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Nitrogen-Rich Salts of 1*H*,1′*H*-5,5′-Bitetrazole-1,1′-diol: Energetic Materials with High Thermal Stability

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1*H*,1′*H*-5,5′-Bitetrazole-1,1′-diol was synthesized starting from glyoxal, which is converted to glyoxime after treatment with hydroxylamine. Chlorination of glyoxime with Cl_2 gas in ethanol and following chloro/azido exchange yields diazidoglyoxime, which is cyclized under acidic conditions (HCl gas in diethyl ether) to give 1*H*,1′*H*-5,5′-bitetrazole-1,1′-diol dihydrate (**1**). A large variety of nitrogen-rich salts of **1** such as the diammonium (**2**), the dihydrazinium (**3**), the bis-guanidinium (**4**), the bis(aminoguanidinium) (**5**), the diaminoguanidinium salt monohydrate (**6**), the triaminoguanidinium salt monohydrate (**7**), the 1-amino-3-nitroguanidinium salt dihydrate (**8**), the diaminouronium salt monohydrate (**9**), the bis(oxalyldihydrazidinium) (**10**), the oxalyldihydrazidinium salt dihydrate (**11**), the 3,6-dihydrazino-1,2,4,5-tetrazinium (**12**), the 5-aminotetrazolium (**13**), the bis(5-amino-1-methyl-1*H*-tetrazolium) salt (**14**), the bis(5-amino-2-methyl-2*H*-tetrazole) adduct (**15**), and the 1,5-diaminotetrazolium salt (**16**) were synthesized by means of Brønsted acid–base or metathesis reactions. All compounds were fully characterized by vibrational spectroscopy (IR and Raman), multinuclear NMR spectroscopy, elemental analysis, and differential scanning calorimetry (DSC) measurements. The crystal structures of **1**–**16** could be determined by using single-crystal X-ray diffraction. The heats of formation of **1**–**16** were calculated by using the atomization method on the basis of CBS-4M enthalpies. With regard to their potential use as cyclotrimethylene trinitramine (RDX) or hexanitrostilbene (HNS) replacements, several detonation parameters such as the detonation pressure, detonation velocity, explosion energy, and explosion temperature were computed using the EXPLO5 code on the basis of the experimental (X-ray) densities and calculated heats of formation. In addition, the sensitivities towards impact, friction, and electrical discharge were tested using the BAM drop hammer, a friction tester, as well as a small-scale electrical discharge device.

Introduction

From an early 21st-century point of view, the practical design of new energetic materials has a long tradition in the materials chemists community. Reaching back at least to the end of the 19th century,[1] when the energetic character of nitrogen-rich materials was first recognized, the development of energetic materials in the 20th century was instead mainly determined by efforts to synthesize cyclic and caged nitramines, as the most prominent examples thereof, RDX,[2] HMX,[3] and CL-20,[4] which cover a wide range of civil and military applications, show. Recent concerns about the environmental impact of energetic materials nowadays have caused a renaissance in the synthesis of so-called green energetic materials,[5] which are based on a high nitrogen content that releases mainly environmentally benign N_2 after decomposition or degradation. Whereas cyclic and caged nitramines decompose into a significant amount of toxic reaction products such as nitro- and nitrosoamines[6] after degradation, the use of nitrogen-rich azoles such as triazole and tetrazole derivatives circumvents the drawbacks, which are related to the use of the above-mentioned nitramines. Not only does the high nitrogen content of triazoles and especially tetrazoles bring the environmental benefit of releasing mainly N_2 after decomposition, it also increases the heat of formation of the compound due to inherently energetic C–N and N–N bonds contained in the molecule. Along with a high heat of formation, a high density, high thermal stability, and low sensitivities towards impact, friction, and electrical discharge of a new material are also amongst the most desirable features when it comes to the synthesis of new energetic compounds with improved detonation performance such as the detonation pressure and the detonation velocity, which both strongly depend on the characteristic values of ρ and enthalpy of formation ($\Delta_f H°$).[7,8]

The authors recently reported on the synthesis and energetic characterization of a series of nitrogen-rich 5,5′-bitetrazololates.[9] These molecules were shown to have excellent thermal stabilities while being comparatively insensitive, despite their very high nitrogen contents of up to 83%.

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A further improvement of the energetic character of tetrazole-containing compounds was demonstrated by the introduction of *N*-oxides,[10–12] in that the density is increased by further possibilities to form hydrogen bonds in the solid state, and also the oxygen content of the molecule is better balanced, thus ensuring a maximum energy output when the compound decomposes to low heat of formation products such as CO_2, H_2O, and N_2.

A very promising candidate that fulfils a variety of the aforementioned desirable properties is 1*H*,1′*H*-5,5′-bitetrazole-1,1′-diol. This dihydroxylated bitetrazole is strongly acidic and bears two protons, which can be easily abstracted by nitrogen-rich bases such as ammonia, guanidine, or even other tetrazole derivatives. We recently described the energetic properties of its dihydroxylammonium salt, which shows great promise for use as an explosive filler in the future.[13] Scheme 2 gives an overview about the 1*H*,1′*H*-5,5′-bitetrazole-1,1′-diolates discussed herein, all of which were structurally characterized by low-temperature single-crystal X-ray diffraction.

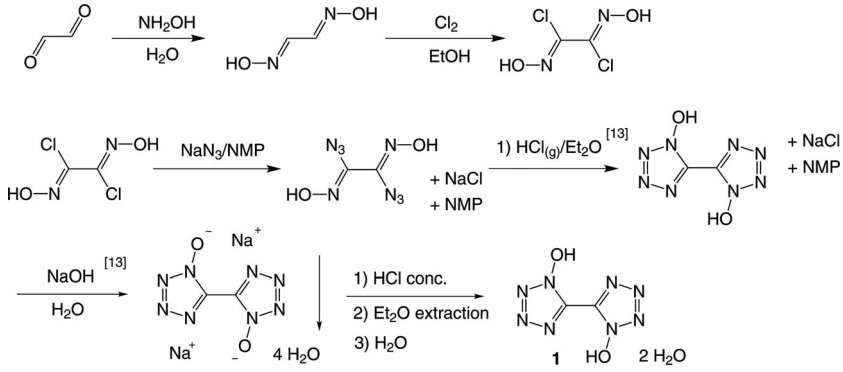
Results and Discussion

Synthesis

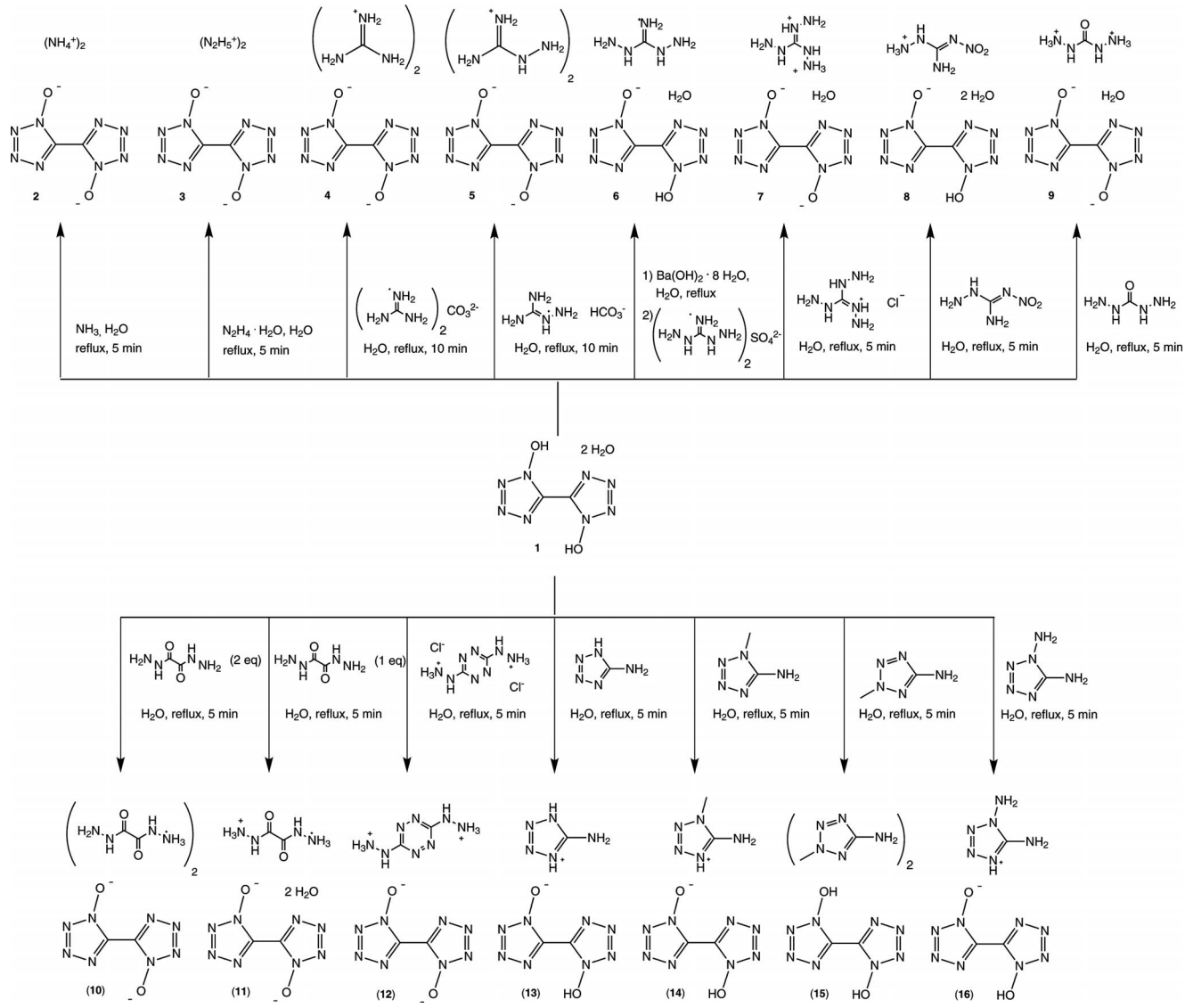
The synthesis of the nitrogen-rich salts **2**–**16** necessarily needs to start with the synthesis of the free acid 1*H*,1′*H*-5,5′-bitetrazole-1,1′-diol (**1**), which is depicted in Scheme 1. Oxidation of 5,5′-bitetrazole by using oxone or hypofluoric acid yields mixtures of the 1,1′-, 1,2′-, and favored 2,2′-dihydroxy derivatives. Tselinskii et al.[14] reported the formation of this dihydroxylated heterocycle in 2001 upon cyclization of diazidoglyoxime, which itself is synthesized by starting from commercially available glyoxal. Glyoxal is treated with hydroxylamine to form glyoxime. Chlorination of glyoxime with Cl_2 gas in ethanol affords dichloroglyoxime, which is cyclized under acidic conditions (HCl gas in diethyl ether) to form **1**. To avoid the isolation of the highly sensitive diazidoglyoxime, the chloro/azido exchange is performed in *N*-methylpyrrolidinone (NMP), whereas the entire mixture of NMP, the dissolved covalent diazide, and precipitated sodium chloride is directly poured onto diethyl ether, a safer procedure that has recently been developed by the authors.[13] After treating the mixture with HCl gas, the cyclized product **1** can be isolated as its disodium salt by filtration after removing diethyl ether and excess amounts of HCl gas, followed by the addition of two equivalents of 2 M NaOH to the NMP-containing mixture. The free acid is obtained by acidifying an aqueous solution of the disodium salt of **1** with concentrated HCl and subsequent extraction of the aqueous solution with diethyl ether (Scheme 1).

Starting from **1**, all compounds except the diamino-, the triaminoguanidinium, and the 3,6-dihydrazino-1,2,4,5-tetrazinium salt **6**, **7**, and **12** were synthesized after treating **1** with stoichiometric amounts of the respective free base or, in the cases of guanidinium and aminoguanidinium salts **4** and **5**, the respective carbonate (**4**) and hydrogen carbonate (**5**). An overview is depicted in Scheme 2. The diaminoguanidinium salt **6** was isolated from a reaction mixture that contained the barium salt of **1** and diaminoguanidinium sulfate after removing the poorly soluble barium sulfate by filtration. The triaminoguanidinium salt **7** crystallized from a mixture that contained the free acid **1** and triaminoguanidinium chloride, and also for the 3,6-dihydrazinium-1,2,4,5-tetrazine salt **12** the respective chloride salt was treated with **1**. With regard to the stoichiometries used in the different reaction mixtures, we anticipated the isolation of 2:1 compounds so that 2:1 stoichiometries were also used in the respective reactions, except for **8**, for which, due to its low water solubility, only one equivalent of 1-amino-3-nitroguanidine was used to avoid precipitation of the base, and for **12**, since the tetrazine derivative was used as its dihydrochloride. However, what we observed was the crystallization of compounds with a 2:1 stoichiometry in the cases of **1**–**4**, **10**, and **15** and, unexpectedly, a 1:1 stoichiometry in the cases of **5**–**8**, **11**–**14**, and **16**, with even double-protonated cations in the cases of **7**, **9**, **11**, and **12**.

Aminoguanidinium chloride was synthesized from aminoguanidinium hydrogen carbonate by acidification with HCl. The resulting aminoguanidinium chloride was treated with hydrazine hydrate (2 equiv.) in 1,4-dioxane under N_2 to form the triaminoguanidinium synthon. Diaminoguanidinium sulfate was obtained from commercially available diaminoguanidinium chloride after ion exchange.[15] Diaminourea[16] and oxalyldihydrazide[17] were obtained from the reaction of hydrazine hydrate with di-



Scheme 1. Synthesis of 1*H*,1′*H*-5,5′-bitetrazole-1,1′-diol (**1**).



