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Thermal Stabilization of Energetic Materials by the Aromatic Nitrogen-Rich Bis(3,4-diamino-1,2,4-triazolium) Cation
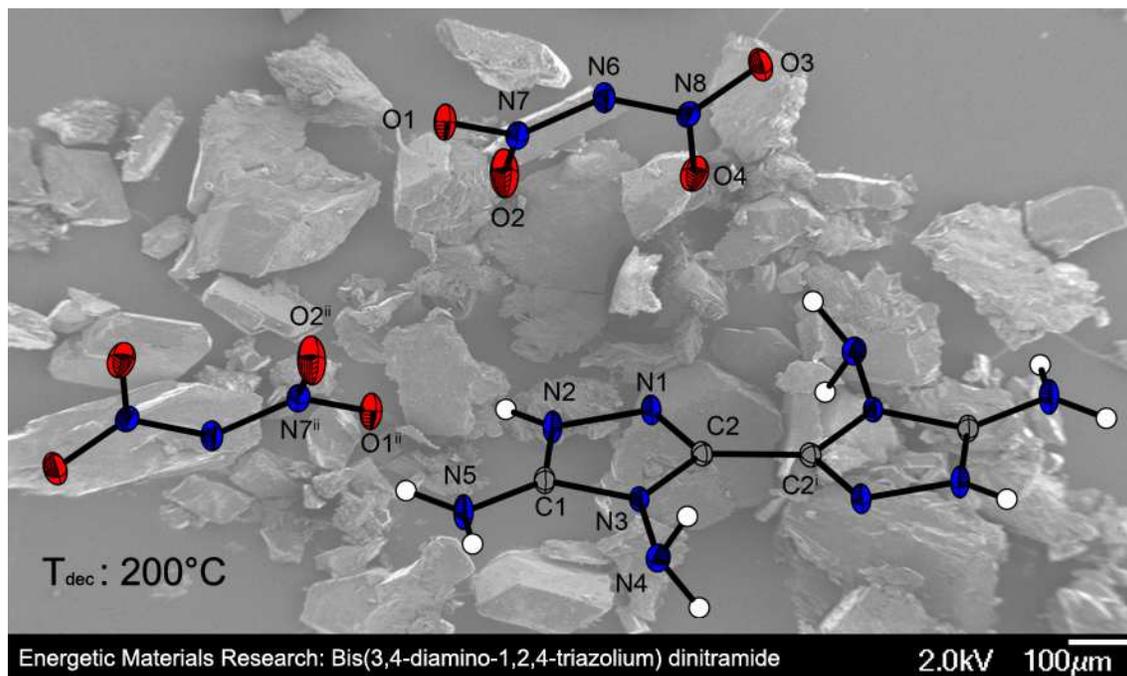
Crystals of the highly energetic material bis(3,4-diamino-1,2,4-triazolium) dinitramide (**2**) representing one of the thermally most stable dinitramide derivatives which is due to the insertion of the long disregarded bis(3,4-diamino-1,2,4-triazolium) cation.

FULL PAPER

Thermal Stabilization of Energetic Materials by the Aromatic Nitrogen-Rich 4,4',5,5'-Tetraamino-3,3'-Bi-1,2,4-Triazolium Cation

Thomas M. Klapötke[*a], Philipp. C. Schmid[a], Simon Schnell[a] and Jörg Stierstorfer[a]

4,4',5,5'-Tetraamino-3,3'-bi-1,2,4-triazole (**1**) was prepared in one step from commonly available starting materials. Compound **1** comprises two combined aromatic triazoles with four amino moieties resulting in a compound which has i) a high temperature stability, ii) a high heat of formation, iii) high density and iv) no sensitivity towards physical stimuli (friction, impact and electrostatic discharge). Interestingly the compound has never been considered as building block in the development of new energetic materials. Therefore **1** was 10 investigated in detail as a potential new nitrogen-rich, temperature stable cation for synthesis of energetic ionic derivatives (**2−13**) as environmentally benign explosives. The cation was combined mostly with oxygen-rich counter-anions such as dinitramide (**2**), 5-nitrotetrazole-2-oxide (**3**), 5-nitrotetrazolate (**4**), nitrate (**5**), tetranitrobisimidazole (**6**), 5,5'-bitetrazole-1,1'-dioxide (**7**), 1,1'-dinitramino-5,5'-bitetrazolate (**8**), 5-nitriminotetrazolate (**9**), 1-methyl-5-nitriminotetrazolate (**10**), perchlorate (**11**), picrate (**12**), nitroformate (**13**). Compounds **2–10** and **13** were characterized by low temperature single–crystal X-ray diffraction. All compounds were investigated by 15 NMR and vibrational (IR, Raman) spectroscopy, mass spectrometry and elemental analysis. The excellent thermal properties were determined by differential thermal analysis (DTA). The sensitivities towards impact, friction, and electrical discharge were investigated using BAM standards and a small scale electrostatic discharge tester. The detonation parameters of those compounds without inclusion of crystal water (**1–3**, **5–8**, **11** and **13**) were calculated using the EXPLO5 (V6.02) code and calculated (CBS-4M) enthalpy of formation values.

Introduction

The highest attention in the research of modern energetic materials in the 20th century was paid on cyclic or caged nitramines, for example 1,3,5-trinitro-1,3,5-triazinane (RDX) and 2,4,6,8,10,12-hexanitro-2,4,6,8,10,12-hexaazaisowurtzitane (CL-20) shown in 25 Figure 1.[1] Since the development of RDX, newly synthesized energetic compounds have to be able to compete with RDX, especially in terms of detonation pressure and detonation velocity, being very important parameters when investigating secondary explosives.[2] Furthermore, stability towards temperature, high 30 density, safe handling, and cheap synthesis are additional properties a new secondary explosive should possess. A high density is vital for a good performance of the energetic material, since the detonation pressure is proportional to its squared density.[2] Next to equal or even enhanced physical properties, the 35 demand for „green", nitrogen-rich energetic materials steadily rises. To reduce the pollution of the environment through commonly used toxic and carcinogenic explosives, like RDX or lead azide, explosives releasing mostly dinitrogen after decomposition gain more and more importance.[3]

40 One approach for synthesizing new energetic compounds is the preparation of energetic salts, which mostly exhibit high densities and high stabilities, due to their high lattice energy.[2] Other than employing alkali metals (Na^+, K^+)[4] as cations, the use of nitrogen-rich cations became more popular, due to (i) the potential hydrogen 45 bond network resulting in less sensitive materials[5] and (ii) a high

positive heat of formation. Latter one mostly results in a high energetic performance as well as a decent oxygen balance.[6]
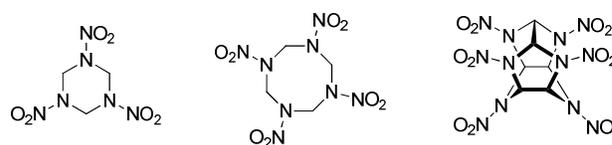

Figure 1. Chemical structure of the commonly used secondary explosive hexogen (RDX, left) and octogen (HMX, middle) as well as CL-20 (right), a potential high-performing alternative.

One approach for synthesizing new energetic compounds is the 55 preparation of energetic salts, which mostly exhibit high densities and high stabilities, due to their high lattice energy.[2] Other than employing alkali metals (Na^+, K^+)[4] as cations, the use of nitrogen-rich cations became more popular, due to (i) the potential hydrogen bond network resulting in less sensitive materials[5] and (ii) a high 60 positive heat of formation. Latter one mostly results in a high energetic performance as well as a decent oxygen balance.[6]

Examples for commonly used nitrogen-rich cations are guanidinium (G^+), aminoguanidinium (AG^+), diaminoguanidinium (DAG^+), triaminoguanidinium (TAG^+), ammonium (NH_4^+), 65 hydroxylammonium (NH_3OH^+) and hydrazinium ($N_2H_5^+$). They strongly vary in their stability towards temperature and in their energetic performance. A common observed trend in simple nitrogen–rich cations is the decrease in temperature stability in the

row G$^+$, AG$^+$, DAG$^+$ and TAG$^+$ whereas the performance increases with increasing number of energetic N–N bonds.[7] To improve the energetic performance of explosives the employment of NH$_4^+$, NH$_3$OH$^+$ and N$_2$H$_5^+$ cations is a valuable strategy. Unfortunately, this usually leads to an increase in mechanical sensitivity and a decrease in temperature stability from NH$_4^+$ over N$_2$H$_5^+$ to NH$_3$OH$^+$.[5,8] Since a high thermal stability seems to be accompanied by a decrease in the energetic performance of energetic salts, currently used nitrogen-rich salts are limited to either their thermal stability or sufficient energetic performance in comparison to RDX.

