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Energetic Derivatives of 4,4′,5,5′-Tetranitro-2,2′-bisimidazole (TNBI)

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Abstract. 4,4′,5,5′-Tetranitro-2,2′-bisimidazole (TNBI) was synthesized by nitration of bisimidazole (BI) and recrystallized from acetone to form a crystalline acetone adduct. Its ammonium salt (**1**) was obtained by the reaction with gaseous ammonia. In order to explore new explosives or propellants several energetic nitrogen-rich 2:1 salts such as the hydroxylammonium (**3**), guanidinium (**4**), aminoguanidinium (**5**), diaminoguanidinium (**6**) and triaminoguanidinium **7** 4,4′,5,5′-tetranitro-2,2′-bisimidazolate were prepared by facile metathesis reactions. In addition, methylated 1,1′-dimethyl-4,4′,5,5′-tetranitro-2,2′-bisimidazole (Me_2TNBI, **8**) was synthesized by the reaction of **2** and dimethyl sulfate. Metal salts of TNBI can also be easily synthesized by using the corresponding metal bases. This was proven by the synthesis of pyrotechnically relevant dipotassium 4,4′,5,5′-tetranitro-2,2′-bisimidazolate (**2**), which is a brilliant burning component e.g. in near-infrared flares. All compounds were characterized by single crystal X-ray diffraction, NMR and vibrational spectroscopy, elemental analysis and DSC. The sensitivities were determined by BAM methods (drophammer and friction tester). The heats of formation were calculated using CBS-4M electronic enthalpies and the atomization method. With these values and mostly the X-ray densities different detonation parameters were computed by the EXPLO5 computer code. Due to the great thermal stability and calculated energetic properties, especially guanidinium salt **4** could be served as a HNS replacement.

Introduction

Most commercial secondary explosives like RDX (hexogen) and HNS (hexanitrostilbene) are highly toxic for human and animal. In terms of performance secondary explosives have parameters like a detonation velocity ($V_{det.}$), detonation pressure (P_{C-J}), heat of detonation ($-\Delta_{Ex}U°$) and a volume of gases (V_0) which is created during their detonation.[1] It is a recent goal to create energetic materials with higher thermostability and lower sensitivity (towards impact (IS), friction (FS), electrostatic discharge (ESD)) and lower toxicity[1] than the current used ones. One approach is the use of azoles in combination with energetic substituents at the carbon atom(s) like nitro or azide groups. Nitrated imidazoles in general were already investigated by Korean scientists and also in our research group due to their thermostabilities and energetic properties.[2,3] For example 1-methyl-2,4,5-trinitroimidazole was investigated, which shows a thermal stability of at least 190 °C[2,4]. In 2007 *Damavarapu* et al. characterized the potassium salt of 2,4,5-trinitroimidazole[2,4]. The synthesis is based upon an alternating nitration/rearrangement strategy starting with commercial available 4-nitroimidazole. Our article reports on derivatives of 4,4′,5,5′-tetranitro-2,2′-bisimidazole (TNBI). The connection of two imidazole rings obtaining 2,2′-bisimidazoles follows the trend of generating larger energetic molecules. This mostly results in higher thermal stability and a more positive oxygen balance, which was also observed in the case of the pernitrated species TNBI. The thermal stability can be further improved by deprotonation and the formation of nitrogen rich 2:1 salts. Synthesis of the 2,2′-bisimidazole was already described by Italian researchers in 1981 in two steps via an bisulfite adduct. It was used for the investigation of methylated copper and zinc dinitrate complexes due to their interesting electronic spectra and ESR data.[5]

Also 4,4′,5,5′-tetranitro-2,2′-bisimidazole (TNBI) was already described by *Cho* et al. in 2005 as a potentially RDX replacement which suffers hygroscopic properties.[6] In 1990 *Cromer* et al. described the crystal structures of TNBI dihydrate and its water-free bis-ammonium salt.[7,8] In 1999 the 3,6-bishydrazine-1,2,4,5-tetrazinium-TNBI salt was described by *Chavez* et al. showing a thermal stability up to 217 °C.[9] *Oxley* et al. carried out thermochemical studies (isothermal thermolysis) on several tetrazine based salts.[10] We today report on several further nitrogen-rich derivatives of TNBI and on its methylated sister compound and their potential use in explosive formulations. In addition, metal salts like the prepared bispotassium salt **2** could serve as pyrotechnically relevant candidates in near IR or visible flares.

Results and Discussion

Synthesis

An overall synthetic protocol is displayed in Scheme 1. The synthesis of 2,2′-bisimidazole (BI) was carried out as described by *Bernaducci* et al.[5] The oxidation of glyoxal with sodium-bisulfite leads to a glyoxal-sodium bisulfite adduct.

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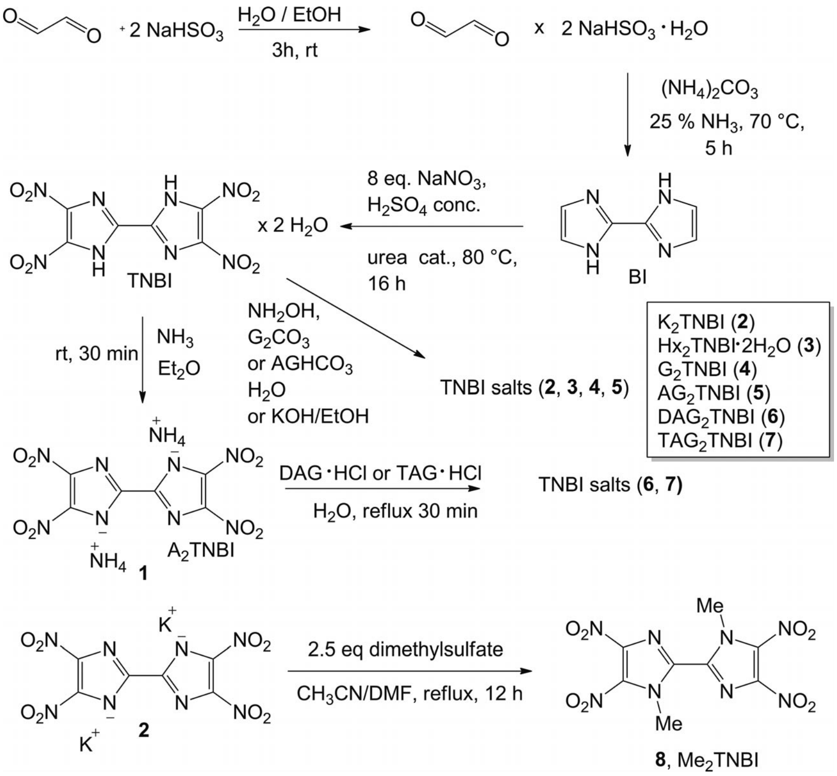

Scheme 1. Synthesis of TNBI salts **2**–**7** and 1,1′-dimethyl-4,4′,5,5′-tetranitro-2,2′-bisimidazole (**8**).

This adduct is more activated to react with concentrated ammonia in an ammonium bicarbonate buffered solution to yield BI. The synthesis was carried out in a scale of 12 g BI. The nitration was performed in conc. sulfuric acid (96–98 %) using eight equivalents sodium nitrate and a catalytic amount of urea. The nitration worked best by stirring the suspension at 85 °C for 16 hours. The maximum yield was 6 g TNBI·$2H_2O$ when 5 g BI was used. After the nitration is poured onto ice-water TNBI can be easily extracted with diethyl ether. The already known bis-ammonium 4,4′,5,5′-tetranitro-2,2′-bisimidazolate (**1**) is synthesized by the reaction with gaseous ammonia.[9] Compound **1** serves as a valuable starting material to generate several salts because of their lower solubility in aqueous solution. The reaction of TNBI with aqueous potassium hydroxide, hydroxylamine solution, guanidinium carbonate or aminoguanidinium bicarbonate, respectively, afforded salts **2** (bispotassium TNBI), **3** (bishydroxylammonium TNBI dihydrate), **4** (bisguanidinium TNBI) and **5** (bisaminoguanidinium TNBI) in good yields and high purities.

