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Nitrogen-Rich Salts Based on Energetic Nitroaminodiazido[1,3,5]triazine and Guanazine

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Abstract: Highly dense nitrogen-rich ionic compounds are potential high-performance energetic materials for use in military and industrial venues. Guanazinium salts with promising energetic anions and a family of energetic salts based on nitrogen-rich cations and the 6-nitroamino-2,4-diazido[1,3,5]-triazine anion (NADAT) were prepared and fully characterized by elemental analysis, IR spectroscopy, ^{1}H NMR and ^{13}C NMR spectroscopy, and differential scanning calorimetry (DSC). The crystal structures of neutral NADAT (**2**) and its biguanidinium salt **5** were determined by single-crystal X-ray diffraction (**2**: orthorhombic, *Pnma*; **5**: monoclinic, *P*2$_1$). Additionally, the isomerization behavior of **2** in solution was investigated by proton-decoupled ^{13}C and ^{15}N NMR spectroscopy. All the new salts exhibit desirable physical properties, such as relatively high densities (1.63–1.78 g cm^{-3}) and moderate thermal stabilities (T_d = 130–196 °C for **3**–**10** and 209–257 °C for **11**–**15**). Theoretical performance calculations (Gaussian 03 and Cheetah 5.0) gave detonation pressures and velocities for the ionic compounds **3**–**15** in the range of 21.0–30.3 GPa and 7675–9048 m s^{-1}, respectively, which makes them competitive energetic materials.

Keywords: detonation performance · heats of formation · energetic compounds · nitrogen heterocycles · X-ray diffraction

Introduction

Energetic materials as controllable storage systems for relatively large amounts of chemical energy are widely applied in military and industrial venues. In the last decade, a unique class of high energetic compounds composed of nitrogen-containing heterocyclic anions and/or cations has been developed to meet the continuing need for improved energetic materials.[1] Recently, salt-based molecules displayed attractive energetic properties due to the special properties of ionic compounds, such as lower vapor pressures and higher densities than their atomically similar nonionic analogues.[2] The present search for energetic salts is mainly directed toward the synthesis of new organic cations and anions, which exhibit high safety, performance, density, and stability. Compounds containing nitroamino groups have been intensively investigated both theoretically and experimentally as energetic materials, because the nitroamino group can offer improved oxygen balance and higher heats of formation.[3] Results from considerable research indicated that R$-$NHNO$_2$ normally can act as a moderate acid, and that the stability of this compound can be dramatically increased by transformation of the $-$NHNO$_2$ moiety into a nitroimino group. For example, 5-nitroaminotetrazole is distinguished as a high-energy compound with low thermal stability. According to thermogravimetric data, the temperature of intensive (explosive) decomposition for 5-nitroaminotetrazole is 132 °C. Concomitantly, salts of 5-nitroaminotetrazole are thermally more stable; the temperature range of their intense decomposition is 200–400 °C, depending on the type of the cation.[4] In addition to the nitroamino group, the azido group is another prominent representative among the energetic groups that contributes heat release approaching 355 kJ per N$_3$ unit.[5] As examples of energetic compounds containing both nitroamino and azido groups, 3-azido-1-nitroazetidine has good thermal stability and good plasticizing properties, and is presently of interest as a plasticizing agent;[6] 1-(2-azidoethyl)-5-nitriminotetrazole has a detonation velocity higher than 8300 m s^{-1}.[7] Unlike neutral compounds that contain both nitroamino and azido groups,[8] the

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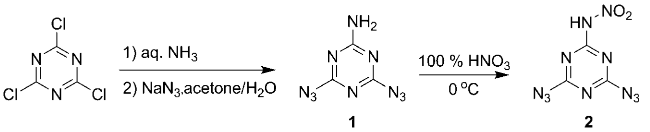
syntheses and energetic properties of salts that contain both nitroamino and azido groups in the cation or anion have not been well investigated.

In this work, we have investigated the energetic properties of salts derived from an anion that contains both nitroamino and azido groups. [1,3,5]Triazine is an ideal backbone for constructing energetic compounds due to its three readily tunable ring positions through which 6-nitroamino-2,4-diazido[1,3,5]triazine (NADAT) and 4,6-dinitroamino-2-azido[1,3,5]triazine might be synthesized. 4,6-Bis(nitroimino)-1,3,5-triazinan-2-one (DNAM), a high energetic s-triazine derivative, has been investigated in detail.[4b,9] In a recently published patent, Fronabarger et al. reported the syntheses of 6-nitroamino-2,4-diazido[1,3,5]triazine and its potassium and rubidium salts;[10] however, the energetic properties and reactivities of these compounds were little studied. Now, we report the syntheses and characterization of salts based on NADAT in combination with nitrogen-rich cations. Salts of 3,4,5-triamino-1,2,4-triazole (guanazine) with promising energetic anions were also prepared and fully characterized here. The detonation properties of these compounds have been calculated and the values suggest that they are insensitive energetic materials.

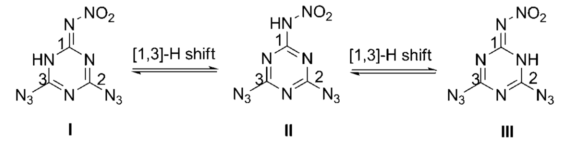
Results and Discussion

As shown in Scheme 1, 6-amino-2,4-diazido[1,3,5]triazine (**1**) was prepared by the selective monoamination of cyanuric chloride with aqueous ammonia at 0 °C followed by azido substitution with sodium azide in acetone/H_2O (1:1).[11] Several reagents for the nitration of the amino group in **1** to give the nitroamino group are available, such as nitric acid in Ac_2O or sulfuric acid,[12] alkyl nitrate in alcohol,[13] and nitronium salt (NO_2BF_4) in acetonitrile.[14] Here, 100 % nitric acid was used for the nitration of **1** to afford 6-nitroamino-2,4-diazido[1,3,5]triazine (NADAT, **2**) as a white powder in 54 % yield.[10] Colorless flat crystals, which were submitted for single-crystal X-ray analysis, can be obtained by recrystallization from hot water. Strong absorption bands at $\tilde{\nu} \approx 1553, 1334,$ and $1279\ \mathrm{cm^{-1}}$ in the IR spectrum of **2** support the successful introduction of the nitro group.



Scheme 1. Syntheses of 6-nitroamino-2,4-diazido[1,3,5]triazine (NADAT, **2**).