Thus, it seems that in many energetic materials, a good energetic performance and low sensitivity exclude each other.[8] Exemplarily this can be observed in the series of five–membered azoles from pyrazole to pentazole. Whereas the pyrazole, containing only two nitrogen atoms exhibits a too small performance but high stability, a pentazole heterocycle, having five nitrogen-atoms in the ring is too sensitive to be taken into account for any applications, but shows high performance.[3a,3f]

R. Centore *et al.* reported the facile synthesis of 4,4',5,5'-tetraamino-3,3'-bi-1,2,4-triazole (**1**).[10] Interestingly this compound has never been described as building block in the development of new energetic materials so far. It only has been characterized by its decomposition point, elemental analysis and mass spectroscopy. A detailed characterization using X-Ray diffraction, elemental analysis and ^{13}C NMR spectrometry as well as the investigation of the energetic properties of compound **1** are missing in literature. Herein we report the synthesis of the temperature stable nitrogen-rich salts of 4,4',5,5'-tetraamino-3,3'-bi-1,2,4-triazole and a detailed investigation on the properties of the resulted energetic materials.
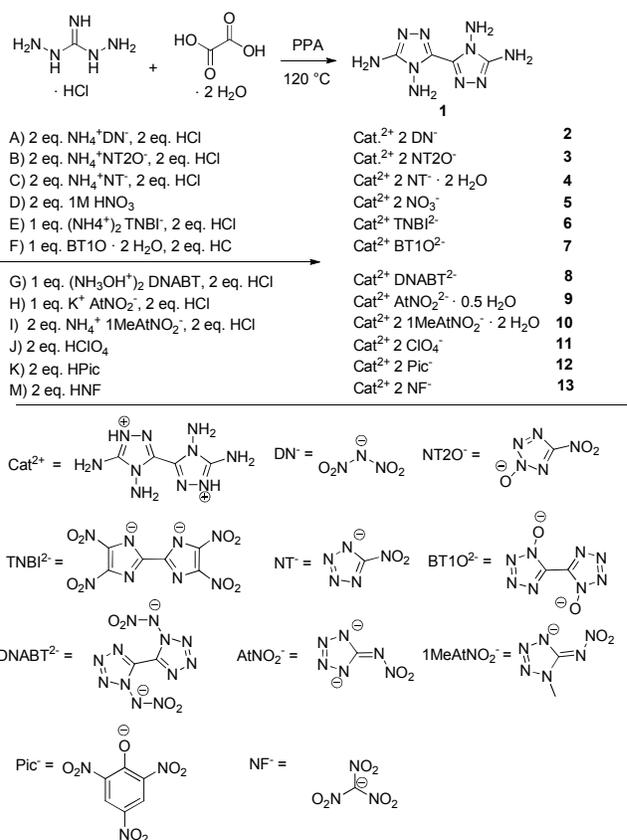
Results and Discussion

Simple One Step Synthesis

4,4',5,5'-Tetraamino-3,3'-bi-1,2,4-triazole (**1**) was synthesized according to an improved literature procedure.[10] By using phosphoric acid (100%) and phosphorus pentoxide, polyphosphoric acid (PPA) is created and utilized as solvent. Diaminoguanidine monohydrochloride and oxalic acid are finely ground in a mortar and then added to the PPA. The temperature is kept at 120°C overnight forming **1**. The energetic salts are received by simple metathesis reactions using compound **1** and different energetic anions as illustrated in Scheme 1.

4,4',5,5'-Tetraamino-3,3'-bi-1,2,4-triazolium dinitramide **2**, 4,4',5,5'-tetraamino-3,3'-bi-1,2,4-triazolium dinitrotetrazolate–2*N*–oxide **3**, 4,4',5,5'-tetraamino-3,3'-bi-1,2,4-triazolium dinitrotetrazolate **4**, and 4,4',5,5'-tetraamino-3,3'-bi-1,2,4-triazolium di–1–methylnitriminotetrazolate dihydrate **10** were formed by a 2:1 stoichiometric reaction of the respective anion, compound **1** and two equivalents of hydrochloric acid in water. The protonation of compound **1** leads to a better solubility in water. 4,4',5,5'-Tetraamino-3,3'-bi-1,2,4-triazolium dinitrate **5**, 4,4',5,5'-tetraamino-3,3'-bi-1,2,4-triazolium diperchlorate **11**, 4,4',5,5'-tetraamino-3,3'-bi-1,2,4-triazolium dipicrate **12** and 4,4',5,5'-tetraamino-3,3'-bi-1,2,4-triazolium dinitroformate **13** are received by adding two equivalents of the anion to one equivalent of compound **1** under aqueous conditions. The nitrogen–rich compounds 4,4',5,5'-tetraamino-3,3'-bi-1,2,4-triazolium tetranitrobis-imidazolate **6**, 4,4',5,5'-tetraamino-3,3'-bi-1,2,4-triazolium 5,5'-bitetrazole-1,1'-dioxide **7**, 4,4',5,5'-tetraamino-3,3'-bi-1,2,4-triazolium 1,1'-dinitramino-5,5'-bitetrazolate **8** and 4,4',5,5'-tetraamino-3,3'-bi-1,2,4-triazolium 5-nitrimino-1*H*-tetrazolate hemihydrate **9** are received by a 1:1 stoichiometric

reaction of the respective anion with compound **1** and two equivalents of hydrochloric acid in water.

A) 2 eq. NH$_4^+$DN$^-$, 2 eq. HCl	Cat.$^{2+}$ 2 DN$^-$ **2**
B) 2 eq. NH$_4^+$NT2O$^-$, 2 eq. HCl	Cat.$^{2+}$ 2 NT2O$^-$ **3**
C) 2 eq. NH$_4^+$NT$^-$, 2 eq. HCl	Cat^{2+} 2 NT$^-$ · 2 H$_2$O **4**
D) 2 eq. 1M HNO$_3$	Cat^{2+} 2 NO$_3^-$ **5**
E) 1 eq. (NH$_4^+$)$_2$ TNBI$^-$, 2 eq. HCl	Cat^{2+} TNBI^{2-} **6**
F) 1 eq. BT1O · 2 H$_2$O, 2 eq. HC	Cat^{2+} BT1O^{2-} **7**
G) 1 eq. (NH$_3$OH$^+$)$_2$ DNABT, 2 eq. HCl	Cat^{2+} DNABT^{2-} **8**
H) 1 eq. K$^+$ AtNO$_2^-$, 2 eq. HCl	Cat^{2+} AtNO$_2^{2-}$ · 0.5 H$_2$O **9**
I) 2 eq. NH$_4^+$ 1MeAtNO$_2^-$, 2 eq. HCl	Cat^{2+} 2 1MeAtNO$_2^-$ · 2 H$_2$O **10**
J) 2 eq. HClO$_4$	Cat^{2+} 2 ClO$_4^-$ **11**
K) 2 eq. HPic	Cat^{2+} 2 Pic$^-$ **12**
M) 2 eq. HNF	Cat^{2+} 2 NF$^-$ **13**

Scheme 1. Synthesis of compound **1** and its salts **2–13** via metathesis reactions

X-Ray Diffraction

The crystal structures of compounds **2–10** and **13** were determined by low temperature X-ray diffraction. Selected parameters of the X-ray determinations are given in Tables S1–S4 in the Supporting Information. The cif files were deposited[11] with the CCDC Nos. 1029064 (**2**), 1029053 (**3**), 1029066 (**4**), 1029061 (**5**), 1029060 (**6**), 1029062 (**7**), 1029053 (**7·2H$_2$O**), 1029058 (**8**), 1029056 (**9**), 1029055 (**9a**), 1029057 (**9b**), 1029054 (**10**), 1029059 (**13**).