Alternatively, the diethyl ether can be evaporated for the most part and KOH/EtOH is added to yield the bispotassium salt **2**. However, it would also be possible to synthesize salts **2**–**7** directly starting with TNBI and the corresponding bases. Crystalline samples of **2**, **5** and **6** (bis-diaminoguanidinium TNBI) and **7** (bis-triaminoguanidinium TNBI) could be obtained by recrystallization from water. **2** and **6** crystallize without inclusion of water, **3** as a dihydrate. **4** is only soluble in DMSO and crystallizes with two additional DMSO molecules. Salts **6** and **7** were synthesized by heating a suspension of **1** with diaminoguanidinium and triaminoguanidinium chloride, respectively, to reflux until a solution is obtained. **6** crystallizes very quickly at approx. 60 °C, **7** crystallizes at 4 °C overnight. In general the purity of all salts can be established best via ^1H and ^{13}C NMR spectroscopy and elemental analysis.

1,1′-Dimethyl-4,4′,5,5′-tetranitro-2,2′-bisimidazole (Me_2TNBI, **8**) was obtained by the reaction of **2** with 2.5 equivalents of dimethylsulfate in CH_3CN/DMF (9:1). We considered that the lack of hydrogen bonds yields to a low melting point but a high decomposition temperature of **8**. A crystalline sample could be obtained from acetone.

During our syntheses we additionally got single crystals of the TNBI·$2H_2O$, potassium-TNBI monohydrate, **4**·DMSO, 1:1 diaminoguanidinium salt (DAGTNBI·H_2O) and **6**, which are all presented in the Supporting Information. Investigations of the alkaline earth metal salts e.g. CaTNBI·$8H_2O$ and BaTNBI·$3H_2O$ will be presented separately with respect to their potential use as pyrotechnic colorants.

Crystal Structures

Due to the moderate water solubility, all compounds except of **4** (from DMSO) were recrystallized from water. TNBI can be either recrystallized from water and acetone yielding the corresponding dihydrate or diacetone adduct, respectively. The structures of compounds **2**–**8** as well as the monoprotonated potassium salt (KTNBI·H_2O) and the 1:1 diaminoguanidinium salt (DAGTNBI·H_2O) were determined by low temperature (173 K) X-ray diffraction. Selected data and parameters of the X-ray determinations are given in the Supporting Information (Tables S1 and S2). Further crystallographic data for the structures have been deposited with the Cambridge Crystallographic Data Centre (CCDC-876136 (TNBI·2H$_2$O), -876137 (TNBI·2 acetone), -877533 (**2**), KTNBI·H$_2$O, 876398 (**3**), 876140 (**4**·2DMSO), 876143 (**5**), 877534 (**6**), 876141 DAGTNBI·H$_2$O, 876142 (**7**), and 876138 (**8**))[11] The molecular structures of TNBI·2H$_2$O, KTNBI·H$_2$O, **4**·2DMSO, DAGTNBI·H$_2$O and **6** are shown in the Supporting Information.

As mentioned in the introduction the structure of TNBI at room temperature has been described in literature.[8] A redetermination of this structure at 173 K is presented in the Supporting Information. First we would like to present the structure of TNBI with two molecules of acetone (Figure 1), which crystallizes in the monoclinic space group $C2/c$ with four formula units per unit cell and calculated density of 1.581 g·cm^{-3}. The structure is similar to that of the dihydrate.[8] Basically, the bisimidazole backbone is found to be planar in all structures except for **8**. The bond length within the imidazoles are between typical C–N single and C=N double bonds representing the aromatic character. The C–C bond connecting both imidazole rings in all structure is significantly shorter (approx. 1.46 Å) than a typical C–C single bond (1.54 Å). Nitro groups are not co-planar with the imidazole rings to avoid electrostatic repulsion of the nitro oxygen atoms. For example, the torsion angle (in TNBI·2 acetone) between the atoms O2–N3–N4–O3 is 44°. The acetone molecules are connected to the TNBI molecules by strong NH···O hydrogen bonds (e.g. N1–H1···O5ii: *d*(D–H) 0.890(18) Å, *d*(H···A) 1.807(19) Å, *d*(D···A) 2.6951(16) Å, ∠(D–H···A) 175.3(16)°.

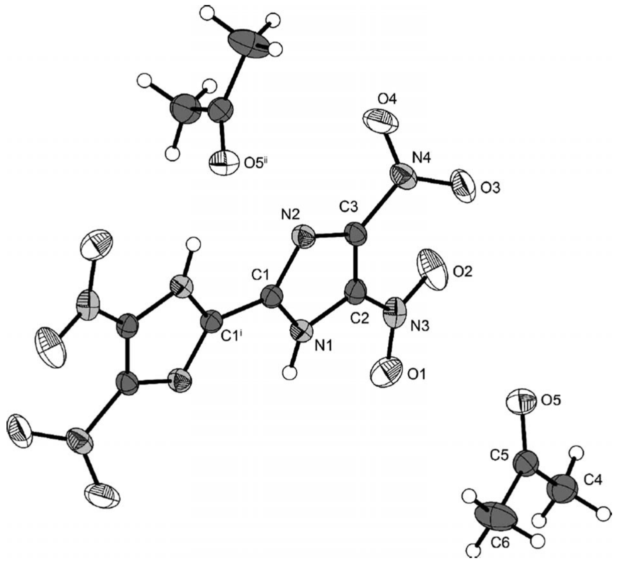

Figure 1. Molecular structure of TNBI·2 acetone showing the labeling scheme. The non-hydrogen atoms are represented by displacement ellipsoids at the 50 % probability level. Symmetry codes (i) 0.5–*x*, 1.5–*y*, –*z*; (ii) 0.5–*x*, 0.5+*y*, 0.5–*z*. Selected bond lengths /Å: O1–N3 1.2267(17), O2–N3 1.2241(17), O3–N4 1.2234(17), O4–N4 1.2229(17), N1–C1 1.3527(19), N1–C2 1.3584(19), N2–C1 1.3312(18), N2–C3 1.3463(19), N3–C2 1.435(2), N4–C3 1.4555(18), C1–C1i 1.449(3), C2–C3 1.375(2), O5–C5 1.2234(18), C4–C5 1.489(2), C5–C6 1.489(2). Selected bond angles /°: C1–N1–C2 105.92(12), C1–N2–C3 104.21(12), O2–N3–O1 125.22(14), O2–N3–C2 118.06(13), O1–N3–C2 116.69(12), O4–N4–O3 125.16(13), O4–N4–C3 116.74(13), O3–N4–C3 118.09(13), N2–C1–N1 112.76(13), N2–C1–C1 124.25(17), N1–C1–C1i 122.99(16), N1–C2–C3 106.18(13), N1–C2–N3 119.33(13), C3–C2–N3 134.29(13), N2–C3–C2 110.92(12), N2–C3–N4 118.87(13), C2–C3–N4 130.15(14), C4–C5–C6 116.95(16). Selected torsion angles /°: O1–N3–C2–N1 –14.47(19), O2–N3–C2–C3 –10.7(2), O3–N4–C3–N2 149.92(13), O4–N4–C3–N2 –29.1(2), N1–C1–C1i–N2 i –0.1(2).

The potassium salt of TNBI (K$_2$TNBI **2**) crystallizes in the monoclinic space group $P2_1/c$ with two formula units per unit cell. The calculated density at –100 °C is 2.126 g·cm^{-3}. The molecular moiety is displayed in Figure 2.