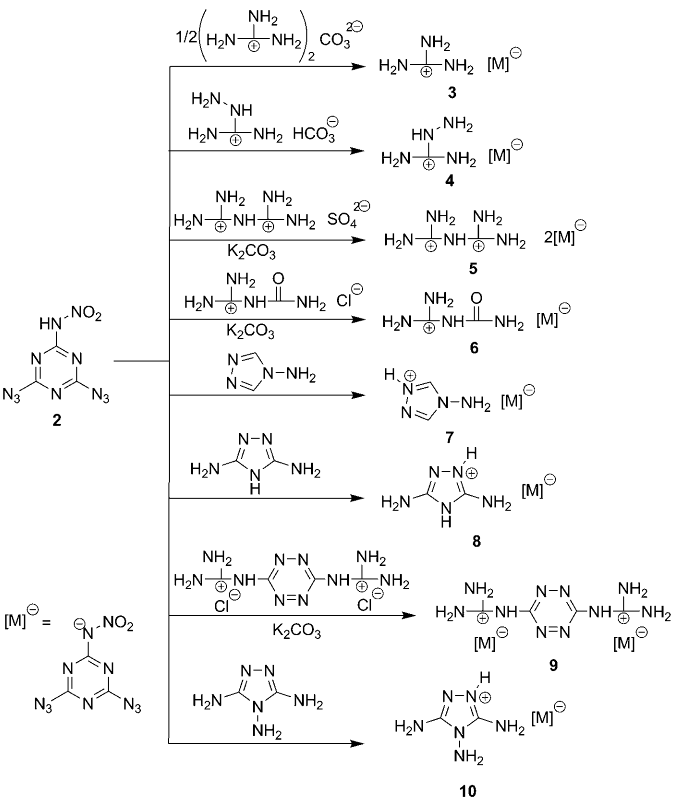
One broad singlet in the ^1H NMR spectrum of **2** appeared at $\delta = 11.57$ ppm. Unusual behavior of **2** in solution was observed in the ^{13}C NMR spectrum acquired in [D_6]DMSO.[10] Five signals at $\delta = 171.7, 164.8, 164.7, 159.8,$ and 151.7 ppm in the proton-decoupled ^{13}C NMR spectrum of **2** recorded at room temperature were found, which indicated that isomerization had occurred for **2** due to a proton shift (Scheme 2). Isomers **I** and **III** are equivalent due to the fast proton movement in solution and display three distinct carbon signals at $\delta = 164.7, 159.8,$ and 151.7 ppm, because of the restricted rotation of the exocyclic C=N bond that resulted in the inequivalence of C2 and C3.[15] Isomer **II** displays two carbon signals at $\delta = 171.7$ and 164.8 ppm due to the free rotation of the exocyclic C–N bond. No signal coalescence but slow compound decomposition was observed when the proton-decoupled ^{13}C NMR spectrum was attempted at 90 °C. The proton-decoupled ^{15}N NMR spectrum of **2** was measured in [D_6]DMSO and seventeen signals ranged from $\delta = 19.62$ to 262.56 ppm with respect to CH_3NO_2 as an external standard were found due to the isomerization (the spectrum is shown in the Supporting Information).



Scheme 2. Isomerization of 6-nitroamino-2,4-diazido[1,3,5]triazine (**2**) in solution through [1,3]-H shift.

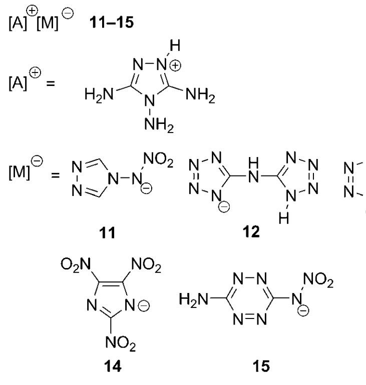
By taking advantage of the inherent high acidity of the nitroamino group, **2** was treated directly with guanidinium carbonate, aminoguanidinium bicarbonate, neutral 4-amino-1,2,4-triazole, 3,5-diamino-1,2,4-triazole, and 3,4,5-triamino-1,2,4-triazole (guanazine) in water to form the corresponding salts **3**, **4**, **7**, **8**, and **10** in excellent yields (Scheme 3). By using potassium carbonate as a base, **2** could be conveniently deprotonated and then underwent metathesis reactions with organic sulfate or halides to achieve the products **5**, **6**, and **9**. The barium or silver salt of **2** was not needed for these metathesis reactions due to the relatively lower solubility of the organic salts compared to that of the potassium salt. However, only the potassium salt of **2** was recovered from the water solution when diaminoguanidinium chloride or triaminoguanidinium chloride were used as reactants under the same conditions. Compound **2** was isolated when 5-aminotetrazolium chloride was used as a cation source, which suggests that 5-aminotetrazole is the more acidic of the two compounds. The barium or silver salt of **2** may need to be prepared in the future in order to obtain additional nitrogen-rich salts based on the NADAT anion.

The three amino groups of guanazine should give rise to the formation of significantly hydrogen-bonded networks, which could result in salts with high densities. This property makes guanazine a reasonable candidate for achieving ionic energetic compounds. Recently, guanazinium[16] and methylguanazinium[17] salts with anions such as perchlorate, nitrate, 5-nitrotetrazolate, dinitramide, and bistetrazolate were synthesized and fully characterized. In our current work, guanazinium salts with such energetic anion counterparts as 4-nitroamino-1,2,4-triazole (**11**),[18] *N*,*N*-bis(1*H*-tetrazol-5-yl)-



Scheme 3. Syntheses of the 6-nitroamino-2,4-diazido[1,3,5]triazine salts **3**–**10**.

amine (**12**),[19] 5-nitroiminotetrazole (**13**),[4] trinitroimidazole (**14**),[20] and 3-amino-6-nitroamino-tetrazine (**15**)[21] were synthesized and their thermal properties were studied.



All ionic compounds **3**–**15** were characterized by IR, ^{1}H NMR, and ^{13}C NMR spectroscopy, and elemental analyses. Three signals at δ = 151.7, 159.8, and 164.8 ppm, assigned to the NADAT anion, were observed in the ^{13}C NMR spectra of compounds **3**–**10**. This result further confirmed the explanation for the five signals in the ^{13}C NMR spectrum of **2** because the electron delocalization of the anion causes the exocyclic nitroamino group to resemble a nitroimino group, which has restricted free rotation of the C–N bond and resulted in the inequivalence of C2 and C3. The proton-decoupled ^{15}N NMR spectrum of salt **6** was also recorded in [D$_6$]DMSO and eleven signals were found in addition to the three signals for the guanylurea cation at δ = −270.26, −291.75, and −296.83 ppm,[22] which clearly indicated the unsymmetric character of the NADAT anion due to the formation of a nitroimino structure (see the spectrum in the Supporting Information).