4,4',5,5'-Tetraamino-3,3'-bi-1,2,4-triazolium dinitramide (**2**) crystallizes from water in the triclinic space group *P*–1 with a density of 1.860 g cm^{-3} at 173 K and one molecule per unit cell. The density of compound **2** is in the same range as of previously reported dinitramides. For example ADN with a density of 1.856 g cm^{-3} at 173K [12] or hydrazinium dinitramide 1.83 g cm^{-3} (298K),[13] show similar densities as the newly reported compound **2**. The torsion angle of N3–C2–C2^i–N1^i equals 0.5(2)° showing that a nearly planar ring–system is formed by the two triazoles. Through the aromaticity of the ring system, the triazoles form almost regular pentagons with angles near 108° and with almost equal bond lengths between the ring atoms of 1.3–1.4 Å. The connecting C–C bond of the triazole–rings with a length of 1.445(3) Å, is significantly shorter than a C–C single bond (1.54 Å). Similar C–C bond lengths can be observed in salts **3–10** and **13**. In comparison to the linking C–C bonds in other 1,2,4–triazoles, for example 3,3'-dinitro-1,1'-dihydroxy-5,5'-bi-1,2,4-triazole and its derivatives, with C–C bond lengths between

1.463(2) Å and 1.438(6) Å, the lengths in compound **2**–**10** and **13** are very similar.[8a, 14] The distance C1–N5 amounts to 1.317(2) Å and thus is remarkably shorter than the distance of the carbon to the nitrogen of the nitro group in 3,3'-dinitro-1,1'-dihydroxy-5,5'-bi-1,2,4-triazole and its derivatives with bond lengths between 1.454(5) Å and 1.427(5) Å.[8a] Moreover, C1–N5 is shorter than other $C_{(triazole)}$–$N_{(amino)}$ distances (1.351(3) Å) of comparable compounds reported in the literature.[15] Compounds **3**–**10** and **13** also show bond lengths around 1.31 Å for the equivalent C–N distance. Figure 2 illustrates the molecular unit of compound **2**, with selected bond lengths and selected bond angles in the caption.
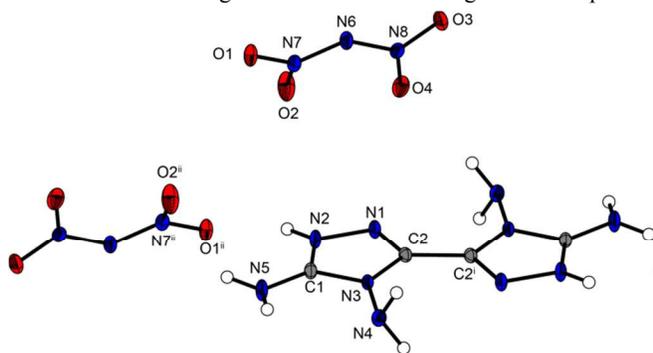

Figure 2. Molecular unit of **2**. Ellipsoids are drawn at the 50% probability level. Selected bond lengths [Å]: N1–N2 1.379(3), N2–C1 1.327(3), C1–N3 1.348(0), N3–C2 1.382(7), C2–N1 1.297(2), C2–C2^i 1.445(3) N3–N4 1.400(2), C1–N5 1.317(2); selected bond angles [°]: N1–N2–C1 111.92(13), N2–C1–N3 106.07(13), C1–N3–C2 106.55(14), N3–C2–N1 111.45(12), C2–N1–N2 104.00(13).

The anhydrous crystal structure of 4,4',5,5'-tetraamino-3,3'-bi-1,2,4-triazolium dinitrotetrazolate–2N–oxide (**3**) is described by the triclinic space group P–1 with a density of 1.833 g cm^{-3} at 173 K and one molecule per unit cell. Compound **3** almost reaches the density of the highly energetic hydroxylammonium nitrotetrazolate–2N–oxide with a density of 1.850(2) g cm^{-3}.[8c] In relation to the nitrogen-rich guanidinium, aminoguanidinium or diaminoguanidinium nitrotetrazolate–2N–oxides with densities of 1.6978(4), 1.697(2) and 1.6867(3) g cm^{-3} respectively, which are more stable than the hydroxylammonium salt, the density of **3** is significantly higher.[8c] The torsion angle of N9–C3–C3^i–N6^i is 0°, making the bicyclic ring system completely planar similar to that of the cation in compound **2**. The angles of the ring-system and bond lengths behave in the same way as described for compound **2**. Likewise the bond lengths and bond angles of the anion correspond to the data reported in literature.[5] The molecular unit is shown in Figure 3, with selected bond lengths and bond angles in the caption.
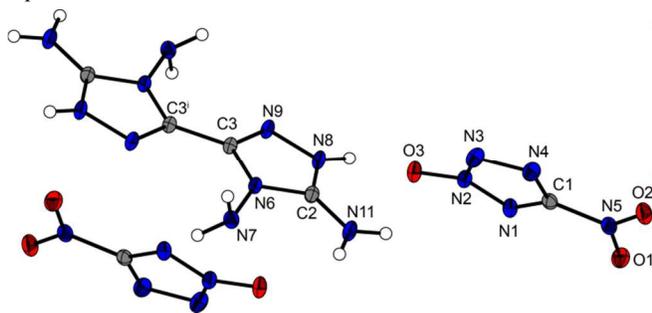

Figure 3. Molecular unit of **3**. Ellipsoids are drawn at the 50% probability level. Selected bond lengths [Å]: C1–N1 1.330(2), N1–

N2 1.324(0), N2–N3 1.338(4), N3–N4 1.336(6), N4–C1 1.317(2), N5–C1 1.441(2), C3–N6 1.380(2), N6–C2 1.358(2), C2–N8 1.330(3), N8–N9 1.380(1), N9–C3 1.302(3), N6–N7 1.400(2), C3–C3^i 1.447(2) C2–N11 1.313(2); selected bond angles [°]: N9–C3–N6 111.47(13), C3–N6–C2 106.46(15), N6–C2–N8 106.09(14), C2–N8–N9 111.74(14), N8–N9–C3 104.24(14), N1–C1–N4 116.17(14), C1–N4–N3 104.48(13), N4–N3–N2 105.46(12), N3–N2–N1 114.54(12), N2–N1–C1 99.34(13).

The energetic compound 4,4',5,5'-tetraamino-3,3'-bi-1,2,4-triazolium dinitrate (**5**) crystallizes anhydrously from water in the triclinic space group P–1 with one molecule per unit cell and a density of 1.779 g cm^{-3} at 173 K. In comparison to compound **2** and **3**, the density of compound **5** is smaller. Compared to hydroxylammonium nitrate with a density of 1.841 g cm^{-3},[16] compound **5** exhibits a smaller density, whereas compound **5** reveals a higher density than guanidinium nitrate (1.410 g cm^{-3}).[17] With a torsion angle of 1.4(2)° of the plane N1–C1–C1^i–N3^i the two triazoles are tilted only slightly more towards each other than in the compounds **2**–**4**. Bond angles and bond lengths of the bicyclic ring system match the data reported above. Figure 4 represents the molecular unit of compound **5**.
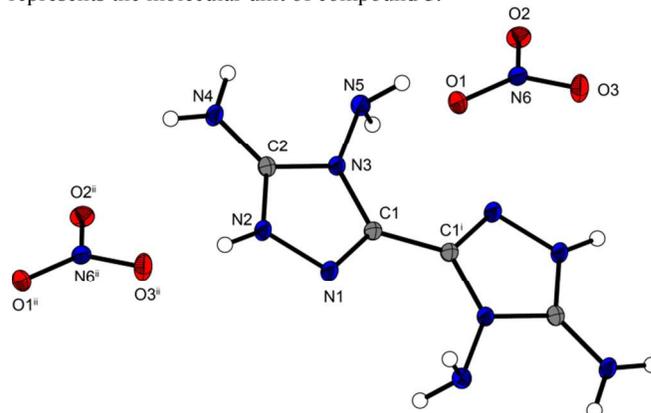

Figure 4. Molecular unit of **5**. Ellipsoids are drawn at the 50% probability level. Selected bond length [Å]: C1–C1^i 1.454(6), C2–N4 1.318(8).

