield, ear protection, body armor, Kevlar gloves, and earthed equipment) should be used at all times.*

1-(2-Hydroxyethyl)-5-nitriminotetrazole (2): 5-Amino-1-(2-hydroxyethyl)tetrazole (4.84 g, 37.5 mmol) was added in small portions to fuming nitric acid (7 mL, 10.5 g, 168 mmol) over 60 min at 0–5 °C in an ice bath. The mixture was stirred for 2 h at 0 °C and overnight at room temp. The mixture was poured into 100 g of ice with stirring and a white solid emerged. After stirring until the ice melted, the mixture was evaporated to dryness under reduced pressure. The product was recrystallized from ethanol/water to yield 6.20 g (35.6 mmol, 95%) of **2**. ^{1}H NMR ([D$_6$]DMSO, 25 °C): δ = 4.85 (s, 1 H, OH), 4.22 (t, 2 H, CH_2OH), 3.77 (t, 2 H, NCH_2) ppm. ^{13}C NMR ([D$_6$]DMSO, 25 °C): δ = 150.9 (CN$_4$), 58.1 (CH$_2$–N), 50.4 (CH$_2$–OH) ppm.

Ammonium 1-(2-Hydroxyethyl)-5-nitriminotetrazolate (3): NH$_3$ (5 mL, 2 M) was added to a solution of 1-(2-hydroxyethyl)-5-nitriminotetrazole (1.74 g, 10 mmol) dissolved in water (10 mL). The clear solution was warmed to 50 °C for 5 min and concentrated with a rotary evaporator. The product was recrystallized from an ethanol/water mixture; yield 82% (1.56 g, 8.17 mmol). DSC (5 °C min^{-1}): 180 °C (m.p.), 205 °C (dec.1), 214 (dec.2). IR (KBr): $\tilde{\nu}$ = 3548 (m), 3476 (s), 3413 (vs), 3236 (m), 1637 (w), 1617 (w), 1507 (m), 1454 (m), 1396 (m), 1384 (m), 1336 (s), 1320 (s), 1255 (w), 1105 (w), 1067 (w), 1045 (w), 889 (w), 862 (w), 775 (w), 740 (w), 622 (w), 480 (w) cm^{-1}. Raman (1064 nm, 500 mW, 25 °C): $\tilde{\nu}$ = 3013 (15), 2993 (32), 2970 (26), 2937 (4), 2893 (7), 1506 (100), 1330 (14), 1256 (7), 1156 (4), 1107 (5), 1049 (3), 1034 (49), 985 (6), 891 (4), 864 (3), 757 (6), 661 (7) cm^{-1}. ^{1}H NMR ([D$_6$]DMSO, 25 °C): δ = 7.12 (t, 4 H, NH$_4^+$), 4.91 (s, 1 H, OH), 4.03 (t, 2 H, N–CH$_2$), 3.66 (t, 2 H, CH$_2$–OH) ppm. ^{13}C NMR ([D$_6$]DMSO, 25 °C): δ = 156.9 (CN$_4$), 58.5 (NCH$_2$), 48.3 (CH$_2$OH) ppm. MS (FAB$^+$): m/z = 18.1 [NH$_4^+$]; MS (FAB$^-$): m/z = 173.0 [C$_3$H$_5$N$_6$O$_3^-$]. C$_3$H$_9$N$_7$O$_3$ (191.15): calcd. C 18.85, H 4.75, N 51.29; found C 18.78, H 4.76, N 51.29. Impact sensitivity: 10 J. Friction sensitivity: 144 N. ESD: 0.15 J.