Scheme 2. Synthesis of the nitrogen-rich salts **2**–**16**.

methylcarbonate or diethylmalonate, respectively. The first step in the synthesis of 3,6-dihydrazino-1,2,4,5-tetrazinium dichloride monohydrate was the reaction of triaminoguanidinium chloride with pentane-2,4-dione to form 3,6-bis[(3,5-dimethyl)pyrazol-1-yl]-1,2-dihydro-1,2,4,5-tetrazine,[18,19] which was subjected to a hydrazinolysis reaction to form 3,6-dihydrazino-1,2,4,5-tetrazine. Further reaction with hydrochloric acid in methanol yielded the dichloride. The methylated 5-aminotetrazoles 1-methyl- and 2-methyl-5-aminotetrazole were obtained by methylation of commercially available 5-aminotetrazole.[20] 1,5-Diaminotetrazole was prepared by the reaction of thiosemicarbazide and sodium azide in the presence of lead(II) oxide and ammonium chloride,[21] and 1-amino-3-nitroguanidine was gained from a hydrazinolysis reaction of nitroguanidine.[22,23]

The solubility of **1** and its nitrogen-rich salts **2**–**16** is only moderate in water, so crystals of **1**–**16** suitable for X-ray single-crystal measurements were obtained after filtration and slow evaporation of the aqueous mother liquors. Efforts to crystallize **1** without crystal water resulted in the formation of a methanol adduct[13] when recrystallized from dry methanol, or the dihydrate **1** when recrystallized from glacial acetic acid or acetonitrile.

Crystal Structures

Suitable single crystals of the described compounds **1**–**16** were picked from the crystallization mixture and mounted in Kel-F oil, transferred to the N_2 stream of an Oxford Xcalibur3 diffractometer with a Spellman generator (voltage 50 kV, current 40 mA) and a KappaCCD detector using a Mo-K_α radiation wavelength of λ = 0.71073 Å. All structures were measured at –100 °C. The data collection and data reduction was carried out with the CrysAlisPro software.[24] The structures were solved with Sir-92,[25] Sir-97,[26] or SHELXS-97,[27] refined with SHELXL-97,[28] and finally checked using the Platon software[29] integrated in the

WinGX software suite.[30] 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.[31] Data and parameters of the measurements and refinements are gathered in Tables S1, S2, and S3 in the Supporting Information. Exact bond lengths, angles, and selected hydrogen bonds are also given in the Supporting Information in Tables S3–S12.

Here, only three examples of the determined crystal structures, which from the crystallographic point of view appear to have interesting properties, are discussed. The discussion of the solid-state structures of the remaining compounds can be found in the Supporting Information.

Despite a reactand stoichiometry of 2:1, diaminoguanidinium salt **6** was only obtained as its monodeprotonated 1′-hydroxy-1*H*,1′*H*-5,5′-bitetrazol-1-olate salt (stoichiometry 1:1) with the inclusion of one molecule of crystal water per molecular unit. Compound **6** crystallizes in the triclinic space group $P\bar{1}$ with two molecules in the unit cell and a density of 1.729 g cm^{-3}. In the structure of **6**, the monodeprotonated anions build long chains along the *a* axis by formation of very strong hydrogen bonds H1^{i}···O2 and H1···O2^{ii}, which are nearly symmetrical and similar to those observed in the HF_2^- anion (Figure 1).

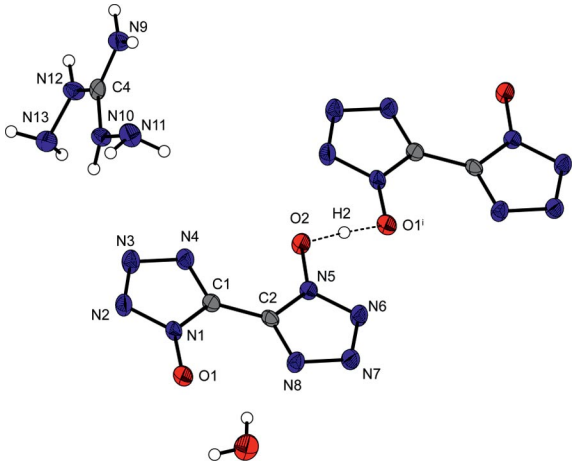


Figure 1. View of a selected detail of the crystal structure of **6** showing the nearly symmetric hydrogen bridge O2–H2···O1^{i}. Ellipsoids are shown at the 50% probability level. Symmetry code: (i) –1 + *x*, *y*, *z*.

In agreement with **6**, triaminoguanidinium salt **7** could be obtained in the crystalline state with one molecule of crystal water as a compound with 1:1 stoichiometry. It crystallizes in the triclinic space group $P\bar{1}$ with two molecules in the unit cell and a comparatively high density of 1.749 g cm^{-3}, which could be explained by the stronger attractive ionic forces between the twice positively/negatively charged ions. The coordination geometry of a single anion consists of interactions with four triaminoguanidinium cations and two hydrate water molecules. There are only very few ionic examples of twice positively charged triaminoguanidinium cations (e.g., its sulfate salt) (Figure 2).[15]

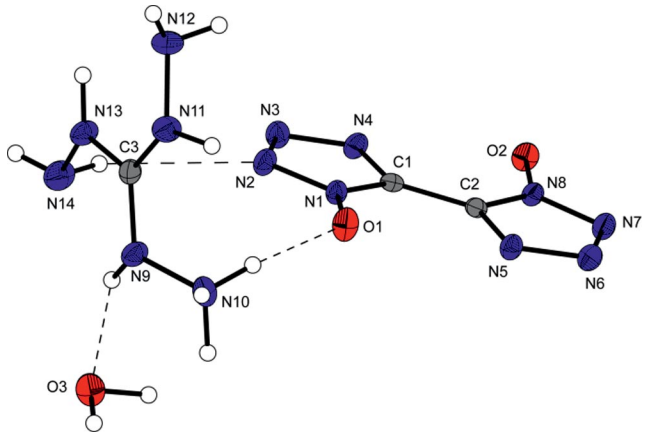


Figure 2. Molecular unit of crystalline **7** with its labeling scheme. Ellipsoids are shown at the 50% probability level.

In the structure of **15**, no proton transfer between **1** as the acid and 2-methyl-5-aminotetrazole as the base is observed. It must be described as a cocrystallization product between the two mentioned species (Figure 3). The fact that 5-amino-2-methyl-2*H*-tetrazole is a weaker base than 5-amino-1-methyl-1*H*-tetrazole has been demonstrated in similar crystal structures before.[32] Compound **15** crystallizes in the monoclinic space group *C*2/*c* with four molecules in the unit cell and a density of 1.608 g cm^{-3}, which is remarkably lower than **14** owing to the lack of ionic attractive forces, although the structure is stabilized by strong hydrogen bonds. The most important, since it is the shortest hydrogen bond, is found between O1^{i}–H1···N8^{ii} with a distance of 1.32(19) Å. This is only slightly longer than the O–H bond length in **1** [1.192(19) Å]. Unlike in all ionic structures described in this work, the two tetrazole moieties in **1** are distorted as evidenced by the torsion angle (N1–C1–C1^{i}–N1^{i}) of –122.98(16)°.

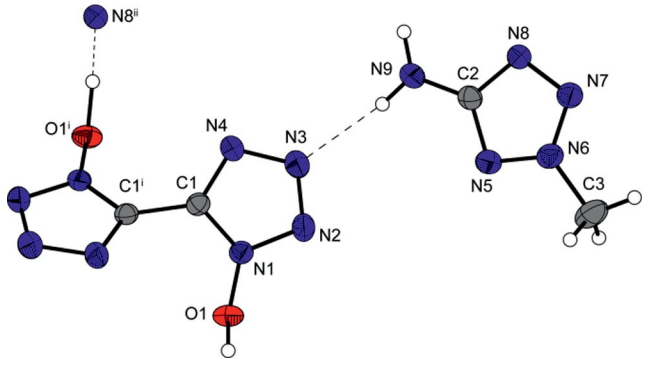


Figure 3. Molecular unit of crystalline **15** with its labeling scheme. Ellipsoids are shown at the 50% probability level. Symmetry codes: (i) –*x*, *y*, 0.5 – *z*; (ii) –*x*, *y*, 0.5 – *z*.

Spectroscopy

NMR Spectroscopy

Compounds **1**–**16** were investigated using ^{1}H and ^{13}C NMR spectroscopy. Additionally, ^{15}N NMR spectra of **1**

as well as of its ammonium salt **2** were recorded. For better comparison, all spectra were measured using [D_6]DMSO as solvent and all chemical shifts are given with respect to TMS (^{1}H, ^{13}C) or nitromethane (^{15}N).

In the proton NMR spectra of **2**, **3**, **10**, **11**, **13**, **14**, and **15**, all N-connected protons contained in the cation are visible as only one singlet, which appears between δ = 7.07 and 8.72 ppm. For the 5-aminotetrazolium salt **13**, an exceptionally high value of δ = 11.90 ppm is observed. Except for the ammonium salt **2**, a fast proton exchange causes the coincidence of the signals of the chemically nonequivalent protons. For the guanidinium derivatives **4**–**8**, the signals of chemically nonequivalent protons can be distinguished well. The NH_2 protons of **4** are visible as a singlet at δ = 7.10 ppm, whereas two singlets appear for the protons of **7** and **8** for NH_2 [δ = 4.46 (**7**), 7.03 ppm (**8**)] and NH [δ = 8.62 (**7**), 8.27 ppm (**8**)]. The amino- and diaminoguanidinium salts **5** and **6** reveal three separated signals for CNHNH_2 [δ = 4.60 (**5**), 5.15 ppm (**6**)], CNH_2 [δ = 7.01 (**5**), 7.10 ppm (**6**)], and $CNHNH_2$ [δ = 8.89 (**5**), 8.50 ppm (**6**)]. In contrast to the hydrazinium salt **3**, in the spectra of the hydrazino-moiety-containing compounds **9** and **12**, the signals for NH [δ = 8.31 (**9**), 9.57 ppm (**12**)] can be distinguished from the signals for NH_3^+ [δ = 7.80 (**9**), 6.38 ppm (**12**)]. Furthermore, the existence of the methyl groups in the cations of **14** and **15** is evidenced by resonances at δ = 3.67 (**14**) and 4.07 ppm (**15**). For the anionic species in **2**–**16**, a single resonance at δ = 134.5–135.8 ppm in the ^{13}C NMR spectrum is observed, which does not significantly differ from the signal of the neutral species **1** (δ = 135.8 ppm). However, this signal differs significantly from the signals observed for the precursor molecules glyoxime (δ = 145.9 ppm), dichloroglyoxime (δ = 131.2 ppm), and diazidoglyoxime (δ =136.5 ppm), which makes NMR spectroscopy the analytical procedure of choice to monitor the completeness of these reactions. A second signal of the cation is visible in each carbon NMR spectrum in the range of δ = 158.6–160.2 ppm for the guanidine derivatives **4**–**8**, in the range of δ = 157.8–159.6 ppm for the carbohydrazide derivatives **9**–**11**, δ = 162.5 ppm for **12**, and δ = 154.2–167.7 ppm for the substituted tetrazolium cations in **13**–**16**, respectively.

In the ^{15}N NMR spectrum of the free acid **1**, a set of four signals according to the four chemically nonequivalent nitrogen atoms of the two tetrazole moieties [C_i symmetry of the 5,5′-bis(tetrazole 1-oxide) molecule] can be found (Figure 4). A partial assignment was undertaken according to a gauge-including atomic orbital (GIAO) NMR spectroscopic calculation with Gaussian 09,[33] which gave the relative NMR spectroscopic shifts of both **1** and **2** in good accordance. Thereafter, the β-nitrogen atoms N3 and N2 are shifted to the lowest field. For unsubstituted 5,5′-bitetrazole, two signals at δ = 3 and –66 ppm are observed,[9] according to the β- (δ = 3 ppm) and the α-nitrogen atoms (δ = –66 ppm). In the spectra of **1** and **2**, N3 is assigned to signals at δ = –2.0 ppm (**1**, **2**) and N2 to signals at δ = –18.7 (**1**) and –19.8 ppm (**2**). A larger difference, however, is observed for the chemical shifts of the α-nitrogen atoms of **1** and **2**, since, unlike N4, N1 is hydroxyl-substituted. For N4, signals at δ = –52.3 (**1**) and –53.6 ppm (**2**) are observed, which is comparable to the chemical shift of the α-nitrogen atoms in unsubstituted 5,5′-bitetrazole (δ = –66 ppm), whereas the signal for the hydroxylated N1 are found at δ = –110.5 (**1**) and –107.5 ppm (**2**), respectively. In the spectrum of **2**, an additional signal at δ = –359.7 ppm for the ammonium cation is visible as a quintet due to NH coupling ($^1J_{N,H}$ = 71.6 Hz).

Vibrational Spectroscopy

The assignments of the observed absorption bands to the corresponding functional groups was undertaken on the basis of values found in literature.[34] The Raman and IR spectra of all investigated compounds show absorptions of the aromatic ring system of the 5,5′-bis(tetrazole 1-oxide) anion at 1350–1550 and 700–1350 cm^{-1} [ν(NN), ν(NCN), γ(CN), δ(aromatic tetrazole oxide ring)], which partially are in the fingerprint region. Furthermore, the N–O$^-$ vibration can barely be observed in a range of 1550–1600 cm^{-1}. In all cases, hydroxyl groups, which are involved in hydrogen

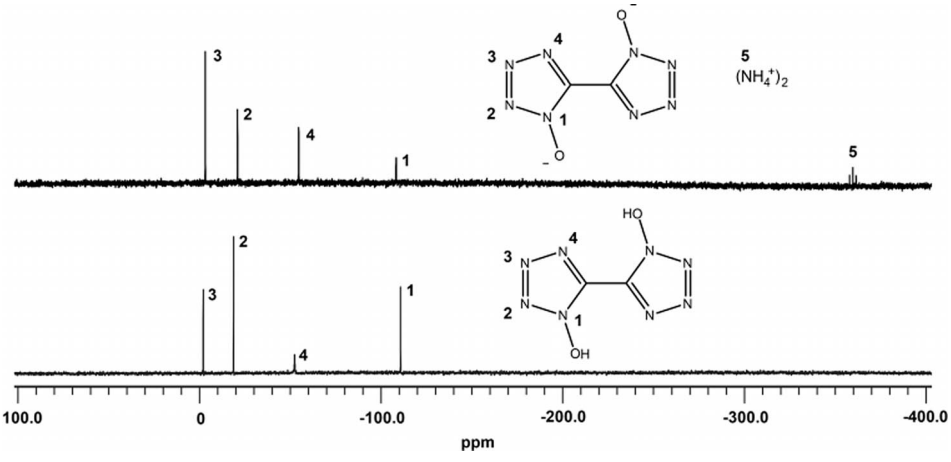


Figure 4. ^{15}N NMR spectra of **1** and **2**. Chemical shifts are given with respect to $MeNO_2$.

bonding, can be detected as absorptions in the range of 3209–3454 cm^{-1} [ν(O–H)].