The anhydrous salt 4,4',5,5'-tetraamino-3,3'-bi-1,2,4-triazolium tetranitro–bisimidazolate (**6**) crystallizes in the monoclinic space group P2$_1$/c with two molecules per unit cell. Compound **6** displays a high density of 1.879 g cm^{-3} at 173 K. The high density may be rationalized due to the strong intra– and intermolecular interactions, which arise through the hydrogen-bond network formed by the combination of the four amino–groups of the cation and the four nitro–groups of the anion, resulting in very long hydrogen bridges. Only the hydrazinium salt of tetranitrobisimidazolate with a density of 1.826 g cm^{-3} (298K) [18] showed a density in the range of compound **6**, whereas other nitrogen-rich salts like the guanidinium (ρ = 1.701 g cm^{-3} at 298K) or aminoguanidinium salt (ρ = 1.698 g cm^{-3} at 298K) exhibit clearly lower densities.[18] The torsion angles of the two bicyclic ring systems show that two nearly planar moieties are formed. The C–C bond of the anion, linking the two rings is in the same dimension as the bond of the cation and comparable to the bond lengths of other tetranitrobisimidazoles.[19] Figure 5 illustrates the molecular unit of compound **6** with selected torsion angles and
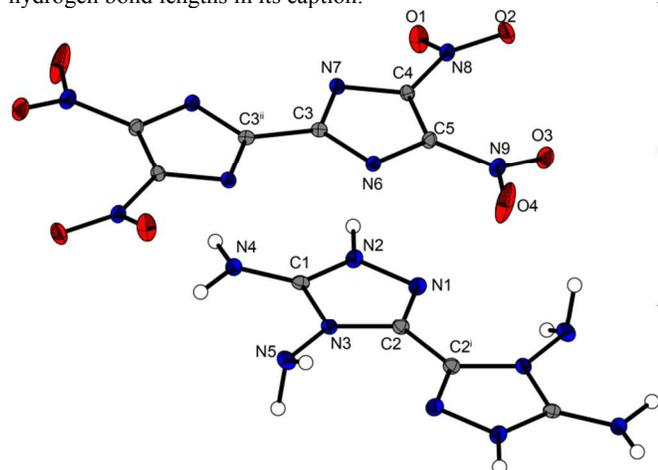
hydrogen bond lengths in its caption.

Figure 5. Molecular unit of **6**. Ellipsoids are drawn at the 50% probability level. Selected bond lengths [Å]: C2–C2^i 1.452(3), C3–C3^i 1.460(3), C1–N4 1.307(3); Selected torsion angles [°]: N1–C2–C2^i–N3^i 1.7(3), N7–C3–C3^i–N6^i 0.9(3); selected hydrogen bond lengths (H···A) [Å]: N2–H2–O4 2.15(3), N4–H4$^{(a)}$–O2 2.56(3), N4–H4$^{(a)}$–O3 2.17(4), N4–H4$^{(a)}$–O1 2.51(3), N5–H5$^{(a)}$–O1 2.48(3), N5–H5$^{(a)}$–O2 2.43(3), N5–H5$^{(a)}$–O3 2.49(3); symmetry codes (i) 1−x, 1−y, −z (ii) 1−x, 1−y, 1−z.

4,4',5,5'-Tetraamino-3,3'-bi-1,2,4-triazolium 5,5'-bitetrazole-1,1'-dioxide (**7**) forms anhydrous crystals as well as crystals containing two water moieties when crystallized from water (**7**·2 H$_2$O). The water free compound **7** crystallizes in the triclinic space group *P*–1 with a density of 1.686 g cm^{-3} at 173 K and one molecule per unit cell. The structure of the dianion has been discussed previously in the literature.[20,21] Compared to other energetic salts of 5,5'-bitetrazole-1,1'-dioxide, e.g. the hydroxylammonium salt TKX–50 ($\rho_{173 K}$ = 1.915 g cm^{-3}), the density of compound **7** is fairly low.[20] However, in comparison to the thermally stable diguanidinium salt 5,5'-bitetrazole-1,1'-dioxide with a density of 1.639 g cm^{-3},[21] compound **7** exhibits a slightly higher density. Figure 6 shows the molecular unit of **7**, with selected bond lengths and torsion angles in the caption. The molecular unit of **7**·2 H$_2$O is illustrated in Figure S2 in the SI.
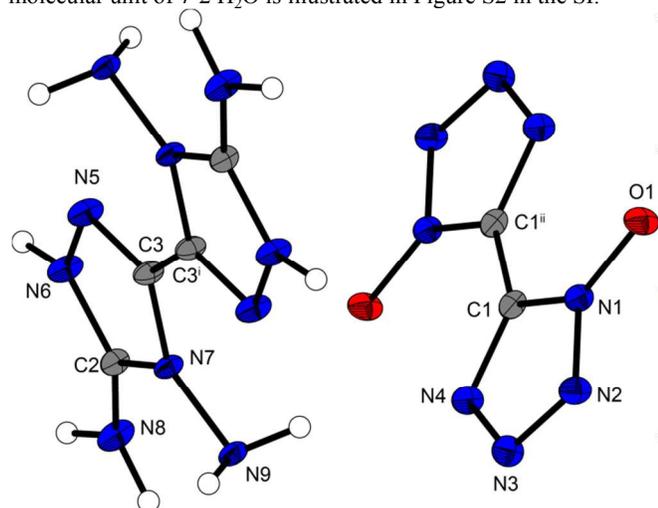

Figure 6. Molecular unit of **7**. Ellipsoids are drawn at the 50% probability level. Selected bond lengths [Å]: C3–C3^i 1.45.1(2),

C2–N8 1.312(3), O1–N1 1.318(2), C1–C1^{ii} 1.446(3), N1–C1 1.347(2), N1–N2 1.345(2), N2–N3 1.314(2), N3–N4 1.342(2), N4–C1 1.333(2); selected torsion angles [°]: N7–C3–C3^i–C5^i 1.3(3), N1–C1–C1^i–N1^i 0.5(3); symmetry codes: (i) −x, 1−y, 1−z; (ii) 1−x, 1−y, z.

The anhydrous energetic compound 4,4',5,5'-tetraamino-3,3'-bi-1,2,4-triazolium 1,1'-dinitramino-5,5'-bitetrazolate (**8**) crystallizes from water in the triclinic space group *P*–1 with a density of 1.778 g cm^{-3} and one formula unit per unit cell. Dipotassium 1,1'-dinitramino-5,5'-bitetrazolate with a density of 2.172 g cm^{-3}, is the only compound containing this anion in literature so far.[4a] The anion of **8** exhibits a larger torsion angle than the corresponding cation, forming a planar cation and a slightly tilted anion. The molecular unit of compound **8** is illustrated in Figure 7.

Figure 7. Molecular unit of **8**. Ellipsoids are drawn at the 50% probability level. Selected bond lengths [Å]: C1–C1^i 1.443(3), C3–C3^i 1.448(2) C2–N11 1.317(2); selected torsion angles [°]: N4–C1–C1^i–N1^i 1.7(3), N8–C3–C3^i–N9^i 0.2(2); symmetry code: (i) 2−x, 1−y, −z (ii) −x, −y, 2−z.