The melting points (T_m) and the decomposition temperatures (T_d) of compounds **3**–**15** were obtained by using differential scanning calorimetry (DSC) from the first heating cycle at a heating rate of 5 °C min^{-1}. As shown in Table 1, for salts **3**–**10** in which the NADAT anion was present, only **5** and **6** appear sufficiently thermally stable, melting at 136 and 152 °C, respectively. For compounds **3**–**10**, thermal degradation temperatures (T_d) are in the range of 130 °C (4-amino-1,2,4-triazolium, **7**) to 196 °C (aminocarbonylguanidinium, **6**). For salts **10**–**15**, which contain the same guanizinium cation, better thermal stability were exhibited with T_d in the range of 191–257 °C. As one of the important physical properties of energetic salts, densities of **3**–**15** were measured by using a gas pycnometer (Table 1) and found to fall in the range of 1.60–1.78 g cm^{-3}. The densities were also estimated by employing our tabulated volume parameters,[23] which agree reasonably well with the experimental values. Oxygen balance (Ω) is used to indicate the degree to which a compound can be oxidized. Compounds **3**–**15** possess negative oxygen balances that are in the range of −24.8 to −62.0 %, which are comparable to TNT (−24.7 %). For compounds **10**–**15**, which contain the same guanazinium cation, trinitroimidazolate **14** shows the best oxygen balance (−12.6 %) due to three nitro groups in the anion. Impact sensitivities of the salts **3**–**13** and **15** were determined by using a BAM Fall hammer apparatus with a 10 kg drop weight with approximately 15 mg samples,[24] and found to be in the range of 20 to >40 J, which places them in the less sensitive class. It is worthwhile to point out that all of the salts are stable upon storing for two years at room temperature without significant change in the ^{1}H and ^{13}C NMR spectra.

Heat of formation ($\Delta_f H$) is another important parameter in evaluating the performance of energetic salts. This property can be calculated with good accuracy from the lattice energy of the salts. The heat of formation of the cations and anions[25] were calculated by using Gaussian 03.[26] The calculated $\Delta_f H$ values of nitrogen-rich cations vary between 350.59 (aminocarbonylguanidinium, **6**) and 1903.56 kJ mol^{-1} (diguanidinotetrazinium, **9**). The $\Delta_f H$ value of the 6-nitroamino-2,4-diazido[1,3,5]triazine anion is 651.80 kJ mol^{-1}, which is higher than the values of the other energetic anions selected for making salts **11**–**15**. The positive heats of formation ($\Delta_f H$) of salts **3**–**15** are calculated by using the Born–Haber energy cycles (see the Experimental Section), and fall in the range of 0.72 (**14**) to 3.68 kJ g^{-1} (**7**).

The performance of a high explosive is characterized by its detonation velocity, *vD* [m s^{-1}], and detonation pressure,

Table 1. Thermal properties of energetic salts.

Salt	ρ[a]	T_m[b]	T_d[c]	Ω[d]	$\Delta_f H_{cation}$[e]	$\Delta_f H_{anion}$[f]	$\Delta_f H_{lat}$[g]	$\Delta_f H_{salt}$[h]		P[i]	vD[j]	IS[k]
	[g cm^{-3}]	[°C]	[°C]	[%]	[kJ mol^{-1}]	[kJ mol^{-1}]	[kJ mol^{-1}]	[kJ mol^{-1}]	[kJ g^{-1}]	[GPa]	[m s^{-1}]	[J]
3	1.60(1.63)		190	−28.4	575.85	651.80	462.04	765.61	2.71	22.2	7859	20
4	1.68(1.64)		168	−29.6	667.41	651.80	461.68	857.53	2.89	26.3	8431	20
5	1.63(1.65)	136	151	−24.8	1618.16	651.80	1346.03	1575.73	2.88	22.7	7866	28
6	1.63(1.69)	152	196	−27.1	350.59	651.80	447.81	554.58	1.71	21.0	7675	40
7	1.68(1.67)		130	−28.6	936.28	651.80	457.81	1130.27	3.68	25.3	8178	25
8	1.67(1.66)		158	−29.8	763.99	651.80	451.62	964.17	3.00	23.9	8073	40
9	1.63(1.63)		193	−27.4	1903.56	651.80	1295.44	1911.72	2.98	22.0	7768	>40
10	1.68(1.68)		191	−30.8	841.98	651.80	447.13	1046.65	3.10	25.2	8280	25
11	1.71(1.63)		219	−42.8	841.98	141.50	488.31	495.16	2.04	27.0	8646	>40
12	1.63(1.63)	170	257	−50.9	841.98	500.1	470.75	871.33	3.26	24.3	8399	>40
13	1.78(1.69)		231	−32.8	841.98	9.8	492.91	358.87	1.47	30.3	9048	>40
14	1.71(1.76)	196[l]	242[l]	−12.6	841.98	−156.68	456.15	229.15	0.72	25.8	8055	–[m]
15	1.64(1.65)	103	209	−62.0	841.98	260.71	496.24	632.98	2.33	24.8	8323	>40

[a] Measured density (calculated density). [b] Melting point. [c] Decomposition temperature. [d] CO oxygen balance (Ω) is an index of the deficiency or excess of oxygen in a compound required to convert all C into CO and all H into H_2O. For a compound with the molecular formula of $C_aH_bN_cO_d$ (without crystal water), $\Omega\ [\%] = 1600\ [(d-a-b/2)/M_w]$. [e] Calculated molar enthalpy for the formation of the cation. [f] Calculated molar enthalpy for the formation of the anion. [g] Calculated molar lattice energy. [h] Calculated molar enthalpy for the formation of the salt. [i] Detonation pressure. [j] Detonation velocity. [k] Impact sensitivity. [l] Measured at a heating rate of 10 °C min^{-1}. [m] Not determined.

P [GPa].[27] These parameters are directly related to the oxygen balance (OB), density, and heat of formation and were calculated based on the traditional Chapman–Jouget thermodynamic detonation theory suggested by Kamlet and Jacobs[28] with the program Cheetah 5.0.[29] The calculated detonation pressures (P) for the new salts fall in the range of 21.0 (**6**) to 30.3 GPa (**13**), and the detonation velocities (vD) are distributed from 7675 (**6**) to 9048 m s^{-1} (**13**). Although the denotation data are lower than the corresponding values for RDX ($P = 33.8$ GPa, $vD = 8750$ m s^{-1}), most of them are superior to TNT ($P = 20.6$ GPa, $vD = 6850$ m s^{-1}) and thus, the investigated compound may be of interest as potential energetic materials. For salts **3**–**10** with the same anion, the aminoguanidinium salt (**4**, $P = 26.3$ GPa, $vD = 8431$ m s^{-1}) exhibits the best performance, and for salts **10**–**15**, which contain the guanazinium cation, the nitroiminotetrazolate (**13**, $P = 30.3$ GPa, $vD = 9048$ m s^{-1}) and 4-nitroamino-1,2,4-triazolate (**11**, $P = 27.0$ GPa, $vD = 8646$ m s^{-1}) exhibit excellent performance.