In the Raman spectrum of the ammonium salt **2**, an absorption at 3075 cm^{-1} [$\nu_{sym}(NH_4^+)$] can be observed, whereas the IR spectrum exhibits several signals in the range of 3047–3180 cm^{-1}, which refer to the asymmetric valence vibrations of the ammonium cation.

Vibrations of the hydrazinium cation in **3** as well as those of the hydrazino groups of diaminourea in compound **9** and the hydrazine moiety in the cation of **12** can be observed in the range of 3059–3434 cm^{-1} [$\nu_{asym}(NH_2/NH_3^+)$] and also in the range of 1535–1620 cm^{-1} [$\delta_{sym}(NH_2/NH_3^+)$, $\delta_{asym}(NH_2/NH_3^+)$]. Furthermore, the carbonyl moiety of the diaminourea cation of **9** reveals a sharp absorption band at 1702 cm^{-1}, whereas the stretching and deformation vibrations of the tetrazine ring (in **12**) are located in the same region as those of the bitetrazole dioxide ring system discussed above.

The spectra of the guanidine derivatives **4**–**8** show absorption bands of valence vibrations of the amino groups at 3000–3500 cm^{-1} [$\nu_{sym}(NH_2)$, $\nu_{asym}(NH_2)$]. Furthermore, deformation vibrations of the amino groups can be found at 1577–1690 cm^{-1} [$\delta_{sym}(NH_2)$, $\delta_{asym}(NH_2)$]. Moreover, valence vibrations of the C–N double bonds in the guanidine part of the cations appear at 1680–1470 cm^{-1} [ν(C=N)]. Another characteristic absorption band of the nitroamine in the cation of **8** is observed at 1262 cm^{-1} in the IR spectrum.

The spectra of both compounds **10** and **11** show the symmetric deformation vibration of the protonated hydrazino groups, the absorption bands of which are located at 1615 cm^{-1} [$\delta_{sym}(NH_3^+)$] and are clearly visible in the Raman spectra. A further strong absorption at 1677 cm^{-1} [$\delta_{asym}(NH_3^+)$] can be assigned to the C=O valence vibration of the carbohydrazide moiety in both compounds. Moreover, the asymmetric valence vibrations of the NH group of the hydrazino moieties is observed at 3029 cm^{-1} [ν_{asym}(NH), **10**] and at 3074 cm^{-1} [ν_{asym}(NH), **11**]. The asymmetric C–H valence vibration of the methyl group in the IR spectra as well as the symmetric one in the Raman spectra of compounds **14** and **15** can be observed at 2960 and 2966 cm^{-1} [$\nu_{sym}(CH_3)$] and at 2850–2960 cm^{-1} [$\nu_{asym}(CH_3)$]. Also, the –CH_3 deformation vibration is visible in absorptions at 1439 [$\delta_{asym}(CH_3)$] and 1390 cm^{-1} [$\delta_{sym}(CH_3)$] in the spectra of **15**.

In contrast to the aminotetrazolium salts **13**–**15**, which have their very sharp absorption bands at 1703 (**13**), 1693 (**14**), and 1659 cm^{-1} (**15**) [$\delta_{asym}(NH_2)$] and 1624 (**13**), 1616 (**14**), and 1627 cm^{-1} (**15**) [$\delta_{sym}(NH_2)$], the diamino-substituted cation in **16** exhibits a broadened signal at 1577–1731 cm^{-1} [$\delta_{sym}(NH_2)$, $\delta_{asym}(NH_2)$] because of the existence of two amino groups.

Thermal Behavior and Sensitivities

Differential scanning calorimetry (DSC) measurements to determine the melt and decomposition temperatures as well as the dehydration temperature of the crystal water that contained free acid **1** and salts **2**–**16** (about 1.5 mg of each energetic material) were performed in covered Al containers with a hole (0.1 mm) in the lid for gas release and a nitrogen flow of 20 mL per minute with a Linseis PT 10 DSC[35] calibrated by standard pure indium and zinc at a heating rate of 5 °C min^{-1}. The decomposition temperatures are given as absolute onset temperatures.

Except for the 1-amino-3-nitroguanidinium salt **8**, the nonionic compound **15**, and the 1,5-diaminotetrazolium salt **16**, the decomposition temperatures for all remaining salts are at or even above 180 °C, which is a necessary requirement for possible RDX replacements, which itself decomposes at about 210 °C. The low decomposition temperature of the 1-amino-3-nitroguanidinium salt **8** is in agreement with other energetic compounds based on this cation in the literature.[23] Also, the low decomposition temperature of **16** is in agreement with other 1,5-diaminotetrazolium-based materials.[36] This is in contrast to the 5-aminotetrazolium salt **13**, which is stable up to 224 °C. A potential reason for the low decomposition temperature of **15** (155 °C) is possibly the lack of ionic attractive forces in the solid state, which can be easily compared to the ionic structure of **14**, the sister compound, which is methylated at the 1-position of the tetrazole ring and is thermally stable up to 192 °C. The highest decomposition temperature is observed for the ammonium salt **2** (290 °C); however, the hydrazinium salt **3** as well as the other hydrazino-moiety-containing compounds **9**–**12** decompose significantly earlier at 220–224 °C (**3**, **9**–**11**) and 180 °C (**12**). A comparison between the guanidinium salts **4**–**7** shows that **4** reveals by far that the highest decomposition temperature is 274 °C, whereas **5**–**7** decompose at 204–210 °C. The loss of crystal water in the hydrated compounds **6**–**9** and **11** can be observed as endothermic steps in the cases of **6** (160 °C), **8** (140 °C, immediately before decomposition), and **11** (110 °C). In **6**, the hydrate water seems to be comparatively strongly bonded by hydrogen bonds, because it cannot be removed before 160 °C. Also, melting points are observed in the DSC traces of **5**, **6**, and **14**–**16**, as evidenced by (additional) endothermic steps. In the cases of **5**, **6**, **14**, and **16**, the materials melt right before decomposition, whereas adduct **15** has a melting point that is somewhat below its decomposition temperature (T_m = 125 °C). For the free acid **1**, which crystallizes as a dihydrate, a decomposition temperature of 214 °C and a dehydration temperature of 115 °C were recorded. By heating the compound to 140 °C for 24 h, the crystal water could completely be removed as evidenced by elemental analysis. However, the crystals were destroyed upon dehydration, so that no crystal structure of the water-free compound could be obtained. Due to its hygroscopicity, dehydrated **1** returns into its dihydrate after standing for several days at ambient humidity. Furthermore, there is no risk of losing the hydrate water at room temperature and low air humidities over time. The missing endothermic event in the DSC curves of the hydrated salts **7** and **9** indicates that either the crystal water was lost after standing at ambient temperatures over time or it is released during decomposition of the salt.

The impact sensitivity tests of compounds **1**–**16** were carried out according to STANAG 4489[37] modified instruction[38] using a BAM (Bundesanstalt für Materialforschung und -prüfung) drop hammer.[39] The friction-sensitivity tests were carried out according to STANAG 4487[40] modified instruction[41] using the BAM friction tester. The classification of the tested compounds resulted from the "UN Recommendations on the Transport of Dangerous Goods."[42] Additionally, all compounds were tested for their sensitivity towards electrical discharge with the Electric Spark Tester ESD 2010 EN.[43]

First, it has to be mentioned that the precursor material diazidoglyoxime, as one would expect for a covalent diazide, was determined to be very impact- and extremely friction-sensitive (IS: 1.5 J, FS: <5 N) and required extreme caution if being isolated. In contrast, cyclized **1** as its dihydrate proved to be impact-insensitive (>4 J) and only moderately sensitive towards friction (216 N). However, the free acid **1**, which was dried at 140 °C for 24 h, revealed sensitivities of 4 J (IS) and 10 ⁿ (FS) and therefore needs to be handled with greater care.

Owing to their impact sensitivity of more than 35–40 J, compounds **2**, **5**, **11**, and **12** can be classified as less sensitive, which in the case of **11** probably can be explained by a dihydrate formation. The guanidinium salt **4** is even insensitive towards impact with a value of more than 40 J. Compounds **3** and **6**–**10** show sensitivities in the range of 9–20 J and therefore can be classified as sensitive towards impact. Expectedly, the protonated tetrazolium salts **13**, **14**, and **16** as well as the hydrogen-bond-stabilized adduct with 2-methyl-5-aminotetrazole (**15**) reveal the lowest values for impact sensitivity and are therefore classified as sensitive (**14**, **15**) or very sensitive towards impact (**13**, **16**). Except for **11**, no apparent desensitization of the materials is observed when hydrate water is included as it is the case for **6**–**9**.

For the friction sensitivity the same trends as for the impact sensitivity were observed. However, a few exceptions were observed [e.g., bishydrazinotetrazinium salt **12**, which is friction-sensitive (80 N) but insensitive towards impact (40 J)]. The opposite behavior is observed for **15**, which is insensitive towards friction (360 N) but impact-sensitive (8 J). Furthermore, again the guanidinium salt **4** is the least sensitive compound (>360 N), and **2**, **10**, and **15** can also be classified as less sensitive. The remaining compounds fill the space between being less sensitive (360 N) to very sensitive (80–10 N), with the 5-aminotetrazolium salt (**13**, 72 N) being the most sensitive compound.

The sensitivity towards electrical discharge next to the compound itself depends on the grain size of the material, whereas larger crystals tend to be less sensitive and powders show enhanced sensitivity. For this reason, the grain size of the materials is given in the Experimental Section. With regard to the grain size, the guanidinium (**4**) as well as the 1-methyl-5-aminotetrazolium salt **14** were determined to be the least sensitive compounds, and the hydrazinium salt **9** (0.10 J) as well as the 1-amino-3-nitroguanidinium (**8**) and the 3,6-dihydrazino-1,2,4,5-tetrazinium salt **12** (both 0.08 J) were determined to be the most sensitive, although it should be mentioned that the human body can generate up to 25 mJ of static electricity through normal activities, which can easily set off the most sensitive explosives, but is well below the value found for the most sensitive compounds presented here.

Theoretical Calculations

Heats of Formation

Usually energetic materials tend to explode in bomb calorimetric measurements. Consequently, doubtful combustion energies are obtained. Therefore, heats of formation of energetic materials mostly are calculated theoretically. In our group we combine the atomization energy method [Equation (1)] with CBS-4M electronic enthalpies (Table 1), which has been shown to be suitable in many recently published studies.[44] CBS-4M energies of the atoms, cations, and anions were calculated with the Gaussian 09 (revision A1) software package[33] and checked for imaginary frequencies. Values for $\Delta_f H°$ (atoms) were taken from the NIST database.[45]

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

Table 1. CBS-4M results and gas phase enthalpies.

	Formula	$-H_{298}$[a] [a.u.]	$\Delta_f H(g)$[b] [kJ mol^{-1}]
1	$C_2H_2N_8O_2$	664.816722	689.1
BTO^-	$C_2HN_8O_2^-$	664.334858	420.7
BTO^{2-}	$C_2N_8O_2^{2-}$	663.687267	587.7
NH_4^+	NH_4^+	56.796608	635.8
$N_2H_5^+$	$N_2H_5^+$	112.030523	774.1
G^+	$CH_6N_3^+$	205.453192	571.9
AG^+	$CH_7N_4^+$	260.701802	671.6
DAG^+	$CH_8N_5^+$	315.949896	772.7
TAG^{2+}	$CH_{10}N_6^+$	371.348640	2012.3
ANQ^+	$CH_6N_5O_2^+$	464.914496	877.0
DAU^{2+}	$CH_7N_4O^+$	335.970626	1726.2
$Oxahy^+$	$C_2H_7N_4O_2^+$	448.979375	550.6
$Oxahy^{2+}$	$C_2H_8N_4O_2^{2+}$	449.181787	1553.2
BHT^{2+}	$C_2H_8N_8^{2+}$	517.532665	2307.0
$5\text{-}AT^+$	$CH_4N_5^+$	313.534215	981.8
$1\text{-}Me\text{-}5\text{-}AT^+$	$C_2H_6N_5^+$	352.779155	935.2
2-Me-5-AT	$C_2H_5N_5$	352.445333	277.8
$1,5\text{-}DAT^+$	$CH_5N_6^+$	368.793548	1053.4

[a] CBS-4M enthalpy at room temperature. [b] Calculated gas phase heat of formation by the atomization equation.

For calculation of the solid-state energy of formation (Table 2) of **1**–**16**, the lattice energy (U_L) and lattice enthalpy (ΔH_L) were calculated from the corresponding molecular volumes (obtained from X-ray elucidations) according to the equations provided by Jenkins and Glasser et al.[46] With the calculated lattice enthalpy (Table 3), the gas-phase enthalpy of formation was converted into the solid-state (standard conditions) enthalpy of formation. In the case of the neutral compounds **1** and **15**, their sublimation enthalpy was calculated with Trouton's rule (ΔH_{sub} [kJ mol]

Table 2. Solid-state energies of formation ($\Delta_f U°$).