In addition the crystal structures of compounds **4**, **7**·2 H$_2$O, **9–10** and **13** were determined and presented in the supplementary information.

Thermal Analysis and compatibility

To identify the decomposition temperatures of compound **1–13** differential thermal analysis (DTA) with a heating rate of 5°C min^{-1} was employed. The results are displayed in Figures 8 and 10.

The decomposition temperature of the neutral compound **1** amounts to a very high temperature of 342°C and thus exceeds the decomposition temperature of the explosives RDX (T$_{dec.}$ = 204°C)[22] and even hexanitrostilbene (T$_{dec.}$ = 316°C).[23] The dinitramide **2** decomposes at 200°C. Dinitramide based ionic energetic materials oftentimes lack in thermal stability. One exception is **FOX-12**. Its decomposition temperature of 215°C is reported at a heating rate of 10°C min^{-1}.[24] For better comparability of **2** with **FOX-12**, ammonium dinitramide (**ADN**) and guanidinium dinitramide (**GDN**), all of them were remeasured on our instrument at a heating rate of 5°C min^{-1} (see Figure 8). **FOX-12** reveals an onset decomposition temperature of 201°C, which is virtually at the same temperature as compound **2**. **GDN** and **ADN** exhibit lower decomposition temperatures of 149°C and 147°C. Table 2 compares the outstanding thermal stability (although being a 1:2 dinitramide salt) with other nitrogen-rich dinitramides.

Compounds **4**, **9** and **10** containing two crystal water moieties each dehydrate at 89°C, 93°C and 104°C respectively. The highest decomposition temperature of the energetic salts of compound **1** could be measured for compound **6** (T$_{dec.}$ = 290°C). Next to compound **6**, compound **5**, **7**, **11** and **12** also show very high thermal stabilities, with onset decomposition temperatures of 275°C, 279°C, 286°C and 284°C, respectively. In comparison to the 1-methylnitriminotetrazolate **10**, which exhibits a fairly low onset of 209 °C, nitriminotetrazolate **9** has a higher decomposition

onset at 232°C. This value is in accordance with the decomposition temperatures of reported nitrogen–rich 1-methylnitrimino-tetrazolates with onset temperatures of around 210°C. [25]
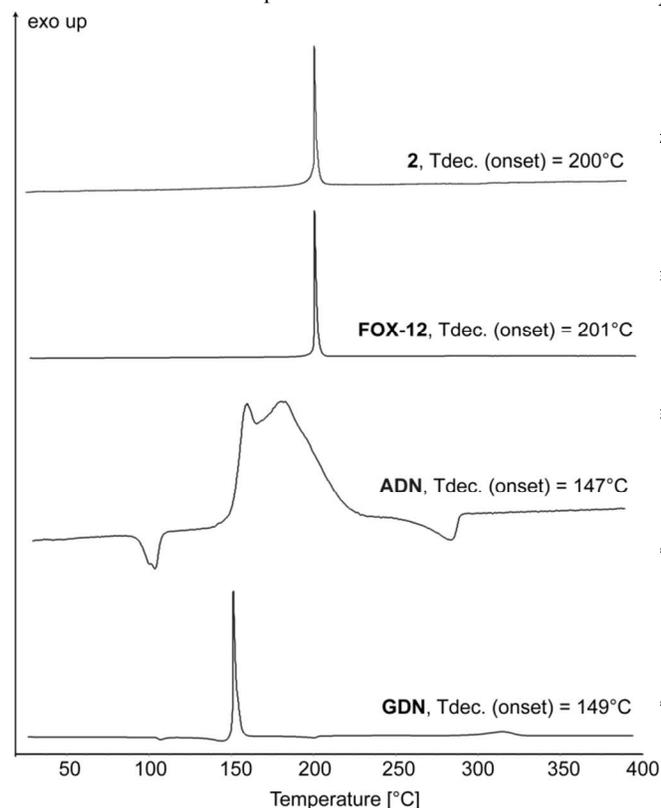

Figure 8. DTA plots of compound **2** in comparison with other nitrogen-rich dinitramide salts, such as *N*-guanylurea-dinitramide (FOX-12), ammonium dinitramide (ADN) and guanidinium dinitramide (GDN) measured with a heating rate of 5°C min⁻¹.

Table 2. Decomposition temperatures of various nitrogen-rich dinitramides [28] in comparison to compound **2**.

Dinitramides	$T_{dec.}$ (onset) [°C]
2	200
FOX-12	201 (215 at 10 °C min⁻¹) [24]
A DN	147
G DN	149
TAG DN	180 [28a]
1,5-DAT DN	135 [28b]
1-Me-AT DN	145 [28b]
2-Me-AT DN	148 [28c]
5-AT DN	117 [28c]
Tz DN	110 [28c]
3,5-DATr DN	164 [28d]
3,6-DHyTT DN	152 [28e]

DN = dinitramide, A = ammonium, G = guanidinium, TAG = triaminoguanidinium, 1,5-DAT = 1,5-diaminotetrazolium, 1-Me-AT = 1-methyl-5-aminotetrazolium, 2-Me-AT = 2-methyl-5-aminotetrazolium, 5-AT = 5-aminotetrazolium, Tz = tetrazolium, 3,5-DATr = 3,5-diaminotriazolium, 3,6-DHyTT = 3,6-dihydrazino-tetrazinium

The nitrotetrazolate **4** decomposes at a temperature of 225°C and thus shows a higher thermal stability than all other reported non-metal nitrotetrazolate salts, with the guanidinium nitrotetrazolate being the most temperature stable ($T_{dec.}$ = 212°C). [5] Through cation metathesis a thermal stabilization of the anion in compound **8** could be achieved. While the potassium salt K₂DNABT decomposes at 200°C [4a], the new energetic compound **8** is thermally stable up to a temperature of 223°C. In comparison to the nitrogen–rich salts, only the ammonium salt (NH₄)₂ DNABT lies in the range of the thermal stability of compound **8**, whereas the hydroxylammonium salt (NH₃OH)₂ DNABT reveals a much lower decomposition temperature of 170°C. [26] The onset decomposition temperature of the nitrotetrazolate–2*N*–oxide **3** equals 220°C showing a much higher thermal stability than other comparable nitrotetrazolate–2*N*–oxides, as the guanidinium salt ($T_{dec.}$ = 211°C), the aminoguanidinium salt ($T_{dec.}$ = 185°C), the diamino-guanidinium salt ($T_{dec.}$ = 174°C), the triaminoguanidinium salt ($T_{dec.}$ = 153°C) or the ammonium salt ($T_{dec.}$ = 173°C). [8c] In comparison to RDX with a decomposition temperature of 204°C [22], salts **2–12** have at least an equivalent thermal stability. Only the nitroformate **13** decomposes at 94°C, which is slightly lower than the ammonium (116°C), guanidinium (113°C) and triaminoguanidinium (105°C) salt but higher than the corresponding aminoguanidinium (71°C) and diaminoguanidinium (82°C) salt. [27]

All explosives have to be coated for practical applications. A prominent mixture of RDX and TNT (ca. 60:40) is called Composition B. A compatibility test of compound **2** with **TNT** reveals that the decomposition temperature of the **2/TNT** mixture is virtually the same as for pure compound **2**, in respect to both, the onset and top of the peak. It can be concluded that dinitramide **2** is compatible with **TNT** as displayed in Figure 9.
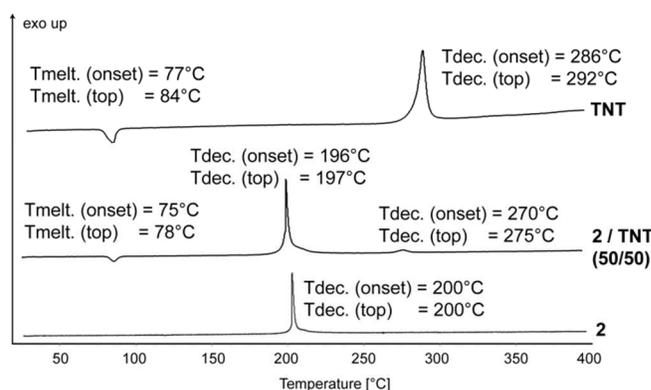

