FULL PAPER

### Nitrogen-Rich 5,5'-Bistetrazolates and their Potential Use in Propellant Systems: A Comprehensive Study

# Niko Fischer, Dániel Izsák, Thomas M. Klapötke,\* Sebastian Rappenglück, and Jörg Stierstorfer<sup>[a]</sup>

Abstract: A large variety of twice-deprotonated nitrogen-rich 5,5'-bistetrazolates, that is, the ammonium (1), hydrazinium (2), hydroxylammonium (3), guanidinium (4), aminoguanidinium (5), diaminoguanidinium (6), triaminoguanidinium (7), and diaminouronium (8) salts, have been synthesized. Energetic compounds 1–8 were fully characterized by single-crystal X-ray diffraction (except 8), NMR spectroscopy, IR

and Raman spectroscopy, and differential scanning calorimetry (DSC) measurements. With respect to their potential use in propellant applications, the sensitivity towards impact, friction, and electrical discharge were determined.

**Keywords:** energetic materials • nitrogen heterocycles • propellants • sensitivities • X-ray diffraction Several propulsion and detonation parameters (e.g., heat of explosion, detonation velocity) were computed by using the EXPLO5 computer code based on calculated (CBS-4M) heats of formation and X-ray densities. Additionally, the performance of **1–8** in various formulations was investigated by calculating the specific energy and specific impulse of the compounds under isochoric conditions.

#### Introduction

Nitrogen-rich materials play an important role in the design of new energetic compounds and their use as propellants, explosives, and pyrotechnics.<sup>[1]</sup> The most promising heterocyclic backbone for the preparation of high-performance energetics is considered to be the tetrazole ring.

Tetrazole ring systems demonstrate high heats of formation that result from inherently energetic nitrogen-nitrogen and nitrogen-carbon bonds, high ring strain, and high density, and have allowed the preparation of a variety of highperformance primary<sup>[2]</sup> and secondary<sup>[3]</sup> explosives, which illustrate their dynamic nature. Depending on the ring substituents and anion/cation pairing, tetrazole-based energetic compounds can span the entire spectrum of sensitivity from insensitive to highly sensitive (primary explosives). Since its discovery in the early 20th century,<sup>[4]</sup> 5,5'-bistetrazole, which has one of the highest nitrogen contents, and in particular its nitrogen-rich salts have been the focus of research for many decades, which has resulted in a wide variety of applications. However, only very few structurally investigated examples of nitrogen-rich salts of 5,5'-bistetrazole are known to literature.<sup>[5]</sup> Owing to its high nitrogen content and high

[a] N. Fischer, D. Izsák, Prof. Dr. T. M. Klapötke, S. Rappenglück, Dr. J. Stierstorfer
Department of Chemistry
Energetic Materials Research
Ludwig Maximilian University
Butenandtstr. 5–13 (D)
81377 München (Germany)
Fax: (+49)89-2180-77492
E-mail: tmk@cup.uni-muenchen.de decomposition temperature, ammonium 5,5'-bistetrazolate was investigated as a gas-generating component in fire-resistant resins and fire-proof adhesives in airbags.<sup>[6]</sup> However, Hiskey et al. have reported on the suitability of several nitrogen-rich 5,5'-bistetrazolates for use as low-smoke pyrotechnic fuels.<sup>[7]</sup> The above-mentioned properties of thermal stability and high nitrogen content make these molecules appropriate materials for investigation as ingredients in gun or rocket propellant systems, particularly considering barrel erosion problems. Barrel corrosion arises from the formation of iron carbide due to the high carbon contents of currently used propellant mixtures, such as M1 (85% nitrocellulose, 10% 2,4-dinitrotoluene, 5% dibutyl phthalate). An increased N<sub>2</sub>/CO ratio in the combustion gases when using nitrogen-rich materials results in the formation of iron nitride in the gun barrel, which has a higher melting point than iron carbide and forms a protective layer on the inside of the gun barrel and helps to increase the lifespan of the equipment by a factor of up to four.<sup>[8]</sup> Additionally, the sensitivity of the material used plays an important role for its safe handling; ideally the materials should be less sensitive than RDX (hexogen). Two very interesting additives currently being developed for use in composite modified double base (CMDB) propellant formulations<sup>[9]</sup> are hydrazinium 5,5'-azotetrazolate<sup>[10,11]</sup> and triaminoguanidinium 5,5'azotetrazolate.<sup>[12,13]</sup> The latter compound is included in the NILE (Navy insensitive low-erosion) propellant mixture, which was developed at NSWC, Indian Head division. The NILE mixture was successfully fielded as a propellant in, for example, the 105 mm Howitzer.<sup>[14]</sup>

Unfortunately, 5,5'-azotetrazolates are not stable under mineral-acidic conditions because neutral 5,5'-azotetrazole decomposes into 5-hydrazinotetrazole, dinitrogen, and



- 4051

formic acid (see Scheme 1).<sup>[15]</sup> The corresponding salts of 5,5'bistetrazole reported herein are stable in acidic media and show performance similar to 5,5'-azotetrazolates. The parent compound, 5,5'-bistetrazole, is easily accessible in high quantities and unlike 5,5'-azotetrazole is stable in acidic media.

#### **Results and Discussion**

**Synthesis**: The synthesis of 5,5'-bistetrazole ( $H_2$ -5,5'-BT) has already been described in the literature;<sup>[4,7]</sup> the basic principle is a ring-closure reaction in a [2+3] dipolar cycloaddition reaction starting from cyanogen. Depending on the literature source, cyanogen can either be prepared and isolated in an additional step and treated with either sodium azide or hydrazoic acid or it can be generated in situ from sodium cyanide and manganese dioxide as the oxidizing agent under acidic conditions and be further treated with sodium azide. Herein, we chose the latter synthetic route because it is the more convenient strategy (Scheme 2).

The workup involves two further steps because the manganese(II) salt of 5,5'-bistetrazole is formed in the first synthetic step. It is treated with sodium carbonate to form the less soluble MnCO<sub>3</sub> and the sodium salt of 5,5'-BT, which stays in solution. The free acid H<sub>2</sub>-5,5'-BT can be precipitated by adding excess concentrated HCl to the mixture. After further recrystallization, the product can be treated with the respective bases to give compounds 1-8 through Brønsted acid-base chemistry or metathesis reactions (Scheme 3).

For compounds 1–3, 7, and 8, the free bases were reacted with an aqueous solution of 5,5'-bistetrazole, whereas for 4 and 5 an aqueous acidic solution of 5,5'-BT was heated to reflux with a suspension of the corresponding carbonates. Diaminoguanidinium salt 6 had to be prepared by a metathesis reaction, in which 5,5'-BT was first converted into the sodium salt. After addition of barium



Scheme 1. Hydrazinium (a) and 1,3,5-triaminoguanidinium 5,5'-azotetrazolate (b) and their decomposition reaction in mineralic acids.







Scheme 3. Synthesis of the nitrogen-rich salts **1–8**. Conditions: i) NH<sub>3</sub>, H<sub>2</sub>O, reflux, 5 min; ii) N<sub>2</sub>H<sub>4</sub>·H<sub>2</sub>O, H<sub>2</sub>O, reflux, 5 min; iii) NH<sub>2</sub>OH, H<sub>2</sub>O, reflux, 5 min; iv) G<sub>2</sub>CO<sub>3</sub>, H<sub>2</sub>O, reflux, 10 min; v) AG<sup>+</sup>HCO<sub>3</sub><sup>-</sup>, H<sub>2</sub>O, reflux, 10 min; vi) NaOH, H<sub>2</sub>O, RT, then BaCl<sub>2</sub>, H<sub>2</sub>O, RT, then DAG<sub>2</sub>SO<sub>4</sub>, reflux, 5 min; vii) TAG, RT; viii) DAU, RT. G = guanidinium, AG = aminoguanidinium, DAG = diaminoguanidinium, TAG = triaminoguanidinium, DAU = diaminouronium.

### **FULL PAPER**

chloride, the barium salt precipitates and can be isolated and further treated with diaminoguanidinium sulfate to obtain 6. The solubility of nitrogen-rich 5,5'-bistetrazolates 1–7 is only moderate in water, so crystals of 1–7 suitable for X-ray single-crystal analysis were obtained after filtration and slow evaporation of the aqueous mother liquors.

**Crystal structures**: Suitable single crystals of the described compounds (1–7) were selected from the crystallization mixture and mounted in Kel-F oil, transferred to the N<sub>2</sub> stream of an Oxford Xcalibur3 diffractometer equipped with a Spellman generator (voltage 50 kV, current 40 mA) and a KappaCCD detector (Mo<sub>Ka</sub> radiation,  $\lambda = 0.71073$  Å). All structures were measured at -100 °C. The data collection and data reduction was carried out by using the CrysAlisPro software.<sup>[16]</sup> The structures were solved by using Sir-92<sup>[17]</sup> or Sir-97,<sup>[17]</sup> refined with Shelxl-97,<sup>[18]</sup> and finally checked using the Platon software<sup>[19]</sup> integrated in the WinGX software suite.<sup>[20]</sup> The non-hydrogen atoms were refined anisotropically and the hydrogen atoms were located and freely re-

fined. The absorptions were corrected by using a SCALE3 ABSPACK multi-scan method.<sup>[21]</sup> Important data and parameters are listed in Table 1.