	$\Delta_f H°$(g)[a] [kJ mol^{-1}]	V_M[b] [nm^3]	U_L[c] [kJ mol^{-1}]	ΔH_L[d] [kJ mol^{-1}]	$\Delta_f H°$(s)[e] [kJ mol^{-1}]	Δn[f]	$\Delta_f U°$(s)[g] [kJ mol^{-1}]	Formula	M_r [g mol^{-1}]	$\Delta_f U°$(s)[h] [kJ kg^{-1}]
1	205.9			91.58[#]	114.3	9	136.6	$C_2H_6N_8O_4$	206.12	662.8
2	1859.4	0.188	1551.4	1558.9	300.5	10	325.3	$C_2H_8N_{10}O_2$	204.15	1592.9
3	2136.0	0.225	1450.9	1458.3	677.7	12	707.4	$C_2H_{10}N_{12}O_2$	234.18	3020.2
4	1731.5	0.292	1316.2	1323.5	408.0	14	442.7	$C_4H_{12}N_{14}O_2$	288.28	1535.5
5	1930.9	0.331	1254.8	1262.3	668.6	16	708.3	$C_4H_{14}N_{16}O_2$	318.31	2225.0
6	951.8[h]	0.242	538.7	542.1	409.6	13.5	443.1	$C_3H_{11}N_{13}O_3$	277.27	1598.2
7	2358.5[h]	0.253	2029.4	2041.8	316.7	14.5	352.6	$C_3H_{12}N_{14}O_3$	292.27	1206.5
8	814.5[h]	0.255	582.5	592.4	222.1	15	259.3	$C_3H_{11}N_{13}O_6$	325.10	797.4
9	2072.3[h]	0.232	2080.6	2093.0	–20.7	13	11.6	$C_3H_{10}N_{12}O_4$	278.23	41.6
10	1688.8	0.365	1208.5	1216.0	472.9	18	517.5	$C_6H_{14}N_{16}O_6$	406.33	1273.5
11	1657.7[h]	0.237	2122.1	2136.9	–479.2	15	–442.0	$C_6H_{12}N_{12}O_6$	324.26	–1363.3
12	2894.7	0.290	1896.9	1906.8	987.9	13	1020.1	$C_4H_8N_{16}O_2$	202.18	3266.7
13	1402.5	0.230	486.5	491.4	911.1	10	935.9	$C_3H_5N_{13}O_2$	255.20	3667.0
14	1355.8	0.254	474.4	479.3	876.5	11	903.8	$C_4H_7N_{13}O_2$	269.18	3356.8
15	1244.7			80.5[i]	1164.2	16	1203.8	$C_6H_{12}N_{18}O_2$	368.34	3268.1
16	1474.0	0.246	478.5	483.4	990.6	11	1017.9	$C_3H_6N_{14}O_2$	270.22	3766.8

[a] Gas-phase enthalpies of formation (those of the ionic compounds are taken as the respective sums of the noninteracting component ions). [b] Molecular volume of the molecular moiety in the crystal structure. [c] Lattice energy calculated by Jenkins and Glasser equations. [d] Lattice enthalpy calculated by Jenkins and Glasser equations. [e] Solid-state molar heat of formation. [f] Change in moles of gaseous components. [g] Molar energy of formation. [h] Energy of formation (mass-dependent). [h] Gas-phase enthalpy of included water has been subtracted. [i] Sublimation enthalpy calculated by the Trouton rule.

Table 3. Energetic properties and detonation parameters of **1**–**8**.

	1	**2**	**3**	**4**	**5**	**6**	**7**	**8**
Formula	$C_2H_6N_8O_4$	$C_2H_8N_{10}O_2$	$C_2H_{10}N_{12}O_2$	$C_4H_{12}N_{14}O_2$	$C_4H_{14}N_{16}O_2$	$C_3H_{11}N_{13}O_3$	$C_3H_{12}N_{14}O_3$	$C_3H_{11}N_{13}O_6$
M_r [g mol^{-1}]	206.12	204.18	234.18	288.28	318.31	277.27	292.27	325.10
IS [J][a]	>40	35	9	>40	40	12	15	10
FS [N][b]	216	360	252	>360	324	168	120	192
ESD-test [J][c]	0.50	0.25	0.10	0.50	0.25	0.25	0.25	0.08
N [%][d]	54.4	68.6	71.8	68.0	70.4	65.7	67.1	56.0
Ω [%][e]	–23.28	–47.02	–47.82	–66.60	–65.35	–49.06	–49.27	–27.06
$T_{dec.}$ [°C][f]	214	290	220	274	228	204	210	140
$\rho_{calcd.}$ [g cm^{-3}][g]	1.811	1.800	1.725	1.639	1.596	1.729	1.749	1.778
$\Delta_f H_m°$ [kJ mol^{-1}][h]	114.3	300.5	677.7	408.0	668.6	409.6	316.7	222.1
$\Delta_f U°$ [kJ kg^{-1}][i]	662.8	1592.9	3020.2	1535.5	2225.0	1598.2	222.1	797.4
Detonation parameters calculated with EXPLO5.05								
$-\Delta_E U°$ [kJ kg^{-1}][j]	5043	4213	5415	3581	4160	4439	2981	5118
T_E [K][k]	3625	2939	3433	2606	2852	3072	2342	3599
p_{CJ} [kbar][l]	331	316	340	233	243	294	246	325
D [m s^{-1}][m]	8764	8817	9159	7917	8111	8598	8028	8796
Gas vol. [L kg^{-1}][n]	810	843	863	806	825	837	844	840
I_{sp} [s][o]	240	211	246	194	212	215	179	241

[a] Impact sensitivity (BAM drop hammer, 1 of 6). [b] Friction sensitivity (BAM friction tester, 1 of 6). [c] Electrostatic discharge device (OZM). [d] Nitrogen content. [e] Oxygen balance.[50] [f] Decomposition temperature from DSC (β = 5 °C/min). [g] Estimated from X-ray diffraction. [h] Calculated (CBS-4M) heat of formation. [i] Calculated energy of formation. [j] Energy of explosion. [k] Explosion temperature. [l] Detonation pressure. [m] Detonation velocity. [n] Assuming only gaseous products. [o] Specific impulse calculated at isobaric (60 bar) rocket conditions.

= 188 T_m [K]).[47] These molar standard enthalpies of formation [$\Delta_f H°$(s)] were used to calculate the molar solid-state energies of formation (ΔU_m) according to Equation (2) (see Tables 3 and 4).

$$\Delta U_m = \Delta H_m - \Delta nRT \quad (2)$$

(Δn is the change in moles of gaseous components)

The solid-state energies of formation range from highly positive values (>3000 kJ kg^{-1}) for the hydrazinium salt (**3**) as well as the bis(hydrazinotetrazinium) (**12**) and the tetrazolium derivatives (**13**–**16**) to negative energies of formation for the oxalyldihydrazidinium salt **11** (–1363 kJ kg^{-1}). Besides **11**, the diaminouronium salt **9** also reveals a comparatively low value of 42 kJ kg^{-1}, which in both cases is due to their high lattice enthalpy (both are 1:1 compounds with double-charged an-/cations) and hydrate formation. The highest energies of formation are found for the tetrazolium derivatives, which have a large number of inherently energetic N–N single and double bonds in combination with a solvent-free crystallization such as for the 5-amino- and 1,5-diaminotetrazolium derivatives **13** (3667 kJ kg^{-1}) and **16** (3767 kJ kg^{-1}).

Table 4. Energetic properties and detonation parameters of **9**–**16**.

	9	**10**	**11**	**12**	**13**	**14**	**15**	**16**	RDX	HMX
Formula	$C_3H_{10}N_{12}O_4$	$C_6H_{14}N_{16}O_6$	$C_4H_{12}N_{12}O_6$	$C_4H_8N_{16}O_2$	$C_3H_5N_{13}O_2$	$C_4H_7N_{13}O_2$	$C_6H_{12}N_{18}O_2$	$C_3H_6N_{14}O_2$	$C_3H_6N_6O_6$	$C_4H_8N_8O_8$
M_r [g mol^{-1}]	278.23	406.33	324.26	202.18	255.20	269.18	368.34	270.22	222.12	296.16
IS [J][a]	20	20	40	40	4	6	8	2	7.5[51]	7[51]
FS [N][b]	240	360	288	80	72	240	360	160	120[51]	112[51]
ESD test [J][c]	0.40	0.40	0.35	0.08	0.30	0.50	0.40	0.35	0.2	0.2
N [%][d]	64.6	55.2	51.8	71.8	71.4	67.6	68.5	65.4	37.84	37.84
Ω [%][e]	–40.26	–51.19	–39.48	–51.24	–40.75	–56.46	–69.50	–41.45	–21.61	–21.61
$T_{dec.}$ [°C][f]	220	224	222	180	224	192	155	170	205	275
$\rho_{calcd.}$ [g cm^{-3}][g]	1.800	1.847	1.885	1.787	1.839	1.762	1.608	1.828	1.858 (90 K)[52]	1.944 (100 K)[53]
$\Delta_f H_m°$ [kJ mol^{-1}][h]	–20.7	472.9	–479.2	987.9	911.1	903.8	1164.2	990.6	86.3	116.1
$\Delta_f U°$ [kJ kg^{-1}][i]	41.6	1273.5	–1363.3	3266.7	3667.0	3356.8	3268.1	3766.8	489.0	492.5
Detonation parameters calculated with EXPLO5.05										
$-\Delta_E U°$ [kJ kg^{-1}][j]	3595	4868	3072	4961	5576	5264	4828	5625	6190	6185
T_E [K][k]	2743	3303	2452	3527	4009	3665	3325	3970	4232	4185
p_{CJ} [kbar][l]	277	333	275	320	358	313	249	361	380	415
D [m s^{-1}][m]	8306	8878	8203	8788	9097	8718	8090	9160	8983	9221
Gas vol. [L kg^{-1}][n]	832	789	826	767	760	751	756	774	734	729
I_{sp} [s][o]	191	217	175	236	250	240	232	252	258	258

[a] Impact sensitivity (BAM drop hammer, 1 of 6). [b] Friction sensitivity (BAM friction tester, 1 of 6). [c] Electrostatic discharge device (OZM). [d] Nitrogen content. [e] Oxygen balance. [f] Decomposition temperature from DSC (β = 5 °C/min). [g] Estimated from X-ray diffraction. [h] Calculated (CBS-4M) heat of formation. [i] Calculated energy of formation. [j] Energy of explosion. [k] Explosion temperature. [l] Detonation pressure. [m] Detonation velocity. [n] Assuming only gaseous products. [o] Specific impulse calculated at isobaric (60 bar) rocket conditions.

Detonation Parameters

The detonation parameters of **1**–**16** (Tables 3 and 4) were calculated by using the program EXPLO5 V5.05.[48] 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.[49] The program is designed to enable the calculation of detonation parameters at the Chapman–Jouguet point. The calculations were performed using the maximum densities according to the crystal structures at low temperatures as well as the solid-state energies of formation and the sum formula of the respective compound.

The calculated detonation parameters are compared to two prominent secondary explosives that are widely used, namely, 1,3,5-trinitro-1,3,5-triazacyclohexane (RDX) and 1,3,5,7-tetranitro-1,3,5,7-tetraazacyclooctane (HMX). For consistency, the low-temperature densities of RDX and HMX were also used. The detonation velocities reach from 7917 (**4**) to 9160 m s^{-1} (**16**), whereas apart from three compounds (**3**, **13**, **16**), the large majority do not reach the detonation velocity calculated for RDX (8983 m s^{-1}), and even the best performing material in terms of its detonation velocity (**16**) does not reach the value calculated for HMX (9221 m s^{-1}). The same argumentation applies to the detonation pressures, for which we find values that range from 233 (**4**) up to 361 kbar (**16**), which is below the values calculated for RDX as well as HMX. It has to be mentioned that for a promising RDX replacement, not only high detonation performance plays an important role, but also the sensitivities needed to meet today's requirements for safe handling, which is rather not the case for **3**, **13**, and **16**. If a material should reveal detonation parameters that exceed those of RDX or even HMX, it is advantageous to have a combination of a high crystal density and at the same time a high energy of formation. Unfortunately, in this study, on the one hand, the densest materials do not have the highest energies of formation, and on the other hand, the compounds with the highest energies of formation do not reveal the highest densities.

Conclusion

From this combined theoretical and experimental study the following conclusions can be drawn.

Firstly, 1*H*,1′*H*-5,5′-bitetrazole-1,1′-diol (**1**) can be deprotonated in aqueous media by using different nitrogen-rich bases. The diammonium (**2**), dihydrazinium (**3**), bis(guanidinium) (**4**), bis-aminoguanidinium (**5**), diaminoguanidinium (**6**), triaminoguanidinium (**7**), 1-amino-3-nitroguanidinium (**8**), diaminouronium (**9**), bis(oxalyldihydrazidinium) (**10**), oxalyldihydrazidinium (**11**), 3,6-dihydrazino-1,2,4,5-tetrazinium (**12**), 5-aminotetrazolium (**13**), 5-amino-1-methyltetrazolium (**14**), 1,5-diaminotetrazolium (**16**) salts, and a bis(2-methyl-5-aminotetrazole) adduct (**15**) were isolated and fully characterized. In the cases of **5**, **7**, **11**, and **12**, a 1:1 stoichiometry of the salts was observed with double-protonated cations and double-deprotonated 1*H*,1′*H*-5,5′-bitetrazole-1,1′-diol. For **2**–**5** and **10**, a cation/anion ratio of 2:1 was observed, whereas in the cases of **6**, **8**, **13**, and **14** a 1:1 stoichiometry with monodeprotonated anions occurs. Compound **15** is an adduct of **1** and 2-

methyl-5-aminotetrazole, which is stabilized by strong hydrogen bonds. With **7**, a rare example of an ionic compound that bears a twice positively charged triaminoguanidinium cation was isolated. In the crystal structures that contain monodeprotonated 1*H*,1′*H*-5,5′-bitetrazole-1,1′-diol, the anions are connected through very strong hydrogen bonds similar to those observed for the HF_2^- anion.