Hydroxylammonium 1-(2-Hydroxyethyl)-5-nitriminotetrazolate (4): 1-(2-Hydroxyethyl)-5-nitriminotetrazole (1.74 g, 10 mmol) was dissolved in hot water (20 mL). An aqueous solution of hydroxylamine (50% w/w, 0.66 g, 10 mmol) was added, the mixture heated to 50 °C for 5 min, and the solvent from the resulting clear solution evaporated in vacuo. A colorless solid formed, which was recrystallized from ethanol to yield **4** as colorless crystals (1.92 g, 9.3 mmol, 93%). DSC [5 °C min^{-1} (°)C]: 133 °C (m.p.), 178 °C (dec. 1), 192 °C (dec. 2). IR (KBr): $\tilde{\nu}$ = 3374 (m), 3135 (m), 3073 (m), 2960 (m), 2933 (m), 2729 (m), 1628 (w), 1546 (m), 1505 (s), 1457 (m), 1431 (m), 1332 (vs), 1265 (m), 1246 (m), 1228 (m), 1163 (w), 1122 (w), 1076 (m), 1037 (m), 1000 (w), 957 (w), 884 (w), 872 (w), 772 (w), 755 (w), 739 (w), 661 (w), 547 (w), 523 (w), 482 (w) cm^{-1}. Raman (1064 nm, 300 mW, 25 °C): $\tilde{\nu}$ = 3014 (2), 2969 (9), 2934 (2), 1507 (100), 1392 (3), 1310 (9), 1231 (2), 1125 (11), 1063 (6), 1039 (32), 1002 (9), 886 (2), 872 (4), 758 (7), 661 (3), 283 (2) cm^{-1}. ^{1}H NMR ([D$_6$]DMSO, 25 °C): δ = 10.09 (s, 4 H, NH$_3$OH$^+$), 4.92 (s, 1 H, OH), 4.08 (t, 2 H, CH_2OH), 3.70 (t, 2 H, NCH_2) ppm. ^{13}C NMR ([D$_6$]DMSO, 25 °C): δ = 157.4 (CN$_4$), 59.1 (NCH$_2$), 48.8 (CH$_2$OH) ppm. MS (FAB$^+$): m/z = 34.0 [NH$_3$OH$^+$]. MS (FAB$^-$): m/z = 172.9 [C$_3$H$_5$N$_6$O$_3^-$]. C$_3$H$_9$N$_7$O$_4$ (207.15): calcd. C 17.39, H 4.38, N 47.33; found C 17.85, H 4.26, N 46.74. BAM drophammer: 15 J. Friction tester: 160 N. ESD: 0.50 J.

Guanidinium 1-(2-Hydroxyethyl)-5-nitriminotetrazolate (5): 1-(2-Hydroxyethyl)-5-nitriminotetrazole (1.74 g, 10 mmol) was dissolved in water (10 mL) in a 50 mL flask. Guanidinium carbonate (0.90 g, 5 mmol) was added and the mixture was heated to reflux for 5 min. The resulting clear solution was concentrated in a rotary evaporator. The product was recrystallized from ethanol/water in 79% yield (1.84 g, 7.92 mmol). DSC (5 °C min^{-1}): 162 °C (m.p.), 223 °C (dec.). IR (KBr): $\tilde{\nu}$ = 3910 (w), 3426 (vs), 3203 (s), 2947 (m), 2885 (m), 2814 (m), 2388 (w), 2217 (w), 1971 (w), 1934 (w), 1662 (vs), 1572 (m), 1544 (w), 1499 (vs), 1458 (s), 1442 (s), 1434 (s), 1380 (s), 1331 (vs), 1307 (vs), 1269 (s), 1248 (s), 1230 (m), 1157 (m), 1108 (s), 1068 (s), 1039 (s), 989 (m), 949 (w), 892 (m), 867 (m), 770 (w), 736 (w), 603 (m), 547 (m), 537 (w), 516 (w), 487 (w), 469 (w) cm^{-1}. Raman (1064 nm, 500 mW, 25 °C): $\tilde{\nu}$ = 3001 (3), 2954 (19), 1501 (100), 1396 (7), 1310 (13), 1111 (5), 1058 (6), 1041 (37), 1010 (15), 868 (3), 757 (3), 435 (1) cm^{-1}. ^{1}H NMR ([D$_6$]DMSO, 25 °C): δ = 6.92 [s, 6 H, C(NH_2)$_3$], 4.91 (s, 1 H, OH), 4.05 (t, 2 H, N–CH_2), 3.67 (dt, 2 H, CH_2–OH) ppm. ^{13}C NMR ([D$_6$]DMSO, 25 °C): δ = 157.9 [C(NH$_2$)$_3$], 156.9 (CN$_4$), 58.6 (NCH$_2$), 48.4 (CH$_2$OH) ppm. MS (FAB$^+$): m/z = 60.1 [CH$_6$N$_3^+$]. MS (FAB$^-$): m/z = 173.0 [C$_3$H$_5$N$_6$O$_3^-$]. C$_4$H$_{11}$N$_9$O$_3$ (233.19): calcd. C 20.60, H 4.75, N 54.06; found C 20.59, H 4.88, N 54.04. Impact sensitivity: > 40 J. Friction sensitivity: 240 N. ESD: 0.25 J.