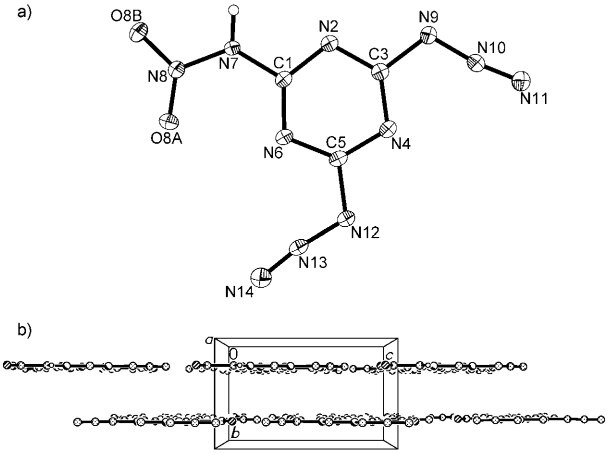


Figure 1. a) Thermal ellipsoid plot (30 %) and labeling scheme for 6-nitroamino-2,4-diazido[1,3,5]triazine (NADAT, **2**). Hydrogen atoms are included but are unlabelled for clarity. b) Packing diagram of **2** viewed down the *a* axis.

X-ray crystallography: Crystals of **2** and its biguanidinium salt **5** that were suitable for X-ray diffraction were obtained by slow recrystallization from water at room temperature. The structures are shown in Figures 1 and 2. Crystallographic and structural refinement data are listed in Table 2. Compound **2** crystallized in the orthorhombic space group *Pnma* with a calculated density of 1.836 g cm^{-3} based on four molecules packed in the unit-cell volume of 807.46(16) Å (Table 2).[30] The X-ray crystallography analysis of **2** revealed that the hydrogen is located on the exocyclic nitrogen that is connected to the nitro group (Figure 1 a). All of the atoms in **2** are strictly coplanar with torsion angles near zero or 180° and the ring C–N bond length in the range of 1.3283–1.3297(14) Å, which is slightly longer than those for unsubstituted [1,3,5]-triazine (1.315–1.319 Å).[31] The distance between the layers is 2.940 Å. For the triazine ring, the C-N-C angles range from 112.51(10) to 112.88(10)° and the N-C-N angles from 126.97(10) to 127.49(10)°. The angles for the two azido groups are 171.63(12) (N11-N10-N9) and 171.92(13) (N14-N13-N12), respectively, which differ not virtually from analogous parameters for the molecules of azido-substituted [1,3,5]-triazines.[32] The planar molecules are assembled through hydrogen bonds and strictly parallel to the (001) plane (Figure 1 b). Intermolecular hydrogen bonds are only formed between N7–H7···N12#1 (2.169(18) Å).

The biguanidinium salt **5** crystallized in the monoclinic space group $P2_1$ with a calculated density of 1.678 g cm^{-3}. The structure consists of two biguanidinium dications, four NADAT anions, and two crystal-water molecules. In contrast to the crystal structure of **2**, the triazine anion moiety in salt **5** is not planar and the two azido groups connected to the same triazine ring are roughly parallel to each other. The exocyclic nitrimino group is twisted out of the plane of the

Table 2. Crystallographic data and structure refinement parameters.

	2	5
formula	$C_3HN_{11}O_2$	$C_8H_1N_{27}O_5$
M_w	223.15	565.44
crystall system	orthorhombic	monoclinic
space gourp	*Pnma*	$P2_1$
a [Å]	14.1327(16)	8.3079(14)
b [Å]	5.8806(7)	26.089(4)
c [Å]	9.7157(11)	10.9765
α [°]	90	90
β [°]	90	109.780
γ [°]	90	90
V [Å^3]	807.46(16)	2238.7
Z	4	4
T [K]	143(2) K	138(2)
λ [Å]	0.71073	0.71073
ρ_{calcd} [g cm^{-3}]	1.836	1.678
μ [mm^{-1}]	0.156	0.141
F(000)	448	1152
crystal size [mm^3]	0.74×0.35×0.08	0.19 x 0.12 x 0.07
θ range [°]	2.54 to 28.40	1.56 to 27.25
no. refl. collected	8133	21358
no. indep. reflections	1101 [R_{int} = 0.0131]	9824 [R_{int} = 0.0421]
data/restraints/parameter	1101/0/99	9824/7/737
GOF on F^2	1.105	1.021
R_1[a] [$I>2\sigma(I)$]	0.0285	0.0604
wR_2[a] [$I>2\sigma(I)$]	0.0847	0.1521
$\Delta\rho$ peak/hole [e Å^{-3}]	0.351 and −0.213	0.774 and −0.403

[a] $R1 = \Sigma||F_o|-|F_c||/\Sigma|F_o|$; $wR2 = \{\Sigma[w(F_o^2-F_c^2)^2]/\Sigma[w(F_o^2)^2]\}^{1/2}$.

triazine ring with a dihedral angle between their planes of 17.89 and 29.16°, respectively. The C−N bond lengths in the ring range from 1.322(6) (N2−C3) to 1.366(5) Å (C1−N2) and the exocyclic C1−N7 bond length is 1.375(5) Å (shorter than in **2**, 1.3860(14) Å), these results indicate the delocalization of the anion electron between the ring and the nitrimino group. The diprotonated biguanidinium cation consists of two planar halves twisted by 42.86°. The packing structure of **5** built up by hydrogen bonds is depicted in Figure 2b viewed along the *a* axis. Each biguanidinium cation is connected to five anions and one water molecule via the terminal amino group through hydrogen bonding to form a stabilized network.

Conclusion

Guanazinium salts with promising energetic anions and a family of energetic salts based on nitrogen-rich cations and the NADAT anion were prepared and fully characterized. The structures of neutral NADAT (**2**) and its biguanidinium salt **5** were analyzed by single-crystal X-ray diffraction, where it was found that **2** is strictly planar but in salt **5** the ring is twisted by the extensive hydrogen-bonding interactions between the cation and anion. All the new salts exhibit desirable physical properties, such as rather high densities (1.63–1.78 g cm^{-3}) and moderate thermal stabilities (T_d = 130–196 °C for **3**–**10** and 191–257 °C for **10**–**15**). The calculated detonation parameters of all new salts (Cheetah 5.0[29]) give detonation pressures and velocities in the range 21.0–30.3 GPa and 7675–9048 m s^{-1}, respectively, which are similar or higher than that of conventional explosives such as TNT or TATB.