Compound 1 crystallizes in the monoclinic space group C2m with two formula units in the unit cell and a calculated density of 1.590 g cm<sup>-3</sup>. The asymmetric unit contains only one quarter of the molecular unit (Figure 1). Therefore, the anion consists of two identical tetrazolate rings. The structure of the bistetrazolate dianion is in agreement with corresponding structures of, for example, the erbium(III) salt described in the literature.<sup>[22]</sup> The N-N bond lengths lie between N-N single bonds (1.48 Å) and N=N double bonds (1.20 Å), and the C-N bonds lie between C-N single (1.47 Å) and C=N double bonds (1.22 Å).<sup>[23]</sup> Both are comparable to other tetrazolates, for example, alkali 5-aminotetrazolates.<sup>[24]</sup> The torsion angles N1-N2-N2<sup>i</sup>-N1<sup>i</sup> (0.0(1)°) and N1-C1-N1<sup>i</sup>-N2<sup>i</sup> (0.2(1)°) indicate a completely planar ring, which together with the bond lengths leads to the assumption of a  $6\pi$  aromatic system. The C1–C1<sup>ii</sup> bond (1.46 Å) is slightly longer than in the neutral 5,5'-bistetrazole.<sup>[25]</sup> How-

Table 1. X-ray data and parameters.<sup>[a]</sup>

	1	2	3	4	5	6	7
formula	$C_2H_8N_{10}$	$C_2H_{10}N_{12}$	$C_2H_8N_{10}O_2$	$C_4H_{12}N_{14}$	$C_4H_{18}N_{16}O_2$	$C_4H_{20}N_{18}O_2$	C4H18N20
$M_{\rm r} [{\rm gmol}^{-1}]$	172.18	202.18	204.18	256.28	322.34	352.38	346.38
crystal system	monoclinic	monoclinic	monoclinic	monoclinic	monoclinic	triclinic	monoclinic
space group	C2/m (No. 12)	<i>P</i> 1̄ (No. 2)	<i>P</i> 1̄ (No. 2)	$P2_1/c$ (No. 14)	$P2_1/n$ (No. 14)	<i>P</i> 1̄ (No. 2)	$P2_1/n$ (No. 14)
color, habit	colorless,	colorless,	colorless,	colorless,	colorless,	colorless,	colorless,
	block	needle	block	rod	rod	needle	rod
size [mm]	$0.30 \times 0.20 \times 0.08$	$0.30\!\times\!0.05\!\times0.05$	$0.15 \times 0.23 \times 0.31$	$0.11 \times 0.14 \times 0.20$	$0.18 \times 0.22 \times 0.23$	$0.13 \times 0.14 \times 0.30$	$0.10 \times 0.11 \times 0.28$
a [Å]	8.8511(8)	3.6096(5)	3.6736(3)	3.588(4)	11.8344(11)	7.3878(6)	10.417(5)
b [Å]	11.1956(9)	7.9134(12)	7.3455(7)	15.014(5)	3.8684(4)	7.5263(8)	3.929(5)
c [Å]	3.6809(4)	8.2992(16)	7.4908(8)	10.048(6)	14.9914(14)	8.1937(8)	18.660(5)
a [°]	90	72.058(15)	102.666(9)	90	90	83.689(8)	90
β [°]	99.608(9)	79.051(14)	95.283(8)	97.362(5)	95.741(9)	70.034(8)	101.092(5)
γ [°]	90	79.132(13)	96.302(8)	90	90	64.158(9)	90
V [Å <sup>3</sup> ]	359.64(6)	219.27(6)	194.61(3)	536.8(7)	682.87(11)	384.98(7)	749.5(10)
Ζ	2	1	1	2	2	1	2
$\rho_{\rm calcd}  [\rm g  cm^{-3}]$	1.590	1.531	1.742	1.586	1.568	1.520	1.535
$\mu [{\rm mm}^{-1}]$	0.125	0.121	0.148	0.122	0.128	0.124	0.120
F(000)	180	106	106	268	340	186	364
$\lambda(Mo_{K\alpha})$ [Å]	0.71073	0.71073	0.71073	0.71073	0.71073	0.71073	0.71073
T [K]	173	173	173	173	173	173	173
$\theta$ range [°]	4.7-27.0	4.3-26.0	4.5-26.5	4.3-26.0	4.3-26.2	4.8-26.0	4.2-26.5
dataset $(h, k, l)$	$-6 \leq h \leq 11$	$-4 \leq h \leq 4$	$-4 \leq h \leq 4$	$-4 \leq h \leq 4$	$-14 \leq h \leq 14$	$-9 \leq h \leq 9$	$-10 \le h \le 13$
	$-14 \leq k \leq 12$	$-6 \leq k \leq 9$	$-9 \leq k \leq 9$	$-18 \le k \le 18$	$-4 \leq k \leq 4$	$-9 \leq k \leq 9$	$-4 \leq k \leq 4$
	$-4 \leq l \leq 3$	$-9 \le l \le 10$	$-9 \leq l \leq 9$	$-12 \le l \le 12$	$-18 \le l \le 11$	$-10 \le l \le 10$	$-23 \le l \le 23$
reflns. collected	1026	1152	2302	5201	3275	3896	3786
independent reflns.	416	868	806	1061	1372	1507	1536
$R_{\rm int}$	0.027	0.020	0.029	0.048	0.034	0.029	0.032
observed reflns	343	580	595	740	1012	1143	1027
parameters	38	84	80	106	136	149	145
$R_1$ (obsd)	0.0320	0.0362	0.0333	0.0356	0.0350	0.0329	0.0325
$wR_2$ (all data)	0.0803	0.0883	0.0782	0.0885	0.0900	0.0815	0.0752
S	1.05	0.88	0.94	0.91	0.97	0.95	0.87
residual density [e Å-3]	-0.29, 0.17	-0.17, 0.21	-0.20, 0.21	-0.17, 0.20	-0.17, 0.20	-0.21, 0.17	-0.15, 0.20
solution	SIR-97	SIR-97	SIR-92	SIR-92	SIR-92	SIR-92	SIR-92
refinement	SHELXL-97	SHELXL-97	SHELXL-97	SHELXL-97	SHELXL-97	SHELXL-97	SHELXL-97
absorption	multi-scan	multi-scan	multi-scan	multi-scan	multi-scan	multi-scan	multi-scan
correction							

[a] CCDC-854127 (1), -854128 (2), -854126 (3), -854129 (4), -854132 (5), -854131 (6), and -854130 (7) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data\_request/cif.

Chem. Eur. J. 2012, 18, 4051-4062

© 2012 Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim



Figure 1. Molecular unit of diammonium 5,5'-bistetrazolate (1). Ellipsoids of non-hydrogen atoms are drawn at the 50% probability level. Bond lengths [Å]: N1–C1 1.334(1), N1–N2 1.342(1), N2–N2<sup>i</sup> 1.314(1), C1–C1<sup>ii</sup> 1.461(2); bond angles [°]: N1-C1-N1<sup>i</sup> 112.1(1), N2-N1-C1 104.4(1), N1-N2-N2<sup>i</sup> 109.6(1), N1-C1-C1<sup>ii</sup> 123.9(1); torsion angles [°]: N1-N2-N2<sup>i</sup> N1<sup>ii</sup> 0.0(1), N1-C1-N1<sup>i</sup>-N2<sup>i</sup> 0.2(1), N1-C1-C1<sup>ii</sup>-N1<sup>ii</sup> -180.0(1), N1-C1-C1<sup>ii</sup>-N1<sup>iii</sup> -0.9(2); symmetry codes: i: x, -y, z; ii: -x, y, 2-z; iii: -x, -y, 2-z; iv: 0.5-x, 0.5-y, 1-z.

ever, the C–C bonds of all structures observed in this work are significantly shorter (mean value 1.46 Å) than typical C–C single bonds of approximately 1.54 Å.<sup>[23]</sup> The N1-C1-C1<sup>ii</sup>-N1<sup>ii</sup> torsion angle is  $-180.0(1)^\circ$ , which shows the complete planarity of the whole anion. In the crystal structure, layers comprised of infinite parallel chains of longitudinal bistetrazolate anions are stacked with ammonium cations between the layers (Figure 2). One ammonium is coordinated by four bistetrazolates, two from each layer above and below the cation, through two crystallographically independ-



Figure 2. A) Layer structure of **1** (view along [010]); B) hydrogen-bonding network with the three most characteristic graph-set descriptors (view along [001]).

ent hydrogen bonds. The resulting hydrogen-bonding network consists of multiple ring patterns, of which  $R_4^4(14)$  and  $R_4^4(10)$  are the most characteristic.

Suitable single crystals of **2** were directly obtained from the mother liquor in the form of fine needles. The compound crystallizes in the triclinic space group  $P\bar{1}$  with one formula unit in the unit cell and a calculated density of 1.531 g cm<sup>-3</sup>. Due to the lower symmetry of the space group, the asymmetric unit contains one half of the molecular unit shown in Figure 3. The bond lengths and angles are never-



Figure 3. Molecular unit of dihydrazinium 5,5'-bistetrazolate (2). Ellipsoids of non-hydrogen atoms are drawn at the 50% probability level. Bond lengths [Å]: N1-C1 1.332(2), N1-N2 1.346(2), N2-N3 1.314(2), N3-N4 1.347(2), N4-C1 1.338(2), C1-C1<sup>i</sup> 1.460(2), N5-N6 1.454(2); bond angles [°]: N1-C1-N4 112.1(1), N2-N1-C1 104.4(1), N1-N2-N3 109.7(1), N2-N3-N4 109.5(1), N3-N4-C1 104.4(1), N1-C1-C1<sup>i</sup> 124.2(1), N4-C1-C1<sup>i</sup> 123.7(1); torsion angles [°]: N1-N2-N3-N4 -0.0(2), N1-C1-N4-N3 0.1(2), N2-N1-C1-N4 -0.1(2), N1-C1-C1-N1 180.0(2), N1-C1-C1-N4 -0.7(3); symmetry codes: i: 1-x, 1-y, -1-z; ii: x, y, -1+z; iii: 1-x, 1-y, -z.

theless almost identical to those in **1**, and so are also the torsion angles. The N5–N6 bond of the hydrazinium is in the range of a N–N single bond and is comparable to the bond in other hydrazinium compounds, such as hydrazinium 5aminotetrazolate<sup>[3]</sup> or hydrazinium tetrafluoroborate.<sup>[26]</sup> The geometry of the hydrogen atoms is staggered. The hydrazinium cation is coordinated by one other cation and three anions, which leads to all hydrogen atoms being involved in the formation of hydrogen bonds (Figure 4). The longest N– H bond and shortest H…A contact is observed in the hydrogen bond involving the two hydrazinium cations, which results in  $C_1^1(3)$  chains.



Figure 4. Coordination sphere of the hydrazinium cation in **2**. Ellipsoids of non-hydrogen atoms are drawn at the 50% probability level. Symmetry codes: i: -1+x, y, z; ii: 2-x, -y, -z; iii: x, y, 1+z; iv: 1-x, 1-y, -z.

4054

### FULL PAPER



Figure 5. Molecular unit of di(hydroxylammonium) 5,5'-bistetrazolate (3). Ellipsoids of non-hydrogen atoms are drawn at the 50% probability level. Selected bond lengths [Å]: N3–N2 1.3128(19), N3–N4 1.3452(18), N4–C1 1.333(2), C1–N1 1.336(2), C1–C1<sup>i</sup> 1.461(3), N1–N2 1.3443(17), O1–N5 1.4181(16); selected bond angles [°]: N2-N3-N4 109.84(12), C1-N4-N3 104.45(13), N4-C1-N1 111.77(13), N4-C1-C1<sup>i</sup> 124.02(18), N1-C1-C1<sup>i</sup> 124.20(18), C1-N1-N2 104.84(13), N3-N2-N1 109.10(12); symmetry codes: i: 2-x, 1-y, 1-z, ii: 1-x, 1-y, 1-z.