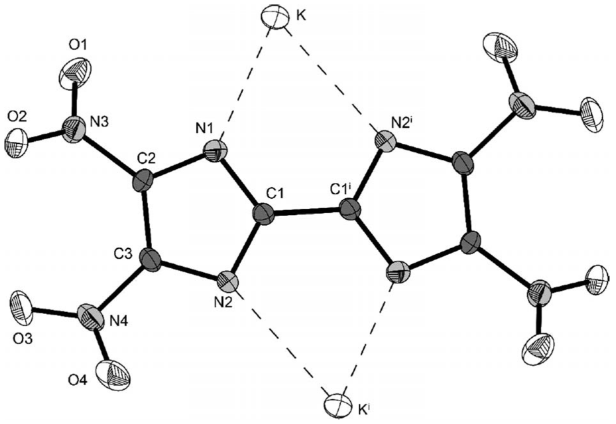

Figure 2. Molecular structure of K$_2$TNBI (**2**) showing the labeling scheme. The non-hydrogen atoms are represented by displacement ellipsoids at the 50 % probability level. Symmetry code (i) 1–*x*, 1–*y*, –*z*. Selected bond lengths /Å: K–N1 2.8213(19), K–N2i 2.948(10), O1–N3 1.230(2), O2–N3 1.236(2), O3–N4 1.226(2), O4–N4 1.231(2), N1–C2 1.343(3), N1–C1 1.348(3), N2–C3 1.342(3), N2–C1 1.353(3), N3–C2 1.435(3), N4–C3 1.438(3), C1–C1i 1.460, C2–C3 1.390(3). Selected bond angles /°: N1–K–N2i 59.90(5). Selected torsion angles /°: O1–N3–C2–N1 28.3(3), O2–N3–C2–N1 –151.7(2), O3–N4–C3–C2 20.5(4), O4–N4–C3–C2 –160.2(2), N1–C1–C1–N2 1.0(3).

As mentioned before, in the molecular structure of **8** which crystallizes in the triclinic space group $P\bar{1}$, the imidazole rings are not co-planar (torsion ∠ N1–C1–C5–N6 = 36.7(4)°). However the C1–C5 bond length is in the same range observed for the other structures. Since no classical hydrogen bonds can be formed the density of 1.703 g cm^{-3} is lower than that of the solvent free compounds investigated in this work. On the other hand, weak non-classical C–H···OH bonds as well as nitro-nitro interactions[12] are present. The nitro groups next to the methyl substituents are twisted significantly more out of the ring plane which can be seen in Figure 3.

Compound **3** crystallizes in the monoclinic space group $P2_1/n$ with a cell volume of 763.6(5) Å^3 and two formula units per unit cell. The molecular moiety is shown in Figure 4. Its density of 1.810 g·cm^{-3} is the highest of the metal-free compounds within this work. Next to the hydroxylammonium cations also the water molecules participate in a strong hydrogen bond network. This may be the reason that it is not possible to dehydrate **3** before decomposition by heating.

In contrast to compound **4** which could only be obtained crystalline with inclusion of two molecules of dimethylsulfoxide, compound **5** was obtained free of water by recrystalli-

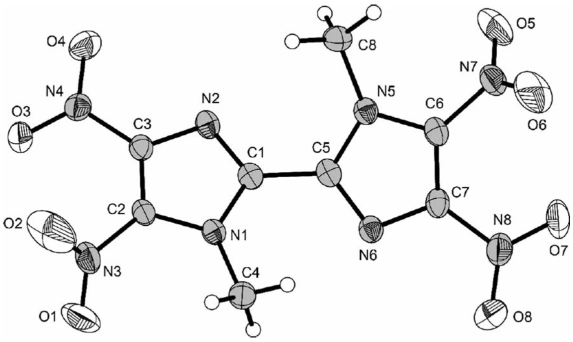

Figure 3. Molecular structure of Me$_2$TNBI (**8**) showing the labeling scheme. The non–hydrogen atoms are represented by displacement ellipsoids at the 50 % probability level. Selected bond lengths /Å: O1–N3 1.201(4), O2–N3 1.205(4), O3–N4 1.223(3), O4–N4 1.218(3), O5–N7 1.226(4), O6–N7 1.204(4), O7–N8 1.228(4), O8–N8 1.222(4), N1–C2 1.359(4), N1–C1 1.368(4), N1–C4 1.473(4), N2–C1 1.326(4), N2–C3 1.351(4), N3–C2 1.459(4), N4–C3 1.440(4), N5–C6 1.366(4), N5–C5 1.367(4), N5–C8 1.479(4), N6–C5 1.321(4), N6–C7 1.349(4), N7–C6 1.454(4), N8–C7 1.440(4), C1–C5 1.461(4), C2–C3 1.358(4), C6–C7 1.357(4). Selected bond angles /°: C2–N1–C1 104.9(2), C2–N1–C4 125.7(3), C1–N1–C4 128.9(3), C1–N2–C3 103.9(2), O1–N3–O2 124.8(3), O1–N3–C2 118.4(3), O2–N3–C2 116.8(3), O4–N4–O3 124.9(3), O4–N4–C3 118.8(3), O3–N4–C3 116.4(3), C6–N5–C5 104.8(2), C6–N5–C8 126.3(3), C5–N5–C8 128.6(3), C5–N6–C7 104.1(2), O6–N7–O5 125.6(3), O6–N7–C6 117.9(3), O5–N7–C6 116.5(3), O8–N8–O7 125.2(3), O8–N8–C7 119.0(3), O7–N8–C7 115.9(3), N2–C1–N1 112.9(3), N2–C1–C5 124.9(3), N1–C1–C5 122.0(3), C3–C2–N1 107.0(2), C3–C2–N3 132.2(3), N1–C2–N3 120.7(3), N2–C3–C2 111.2(3), N2–C3–N4 121.7(3), C2–C3–N4 127.0(3), N6–C5–N5 113.0(3), N6–C5–C1 124.1(3), N5–C5–C1 122.7(3), C7–C6–N5 106.7(3), C7–C6–N7 132.0(3), N5–C6–N7 121.4(3), N6–C7–C6 111.3(3), N6–C7–N8 121.1(3), C6–C7–N8 127.6(3). Selected torsion angles /°: N1–C1–C5–N6 36.7(4), O1–N3–C2–N1 –60.9(4), O2–N3–C2–N1 –119.8(4), O4–N4–C3–N2 –11.0(4), O3–N4–C3–N2 –169.8(3), O6–N7–C6–N5 124.5(3), O5–N7–C6–N5 –54.3(4), O8–N8–C7–N6 –13.6(5), O7–N8–C7–N6 166.3(3).

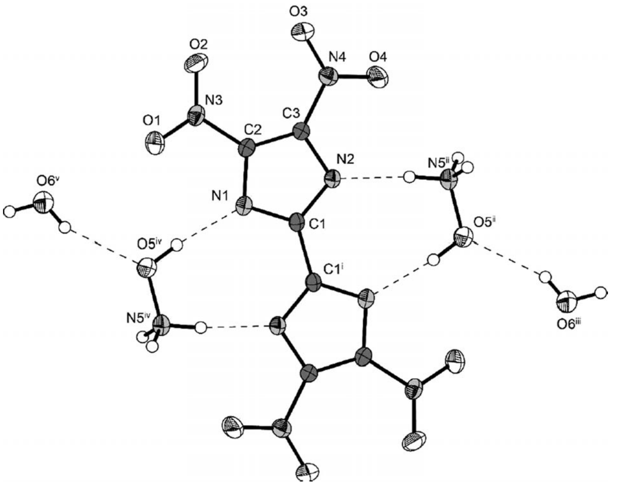

Figure 4. Molecular structure of bishydroxylammonium tetranitrobisimidazolate dihydrate (**3**) showing the labeling scheme. The non-hydrogen atoms are represented by displacement ellipsoids at the 50 % probability level. Symmetry codes (i) 1–*x*, –*y*, –*z*; (ii) 1–*x*, 1–*y*, –*z*; (iii) 0.5+*x*, 0.5–*y*, –0.5+*z*; (iv) *x*, –1+*y*, *z*; (v) 0.5–*x*, –0.5+*y*, 0.5–*z*. Selected bond lengths /Å: O1–N3 1.2269(17), O2–N3 1.2193(17),O3–N4 1.2207(16), O4–N4 1.2256(17), N1–C1 1.3474(18), N1–C2 1.3484(19), N2–C3 1.3409(18), N2–C1 1.3469(19), N3–C2 1.4391(19), N4–C3 1.445(2), C2–C3 1.394(2), O5–N5 1.4141(17); Selected bond angles /°: C1–N1–C2 –103.20(12), C3–N2–C1 103.89(12), O2–N3–O1 123.56(13), O2–N3–C2 119.39(12), O1–N3–C2 117.05(13), O3–N4–O4 123.13(14), O3–N4–C3 119.77(13), O4–N4–C3 117.09(12), N2–C1–N1 114.85(13), N2–C1–C1 122.03(16), N1–C1–C1 123.11(16), N1–C2–C3 109.29(13), N1–C2–N3 117.99(13), C3–C2–N3 132.71(14), N2–C3–C2 108.77(13), N2–C3–N4 117.21(13), C2–C3–N4 134.02(13); Selected torsion angles /°: O2–N3–C2–N1 –174.21(13), O1–N3–C2–N1 5.3(2), O3–N4–C3–N2 –176.41(13), O4–N4–C3–N2 3.3(2), N1–C2–C3–N2^{i} 0.21(17).

