

Nitroimino-tetrazolates and Oxy-nitroimino-tetrazolates

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Abstract: Highly energetic 1,1'-ethylenebis(oxy)bis(5-nitroimino-tetrazolate) salts were obtained by reacting equimolar quantities of the acidic 1,1'-ethylenebis(oxy)bis(5-nitroimino-tetrazole) and energetic bases in aqueous solution. Additionally, metathesis of silver 1,1'-ethylenebis(oxy)bis(5-nitroimino-tetrazolate) with diaminoguanidinium chloride or triaminoguanidinium chloride gave the corresponding oxy-nitroimino-tetrazolate salt. These salts were fully characterized using IR and multinuclear NMR spectroscopy, elemental analysis, and differential scanning calorimetry (DSC), and, in some cases, **2**·2H₂O, **8**·2H₂O, **10**, **13**·2H₂O and **14**, with single crystal X-ray structuring. The heats of formation for all compounds were calculated with Gaussian 03 and then combined with measured densities to determine detonation pressures (*P*) and velocities (*D*) of the energetic materials (Cheetah 5.0). The impact sensitivities of all salts were found to be less than those of the parent compounds. The physical and detonation properties of these oxy-nitroimino-tetrazolate salts are comparable to the analogous newly prepared diaminoguanidinium and triaminoguanidinium 1,1'-ethylenebis(5-nitroimino-tetrazolate)s.

Introduction

Nitroimino-tetrazole families,¹ which are five-membered aromatic heterocycles with a nitroimine substituent, are one approach in the development of new energetic materials. They are very useful as less toxic energetic materials. Most of the compounds exhibit positive heats of formation owing to their high nitrogen content and to their excellent thermal stabilities arising from their aromaticity.^{1a} 1-Methyl-5-nitroimino-tetrazole was first prepared and characterized (*pK* = 2.72, melting point = 158–160 °C) nearly 50 years ago.² It was of interest to examine the reactivity of the relatively acidic hydrogen of the tetrazole ring. Recently, the Klapötke group reported more information about the calculated detonation properties of 1-methyl-5-nitroimino-tetrazole, confirmed a synthetic method for preparing substituted nitroimino-tetrazoles in better yields, and established structure by single-crystal X-ray diffraction analysis.³ Moreover, synthesis and characterization of various guanidinium nitroimino-tetrazolate salts, which can be prepared from silver nitroimino-tetrazolate by metathesis, were reported as high energy density materials.⁴

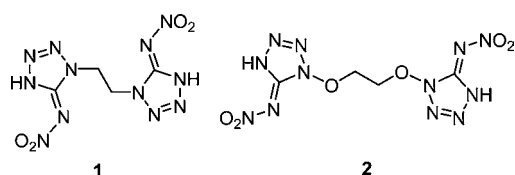


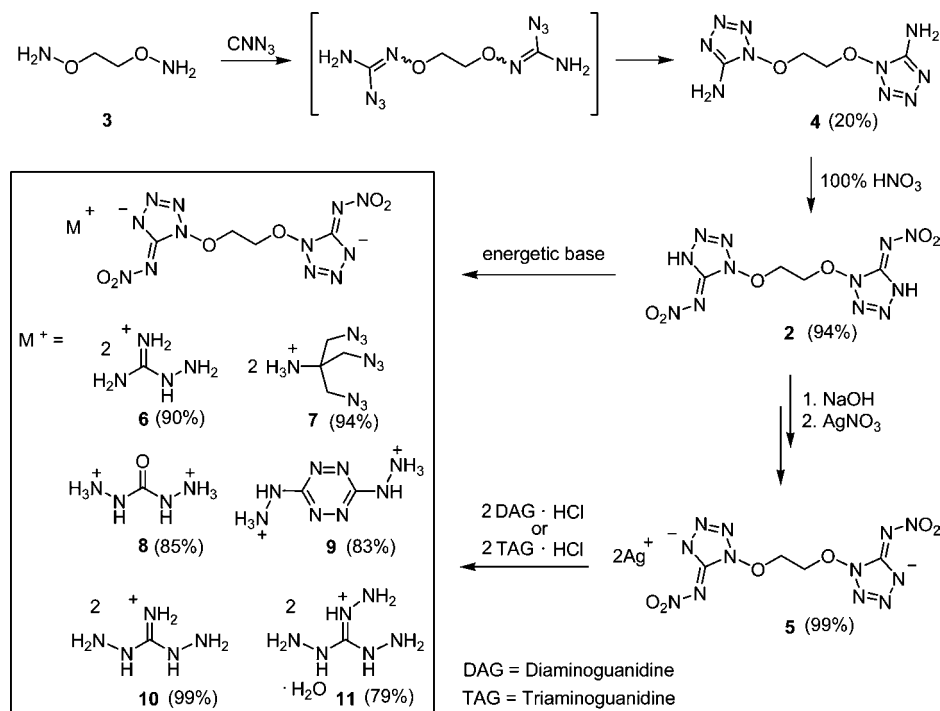
Figure 1. Bis(5-nitroimino-tetrazole) **1** and **2**.

One high nitrogen system extensively studied by the Idaho group is the substituted nitroimino-tetrazole. By employing an alternate route, we reported the effective synthesis of the disubstituted 5-nitroimino-tetrazoles, 1,1'-ethylenebis(5-nitroimino-tetrazole) (**1**)⁵ and 1,1'-ethylenebis(oxy)bis(5-nitroimino-tetrazole) (**2**)⁶ (Figure 1). The development of disubstituted 5-aminotetrazole compounds was extended by the utilization of an excellent in situ method which involved reactions of cyanogen azide⁷ and primary amines. Nitration of these aminotetrazoles using 100% nitric acid has been shown to form disubstituted nitroimino-tetrazole derivatives. Compound **1** exhibits a high measured density of 1.858 g cm⁻³; calculated heat of formation of 3.63 kJ g⁻¹; detonation pressure of 38.19 GPa; and a detonation velocity of 9329 m s⁻¹. The values of the detonation properties of compound **2** (*P* = 38.38 GPa, *D* = 9200 m s⁻¹) are as high as for compound **1** and its oxygen percentage is slightly improved. Impact sensitivity measurements on oxy-nitroimino-tetrazole **2** indicate that it is very sensitive to shock; accordingly it should be handled with caution and in small amounts. For this reason, **2** needs to be desensitized perhaps by salt formation. Recently we reported that reduced sensitivity

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Scheme 1. Synthesis of 1,1'-Ethylenebis(oxy)bis(5-nitroimino-tetrazolate) Salts



was obtained by making energetic salts of compound **1** and energetic bases.⁸ The formation of salts of the nitroimino-tetrazole led to an enhanced thermal stability and less or equal impact sensitivity compared to those of a neutral compound.

The aim of this work was to prove the structures of important crystalline energetic salts using X-ray diffraction analysis and to discover new and potent nitroimino-tetrazolate salts. Oxy-5-nitroimino-tetrazolate salts are of interest as ionic energetic materials, which have good thermal stabilities and low impact sensitivities, and which deserve closer attention by researchers because they are closely linked with the safety of handling and application of explosives. Here, we compare properties of the new oxy-nitroimino-tetrazolate salts with new as well as our previously reported nitroimino-tetrazolate salts.⁸

Results and Discussion

The reaction of ethylene(oxyphthalimide), which was prepared via the treatment of 1,2-dibromoethane with *N*-hydroxyphthalimide according to the literature procedure, called Gabriel Amine Synthesis, gave the ethylenebis(oxyamine) **3** by hydrazinolysis.⁹ A convenient method for the synthesis of 1,1'-ethylenebis(oxy)bis(5-aminotetrazole) **4** from **3** and cyanogen azide without the intermediate isolation of imindoylazide was developed and resulted in the preparation of the target oxy-aminotetrazole **4** in 20% yield. The corresponding high energetic

oxy-nitroimino-tetrazole **2** was prepared from oxy-aminotetrazole **4** in good yield by a nitration procedure from the literature.⁶ All attempts to remove water molecules in the crystal of **2**·2H₂O to give **2** at 60 °C under high vacuum were successful. However, violent detonations during attempted elemental analyses determinations, compound **2** and **2**·2H₂O were not analyzed.

Fortunately, it was possible to perform single-crystal X-ray diffraction analysis for **2**·2H₂O. The energetic salts **6**–**9** were generally obtained by acid–base reactions between **2** and energetic bases in aqueous solutions (Scheme 1).

Also, in Scheme 1 is shown the syntheses of the diaminoguanidinium and triaminoguanidinium oxy-nitroimino-tetrazolate salts. Two energetic salts, **10** and **11**, were synthesized using silver 1,1'-ethylenebis(oxy)bis(5-nitroimino-tetrazolate) (**5**), which was obtained by metathesis of sodium 1,1'-ethylenebis(oxy)bis(5-nitroimino-tetrazolate) and silver nitrate, with the corresponding chloride salts. After stirring for four hours, silver chloride from the suspension was filtered and the filtrate was dried. The structures of 1,1'-ethylenebis(oxy)bis(5-nitroimino-tetrazole) (**2**) and its salts are supported by IR, and ¹H, ¹³C, and ¹⁵N NMR spectroscopic data as well as elemental analysis.