Aminoguanidinium 1-(2-Hydroxyethyl)-5-nitriminotetrazolate (6): 1-(2-Hydroxyethyl)-5-nitriminotetrazole (1.74 g, 10 mmol) was dissolved in water (10 mL) in a 50 mL flask. Aminoguanidinium hydrogencarbonate (1.36 g, 10 mmol) was added to the solution and the mixture was heated to reflux for 5 min. The resulting clear solution was concentrated with a rotary evaporator. The product was recrystallized from an ethanol/water mixture in 81% yield (2.00 g, 8.07 mmol). DSC (5 °C min^{-1}): 135 °C (m.p.), 225 °C (dec.). IR (KBr): $\tilde{\nu}$ = 3425 (vs), 3387 (vs), 3337 (vs), 3309 (vs), 3188 (s), 3021 (m), 2953 (m), 2901 (m), 2343 (w), 1996 (w), 1688 (vs), 1658 (s), 1596 (w), 1513 (vs), 1471 (m), 1455 (s), 1438 (m), 1423 (m), 1383 (s), 1340 (vs), 1306 (vs), 1270 (s), 1149 (m), 1110 (m), 1060 (m), 1052 (m), 1038 (m), 976 (w), 954 (w), 888 (w), 863 (w), 772 (w), 751 (w), 733 (w), 701 (w), 666 (w), 624 (w), 558 (m), 534 (m), 508 (w), 485 (w) cm^{-1}. Raman (1064 nm, 500 mW, 25 °C): $\tilde{\nu}$ = 3339 (3), 3247 (6), 3006 (5), 2982 (20), 2954 (16), 2903 (4), 1507 (100), 1386 (3), 1326 (35), 1113 (9), 1053 (4), 1038 (58), 976 (7), 891 (5), 863 (4), 753 (10), 669 (5), 506 (7), 443 (3) cm^{-1}. ^{1}H NMR ([D$_6$]DMSO, 25 °C): δ = 8.54 (s, 1 H, C–NH–NH$_2$), 7.23 [s, 2 H, (NH_AH$_B$)$_2$], 6.70 [s, 2 H, (NH$_A$$H_B$)$_2$], 4.89 (s, 1 H, O$H$), 4.66 (s, 2 H, NH–N$H_2$), 4.04 (t, 2 H, NC$H_2$), 3.65 (t, 2 H, C$H_2$OH) ppm. ^{13}C NMR ([D$_6$]-DMSO, 25 °C): δ = 158.7 [C(NH$_2$)$_2$(NHNH$_2$)], 157.0 (CN$_4$), 58.5

(N*C*H$_2$), 48.3 (*C*H$_2$OH) ppm. MS (FAB$^+$): *m*/*z* = 75 [$CH_7N_4^+$]. MS (FAB$^-$): *m*/*z* = 173.0 [$C_3H_5N_6O_3^-$]. $C_4H_{12}N_{10}O_3$ (248.22): calcd. C 19.36, H 4.87, N 56.43; found C 19.30, H 4.89, N 56.55. Impact sensitivity: 10 J. Friction sensitivity: 192 N. ESD: 0.15 J.