Secondly, the free acid **1**, which crystallizes as a dihydrate (IS: >40 J, FS: 216 N), can be dehydrated at 140 °C (24 h), thereby resulting in remarkably enhanced sensitivities (IS 4 J, FS: 10 [n]). However, water-free **1** is hygroscopic and thus turns into the dihydrate over time at ambient conditions. The dihydrate does not lose its crystal water over time, even at low air humidities.

Thirdly, the highest thermal stability (290 °C) is observed for the diammonium salt **2**, which we call ABTOX (ammonium BTO explosive). As expected, the 3-amino-1-nitroguanidinium salt **8** decomposes at the lowest observed temperature of 140 °C, which is due to the thermal instability of the 3-amino-1-nitroguanidinium cation.[23]

And finally, the most promising compounds in terms of explosive performance are the dihydrazinium salt **3** (D = 9159 m s^{-1}, p_{CJ} = 340 kbar, I_{sp} = 246 s), the 5-aminotetrazolium salt **13** (D = 9097 m s^{-1}, p_{CJ} = 358 kbar, I_{sp} = 250 s), and the 1,5-diaminotetrazolium salt **16** (D = 9160 m s^{-1}, p_{CJ} = 361 kbar, I_{sp} = 252 s); however, their utility as RDX replacements is restricted by their high sensitivities (**3**: IS: 9 J, FS: 252 N; **13**: IS: 4 J, FS: 72 N; **16**: IS: 2 J, FS: 160 N).

Experimental Section

Caution! 1*H*,1′*H*-5,5′-Bitetrazole-1,1′-diol and its salts are energetic materials with increased sensitivities towards shock and friction. Therefore, proper safety precautions (safety glass, face shield, earthed equipment and shoes, Kevlar gloves, and ear plugs) have to be applied when synthesizing and handling the described compounds.

All chemicals and solvents were employed as received (Sigma–Aldrich, Fluka, Acros). ^{1}H, ^{13}C, and ^{15}N NMR spectra were recorded with a JEOL Eclipse 270, JEOL EX 400, or a JEOL Eclipse 400 instrument. The chemical shifts quoted in ppm in the text refer to typical standards such as tetramethylsilane (^{1}H, ^{13}C) or nitromethane (^{15}N). To determine the melting and decomposition temperatures of the described compounds, a Linseis PT 10 DSC (heating rate 5 °C min^{-1}) was used. Infrared spectra were measured with a Perkin–Elmer Spectrum One FTIR spectrometer as KBr pellets. Raman spectra were recorded with a Bruker MultiRAM Raman Sample Compartment D418 equipped with an Nd:YAG laser (1064 nm) and an LN-Ge diode as detector. Mass spectra of the described compounds were measured with a JEOL MStation JMS 700 using FAB technique. To measure elemental analyses, a Netsch STA 429 simultaneous thermal analyzer was employed. 5,5′-Bis(1-hydroxytetrazole) was synthesized according to a modified literature procedure.[13]

CCDC-884561 (for **1**), -895972 (for **2**), -895963 (for **3**), -895965 (for **4**), -895973 (for **5**), -895969 (for **6**), -895970 (for **7**), -895977 (for **8**), -895964 (for **9**), -895967 (for **10**), -895975 (for **11**), -895974 (for **12**), -895966 (for **13**), -895976 (for **14**), -895971 (for **15**), and -895968 (for **16**) 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.

Glyoxime: NaOH (27.5 g, 0.69 mol) was dissolved in water (75 mL) and the solution was cooled to 0 °C in a salt ice bath. Hydroxylammonium chloride (69.5 g, 1.00 mol) was added while stirring. Glyoxal (72.5 g, 0.50 mol, 40% w/w in H_2O) was added to the obtained solution while the temperature was kept below 10 °C. After complete addition of the glyoxal, the solution was further chilled in the salt ice bath until glyoxime precipitated. The solid was removed by suction filtration and washed with a little ice water to remove the remaining sodium chloride.

Dichloroglyoxime: Glyoxime (17.6 g, 200 mmol) was suspended in ethanol (200 mL). Cl_2 gas was bubbled through the suspension at –20 °C until the green suspension turned into a yellowish solution. The solution was warmed slowly to room temperature while releasing dissolved chlorine. Then the solvent was removed under vacuum and the remaining solid was resuspended in chloroform (50 mL), stirred for 15 min at room temperature and filtered to yield 26.6 g (85%) of the colorless product. ^{1}H NMR ([D$_6$]DMSO, 25 °C): δ = 13.10 ppm. ^{13}C NMR ([D$_6$]DMSO, 25 °C): δ = 131.2 ppm. $C_2H_2Cl_2N_2O_2$ (156.96): calcd. C 15.30, H 1.28, N 17.85; found C 15.65, H 1.25, N 17.49.

Diazidoglyoxime: Dichloroglyoxime (3.13 g, 20 mmol) was dissolved in dimethyl formamide (40 mL). At 0 °C, sodium azide (2.93 g, 45 mmol) was added. The suspension was stirred for 20 min at 0 °C and water (100 mL) was added. The precipitate was filtered, washed with water (100 mL), and air-dried to yield 2.85 g (84%) of the colorless product. DSC (5 °C min^{-1}): 170 °C (dec.). IR (atr): $\tilde{\nu}$ = 3209 (w), 2170 (w), 2123 (w), 1622 (w), 1400 (w), 1361 (w), 1286 (m), 1013 (vs), 930 (m), 920 (s), 855 (s), 731 (s) cm^{-1}. Raman (1064 nm, 300 mW, 25 °C): $\tilde{\nu}$ = 2166 (8), 2129 (5), 2091 (3), 1621 (100), 1457 (14), 1390 (12), 1216 (19), 1034 (3), 882 (20), 672 (3), 442 (6) cm^{-1}. ^{1}H NMR ([D$_6$]DMSO, 25 °C): δ = 12.08 ppm. ^{13}C NMR ([D$_6$]DMSO, 25 °C): δ = 136.5 ppm. $C_2H_2N_8O_2$ (170.09): calcd. C 14.12, H 1.19, N 65.88; found C 14.38, H 1.46, N 66.01. BAM drop hammer: 1.5 J; friction tester: <5 N; ESD: 7 mJ.

1*H*,1′*H*-5,5′-Bitetrazole-1,1′-diol Dihydrate (1): Diazidoglyoxime (1.70 g, 10 mmol) was suspended in diethyl ether (100 mL), which was cooled to 0 °C in a salt ice bath. HCl was bubbled through the suspension while the temperature was maintained below 20 °C, until saturation of the diethyl ether, indicated by a drop in the temperature back to 0–5 °C, was reached. The flask was stoppered tightly, and the reaction mixture was stirred overnight at room temperature under a slight overpressure of HCl, which formed upon warming the mixture to room temperature. The HCl overpressure was released carefully, and the mixture was evaporated either overnight at room temperature in an open dish or in 1–2 h at 50 °C. After most of the diethyl ether had evaporated, water (20 mL) was added to result in a clear solution. A remaining colorless precipitate indicated uncompleted conversion of diazidoglyoxime to 1*H*,1′*H*-5,5′-bitetrazole-1,1′-diol. The water was evaporated again on a rotary evaporator to remove the remaining HCl and diethyl ether, thus yielding crude **1** as a colorless solid, which could be further purified by recrystallization from hot water, yield 1.90 g (9.2 mmol, 92%). DSC (5 °C min^{-1}): 115 °C (dehydr.), 214 °C (dec.). IR (KBr): $\tilde{\nu}$ = 3229 (m), 1665 (m), 1411 (w), 1375 (w), 1302 (w), 1208 (w), 1144 (m), 995 (s), 714 (w), 662 (w) cm^{-1}. Raman (1064 nm, 300 mW, 25 °C): $\tilde{\nu}$ = 1608 (100), 1270 (26), 1157 (46), 1133 (38), 1019 (22), 766 (31), 738 (13), 693 (4), 597 (6), 402 (29) cm^{-1}. ^{1}H NMR ([D$_6$]DMSO, 25 °C): δ = 6.80 ppm. ^{13}C NMR ([D$_6$]DMSO, 25 °C): δ = 135.8 ppm. ^{15}N NMR ([D$_6$]DMSO, 25 °C): δ = –2.0

(N3), –18.7 (N2), –52.3 (N4), –110.5 (N1) ppm. $C_2H_6N_8O_4$ (206.12): calcd. C 11.65, H 2.93, N 54.36; found C 12.18, H 2.81, N 54.04. BAM drop hammer: >40 J; friction tester: 216 N; ESD: 0.5 J.

Diammonium 1*H*,1′*H*-5,5′-Bitetrazole-1,1′-diolate (2): 1*H*,1′*H*-5,5′-Bitetrazole-1,1′-diol dihydrate (2.06 g, 10 mmol) was suspended in aqueous ammonia (2 mol L^{-1}, 10 mL). The mixture was heated after adding water (90 mL). After boiling, the mixture became clear. The solution was cooled to room temperature, the colorless crystalline residue was filtered, and 1.14 g (5.57 mmol, 56% yield) was obtained. DSC (5 °C min^{-1}): 290 °C (dec.). IR (KBr): $\tilde{\nu}$ = 3180 (s), 3047 (s), 2851 (s), 2150 (w), 1817 (w), 1668 (w), 1433 (s), 1400 (vs), 1352 (s), 1231 (s), 1165 (s), 1046 (m), 997 (m), 727 (m), 501 (m) cm^{-1}. Raman (1064 nm, 300 mW, 25 °C): $\tilde{\nu}$ = 3075 (1), 1605 (100), 1463 (3), 1278 (2), 1245 (23), 1118 (8), 1000 (7), 774 (8), 740 (3), 616 (3), 408 (4), 281 (3), 120 (14), 102 (18), 81 (16) cm^{-1}. ^1H NMR ([D$_6$]DMSO, 25 °C): δ = 7.07 (s, NH_4^+) ppm. ^{13}C NMR ([D$_6$]-DMSO, 25 °C): δ = 134.8 (CN_4O) ppm. ^{15}N NMR ([D$_6$]DMSO, 25 °C): δ = –2.0 (N3), –19.8 (N2), –53.6 (N4), –107.5 (N1) ppm. MS (FAB$^-$): *m*/*z* = 169.0 [$C_2N_8O_2^-$]; MS (FAB$^+$): *m*/*z* = 18.1 [NH_4^+]. $C_2H_8N_{10}O_2$ (204.15): calcd. C 11.77, H 3.95, N 68.61; found C 12.14, H 3.69, N 68.18. BAM drop hammer: 35 J; friction tester: 360 N; ESD: 0.25 J.

Dihydrazinium 1*H*,1′*H*-5,5′-Bitetrazole-1,1′-diolate (3): 1*H*,1′*H*-5,5′-Bitetrazole-1,1′-diol dihydrate (2.06 g, 10 mmol) was suspended in a few milliliters of water, and hydrazine hydrate (1.00 g, 20 mmol) was added to the clear solution. The mixture was heated and filtered. Compound **3** was obtained as small colorless crystalline needles to yield 0.95 g (4.05 mmol, 41%). DSC (5 °C min^{-1}): 220 °C (dec.). IR (KBr): $\tilde{\nu}$ = 3434 (w), 3322 (s), 3294 (s), 3189 (s), 2958 (s), 2864 (s), 2743 (s), 2642 (s), 2133 (m), 1832 (w), 1620 (s), 1578 (m), 1529 (m), 1511 (m), 1420 (s), 1408 (s), 1347 (m), 1232 (s), 1170 (s), 1117 (s), 1096 (s), 1046 (w), 1038 (w), 998 (m), 970 (vs), 732 (m), 712 (w), 523 (w), 495 (w) cm^{-1}. Raman (1064 nm, 300 mW, 25 °C): $\tilde{\nu}$ = 3294 (1), 3196 (2), 2006 (1), 1605 (100), 1476 (1), 1458 (2), 1399 (2), 1241 (21), 1139 (7), 1109 (8), 1007 (7), 974 (6), 782 (9), 739 (3), 613 (3), 406 (6) cm^{-1}. ^1H NMR ([D$_6$]DMSO, 25 °C): δ = 7.20 (s, $NH_2NH_3^+$) ppm. ^{13}C NMR ([D$_6$]DMSO, 25 °C): δ = 134.9 (CN_4O) ppm. MS (FAB$^+$): *m*/*z* = 33.1 [$N_2H_5^+$]; MS (FAB$^-$): *m*/*z* = 169.0 [$C_2HN_8O_2^-$]; $C_2H_{10}N_{12}O_2$ (234.18): calcd. C 10.26, H 4.30, N 71.77; found C 10.71, H 3.97, N 71.17; BAM drop hammer: 9 J; friction tester: 252 N; ESD: 0.1 J.