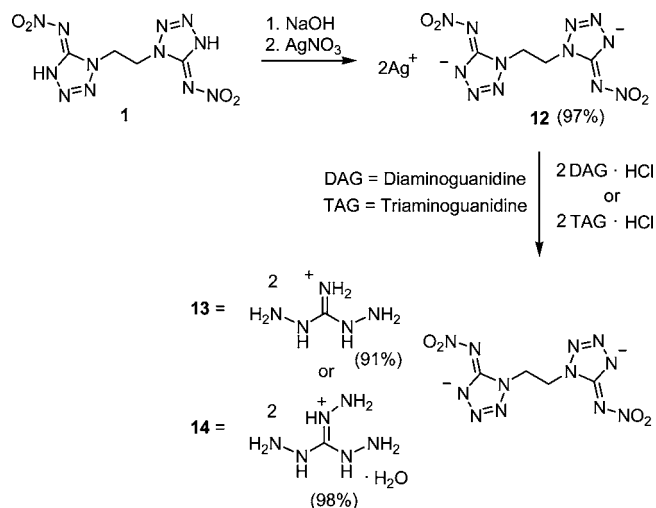
Next similar successful attempts were made to prepare bis(diaminoguanidinium) 1,1'-ethylenebis(5-nitroimino-tetrazolate) (**13**) and bis(triaminoguanidinium) 1,1'-ethylenebis(5-nitroimino-tetrazolate) (**14**) in good yields by metathesis with silver salt **12** (Scheme 2). The structures of **13** and **14** are supported by IR, and ¹H, ¹³C, and ¹⁵N NMR spectroscopic data as well as elemental analysis. Salt **14** also could be prepared by metathesis reactions of barium 1,1'-ethylenebis(oxy)bis(5-aminotetrazolate) with the corresponding triaminoguanidinium sulfate in a yield of 74%.

Crystal Structure Analysis. Data collection was performed, and the unit cell was initially refined using APEX2 [v2.1-0].^{10a} Data reduction was performed using SAINT [v7.34A]^{10b} and XPREP [v2005/2].^{10c} Corrections were applied for Lorentz,

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Scheme 2. Synthesis of 1,1'-Ethylenebis(5-nitroimino-tetrazolate) Salts by Metathesis

polarization, and absorption effects using SADABS [v2004/1].^{10d} The structure was solved and refined with the aid of the programs in the SHELXTL-plus [v6.12] system of programs.^{10e} The full-matrix least-squares refinement on F^2 included atomic coordinates and anisotropic thermal parameters for all non-H atoms. The H atoms were included using a riding model. Selected data and parameters of the X-ray determinations are given in Table 1. Further information about crystal structure determinations is given in the Supporting Information.

As expected and found in several selected structures including 1,1'-ethylenebis(oxy)bis(5-nitroimino-tetrazole) dihydrate ($2 \cdot 2\text{H}_2\text{O}$) and its salts ($8 \cdot 2\text{H}_2\text{O}$ and **10**) and 1,1'-ethylenebis(5-nitroimino-tetrazolate) salts ($13 \cdot 2\text{H}_2\text{O}$ and **14**) discussed in this work, the nitroimino-tetrazole ring is nearly planar, building an aromatic system, which can be seen at the torsion angle N1–N2–N3–N4 of between $0.14(14)^\circ$ and $0.71(15)^\circ$. The ring moieties of $2 \cdot 2\text{H}_2\text{O}$, $8 \cdot 2\text{H}_2\text{O}$, **10**, $13 \cdot 2\text{H}_2\text{O}$, and **14** are in agreement with the geometry observed for 5-nitroimino-tetrazoles and their salts.^{3–6,8} The N2–N3 bond lengths of all structures of $2 \cdot 2\text{H}_2\text{O}$, $8 \cdot 2\text{H}_2\text{O}$, **10**, $13 \cdot 2\text{H}_2\text{O}$, and **14** lie between 1.271 and 1.294 Å, which are typical values observed for the nitroimino-tetrazoles and their anions. We observed that, for the N2–N3 bond lengths, neutral compounds **1** (1.271 Å) and $2 \cdot 2\text{H}_2\text{O}$ (1.271 Å) are slightly shorter than their salts (between 1.291 and 1.294 Å).

1,1'-Ethylenebis(oxy)bis(5-nitroimino-tetrazole) dihydrate ($2 \cdot 2\text{H}_2\text{O}$) crystallizes in the monoclinic space group $C2/c$ with four molecules in the unit cell (Figure 2), and has a density of 1.684 g cm^{-3} (at 296 K) (Table 1). The C–N and N–N bonds of the tetrazole ring are in a range similar to that observed in **1**.⁵ The N1–O10 distances (1.3591 Å) in **2** are found to be shorter than the N–C distances (1.460 Å) in compound **1**. The tetrazole ring [torsion angle N1–N2–N3–N4 $0.71(15)^\circ$] is planar, which is a condition of the 6π aromaticity, and the nitroimine group [torsion angle N4–C5–N6–N7 $1.3(2)^\circ$] is also almost planar out of this ring. In contrast to this, the ethoxy unit [torsion angle C5–N1–O10–C11 $-84.65(14)^\circ$] is significantly bent from the ring plane. The packing structure of $2 \cdot 2\text{H}_2\text{O}$ is strongly influenced by strong hydrogen bonds between H_2O and **2**. These extensive hydrogen-bonding interactions between oxygen atom O1S from water and N4 [N4...O1S 2.6854(16)] can be seen in Figure 2b along the b axis.

Compound **8**· $2\text{H}_2\text{O}$ crystallized in a triclinic cell in the space group $P\bar{1}$ with two molecules in the unit cell. The tetrazole ring of **8**· $2\text{H}_2\text{O}$ is nearly planar and four similar bond lengths are observed [N1–N2 = 1.336(16) Å, N3–N4 = 1.369(19) Å, N4–C5 = 1.326(16) Å, N1–C5 = 1.349(18) Å], and shows the delocalization of the negative charge from the ring (Figure 3). The main change observed is the bond length of N2–N3 which corresponds to the N4 nitrogen atom that undergoes deprotonation in **1**. Deprotonation results in a lengthening of the N1–N2 and N3–N4 distances (~ 0.01 Å) and a shortening of the N2–N3 bond (~ 0.02 Å). These distances are considerably longer than N2–N3 double bonds (1.291(2) Å) but significantly shorter than the O10–C11 [1.461(17) Å] or N1–O10 [1.363(14) Å] single bond. The nitroimine unit lies in the plane of the tetrazole ring as clearly shown by the C5–N6–N7–O9 torsion angle of $-0.57(18)^\circ$ and C5–N6–N7–O8 torsion angle of $-179.27(11)^\circ$, in which the oxygen atoms O8 and O9 are twisted slightly out of the plane. The ethoxy unit does not lie in the plane of the tetrazole ring [torsion angle C5–N1–O10–C11 of $91.50(15)^\circ$]. The observed angle in the tetrazolate matches the typical values found in the literature for oxy-nitroimino-tetrazolate.⁶

The colorless crystals of **10** were grown by slow evaporation of an aqueous solution. The unit cell of **10**, which crystallizes with a calculated density of 1.675 g cm^{-3} (296(2) K) in the monoclinic space group $P\bar{1}$, contains two formula moieties. The bond lengths and angles of the diaminoguanidinium cation correspond to the values of diaminoguanidinium 1-methyl-5-nitroimino-tetrazolate.⁴ Between the oxy-nitroimino-tetrazolates, a torsion angle O10–C11–C12–O13 of $-54.70(17)^\circ$ is observed (Figure 4).

The bond lengths in oxy-5-nitroimino-tetrazolate are very similar to the values found and discussed for $8 \cdot 2\text{H}_2\text{O}$. The packing of **10** is also characterized by a three-dimensional network (see Supporting Information), whereby several weak hydrogen bonds are formed between the nitrogen atom of the diaminoguanidinium cation and the nitrogen or oxygen atom of the oxy-nitroimino-tetrazolate anion.

Diaminoguanidinium 1,1'-ethylenebis(5-nitroimino-tetrazolate) $13 \cdot 2\text{H}_2\text{O}$ crystallizes in the monoclinic crystal system in the space group $P2_1/c$. By including four molecular moieties in the unit cell, the calculated density is 1.636 g cm^{-3} . In general, the diaminoguanidine cations have geometries found in diaminoguanidinium sulfate.¹¹ This cation is nearly planar with torsion angle (N26–C21–N22–N23 $176.96(12)^\circ$) and C–N bond lengths observed between 1.3284 and 1.3310 Å. Two nitroimino-tetrazole anions in the molecule exhibit coplanar geometry with torsion angle N1–C10–C11–N12 $179.29(10)$ (Figure 5).