Diaminoguanidinium 1-(2-Hydroxyethyl)-5-nitriminotetrazolate (7): 1-(2-Hydroxyethyl)-5-nitriminotetrazole (2.62 g, 15 mmol) was dissolved in warm water (approx. 20 mL). The clear solution was mixed with a solution of $AgNO_3$ (2.55 g, 15 mmol) in water (approx. 10 mL). The resulting mixture was stirred for 5 min at room temp. in the darkness. The white precipitate was separated by centrifugation, washed twice with water until free of acid, and resuspended in water (approx. 20 mL). The suspension of silver-1-(2-hydroxyethyl)-5-nitriminotetrazolate was mixed with a solution of diaminoguanidinium iodide (3.26 g, 15 mmol) in warm water (approx. 15 mL). The mixture was stirred for 30 min at 30 °C in darkness. The AgI precipitate was removed by filtration. The clear solution was evaporated to dryness under reduced pressure, and the product was recrystallized from ethanol/water; yield 71% (2.80 g, 10.65 mmol). DSC (5 °C min^{-1}): 110 °C (m.p.), 208 °C (dec.). IR (KBr): $\tilde{\nu}$ = 3441 (s), 3339 (vs), 3289 (vs), 2981 (w), 2955 (w), 2352 (w), 1674 (vs), 1629 (vs), 1556 (w), 1508 (vs), 1455 (s), 1446 (s), 1421 (m), 1344 (vs), 1318 (vs), 1268 (s), 1231 (m), 1174 (m), 1112 (m), 1063 (m), 1049 (m), 1031 (m), 971 (m), 918 (w), 879 (w), 864 (w), 778 (w), 742 (w), 670 (w), 520 (w) cm^{-1}. Raman (1064 nm, 500 mW, 25 °C): $\tilde{\nu}$ = 3340 (3), 3262 (8), 3002 (3), 2984 (15), 2956 (5), 2892 (3), 1505 (100), 1341 (18), 1274 (7), 1177 (3), 1111 (7), 1052 (4), 1033 (30), 992 (8), 936 (5), 865 (5), 748 (7), 671 (4), 489 (3) cm^{-1}. ^{1}H NMR ([D$_6$]DMSO, 25 °C): δ = 8.55 [s, 2 H, C(–N*H*–NH$_2$)$_2$], 7.14 (s, 2 H, C=N*H$_2$*), 4.93 (s, 1 H, OH), 4.59 [s, 4 H, C(–NH–N*H$_2$*)$_2$], 4.07 (t, 2 H, N–C*H$_2$*), 3.70 (t, 2 H, C*H$_2$*–OH) ppm. ^{13}C NMR ([D$_6$]DMSO, 25 °C): δ = 160.3 [*C*(NH–NH$_2$)$_2$(NH$_2$)$^+$], 157.6 (*C*N$_4$), 59.1 (N*C*H$_2$), 48.8 (*C*H$_2$OH) ppm. MS (FAB$^+$): *m*/*z* = 90.1 [$CH_8N_5^+$]. MS (FAB$^-$): *m*/*z* = 173.0 [$C_3H_5N_6O_3^-$]. $C_4H_{13}N_{11}O_3$ (263.22): calcd. C 18.25, H 4.98, N 58.53; found C 18.17, H 4.87, N 58.07. Impact sensitivity: > 40 J. Friction sensitivity: 144 N. ESD: 0.20 J.