Figure 9. Compatibility measurements of dinitramide **2** with **TNT**

Sensitivities

Compounds **1–13** were tested for their sensitivity towards friction and impact by employment of BAM methods as described in the supporting information. Compounds **1–13** show a wide range of sensitivities towards impact. While the neutral compound **1** as well as compound **6, 7** and **9** can be classified as insensitive towards impact (<40 J), compounds **2, 3, 8** and **11** show very high sensitivities from 6 J (**3**) to up to 3 J (**8**). The dinitramide **2** with an impact sensitivity of 5 J is in the range of the sensitivities towards impact observed for other nitrogen-rich dinitramides (ADN: 5 J [29], TAG DN: 2 J). [28a] The impact sensitivity of compound **3** (6 J) is comparable to the impact sensitivities of the corresponding

hydroxylammonium or the ammonium salt with impact sensitivities of 4 J and 7 J respectively, but does not reach the stability of the diaminoguanidnium nitrotetrazolate–2N–oxide (20 J) or the guanidinium salt, which is insensitive.[8c] Compound **8** exhibits the highest sensitivity towards impact stimuli with 3 J, which arises from the highly sensitive anion. The corresponding hydroxylammonium and ammonium salts reveal an impact sensitivity of 2 J, and thus lie in the same range as compound **8**.[26]
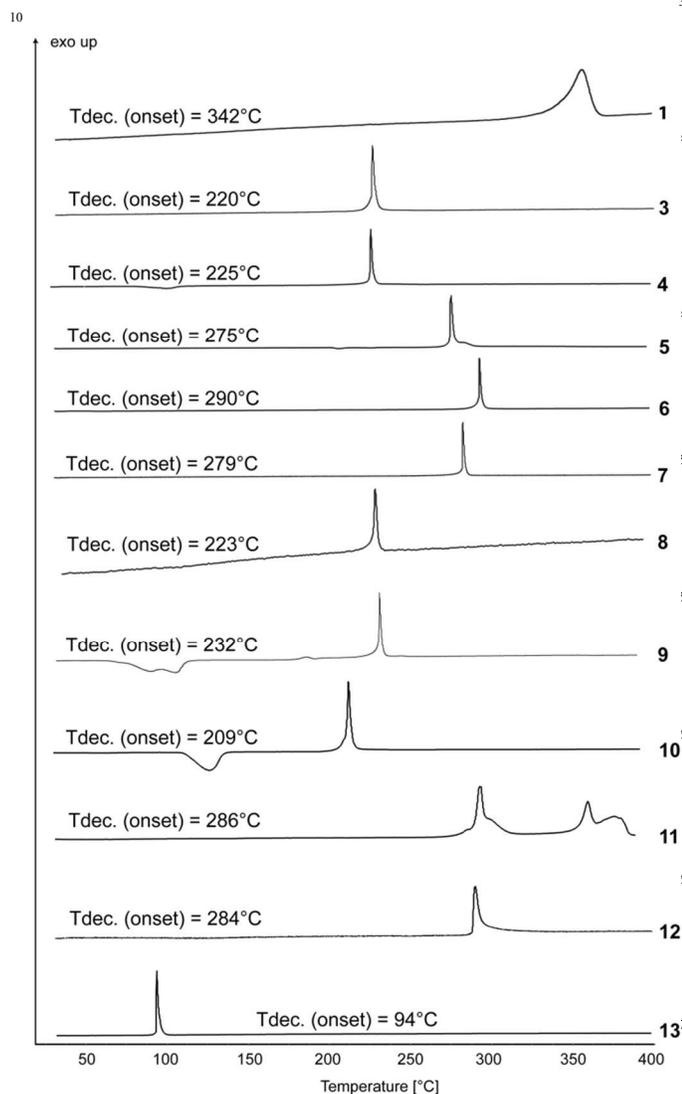

Figure 10. DTA plots of compounds **1** and **3–13** measured with a heating rate of 5 °C min^{-1}.

Compound **13** exhibits a sensitivity of 4 J. Compounds **4**, **10** and **12** are fairly insensitive with sensitivities >30 J. In comparison to previously reported nitrogen-rich salts of 1-methyl-5-nitrimino-tetrazole, an impact sensitivity of up to 35 J is very high, especially because the aminoguanidinium or triaminoguanidinium salts exhibit values in the range of 10 J.[25] The nitrate salt **5** (15 J), shows an moderate sensitivity towards friction. All compounds thus at least lie in the range (**2**, **3**, **8**, **11** and **13**) of RDX (7.5 J)[30], or reveal higher stabilities towards impact.

Except for compound **8** and **11**, the energetic salts as well as the neutral compound **1** are insensitive towards friction (360 N).

Noticeable is the friction insensitivity of the dinitramide compound **2**, since the previously reported nitrogen–rich salts, exemplary the triaminoguanidinium dinitramide (24 N)[28a] or ammonium dinitramide (72 N)[29], exhibit high sensitivities towards friction. In addition the friction insensitivity of the nitrotetrazolate–2N–oxide **3** exceeds the values reported for other nitrogen–rich nitrotetrazolate–2N–oxides, which reach from the guanidinium nitrotetrazolate–2N–oxide (252 N) to the hydroxylammonium salt with a friction sensitivity of 60 N, by far.[8c] The perchlorate **11** and nitroformate **13** have a slightly higher sensitivity towards friction stimuli (240 N and 160 N). Thus compounds **1–7** and **9–12** reveal much lower sensitivity towards friction than RDX (FS_{RDX} = 120 N).[30] The ESD measurements show that compounds **1–7** and **9–13** are less sensitive towards electrostatic discharge (**1**, **5**, **7**, **9**: 1.5 J, **2**, **3**, **13**: 0.8 J **12**: 0.75 J, **11**: 0.6 J, **10**: 0.5 J, **6**: 0.4 J, **4**: 0.3 J) than sensitive compound **8** (0.05 J) or RDX (0.2 J).

Energetic Performance

The values for the enthalpies of formation are calculated with the atomization method, using electronic energies (CBS-4M method) at room temperature (see supplementary information). The heats and energies of formation for compounds **1–3**, **5–8**, **11** and **13** are given in Table 3.

Calculation of the detonation parameters of **1–3**, **5–8**, **11** and **13** was performed with the program package EXPLO5 (version 6.02).[31] The program is based on the chemical equilibrium, steady-state model of detonation. It uses the Becker–Kistiakowsky–Wilson equation of state (BKW EOS) for gaseous detonation products and Cowan–Fickett's equation of state for solid carbon. For these calculations low temperature X-ray densities were converted to room temperature values with the equation $\rho_{298K} = \rho_T / (1+\alpha_V(298-T_0)$; $\alpha_V = 1.5 \ 10^{-4} \ K^{-1}$.[32] In order to verify this approximation, crystals of compound **2** have been measured at 100K, 173K and 298K (see SI). The measured X-ray density of 1.819 g cm^{-3} (298K) is virtually the same as the recalculated density of 1.826 g cm^{-3} (298K). The marginal influence on the calculated detonation performances is illustrated in Table 3.

The calculated detonation parameters are summarized in Table 3 and compared to the values calculated for **FOX-12** and **RDX**. The energetic performances of compounds **6–8**, **11** and **13** are discussed in detail in the Supporting Information.

Compared to the energetic salts, compound **1** reveals a fairly high heat of formation of 472 kJ mol^{-1}. The dinitramide **2** exhibits a heat of formation of 302 kJ mol^{-1}. Compared to **ADN** with a heat of formation of –150 kJ mol^{-1}, or hydroxylammonium dinitramide with a heat of formation of –34 kJ mol^{-1}, the calculated heat of formation of compound **2** is significantly higher.[13] Additionally in comparison to **RDX** and **FOX–12** with heats of formation of 70 kJ mol^{-1} and –355 kJ mol^{-1}, a higher value is obtained as well. Compound **3** comprises a highly positive heat of formation of 761 kJ mol^{-1}.