The geometry of the triaminoguanidine cation is comparable to that observed for triaminoguanidinium sulfate in the literature.¹¹ The positive charge is delocalized as supported by similar C–N bond lengths C21–N22 = 1.328(2) Å, C21–N24 = 1.323(2) Å, C21–N26 = 1.324(2) Å and a planar system. The hydrazine bonds of triaminoguanidine cation have similar lengths between 1.401(2) and 1.413(2) (Figure 6). The constitution of the nitroimino-tetrazole anion is comparable to those observed for $13 \cdot 2\text{H}_2\text{O}$. However, the nitroimino-tetrazolate rings are considerably twisted relative to each other with a torsion angle N1–C10–C11–N12 at $57.2(2)^\circ$.

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Table 1. Crystallographic Data for **2**·2H₂O, **8**·2H₂O, **10**, **13**·2H₂O, and **14**

	2 ·2H ₂ O	8 ·2H ₂ O	10	13 ·2H ₂ O	14
formula	C ₄ H ₁₀ N ₁₂ O ₈	C ₅ H ₁₆ N ₁₆ O ₉	C ₆ H ₂₀ N ₂₂ O ₆	C ₆ H ₂₄ N ₂₂ O ₆	C ₆ H ₂₄ N ₂₄ O ₅
fw	354.24	444.34	496.44	500.47	512.49
space group	C2/c	P1	P1	P2 ₁ /c	P2 ₁ /c
<i>a</i> (Å)	26.767(6)	7.7035(3)	7.5429(5)	14.251(2)	14.1339(17)
<i>b</i> (Å)	4.8803(10)	10.8458(4)	8.9642(6)	12.9147(19)	22.245(3)
<i>c</i> (Å)	10.707(2)	10.9203(4)	15.2214(11)	11.0418(17)	6.8288(8)
α (deg)	90	79.481(1)	80.376(2)	90	90
β (deg)	92.639(3)	76.778(1)	82.322(2)	91.008(2)	94.726(2)
γ (deg)	90	77.897(1)	77.146(2)	90	90
<i>V</i> (Å ³)	1397.2(5)	859.74(6)	984.31(12)	2031.9(5)	2139.7(4)
<i>Z</i>	4	2	2	4	4
λ (Å)	0.71073	0.71073	0.71073	0.71073	0.71073
<i>T</i> (K)	296(2)	296(2)	296(2)	296(2)	296(2)
<i>D</i> _{calcd} (g cm ⁻³)	1.684	1.716	1.675	1.639	1.591
μ (mm ⁻¹)	0.157	0.157	0.144	0.140	0.134
<i>R</i> ₁ [<i>I</i> > 2 σ (<i>I</i>)] ^a	0.0317	0.0331	0.0383	0.0341	0.0426
<i>wR</i> ₂ [<i>I</i> > 2 σ (<i>I</i>)] ^b	0.0880	0.0853	0.0951	0.0875	0.0951

^a $R_1 = \sum ||F_o| - |F_c|| / \sum |F_o|$. ^b $wR_2 = \{\sum [w(F_o^2 - F_c^2)^2] / \sum [w(F_o^2)]\}^{1/2}$.

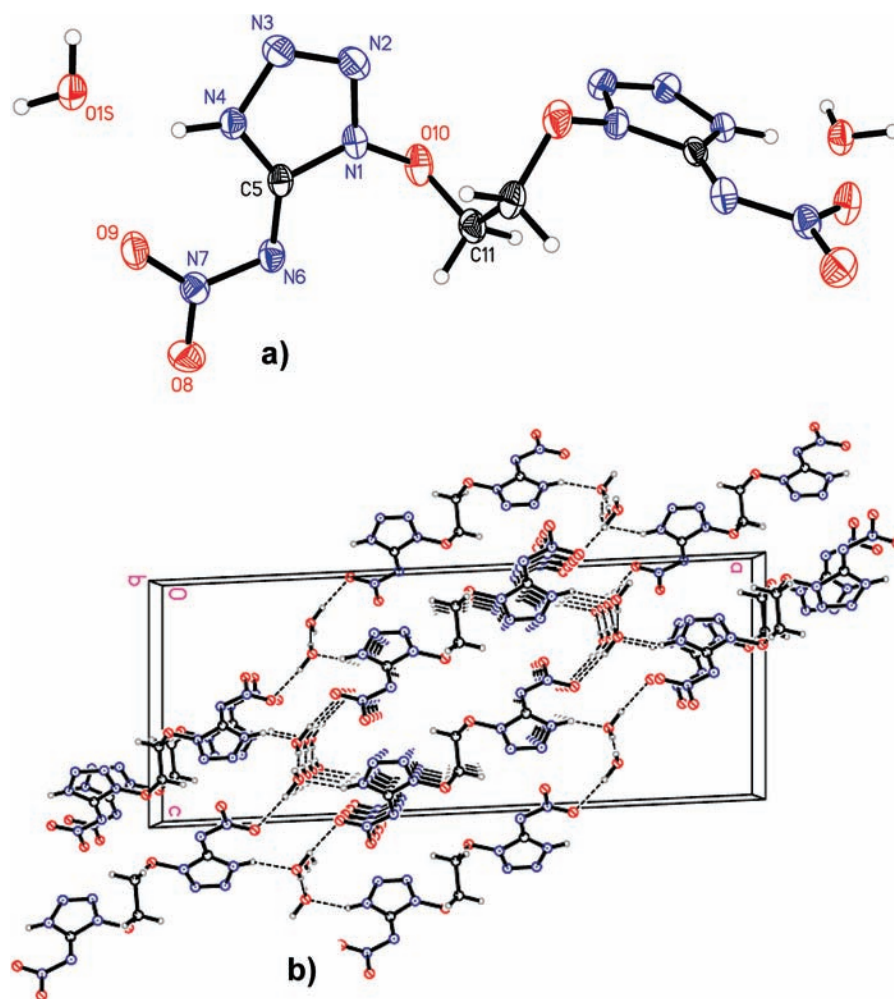


Figure 2. (a) View of the molecular unit of **2**·2H₂O. Thermal ellipsoids represent 50% probability. (b) Unit cell view along the *b* axis. Selected bond lengths [Å]: N1–N2 1.3479(18), N2–N3 1.2715(18), N3–N4 1.3605(17), N4–C5 1.3315(18), N1–C5 1.3553(17), C5–C6 1.3296(18), N6–N7 1.3472(16), N1–O10 1.3618(15), O10–C11 1.4589(19).

The ¹⁵N NMR chemical shift data of the 1,1'-ethylenebis(oxy)-bis(5-nitroimino-tetrazolate) salts **6**–**11** and 1,1'-ethylenebis(5-nitroimino-tetrazolate) salts **13** and **14** are presented in Table 2. On the basis of the values of the chemical shifts of guanidine or hydrazine moieties, NH, NH₂, and NH₃⁺ groups can be assigned to the resonances at highest field on the basis of

comparison with the literature^{4,11} (see Experimental Section). The assignment of the resonance peaks between the coordinated nitrogen atoms of nitroimino-tetrazoles **2** can be achieved mainly on the basis of the fact that N1 has one oxygen, one carbon, and one nitrogen atom as nearest neighbors, while N4 has one carbon and one nitrogen. Dependency of the resonance shift in

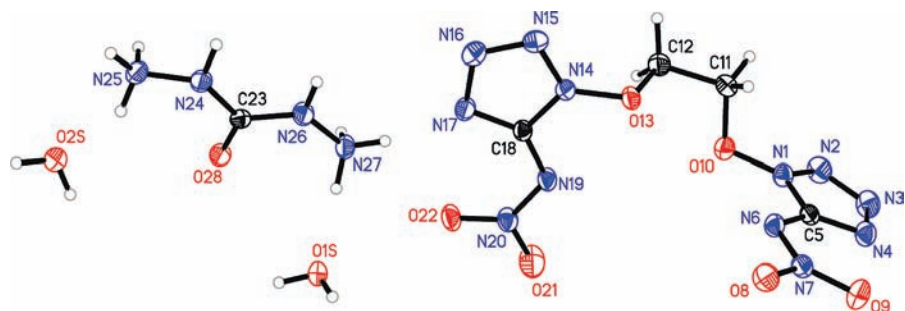


Figure 3. View of the molecular unit of **8**·2H₂O. Thermal ellipsoids represent 50% probability. Selected torsion angles [deg]: C5–N6–N7–O9 –0.57(18), C5–N6–N7–O8 –179.27(11), C5–N1–O10–C11 91.50(15).