zation from water. It crystallizes in the triclinic space group $P\bar{1}$ with one formula unit per unit cell and a calculated density of 1.751 g•cm^{-3}. All hydrogen atoms of the aminoguanidinium cation participate in hydrogen bonds, a few of them illustrated in Figure 5.

The triaminoguanidinium salt **7** also crystallizes in the triclinic space group $P\bar{1}$ with one formula unit per unit cell. The molecular structure is shown in Figure 6. Its calculated crystal density (1.722 g•cm^{-3}) is slightly lower than those of **5** (1.806 g•cm^{-3}) and **6** (1.758 g•cm^{-3}). In the crystal packing the anions and cations are orientated almost perpendicularly to each other.

Energetic Properties

Due to their high combined nitrogen and oxygen content (N+O ≈ 70 %), but low sensitivities (see below) TNBI and its salts are energetic materials which could serve as high-explosives or also propellants. With respect to the thermal stability, compound **4** (without DMSO) shows the highest decomposition temperature ($T_{\text{dec.}}$ = 328 °C) and is a potential HNS replacement ($T_{\text{dec.}}$ = 337 °C[13] but lower explosive performance 7000 ms^{-1}[14]). The other salts show thermal-stabilities between 152 (**7**) and 206 °C (**5**). DSC plots are shown in Figure 7. Compound **8** has an melting area at approx. 236 °C. Unfortunately, the gap between the melting and decomposition point ($T_{\text{dec.}}$ = 258 °C) is too small for being a suitable meltcast explosive (for comparison TNT (2,4,6-trinitrotoluene) melts at 80 °C and decompose not before 310 °C)[12].

For safety issues the sensitivities towards impact, friction and electrostatic discharge were determined by BAM methods (see Experimental Section) and listed in Table 1. Regarding the impact values, **3** and **7** are the most sensitive (6 J) ones. This value is in the range of those observed for RDX (7 J) and PETN (5 J).[15] According to the "UN recommendations of the transport of dangerous goods"[16] they are classified as sensitive. Compounds **4** and **8** are completely insensitive towards impact (>40 J). Compounds **4** and **5** are insensitive (> 360 N) in terms of their friction sensitivity. Interestingly, salt **6** is the most sensitive one (252 N) which is classified as sensitive. All compounds are not susceptible towards electrical sparks.

Several detonation parameters of **3**–**8** were calculated by the EXPLO5.04 computer code.[17–19] The program is based on the input of the energy of formation (kJ•kg^{-1}), density (g•cm^{-3}) and the sum formula. For all compounds, except for **4**, their maximum X-ray densities at –173 K were used. The density of **4** (1.80 g•cm^{-3}) was measured with a Quantachrome helium gas pycnometer. The heats of formation (Table 1) were calcu-

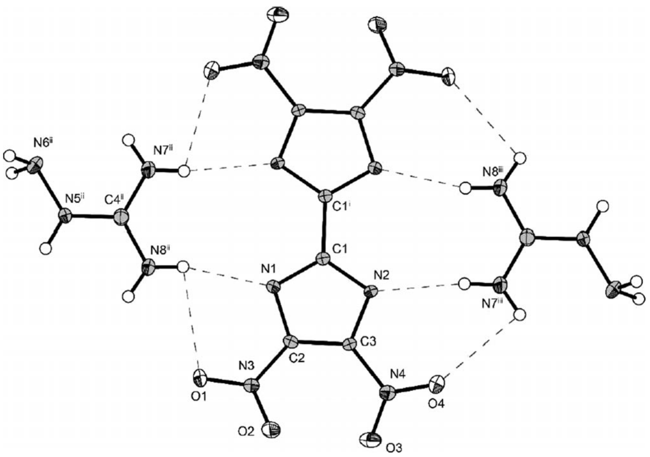

Figure 5. Molecular structure of bisaminoguanidinium tetranitrobisimidazolate (**4**) showing the labeling scheme. The non-hydrogen atoms are represented by displacement ellipsoids at the 50 % probability level. Symmetry codes: (i) –*x*, 1–*y*, –*z*; (ii) 1–*x*, 1–*y*, –*z*; (iii) –1+*x*, *y*, *z*., Selected bond lengths /Å: O1–N3 1.2286(19), O2–N3 1.2405(18), O3–N4 1.2281(19), O4–N4 1.2356(19), N1–C1 1.352(2), N1–C2 1.354(2), N2–C3 1.344(2), N2–C1 1.358(2), N3–C2 1.423(2), N4–C3 1.436(2), C1–C1 1.461(3), C2–C3 1.387(2), N5–C4 1.335(2), N5–N6 1.411(2), N7–C4 1.318(2), N8–C4 1.324(2); Selected bond angles /°:C1–N1–C2 102.57(14), C3–N2–C1 102.50(14), O1–N3–O2 122.54(14), O1–N3–C2 119.73(14), O2–N3–C2 117.71(14), O3–N4–O4 123.35(15), O3–N4–C3 119.09(15), O4–N4–C3 117.54(14), N1–C1–N2 115.66(15), N1–C1–C1 122.28(19), N2–C1–C1[i] 122.06(19), N1–C2–C3 109.34(14), N1–C2–N3 121.10(15), C3–C2–N3 129.26(15), N2–C3–C2 109.94(14), N2–C3–N4 119.58(15), C2–C3–N4 130.38(15), C4–N5–N6 118.05(15), N7–C4–N8 121.32(17), N7–C4–N5 120.12(17), N8–C4–N5 118.56(16); Selected torsion angles /°: O1–N3–C2–N1 18.6(2), O2–N3–C2–N1 –160.03(15), O3–N4–C3–N2 146.31(16), O4–N4–C3–N2 32.0(2), N2–C1–C1[i]–N1[i] 0.56 (3).