Bis(guanidinium) 1*H*,1′*H*-5,5′-Bitetrazole-1,1′-diolate (4): 1*H*,1′*H*-5,5′-Bitetrazole-1,1′-diol dihydrate (2.06 g, 10 mmol) was suspended in a few milliliters of water, and guanidinium carbonate (1.08 g, 12 mmol) was added. The mixture was heated to reflux for 10 min and filtered. After cooling the filtrate to room temperature, **4** precipitated as colorless crystalline needles, yield 2.00 g (6.94 mmol, 69%). DSC (5 °C min^{-1}): 274 °C (dec.). IR (KBr): $\tilde{\nu}$ = 3454 (s), 3376 (s), 3089 (s), 2192 (w), 1652 (vs), 1583 (m), 1424 (s), 1385 (m), 1347 (m), 1289 (w), 1234 (m), 1169 (m), 1139 (m), 1068 (m), 1014 (w), 999 (m), 744 (m), 595 (w), 543 (w), 530 (w), 513 (m), 490 (w) cm^{-1}. Raman (1064 nm, 300 mW, 25 °C, cm^{-1}): $\tilde{\nu}$ = 3197 (2), 1603 (100), 1458 (4), 1233 (17), 1152 (12), 1120 (6), 1017 (33), 791 (9), 739 (2), 621 (2), 545 (5), 422 (3), 409 (4), 292 (6), 179 (4), 128 (18), 100 (18) cm^{-1}. ^1H NMR ([D$_6$]DMSO, 25 °C): δ = 7.10 [s, $C(NH_2)_3$] ppm. ^{13}C NMR ([D$_6$]DMSO, 25 °C): δ = 158.6 [$C(NH_2)_3$], 134.6 (CN_4O) ppm. MS (FAB$^+$): *m*/*z* = 60.1 [$CH_6N_3^+$]; MS (FAB$^-$): *m*/*z* = 169.0 [$C_2HN_8O_2^-$]; $C_4H_{12}N_{14}O_2$ (288.23): calcd. C 16.67, H 4.20, N 68.03; found C 16.95, H 3.94, N 67.45; BAM drop hammer: >40 J; friction tester: >360 N; ESD: 0.5 J.

Bis(aminoguanidinium) 1*H*,1′*H*-5,5′-Bitetrazole-1,1′-diolate (5): 1*H*,1′*H*-5,5′-Bitetrazole-1,1′-diol dihydrate (2.06 g, 10 mmol) was suspended in a few milliliters of water. After two equivalents of aminoguanidinium hydrogen carbonate (2.72 g, 20 mmol) were added, the mixture was heated until boiling for 10 min, and the hot solution was filtered. The solvent was slowly evaporated from the filtrate to yield 1.94 g (6.09 mmol, 61%) of **5** as colorless crystals. DSC (5 °C min^{-1}): 208 °C (m.p.), 228 °C (dec.). IR (KBr): $\tilde{\nu}$ = 3432 (s), 3308 (s), 3180 (s), 2344 (w), 1678 (vs), 1416 (m), 1424 (s), 1384 (m), 1352 (w), 1234 (m), 1208 (w), 1176 (w), 1101 (w), 994 (m), 957 (w), 730 (w), 712 (w), 677 (w), 643 (w), 515 (w), 494 (w) cm^{-1}. Raman (1064 nm, 300 mW, 25 °C): $\tilde{\nu}$ = 3302 (2), 3245 (3), 3184 (4), 1673 (2), 1613 (100), 1590 (32), 1452 (2), 1292 (2), 1241 (23), 1214 (2), 1147 (10), 1133 (6), 1114 (9), 1009 (7), 968 (10), 778 (10), 736 (2), 637 (1), 612 (4), 512 (4), 423 (2), 339 (1), 289 (11), 177 (10), 145 (10), 95 (23) cm^{-1}. ^1H NMR ([D$_6$]DMSO, 25 °C): δ = 8.89 (s, 1 H, $CNHNH_2$), 7.01 [s, 4 H, $C(NH_2)_2$], 4.60 (s, 2 H, $NHNH_2$) ppm. ^{13}C NMR ([D$_6$]DMSO, 25 °C): δ = 159.4 [$C(NH_2)_2NHNH_2$], 134.7 (CN_4O) ppm. MS (FAB$^+$): *m*/*z* = 75.1 [$CH_7N_4^+$]; MS (FAB$^-$): *m*/*z* = 169.0 [$C_2HN_8O_2^-$]. $C_4H_{14}N_{16}O_2$ (318.26): calcd. C 15.10, H 4.43, N 70.42; found C 15.41, H 4.24, N 69.46. BAM drop hammer: 40 J; friction tester: 324 N; ESD: 0.25 J.

Diaminoguanidinium 1′-Hydroxy-1*H*,1′*H*-5,5′-bitetrazol-1-olate Monohydrate (6): 1*H*,1′*H*-5,5′-Bitetrazole-1,1′-diol dihydrate (2.06 g, 10 mmol) was suspended in a few milliliters of water. $Ba(OH)_2{\cdot}8H_2O$ (3.16 g, 10 mmol) was added to the clear solution, and the mixture was heated until boiling to obtain a white, poorly soluble deposit. The white barium salt was filtered off under vacuum and dried. The substance was proved to be anhydrous by elemental analysis. Afterwards, the white powder was suspended in water to mix it with diaminoguanidinium sulfate (5.72 g, 20 mmol). $BaSO_4$ was filtered off and **6** precipitated from the filtrate as clear crystalline agglomerates to yield 1.52 g (5.48 mmol, 55%). DSC (5 °C min^{-1} °C): 160 °C (dehydr.), 200 °C (m.p.), 204 °C (dec.). IR (KBr): $\tilde{\nu}$ = 3437 (s), 3338 (vs), 3301 (s), 2302 (w), 1690 (s), 1670 (s), 1628 (m), 1602 (m), 1458 (w), 1408 (w), 1369 (s), 1340 (w), 1269 (m), 1179 (s), 1148 (s), 1085 (s), 1022 (s), 867 (s), 758 (s), 710 (m), 692 (m), 631 (s), 491 (w) cm^{-1}. Raman (1064 nm, 300 mW, 25 °C): $\tilde{\nu}$ = 3338 (3), 3290 (2), 3237 (2), 1615 (100), 1469 (2), 1250 (33), 1180 (2), 1122 (9), 1150 (15), 1132 (16), 1009 (6), 924 (5), 763 (3), 739 (3), 695 (2), 540 (3), 411 (5) cm^{-1}. ^1H NMR ([D$_6$]DMSO, 25 °C): δ = 8.50 [s, 2 H, $C(NH)_2$], 7.10 (s, 2 H, $C{=}NH_2^+$), 5.15 [s, 4 H, $(NHNH_2)_2$] ppm. ^{13}C NMR ([D$_6$]DMSO, 25 °C): δ = 160.2 ($C{=}NH_2^+$), 135.7 (CN_4O) ppm. MS (FAB$^+$): *m*/*z* = 90.1 [$CH_8N_5^+$]; MS (FAB$^-$): *m*/*z* = 169.0 [$C_2HN_8O_2^-$]. $C_3H_{11}N_{13}O_3$ (277.20): calcd. C 13.00, H 4.00, N 65.69; found C 13.79, H 3.31, N 67.46. BAM drop hammer: 12 J; friction tester: 168 N; ESD: 0.25 J.

Triaminoguanidinium 1′-Hydroxy-1*H*,1′*H*-5,5′-bitetrazol-1-olate Monohydrate (7): 1*H*,1′*H*-5,5′-Bitetrazole-1,1′-diol dihydrate (2.06 g, 10 mmol) was suspended in a few milliliters of water, and triaminoguanidinium chloride (2.81 g, 20 mmol) was added to the clear solution. The mixture was briefly heated to reflux and filtered. From the filtrate, **7** crystallizes as small crystalline needles to give 2.43 g (8.32 mmol, 83%). DSC (5 °C min^{-1}): 210 °C (dec.). IR (KBr): $\tilde{\nu}$ = 3364 (m), 3320 (s), 3209 (s), 2994 (m), 1683 (vs), 1615 (m), 1585 (m), 1508 (w), 1410 (s), 1384 (m), 1338 (m), 1235 (m), 1202 (m), 1150 (m), 1128 (m), 1057 (m), 1013 (m), 989 (m), 949 (m), 779 (w), 733 (m), 638 (m), 567 (m), 496 (w) cm^{-1}. Raman (1064 nm, 300 mW, 25 °C): $\tilde{\nu}$ = 3362 (3), 3270 (7), 3171 (7), 1680 (5), 1657 (5), 1602 (100), 1456 (4), 1374 (2), 1232 (25), 1171 (2), 1135 (13), 1110 (14), 1002 (8), 890 (11), 779 (14), 740 (4), 646 (3), 613 (5), 424 (9), 406 (6), 289 (6), 143 (24), 118 (15), 100 (41), 83 (34) cm^{-1}. ^1H NMR ([D$_6$]DMSO, 25 °C): δ = 8.62 [s, 3 H, $C(NH)_3$], 4.46 [s, 6 H, $C(NHNH_2)_3$] ppm. ^{13}C NMR ([D$_6$]DMSO, 25 °C): δ = 159.7 [$C(NHNH_2)_3$], 134.5 (CN_4O) ppm. MS (FAB$^+$):

m/z = 105.1 [$CH_9N_6^+$]; MS (FAB⁻): *m/z* = 169.0 [$C_2HN_8O_2^-$]. $C_3H_{12}N_{14}O_3$ (292.22): calcd. C 12.33, H 4.14, N 67.10; found C 13.17, H 4.51, N 73.36. BAM drop hammer: 15 J; friction tester: 120 N; ESD: 0.25 J.

1-Amino-3-nitroguanidinium 1′-Hydroxy-1*H*,1′*H*-5,5′-bitetrazol-1-olate Dihydrate (8): 1*H*,1′*H*-5,5′-Bitetrazole-1,1′-diol dihydrate (0.59 g, 2.87 mmol) was dissolved in warm water (5 mL), and a solution of 1-amino-3-nitroguanidine (0.34 g, 2.87 mmol) in hot water (10 mL) was added. After boiling and stirring the mixture for a few minutes, **8** precipitated as thin, colorless plates upon cooling the solution to room temperature. Single crystals suitable for X-ray crystallography in this case were grown from a 40% aqueous solution of HF. DSC (5 °C min⁻¹): 138 °C (dehydr.), 140 °C (dec.). IR (KBr): $\tilde{\nu}$ = 3494 (m), 3373 (s), 3285 (m), 3197 (m), 3097 (s), 2677 (m), 1644 (m), 1577 (m), 1469 (m), 1377 (s), 1262 (vs), 1248 (s), 1166 (w), 1153 (w), 1116 (m), 1074 (m), 1024 (w), 1002 (w), 910 (w), 820 (m), 763 (s), 729 (m), 646 (s), 460 (w) cm⁻¹. Raman (1075 nm, 300 mW, 25 °C): $\tilde{\nu}$ = 3092 (1), 1628 (100), 1491 (3), 1475 (2), 1392 (2), 1257 (30), 1152 (13), 1015 (5), 913 (9), 799 (7), 738 (3), 621 (7), 445 (3), 404 (4), 361 (7), 282 (7) cm⁻¹. ^{1}H NMR ([D$_6$]DMSO, 25 °C): δ = 9.34 (s, 1 H, CN_4OH), 8.27 (s, 1 H, $NHNH_2$), 7.03 (s, 4 H, $NHNH_2$, NH_2) ppm. ^{13}C NMR ([D$_6$]DMSO, 25 °C): δ = 160.0 [$C(NH_2)(NHNH_2)(NNO_2)$], 135.7 (CN_4O) ppm. MS (FAB⁺): *m/z* = 120.1 [$CH_6N_5O_2^+$]; MS (FAB⁻): *m/z* = 169.0 [$C_2HN_8O_2^-$]. $C_3H_{11}N_{13}O_6$ (325.20): calcd. C 11.08, H 3.41, N 55.99; found C 11.54, H 3.27, N 55.96. BAM drop hammer: 10 J; friction tester: 192 N; ESD: 0.08 J (at grain size 100–500 μm).

Diaminouronium 1*H*,1′*H*-5,5′-Bitetrazole-1,1′-diolate Monohydrate (9): 1*H*,1′*H*-5,5′-Bitetrazole-1,1′-diol dihydrate (2.06 g, 10 mmol) was suspended in a few milliliters of water. Diaminourea (1.81 g, 20 mmol) was added to the clear solution. The mixture was briefly heated to reflux and filtered. After cooling to room temperature, **9** precipitated as crystalline needles, yield 2.56 g (9.20 mmol, 92%). DSC (5 °C min⁻¹): 220 °C (dec.). IR (KBr): $\tilde{\nu}$ = 3617 (m), 3545 (m), 3274 (s), 2964 (s), 2659 (s), 2126 (w), 2049 (w), 1702 (m), 1608 (s), 1535 (vs), 1427 (s), 1413 (s), 1385 (m), 1356 (w), 1269 (w), 1233 (s), 1171 (s), 1048 (m), 1006 (w), 996 (w), 978 (w), 729 (m), 565 (w), 504 (w) cm⁻¹. Raman (1064 nm, 300 mW, 25 °C): $\tilde{\nu}$ = 1709 (2), 1616 (100), 1474 (5), 1289 (2), 1246 (18), 1202 (4), 1144 (11), 1122 (9), 1008 (7), 1000 (4), 980 (4), 778 (8), 744 (3), 614 (4), 411 (3) cm⁻¹. ^{1}H NMR ([D$_6$]DMSO, 25 °C): δ = 8.31 [s, $C(NHNH_2)_2$], 7.80 [s, $C(NHNH_2)_2$] ppm. ^{13}C NMR ([D$_6$]DMSO, 25 °C): δ = 135.7 (CN_4O), 159.6 [$C(NHNH_2)_2$] ppm. MS (FAB⁺): *m/z* = 91.1 [$CH_7N_4^+$]; MS (FAB⁻): *m/z* = 169.0 [$C_2HN_8O_2^-$]. $C_3H_{10}N_{12}O_4$ (278.19): calcd. C 12.95, H 3.62, N 60.42; found C 13.29, H 3.28, N 60.21. BAM drop hammer: 20 J; friction tester: 240 N; ESD: 0.4 J.