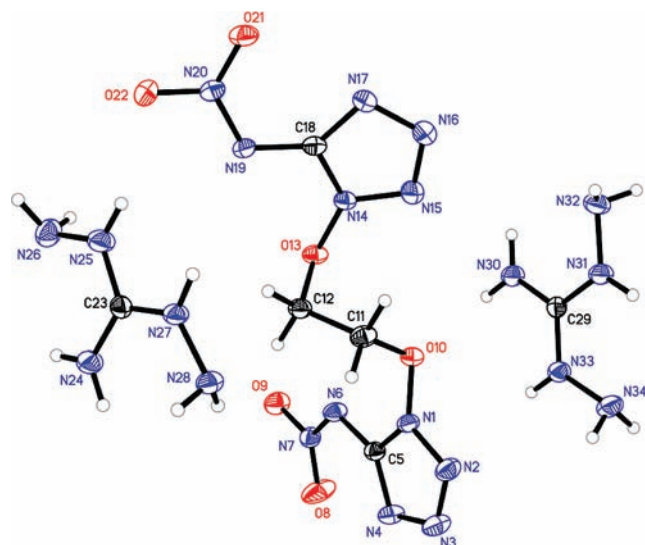


Figure 4. View of the molecular unit of **10**. Thermal ellipsoids represent 50% probability.

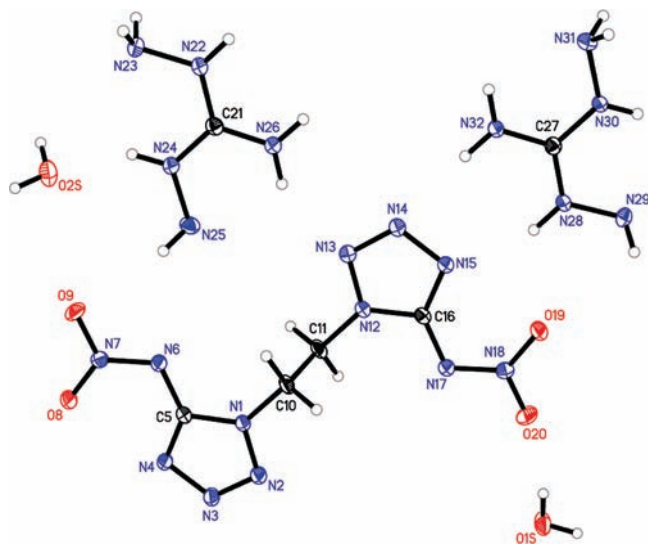


Figure 5. View of the molecular unit of **13**·2H₂O. Thermal ellipsoids represent 50% probability. Selected bond lengths [Å]: N1–N2 1.3498(16), N2–N3 1.2940(16), N3–N4 1.3590(16), N4–C5 1.3344(17), N1–C5 1.3614(16), N1–C10 1.4587(16), C5–N6 1.3631(17), C10–C11 1.5224(18). Selected torsion angles [deg]: C5–N1–C10–C11 –97.99(15), N1–C10–C11–N12 179.29(10).

the ¹⁵N NMR can thus be used to assign the ¹⁵N signals in the tetrazole ring and to distinguish from the substituted and nonsubstituted nitrogen atoms. In Table 2, the resonance for

N1 (–117 ppm) of **2** with an alkoxy substituent are observed at a relatively lower field than the alkyl-substituted N1 of **1** (–170.6 ppm) in the tetrazole ring because of the strong electronegativity effect. By comparison with neutral nitroimino-tetrazole **1** and **2** (Table 2), the N4 resonance for the deprotonated nitroimino-tetrazole, **6–11**, **13** and **14** is observed at considerably lower field (50–80 ppm) than for the former compounds, **1** and **2**. The assignments are based on the values of the chemical shifts reported for nitroimino-tetrazolate salts in the literature.^{3–6,8}

The ¹⁵N NMR spectra of nitroimino-tetrazolate salts were measured in DMSO[D₆] solution, and chemical shifts are given with respect to CH₃NO₂ as external standard. In Figure 7, selected ¹⁵N NMR spectra of **7**, **9**, **11**, and **14** are shown.

In the case of compound **7**, the signals for the N_α (–317.5 ppm) from azide (R–N₃: R–N_αN_βN_γ) and ammonium cation (–336.9 ppm) appear at the highest field. N_β and N_γ are at –134.9 ppm and –171.1 ppm, respectively. Comparison of the resonances observed for the oxy-5-nitroimino-tetrazolate anion in this study shows the expected shifts.¹³ Compound **9** signals for the hydrazinium cation bonded to tetrazine appear at the highest field (NH and NH₂). The chemical shift of N7 (–26.7 ppm) in the tetrazine ring,⁸ and those for the alkoxy-nitroimino-tetrazolate anion were assigned on the basis of comparison with literature values.⁶ The spectrum of **11** with eight signals at –319.6 (NH₂), –279.2 (NH), –151.0 (N5), –115.9 (N1), –64.1 (N4), –19.4 (N3), –4.4 (NO₂), 3.5 (N2) is shown. The signals for N1, which has oxygen as a neighbor in the tetrazole ring appear as expected at lower field (–115.9 ppm) compared with the N1 position (–166.7 ppm) of triaminoguanidinium 1,1'-ethylene bis(5-nitroimino-tetrazolate) (**14**). The assignments are based on the literature values of the remainder of the peaks which are essentially unchanged for the nitroimino-tetrazole group.^{3–6,8}

Physical Properties. Heat of formation is one of the important characteristics for energetic salts which is directly related to the number of nitrogen–nitrogen bonds in an ionic species.¹⁴ All quantum chemical calculations were carried out using the program package Gaussian 03 (Revision D.01).¹⁵ The geometric optimization of the structures and frequency analyses was accomplished by using the B3LYP with the 6-31+G** basis set,¹⁶ and single-point energies were calculated at the MP2/6-

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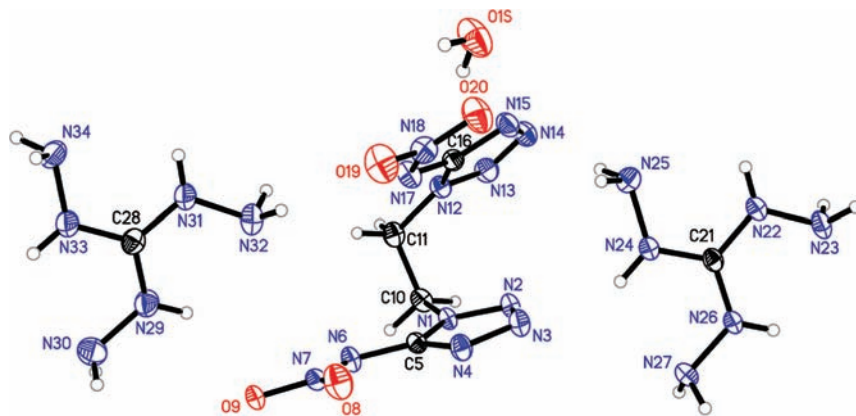


Figure 6. View of the molecular unit of **14**. Thermal ellipsoids represent 50% probability.

Table 2. Comparison of the ^{15}N NMR Chemical Shifts (ppm) of Nitroimino-tetrazole **1**, Oxy-nitroimino-tetrazole **2**, and Their Salts^a

compd	N1	N2	N3	N4	N5	N6 (NO ₂)
1 ^b	-170.6	-20.1	-24.7	-154.3	-156.8	-15.5
2	-117.0	-10.6	-24.5	-124.3	-154.7	-17.8
6	-125.5	-6.3	-28.7	-74.4	-160.0	-14.3
7	-125.5	-6.1	-28.8	-74.7	-160.0	-13.9
8	-118.6	-0.1	-21.6	-71.2	-152.9	-6.9
9	-118.8	-0.6	-21.8	-72.4	-153.0	-7.0
10	-116.1	3.2	-19.5	-64.6	-150.9	-4.7
11	-115.9	3.5	-19.4	-64.1	-151.0	-4.4
13	-166.7	-21.5	5.5	-73.2	-157.7	-14.5
14	-166.7	-21.5	5.5	-73.0	-157.8	-14.4

^a All shifts were measured with [D₆]DMSO at 30 °C. ^b At 55 °C.