Single crystals of di(hydroxylammonium) 5,5'-bistetrazolate (3) crystallized in the triclinic  $(P\bar{1})$  space group with one molecular moiety (Figure 5) in the unit cell. Its density of 1.742 g cm<sup>-3</sup> is the highest of the salts investigated herein and is comparable to the neutral compound  $(1.738 \text{ g cm}^{-3})$ .<sup>[25]</sup> The structure of the dianion is in agreement with those of 1 and 2.

Compounds 4 and 5 (Figures 6 and 7) crystallize in the monoclinic space groups  $P2_1/c$  (4) and  $P2_1/n$  (5) with two



Figure 6. Molecular unit of bis(guanidinium) 5,5'-bistetrazolate (4). Ellipsoids of non-hydrogen atoms are drawn at the 50% probability level. Symmetry codes: i: 2-x, -y, 2-z; ii: 1-x, -y, 2-z.

formula units per unit cell and densities of 1.586 gcm<sup>-3</sup> (**4**) and 1.568 gcm<sup>-3</sup> (**5**). Diaminoguanidinium salt dihydrate **6** (Figure 8) crystallizes in the triclinic space group  $P\bar{1}$  with a density of 1.520 gcm<sup>-3</sup>, which is the lowest density observed herein. Triaminoguanidinium salt **7** (Figure 9) crystallizes in the monoclinic space group  $P2_1/n$  and has a density of 1.535 gcm<sup>-3</sup>. Crystals of compound **8** were also obtained by recrystallization from water and measured by XRD. However, the refinement could not be finished due to a twinning problem along the *c* axis. The cell volume of 606.68 Å<sup>3</sup> was used to calculate a density of 1.742 gcm<sup>-3</sup>, which is equal to that observed for **3**. Of guanidines **4–7**, compounds **5** and **6** 



Figure 7. Molecular unit of bis(aminoguanidinium) 5,5'-bistetrazolate (5). Ellipsoids of non-hydrogen atoms are drawn at the 50% probability level. Symmetry code: i: 1-x, 1-y, 1-z.



Figure 8. Molecular unit of bis(diaminoguanidinium) 5,5'-bistetrazolate (6). Ellipsoids of non-hydrogen atoms are drawn at the 50% probability level. Symmetry codes: i: 1-x, 1-y, -z; ii: 1-x, 1-y, -z; iii: -x, 1-y, -z.



Figure 9. Molecular unit of bis(triaminoguanidinium) 5,5'-bistetrazolate (7). Ellipsoids of non-hydrogen atoms are drawn at the 50% probability level. Symmetry codes: i:2-x, -y, 1-z; ii:1.5-x, -0.5+y, 0.5-z; iii:2.5-x, 0.5+y, 0.5-z.

crystallized as dihydrates, whereas **4** and **7** were obtained as solvent-free crystals. The structures of the guanidines are in agreement with those observed for other guanidinium tetrazolates in the literature,<sup>[27]</sup> which participate strongly in many classical hydrogen bonds. Regarding the structure of the dianions, all compounds show planar geometries comparable to that discussed in detail for compound **1**.

**Spectroscopy**: All compounds described were investigated by using <sup>1</sup>H and <sup>13</sup>C NMR spectroscopy. Additionally a <sup>14</sup>N NMR spectrum was recorded for ammonium salt **1**. For better comparison all spectra (except for **1** and **7**) were measured in  $[D_6]DMSO$  as the solvent and all chemical shifts are given with respect to TMS (<sup>1</sup>H, <sup>13</sup>C).

Proton signals for the C-N $H_2$  protons of the guanidinium derivatives can be found at  $\delta = 7.73$  (4, 5) and 7.76 ppm (6). Due to the presence of both NH and  $NH_2$  groups in 5, 6, and 7, additional resonances at  $\delta = 4.63 - 4.77$  (NHNH<sub>2</sub>) and 9.61-9.65 ppm (NH) are observed. Due to the poor solubility of 1 and 7 in DMSO,  $D_2O$  was used instead and thus only one singlet is observed in both proton spectra due to fast proton exchange. Because of fast proton exchange in the protonated 1,3-diaminourunium cation of 8, only a broad signal at  $\delta = 7.22$  ppm is observed for all protons. The measured <sup>13</sup>C NMR spectra of all guanidine derivatives reveal a single resonance at  $\delta = 154.6 - 155.1$  ppm, which can be assigned to the bistetrazolate ring carbon atom. The guanidine carbon atom signal is found at  $\delta = 158.9 - 160.6$  ppm for 4, 5, and 6, but not for 7, the NMR spectrum of which was measured in D<sub>2</sub>O. The <sup>13</sup>C NMR spectrum of 8 reveals two single resonances at  $\delta = 150.1$  ppm for the bistetrazolate ring carbon and at  $\delta = 161.1$  ppm for the urea carbonyl group of the cation. Unfortunately no <sup>1</sup>H or <sup>13</sup>C NMR spectrum could be recorded for ammonium salt 1 in DMSO due to its low solubility in this solvent, however the spectra recorded in D<sub>2</sub>O show the expected signals. The <sup>14</sup>N NMR spectrum reveals a sharp singlet for the ammonium cation at  $\delta =$ -356 ppm and two singlets at  $\delta = -66$  and 3 ppm assigned to the two nonequivalent nitrogen atoms in the 5,5'-bistetrazolate anion. In the proton spectrum of the hydrazinium (2) and hydroxylammonium (3) salt, a singlet at  $\delta = 7.20$  (2) and 10.50 ppm (3) is observed, which nicely demonstrates the lower  $pK_a$  value of protonated hydroxylamine compared to the hydrazinium monocation, which is shown by the downfield shift in the spectrum of 3 compared to 2. The bistetrazole carbon atom signals are found at  $\delta\!=\!152.6$  (3) and 154.5 ppm (2), respectively, which is the same region as observed for the guanidinium derivatives.

IR and Raman spectroscopy were used for the identification of structural elements and functional groups in all compounds. Absorptions were assigned according to values reported in the literature.<sup>[28,29]</sup> The characteristic vibrations of the bistetrazole system were observed in all IR spectra, including the bistetrazole framework vibrations at 1011 to 1184 cm<sup>-1</sup>, the asymmetric and symmetric stretching vibrations of the N1-C1-N4 fragment<sup>[30]</sup> in the range of 1299 to 1335 cm<sup>-1</sup> and the stretching vibration of the cyclic C=N bond at 1650 to 1890 cm<sup>-1</sup>. The latter is in the same range as the C=N stretching vibration of the guanidine derivatives. Due to the presence of amino groups, N-H and NH<sub>2</sub> wagging absorptions can be observed between 603 and 781 cm<sup>-1</sup> and the corresponding bending vibrations appear in the range of 1536 to 1614 cm<sup>-1</sup>. In compound **8**, N–H and NH<sub>2</sub> bending vibrations are in the same range as the C=O stretching vibration of 1,3-diaminourea. N-H stretching vibrations are partly shifted to lower frequencies by H-bonding effects, and can be found between 3092 and  $3470 \text{ cm}^{-1}$ . In the spectra of 4, 5, and 8, two well-defined sharp characteristic absorptions due to the asymmetric and symmetric N-H stretching vibrations of the primary amino groups appear at 3350 to  $3449 \text{ cm}^{-1}$  (4), 3345 to  $3409 \text{ cm}^{-1}$  (5), and 3185 to 3296  $\text{cm}^{-1}$  (8). All Raman spectra show the characteristic and very intense signal of the 5,5'-bistetrazole C-C bond at 1582 to 1591 cm<sup>-1</sup>, which has a partial double-bond character, as can be seen from the bond lengths discussed above in the X-ray crystallography section, and very weak N-H vibrations at 3166 to 3429 cm<sup>-1</sup>. However, bistetrazole framework vibrations are visible in all Raman spectra in the range of 1013 to 1207 cm<sup>-1</sup>. The measured IR and Raman spectra correspond very well and verify the structural elements in all investigated compounds.

Sensitivities and thermal behavior: The impact sensitivity tests were carried out according to STANAG 4489<sup>[31]</sup> modified instructions<sup>[32]</sup> by using a BAM (Bundesanstalt für Materialforschung) drop hammer.<sup>[33]</sup> The friction sensitivity tests were carried out according to STANAG 4487<sup>[34]</sup> modified instructions<sup>[35]</sup> by using the BAM friction tester. The classification of the tested compounds results from the "UN Recommendations on the Transport of Dangerous Goods".[36] All compounds were tested for sensitivity towards electrical discharge by using the Electric Spark Tester ESD 2010 EN.<sup>[37]</sup> Generally, all investigated materials showed surprisingly low sensitivities towards both impact and friction despite their high nitrogen contents. Compounds 1, 2, 4, 5, and 8 are classified as less sensitive towards impact (2, 4, 5: 40 J; 1, 8: 35 J), whereas 3, 6, and 7 are classified as sensitive (3: 10 J; 6: 30 J; 7: 15 J). As expected, the hydroxylammonium and the triaminoguanidinium salt are the most sensitive towards impact, which is partly due to the low carbon content of the cation and, therefore, the highest nitrogen content for the ionic compounds, and partly due to the fact that both species crystallize without the inclusion of crystal water. This trend is also observed for the friction sensitivity. The hydroxylammonium (3: 240 N), the aminoguanidinium (5: 324 N), and the triaminoguanidinium (7: 285 N) salts are classified as sensitive towards friction, whereas 2, 6, and 8 are less sensitive (2, 6, 8: 360 N). The ammonium and the guanidinium salts did not show any response and are, therefore, classified as insensitive (1,4:>360 N). The inclusion of water, as in the case of 5 and 6, usually also plays a role, but because the materials are comparatively insensitive no obvious trend for the desensitization of 5 and 6 was observed. The sensitivity towards electrostatic discharge for most of the substances is low, with values between 0.50 for **8** and 1.0 J for **4** and **5**. However, the hydrazinium (**2**: 0.23 J) and the hydroxylammonium (**3**: 0.10 J) salts do not follow this trend. The observed results of the impact sensitivity testing are comparable to the results observed by Hiskey et al. They also determined the impact sensitivities of the diammonium, the dihydrazinium, and the dihydroxylammonium salt by using a different method, and stated that those fuels are fairly insensitive when not mixed with an oxidizer, such as ammonium perchlorate.<sup>[7]</sup>