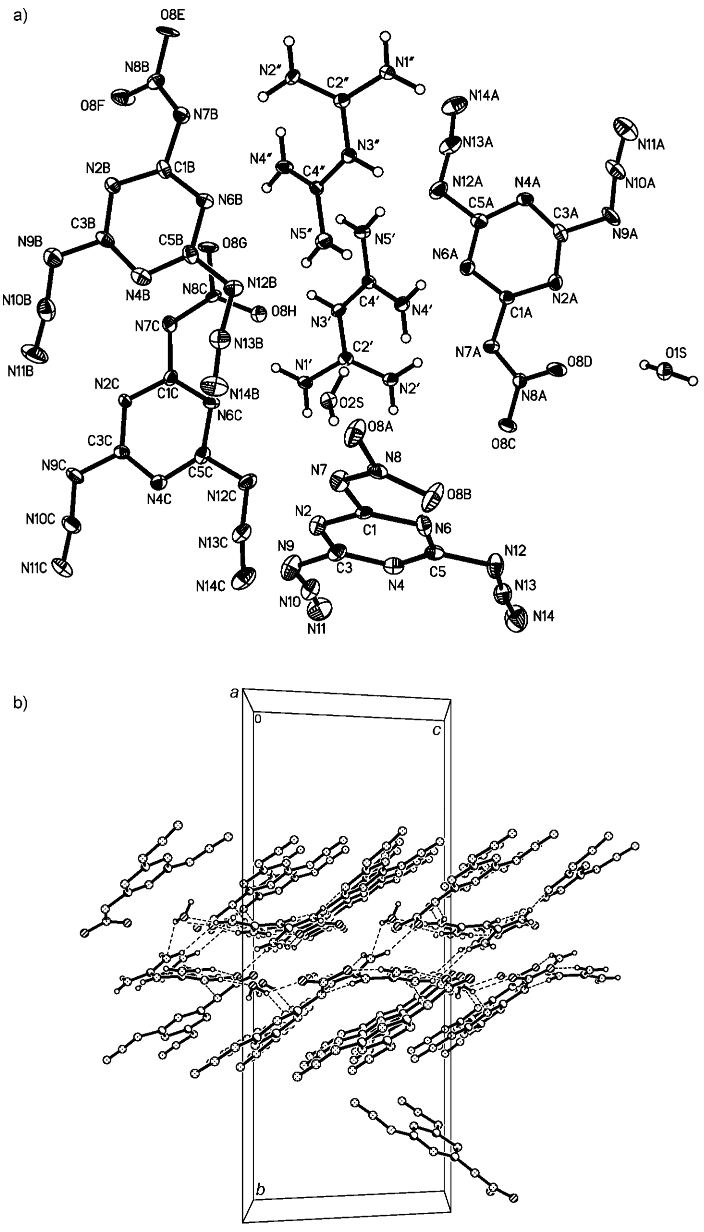
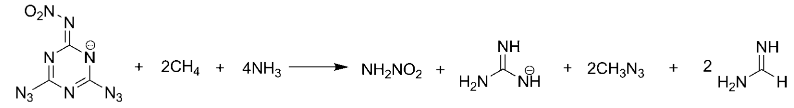


Figure 2. a) Thermal ellipsoid plot (30 %) and labeling scheme for salt **5**. Hydrogen atoms are included but are unlabelled for clarity. b) Packing diagram of **5** viewed down the *a* axis. Dashed lines indicate hydrogen bonding.

Experimental Section

Caution: Although none of the compounds described herein has exploded or detonated in the course of this research, these materials should be handled with extreme care by using the best safety practices because the nitrogen content is very high.

X-ray analyses: A clear colorless plate of dimensions 0.74×0.35×0.08 mm^3 for **2** or a colorless prism crystal of dimensions 0.19×0.12×0.07 mm^3 for **5** was mounted on a MiteGen MicroMesh by using a small amount of Cargille Immersion Oil. Data were collected on a Bruker

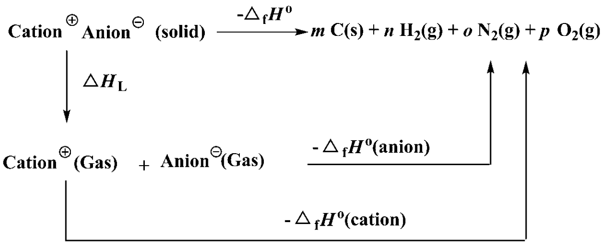


Scheme 5. Isodesmic reactions for calculating the heat of formation of the NADAT anion.

three-circle platform diffractometer equipped with a SMART APEX II CCD detector. The crystals were irradiated by using graphite monochromated $Mo_{K\alpha}$ radiation (λ = 0.71073). An MSC X-Stream low temperature device was used to keep the crystals at a constant 143(2) K for **2** or 138(2) K for **5** during data collection. Data collection was performed and the unit cell was initially refined by using APEX2 [v2004/1].[33] Data reduction was performed by using SAINT [v7.34A][34] and XPREP [v6.12].[35] Corrections were applied for Lorentz, polarization, and absorption effects by using SADABS [v2.10].[36] The structure was solved and refined with the aid of the programs in the SHELXTL-plus [v6.12] system of programs.[37] The full-matrix least-squares refinement on F^2 included atomic coordinates and anisotropic thermal parameters for all non-hydrogen atoms. The hydrogen atoms were included by using a riding model. CCDC-789261 and 789262 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.

Computational details: Computations were performed with the Gaussian 03 program.[26] The geometric optimization of the structures based on single-crystal structures, where available, and frequency analyses were carried out by using the B3-LYP functional with 6-31+G** basis set,[38] and single energy points were calculated at the MP2/6-311++G** level. All of the optimized structures were characterized to be true local energy minima on the potential energy surface without imaginary frequencies.

Based on a Born–Haber energy cycle (Scheme 4), the heat of formation of a salt can be simplified by Equation (1):



Scheme 4. Born–Haber cycle for the formation of energetic salts.

$$\Delta_f H^o(\text{salt, 298 K}) = \Delta_f H^o(\text{cation, 298 K}) + \Delta_f H^o(\text{anion, 298 K}) - \Delta H_L \tag{1}$$

where ΔH_L is the lattice energy of the ionic salts that could be predicted by Equation (2), as suggested by Jenkins et al.[39] as:

$$\Delta H_L = U_{POT} + [P(nM/2-2)+q(n_X/2-2)]RT \tag{2}$$

where n_M and n_X depend on the nature of the ions M_p^+ and X_q^-, respectively, and are equal to 3 for monatomic ions, 5 for linear polyatomic ions, and 6 for nonlinear polyatomic ions. The lattice potential energy U_{POT} [Eq. (3)] can be calculated as follows:

$$U_{POT}/\text{kJ mol}^{-1} = \gamma\ (\rho_m/M_m)^{1/3} + \delta \tag{3}$$

where ρ_m [g cm^{-3}] is the density, M_m is the chemical formula mass of the ionic material, and values for *g* and the coefficients γ [kJ mol^{-1}cm] and δ [kJ mol^{-1}]) were taken from the literature.[39]