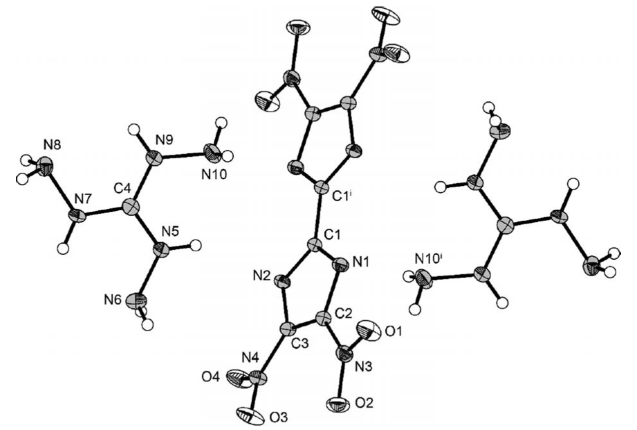

Figure 6. Molecular structure of bistriaminoguanidinium tetranitrobisimidazolate (**7**) showing the labeling scheme. The non-hydrogen atoms are represented by displacement ellipsoids at the 50 % probability level. Symmetry codes: (i) 2–*x*, 1–*y*, 1–*z*. Selected bond lengths /Å: O1–N3 1.2313(17), O2–N3 1.2390(17), O3–N4 1.2320(17), O4–N4 1.2258(17), N1–C1 1.3454(19), N1–C2 1.3458(19), N2–C3 1.3467(19), N2–C1 1.3528(19), N3–C2 1.4429(19), N4–C3 1.4384(19), C1–C1i 1.465(3), C2–C3 1.400(2); Selected bond angles /°: C1–N1–C2 102.95(12), C3–N2–C1 103.26(12), O1–N3–O2 123.40(13), O1–N3–C2 117.48(13), O2–N3–C2 119.12(13), O4–N4–O3 122.73(13), O4–N4–C3 118.23(12), O3–N4–C3 119.02(12), N1–C1–N2 115.54(12), N1–C1–C1i 123.04(16), N1–C2–C3 109.58(13), N1–C2–N3 117.98(13), C3–C2–N3 132.40(13), N2–C3–C2 108.67(13), N2–C3–N4 118.20(13), C2–C3–N4 133.12(13); Selected torsion angles /°: O1–N3–C2–N1 12.79(19), O2–N3–C2–N1 –166.49(13), O4–N4–C3–N2 17.5(2), O3–N4–C3–N2 –161.12(14), N1–C1–C1i–N2i 1.2 (2).

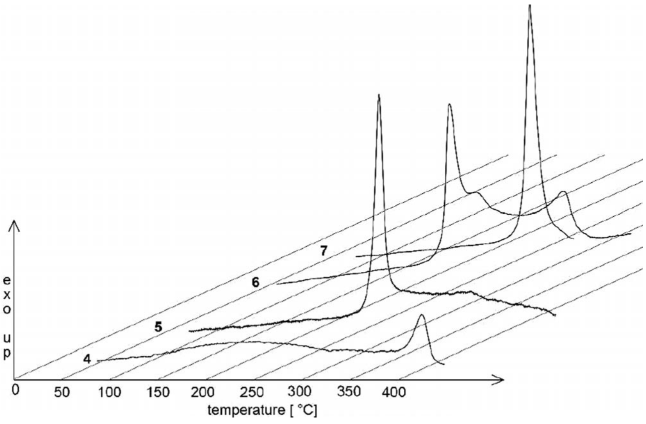

Figure 7. DSC plots of compounds **4**–**7** measured with a heating rate of 5 K·min^{-1} (exo-up). Onset temperatures: 328 °C (**4**), 206 °C (**5**), 197 (**6**), 152 °C (**7**).

lated with the atomization method (Equation 1) using CBS-4M enthalpies summarized in Table 2.[20,21] The gas phase enthalpies of formation $\Delta H_m(g)$ were converted into the solid state enthalpies of formation ($\Delta H_m(s)$) either by using the *Jenkins*' equations for X_2Y salts[22] (for ionic derivatives) or the Trouton rule[23] (**8**).

$$\Delta_f H^\circ_{(g,\,M,\,298)} = H_{(M,\,298)} - \sum H^\circ_{(Atoms,\,298)} + \sum \Delta_f H^\circ_{(Atoms,\,298)} \qquad (1)$$

Lastly, the molar standard enthalpies of formation (ΔH_m) were used to calculate the molar solid state energies of formation (ΔU_m) according to Equation (2) (Table 1).

$\Delta U_m = \Delta H_m - \Delta n\, RT$ (Δn being the change of moles of gaseous components) (2)

The most positive heat of formation (639 kJ·mol^{-1}) was achieved for the triaminoguanidinium salt **7**, which has the largest number of N–N single bonds. The hydroxylammonium salt **3** has a negative value (–516 kJ·mol^{-1}) due to the inclusion of two molecules of crystal water. Although of this negative value **3** is one of the best compounds investigated in this work in terms of performance (detonation energy, velocity and pressure). The guanidinium salts show the general trend of improving performance with rising number of N–N single bonds in the cations. The highest detonation velocity was calculated for **7**, which is much higher than that of HNS (7000 m·s^{-1})[14] and in the range that of PETN (8400 m·s^{-1}).[13] Most thermally stable **4** has also a good calculated detonation performance. In order to investigate the ignitability and explosiveness of **4**, a small scale reactivity test (SSRT)[24] was performed.

The SSRT was carried out in comparison to HNS in which a defined volume (HNS: 470 mg, density: 1.74 g·cm^{-3}, **4**: 485 mg, density: 1.80 g·cm^{-3}) was pressed into a perforated steel block (Figure 8). This was topped with a commercially available detonator (Orica, DYNADET-C2–0ms). Initiation of

Table 1. Energetic properties of compounds **3–8**.

	3*	**4**	**5**	**6**	**7**	**8**
Formula	$C_6H_{12}N_{10}O_{14}$	$C_8H_{12}N_{14}O_8$	$C_8H_{12}N_{16}O_8$	$C_8H_{16}N_{18}O_8$	$C_8H_{18}N_{20}O_8$	$C_8H_6N_8O_8$
FW /g·mol^{-1}	416.22	432.27	462.39	492.33	522.36	342.01
IS /J $^{a)}$	> 6 (500 µm)	> 40 (500 µm)	> 20 (500 µm)	> 17 (500 µm)	> 6 (500 µm)	> 40 (500 µm)
FS /N $^{b)}$	> 288 (500 µm)	> 360 (500 µm)	> 360 (500 µm)	>252 (500 µm)	> 288 (500 µm)	> 292 (500 µm)
ESD /J $^{c)}$	> 0.3 (500 µm)	> 1.0 (500 µm)	> 1.0 (500 µm)	> 0.4 (500 µm)	> 0.2 (500 µm)	> 0.1 (500 µm)
N /% $^{d)}$	33.65	45.36	48.48	51.21	53.63	32.75
Ω /% $^{e)}$	–23.06	–51.8	–51.91	–51.99	–52.1	–51.34
$T_{\mathrm{Dec.}}$ /°C $^{f)}$	186	328	206	197	152	236(T_{m}), 258 (T_{dec})
ρ /g·cm^{-3} $^{g)}$	1.81	1.80 (pyc.)	1.75	1.76	1.71	1.70
$\Delta_f H_m°$ /kJ·mol^{-1} $^{h)}$	–515.9	–114.5	171.1	399.3	638.7	145.3
$\Delta_f U°$ /kJ·kg^{-1} $^{i)}$	–1138.1	–17.0	473.4	916.6	1319.0	504.1
EXPLO5.04 values:						
$-\Delta_{\mathrm{Ex}}U°$ /kJ·kg^{-1} $^{j)}$	5015	4172	4486	4770	5030	4984
T_{det} /K $^{k)}$	3619	3098	3229	3351	3418	3732
P_{CJ} /kbar $^{l)}$	311	266	268	286	281	242
$V_{Det.}$ /m·s^{-1} $^{m)}$	8362	8070	8138	8377	8388	7604
V_o /L·kg^{-1} $^{n)}$	740	429	750	769	785	624

a) Impact sensitivity (BAM drophammer, 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); g) from X-ray diffraction; h) calculated (CBS-4M) heat of formation; i) energy of formation; j) energy of explosion; k) explosion temperature; l) detonation pressure; m) detonation velocity; n) assuming only gaseous products; * all values for dihydrate.

Table 2. CBS-4M calculation results and molecular volumes.