Differential scanning calorimetry (DSC) measurements to determine the melting and decomposition temperatures of 1-8 (about 1.5 mg of each energetic material) were performed in covered Al-containers with a hole (0.1 mm) in the lid for gas release and a nitrogen flow of 20 mLmin<sup>-1</sup> on a Linseis PT 10 DSC<sup>[38]</sup> calibrated by standard pure indium and zinc at a heating rate of 5°C min<sup>-1</sup>. The decomposition temperatures are given as absolute onset temperatures. It is very remarkable that despite their very high nitrogen content, except for 2 and 8, none of the compounds show any decomposition at temperatures below 200°C. Even the hydroxylammonium (3) and triaminoguanidinium salts (7) decompose at temperatures of 205 (3) and 207 °C (7), which is in the same range as observed for RDX (hexogen), whereas the ammonium (1) and guanidinium salts (4) reach decomposition temperatures as high as 312 (1) and 316°C (4), which is comparable to the melting- and decomposition point of HNS (hexanitrostilbene, a highly thermally stable explosive). The remaining compounds fill the range between these extreme values, with the lowest temperature being recorded for 6 (208°C) up to 234 and 237°C for 2 and 8 and 251 °C for 5. The ammonium (1), hydroxylammonium (3), and triaminoguanidinium salts (7) do not show any endothermic steps in their DSC curve before decomposition, whereas the guanidinium (4), aminoguanidinium (5), and diaminoguanidinium salts (6) melt directly before they decompose, as indicated by endothermic steps observed prior to their exothemic decomposition peaks. Two salts, namely, the hydrazinium (2) and the diaminouronium salts (8), show one or more endothermic peaks in their respective DSC curves at 165, 185, and 217°C (2), and at 175°C (8). These observations are in accordance with results published by Hiskey et al.,<sup>[7]</sup> who found that the dihydrazinium salt loses

Table 3. Solid-state energies of formation  $(\Delta_f U^{\circ})$ 

hydrazine at temperatures starting from 130 °C in a thermogravimetric analysis experiment. The lower temperature compared to 165 °C as observed in our case can be explained by the lower heating rate used by Hiskey et al.  $(0.1 °Cmin^{-1})$ . The same could be true for the diaminouronium salt because the cation in **8** is also a hydrazine derivative, however, a thermogravimetrical analysis would be necessary to support this assumption.

#### **Theoretical calculations**

*Heats of formation*: Usually energetic materials tend to explode in bomb calorimetric measurements and consequently doubtful combustion energies are obtained. Therefore, the heats of formation of energetic materials are mostly calculated theoretically. In our group, we combine the atomization energy method [Eq. (1)] with CBS-4M electronic energies are approximately of the second seco

Table 2. CBS-4M results and gas-phase enthalpies.

	Formula	$-H^{298}$ [a.u.]	$\Delta_{\rm f} H({\rm g})  [{\rm kJ}  {\rm mol}^{-1}]$
$BT^{2-}$	$C_2 N_8^{2-}$	513.511502	596.7
$NH_4$ +	$NH_4$ +	56.796608	635.8
$N_2H_5$ +	$N_{2}H_{5}^{+}$	112.030523	774.1
Hx+	$H_4NO^+$	131.863229	687.2
G+	CH <sub>6</sub> N <sub>3</sub> +	205.453192	571.9
AG+	$CH_7N_4$ +	260.701802	671.6
DAG+	CH <sub>8</sub> N <sub>5</sub> +	315.949896	772.7
TAG+	$CH_9N_6^+$	371.197775	874.3
DAU+	$\rm CH_7N_4O^+$	335.795706	651.3

gies (Table 2), which has been shown to be suitable in many recently published studies.<sup>[39]</sup> CBS-4M energies of the atoms, cations, and anions were calculated by using the Gaussian 09 (revision A1) software package<sup>[42]</sup> and checked for imaginary frequencies. Values for  $\Delta_{\rm f} H^{\circ}$  (atoms) were taken from the NIST database.<sup>[43]</sup>

$$\Delta_{\rm f} H^{\circ}_{({\rm g},{\rm M},298)} = H_{({\rm M},298)} - \sum H^{\circ}_{({\rm Atoms},298)} + \sum \Delta_{\rm f} H^{\circ}_{({\rm Atoms},298)} \quad (1)$$

For calculation of the solid-state energy of formation (Table 3) of **4–8**, the lattice energy  $(U_L)$  and lattice enthalpy  $(\Delta H_L)$  were calculated from the corresponding molecular volumes (obtained from X-ray elucidations) according to

		8		)-						
	Formula	$\Delta_{\rm f} H^{\rm o}({ m g})$ [kJ mol <sup>-1</sup> ]	V <sub>M</sub> [nm <sup>3</sup> ]	$U_{\rm L}$ [kJ mol <sup>-1</sup> ]	$\frac{\Delta H_{\rm L}}{[\rm kJmol^{-1}]}$	$\Delta_{\rm f} H^{\circ}({ m s})$ [kJ mol <sup>-1</sup> ]	$\Delta n$	$\Delta_{\rm f} U^{\circ}({ m s})$ [kJ mol <sup>-1</sup> ]	M [g mol <sup>-1</sup> ]	$\Delta_{\rm f} U^{\rm o}({ m s})$ [kJ kg <sup>-1</sup> ]
1	$C_2H_8N_{10}$	1868.3	0.180	1578.4	1589.3	279.0	9	301.4	172.18	1750.0
2	$C_2 H_{10} N_{12}$	2144.9	0.219	1465.9	1476.9	668.1	11	695.3	202.18	3438.2
3	$C_2 H_8 N_{10} O_2$	1971.1	0.195	1532.7	1543.6	427.5	10	452.3	204.18	2215.0
4	$C_4H_{12}N_{14}$	1740.5	0.268	1358.8	1369.7	370.8	13	403.0	256.28	1572.5
5	$C_4 H_{18} N_{16} O_2$	1459.2 <sup>[a]</sup>	0.291	1317.2	1328.1	131.1	18	175.7	322.34	545.1
6	$C_4 H_{20} N_{18} O_2$	1661.3 <sup>[a]</sup>	0.335	1249.2	1260.2	401.2	20	450.8	352.38	1279.1
7	$C_4 H_{18} N_{20}$	2345.2	0.374	1196.9	1207.8	1137.4	19	1184.5	346.38	3419.2
8	$C_4 H_{14} N_{16} O_2$	1899.3	0.300	1302.8	1313.7	585.6	16	625.3	318.34	1964.2

[a] Value has been corrected  $(-483.4 \text{ kJ mol}^{-1})$  due to dihydrate formation.

Chem. Eur. J. 2012, 18, 4051-4062

© 2012 Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim

A EUROPEAN JOURNAL

Table 4. Composition of the calculated gun propellant charges.

Formulation	Components	Ratio [wt %]
M1	NC (13.25)/2,4-DNT <sup>[a]</sup> /DBP <sup>[b]</sup> /DPA <sup>[c]</sup>	86/10/3/1
EX-99	RDX/CAB <sup>[d]</sup> /BDNPA/F <sup>[e]</sup> /NC (13.25)	76/12/8/4
HN-1	RDX/TAGzT/CAB <sup>[d]</sup> /BDNPA/F <sup>[e]</sup> /NC	56/20/12/8/4
	(13.25)	
HN-2	RDX/TAGzT/FOX-12 <sup>[f]</sup> /CAB <sup>[d]</sup> /BDNPA/F <sup>[e]</sup> /	40/20/16/12/
	NC (13.25)	8/4
HN-1 <b>·1</b> –4;	RDX/1-4; 7; 8/CAB <sup>[d]</sup> /BDNPA/F <sup>[e]</sup> /NC	56/20/12/8/4
7; 8	(13.25)	
HN-2 <b>·1</b> –4;	RDX/1-4; 7; 8/FOX-12 <sup>[f]</sup> /CAB <sup>[d]</sup> /BDNPA/	40/20/16/12/
7; 8	F <sup>[e]</sup> /NC (13.25)	8/4

[a] 2,4-Dinitrotoluene. [b] Dibutyl phthalate. [c] Diphenyl amine. [d] Cellulose acetate butyrate. [e] 1:1 mixture of bis(2,2-dinitroprop-1-yl)acetal and -formal. [f] 1,1-Dinitro-2,2-diaminoethylene.

the equations provided by Jenkins et al.<sup>[42]</sup> With the calculated lattice enthalpy (Table 3), the gas-phase enthalpy of formation was converted into the solid-state (standard conditions) enthalpy of formation. These molar standard enthalpies of formation ( $\Delta H_{\rm m}$ ) were used to calculate the molar solid-state energies of formation ( $\Delta U_{\rm m}$ , see Table 4) according to Equation (2):

$$\Delta U_{\rm m} = \Delta H_{\rm m} - \Delta n R T \tag{2}$$

in which  $\Delta n$  is the change in moles of gaseous components.

Gun propellant evaluations: The most important parameters for gun propellant formulations are the specific energy  $f_{\rm E}$ ([Jg<sup>-1</sup>],  $f_{\rm E} = nRT_{\rm c}$ ), the combustion temperature  $T_{\rm c}$  [K], the co-volume  $b_{\rm E}$  [cm<sup>3</sup>g<sup>-1</sup>], and the pressure  $p_{\rm max}$  ([bar], 3000– 4000 bar) while assuming isochoric combustion. These parameters and furthermore the N<sub>2</sub>/CO ratio can be calculated with the program package EXPLO5 (v. 5.04),<sup>[43]</sup> with an error of usually less than 5% (loading densities ca. 0.2 g cm<sup>-3</sup>) when the maximum pressure, the specific energy, and the co-volume are considered.