Triaminoguanidinium 1-(2-Hydroxyethyl)-5-nitriminotetrazolate (8): 1-(2-Hydroxyethyl)-5-nitriminotetrazole (1.74 g, 10 mmol) was dissolved in water (10 mL) and triaminoguanidine (1.04 g, 10 mmol) was added under nitrogen. The free base dissolved immediately, the mixture was warmed to 40 °C for 5 min., and the clear solution was evaporated to dryness. Recrystallization of the crude material from ethanol/water affords 2.20 g (7.91 mmol, 79%) of **8** as colorless crystals. DSC (5 °C min^{-1}): 142 °C (m.p.), 215 °C (dec.). IR (KBr): $\tilde{\nu}$ = 3552 (s), 3477 (s), 3414 (vs), 3348 (s), 3213 (s), 1685 (s), 1637 (m), 1617 (s), 1508 (s), 1451 (s), 1423 (m), 1392 (s), 1360 (s), 1337 (s), 1267 (m), 1241 (m), 1227 (m), 1202 (m), 1160 (w), 1128 (m), 1111 (m), 1073 (m), 1054 (w), 1034 (w), 990 (m), 952 (m), 884 (w), 861 (w), 778 (w), 749 (w), 702 (w), 637 (m), 608 (m), 511 (w), 483 (m) cm^{-1}. Raman (1064 nm, 500 mW, 25 °C): $\tilde{\nu}$ = 3345 (13), 3321 (13), 3267 (18), 3007 (7), 2966 (14), 2883 (6), 1687 (3), 1513 (100), 1459 (5), 1423 (7), 1341 (19), 1274 (9), 1110 (12), 1035 (49), 991 (8), 752 (10), 671 (5), 512 (3), 483 (5) cm^{-1}. ^{1}H NMR (D$_2$O, 25 °C): δ = 4.67 [s, 10 H, C(-N*H*-NH$_2$)$_3$, -OH], 4.25 (t, 2 H, NC*H$_2$*), 3.85 (t, 2 H, C*H$_2$*OH) ppm. ^{13}C NMR (D$_2$O, 25 °C): δ = 159.6 [C(-N*H*-NH$_2$)$_3$], 156.2 (*C*N$_4$), 59.2 (N*C*H$_2$), 48.8 (*C*H$_2$OH) ppm. MS (FAB$^+$): *m*/*z* = 105.1 [$CH_9N_6^+$]. MS (FAB$^-$): *m*/*z* = 173.0 [$C_3H_5N_6O_3^-$]. $C_4H_{14}N_{12}O_3$ (278.23): calcd. C 17.27, H 5.07, N 60.41; found C 17.13, H 4.88, N 60.27. Impact sensitivity: 18 J. Friction sensitivity: > 360 N. ESD: 0.80 J.

Azidoformamidinium 1-(2-Hydroxyethyl)-5-nitriminotetrazolate (9): 1-(2-Hydroxyethyl)-5-nitriminotetrazole (2.62 g, 15 mmol) was dissolved in warm water (approx. 20 mL). The clear solution was mixed with a solution of $AgNO_3$ (2.55 g, 15 mmol) in water (10 mL). The mixture was stirred for 5 min at room temperature in the darkness. The white precipitate was separated by centrifugation, washed twice with water until free of acid, and finally resuspended in water (approx. 20 mL). This suspension of silver 1-(2-hydroxyethyl)-5-nitriminotetrazolate was mixed with a solution of azidoformamidinium chloride (1.82 g, 15 mmol) in warm water (approx. 15 mL). This mixture was stirred for 30 min at 30 °C in darkness. The AgCl precipitate was removed by filtration. The clear solution was evaporated to dryness under reduced pressure, and the product was recrystallized from ethanol/water to yield 2.88 g (11.1 mmol, 74%) of **9** as very fine needles. Unfortunately no crystals suitable for X-ray crystallography were obtained. DSC (5 °C min^{-1}): 154 °C (dec.). IR (KBr): $\tilde{\nu}$ = 3551 (m), 3474 (s), 3413 (vs), 3236 (w), 2984 (m), 2962 (m), 2643 (w), 2102 (w), 2023 (w), 1911 (w), 1637 (m), 1618 (m), 1578 (vs), 1491 (s), 1454 (m), 1426 (m), 1403 (m), 1364 (m), 1330 (s), 1266 (s), 1222 (m), 1153 (m), 1050 (s), 1033 (s), 991 (m), 949 (m), 887 (m), 871 (m), 862 (m), 777 (w), 724 (m), 684 (w), 668 (w), 583 (m), 523 (m), 485 (w) cm^{-1}. Raman (1064 nm, 500 mW, 25 °C): $\tilde{\nu}$ = 3006 (21), 2988 (46), 2963 (76), 2956 (71), 2903 (16), 1589 (100), 1465 (11), 1450 (9), 1429 (12), 1411 (33), 1404 (41), 1362 (13), 1307 (7), 1258 (8), 1225 (34), 1158 (3), 1043 (18), 995 (13), 952 (4), 874 (11), 863 (11), 778 (3), 762 (17), 724 (3), 670 (10), 524 (9), 488 (7), 449 (5), 327 (3), 278 (11) cm^{-1}. ^{1}H NMR ([D$_6$]DMSO, 25 °C): δ = 9.36 [s, 5 H, {C–(NH$_2$)$_2$}, –OH], 4.23 (t, 2 H, NC*H$_2$*), 3.77 (t, 2 H, C*H$_2$*OH) ppm. ^{13}C NMR ([D$_6$]DMSO, 25 °C): δ = 156.8 (*C*N$_4$), 150.7 [*C*(NH$_2$)$_2$], 58.1 (N*C*H$_2$), 50.4 (*C*H$_2$OH) ppm. MS (FAB$^+$): *m*/*z* = 86.1 [$CH_4N_5^+$]. MS (FAB$^-$): *m*/*z* = 173.0 [$C_3H_5N_6O_3^-$]. $C_4H_9N_{11}O_3$ (259.19): calcd. C 18.54, H 3.50, N 59.45; found C 19.71, H 3.62, N 49.60. Impact sensitivity: 9 J. Friction sensitivity: 120 N. ESD: 0.15 J.