M	$-H^{298}$ /a.u.	$\Delta_f H°$(g,M) /kcal·mol^{-1}	V_{M} /nm^3
Me_2TNBI	1346,195338	57.5	
TNBI^{2-}	1266.677508	–8.1	
G$^+$	205.453192	136.6	
AG$^+$	260.701802	160.4	
DAG$^+$	315.949896	184.5	
TAG$^+$	371.197775	208.8	
NH_4O^+	131.863229	164.1	
3		320.1*	0.333*
4		265.1	0.417
5		312.7	0.439
6		361.0	0.465
7		409.5	0.504

* without crystal water

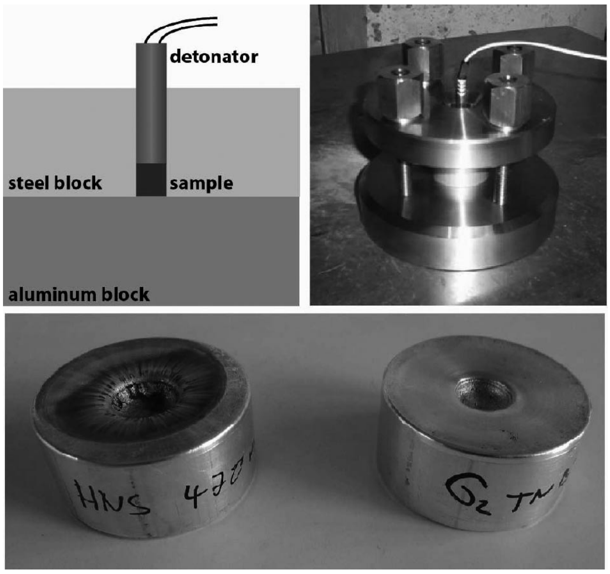

Figure 8. Dented steel block of HNS (left) and **4** (right).

the tested explosive resulted in denting a separate aluminum block, which was placed right underneath the steel block. The volume of the dent was then filled with sand to compare the performance of HNS and **4**. The test showed that HNS is superior and the dent could be filled with 672 mg sand in comparison to **4** (472 mg). The smaller dent of **4** could be caused by a larger critical diameter of **4**, which should influence the SSRT dramatically.

Conclusions

From this experimental study the following conclusions can be drawn:

- TNBI can be synthesized in good yields and purities by nitration of 2,2′-bisimidazole.
- The bis-potassium salt (**2**) crystallizes without crystal water and could be used for near infrared based combustion mixtures.
- 2:1 salts of TNBI can be synthesized either with corresponding bases (e.g. hydroxides, carbonates) or metathesis reactions using hydrochloride derivatives.

- Enhanced performance of compounds **3**–**7** correlates with higher sensitivities towards impact, friction and electrostatic discharge.
- Bis-hydroxylammonium TNBI (**3**) although crystallizing as a dihydrate has the best energetic properties related to secondary explosive applications (highest detonation pressure), highest density (1.81 g•cm^{-3}).
- Bis-guanidinium TNBI (**4**) has a high decomposition temperature (328 °C), low sensitivities and was successfully detonated in a small-scale reactivity test.
- Me_2TNBI (**8**) cannot be used as a suitable melt castable explosive because of its small melting range.
- All crystal structures of the herein investigated compounds were determined by low temperature single crystal X-ray diffraction.

Experimental Section

General Procedures

Raman spectra were recorded with a Bruker MultiRAM FT–Raman fitted with a liquid nitrogen cooled germanium detector and a Nd:YAG laser (λ = 1064 nm), infrared spectra were measured with a Perkin–Elmer Spectrum BXFTIR spectrometer equipped with a Smiths DuraSampl*IR* II ATR device. All spectra were recorded at ambient temperature, the samples were solids. NMR spectra were recorded at 25 °C with a JEOL Eclipse 400 ECX instrument, and chemical shifts were determined with respect to external Me_4Si (^{1}H, 400.2 MHz; ^{13}C, 100.6 MHz), $MeNO_2$ (^{14}N, 29.0 MHz;). Mass spectrometric data were obtained with a JEOL MStation JMS 700 spectrometer (DCI+). Elemental analysis (C/H/N) were performed with a Elementar Vario EL analyzer. Melting points were determined in capillaries with a Büchi Melting Point B–540 instrument and are uncorrected. Decomposition points were determined by Differential Scanning Calorimetry (DSC) measurements with a Linseis DSC–PT10, using a heating rate of 5 K•min^{-1}. Pycnometric measurements were carried out with a Quantachrome helium gas pycnometer. Sensitivity data (impact and friction) were performed using a drophammer and friction tester analog to BAM (Bundesanstalt für Materialforschung und -prüfung)[25]. Electrostatic sensitivities were measured with a OZM small scale electrostatic discharge tester.[26] Quantum chemical calculations were performed with the Gaussian09 software.[27]

XRD was performed on an Oxford Xcalibur3 diffractometer with a Spellman generator (voltage 50 kV, current 40 mA) and a KappaCCD detector using Mo-K_α radiation (λ = 0.71073 Å). The data collection and reduction was carried out using the CRYSALISPRO software.[28] The structures were solved either with SHELXS-97[29] or SIR-92,[30] refined with SHELXL-97[31] and finally checked using the PLATON[32] software integrated in the WINGX[33] software suite. The absorptions were corrected with a Scale3 Abspack multi-scan method. Cif files can be obtained free of charge using the CCDC Nos. from the Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

CAUTION! All high nitrogen and oxygen containing compounds are potentially explosive energetic materials, although no hazards were observed during preparation and handling these compounds. Nevertheless, this necessitates additional meticulous safety precautions (earthed equipment, Kevlar® gloves, Kevlar® sleeves, face shield, leather coat, and ear plugs).

Synthesis of 2,2′-Bisimidazole (BI)

Sodium bisulfite (36.6 g, 351 mmol) was dissolved in water (180 mL) and ethanol (100 mL) was added. Afterwards, an aqueous glyoxal solution (25.54 g, 176 mmol, 40 %) was added. The solution was stirred for 1.5 hours at ambient temperature. The white adduct was filtered and washed with ethanol and diethyl ether to yield the glyoxal-sodium bisulfite-hydrate adduct (50.6 g, 175 mmol). The adduct was dissolved in aqueous ammonia (275 mL, 25 %) and ammonium carbonate (10 g) was added. The solution was heated to reflux for 4 hours and cooled down to ambient temperature. After filtration and washing with ethanol and diethyl ether 2.2 g (16 mmol 40 %) could be obtained. The synthesis can be up-scaled by using the fivefold amount of each reagent yielding 12 g BI. **EA** ($C_6H_6N_4$ 134.14 g•mol^{-1}) exp.(calc.): C: 53.50 (53.72), H: 4.16 (4.51), N: 41.54 (41.77) %; **^{1}H NMR** (d_6 DMSO, 25 °C,): δ = 12.58 (s, br, 1H, NH), 7.13 (s, 1 H, $H_{arom.}$), 7.00 (s, 1H, $H_{arom.}$) ppm; **^{13}C{^{1}H} NMR** (d_6 DMSO, 25 °C): δ = 139.8 (s, 2C, C2/2’), 128.8 (s, 2C, C4/4’), 117.9 (s, 2C, C5/5’) ppm.

Synthesis of 4,4′,5,5′-Tetranitro-2,2′-bisimidazole (TNBI)

Sodium nitrate (18 g 0.2 mol) and urea (0.02 g 0.33 mmol) were suspended in concentrated sulfuric acid (30 mL) at 0 °C. Afterwards, bisimidazole (5.0 g 37.0 mmol) was added in small portions. The suspension was stirred for one hour at ambient temperature and was subsequently heated to 85–90 °C for 16 hours. After that the suspension was put onto ice-water (100 mL). The product precipitated immediately. It was filtered off and washed with ice water (4 × 50 mL) to obtain 6.6 g TNBI•$2H_2O$ (51 %) as a pale yellow powder. **EA** ($C_6H_2N_8O_8$•$2H_2O$, 350.14 g•mol^{-1}): exp. (calc.): C: 22.52 (22.58), N: 31.71 (32.00), H: 1.55 (1.73) %; **^{1}H NMR** (d_6-DMSO, 25 °C): δ = 8.95 (2H, N–H) ppm; **^{13}C{^{1}H} NMR** (d_6-DMSO, 25 °C): δ = 138.8 (1C, C–C), 139.1 (1C, C4,C5–NO_2) ppm; **Sensitivities:** IS > 40 J; FS: > 240 N; ESD: > 1.0 J

Bisammonium-4,4′,5,5′-tetranitro-2,2′-bisimidazolate (1)