Table 4 contains the compositions of the calculated gun propellant charges. M1 is a typical single-base propellant based on nitrocellulose (NC), used for large caliber artillery guns.<sup>[44]</sup> The drawbacks of this formulation are the relatively low performance and the toxicity of almost all ingredients.<sup>[45]</sup> EX-99 is a typical formulation for large naval guns and contains high amounts of the highly energetic RDX.<sup>[46]</sup> The formulations herein referred to as High-Nitrogen 1 and 2 (HN-1 and HN-2, respectively) are two erosion-reduced formulations derived from EX-99, which contain the nitrogen-rich compound bis(triaminoguanidinium) 5,5'-azobistetrazolate (TAGzT, 82% nitrogen). Synthesized compounds 1-8 (except for 5 and 6 due to the formation of hydrates) were calculated in formulations based on HN-1 and HN-2, in which they replace the TAGzT. The heats of formation were either taken from the EXPLO5 database, from the literature (BDNPA/F),<sup>[47]</sup> or calculated in this study.

The combustion parameters of the formulations were calculated assuming isochoric conditions by using the virial

Table 5. Calculated	performance of the	gun propellant	charges
---------------------	--------------------	----------------	---------

	$T_{\rm c}  [{ m K}]$	$p_{\rm max}$ [bar]	$f_{\rm E}  [{\rm kJ}  {\rm g}^{-1}]$	$b_{\rm E}  [{\rm cm}^3 {\rm g}^{-1}]$	N <sub>2</sub> /CO [w/w]
M1	2834	2591	1.005	1.125	0.23
EX-99	3406	3249	1.257	1.129	0.71
HN-1	2922	3042	1.161	1.185	0.95
HN-2	2735	2848	1.088	1.181	1.05
<b>1</b> HN-1	2798	2890	1.103	1.181	0.95
1 HN-2	2610	2691	1.030	1.174	1.06
<b>2</b> HN-1	2975	3109	1.186	1.187	0.96
<b>2</b> HN-2	2783	2910	1.111	1.183	1.06
<b>3</b> HN-1	3130	3157	1.211	1.164	0.87
3 HN-2	2928	2964	1.138	1.163	0.96
<b>4</b> HN-1	2737	2830	1.080	1.183	0.90
4 HN-2	2556	2635	1.008	1.175	1.01
7 HN-1	2942	3091	1.178	1.190	0.93
7 HN-2	2756	2896	1.105	1.185	1.03
8 HN-1	2960	3037	1.161	1.176	0.87
8 HN-2	2770	2845	1.089	1.172	0.96

equation of state with a loading density of  $0.2 \text{ g cm}^{-3}$ ; the results are compiled in Table 5.

As expected from the ingredients, the M1 and EX-99 formulations have the worst N2/CO ratios, but EX-99 also has the highest performance. The formulations based on HN-1 have generally higher performance than those based on HN-2, due to the higher content of RDX, but also have higher combustion temperatures  $(T_c)$  and N<sub>2</sub>/CO ratios that are lower by about 0.1. The most promising compound is the hydrazinium salt 2, which outperforms HN-2 itself, with an  $f_{\rm E}$  of 1.111 kJ g<sup>-1</sup>, a  $p_{\rm max}$  of 2910 bar, and, together with 1, the best  $N_2$ /CO ratio of 1.06. The  $T_c$  value of 2783 K is comparable to the triaminoguanidinium-based formulations HN-2 ( $T_c = 2735$  K) and **7** HN-2 ( $T_c = 2756$  K). Guanidinium salt formulation 4 HN-2 has the lowest  $T_c$  value of 2556 K, but also the lowest general performance. Figure 10 illustrates the calculated performances of M1, EX-99, HN-2, and the HN-2 analogues of 1, 2, 4, and 7. As expected, the formulations with 3 and 8 show the worst  $N_2/CO$  ratios due to the higher oxygen content at the expense of the nitrogen content. Additionally, compound 3 has the highest specific energy in both HN-1 and HN-2 formulations, outperforming the original formulations.

Detonation parameters and specific impulse: Although compounds 1–8 show promise as alternative additives in gun propellants, they nevertheless detonate when stimulated by using a primary explosive in combination with a booster charge. All compounds show better detonation behavior than TNT (trinitrotoluene), compound 3 is even better than RDX (hexogen). Table 6 shows the detonation values of 1–8 calculated by using the EXPLO5.04 software, the heats of formation, and X-ray densities. In addition, the specific impulse of the pure compounds when used as monopropellants was calculated assuming rocket propellant conditions (isobaric combustion with a chamber pressure of 60 bar).



Figure 10. Comparison of the calculated performances of M1, EX-99, HN-2, **2** HN-2, **3** HN-2 and **7** HN-2. For each formulation, column 1:  $T_c$  [K], column 2:  $p_{max}$  [bar], column 3:  $f_E$  [J g<sup>-1</sup>], column 4: N<sub>2</sub>/CO/0.001.

Table 6. Calculated specific impulses, nitrogen contents, oxygen balances, and detonation parameters of **1–8**.

	$I_{\rm sp} \\ [{\rm s}^{-1}]^{[{\rm a}]}$	N [%] <sup>[b]</sup>	$\Omega$ $[\%]^{[c]}$	$ ho [gcm^{-3}]^{[d]}$	$-\Delta_{\rm E} U^{\circ}$ [kJ kg <sup>-1</sup> ] <sup>[e]</sup>	$T_{\rm E}$ [K] <sup>[f]</sup>	p <sub>C-J</sub> [kbar] <sup>[g]</sup>	$V_{\text{Det.}} = [m  \text{s}^{-1}]^{[h]}$	V <sub>0</sub> [L kg <sup>-1</sup> ] <sup>[i]</sup>
1	172.3	81.36	-74.34	1.590	2415	1976	189	7417	826
2	225.2	83.13	-71.21	1.531	4126	2744	236	8265	853
3	227.9	68.61	-47.02	1.742	4829	3243	317	8854	843
4	165.8	76.53	-87.41	1.586	2239	1869	176	7199	790
5	174.6	69.54	-74.46	1.568	2656	2049	193	7504	859
6	190.1	71.56	-72.65	1.520	3284	2320	205	7711	872
7	224.1	80.89	-78.53	1.535	4129	2698	238	8181	846
8	204.8	70.42	-65.35	1.742	3893	2676	288	8562	824

[a] Specific impulse. [b] Nitrogen content. [c] Oxygen balance.<sup>[48]</sup> [d] Density calculated from X-ray structure. [e] Energy of explosion. [f] Explosion temperature. [g] Detonation pressure. [h] Detonation velocity. [i] Volume of detonation gases.

#### Conclusion

From this combined theoretical and experimental study, several conclusions can be drawn. Deprotonation of 5,5'-bistetrazole with nitrogen-rich bases leads to a variety of compounds, namely, the diammonium salt (1), the dihydrazinium salt (2), the di(hydroxylammonium) salt (3), the bis(guanidinium) salt (4), the bis(aminoguanidinium) salt (5), the bis(diaminoguanidinium) salt (6), the bis(triaminoguanidinium) salt (7), and the bis(diaminouronium) salt (8), which were prepared in high yields and good purity. Only the double-deprotonated 5,5'-bistetrazolates could be isolated even when using stoichiometric amounts (1.0 equiv) of the

## FULL PAPER

corresponding bases. The crystal structures of 1-7 were determined by low-temperature single-crystal X-ray diffraction. The compounds crystallize in the space groups  $P\bar{1}$  (2, 3, 6), C2/m (1),  $P2_1/c$  (4), and  $P2_1/n$ (5, 7) with densities between 1.520 (for the bis(aminoguanidinium) salt dihydrate) and  $1.742 \text{ g cm}^{-3}$  (for the di(hydroxylammonium) salt). Additionally, all compounds were fully characterized by using vibrational spectroscopy (IR and Raman), <sup>1</sup>H and <sup>13</sup>C NMR spectroscopy, mass spectrometry, and elemental analysis. The thermal stabilities of 1-8 were investigated by DSC. All compounds decompose at temperatures higher than 200°C, with the guanidinium salt being the most thermally stable salt (316°C).

The sensitivity of compounds **1–8** towards friction, impact, and electrostatic discharge were investigated by BAM methods.

Compounds 1–8 were found to have impact sensitivities between 10 (3, sensitive) and 40 J (2, 4, 5, less sensitive), friction sensitivities of between 240 (3, sensitive) and > 360 N (1, 4, insensitive), and ESD sensitivities of between 0.1 (3) and 1.0 J (4, 5). Therefore, the hydroxylammonium salt 3 is the most sensitive, whereas the guanidinium salt 4 is the least sensitive compound. However, all materials are less sensitive than commonly used high explosives, such as RDX.

By using calculated heats of formation and loading densities of  $0.2 \text{ g cm}^{-3}$ , the isochoric combustion parameters (specific energy, combustion temperature, pressure, co-volume, and N<sub>2</sub>/CO ratios) for formulations of **1–4**, **7**, and **8** were calculated with

the EPXLO5 program and compared to common formulations found in the literature. The most promising compound for gun propellant formulations is **2**, which has a specific energy of  $1.111 \text{ kJ g}^{-1}$ , a pressure of 2910 bar, a combustion temperature of 2783 K, and an N<sub>2</sub>/CO ratio of 1.06. Formulations with **1**, **3**, **4**, **7**, and **8** are similar in performance to formulations reported in the literature.

#### **Experimental Section**

Caution! 5,5'-Bistetrazole and its salts are energetic materials with increased sensitivities towards shock and friction. Therefore, proper safety

precautions (safety glass, face shield, earthed equipment and shoes, Kevlar gloves, and ear plugs) have to be applied while synthesizing and handling the described compounds.