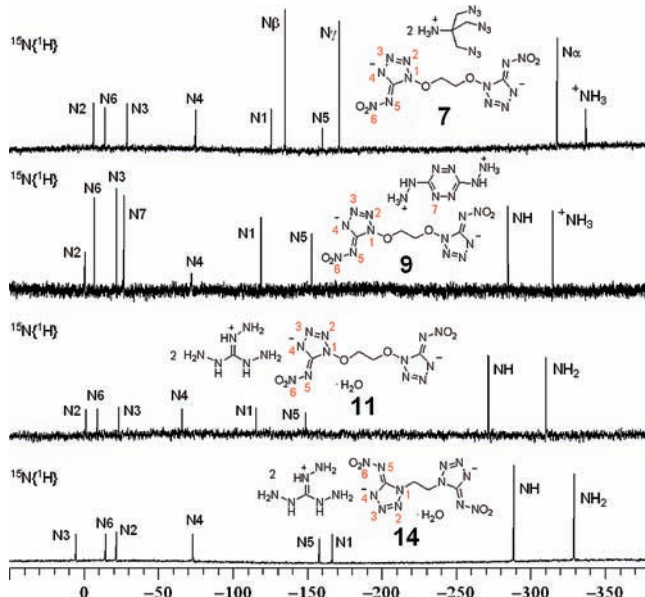
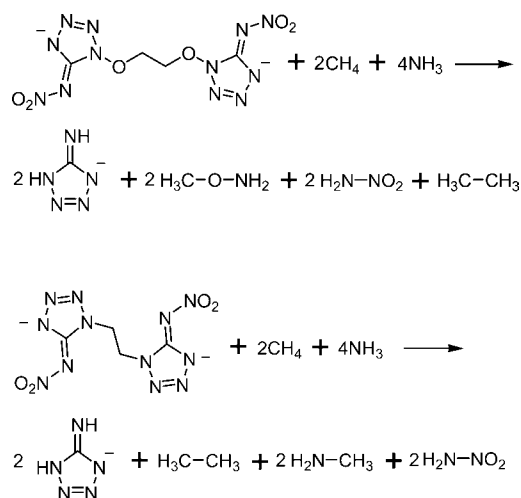


Figure 7. Selected ^{15}N NMR spectra of nitroimino-tetrazolate salts.

311++G** level. Atomization energies were calculated by the G2 method.¹⁷ All of the optimized structures were characterized

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Scheme 3. Isodesmic Reactions of the Bis(nitroimino-tetrazolate) Anions



to be true local energy minima on the potential-energy surface without imaginary frequencies. The remaining task is to determine the heats of formation of the cations and anions, which are computed by using the method of isodesmic reactions (Scheme 3).

The enthalpy of an isodesmic reaction (ΔH_f°) is obtained by combining the MP2/6-311++G** energy difference for the reaction, the scaled zero-point energies (B3LYP/6-31+G**), and other thermal factors (B3LYP/6-31+G**). Thus, the heats of formation of the cations and anions being investigated can be extracted readily (Table 3).

On the basis of Born–Haber energy cycles (Figure 8), the heats of formation of ionic salts can be simplified by eq 1:

$$\Delta H_f^{\circ}(\text{ionic salt}, 298 \text{ K}) = \Delta H_f^{\circ}(\text{cation}, 298 \text{ K}) + \Delta H_f^{\circ}(\text{anion}, 298 \text{ K}) - \Delta H_L \quad (1)$$

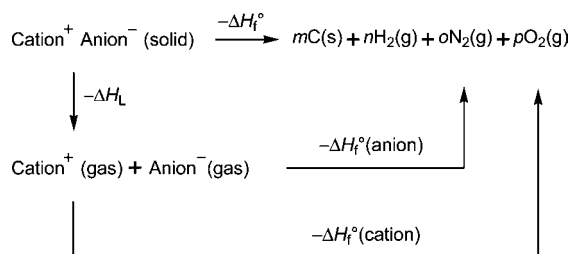
The lattice potential energies (U_{POT}) and lattice enthalpies (ΔH_L) were calculated according to the followed equations provided by Jenkins and are summarized¹⁸ in which ΔH_L is the lattice energy of the ionic salt. The ΔH_L value can be predicted by the formula, eq 2,¹⁸ where U_{POT} is the lattice potential energy, n_M and n_X depend on the nature of the ions M_p^+ and X_q^- , respectively, and are equal to three for monatomic

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Table 3. Physical Properties of Oxy-nitroimino-tetrazolate Salts **6–11** Compared with Nitroimino-tetrazolate Salts

compd	T_m [°C] ^a	T_{dec} [°C] ^b	density [g cm ⁻³] ^c	P [GPa] ^e	D [m s ⁻¹] ^f	IS [J] ^g	OB [%] ^h
6	–	200	1.602	1029 (2.21)	26.78	8472	6
7	–	151	1.597	2944 (4.14)	26.56	8377	<1
8	–	130, 146	1.695	1134 (2.78)	32.20	8789	6
8 ·2H ₂ O	127	156	1.716 ⁱ	–	–	–	2
8 ·4H ₂ O	71, 78, 129	147	1.647	–	–	–	8
9	–	147	1.780	1270 (2.76)	33.25	9030	2
9 ·2H ₂ O	72	131	1.683	–	–	–	–
10	160	164	1.675 ⁱ	1254 (2.53)	28.72	8741	5
11	95, 160	162	1.607	1487 (2.82)	29.36	8840	4
13	–	220	1.577	1233 (2.66)	26.51	8568	7
13 ·2H ₂ O	202	218	1.639 ⁱ	–	–	–	>40
14	132	195	1.601	1458 (2.95)	28.64	8860	>40
AG I-8 ^j	–	255	1.610	993 (2.29)	26.27	8531	10
TAA I-8 ^k	–	186	1.600	2922 (4.31)	26.45	8429	5
CH I-8 ^l	–	203	1.722	1094 (2.91)	31.98	8957	10
TH I-8 ^m	–	203	1.820	1231 (2.87)	34.25	9305	15
RDX ⁿ	–	230	1.816	92.6 (0.42)	35.17	8977	7.4

^a Melting point. ^b Thermal decomposition temperature (onset) under nitrogen gas (DSC, 10 °C min⁻¹). ^c From gas pycnometer (25 °C). ^d Heat of formation (calculated via Gaussian 03). ^e Calculated detonation pressure (Cheetah 5.0). ^f Calculated detonation velocity (Cheetah 5.0). ^g Impact sensitivity (BAM drophammer). ^h OB = oxygen balance (%) for C_aH_bO_cN_d: 1600 × (c - 2a - b/2)/M_w, M_w = molecular weight of salt. ⁱ X-ray density (23 °C). ^j Bis(aminoguanidinium) 1,1'-ethylenebis(5-nitroimino-tetrazolate): ref 8. ^k Bis[1,3-diazido-2-(azidomethyl)-2-propylammonium] 1,1'-ethylenebis(5-nitroimino-tetrazolate): ref 13. ^l Carbohydrazinium 1,1'-ethylenebis(5-nitroimino-tetrazolate): ref 8. ^m 1,2,4,5-Tetrazino-3,6-bis(hydrazinium) 1,1'-ethylenebis(5-nitroimino-tetrazolate): ref 8. ⁿ Reference 22.

**Figure 8.** Born–Haber cycle for the formation of nitroimino-tetrazolate salts.

ions, five for linear polyatomic ions, and six for nonlinear polyatomic ions.

$$\Delta H_L = U_{\text{POT}} + [p(n_M/2 - 2) + q(n_X/2 - 2)]RT \quad (2)$$

The equation for the lattice potential energy, U_{POT} , takes the form of eq 3,

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

where ρ_m is the density (g cm⁻³), M_m is the chemical formula mass of the ionic material (g), and the coefficients γ (kJ mol⁻¹ cm) and δ (kJ mol⁻¹) are assigned literature values.¹⁸

In Table 3 it is shown that all nitroimino-tetrazolate salts are highly endothermic compounds. The enthalpies of energetic materials are controlled by the molecular structure of the compounds. Consequently, heterocycles with higher nitrogen content, especially tetrazole, show higher heats of formation. All of the new compounds (**6–11**, **13**, and **14**) exhibit positive heats of formation ranging between 2.21 and 4.14 kJ g⁻¹. Bis[1,3-diazido-2-(azidomethyl)-2-propylammonium] 1,1'-ethylenebis(oxy)bis(5-nitroimino-tetrazolate) (**9**) has the highest value at 4.14 kJ g⁻¹ which is comparable to salt (**TAA I-8**)¹³ of the same cation and anion **1**²⁻ with a high positive heat of formation (4.31 kJ g⁻¹). Impact sensitivity measurements were made using standard BAM Fallhammer techniques.¹⁹ Listed in Table 3 are impact sensitivities ranging from those of the relatively less sensitive **6**, **8**, **8**·4H₂O, **9**·2H₂O, **10**, **11**, and **13**, between 4 and 8 J to the very sensitive compounds **7**, **8**·2H₂O,

and **9** between 1 and 2 J. Compounds **13**·2H₂O and **14** are not impact sensitive. Thermal stabilities of the energetic compounds were studied with differential scanning calorimetry (DSC) at a scan rate of 10 °C min⁻¹. All nitroimino-tetrazolates decomposed between 130 and 220 °C (see DSC traces for all compounds in the Supporting Information). As expected, the thermal stabilities for all energetic salts are higher for the neutral compounds **1** (194 °C) and **2** (125 °C). The most thermally stable derivatives of **2** and **1** are the aminoguanidinium salts **6** and **AG I-8** where decomposition occurred at 200 and 255 °C, respectively (Table 3). By using the calculated values of the heats of formation and the experimental values for the densities (gas pycnometer or X-ray values) of the new highly energetic nitroimino-tetrazolate salts, **6–11**, **13**, and **14**, the detonation pressures (P) and detonation velocities (D) were calculated on the basis of traditional Chapman–Jouget thermodynamic detonation theory using Cheetah 5.0 (Table 3).²⁰ The calculated detonation pressures of nitroimino-tetrazolate salts lie in the range between $P = 26.51$ and $P = 33.25$ GPa (comparable to TATB = 31.15, RDX = 35.17 GPa). Detonation velocities lie between $D = 8377$ and $D = 9030$ m s⁻¹ (comparable to TATB = 8114, RDX = 8977 m s⁻¹). These properties coupled with the rather high thermal and hydrolytic stabilities make these high-nitrogen materials attractive candidates for energetic applications. The oxygen balance (OB) is the index of the deficiency or excess of oxygen in a compound required to convert all carbon into carbon dioxide, and all hydrogen into water; for a compound with the molecular formula of C_aH_bN_cO_d, OB (%) = 1600 × (d - 2a - b/2)/M_w (Table 3). The relatively