For neutral **1** a fairly high detonation velocity of 8944 m s^{-1} and a detonation pressure of 285 kbar was calculated. The highest detonation velocity of 9053 m s^{-1} within this work was calculated for dinitramide **2**. It is also higher than that of **RDX** (8861 m s^{-1}) and **FOX–12** (8323 m s^{-1}). When comparing the detonation pressures, compound **2** shows a value in the range of RDX (345 kbar) and a much higher value than **FOX–12** (265 kbar). Compared to **RDX**, compound **3** has a very similar detonation velocity of 8857 m s^{-1} and a slightly lower detonation pressure of 306 kbar. The corresponding hydroxylammonium salt has higher

detonation velocity (9499 m s^{-1}) and detonation pressure (410 kbar).[8c] The other reported nitrotetrazolate–2N–oxides show detonation parameters in the range of compound **3** (NH$_4$ NT2O p_{C-J} = 322 kbar, D = 8885 m s^{-1}) or exhibit lower values (G$^+$, AG$^+$, DAG$^+$, TAG$^+$ salts).[8c] The nitrate **5** has a detonation velocity of 8334 m s^{-1} and a detonation pressure of 260 kbar. The lowest detonation pressure (221 kbar) and velocity (8081 m s^{-1}) of the compounds discussed is exhibited by compound **7**.

A small scale reactivity test (SSRT, for a detail setup description see supporting information) was conducted to assess the explosive performance of **2** in comparison to **RDX** and **FOX–12**. From measuring the volumes of the dents (Table 4), it can be concluded that the small scale explosive performance of **2** is slightly lower than that of commonly used **RDX**, but exceeds that of **FOX–12** by far.

The toxicity to aquatic life was investigated using the luminescent marine bacterium *Vibrio fischeri* (for a detail setup description see SI).[33]

For the dinitramide **2** and **FOX-12** we observed EC$_{50}$ values of 3.78 g L^{-1} and 3.58 g L^{-1} after an incubation time of 30 min. With a value higher than 1.00 g L^{-1} a compound can be considered as non toxic. The toxicity test demonstrates the low toxicity of **2** and **FOX–12** compared to **RDX** (Table 4).

Table 4. Values for the SSRT and toxicity test of compound **2** compared to **FOX-12** and **RDX**

SSRT		
Compound	Weight [mg]	Dent [mg SiO$_2$]
2	524	772
FOX-12	503	579
RDX	504	858
Toxicity assessment:		
Compound	EC$_{50}$ (15 min)	EC$_{50}$ (30 min)
2	-	3.78
FOX-12	2.15	3.58
RDX	0.237	0.239

Spectroscopy

Compounds **1–13** were characterized by ^{1}H NMR and ^{13}C NMR spectroscopy. Compound **1** shows two broad signals at 5.91 and 5.81 ppm representing two –NH$_2$ groups each. These values match the chemical shifts already reported in literature (5.90 and

5.80 ppm).[10] Carbon resonances of poorly soluble **1** could only be observed in a ^{13}C NMR long-time measurement (pulse delay >2 s, > 8000 scans). The resulting spectrum shows two sharp peaks at 155.4 (C–NH$_2$) and 139.4 ppm (C–C).

The ^{1}H NMR spectra of compounds **2–5**, **8** and **11–13**, which all contain only N–connected protons, each reveals two similar broad signals with chemical shifts of 8.64–8.56 ppm and 6.16–6.08 ppm. With two broad signals at 8.10 and 6.17 ppm the energetic salt **6** shows chemical shifts, which are slightly shifted upfield compared to the signals of the bulk of the compounds. The proton signals of compound **7** and **9** are slightly shifted upfield to 7.65 and 6.00 ppm and 7.82 and 6.05 ppm respectively. In comparison compound **10**, which is the 1–methyl derivative of compound **9**, shows an even greater chemical shift upfield to 6.89 and 4.64 ppm.

The chemical shifts of the carbon–atoms of the cations in compound **2–13** are slightly shifted upfield compared to neutral compound **1**. The chemical shifts of all carbons in the cations of compounds **2–13** exhibit very sharp signals in a similar range. The carbon of the C–NH$_2$ group shows a chemical shift between 153.6 and 151.9 ppm, whereas the chemical shift of the C–C carbon lies between 138.5 and 137.7 ppm.

IR and Raman spectra for compounds **1–13** were measured and the frequencies were assigned according to commonly observed values in the literature.[5, 34]

In the IR–spectrum of compound **1** the stretching vibration of the N–H bond is observed between 3500 and 3300 cm^{-1}, whereas the deformation vibration shows a strong band at 1537 cm^{-1} in the IR spectrum and a very weak band at 1551 cm^{-1} in the Raman spectrum. The strongest band observed in the IR spectrum is the C=N stretch at 1626 cm^{-1}. Another characteristic band of the triazole–ring is observed at 1317 cm^{-1} representing the C–N stretch. These values are very similar to the ones reported for substituted 1,2,4–triazoles.[35] The vibration of the carbon–amine bond appears at 1085 cm^{-1} and the C–C vibration of the carbons linking the two rings together occurs at 1022 cm^{-1}. These bands can all be observed for the cations of compounds **2–13** at very similar values.

The ^{13}C NMR peaks as well as the IR and Raman bands of the anions all match the values of the literature and are discussed in detail in the supplementary information.

Table 3. Energetic Properties and detonation parameters of compounds **1–3**, **5–8**, **11** and **13** compared to RDX and FOX-12.

	1	2	3	5	6	7	8	11	13	RDX	FOX-12
Formula	C$_4$H$_8$N$_{10}$	C$_4$H$_{10}$N$_{16}$O$_8$	C$_6$H$_{10}$N$_{20}$O$_6$	C$_4$H$_{10}$N$_{12}$O$_6$	C$_{10}$H$_{10}$N$_{18}$O$_8$	C$_6$H$_{10}$N$_{18}$O$_2$	C$_6$H$_{10}$N$_{22}$O$_4$	C$_4$H$_{10}$N$_{10}$O$_8$Cl$_2$	C$_6$H$_{10}$N$_{16}$O$_{12}$	C$_3$H$_6$N$_6$O$_6$	C$_2$H$_7$N$_7$O$_5$
FW [g mol^{-1}]	196.17	410.22	458.11	322.20	510.30	366.26	454.29	397.09	498.24	222.12	209.12
IS [J][a]	40	5	6	15	40	40	3	5	4	7.5	30
FS [N][b]	360	360	360	360	360	360	10	240	160	120	350
ESD [J][c]	1.5	0.8	0.8	1.5	0.4	1.5	0.05	0.9	0.8	0.20	1.5
N [%][d]	71.40	54.63	61.13	52.17	49.41	68.84	67.83	35.27	44.98	37.84	46.89
Ω [%][e]	−97.87	−19.50	−38.40	−34.76	−53.30	−65.52	−45.79	−16.11	−16.06	−21.61	−19.13
$T_{dec.}$ [°C][f]	342	200	220	275	290	279	223	286	94	204	201
ρ [g cm^{-3}] (298K)[g]	1.68 (pyc.)	1.826 (1.819)[h]	1.799	1.746	1.844	1.655	1.745	1.870	1.837	1.806	1.754
$\Delta_f H°$ [kJ mol^{-1}][i]	472.0	301.5 (302.8)[h]	761.2	−153.2	20.9	597.4	1107.7	−23.1	173.4	70.3	−355.0
$\Delta_f U°$ [kJ kg^{-1}][j]	2520.3	837.7 (840.9)[h]	1758.3	−367.7	258.6	1733.7	2536.6	35.4	442.5	417.0	−1585.0
EXPLO V6.02 values:											
$-\Delta_E U°$ [kJ kg^{-1}][k]	3101	4955 (4956)[h]	4696	3871	3533	3262	4672	4589	5226	5845	3694
T_E [K][l]	2088	3407 (3422)[h]	3293	2790	2668	2446	3266	3492	3642	3810	2703
p_{C-J} [kbar][m]	258	338 (338)[h]	306	260	260	221	288	299	343	345	265
D [m s^{-1}][n]	8944	9053 (9022)[h]	8857	8334	8237	8081	8804	8290	8879	8861	8323
V_0 [L kg^{-1}][o]	812	843 (843)[h]	822	867	736	819	833	792	780	785	893

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 recalculated from low temperature X-ray densities ($\rho_{298K} = \rho_T / (1+\alpha_V(298-T_0))$; α_V = 1.5 10^{-4} K^{-1}); h in parenthesis values for the density obtained from the X-ray measurmnet at 298K; i calculated (CBS-4M) heat of formation; j calculated energy of formation; k energy of explosion; l explosion temperature; m detonation pressure; n detonation velocity; o assuming only gaseous products.