All chemicals and solvents were employed as received (Sigma-Aldrich, Fluka, Acros). <sup>1</sup>H and <sup>13</sup>C NMR spectra were recorded by using a JEOL Eclipse 270, JEOL EX 400 or a JEOL Eclipse 400 instrument. The chemical shifts are quoted in ppm and refer to typical standards, such as tetramethylsilane (<sup>1</sup>H, <sup>13</sup>C) and nitromethane (<sup>14</sup>N). To determine the melting and decomposition temperatures of the described compounds, a Linseis PT 10 DSC instrument (heating rate 5°Cmin<sup>-1</sup>) was used. Infrared spectra were measured as KBr pellets by using a Perkin-Elmer Spectrum One FT-IR spectrometer. Raman spectra were recorded by using a Bruker MultiRAM Raman Sample Compartment D418 equipped with a Nd-YAG laser ( $\lambda = 1064$  nm) and a LN-Ge diode as the detector. Mass spectra of the described compounds were measured by using a JEOL MStation JMS 700 spectrometer and the FAB technique. To record elemental analyses, a Netsch STA 429 simultaneous thermal analyzer was used. 5,5'-Bistetrazole was synthesized according to a literature procedure.[7]

Diammonium 5,5'-bistetrazolate (1): 5,5'-Bistetrazole (5.52 g, 40.0 mmol) was dissolved in warm water (20 mL) and aqueous half-concentrated ammonia (100 mL) was added. Water was added to the reaction mixture, which was heated to reflux, until a clear solution was obtained (40 mL). After heating to reflux for 20 min, the reaction mixture was cooled to RT and then stored for 20 h at 4°C. The precipitate was filtered off, washed with a small amount of water and plentiful ethanol, and dried in medium vacuum to give the title compound as colorless needles (yield: 5.25 g, 30.5 mmol, 76%). DSC (5°Cmin<sup>-1</sup>): 312°C (decomp.); <sup>1</sup>H NMR (D<sub>2</sub>O, 60°C):  $\delta = 4.80$  ppm (s, NH<sub>4</sub><sup>+</sup>, H<sub>2</sub>O); <sup>13</sup>C NMR ([D<sub>6</sub>]DMSO, 25°C):  $\delta =$ 155.2 ppm (N<sub>4</sub>C-CN<sub>4</sub>); <sup>14</sup>N NMR ([D<sub>6</sub>]DMSO, 25 °C):  $\delta = -356$  (NH<sub>4</sub><sup>+</sup>), -66 (CN<sub>4</sub>), 3 ppm (CN<sub>4</sub>); IR (ATR):  $\tilde{\nu} = 3170$  (w), 2984 (w), 2875 (w), 2360 (w), 2341 (w), 2140 (w), 1880 (w), 1722 (w), 1692 (m), 1680 (m), 1432 (s), 1327 (s), 1302 (s), 1184 (s), 1147 (s), 1084 (m), 1051 (m), 1016 (s), 732 cm<sup>-1</sup> (w); Raman (1064 nm, 250 mW, 25 °C):  $\tilde{\nu} = 3005$  (8), 1588 (100), 1568 (9), 1208 (22), 1144 (8), 1116 (33), 1109 (8), 1074 (26), 784 cm<sup>-1</sup> (5); MS (FAB<sup>+</sup>): m/z: 18.0 [NH<sub>4</sub><sup>+</sup>]; MS (FAB<sup>-</sup>): m/z: 137.0 [C<sub>2</sub>HN<sub>8</sub><sup>-</sup>]; elemental analysis calcd (%) for C<sub>2</sub>H<sub>8</sub>N<sub>10</sub>O (172.15): C 13.95, H 4.68, N 81.36; found: C 14.36, H 4.46, N 81.36; BAM drophammer: 35 J; friction tester: >360 N; ESD: 0.60 J (at grain size 500-1000 µm).

Dihydrazinium 5,5'-bistetrazolate (2): 5,5'-Bistetrazole (2.76 g. 20.0 mmol) was suspended in warm water (5 mL) and hydrazine hydrate (5.01 g, 100 mmol, 5.00 equiv) was added. The reaction mixture was heated to reflux for 20 min, then cooled to RT and stored at  $4\,^{o}\!\mathrm{C}$  for 5 h. The resulting precipitate was filtered off and washed with a small amount of water, ethanol, and diethyl ether to give the title compound as colorless, fine needles (yield: 0.50 g, 2.47 mmol, 12%). DSC (5°Cmin<sup>-1</sup>): 234°C (decomp.); <sup>1</sup>H NMR ([D<sub>6</sub>]DMSO, 25°C):  $\delta = 7.20$  ppm (brs,  $NH_2NH_3^+$ ); <sup>13</sup>C NMR ([D<sub>6</sub>]DMSO, 25 °C):  $\delta = 154.5$  ppm (N<sub>4</sub>C-CN<sub>4</sub>); IR (ATR):  $\tilde{\nu} = 3235$  (m), 3142 (m), 2883 (m, br), 2574 (s, br), 2350 (m), 2248 (m, br), 1613 (m, br), 1549 (m), 1529 (m), 1328 (s), 1306 (m), 1185 (m), 1167 (m), 1120 (vs), 1079 (s), 1051 (s), 1019 (s), 968 (vs), 728 cm<sup>-1</sup> (m); Raman (1064 nm, 250 mW, 25 °C):  $\tilde{\nu} = 3151$  (6), 1586 (100), 1563 (10), 1210 (16), 1141 (8), 1113 (27), 1078 (18), 971 (11), 782 cm<sup>-1</sup> (6); MS (FAB<sup>+</sup>): *m*/*z*: 33.0 [N<sub>2</sub>H<sub>5</sub><sup>+</sup>]; MS (FAB<sup>-</sup>): *m*/*z*: 137.0 [C<sub>2</sub>HN<sub>8</sub><sup>-</sup>]; elemental analysis calcd (%) for  $C_2H_{10}N_{12}$  (202.18): C 11.88, H 4.99, N 81.13; found: C 12.30, H 4.62, N 81.15; BAM drophammer: 40 J; friction tester: 360 N; ESD: 0.23 J (at grain size 100-500 µm).

**Dihydroxylammonium 5,5'-bistetrazolate (3)**: 5,5'-Bistetrazole (1.38 g, 10 mmol) was dissolved in hot water (20 mL). A solution of hydroxylamine (50 % w/w in H<sub>2</sub>O, 1.32 g, 20 mmol, 2.00 equiv) was added slowly and the resulting clear solution was evaporated under vacuum. The colorless solid residue was recrystallized from ethanol/water to give **3** as colorless, fine needles suitable for X-ray crystallography (yield: 1.79 g, 8.8 mmol, 88%). Alternatively, single crystals could be obtained by slow evaporation of the mother liquor. DSC (5°Cmin<sup>-1</sup>): 205°C (decomp.); <sup>1</sup>H NMR ([D<sub>6</sub>]DMSO, 25°C):  $\delta$ =10.50 ppm (s, 8H; NH<sub>3</sub>OH); <sup>13</sup>C NMR ([D<sub>6</sub>]DMSO, 25°C):  $\delta$ =152.6 ppm (N<sub>4</sub>C-CN<sub>4</sub>); IR (KBr):  $\tilde{\nu}$ =3425 (m), 3030 (vs), 2815 (s), 2744 (s), 2203 (m), 2056 (m), 1987 (m), 1626 (m), 1534 (m), 1385 (w), 1339 (m), 1314 (m), 1247 (s), 1184 (m), 1145 (m), 1095 (w), 1056 (m), 1030 (m), 1000 (m), 769 (m), 725 cm<sup>-1</sup> (m); Raman (1064 nm, 350 mW, 25 °C):  $\tilde{\nu}$ =2958 (1), 2752 (1), 1591 (100), 1436 (2), 1251 (1), 1205 (17), 1144 (9), 1224 (34), 1093 (17), 1002 (22), 779 (3), 426 (5), 387 cm<sup>-1</sup> (8); MS (FAB<sup>+</sup>): *m*/*z*: 34.0 [NH<sub>3</sub>OH<sup>+</sup>]; MS (FAB<sup>-</sup>): *m*/*z*: 137.0 [C<sub>2</sub>HN<sub>8</sub><sup>-</sup>]; elemental analysis calcd (%) for C<sub>2</sub>H<sub>8</sub>N<sub>10</sub>O<sub>2</sub> (204.15): C 11.77, H 3.95, N 68.61; found: C 12.25, H 3.74, N 68.01; BAM drophammer: 10 J; friction tester: 240 N (neg.); ESD: 0.10 J (at grain size 100– 500 um).

Bis(guanidinium) 5,5'-bistetrazolate (4): A solution of guanidine carbonate (1.80 g, 9.99 mmol, 1.00 equiv) in  $H_2O$  (10 mL) was added to a solution of 5,5'-bistetrazole (1.38 g, 9.99 mmol, 1.00 equiv) in H<sub>2</sub>O (15 mL). The resulting solution was heated until all solids were dissolved, then filtered. Slow evaporation of the solvent gave colorless crystals of compound 4 that were suitable for X-ray diffraction (yield: 1.88 g, 7.34 mmol, 73%). DSC (5°Cmin<sup>-1</sup>): 316 (m.p.), 319°C (decomp.); <sup>1</sup>H NMR ([D<sub>6</sub>]DMSO, 25 °C):  $\delta$  = 7.73 ppm (s, 6H; NH<sub>2</sub>); <sup>13</sup>C NMR ([D<sub>6</sub>]DMSO, 25°C):  $\delta = 158.9$  (C(NH<sub>2</sub>)<sub>3</sub>), 154.9 ppm (N<sub>4</sub>C-CN<sub>4</sub>); IR (KBr):  $\tilde{\nu} = 3449$ (vs), 3350 (s), 3092 (s), 2194 (w), 1707 (m), 1650 (vs), 1584 (m), 1384 (m), 1327 (m), 1308 (m), 1183 (m), 1142 (m), 1088 (w), 1044 (w), 1017 (w), 726 (w), 603 (m), 543 cm<sup>-1</sup> (m); Raman (1064 nm, 300 mW, 25 °C):  $\tilde{\nu} =$ 3177 (2), 1592 (100), 1563 (3), 1207 (7), 1139 (4), 1123 (20), 1073 (26), 1014 (50), 780 (4), 542 (20), 483 (3), 421 (4), 382 (7), 167 (13), 156 (5), 131 (5), 115 (68), 107 (12), 70 cm<sup>-1</sup> (6); MS (FAB<sup>+</sup>): m/z: 60.1 [CH<sub>6</sub>N<sub>3</sub><sup>+</sup>]; MS (FAB<sup>-</sup>): m/z: 137.0 [C<sub>2</sub>HN<sub>8</sub><sup>-</sup>]; elemental analysis calcd (%) for C4H12N14 (256.23): C 18.75, H 4.72, N 76.53; found: C 19.06, H 4.46, N 75.24; BAM drophammer: 40 J; friction tester: > 360 N; ESD: 1.0 J (at grain size 100-500 μm).