(19) (a) <http://www.bam.de/en/index.htm>. (b) A portion of 20 mg of nitroimino-tetrazolate salts was subjected to a drop-hammer test using a 5- or 10-kg weight. A range in impact sensitivities according to the UN Recommendations (insensitive > 40 J; less sensitive ≥ 35 J; sensitive ≥ 4 J; very sensitive ≤ 3 J).

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(21) Krause, H. H. In *Energetic Materials*; Teipel, U., Ed.; VCH: Weinheim, 2005; pp 1–25.

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moderate oxygen balances of **8** and **9** are -35% and -42% , respectively. Incorporation of one additional oxygen atom from the oxyethylene link to the nitroimino-tetrazole moiety slightly improves the oxygen balance of the corresponding compounds and may eventually result in higher exothermicities of the combustion and detonation processes.

Conclusions

Oxy-5-nitroimino-tetrazolate salts (**6–11**) were synthesized and characterized in order to develop new energetic materials. Oxyamine and cyanogen azide were used as starting materials for the preparation of the oxy-aminotetrazole. The latter was converted into oxy-nitroimino-tetrazole **2** by nitration with 100% nitric acid in a neat reaction. The 1,1'-ethylenebis(oxy)bis(5-nitroimino-tetrazolate) salts were fully characterized using IR and multinuclear NMR (^1H , ^{13}C , ^{15}N) spectroscopy, elemental analysis, and in some cases, single-crystal X-ray structuring was done. Compound **2** is a very sensitive and highly energetic compound which should be assigned to the class of primary explosives and only be handled with appropriate precautions.

Although all of the energetic salts exhibit lower densities ($1.577\text{--}1.780\text{ g cm}^{-3}$) than the neutral nitroimino-tetrazole **2** (1.805 g cm^{-3}), they have better thermal stabilities. Selected oxy-nitroimino-tetrazolate salts **8**, **9**, and **11** show good heats of formation (for **8**: 2.78 kJ g^{-1} , **9**: 2.76 kJ g^{-1} , **11**: 2.82 kJ g^{-1}), good detonation pressures (for **8**: 32.20 GPa , **9**: 33.25 GPa , **11**: 29.36 GPa), good detonation velocities (for **8**: 8789 m s^{-1} , **9**: 9030 m s^{-1} , **11**: 8840 m s^{-1}). Calculated detonation values of these compounds are comparable to those of explosives such as RDX ($P = 35.17\text{ GPa}$, $D = 8977\text{ m s}^{-1}$). To compare properties, new energetic salts **13** and **14** based on 1,1'-ethylenebis(5-nitroimino-tetrazole) **1** were synthesized and characterized. While the detonation properties of salts derived from precursors **1** and **2** are similar, for salts of **1** the thermal stabilities and impact sensitivities are better than those for **2**, oxy-nitroimino-tetrazolate salts **6–11**. Finally, all of the new energetic salts are highly endothermic compounds, have high performances and increased thermal or impact sensitivity values in comparison to those of the neutral compounds **1** and **2** which might be of interest for future applications as environmentally friendly and high-performing nitrogen or oxygen-rich materials.

Experimental Section

Safety Precautions. While we have experienced no difficulties with the impact instability of the 1,1'-ethylenebis(5-nitroimino-tetrazole) **1**, 1,1'-ethylenebis(oxy)bis(5-aminotetrazole) **2**, and their salts (**6–11**, **13**, and **14**), they must be synthesized only in 1–2 mmol amounts. Manipulations must be carried out in a hood behind a safety shield. Eye protection and leather gloves must be worn. Caution should be exercised at all times during the synthesis, characterization, and handling of any of these materials, and mechanical actions involving scratching or scraping must be avoided.

General Methods. ^1H , ^{13}C , and ^{15}N NMR spectra were recorded on a 300 MHz (Bruker AVANCE 300) and 500 MHz (Bruker AVANCE 500) nuclear magnetic resonance spectrometers operating at 300.13, 75.48, and 50.69 MHz, respectively, by using DMSO- d_6 as solvent and locking solvent unless otherwise stated. The melting and decomposition points were obtained on a differential scanning calorimeter (TA Instruments Company, model Q10) at a scan rate of $10\text{ }^\circ\text{C min}^{-1}$. IR spectra were recorded using KBr pellets for solids on BIORAD model 3000 FTS spectrometer. Densities of the nitroimino-tetrazole and their salts were determined at $25\text{ }^\circ\text{C}$ by employing a Micromeritics AccuPyc 1330 gas pycnometer. Mass spectra (Shimadzu GCMS-QP5050) were measured by using solid

probe insertion (EI). Elemental analyses were carried out using an Exeter CE-440 elemental analyzer. Details of the X-ray diffraction analysis of compounds **2**· $2\text{H}_2\text{O}$, **8**· $2\text{H}_2\text{O}$, **10**, **13**· $2\text{H}_2\text{O}$, and **14** are provided in Supporting Information. Data were collected on a Bruker three-circle platform diffractometer equipped with a SMART PLATINUM 135 CCD detector.

1,1'-Ethylenebis(oxy)bis(5-nitroimino-tetrazole) (2).⁶ At $0\text{ }^\circ\text{C}$, 2 mmol 1,1'-ethylenebis(oxy)bis(5-aminotetrazole) was added in small portions to 5 mL 100% HNO_3 . The reaction mixture was stirred at ambient temperature for 18 h. The solution was poured into ca. 20 g ice. After stirring for 3 h, the product was precipitated (if not, water should be evaporated in air), filtered, washed with a small amount of cold water, and dried in air at room temperature. The crystal water of $2\cdot 3\text{H}_2\text{O}$ could be removed under high vacuum at $60\text{ }^\circ\text{C}$. $2\cdot 3\text{H}_2\text{O}$ was recrystallized with water and formed $2\cdot 2\text{H}_2\text{O}$ as white crystals.

Yield: 94%; White solid; $T_{\text{dec}} 125\text{ }^\circ\text{C}$ (onset); IR (KBr) $\tilde{\nu}$ 3421, 3288, 3027, 1593, 1494, 1426, 1322, 1216, 1045, 1026, 1001, 978, 878, 842, 779, 694, 675, 631; ^1H NMR δ 10.49 (s, 2H, H-tetrazole), 4.77 (s, 4H, CH_2); $^{13}\text{C}\{^1\text{H}\}$ NMR δ 147.0, 76.9; $^{15}\text{N}\{^1\text{H}\}$ NMR δ -10.6 (N2), -17.8 (N6), -24.5 (N3), -117.0 (N1), -124.3 (N4), -154.7 (N5); MS (EI) m/z : 319 (0.2), 68 (8), 63 (2.4), 46 (100), 44 (61); *Caution!* During elemental analysis the compound exploded and was not determinable. The structure of $2\cdot 2\text{H}_2\text{O}$ is supported by single crystal X-ray analysis.

1,1'-Ethylenebis(oxy)bis(5-nitroimino-tetrazole) (2) Trihydrate.⁶ White solid; Yield 94%, $T_{\text{m}} 109\text{ }^\circ\text{C}$ (H_2O), $T_{\text{dec}} 143\text{ }^\circ\text{C}$ (onset); IR (KBr) $\tilde{\nu}$ 3419, 2898, 2727, 2645, 1592, 1498, 1425, 1333, 1247, 1053, 968, 916, 879, 840, 696, 681; ^1H NMR δ 6.54 (8H, H-tetrazole and $3\text{H}_2\text{O}$), 4.76 (s, 4H, CH_2); $^{13}\text{C}\{^1\text{H}\}$ NMR δ 147.1, 76.9; *Caution!* during elemental analysis the compound exploded and was not determinable.