The heats of formation of the cations and anions were computed by using the method of isodesmic reactions. The isodesmic reactions for NADAT anions are shown in Scheme 5. The enthalpy of the reaction ($\Delta_r H^0_{298}$) is obtained by combining the MP2/6-311++G** energy difference for the reaction, the scaled zero point energies, and other thermal factors. Thus, the heats of formation of the species being investigated can be readily extracted. With the value of the heats of formation and density of the energetic salts, the detonation pressures (*P*) and detonation velocities (*vD*) were calculated based on the traditional Chapman–Jouget thermodynamic detonation theory by using Cheetah 5.0.[29]

General methods for characterization: ^{1}H and ^{13}C NMR spectra were recorded on a 300 MHz nuclear magnetic resonance spectrometer operating at 300.13, and 75.48 MHz, respectively, by using [D$_6$]DMSO as solvent unless otherwise indicated. Chemical shifts were reported relative to Me_4Si. The melting and decomposition points were recorded on a differential scanning calorimeter (DSC) at a scan rate of 5 °C min^{-1} in closed Al containers with a nitrogen flow of 50 mL min^{-1}. The melting points and the temperatures of decomposition are given as onset temperatures. IR spectra were recorded by using KBr pellets. Densities were measured at room temperature by using a Micromeritics Accupyc 1330 gas pycnometer. Elemental analyses were obtained by using a CE-440 elemental analyzer (EAI Exeter Analytical).

6-Amino-2,4-diazido[1,3,5]triazine (1): Compound **1** was synthesized according to the literature method.[8] ^{1}H NMR (300 MHz, [D$_6$]DMSO): δ = 7.93 ppm (s, 2H); ^{13}C NMR (75 MHz, [D$_6$]DMSO): δ = 169.7, 167.9 ppm; IR (KBr): $\tilde{\nu}$ = 3335, 3197, 2732, 2237, 2216, 2149, 1663, 1557, 1513, 1366, 1308, 1246, 1193, 930, 802, 633 cm^{-1}.

2-Nitroamino-4,6-diazido[1,3,5]triazine (2):[7] 6-Amino-2,4-diazido-[1,3,5]-triazine (**1**) (1.35 g, 7.6 mmol) was added to nitric acid (100 %, 15 mL) as a solid in portions, while the temperature was maintained below 5 °C. After the addition of the starting material, the reaction mixture was stirred at 0 °C for 30 min, and then warmed to room temperature slowly and stirred for a further 3 h. The clear yellow mixture was poured onto ice (50 g) and stirred for 30 min. The resulting precipitate was collected by filtration, washed with cold water (3 mL), and dried in air to give the desired product **2** as a white powder (0.92 g, 54 %). Colorless flat crystals were obtained by recrystallization from hot water. DSC: 173 °C (onset, decomp); ^{1}H NMR (300 MHz, [D$_6$]DMSO): δ = 10.92 ppm (s, 1H); ^{13}C NMR (75 MHz, [D$_6$]DMSO): δ = 171.7, 164.8, 164.7, 159.8, 151.7 ppm; IR (KBr): $\tilde{\nu}$ = 3200, 2797, 2344, 2280, 2153, 1621, 1553, 1392, 1334, 1279, 1193, 1069, 964, 806, 697 cm^{-1}; MS (EI): *m/z*: 224 (2) $[M+1]^+$, 223 (29) $[M]^+$, 179 (6), 107 (18), 93 (7), 67 (41), 54 (51), 46 (100), 41 (57); elemental analysis calcd (%) for $C_3HN_{11}O_2$ (223.11): C 16.15, H 0.45, N 69.06; found: C 15.91, H 0.33, N 68.53.

Potassium 2-nitroamino-4,6-diazido[1,3,5]triazinate monohydrate: A solution of potassium hydroxide (230 mg, 4.1 mmol) in water (3 mL) was added to a suspension of NADAT (**2**) (892 mg, 4.0 mmol) in methanol (20 mL) at room temperature with stirring. After stirring for 1 h, the reaction mixture was filtered, the filtrate was concentrated to 5 mL, and held at 5 °C overnight. The resulting precipitate was collected by filtration, washed with cold methanol (3 mL), and dried in air to give the desired product as a colorless crystalline solid (0.98 g, 88 %) (thermally sensitive, exploded during elemental analyses). IR (KBr): $\tilde{\nu}$ = 3433, 2398, 2201, 2145, 1633, 1576, 1506, 1422, 1381, 1349, 1238, 1203, 1177, 1015, 979, 800 cm^{-1}; elemental analysis calcd (%) for $C_3KN_{11}O_2\ H_2O$ (279.22): C 12.90, H 0.72, N 55.18; found: C 12.95, H 0.60, N 54.42.

Guanidinium 2-nitroamino-4,6-diazido[1,3,5]triazinate (3): A solution of guanidinium carbonate (54 mg, 0.3 mmol) in water (3 mL) was added to a suspension of NADAT (**2**) (134 mg, 0.6 mmol) in water (10 mL) at room temperature with stirring. After stirring for 1 h, the reaction mixture was filtered, the filtrate was concentrated to 5 mL, and held at 5 °C overnight. The resulting precipitate was collected by filtration, washed with cold methanol (3 mL), and dried in air to afford the desired product as a colorless crystalline solid (0.154 g, 91 %). DSC: m.p. 190 °C (decomp); $\rho = 1.60\,\mathrm{g\,cm^{-3}}$, ^{1}H NMR (300 MHz, [D$_6$]DMSO): $\delta = 6.89$ ppm (br s, 6H); ^{13}C NMR (75 MHz, [D$_6$]DMSO): $\delta = 164.8, 159.8, 159.2, 151.7$ ppm; IR (KBr): $\tilde{\nu} = 3434, 3344, 3262, 3206, 2791, 2344, 2201, 2156, 1670, 1599, 1497, 1431, 1323, 1258, 1221, 1097, 779\,\mathrm{cm^{-1}}$; elemental analysis calcd (%) for $C_4H_6N_{14}O_2$ (282.18): C 17.03, H 2.14, N 69.49; found: C 17.14, H 2.04, N 68.34.

Aminoguanidinium 2-nitroamino-4,6-diazido[1,3,5]triazinate (4): The same method was used as described for compound **3** from aminoguanidinium bicarbonate (136 mg, 1.0 mmol) to form the product as a white solid (279 mg, 94 % yield). DSC: m.p. 168 °C (decomp); $\rho = 1.68\,\mathrm{g\,cm^{-3}}$; ^{1}H NMR (300 MHz, [D$_6$]DMSO): $\delta = 9.03$ (br s, 1H), 7.21 (br s, 2H), 6.60 (br s, 2H), 4.69 ppm (br s, 2H); ^{13}C NMR(75 MHz, [D$_6$]DMSO): $\delta = 164.8, 160.7, 160.1, 151.7$ ppm; IR (KBr): $\tilde{\nu} = 3430, 3340, 3156, 2398, 2274, 2195, 2142, 1668, 1625, 1553, 1507, 1418, 1370, 1338, 1263, 1220, 1092, 807\,\mathrm{cm^{-1}}$; elemental analysis calcd (%) for $C_4H_7N_{15}O_2$ (297.20): C 16.17, H 2.37, N 70.69; found: C 16.39, H 2.71, N 68.56.