Bis(aminoguanidinium) 5,5'-bistetrazolate dihydrate (5): A suspension of aminoguanidine bicarbonate (2.73 g, 20.1 mmol, 2.00 equiv) in H<sub>2</sub>O (30 mL) was added to a solution of 5,5'-bistetrazole (1.38 g, 9.99 mmol, 1.00 equiv) in H<sub>2</sub>O (15 mL). The resulting suspension was diluted with  $\mathrm{H_{2}O}$  (45 mL) and heated to reflux until all solids were dissolved. Slow evaporation of the solvent gave colorless crystals of compound 5 that were suitable for X-ray diffraction (yield: 1.72 g, 6.01 mmol, 60%). DSC (5°Cmin<sup>-1</sup>): 247 (m.p.), 251°C (decomp.); <sup>1</sup>H NMR ([D<sub>6</sub>]DMSO, 25°C):  $\delta = 9.65$  (brs, 1H; NH), 7.73 (brs, 4H; C-(NH<sub>2</sub>)<sub>2</sub>) 4.73 ppm (s, 2H;  $\delta = 159.7$  $NHNH_2$ ; <sup>13</sup>C NMR ([D<sub>6</sub>]DMSO, 25°C): (C- $(NHNH_2)(NH)NH_2)$ , 155.1 ppm  $(N_4C-CN_4)$ ; IR (KBr):  $\tilde{v} = 3409$  (vs), 3345 (vs), 3162 (vs), 2994 (s), 2891 (s), 2175 (w), 1690 (vs), 1668 (vs), 1553 (w), 1463 (m), 1384 (w), 1327 (s), 1299 (m), 1223 (w), 1169 (m), 1145 (m), 1079 (w), 1042 (w), 1015 (m), 983 (m), 957 (m), 758 (w), 728 (w), 687 (m), 607 (m), 511 (w), 463 cm<sup>-1</sup> (w); Raman (1064 nm, 300 mW, 25°C):  $\tilde{\nu}$ =3347 (2), 3279 (5), 3166 (1), 1670 (3), 1587 (100), 1564 (10), 1423 (2), 1194 (8), 1142 (5), 1108 (32), 1073 (19), 973 (11), 783 (4), 626 (3), 512 (7), 480 (1), 424 (9), 394 (6), 329 (2), 133 (39), 100 (7), 70 cm<sup>-1</sup> (13); MS (FAB<sup>+</sup>): m/z: 75.0 [CH<sub>7</sub>N<sub>4</sub><sup>+</sup>]; MS (FAB<sup>-</sup>): m/z: 136.9  $[C_2HN_8^-]$ ; elemental analysis calcd (%) for  $C_4H_{18}N_{16}O_2$  (322.29): C 14.91, H 5.63, N 69.54; found: C 15.21, H 5.56, N 69.42; BAM drophammer: 40 J; friction tester: 324 N; ESD: 1.0 J (at grain size 500-1000 µm).

Bis(diaminoguanidinium) 5,5'-bistetrazolate dihydrate (6): A solution of bis(diaminoguanidinium) sulfate (1.26 g, 4.56 mmol, 1.00 equiv) in H<sub>2</sub>O (10 mL) was added to a solution of barium 5,5'-bistetrazolate tetrahydrate (1.58 g, 4.57 mmol, 1.00 equiv) in H<sub>2</sub>O (40 mL). Filtration and slow evaporation of the solvent gave colorless crystals of compound  ${\bf 6}$  that were suitable for X-ray diffraction (yield: 1.23 g, 3.49 mmol, 77 %). DSC  $(5^{\circ}C min^{-1})$ : 97 (H<sub>2</sub>O), 204 (m.p.), 208°C (decomp.); <sup>1</sup>H NMR  $([D_6]DMSO, 25^{\circ}C): \delta = 9.61$  (brs 2H; NH), 7.64 (s, 2H; C-NH<sub>2</sub>), 4.63 ppm (s, 4H; NHNH<sub>2</sub>); <sup>13</sup>C NMR ([D<sub>6</sub>]DMSO, 25 °C):  $\delta$  = 160.6 (C- $(NHNH_2)_2NH_2)$ , 155.1 ppm  $(N_4C-CN_4)$ ; IR (KBr):  $\tilde{\nu} = 3470$  (s), 3435 (s), 3341 (vs), 3329 (vs), 3195 (vs), 2906 (s), 2252 (w), 2185 (w), 1672 (vs), 1590 (m), 1416 (m), 1384 (m), 1325 (s), 1302 (m), 1205 (m), 1184 (s), 1146 (w), 1081 (w), 1043 (w), 1018 (s), 986 (m), 781 (w), 742 (w), 663 (m), 593 (m), 473 cm<sup>-1</sup> (w); Raman (1064 nm, 300 mW, 25 °C):  $\tilde{\nu} = 3330$ (3), 3219 (6), 1670 (2), 1585 (100), 1565 (5), 1417 (2), 1206 (17), 1185 (2), 1146 (3), 1129 (4), 1109 (29), 1072 (18), 922 (12), 783 (3), 655 (2), 547 (4), 471 (1), 425 (8), 402 (5), 366 (3), 282 (3), 224 cm<sup>-1</sup> (3); MS (FAB<sup>+</sup>): *m/z*: 90.1 [CH<sub>8</sub>N5<sup>+</sup>]; MS (FAB<sup>-</sup>): m/z: 137.0 [C<sub>2</sub>HN<sub>8</sub><sup>-</sup>]; elemental analysis

4060 -

calcd (%) for  $C_4H_{20}N_{18}O_2$  (352.32): C 13.64, H 5.72, N 71.56; found: C 14.22, H 5.46, N 71.16; BAM drophammer: 30 J; friction tester: 360 N; ESD: 0.70 J (at grain size 100–500  $\mu$ m).

Bis(triaminoguanidinium) 5,5'-bistetrazolate (7): Triaminoguanidine (1.04 g, 9.99 mmol, 1.00 equiv) was added to a solution of 5,5'-bistetrazole (1.45 g, 10.5 mmol, 1.05 equiv) in H<sub>2</sub>O (25 mL). Filtration and slow evaporation of the solvent gave slightly purple crystals of 7 that were suitable for X-ray diffraction (yield: 1.42 g, 4.10 mmol, 82%). DSC (5°Cmin<sup>-1</sup>): 207 °C (decomp.); <sup>1</sup>H NMR (D<sub>2</sub>O, 25 °C):  $\delta = 4.77$  ppm (s, 6H; NH<sub>2</sub>); <sup>13</sup>C NMR (D<sub>2</sub>O, 25 °C):  $\delta = 154.6$  ppm (N<sub>4</sub>C-CN<sub>4</sub>); IR (KBr):  $\tilde{\nu} = 3340$ (m), 3320 (s), 3289 (m), 3211 (vs), 3139 (s), 2178 (w), 1685 (vs), 1614 (m), 1451 (w), 1383 (w), 1335 (m), 1322 (m), 1303 (m), 1224 (w), 1177 (w), 1171 (w), 1157 (m), 1128 (s), 1078 (w), 1043 (w), 1017 (m), 1011 (m), 952 (s), 764 (w), 732 (w), 638 (w), 611 (m), 566 cm<sup>-1</sup> (w); Raman (1064 nm, 300 mW, 25 °C):  $\tilde{\nu} = 3340$  (5), 3292 (2), 3240 (2), 3195 (11), 1686 (4), 1664 (1), 1582 (100), 1564 (7), 1457 (2), 1423 (2), 1339 (3), 1198 (26), 1158 (4), 1137 (5), 1111 (38), 1073 (27), 1026 (2), 885 (12), 783 (4), 650 (1), 608 (2), 478 (2), 431 (8), 393 (4), 295 (3), 265 cm<sup>-1</sup> (2); MS (FAB<sup>+</sup>): m/z: 105.1  $[CH_9N_6^+]; MS (FAB^-): m/z: 137.0 [C_2HN_8^-];$  elemental analysis calcd (%) for  $C_4 H_{18} N_{20}$  (346.32): C 13.87, H 5.24, N 80.89; found: C 14.02, H 4.87, N 79.21; BAM drophammer: 15 J; friction tester: 285 N; ESD: 0.70 J (at grain size 100-500 µm).

Bis(diaminouronium) 5,5'-bistetrazolate dihydrate (8): Diaminourea (1.81 g, 20.1 mmol, 2.00 equiv) in  $\mathrm{H_{2}O}$  (25 mL) was added to a solution of 5,5'-bistetrazole (1.39 g, 10.1 mmol, 1.00 equiv) in H<sub>2</sub>O (30 mL). The solvent was removed under reduced pressure and the residue was recrystallized from EtOH/H2O (1:4) to give colorless crystals of compound 8 (yield: 2.84 g, 8.92 mmol, 88%). DSC (5°C min<sup>-1</sup>): 174 (m.p.), 237°C (decomp.); <sup>1</sup>H NMR ([D<sub>6</sub>]DMSO, 25°C):  $\delta = 7.22$  ppm (br s, 7H); <sup>13</sup>C NMR ([D<sub>6</sub>]DMSO, 25°C):  $\delta = 161.1$  (C=O), 150.1 ppm (N<sub>4</sub>C-CN<sub>4</sub>); IR (KBr):  $\tilde{\nu} = 3296$  (vs), 3185 (vs), 2996 (vs), 2718 (vs), 2490 (vs), 2225 (s), 2083 (s), 1739 (w), 1681 (s), 1646 (vs), 1621 (vs), 1590 (vs), 1560 (vs), 1536 (vs), 1384 (m), 1335 (vs), 1306 (vs), 1251 (m), 1225 (s), 1183 (s), 1144 (s), 1122 (vs), 1092 (s), 1056 (m), 1015 (s), 977 (m), 817 (m), 727 (s), 702 (s), 534 (w), 504 cm<sup>-1</sup> (w); Raman (1064 nm, 300 mW, 25 °C):  $\tilde{\nu} =$ 3297 (1), 3184 (4), 1679 (2), 1588 (100), 1560 (6), 1432 (2), 1340 (2), 1325 (5), 1226 (2), 1204 (22), 1143 (9), 1119 (28), 1092 (19), 1017 (5), 975 (9), 780 (4), 512 (7), 426 (12), 385 (9), 365 (3), 192 (7), 161 (3), 144 (34), 126 (9), 107 (42), 90 (27), 67 cm<sup>-1</sup> (3); MS (FAB<sup>+</sup>): m/z: 91.0 [CH<sub>7</sub>N<sub>4</sub>O<sup>+</sup>]; MS (FAB<sup>-</sup>): m/z: 137.0 [C<sub>2</sub>HN<sub>8</sub><sup>-</sup>]; elemental analysis calcd (%) for C4H18N16O4 (318.26): C 15.10, H 4.43, N 70.42; found: C 15.46, H 4.10, N 69.48; BAM drophammer: 35 J; friction tester: 360 N; ESD: 0.50 J (at grain size 100-500 µm).