1,1'-Ethylenebis(oxy)bis(5-aminotetrazole) (4).⁶ At $0\text{ }^\circ\text{C}$, 10 mmol cyanogen bromide was dissolved in 50 mL dry acetonitrile and 40 mmol dry sodium azide was added. The reaction mixture was stirred at $0\text{ }^\circ\text{C}$ for 4 h. The inorganic salt was filtered off (after filtering, the salt must be dissolved in cold water quickly). The cyanogen azide solution is added to a solution containing 2.5 mmol bis(oxyamino)ethane⁹ in 20 mL water at $0\text{ }^\circ\text{C}$. After stirring overnight at ambient temperature, the solvent was removed by blowing air over the liquid surface. The product **4** was purified by washing with water and acetonitrile.

Light-brown solid; yield 20%; $T_{\text{dec}} 175\text{ }^\circ\text{C}$ (onset); IR (KBr) $\tilde{\nu}$ 3331, 3150, 1661, 1603, 1449, 1314, 1263, 1106, 1032, 1014, 858; ^1H NMR δ 7.10 (s, 4H, NH_2), 4.65 (s, 4H, CH_2); $^{13}\text{C}\{^1\text{H}\}$ NMR δ 149.3, 76.4; $^{15}\text{N}\{^1\text{H}\}$ NMR δ 1.3 (N3), -25.0 (N2), -87.7 (N4), -127.2 (N1), -328.7 (NH_2); EA ($\text{C}_8\text{H}_8\text{N}_{10}\text{O}_2$, 228.17) calcd: C, 21.06; H, 3.53; N, 61.39%. Found: C, 21.37; H, 3.55; N, 60.34%. Impact sensitivity: 4 J.

Silver 1,1'-Ethylenebis(oxy)bis(5-nitroimino-tetrazolate) (5). Silver nitrate (680 mg, 4 mmol) was dissolved in 10 mL of water and added to a solution of sodium 1,1-ethylenebis(oxy)bis(5-nitroimino-tetrazolate), which was obtained from 636 mg (2.00 mmol) 1,1'-ethylenebis(oxy)bis(5-nitroimino-tetrazole) (**2**) and 160 mg (4.00 mmol) sodium hydroxide in 50 mL of water. The silver salt precipitated immediately as a white powder. The suspension was stirred for 5 h under ambient temperature. The product was filtered off and dried with air overnight. White solid **5** was obtained in a yield of 99% (1.05 mg, 1.97 mmol).

White solid; $T_{\text{dec}} 200\text{ }^\circ\text{C}$ (onset); IR (KBr) $\tilde{\nu}$ 3433, 1518, 1464, 1430, 1400, 1333, 1265, 1095, 1009, 892, 847, 772, 583; EA ($\text{C}_4\text{H}_4\text{Ag}_2\text{N}_{12}\text{O}_6$, 531.89) calcd: C, 9.03; H, 0.76; N, 31.60%. Found: C, 9.12; H, 0.81; N, 31.40%; *Caution!* During elemental analysis the compound exploded.

Bis(aminoguanidinium)-1,1'-ethylenebis(oxy)bis(5-nitroimino-tetrazolate) (6). The reaction of 318 mg (1.00 mmol) 1,1'-ethylenebis(oxy)bis(5-nitroimino-tetrazole) **2**⁶ with 210 mg (2.00

mmol) aminoguanidine bicarbonate in 10 mL water at 70 °C for 30 min gave a white solid (420 mg, 0.901 mmol, 90%) after air drying.

T_{dec} 200 °C (onset); IR (KBr) $\tilde{\nu}$ 3396, 3343, 3281, 3192, 3117, 1676, 1508, 1449, 1424, 1379, 1317, 1287, 1221, 1092, 1026, 1002, 889, 588, 509, 476; $^1\text{H NMR}$ δ 8.54 (s, 2H, NH), 7.19 (br s, 4H, NH₂), 6.80 (br s, 4H, NH₂), 4.64 (br s, 8H, NH₂ and CH₂ overlap); $^{13}\text{C}\{^1\text{H}\}$ NMR δ 158.8, 150.8, 76.2; $^{14}\text{N NMR}$ δ -13.6 (NO₂); $^{15}\text{N}\{^1\text{H}\}$ NMR δ -14.3 (NO₂), -6.3, -28.7, -74.4 (N⁻), -125.5, -160.0, -283.4, -306.9 (br), -313.1 (br), -325.1; EA (C₆H₁₈N₂₀O₆, 466.34) calcd: C, 15.45; H, 3.89; N, 60.07%. Found: C, 15.41; H, 3.79; N, 59.91%.

Bis[1,3-diazo-2-(azidomethyl)-2-propylammonium]-1,1'-ethylenebis(oxy)bis(5-nitroimino-tetrazolate) (7). The reaction of 318 mg (1.00 mmol) of 1,1'-ethylenebis(oxy)bis(5-nitroimino-tetrazole) **2**⁶ with 392 mg (2.00 mmol) 2-amino-1,3-diazo-2-(azidomethyl)propane²² in 10 mL water at ambient temperature gave colorless crystals of **7** (640 mg, 0.943 mmol, 94%) after air drying.

T_{dec} 151 °C (onset); IR (KBr) $\tilde{\nu}$ 3420, 3032, 2931, 2869, 2803, 2114 (N₃), 1600, 1536, 1510, 1445, 1425, 1379, 1313, 1283, 1223, 1080, 963, 880; $^1\text{H NMR}$ δ 8.49 (br s, 6H, NH₃⁺), 4.64 (s, 4H, CH₂), 3.74 (s, 12H, CH₂); $^{13}\text{C}\{^1\text{H}\}$ NMR δ 150.8, 76.1, 57.7, 51.6; $^{15}\text{N}\{^1\text{H}\}$ NMR δ -6.1, -13.9 (NO₂), -28.8, -74.7 (N⁻), -125.5, -134.9 (N_β), -160.0, -171.1 (N_γ), -317.5 (N_α), -336.9 (NH₃⁺); EA (C₁₂H₂₂N₃₂O₆, 710.51) calcd: C, 20.29; H, 3.12; N, 63.08%. Found: C, 20.72; H, 3.05; N, 62.03%. *Caution!* During elemental analysis the compound exploded.

Carbohydrazinium 1,1'-ethylenebis(oxy)bis(5-nitroimino-tetrazolate) (8) Tetrahydrate. The reaction of 318 mg (1.00 mmol) 1,1'-ethylenebis(oxy)bis(5-nitroimino-tetrazole) (**2**) with 90.0 mg (1.00 mmol) carbohydrazide in 10 mL water at ambient temperature for 20-min stirring precipitated a white solid, which was filtered and dried. **8**·4H₂O (410 mg, 0.854 mmol, 85%). **8**·4H₂O was recrystallized with water and formed **8**·2H₂O as colorless crystals.

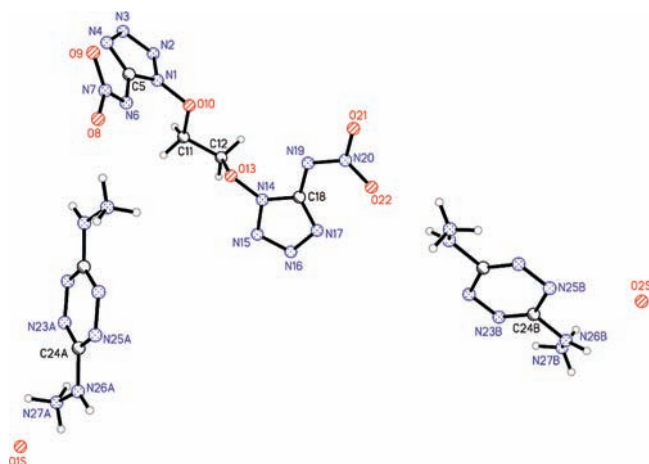
T_{m} 71 (H₂O), 78 (H₂O), and 129 °C (H₂O); T_{dec} 147 °C (onset); IR (KBr) $\tilde{\nu}$ 3569, 3448, 3348, 3090, 3020, 2956, 2853, 2736, 1707, 1636, 1617, 1524, 1444, 1399, 1362, 1328, 1288, 1272, 1241, 1099, 1044, 902; $^1\text{H NMR}$ δ 9.63 (br s, 2H, NH), 4.64 (s, 4H, CH₂), 4.57 (br s, 10H, NH₃⁺ and H₂O); $^{13}\text{C}\{^1\text{H}\}$ NMR δ 157.0, 150.4, 76.2; EA (C₅H₂₀N₁₆O₁₁, 480.31) calcd: C, 12.50; H, 4.20; N, 46.66%. Found: C, 12.52; H, 4.33; N, 46.73%.

Carbohydrazinium 1,1'-Ethylenebis(oxy)bis(5-nitroimino-tetrazolate) (8) Dihydrate. Colorless crystals; T_{m} 127 °C (H₂O); T_{dec} 156 °C (onset); IR (KBr) $\tilde{\nu}$ 3447, 3235, 3038, 2959, 2923, 2691, 1729, 1634, 1597, 1559, 1524, 1439, 1393, 1341, 1320, 1282, 1240, 1185, 1088, 1027, 899, 853, 772, 621, 528, 441; EA (C₅H₁₆N₁₆O₉, 444.28) calcd: C, 13.52; H, 3.63; N, 50.44%. Found: C 13.43; H, 3.44; N, 50.23%; Impact sensitivity: 2 J. The structure of **8**·2H₂O is supported by single-crystal X-ray analysis.