Bis(oxalyldihydrazidinium) 1*H*,1′*H*-5,5′-Bitetrazole-1,1′-diolate (10): 1*H*,1′*H*-5,5′-Bitetrazole-1,1′-diol dihydrate (2.06 g, 10 mmol) was suspended in a few milliliters of water, and oxalyldihydrazide (2.36 g, 20 mmol) was added. The mixture was briefly heated to reflux and filtered. After cooling to room temperature, **10** precipitated as small crystalline needles to yield 3.57 g (8.79 mmol, 88%). DSC (5 °C min⁻¹): 224 °C (dec.). IR (KBr): $\tilde{\nu}$ = 3423 (m), 3316 (m), 3269 (s), 3029 (s), 2340 (w), 1677 (vs), 1607 (s), 1579 (s), 1512 (s), 1429 (s), 1412 (s), 1348 (m), 1290 (m), 1256 (m), 1239 (s), 1175 (m), 1148 (m), 1077 (m), 971 (m), 927 (m), 831 (m), 780 (w), 730 (m), 712 (w), 636 (w), 536 (m), 498 (m), 479 (m) cm⁻¹. Raman (1064 nm, 300 mW, 25 °C): $\tilde{\nu}$ = 3318 (1), 3259 (2), 2017 (1), 1715 (4), 1674 (2), 1615 (100), 1542 (9), 1471 (2), 1320 (12), 1285 (4), 1245 (13), 1211 (2), 1139 (12), 1119 (8), 1071 (1), 1003 (4), 977 (3), 932 (6), 776 (5), 744 (4), 617 (1), 525 (1), 503 (1), 433 (2), 407 (5), 363 (2), 327 (2), 296 (3), 271 (3), 158 (38), 98 (11), 67 (6) cm⁻¹. ^{1}H NMR ([D$_6$]DMSO, 25 °C): δ = 7.74 (s) ppm. ^{13}C NMR ([D$_6$]DMSO, 25 °C): δ = 135.7 (CN_4O), 158.1 (C=O) ppm. MS (DEI⁺): *m/z* = 118.1 [$C_2H_6N_4O_2^{+\cdot}$]; MS (FAB⁻): *m/z* = 169.1 [$C_2HN_8O_2^-$]. $C_6H_{14}N_{16}O_6$ (406.28): calcd. C 17.74, H 3.47, N 55.16; found C 17.80, H 3.24, N 54.41. BAM drop hammer: 20 J; friction tester: 360 N; ESD: 0.4 J.

Oxalyldihydrazidinium 1*H*,1′*H*-5,5′-Bitetrazole-1,1′-diolate Dihydrate (11): 1*H*,1′*H*-5,5′-Bitetrazole-1,1′-diol dihydrate (1.03 g, 5 mmol) was suspended in a few milliliters of water, and oxalyldihydrazide (0.59 g, 5 mmol) was added. The mixture was briefly heated to reflux and filtered. After cooling to room temperature, **11** was obtained as small crystalline needles to give 1.41 g (4.35 mmol, 87%). DSC (5 °C min⁻¹): 110 °C (dehydr.), 222 °C (dec.). IR (KBr): $\tilde{\nu}$ = 3871 (w), 3428 (s), 3074 (s), 2837 (s), 2730 (s), 2043 (m), 1676 (vs), 1585 (m), 1523 (s), 1431 (s), 1415 (s), 1358 (m), 1265 (m), 1241 (s), 1209 (m), 1173 (m), 1040 (m), 1000 (m), 811 (m), 735 (m), 715 (w), 616 (w), 532 (m), 471 (w) cm⁻¹. Raman (1064 nm, 300 mW, 25 °C): $\tilde{\nu}$ = 1706 (5), 1660 (2), 1615 (100), 1591 (4), 1555 (2), 1478 (2), 1334 (3), 1287 (1), 1248 (18), 1216 (3), 1139 (6), 1116 (9), 1008 (5), 929 (5), 779 (4), 744 (3), 631 (2), 520 (2), 416 (4), 397 (3), 322 (1), 287 (4), 266 (2), 162 (12), 151 (15), 124 (20), 88 (17), 66 (5) cm⁻¹. ^{1}H NMR ([D$_6$]DMSO, 25 °C): δ = 7.53 [s, $(NHNH_3^+)_2$] ppm. ^{13}C NMR ([D$_6$]DMSO, 25 °C): δ = 157.8 (C=O), 135.7 (CN_4O) ppm. MS (DEI⁺): *m/z* = 118.1 [$C_2H_6N_4O_2^{+\cdot}$]; MS (DCI⁺): *m/z* = 119.14 [$C_2H_7N_4O_2^{+\cdot}$]; MS (FAB⁻): *m/z* = 169.1 [$C_2HN_8O_2^-$]. $C_4H_{12}N_{12}O_6$ (324.21): calcd. C 14.82, H 3.73, N 51.84; found C 15.14, H 3.52, N 51.32. BAM drop hammer: 40 J; friction tester: 288 N; ESD: 0.35 J.

3,6-Bishydrazino-1,2,4,5-tetrazinium 1*H*,1′*H*-5,5′-Bitetrazole-1,1′-diolate (12): 1*H*,1′*H*-5,5′-Bitetrazole-1,1′-diol dihydrate (0.37 g, 1.8 mmol) was suspended in a few milliliters of water, and 3,6-dihydrazino-1,2,4,5-tetrazinium dichloride monohydrate (0.41 g, 1.8 mmol), previously dissolved in a few milliliters of water was added. The mixture was heated until boiling to obtain a clear solution. After cooling to 10 °C, **12** precipitated as a red flaky deposit, which was filtered and washed with a little cold water, yield 0.36 g (1.15 mmol, 64%) of small, orange crystals. DSC (5 °C min⁻¹): 180 °C (dec.). IR (KBr): $\tilde{\nu}$ = 3424 (m), 3259 (s), 3059 (m), 2923 (m), 2857 (m), 2657 (m), 2005 (w), 1620 (m), 1573 (m), 1535 (s), 1495 (s), 1426 (vs), 1359 (w), 1327 (w), 1242 (s), 1175 (m), 1159 (m), 1098 (w), 1053 (m), 1000 (w), 939 (m), 856 (m), 730 (m), 706 (m), 595 (m), 508 (w), 464 (w) cm⁻¹. Raman (1064 nm, 300 mW, 25 °C): $\tilde{\nu}$ = 3260 (2), 1907 (1), 1615 (100), 1550 (2), 1515 (3), 1490 (7), 1314 (3), 1286 (2), 1247 (21), 1221 (2), 1165 (2), 1141 (10), 1115 (8), 1077 (2), 1008 (7), 876 (8), 816 (2), 777 (7), 740 (3), 702 (1), 671 (3), 613 (4), 467 (4), 435 (3), 415 (3), 293 (9), 198 (3), 157 (7), 127 (18), 115 (47), 105 (54), 90 (34) cm⁻¹. ^{1}H NMR ([D$_6$]DMSO, 25 °C): δ = 9.57 (s, 2 H, $NHNH_3^+$), 6.38 (s, 6 H, $NHNH_3^+$) ppm. ^{13}C NMR ([D$_6$]DMSO, 25 °C): δ = 162.5 (C_2N_4), 135.7 (CN_4O) ppm. MS (FAB⁻): *m/z* = 169.1 [$C_2HN_8O_2^-$]. $C_4H_8N_{16}O_2$ (312.21): calcd. C 15.39, H 2.58, N 71.78; found C 15.79, H 2.49, N 70.58. BAM drop hammer: 40 J; friction tester: 80 N; ESD: 0.08 J.

5-Aminotetrazolium 1′-Hydroxy-1*H*,1′*H*-5,5′-bitetrazol-1-olate (13): 1*H*,1′*H*-5,5′-Bitetrazole-1,1′-diol dihydrate (2.06 g, 10 mmol) was suspended in a few milliliters of water, and 5-aminotetrazole (1.70 g, 20 mmol) was added. The mixture was briefly heated to reflux and filtered. After cooling to room temperature, **13** crystallized as colorless needles, yield 2.31 g (9.05 mmol, 91%). DSC (5 °C min⁻¹): 224 °C (dec.). IR (KBr): $\tilde{\nu}$ = 3407 (s), 3325 (s), 3281 (m), 3167 (m), 2965 (m), 2837 (m), 2720 (s), 2565 (m), 2508 (m), 1703 (vs), 1594 (m), 1489 (m), 1451 (w), 1407 (w), 1370 (m), 1322

(m), 1281 (m), 1140 (m), 1080 (m), 1056 (m), 999 (s), 809 (s), 522 (m), 456 (w) cm^{-1}. Raman (1064 nm, 300 mW, 25 °C): $\tilde{\nu}$ = 1698 (1), 1624 (100), 1592 (3), 1496 (17), 1322 (3), 1297 (1), 1260 (26), 1143 (6), 1130 (11), 1063 (10), 1018 (3), 819 (1), 787 (2), 743 (8), 653 (1), 411 (3), 403 (2), 295 (5), 173 (9), 129 (18), 121 (18), 111 (15), 97 (45), 77 (25) cm^{-1}. ^{1}H NMR ([D$_6$]DMSO, 25 °C): δ = 11.90 [s, CNH_2, $(NH)_2^+$] ppm. ^{13}C NMR ([D$_6$]DMSO, 25 °C): δ = 155.7 ($CH_4N_5^+$), 135.8 (CN_4O) ppm. MS (FAB$^+$): *m/z* = 86.1 [$CH_4N_5^+$]; MS (FAB$^-$): *m/z* = 169.0 [$C_2HN_8O_2^-$]. $C_3H_5N_{13}O_2$ (255.16): calcd. C 14.12, H 1.98, N 71.36; found C 14.50, H 1.91, N 70.90. BAM drop hammer: 4 J; friction tester: 72 N; ESD: 0.3 J.

1-Methyl-5-aminotetrazolium 1′-Hydroxy-1*H*,1′*H*-5,5′-bitetrazol-1-olate (14): 1*H*,1′*H*-5,5′-Bitetrazole-1,1′-diol (2.06 g, 10 mmol) was suspended in a few milliliters of water, and 5-amino-1-methyl-1*H*-tetrazole (1.98 g, 20 mmol) was added. The mixture was heated and filtered. After cooling to room temperature, **14** crystallized as colorless blocks to yield 1.07 g (3.98 mmol, 40%). DSC (5 °C min^{-1}): 188 °C (m.p.), 192 °C (dec.). IR (KBr): $\tilde{\nu}$ = 3496 (m), 3398 (s), 3296 (m), 3126 (m), 3061 (m), 2950 (m), 2850 (m), 2752 (m), 2676 (m), 1693 (vs), 1514 (w), 1465 (w), 1424 (w), 1367 (m), 1273 (m), 1240 (w), 1138 (m), 1116 (m), 1084 (m), 1042 (m), 1007 (w), 963 (m), 847 (m), 779 (w), 759 (m), 713 (m), 661 (w), 621 (m) cm^{-1}. Raman (1075 nm, 300 mW, 25 °C): $\tilde{\nu}$ = 3032 (4), 3012 (2), 2960 (9), 2822 (2), 1712 (1), 1616 (100), 1513 (1), 1464 (2), 1422 (4), 1366 (2), 1275 (5), 1252 (34), 1131 (15), 1112 (10), 1063 (1), 1039 (5), 1013 (4), 969 (2), 781 (25), 741 (5), 671 (5), 623 (1), 475 (2), 412 (4), 314 (5), 292 (5), 231 (6) cm^{-1}. ^{1}H NMR ([D$_6$]DMSO, 25 °C): δ = 8.72 (br. s, NH, NH_2, OH), 3.67 (s, CH_3) ppm. ^{13}C NMR ([D$_6$]DMSO, 25 °C): δ = 155.6 (CN_4), 135.8 (CN_4O), 32.2 (CH_3) ppm. MS (FAB$^+$): *m/z* = 100.0 [$C_2H_6N_5^-$]; MS (FAB$^-$): *m/z* = 169.0 [$C_2HN_8O_2^-$]; $C_4H_7N_{13}O_2$ (269.08): calcd. C 17.85, H 2.62, N 67.64; found C 18.27, H 2.60, N 67.09. BAM drop hammer: 6 J; friction tester: 240 N; ESD: 0.50 J (at grain size 500–1000 μm).

1*H*,1′*H*-5,5′-Bitetrazole-1,1′-diol·2(5-Amino-2-methyl-2*H*-tetrazole) (15): 1*H*,1′*H*-5,5′-Bitetrazole-1,1′-diol dihydrate (2.06 g, 10 mmol) was suspended in a few milliliters of water, and 5-amino-2-methyl-2*H*-tetrazole (1.98 g, 20 mmol) was added. The mixture was briefly heated to reflux and filtered. After cooling to room temperature, **15** precipitated as clear crystals to yield 0.98 g (2.66 mmol, 27%). DSC (5 °C min^{-1}): 125 °C (m.p.), 155 °C (dec.). IR (KBr): $\tilde{\nu}$ = 3403 (s), 3344 (s), 3212 (m), 2743 (w), 2400 (w), 1659 (vs), 1596 (s), 1439 (m), 1287 (m), 1159 (s), 1130 (m), 1064 (m), 896 (m), 781 (m), 748 (m), 710 (m), 653 (m), 487 (m) cm^{-1}. Raman (1064 nm, 300 mW, 25 °C): $\tilde{\nu}$ = 3220 (7), 3047 (9), 3029 (14), 2966 (49), 1847 (4), 1771 (4), 1714 (4), 1671 (7), 1627 (100), 1438 (18), 1414 (8), 1390 (16), 1328 (4), 1268 (27), 1150 (18), 1091 (10), 1065 (11), 1015 (24), 807 (5), 768 (18), 724 (10), 647 (51), 562 (10), 493 (18), 409 (19), 324 (15), 305 (6), 276 (7), 207 (21), 138 (71) cm^{-1}. ^{1}H NMR ([D$_6$]DMSO, 25 °C): δ = 7.26 (s, 2 H, CNH_2), 4.07 (s, 3 H, NCH_3) ppm. ^{13}C NMR ([D$_6$]DMSO, 25 °C): δ = 167.7 (CNH_2), 135.8 (CN_4O), 39.4 (NCH_3) ppm. MS (FAB$^+$): *m/z* = 100.1 [$C_2H_6N_5^+$]; MS (FAB$^-$): *m/z* = 169.1 [$C_2HN_8O_2^-$]. $C_6H_{12}N_{18}O_2$, (368.28): calcd. C 19.57, H 3.28, N 68.46; found C 20.08, H 3.24, N 68.50. BAM drop hammer: 8 J; friction tester: 360 N; ESD: 0.4 J.