#### Acknowledgements

Financial support of this work by the Ludwig Maximilian University of Munich (LMU), the U.S. Army Research Laboratory (ARL), the Armament Research, Development and Engineering Center (ARDEC), the Strategic Environmental Research and Development Program (SERDP), and the Office of Naval Research (ONR Global, title: "Synthesis and Characterization of New High Energy Dense Oxidizers (HEDO) -NICOP Effort") under contract nos. W911NF-09-2-0018 (ARL), W911NF-09-1-0120 (ARDEC), W011NF-09-1-0056 (ARDEC), and 10 WPSEED01-002/WP-1765 (SERDP) is gratefully acknowledged. The authors acknowledge collaborations with Dr. Mila Krupka (OZM Research, Czech Republic) for the development of new testing and evaluation methods for energetic materials and Dr. Muhamed Sucesca (Brodarski Institute, Croatia) for the development of new computational codes to predict the detonation and propulsion parameters of novel explosives. We are indebted to and thank Drs. Betsy M. Rice and Brad Forch (ARL, Aberdeen, Proving Ground, MD) and Mr. Gary Chen (ARDEC, Picatinny Arsenal, NJ) for many helpful and inspired discussions and support of our work. Mr. Stefan Huber is thanked for performing the sensitivity tests

[2] M. H. V. Huynh, M. A. Hiskey, T. J. Meyer, M. Wetzler, Proc. Natl. Acad. Sci. USA 2006, 103, 5409–5412.

**FULL PAPER** 

- [3] N. Fischer, T. M. Klapötke, S. Scheutzow, J. Stierstorfer, Cent. Eur. J. Energ. Mater. 2008, 5, 3–18.
- [4] E. Oliveri-Mandala, T. Passalacqua, Gazz. Chim. Ital. 1914, 43(II), 465–475.
- [5] a) Y. Guo, G.-H. Tao, Z. Zeng, H. Gao, D. A. Parrish, J. M. Shreeve, *Chem. Eur. J.* 2010, *16*, 3753–3762.
- [6] S. Hachiya, M. Sato (Jpn. Kokai Tokkyo) JP 2006096860A 20060413, 2006.
- [7] D. E. Chavez, M. A. Hiskey, D. L. Naud, J. Pyrotech. 1999, 10, 17– 36.
- [8] T. M. Klapötke in *Chemistry of High-Energy Materials*, de Gruyter, Berlin, 2011, 90–91.
- [9] R. Sivabalan, N. Senthilkumar, B. Kavitha, S. N. Asthana, J. Therm. Anal. Calorim. 2004, 78, 781–792.
- [10] R. Sivabalan, M. Anniyappan, S. J. Pawar, M. B. Talawar, G. M. Gore, S. Venugopalan, B. R. Gandhe, J. Hazard. Mater. 2006, 137, 672–680.
- [11] A. Hammerl, T. M. Klapötke, H. Nöth, M. Warchhold, *Inorg. Chem.* 2001, 40, 3570–3575.
- [12] a) M. Tremblay, Can. J. Chem. 1965, 43, 1230; b) M. A. Hiskey, N. Goldman, J. R. Stine, J. Energ. Mater. 1998, 16, 119; c) A. Hammerl, M. A. Hiskey, G. Holl, T. M. Klapötke, K. Polborn, J. Stierstorfer, J. J. Weigand, Chem. Mater. 2005, 17, 3784–3793.
- [13] B. C. Tappan, A. N. Ali, S. F. Son, T. B. Brill, Propellants Explos. Pyrotech. 2006, 31, 163–168.
- [14] C. M. Michienzi, C. J. Campagnuolo, E. G. Tersine, C. D. Knott, NDIA IM/EM Symposium October 11–14, 2010, Munich, Germany, http://www.imemg.org/.
- [15] A. Hammerl, G. Holl, M. Kaiser, T. M. Klapötke, P. Mayer, H. Nöth, H. Piotrowski, M. Warchhold, *Eur. J. Inorg. Chem.* 2002, 834– 845.
- [16] CrysAlisPro Oxford Diffraction Ltd., Version 171.33.41, 2009.
- [17] a) SIR92: A. Altomare, G. Cascarano, C. Giacovazzo, A. Guagliardi, J. Appl. Crystallogr. 1993, 26, 343; b) SIR97: A. Altomare, M. C. Burla, M. Camalli, G. L. Cascarano, C. Giacovazzo, A. Guagliardi, A. G. G. Moliterni, G. Polidori, R. Spagna, J. Appl. Crystallogr. 1999, 32, 115–119.
- [18] G. M. Sheldrick SHELXS-97, Program for Crystal Structure Solution, Universität Göttingen, 1997.
- [19] PLATON, Utrecht University, Utrecht, The Netherlands, A. L. Spek, 1998.
- [20] L. J. Farrugia, J. Appl. Crystallogr. 1999, 32, 837-838.
- [21] Empirical absorption correction using spherical harmonics, implemented in SCALE3 ABSPACK scaling algorithm (CrysAlisPro Oxford Diffraction, v. 171.33.41, 2009).
- [22] P. J. Eulgem, A. Klein, N. Maggiarosa, D. Naumann, R. W. H. Pohl, *Chem. Eur. J.* 2008, 14, 3727–3736.
- [23] A. F. Holleman, E. Wiberg, N. Wiberg, *Lehrbuch der Anorganischen Chemie*, 102. Auflage, Walter de Gruyter, Berlin, 2007.
- [24] V. Ernst, T. M. Klapötke, J. Stierstorfer, Z. Anorg. Allg. Chem. 2007, 633, 879–887.
- [25] P. J. Steel, J. Chem. Crystallogr. 1996, 26, 399-402.
- [26] M. Kowalewski, P. Mayer, A. Schulz, A. Villinger, Acta Crystallogr. Sect. E 2006, 62, i248–i249.
- [27] T. Fendt, N. Fischer, T. M. Klapötke, J. Stierstorfer, *Inorg. Chem.* 2011, 50, 1447–1458.
- [28] M. Hesse, H. Meier, B. Zeeh, Spektroskopische Methoden in der Organischen Chemie, 7th ed., Thieme, Stuttgart, Germany, 2005.
- [29] G. Socrates, Infrared and Raman Characteristics Group Frequencies, 3rd ed., John Wiley & Sons, Chichester, 2004.
- [30] T. M. Klapötke, P. Mayer, C. Miro Sabate, J. M. Welch, N. Wiegand, *Inorg. Chem.* 2008, 47, 6014–6027.
- [31] NATO standardization agreement (STANAG) on explosives, *Impact Sensitivity Tests*, no. 4489, 1st ed., Sept. 17, 1999.

#### CHEMISTRY

A EUROPEAN JOURNAL

- [32] WIWEB-Standardarbeitsanweisung 4-5.1.02, Ermittlung der Explosionsgefährlichkeit, hier der Schlagempfindlichkeit mit dem Fallhammer, Nov. 8, 2002.
- [33] http://www.bam.de.
- [34] NATO standardization agreement (STANAG) on explosives, *Fric*tion Sensitivity Tests, no. 4487, 1st ed., Aug. 22, 2002.
- [35] WIWEB-Standardarbeitsanweisung 4-5.1.03, Ermittlung der Explosionsgefährlichkeit oder der Reibeempfindlichkeit mit dem Reibeapparat, Nov. 8, 2002.
- [36] Impact: insensitive >40 J, less sensitive  $\ge$ 35 J, sensitive  $\ge$ 4 J, very sensitive  $\le$ 3 J; friction: insensitive >360 N, less sensitive =360 N, sensitive 360–80 N, very sensitive  $\le$ 80 N, extreme sensitive  $\le$ 10 N. According to the UN Recommendations on the Transport of Dangerous Goods (+) indicates not safe for transport.
- [37] http://www.ozm.cz.
- [38] http://www.linseis.com.
- [39] T. Altenburg, T. M. Klapötke, A. Penger, J. Stierstorfer, Z. Anorg. Allg. Chem. 2010, 636, 463–471.
- [40] Gaussian 09, Revision A.1, M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, B. Mennucci, G. A. Petersson, H. Nakatsuji, M. Caricato, X. Li, H. P. Hratchian, A. F. Izmaylov, J. Bloino, G. Zheng, J. L. Sonnenberg, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, J. A. Montgomery, Jr., J. E. Peralta, F. Ogliaro, M. Bearpark, J. J. Heyd, E. Brothers, K. N. Kudin, V. N. Staroverov, R. Kobayashi, J. Normand, K. Raghavachari, A. Rendell, J. C. Burant, S. S. Iyengar, J. Tomasi, M. Cossi, N. Rega, J. M. Millam, M. Klene, J. E. Knox,

J. B. Cross, V. Bakken, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. W. Ochterski, R. L. Martin, K. Morokuma, V. G. Zakrzewski, G. A. Voth, P. Salvador, J. J. Dannenberg, S. Dapprich, A. D. Daniels, Ö. Farkas, J. B. Foresman, J. V. Ortiz, J. Cioslowski, and D. J. Fox, Gaussian, Inc., Wallingford CT, **2009**.

- [41] NIST Chemistry WebBook, NIST Standard Reference Database Number 69 (Eds.: P. J. Linstrom, W. G. Mallard), National Institute of Standards and Technology, Gaithersburg MD, 20899, http://webbook.nist.gov, (retrieved October 27, 2011).
- [42] a) H. D. B. Jenkins, H. K. Roobottom, J. Passmore, L. Glasser, *Inorg. Chem.* **1999**, *38*, 3609–3620; b) H. D. B. Jenkins, D. Tudela, L. Glasser, *Inorg. Chem.* **2002**, *41*, 2364–2367.
- [43] M. Sućeska, EXPLO5.04 program, Zagreb, Croatia, 2010.
- [44] K. M. Dontsova, J. C. Pennington, C. Hayes, J. Šimunek, C. W. Williford, *Chemosphere* 2009, 77, 597–603.
- [45] United States Environmental Protection Agency, http://www.epa.gov/.
- [46] C. M. Walsh, C. D. Knott, C. S. Leveritt, *Reduced Erosion Additive for a Propelling Charge*, US 6984275 B1, 2006.
- [47] F. Volk, H. Bathelt, Propellants Explos. Pyrotech. 1997, 22, 120–124.
- [48] Calculation of oxygen balance:  $\Omega$  [%]=(wO-2xC-1/2yH-2zS)1600/M. (w: number of oxygen atoms, x: number of carbon atoms, y: number of hydrogen atoms, z: number of sulfur atoms, M: molecular weight).

Received: November 28, 2011 Published online: February 24, 2012