Carbohydrazinium 1,1'-Ethylenebis(oxy)bis(5-nitroimino-tetrazolate) (8). White solid; T_{dec} 130 °C (onset), 146 °C (onset); IR (KBr) $\tilde{\nu}$ 3435, 2967, 2706, 1730, 1612, 1597, 1519, 1438, 1376, 1321, 1287, 1093, 1023; $^1\text{H NMR}$ δ 9.62 (br s, 2H, NH), 8.63 (br s, 6H, NH₃⁺), 4.64 (s, 4H, CH₂); $^{13}\text{C}\{^1\text{H}\}$ NMR δ 157.0, 150.4, 76.2; $^{15}\text{N}\{^1\text{H}\}$ NMR δ -0.1 (N₂), -6.9 (NO₂), -21.6 (N₃), -71.1 (N⁻), -118.6 (N₁), -152.9 (N₅), -277.3 (NH), -317.1 (NH₃⁺); EA (C₅H₁₂N₁₆O₇, 408.25) calcd: C, 14.71; H, 2.96; N, 54.89%. Found: C 14.64; H, 2.97; N, 54.12%.

1,2,4,5-Tetrazino-3,6-bis(hydrazinium)-1,1'-ethylenebis(oxy)bis(5-nitroimino-tetrazolate) (9) Dihydrate. The reaction of 318 mg (1.00 mmol) 1,1'-ethylenebis(oxy)bis(5-nitroimino-tetrazole) (**2**) with 142 mg (1.00 mmol) 3,6-dihydrazino-1,2,4,5-tetrazine²³ in 50 mL water at ambient temperature for 10 min gave light-red crystals **9**·2H₂O (410 mg, 0.826 mmol, 83%) after air drying (Figure 9).

Light-red crystals; T_{m} 72 °C (H₂O); T_{dec} 131 °C (onset); IR (KBr) $\tilde{\nu}$ 3424, 3220, 2849, 1624, 1528, 1447, 1395, 1324, 1281, 1184,



Silver 1,1'-Ethylenebis(5-nitroimino-tetrazolate) (12). Silver nitrate (2.38 g, 14.0 mmol) was dissolved in 50 mL of water and added to a solution of sodium 1,1'-ethylenebis(5-nitroimino-tetrazolate), which was obtained 2.00 g (6.99 mmol) 1,1'-ethylenebis(5-nitroimino-tetrazole) (**1**)⁵ and 560 mg (14.0 mmol) sodium hydroxide in 100 mL of water. The silver salt precipitated immediately as a white powder. The suspension was stirred for 5 h under ambient temperature. The product was filtered and dried with air overnight. White solid **12** was obtained in a yield of 97% (3.40 g, 1.97 mmol).

White solid; T_{dec} 270 °C (onset); IR (KBr) $\tilde{\nu}$ 3441, 3022, 1629, 1510, 1458, 1434, 1381, 1302, 1229, 1109, 1026, 884, 733, 708; EA (C₄H₄Ag₂N₁₂O₄, 499.89) calcd: C, 9.61; H, 0.81; N, 33.62%. Found: C 9.44; H, 0.64; N, 33.01%. Density: 2.974 g cm⁻³.

Bis(diaminoguanidinium)-1,1'-ethylenebis(5-nitroimino-tetrazolate) (13) Dihydrate. To an aqueous suspension of 1.50 g (3.00 mmol) silver 1,1'-ethylenebis(5-nitroimino-tetrazolate) (**12**) in 60 mL H₂O was added 754 mg (6.01 mmol) diaminoguanidine hydrochloride. After stirring at ambient temperature for 6 h, silver salt was removed by 3 times filtration, and the solvent was removed under air. A 1.37 g portion (2.74 mmol, 91%) of colorless crystal **13**·2H₂O was obtained.

Colorless crystals; T_{m} 96 (H₂O), 202 °C; T_{dec} 218 °C (onset); IR (KBr) $\tilde{\nu}$ 3557, 3437, 3358, 3314, 3258, 3178, 3074, 2968, 1677, 1636, 1504, 1456, 1436, 1385, 1345, 1303, 1260, 1165, 1105, 1036, 961, 884, 775, 748, 694, 635, 525; ¹H NMR δ 8.54 (s, 4H), 7.13 (s, 4H), 4.59 (s, 8H, NH₂), 4.44 (s, 4H, CH₂), 3.35 (s, 4H, H₂O); ¹³C{¹H} NMR δ 159.7, 157.0, 43.8; EA (C₆H₂₄N₂₂O₆, 500.40) calcd: C, 14.40; H, 4.83; N, 61.58%. Found: C, 14.44; H, 4.63; N, 61.58%. The structure of **13**·2H₂O is supported by single crystal X-ray analysis.

Bis(diaminoguanidinium)-1,1'-ethylenebis(5-nitroimino-tetrazolate) (13). White solid; T_{m} 202 °C; T_{dec} 220 °C (onset); IR (KBr) $\tilde{\nu}$ 3402, 3322, 3256, 3010, 1686, 1636, 1509, 1471, 1439, 1384, 1348, 1326, 1307, 1263, 1238, 1214, 1175, 1105, 1034, 1025, 965, 891, 777, 741, 699, 591; ¹H NMR δ 8.57 (s, 4H), 7.15 (s, 4H), 4.60 (s, 8H, NH₂), 4.48 (s, 4H, CH₂); ¹³C{¹H} NMR δ 159.9, 157.0, 44.1; ¹⁴N NMR δ -13.9 (br s, NO₂); ¹⁵N{¹H} NMR δ 5.5, -14.5 (NO₂), -21.5, -73.2 (N⁻), -157.7, -166.7, -287.3, -311.7, -327.1; EA (C₆H₂₀N₂₂O₄, 464.37) calcd: C, 15.52; H, 4.34; N, 66.36%. Found: C, 15.49; H, 4.29; N, 66.11%.

Bis(triaminoguanidinium)-1,1'-ethylenebis(5-nitroimino-tetrazolate) Hydrate (14). Method 1. To an aqueous suspension of 1.50 g (3.00 mmol) silver 1,1'-ethylenebis(5-nitroimino-tetrazolate) (**12**) in 60 mL H₂O was added 843 mg (6.00 mmol) triaminoguanidine hydrochloride. After stirring at ambient temperature for 6 h, silver salts were removed by 3 times filtration, and the solvent was removed under air. A 1.51 g portion (2.95 mmol, 98%) of colorless crystals **14** was obtained.

Method 2. The reaction of 572 mg (2.00 mmol) 1,1'-ethylenebis(5-nitroimino-tetrazole) (**1**) with 316 mg (1.00 mmol) barium hydroxide octahydrate in 100 mL water at ambient temperature gave barium 1,1'-ethylenebis(5-nitroimino-tetrazolate) as a white solid (810 mg, 1.92 mmol, 96%). To an aqueous suspension of 810 mg (1.92 mmol) barium 1,1'-ethylenebis(5-nitroimino-tetrazolate) in 50 mL H₂O was added 588 mg (1.92 mmol) triaminoguanidinium sulfate. After stirring at 40 °C for 30 min, precipitated barium sulfate were removed by filtration, and the filtrate was removed under air. The white crystal **14** (730 mg, 1.42 mmol, 74%) was formed.

Colorless crystals; T_{m} 131 °C (H₂O); T_{dec} 195 °C (onset); IR (KBr) $\tilde{\nu}$ 3613, 3433, 3339, 3216, 3025, 1686, 1605, 1505, 1451, 1424, 1389, 1290, 1252, 1229, 1189, 1142, 1038, 991, 947, 882, 775, 741, 652, 596; ¹H NMR δ 8.57 (s, 6H, NH), 4.47 (s, 16H, CH₂, NH₂, and H₂O); ¹³C{¹H} NMR δ 159.2, 157.1, 44.1; ¹⁴N NMR δ -13.8 (br s, NO₂); ¹⁵N{¹H} NMR δ 5.5, -14.4 (NO₂), -21.5, -73.0 (N⁻), -157.8, -166.7, -288.4, -328.8; EA (C₆H₂₄N₂₄O₅, 512.41) calcd: C, 14.06; H, 4.72; N, 65.60%. Found: C, 14.10; H, 4.78; N, 65.22%. The structure of **14** is supported by single crystal X-ray analysis.

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Supporting Information Available: X-ray crystallographic files in CIF format for **2**·2H₂O, **8**·2H₂O, **10**, **13**·2H₂O, and **14** and ¹H, ¹³C, and ¹⁵N NMR spectra of all products. DSC scans of all compounds. Complete reference 15. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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