Diaminouronium 1-(2-Hydroxyethyl)-5-nitriminotetrazolate (10): 1-(2-Hydroxyethyl)-5-nitriminotetrazole (1.74 g, 10 mmol) was dissolved in water (10 mL) and diaminourea (0.90 g, 10 mmol) was added to the clear solution. The free base dissolved immediately, the mixture was warmed to 50 °C for 5 min, and the solution was evaporated to dryness. Recrystallization of the crude material from ethanol/water affords 2.34 g (8.86 mmol, 86%) of **10** as a colorless solid. Unfortunately, no crystals suitable for X-ray crystallography by recrystallization either from water, dimethyl formamide or an ethanol/water mixture were obtained. DSC (5 °C min^{-1}): 136 °C (m.p.), 191 °C (dec.). IR (KBr): $\tilde{\nu}$ = 3460 (m), 3377 (m), 3335 (m), 3295 (m), 3230 (m), 3121 (m), 3024 (w), 2962 (w), 2946 (w), 2896 (w), 2796 (w), 2694 (w), 2379 (w), 2030 (w), 1691 (m), 1624 (m), 1504 (s), 1458 (m), 1430 (m), 1376 (s), 1337 (s), 1311 (vs), 1253 (m), 1234 (m), 1176 (m), 1158 (m), 1117 (m), 1059 (m), 1035 (m), 996 (w), 970 (m), 940 (w), 879 (w), 871 (w), 773 (w), 747 (w), 742 (w), 687 (w), 664 (m), 583 (m), 567 (m), 527 (w) cm^{-1}. Raman (1064 nm, 500 mW, 25 °C): $\tilde{\nu}$ = 3377 (1), 3333 (1), 3298 (2), 3025 (3), 2971 (10), 2898 (2), 1690 (3), 1548 (3), 1502 (100), 1458 (2), 1418 (3), 1375 (7), 1336 (28), 1281 (3), 1231 (2), 1177 (6), 1118 (17), 1052 (7), 1035 (62), 999 (4), 972 (4), 939 (3), 881 (7), 749 (10), 666 (7), 586 (3), 490 (4), 444 (3), 385 (3), 308 (13), 274 (11) cm^{-1}. ^{1}H NMR ([D$_6$]DMSO, 25 °C): δ = 7.75 (s, 8 H, –NH–NH$_2$, NH–NH$_3$, –OH), 4.08 (t, 2 H, NC*H$_2$*), 3.70 (t, 2 H, C*H$_2$*OH) ppm. ^{13}C NMR ([D$_6$]DMSO, 25 °C): δ = 159.4 [C(–N*H*–NH$_2$)(–NH–NH$_3$)], 157.3 (*C*N$_4$), 59.1 (N*C*H$_2$), 48.9 (*C*H$_2$OH) ppm. MS (FAB$^+$): *m*/*z* = 91.0 [$CH_7N_4O^+$]. MS (FAB$^-$): *m*/*z* = 173.0 [$C_3H_5N_6O_3^-$]. $C_4H_{14}N_{10}O_4$ (264.20): calcd. C 18.18, H 4.58, N 53.01; found C 18.29, H 4.52, N 52.18. Impact sensitivity: 40 J. Friction sensitivity: 288 N. ESD: 0.60 J.

CCDC-819225 (for **3**), -819228 (for **4**), -819226 (for **5**), -819227 (for **6**), -815408 (for **7**), and -819224 (for **8**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

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