Biguanidinium 2-nitroamino-4,6-diazido[1,3,5]triazinate monohydrate (5): A solution of potassium carbonate (69 mg, 0.5 mmol) in water (3 mL) was added to a suspension of NADAT (**2**) (223 mg, 1.0 mmol) in water (15 mL) at room temperature with stirring. The reaction mixture became a clear yellow solution, and then biguanidinium sulfate (100 mg, 0.5 mmol) in water (5 mL) was added. A white solid precipitated slowly. After stirring for 1 h, the reaction mixture was heated to ensure complete dissolution of the solid. After standing at room temperature overnight, the resulting colorless crystalline solid was collected by filtration, washed with cold water (3 mL), and dried in air to give the desired product as a colorless flat crystal (262 mg, 93 %), DSC: m.p. 136 °C, 151 °C (onset, decomp); $\rho = 1.63\,\mathrm{g\,cm^{-3}}$; ^{1}H NMR (300 MHz, [D$_6$]DMSO): $\delta = 8.10$ (s, 8H), 4.98 ppm (br s, 1H); ^{13}C NMR (75 MHz, [D$_6$]DMSO): $\delta = 164.8, 159.8, 156.7, 151.7$ ppm; IR (KBr): $\tilde{\nu} = 3626, 3346, 3182, 3077, 2828, 2395, 2256, 2195, 2139, 1711, 1568, 1514, 1420, 1371, 1343, 1261, 1086, 806\,\mathrm{cm^{-1}}$; elemental analysis calcd (%) for $C_8H_9N_{27}O_4\cdot H_2O$ (565.35): C 17.00, H 1.96, N 66.89; found: C 16.79, H 1.81, N 66.52.

Aminocarbonylguanidinium 2-nitroamino-4,6-diazido[1,3,5]triazinate monohydrate (6): The same method was used as described for compound **5** but by using aminocarbonylguanidinium chloride to give the product as colorless crystalline solid (246 mg, 72 % yield). DSC: m.p. 152 °C, 196 °C (onset, decomp); $\rho = 1.64\,\mathrm{g\,cm^{-3}}$; ^{1}H NMR (300 MHz, [D$_6$]DMSO): $\delta = 8.64$ (br s, 4H), 7.12 ppm (br s, 2H); ^{13}C NMR (75 MHz, [D$_6$]DMSO): $\delta = 164.8, 159.8, 156.8, 155.7, 151.7$ ppm; IR (KBr): $\tilde{\nu} = 3628, 3342, 3188, 3047, 2789, 2398, 2195, 2137, 1732, 1699, 1561, 1516, 1416, 1342, 1261, 1221, 1080, 706\,\mathrm{cm^{-1}}$; elemental analysis calcd (%) for $C_5H_7N_{15}O_3\cdot H_2O$ (343.22): C 17.50, H 2.64, N 61.21; found: C 17.75, H 2.41, N 61.98.

4-Amino-1,2,4-triazolium 2-nitroamino-4,6-diazido[1,3,5]triazinate (7): A mixture of 4-amino-1,2,4-triazole (67 mg, 0.8 mmol) and NADAT (**2**) (178 mg, 0.8 mmol) in acetonitrile (15 mL) was heated at reflux and stirred overnight. After removing the solvent, the residue was recrystallized from methanol (10 mL)/diethyl ether (5 mL) to afford the desired product as colorless crystalline solid (224 mg, 91 %). DSC: m.p. 130 °C (decomp); $\rho = 1.68\,\mathrm{g\,cm^{-3}}$; ^{1}H NMR (300 MHz, [D$_6$]DMSO): $\delta = 9.41$ (s, 2H), 8.20 ppm (br s, 3H); ^{13}C NMR (75 MHz, [D$_6$]DMSO): $\delta = 164.8, 159.8, 151.7, 145.3$ ppm; IR (KBr): $\tilde{\nu} = 3441, 3330, 3231, 3111, 2371, 2191, 2141, 1644, 1565, 1519, 1451, 1339, 1249, 1206, 800\,\mathrm{cm^{-1}}$; elemental analysis calcd (%) for $C_5H_5N_{15}O_2$ (307.19): C 19.55, H 1.64, N 68.39; found: C 19.82, H 1.55, N 68.08.

3,5-Diamino-1,2,4-triazolium 2-nitroamino-4,6-diazido[1,3,5]triazinate (8): A solution of 3,5-diamino-1.2,4-triazole (80 mg, 0.8 mmol) in water or acetonitrile (5 mL) was added to a suspension of NADAT (**2**) (178 mg, 0.8 mmol) in water or acetonitrile (10 mL) at room temperature with stirring. After stirring for 4 h, the resulting precipitate was collected by filtration, washed with cold methanol (5 mL), dried in air to afford the desired product as a white solid (242 mg, 94 %). DSC: 158 °C (onset, decomp); $\rho = 1.67\,\mathrm{g\,cm^{-3}}$; ^{1}H NMR (300 MHz, [D$_6$]DMSO): $\delta = 7.51$ ppm (br s, 4H); ^{13}C NMR (75 MHz, [D$_6$]DMSO): $\delta = 164.8, 159.8, 152.7, 151.7$ ppm; IR (KBr): $\tilde{\nu} = 3404, 3369, 3246, 3133, 2677, 2362, 2192, 2139, 1666, 1568, 1512, 1370, 1345, 1261, 1227, 1009, 802\,\mathrm{cm^{-1}}$; elemental analysis calcd (%) for $C_5H_6N_{16}O_2$ (322.1) C 18.64; H 1.88, N 69.55; found: C 18.66, H 1.73, N 69.02.

1,2,4,5-Tetrazino-3,6-diguanidinium 2-nitroamino-4,6-diazido[1,3,5]-triazinate (9): The same method was used as described for compound **5** by starting from 3,6-diguanidinium-1,2,4,5-tetrazine dichloride (134.5 mg, 0.5 mol) in water (80 mL) to form the product as a red solid (242 mg, 75 % yield). DSC 193 °C (onset, decomp); $\rho = 1.63\,\mathrm{g\,cm^{-3}}$; ^{1}H NMR (300 MHz, [D$_6$]DMSO): $\delta = 8.06$ ppm (br s, 10H); ^{13}C NMR (75 MHz, [D$_6$]DMSO): $\delta = 164.8, 159.9, 159.8, 155.9, 151.7$ ppm; IR (KBr): $\tilde{\nu} = 3389, 3195, 3073, 2197, 2142, 1698, 1609, 1568, 1512, 1433, 1342, 1268, 1233, 1033, 808\,\mathrm{cm^{-1}}$; elemental analysis calcd (%) for $C_{10}H_{10}N_{32}O_4$ (642.40): C 18.70, H 1.57, N 69.77; found: C 18.88, H 1.52, N 69.59.