Journal of Materials Chemistry

FULL PAPER

Experimental Part

General methods and procedures as well as synthesis of **3–13** are described in the SI.

4,4',5,5'-Tetraamino-3,3'-bi-1,2,4-triazole (1)

4,4',5,5'-Tetraamino-3,3'-bi-1,2,4-triazole (**1**) was synthesized slightly modified according to the literature:[10] Phosphorus pentoxide (10 g, 70.4 mmol) was slowly dissolved in phosphoric acid (30 g, 306 mmol), which was preheated to 50 °C. A finely ground mixture of oxalic acid dihydrate (3.15 g, 25.0 mmol, 1.0 eq) and diaminoguanidine monohydrochloride (8.29 g, 66 mmol, 2.6 eq.) was slowly added to the preheated solution After complete addition, the viscous mixture was slowly heated to 120 °C and gas evolution of HCl was observed. The mixture was kept at 120 °C for 4 h and was then cooled to room temperature under stirring. 150 mL ice water was poured into the mixture and a white precipitate was formed. About 75 mL of 10 M NaOH was used to neutralize the reaction mixture, changing the color of the suspension from white to brown. The precipitate was filtered, washed repeatedly with water and air dried to obtain crude compound **1** as a brownish solid. Yield: 1.39 g, 7.09 mmol, 28%. For purification the crude product was recrystallized with hydrochloric acid or glacial acetic acid. Compound **1** (1000 mg, 5.10 mmol, 1.00 eq.) was added slowly to glacial acid. The mixture was heated until compound **1** completely dissolved. The mixture was removed from the heating bath and was left to cool to room temperature. After filtration and repeated washing with water the residue was dried in a nitrogen flow before drying the substance in oven at 100 °C over night. Then the solid was suspended in 50 mL water and basified with about 1 mL of 10 M NaOH. The suspension was filtered and the residue was air dried to receive pure compound **1** as a white solid. Yield: 696 mg, 3.55 mmol, 70%. DTA (5 °C min^{-1}) onset: 342 °C (dec.); IR (ATR, cm^{-1}): ν = 3782(vw), 3400(m), 3341(m), 3278(m), 3142(w), 2348(vw), 1626(vs), 1537(s), 1478(m), 1421(w), 1317(w), 1252(vw), 1232(vw), 1085(m), 1022(m), 987(vs), 935(m), 799(vw), 778(vw), 723(m), 678(vw), 664(vw); Raman (1064 nm, 300 mW, 25 °C, cm^{-1}): ν = 3258(4), 3171(3), 1592(100), 1551(11), 1510(4), 1393(4), 1289(7), 1087(10), 1034(6), 811(16), 712(6), 621(3), 374(3), 330(4), 268(4), 110(12), 93(7); ^{1}H NMR ([D$_6$]DMSO): δ = 5.91 (br s, 4H), 5.81 ppm (br s, 4H); ^{13}C NMR ([D$_6$]DMSO): δ = 155.4 (s, C–NH$_2$), 139.4 ppm (s, C–C) ; m/z (DEI$^+$): 196.2 (C$_4$H$_8$N$_{10}$); EA (C$_4$H$_8$N$_{10}$, 196.17): C 24.49, H 4.11, N 71.40; found: C 25.04, H 4.04, N 69.93; BAM impact: 40 J, BAM friction: 360 N, ESD: 1.5 J (at grain sizes: <100 μm).

4,4',5,5'-Tetraamino-3,3'-bi-1,2,4-triazolium dinitramide (2)

To a suspension of 4,4',5,5'-tetraamino-3,3'-bi-1,2,4-triazole (**1**) (392 mg, 2.00 mmol, 1.00 eq.) and ammonium dinitramide (496 mg, 4.00 mmol, 2.00 eq.) in water was added 1 mL 1 M hydrochloric acid. The mixture was heated until all components were dissolved and the mixture was left to crystallize over night. The product was received in form of slightly brownish crystals. Yield: 416 mg, 1.01 mmol, 51%. DTA (5 °C min^{-1}) onset: 200 °C (dec.); IR (ATR, cm^{-1}): ν = 3278(m), 3142(m), 3088(m), 2854(m), 1695(vs), 1602(m), 1596(m), 1554(m), 1516(s), 1470(m), 1417(m), 1352(m), 1339(m), 1306(m), 1258(m), 1172(s), 1082(w), 992(vs), 954(m), 790(m), 778(m), 706(w), 672(w), 672(w); Raman (1064 nm, 300 mW, 25 °C, cm^{-1}): ν = 3176(1), 1695(2), 1642(100), 1560(2), 1532(1), 1436(6), 1377(1), 1339(2), 1288(14), 1124(2), 1079(7), 1022(2), 805(20), 713(7), 602(6), 492(1), 415(1), 387(2), 328(3), 286(2), 264(2), 175(3), 150(7), 150(7), 121(12), 90(11); ^{1}H NMR ([D$_6$]DMSO): δ = 8.56 (br s, 4 H), 6.08 ppm (br s, 6 H); ^{13}C NMR ([D$_6$]DMSO): δ = 152.0 (s, C–NH$_2$), 137.8 ppm (s, C–C); m/z (FAB$^-$): 106.0 (N$_3$O$_4^-$), m/z (FAB$^+$): 197.0 (C$_4$H$_9$N$_{10}^+$); EA (C$_4$H$_{10}$N$_{16}$O$_8$, 410.22): C 11.71, H 2.46, N 54.63; found: C 12.04, H 2.55, N 53.96; BAM impact: 5 J, BAM friction: 360 N, ESD: 0.8 J (at grain sizes <100 μm).

Conclusions

The aromatic, nitrogen-rich 4,4',5,5'-tetraamino-3,3'-bi-1,2,4-triazole (**1**) was synthesized starting from commercially available diaminoguanidine hydrochloride and oxalic acid in poly phosphoric acid. **1** shows an amazing thermal stability in its neutral (342 °C) as well as protonated form. Through simple anion metathesis a number of new energetic salts (**2–13**) were obtained and characterized in detail. These energetic ionic derivatives were extensively characterized for their physico-chemical properties (e.g. stability, sensitivity, compatibility) and detonation parameters based on computed enthalpies of formation were calculated with the EXPLO5 computer code. The dinitramide salt **2** has a heat of formation of 301.5 kJ mol^{-1}, a detonation pressure of 338 kbar and a detonation velocity of 9053 m s^{-1}, which are remarkably high compared to other nitrogen-rich dinitramide salts as **FOX–12**. Moreover, dinitramide **2** was measured to be less toxic tan **RDX** in aqueous media. Fundamental compatibility tests demonstrate the compatibility of **2** with 2,4,6-trinitrotoluene (TNT)**.**
The high decomposition temperature (200 °C, determined by DTA at a heating rate of 5 °C min^{-1}) of dinitramide **2** is superior over nearly all dinitramides described in literature so far. The great thermal stability of the described energetic salts demonstrate the great value of **1** over other nitrogen rich cations as guanidine, aminoguanidine or triaminoguanidine in future synthesis of new ionic energetic materials.

Acknowledgements

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