When TNBI was extracted with diethyl ether (starting with 5 g BI) anhydrous ammonia was bubbled through the solution. The ammonium salt precipitated immediately. The solid was filtered and washed with diethyl ether to obtain 6.5 g of **1** (95 % relating to TNBI). **EA** ($C_6H_8N_{10}O_8$ 348.20 g•mol^{-1}) exp. (calc.): C: 19.98 (20.37), N: 39.96 (40.23), H: 2.11 (2.32) %; **^{1}H NMR** (d_6-DMSO, 25 °C): δ = 7.25 (8H, NH_4^+) ppm; **^{13}C{^{1}H} NMR** (d_6-DMSO, 25 °C): δ = 141.0 (1C, C–C), 144.9 (1C, C4,C5–NO_2) ppm; **Raman:** 1/λ [(%)] = 1562 (100), 1540 (15), 1496 (10), 1478 (20), 1389 (12), 1344 (19), 1302 (57), 1257 (88), 1026 (19), 867 (21), 771 (8), 758 (10), 688 (2), 432 (3), 397 (6) cm^{-1}; **IR:** (ATR) 1/λ = 3262 (m, br), 1492 (s), 1481 (s), 1440 (w), 1390 (s), 1368 (s), 1306 (s), 1246 (s), 1114 (m), 951 (m), 855 (m), 802 (vs), 754 (m), 706 (m) cm^{-1}; **MS** (FAB (–)): m/z = 311.98 (100), 312.99 (10), 313.99 (2); (FAB (+) m/z): 18.03 (100). **Sensitivities:** IS > 9 J; FS : > 240 N; ESD: > 1.0 J.

Bispotassium-4,4′,5,5′-tetranitro-2,2′-bisimidazolate (2)

The precipitated TNBI•$2H_2O$ can be purified by extraction with diethyl ether (4 × 100 mL). After evaporation of the solvent until a remaining of 5–10 mL, an excess (approx. 50 mL) KOH/EtOH (0.5 M) was added and the water-free orange bis-potassium salt (**2**) precipitated. To get rid of the precipitated excess KOH, the solid was washed with ice water and EtOH. **EA** ($K_2C_6N_8O_8$ 390.31 g•mol^{-1}) exp. (calc.): C: 18.52 (18.46), N: 28.66 (28.71), H: 0.0 (0.0) %; **^{1}H NMR** (d_6-DMSO, 25 °C): $\delta = 8.95$ (2H, N–H) ppm; **^{13}C{^{1}H} NMR** (d_6-DMSO, 25 °C): $\delta = 141.0$ (1C, C–C), 144.9 (1C, C4, C5–NO_2) ppm; **Sensitivities:** IS $>$ 40 J; FS: $>$ 240 N; ESD: $>$ 1.0 J.

Synthesis of Bishydroxylammonium 4,4′,5,5′-Tetranitro-2,2′-bisimidazolate Dihydrate (3)

TNBI·2H_2O (350 mg 1mmol) was dissolved in diethyl ether (20 mL). Hydroxylamine-monohydrate (0.25 mL, 50 wt.-%) was added and the resulting suspension was stirred for 30 min at ambient temperature. After filtering and washing with diethyl ether, the crude product can be recrystallized from water to yield **3** (300 mg 72 %). **DSC** (5 K·min^{-1}): $T_{dec} = 186$ °C; **EA** ($C_6H_8N_{10}O_{10}\cdot 2H_2O$ 416.22 g·mol^{-1}) exp. (calc.): C: 17.50 (17.31), N: 33.36 (33.65), H: 2.61 (2.91) %; **^{1}H NMR** (d_6-DMSO, 25 °C): $\delta = 10.35$ (s, br, 1H, N–OH) ppm; **^{13}C{^{1}H} NMR** (d_6-DMSO, 25 °C): $\delta = 140.4$ (2C, C2,2‘), 143.4 (4C, C4,4‘,5,5‘ –NO_2) ppm; **^{14}N NMR{^{1}H}** (d_6-DMSO, 25 °C) $\delta = -25$ (4N, –NO_2), –349 (1N, O–NH_3) ppm; **Raman**: 1/λ [(%)] = 2060 (8), 1603 (19), 1564 (100), 1486 (35), 1388 (22), 1352 (28), 1304 (53), 1266 (64), 1217 (19), 1043 (20), 870 (26), 757 (17), 397 (18) cm^{-1}; **IR** (ATR): 1/λ = 3638 (m, br), 3332 (vw), 3274 (vw), 3216 (vw), 2504 (w), 2086 (vw), 1609 (vw), 1594 (vw), 1509 (s), 1462 (s), 1399 (s), 1348 (m), 1311 (s), 1262 (vs), 1226 (m), 1187 (s), 1115 (m), 996 (w), 966 (w), 927 (vw), 855 (vs), 752 (m), 697 (m), 655 (w), 614 (vw) cm^{-1}; **Sensitivities**: IS $>$ 6 J; FS: 288 N; ESD: 0.2 J.

General Procedure for the Syntheses of Compounds 4 and 5

TNBI dihydrate (350 mg, 1mmol) was suspended in water (10 mL). Adding guanidinium carbonate (200 mg, 1.1 mmol) or aminoguanidinium bicarbonate (300 mg, 2.2 mmol) resulted in precipitation of the corresponding orange 2:1 salt. Afterwards, the salts could be washed with a lot of water to yield 400 mg of **4** (93 %) and 425 mg of **5** (92 %).

Bisguanidinium-4,4′,5,5′-tetranitro-2,2′-bisimidazolate (4): DSC (5 K·min^{-1}): $T_{dec} = 328$ °C; **EA** ($C_8H_{12}N_{14}O_8$ 432.27 g·mol^{-1}) exp. (calc.): C:22.38 (22.23); N: 45.09 (45.36); H: 2.67 (2.80) %; **^{1}H NMR** (d_6-DMSO, 25 °C): $\delta = 7.12$ (s, br, 6H, NH_2) ppm; **^{13}C{^{1}H} NMR** (d_6-DMSO, 25 °C): $\delta = 140.8$ (2C, C2,2‘), 144.1 (4C, C4,4‘,5,5‘ –NO_2), 158.4 (1C, –(NH_2) ppm; **^{14}N{^{1}H} NMR** (d_6-DMSO, 25 °C): $\delta = -20$ (4N, –NO_2) ppm; **MS:** (FAB (–)) m/z = 311.98 (100), 312.99 (10), 313.99 (2); (FAB (+)) m/z = 60.06 (100), 61.06 (2); **Raman:** 1/λ [(%)] = 1551 (100), 1536 (18), 1490 (5), 1465 (19), 1396 (7), 1348 (17), 1303 (42), 1363 (6), 1216 (60), 1111 (3), 1026 (15), 868 (16), 762 (6), 684 (4), 517 (3) cm^{-1}; **IR** (ATR): 1/λ = 3424 (m), 3280 (w), 3116 (m), 1738 (w), 1664 (s), 1650 (s), 1574 (w), 1483 (s), 1460 (s), 1385 (s), 1372 (vs), 1304 (s), 1197 (vs), 1111 (m), 1015 (w), 1015 (w), 945 (w), 858 (m), 820 (vs) cm^{-1}**; Sensitivities:** IS $>$ 40 J; FS: $>$ 240 N; ESD: $>$ 1.0 J