Guanizinium 2-nitroamino-4,6-diazido[1,3,5]triazinate (10): A solution of guanazine (69 mg, 0.6 mmol) in water (5 mL) was added to a suspension of NADAT (**2**) (134 mg, 0.6 mmol) in water (10 mL) at room temperature with stirring. A white solid precipitated slowly. After stirring for 3 h, the reaction mixture was heated to ensure that the entire solid was dissolved. After standing at room temperature overnight, the resulting colorless crystalline solid was collected by filtration, washed with cold water (5 mL), and dried in air to give the desired product as colorless needles (181 mg, 90 %). DSC: m.p. 191 °C (decomp); $\rho = 1.68\,\mathrm{g\,cm^{-3}}$; ^{1}H NMR (300 MHz, [D$_6$]DMSO): $\delta = 7.06$ (br s, 4H), 5.57 ppm (s, 2H); ^{13}C NMR (75 MHz, [D$_6$]DMSO): $\delta = 164.8, 159.8, 151.7, 151.3$ ppm; IR (KBr): $\tilde{\nu} = 3357, 3277, 3257, 2951, 2734, 2410, 2268, 2195, 2144, 1699, 1669, 1553, 1511, 1415, 1358, 1175, 1014, 903, 804, 708\,\mathrm{cm^{-1}}$; elemental analysis calcd (%) for $C_5H_7N_{17}O_2$ (337.22): C 17.81, H 2.09, N 70.61; found: C 17.77, H 1.91, N 70.03.

General method for the preparation of guanizinium salts

Guanizinium 4-nitroamino-1,2,4-triazolate (11): A solution of 4-nitroamino-1,2,4-triazole (129 mg, 1.0 mmol) in water (2 mL) was added to a solution of guanazine (114 mg, 1.0 mmol) in water (10 mL) at room temperature with stirring. A white solid precipitated slowly. After stirring for 4 h, the reaction mixture was heated to ensure that all solid was dissolved. After standing at room temperature overnight, the resulting solid was collected by filtration, washed with cold methanol (3 mL), and dried in air to give the desired product as a colorless crystalline solid (231 mg, 95 %). DSC: 219 °C (onset, decomp); $\rho = 1.71\,\mathrm{g\,cm^{-3}}$; ^{1}H NMR (300 MHz, [D$_6$]DMSO): $\delta = 8.32$ (s, 2H), 7.08 (br s, 4H), 5.59 ppm (s, 2H); ^{13}C NMR (75 MHz, [D$_6$]DMSO): $\delta = 151.3, 143.1$ ppm; IR (KBr): $\tilde{\nu} = 3411, 3370, 3294, 3194, 3113, 1702, 1668, 1622, 1516, 1389, 1294, 1074, 964\,\mathrm{cm^{-1}}$; elemental analysis calcd (%) for $C_4H_9N_{11}O_2$ (243.19): C 19.76, H 3.73, N 63.36; found: C 19.66, H 3.67, N 63.05.

Guanizinium 5-(5'-tetrazolylamino)tetrazolate monohydrate (12): Colorless crystalline solid (235 mg, 82 %); DSC: m.p. 170 °C, 257 °C (onset, decomp); $\rho = 1.63\,\mathrm{g\,cm^{-3}}$; ^{1}H NMR (300 MHz, [D$_6$]DMSO): $\delta = 7.03$ (br s, 9H), 5.65 ppm (s, 2H); ^{13}C NMR (75 MHz, [D$_6$]DMSO): $\delta = 157.5, 151.4$ ppm; IR (KBr): $\tilde{\nu} = 3340, 3285, 3159, 2982, 1669, 1645, 1564, 1512, 1315, 1240, 1038, 887\,\mathrm{cm^{-1}}$; elemental analysis calcd (%) for $C_4H_9N_{15}\cdot H_2O$ (285.23): C 16.84, H 3.89, N 73.66; found: C 17.20, H 3.61, N 74.47.

Guanizinium 5-nitroiminotetrazolate (13): Colorless crystalline solid (212 mg, 87 % yield); DSC: 231 °C (onset, decomp); $\rho = 1.78\,\mathrm{g\,cm^{-3}}$; ^{1}H NMR (300 MHz, [D$_6$]DMSO): $\delta = 7.08$ (br s, 4H), 5.60 ppm (s, 2H); ^{13}C NMR (75 MHz, [D$_6$]DMSO): $\delta = 159.2, 151.3$ ppm; IR (KBr): $\tilde{\nu} = 3468, 3387, 3323, 3208, 3136, 1665, 1552, 1447, 1333, 1244, 1094, 882\,\mathrm{cm^{-1}}$; elemental analysis calcd (%) for $C_3H_8N_{12}O_2$ (244.17): C 14.76, H 3.30, N 68.84; found: C 14.79, H 3.27, N 68.67.

Guanizinium trinitroimdazolate (14): Colorless crystalline solid (295 mg, 93 %); DSC: m.p. 196 °C; thermogravimetric analysis: 242 °C (onset, decomp); $\rho = 1.71\,\mathrm{g\,cm^{-3}}$; ^{1}H NMR (300 MHz, [D$_6$]DMSO): $\delta = 12.45$ (br s, 1H), 7.07 (br s, 4H), 5.57 ppm (s, 2H); ^{13}C NMR (75 MHz, [D$_6$]DMSO): $\delta = 151.3$ ppm; IR (KBr): $\tilde{\nu} = 3472, 3312, 3248, 3156, 1705, 1663, 1625, 1542, 1329, 1111, 870\,\mathrm{cm^{-1}}$; elemental analysis calcd (%) for $C_5H_7N_{11}O_6$ (317.18): C 18.93, H 2.22, N 48.58; found: C 18.89, H 2.00, N 48.20.

Guanizinium 6-amino-3-nitroamino-1,2,4,5-tetrazinate monohydrate (15): Red crystalline solid (245 mg, 85 % yield); DSC: m.p. 103 °C, 209 °C (onset, decomp); $\rho = 1.64\,\mathrm{g\,cm^{-3}}$; ^{1}H NMR (300 MHz, [D$_6$]DMSO): $\delta = 7.38$ (s, 2H), 7.06 (s, 4H), 5.62 ppm (s, 2H); ^{13}C NMR (75 MHz, [D$_6$]DMSO): $\delta = 164.9, 163.0, 151.3$ ppm; IR (KBr): $\tilde{\nu} = 3518, 3416,$

3305, 3166, 1703, 1655, 1509, 1373, 1304, 1056, 964 cm^{-1}; elemental analysis calcd (%) for $C_4H_9N_{13}O_2{\cdot}H_2O$ (289.22): C 16.61, H 3.83, N 62.96; found: C 16.48, H 3.73, N 62.50.

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