1,5-Diaminotetrazolium 1′-Hydroxy-1*H*,1′*H*-5,5′-bitetrazol-1-olate (16): 1*H*,1′*H*-5,5′-Bitetrazole-1,1′-diol dihydrate (2.06 g, 10 mmol) was suspended in a few milliliters of water, and 1,5-diaminotetrazole (2.04 g, 20 mmol) was added. The mixture was heated and filtered. After cooling to room temperature, **16** crystallized from the aqueous solution to give 2.60 g (9.62 mmol, 96%) of **16**. DSC (5 °C min^{-1}): 160 °C (m.p.), 170 °C (dec.). IR (KBr): $\tilde{\nu}$ = 3322 (s), 3325 (s), 3225 (s), 3153 (s), 2791 (w), 2692 (w), 2439 (w), 2241 (w), 1731 (m), 1655 (vs), 1577 (m), 1487 (w), 1470 (w), 1368 (w), 1329 (s), 1134 (w), 1109 (m), 1077 (m), 1002 (m), 931 (m), 745 (m), 687 (m), 605 (m), 486 (w) cm^{-1}. Raman (1064 nm, 300 mW, 25 °C): $\tilde{\nu}$ = 3322 (7), 3247 (8), 3157 (9), 1671 (8), 1618 (20), 1547 (30), 1498 (6), 1328 (23), 1306 (32), 1250 (5), 1135 (6), 1106 (26), 1079 (10), 1000 (4), 957 (3), 792 (100), 698 (20), 497 (2), 322 (34), 231 (16), 138 (22), 105 (44), 92 (37), 78 (62) cm^{-1}. ^{1}H NMR ([D$_6$]DMSO, 25 °C): δ = 7.87 [s, CNH_2, $N(NH_2)$, NH^+] ppm. ^{13}C NMR ([D$_6$]-DMSO, 25 °C): δ = 154.2 ($CH_5N_6^+$), 135.8 (CN_4O) ppm. MS (FAB$^+$): *m/z* = 101.1 [$CH_5N_6^+$]; MS (FAB$^-$): *m/z* = 169.1 [$C_2HN_8O_2^-$]. $C_3H_6N_{14}O_2$ (270.17): calcd. C 13.34, H 2.24, N 72.58; found C 13.95, H 2.23, N 75.97. BAM drop hammer: 2 J; friction tester: 160 N; ESD: 0.35 J.

Supporting Information (see footnote on the first page of this article): Description of crystal structures of compounds **1**–**5**, **8**–**14** and **16**; tables of crystallographic details (mesurements and refinements, bond lengths, bond angles and hydrogen bonds.

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[1] J. Thiele, *Justus Liebigs Ann. Chem.* **1898**, *203*, 57–75.
[2] W. E. Bachmann, J. C. Sheehan, *J. Am. Chem. Soc.* **1949**, *71*, 1842–1845.
[3] H. Fischer, *Chem. Ber.* **1949**, *82*, 192–193.
[4] A. T. Nielsen, A. P. Chafin, S. L. Christian, D. W. Moore, M. P. Nadler, R. A. Nissan, D. J. Vanderah, R. D. Gilardi, C. F. George, J. L. Flippen-Anderson, *Tetrahedron* **1998**, *54*, 11793–11812.
[5] a) H. Gao, J. M. Shreeve, *Chem. Rev.* **2011**, *111*, 7377–7436; b) R. Haiges, S. Schneider, T. Schroer, K. O. Christe, *Angew. Chem.* **2004**, *116*, 5027; *Angew. Chem. Int. Ed.* **2004**, *43*, 4919–4924; c) D. E. Chavez, M. A. Hiskey, D. L. Naud, D. Parrish, *Angew. Chem.* **2008**, *120*, 8431; *Angew. Chem. Int. Ed.* **2008**, *47*, 8307–8309; d) M. B. Talawar, R. Sivabalan, T. Mukundan, H. Muthurajan, A. K. Sikder, B. R. Gandhe, A. Subhananda Rao, *J. Hazard. Mater.* **2009**, *161*, 589–607; e) O. S. Bushuyev, P. Brown, A. Maiti, R. H. Gee, G. R. Peterson, B. L. Weeks, L. J. Hope-Weeks, *J. Am. Chem. Soc.* **2012**, *134*, 1422–1425.
[6] S. A. Meyer, A. J. Marchand, J. L. Hight, G. H. Roberts, L. B. Escalon, L. S. Inouye, D. K. MacMillan, *J. Appl. Toxicol.* **2005**, *25*, 427–434.
[7] T. M. Klapötke, in: *High Energy Density Materials*, Springer, Berlin, Heidelberg, **2007**.

[8] D. E. Chavez, M. A. Hiskey, R. D. Gilardi, *Angew. Chem.* **2000**, *112*, 1861; *Angew. Chem. Int. Ed.* **2000**, *39*, 1791–1793.
[9] N. Fischer, D. Iszak, T. M. Klapötke, S. Rappenglück, J. Stierstorfer, *Chem. Eur. J.* **2012**, *18*, 4051–4062.
[10] M. Göbel, K. Karaghiosoff, T. M. Klapötke, D. G. Piercey, J. Stierstorfer, *J. Am. Chem. Soc.* **2010**, *132*, 17216–17226.
[11] T. M. Klapötke, D. G. Piercey, J. Stierstorfer, *Chem. Eur. J.* **2011**, *17*, 13068–13077.
[12] A. M. Churakov, V. A. Tartakovsky, *Chem. Rev.* **2004**, *104*, 2601–2616.
[13] N. Fischer, D. Fischer, T. M. Klapötke, D. Piercey, J. Stierstorfer, *J. Mater. Chem.* **2012**, *22*, 20418–20422.
[14] I. V. Tselinskii, S. F. Mel′nikova, T. V. Romanova, *Russ. J. Org. Chem.* **2001**, *37*, 430–436.
[15] T. M. Klapötke, P. Mayer, J. Stierstorfer, *Phosphorus Sulfur Silicon Relat. Elem.* **2009**, *184*, 2393–2407.
[16] Z. Li, W. Zhu, J. Yu, X. Ma, Z. Lu, S. Xiao, *Synth. Commun.* **2006**, *36*, 2613–2619.
[17] T. Curtius, K. Hochschwender, *J. Prakt. Chem.* **1915**, *91*, 415–441.
[18] K. Y. Lee, M. D. Coburn, *US 4733610*, **1988**, *28*, 1–2.
[19] M. D. Coburn, G. A. Buntain, B. W. Harris, *J. Heterocycl. Chem.* **1991**, *28*, 2049–2050.
[20] R. A. Henry, W. G. Finnegan, *J. Am. Chem. Soc.* **1954**, *76*, 923–926.
[21] P. N. Gaponik, V. P. Karavai, *Chem. Heterocycl. Compd.* **1984**, 1683–1686.
[22] J. A. Castillo-Melendez, B. T. Golding, *Synthesis* **2004**, *10*, 1655–1663.
[23] N. Fischer, T. M. Klapötke, J. Stierstorfer, *Z. Naturforsch. B* **2012**, *67*, 573–588.
[24] CrysAlisPro Oxford Diffraction Ltd., Version 171.33.41, **2009**.
[25] A. Altomare, G. Cascarano, C. Giacovazzo, A. Guagliardi, *J. Appl. Crystallogr.* **1993**, *26*, 343.
[26] A. Altomare, M. C. Burla, M. Camalli, G. L. Cascarano, C. Giacovazzo, A. Guagliardi, A. G. G. Moliterni, G. Polidori, R. Spagna, *J. Appl. Crystallogr.* **1999**, *32*, 115–119.
[27] G. M. Sheldrick, *SHELXS-97*, Program for Crystal Structure Solution, University of Göttingen, **1997**.
[28] G. M. Sheldrick, *SHELXL-97*, Program for the Refinement of Crystal Structures, University of Göttingen, Germany, **1997**.
[29] A. L. Spek, *PLATON*, A Multipurpose Crystallographic Tool, Utrecht University, Utrecht, The Netherlands, **1998**.
[30] L. J. Farrugia, *J. Appl. Crystallogr.* **1999**, *32*, 837–838.
[31] Empirical absorption correction using spherical harmonics, implemented in SCALE3 ABSPACK scaling algorithm (CrysAlisPro, Oxford Diffraction Ltd., v. 171.33.41, **2009**).
[32] N. Fischer, T. M. Klapötke, J. Stierstorfer, *Z. Anorg. Allg. Chem.* **2009**, *635*, 271–281.
[33] M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, B. Mennucci, G. A. Petersson, H. Nakatsuji, M. Caricato, X. Li, H. P. Hratchian, A. F. Izmaylov, J. Bloino, G. Zheng, J. L. Sonnenberg, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, J. A. Montgomery Jr, J. E. Peralta, F. Ogliaro, M. Bearpark, J. J. Heyd, E. Brothers, K. N. Kudin, V. N. Staroverov, R. Kobayashi, J. Normand, K. Raghavachari, A. Rendell, J. C. Burant, S. S. Iyengar, J. Tomasi, M. Cossi, N. Rega, J. M. Millam, M. Klene, J. E. Knox, J. B. Cross, V. Bakken, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. W. Ochterski, R. L. Martin, K. Morokuma, V. G. Zakrzewski, G. A. Voth, P. Salvador, J. J. Dannenberg, S. Dapprich, A. D. Daniels, Ö. Farkas, J. B. Foresman, J. V. Ortiz, J. Cioslowski, D. J. Fox, *Gaussian 09*, revision A.1, Gaussian, Inc., Wallingford CT, **2009**.
[34] M. Hesse, H. Meier, B. Zeeh, in: *Spektroskopische Methoden in der organischen Chemie*, Vol. 6, Thieme, Stuttgart, New York, **2002**.
[35] http://www.linseis.com.
[36] T. M. Klapötke, F. A. Martin, J. Stierstorfer, *Chem. Eur. J.* **2012**, *18*, 1487–1501.
[37] NATO standardization agreement (STANAG) on explosives, impact sensitivity tests, no. 4489, 1st ed., Sept. 17, **1999**.
[38] WIWEB-Standardarbeitsanweisung 4-5.1.02, Ermittlung der Explosionsgefährlichkeit, hier der Schlagempfindlichkeit mit dem Fallhammer, Nov. 8, **2002**.
[39] a) http://www.bam.de; b) www.reichel&partner.de.
[40] NATO standardization agreement (STANAG) on explosive, friction sensitivity tests, no. 4487, 1st ed., Aug. 22, **2002**.
[41] WIWEB-Standardarbeitsanweisung 4-5.1.03, Ermittlung der Explosionsgefährlichkeit oder der Reibeempfindlichkeit mit dem Reibeapparat, Nov. 8, **2002**.
[42] Impact: insensitive >40 J, less sensitive >35 J, sensitive >4 J, very sensitive <3 J. Friction: insensitive >360 N, less sensitive = 360 N, sensitive >80 [n], very sensitive >10 N, extremely sensitive <10 N. According to the UN Recommendations on the Transport of Dangerous Goods, (+) indicates not safe for transport.
[43] http://www.ozm.cz.
[44] E. F. C. Byrd, B. M. Rice, *J. Phys. Chem. A* **2006**, *110*, 1005–1013.
[45] P. J. Linstrom, W. G. Mallard (Eds.), in: *NIST Chemistry WebBook*, NIST Standard Reference Database Number 69, National Institute of Standards and Technology, Gaithersburg MD, 20899, http://webbook.nist.gov (retrieved October 27, **2011**).
[46] a) H. D. B. Jenkins, H. K. Roobottom, J. Passmore, L. Glasser, *Inorg. Chem.* **1999**, *38*, 3609–3620; b) H. D. B. Jenkins, D. Tudela, L. Glasser, *Inorg. Chem.* **2002**, *41*, 2364–2367.
[47] a) M. S. Westwell, M. S. Searle, D. J. Wales, D. H. Williams, *J. Am. Chem. Soc.* **1995**, *117*, 5013–5015; b) F. Trouton, *Philos. Mag.* **1884**, *18*, 54–57.
[48] M. Sućeska, EXPLO5.05 program, Zagreb, Croatia, **2012**.
[49] M. Sućeska, *Propellants Explos. Pyrotech.* **1991**, *16*, 197–202.
[50] Calculation of oxygen balance: Ω [%] = (wO – 2xC – 1/2yH – 2zS)1600/M (w: number of oxygen atoms, x: number of carbon atoms, y: number of hydrogen atoms, z: number of sulfur atoms, M: molecular weight).
[51] R. Mayer, J. Köhler, A. Homburg, in: *Explosives*, vol. 5, Wiley-VCH, Weinheim, Germany, **2002**.
[52] P. Hakey, W. Ouellette, J. Zubieta, T. Korter, *Acta Crystallogr., Sect. E* **2008**, *64*, o1428/1–o1428/6.
[53] J. R. Deschamps, M. Frisch, D. Parrish, *J. Chem. Crystallogr.* **2011**, *41*, 966–970.

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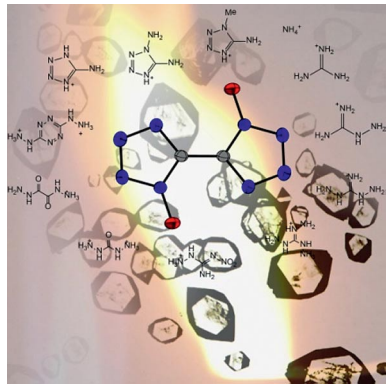
FULL PAPER

Energetic Materials

Fifteen nitrogen-rich energetic salts of 1*H*,1′*H*-5,5′-bitetrazole-1,1′-diol were synthesized and characterized. The energetic investigation partly showed candidates that performed very well with respect to detonation and combustion applications. They combine good thermal and chemical stabilities with acceptable sensitivities and synthetic costs.



Keywords: Energetic materials / Nitrogen heterocycles / Nitrogen-rich compounds