Bisaminoguanidinium-4,4′,5,5′-tetranitro-2,2′-bisimidazolate (5): DSC (5 K·min^{-1}): $T_{dec} = 206$ °C; **EA** ($C_8H_{14}N_{16}O_8$ 462.30 g·mol^{-1}) exp. (calc.): C: 21.17 (20.48), N: 48.55 (48.48), H: 2.82 (3.05) %; **^{1}H NMR** (d_6-DMSO, 25 °C): $\delta = 4.70$ (s, 2H, N–NH_2), 7.02 (s, br, 4H, –NH_2), 8.85 (s, br, 1H, C–NH) ppm; **^{13}C{^{1}H} NMR** (d_6-DMSO, 25 °C): $\delta = 140{,}6$ (2C, C2,2‘), 144.5 (4C, C4,4‘,5,5‘ –NO_2), 159.41 (1C, aminoguanidine) ppm; **^{14}N{^{1}H} NMR** (d_6-DMSO, 25 °C): $\delta = -25$ (4N, –NO_2) ppm, **IR** (ATR**):** 1/λ = 3423 (m), 3382 (w), 3290 (m), 3109 (m, br), 2649 (w), 2408 (vw), 1666 (s), 1593 (w), 1519 (m), 1464 (vs), 1373 (vs), 1302 (vs), 1258 (m), 1238 (m), 1192 (vs, br), 1111 (vs), 994 (m), 946 (m), 910 (s, br), 856 (s), 811 (vs), 750 (vs), 723 (m), 702 (s) cm^{-1}; **Sensitivities:** IS $>$ 20 J; FS : 360 N; ESD: $>$ 1.0 J

General Procedure for the Syntheses of Compounds 6 and 7

Compound **1** (348 mg 1 mmol) was suspended in water (10 mL). Afterwards, DAG·HCl (260 mg, 1.1 mmol) or TAG·HCl (300 mg, 1.1 mmol), respectively, was added. The corresponding suspension was heated to reflux for 1 h. The DAG_2TNBI precipitated immediately, whereas the TAG_2TNBI crystallized overnight in the fridge at 4 °C. Both compounds can be filtered and washed with ice water to yield 400 mg of **6** (81 %) and 420 mg of **7** (80 %).

Bis-diaminoguanidinium-4,4′,5,5′-tetranitro-2,2′bisimidazolate (6): DSC (5 K·min^{-1}): T_{dec} = 195 °C; **EA** ($C_8H_{16}N_{18}O_8$ 492.33 g·mol^{-1}) (exp. (calc.): C: 19.82 (19.52), N: 50.56 (51.21), H: 3.14 (3.28) %; **^{1}H NMR** (d_6-DMSO, 25 °C): $\delta = 4.48$ (s, br, 4H, N–NH_2), 7.12 (s, br, 2H, –NH_2), 8.57 (s, br, 2H, C–NH) ppm; **^{13}C{^{1}H} NMR** (d_6-DMSO, 25 °C): $\delta = 140.9$ (2C, C2,2‘), 144.7 (4C, C4,4‘,5,5‘ –NO_2), 160.2 (1C, diaminoguanidine) ppm; **^{14}N{^{1}H} NMR** (d_6-DMSO, 25 °C): $\delta = -18$ (4N, –NO_2) ppm; **MS:** (FAB (–)) m/z = 311.98 (100), 312.99 (10), 313.99 (2); (FAB (+) m/z) : 90.08 (100), 91.08 (3); **Raman:** 1/λ [(%)] = 1553 (100), 1542 (43), 1447 (25), 1380 (10), 1346 (18), 1307 (46), 1224 (50), 1182 (18), 1029 (10), 989 (6), 930 (5), 866 (23), 700 (5), 527 (5), 434 (5) cm^{-1}; **IR** (ATR): 1/λ = 3480 (w), 3376 (w), 3348 (w), 3312 (w), 3055 (w, br), 1675 (s), 1562 (w), 1516 (m), 1489 (m), 1443 (s), 1393 (s), 1361 (vs), 1300 (vs), 1264 (w), 1212 (s), 1172 (vs), 986 (s), 962 (vs), 946 (s), 856 (s), 811 (vs), 756 (m), 698 (s), 637 (vs, br) cm^{-1}; **Sensitivities:** IS $>$ 17 J; FS: 252 N; ESD: 0.4 J

Bis-triaminoguanidinium-4,4′,5,5′-tetranitro-2,2′-bisimidazolate (7): DSC (5 K·min^{-1}): 152; **EA** ($C_8H_{18}N_{20}O_8$ 522,36 g·mol^{-1}) **exp. (calc.):** C: 18.65 (18.39), N: 53.48 (53.63), H: 3.34 (3.47) %; **^{1}H NMR** (d_6-DMSO, 25 °C): $\delta = 4.48$ (s, br, 6H, N–NH_2), 8.59 (s,br, 3H, C–NH) ppm; **^{13}C{^{1}H} NMR** (d_6-DMSO, 25 °C): $\delta = 141.0$ (2C, C2,2‘), 144.9 (4C, C4,4‘,5,5‘ –NO_2), 159,6 (1C, guanidine) ppm; **^{14}N{^{1}H} NMR** (d_6-DMSO, 25 °C): $\delta = -26$ (4N, –NO_2) ppm; **MS:**(FAB (+)) m/z = 105.12 (100), 104.12 (3); **Raman:** 1/λ [(%)] = 1557 (100), 1545 (39), 1517 (8), 1451 (17), 1443 (17), 1379 (9), 1340 (14), 1299 (52), 1223 (66), 1145 (4), 1027 (14), 865 (15), 754 (5), 697 (3), 527 (4), 405 (5) cm^{-1}; **IR** (ATR): 1/λ = 3381 (vw), 3340 (w), 3144 (w), 2430 (vw, br), 1670 (m), 1589 (w, br), 1519 (m), 1495 (m), 1445 (m, br), 1389 (s), 1361 (s), 1306 (s), 1219 (s, br), 1108 (m), 1027 (m), 945 (s), 886 (s, br), 854 (vs), 752 (s) 705 (vs) 639 (vs) 606 (s) cm^{-1}; **Sensitivities:** IS $>$ 6 J; FS: 288 N; ESD: 0.2 J

1,1′-Dimethyl,4,4′,5,5′-tetranitro-2,2′-bisimidazole (8)

Bispotassium-4,4′,5,5′-tetranitro-bisimidazolate (390.1 mg 1mmol) was suspended in acetonitrile (20 mL) and dimethylsulfate (0.2 mL, 2 mmoL) was added at ambient temperature. The suspension was heated to reflux and DMF (2–3 mL) was added until a solution had been obtained. After heating to reflux for 16 h, all solvents were removed in vacuo. The residue was boiled in water, hot filtered and washed with water to yield bright-shining **8** (212 mg 62 %) after drying in a 60 °C oven for 12 h. **DSC** (5 K·min^{-1}): $T_m = 236$ °C, $T_{dec} = 258$ °C; **EA** ($C_8H_6N_8O_8$ 342.04 g·mol^{-1}): exp.(calc.): C: 27.91 (28.08), N: 32.44 (32.75); H: 1.92 (1.77) %; **^{1}H NMR** (d_6-DMSO, 25 °C): $\delta = 4.28$ (6H,CH_3) ppm, **^{13}C{^{1}H} NMR** (d_6-DMSO, 25 °C): $\delta = 35.7$ (2C, C1,C1’) 132.2 (2C, C3,C3’), 133.3 (1C, C4–NO_2), 139.6 (1C, C5–NO_2) ppm. **MS** (EI) m/z = 343.03 (12.94 % MH^+), 342.03 (100 %, M^+), 326.03 (11.45 %MH^+–CH_3), 325.03 (97.67 %), 313.02 (14.07 %, M–2CH_3+1H), 312.02 (61.83 %, M–2CH_3+2H). **IR** (ATR) 1/λ = 1567 (w), 1534 (s), 1454 (m), 1408 (m), 1384 (m), 1342 (m), 1301 (s), 1164 (w), 1082 (w), 1040 (w), 850 (s), 813 (vs), 744 (m), 687 (m) cm^{-1}. **Raman** 1/λ [(%)] = 2977 (8), 1584 (100), 1567 (51), 1534 (31), 1490 (4), 1387 (16), 1344 (54), 1312 (56), 1208 (8), 1145 (3), 1054 (8), 874 (3), 817 (9), 778 (5), 764 (6), 742 (6), 292 (4), 240 (3) cm^{-1}. **Sensitivities:** IS > 40 J; FS: 292 N; ESD: 0.1 J.

Supporting Information (see footnote on the first page of this article): X-ray data and parameters and additional structure descriptions.

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