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Asymmetrically substituted 5,5′-bistriazoles – nitrogen-rich materials with various energetic functionalities†

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In this contribution the synthesis and full structural and spectroscopic characterization of three asymmetrically substituted bis-1,2,4-triazoles, along with different energetic moieties like amino, nitro, nitrimino and azido moieties, is presented. Additionally, selected nitrogen-rich ionic derivatives have been prepared and characterized. This comparative study on the influence of these energetic moieties on structural and energetic properties constitutes a complete characterization including IR, Raman and multinuclear NMR spectroscopy. Single crystal X-ray crystallographic measurements were performed and provide insight into structural characteristics as well as inter- and intramolecular interactions. The standard enthalpies of formation were calculated for all compounds at the CBS-4M level of theory, revealing highly positive heats of formation for all compounds. The detonation parameters were calculated using the EXPLO5 program and compared to the common secondary explosive RDX as well as recently published symmetric bistriazoles. As expected, the measured sensitivities to mechanical stimuli and decomposition temperatures strongly depend on the energetic moiety of the triazole ring. All compounds were characterized in terms of sensitivities (impact, friction, electrostatic) and thermal stabilities, the ionic derivatives were found to be thermally stable, insensitive compounds.

Introduction

In the past, the chemistry of explosives has been largely guided by intuition, experience and testing. Nowadays, a better understanding of the basic principles and relationships which are necessary to predict the properties of an energetic material leads to a more rational design of novel compounds with tailored properties. The academic research mainly focuses on the work with energetic systems to determine factors affecting stability and performance and to bring new strategies into the design of energetic materials.

The main challenge is the desired combination of a large energy content with a maximum possible chemical stability to ensure safe synthesis and handling. Modern heterocyclic energetic compounds derive their energy not only from the oxidation of their carbon backbone, but additionally from ring or cage strain, high-nitrogen content and high heats of formation.[1–6] Nitrogen-rich heterocycles are promising compounds that fulfill many requirements in the challenging field of energetic materials research.[5,7–11] A prominent family of novel high-energy-density materials (HEDMs) are azole-based compounds, since they are generally highly endothermic with high densities and low sensitivities towards outer stimuli. Owing to the high positive heats of formation resulting from the large number of N–N and C–N bonds[12] and the high level of environmental compatibility, triazole and tetrazole compounds have been studied over the last couple of years with growing interest.

Many energetic compounds that combine the triazole backbone with energetic moieties have been synthesized over the last few decades. Examples for these kinds of molecules are 5-amino-3-nitro-1,2,4-triazole (ANTA),[13] 2-azido-5-nitramino-1,2,4-triazole[14] or trinitromethyl-substituted triazoles.[15] Bridged compounds like 5,5′-dinitro-3,3′-azo-1,2,4-triazole (DNAT)[16] or the analogue nitrimino-compound (DNAAT)[17] have already been investigated and show remarkably high decomposition temperatures and excellent energetic properties. Recently investigated symmetrically substituted bistriazoles connected *via* C–C bonds show promising properties as energetic materials.[18–27]

The focus of this contribution is on the full structural and spectroscopic characterization of three different asymmetrically substituted bis-1,2,4-triazoles along with energetic moieties like amino, nitro, nitramino and azido groups. We present a comparative study on the influence of those energetic moieties on structural and energetic properties in comparison to literature

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known symmetric 5-5′-bistriazoles. The potential application of the synthesized compounds as energetic materials will be studied and evaluated using the experimentally obtained values for the thermal decomposition, the sensitivity data, as well as the calculated performance characteristics.

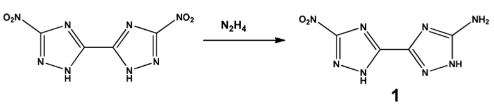
Results and discussion

Synthesis

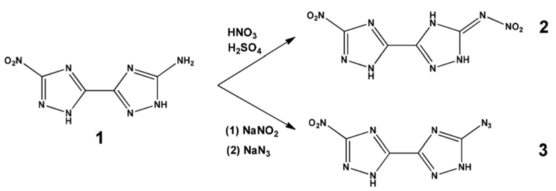
3,3′-Diamino-5,5′-bis(1*H*-1,2,4-triazole) and 3,3′-dinitro-5,5′-bis-(1*H*-1,2,4-triazole) were synthesized according to the literature.[27] The synthesis is based on the reaction of oxalic acid and aminoguanidinium bicarbonate in concentrated hydrochloric acid and subsequent cyclisation in basic media. Oxidation of 3,3′-diamino-5,5′-bis(1*H*-1,2,4-triazole) was accomplished by the well known Sandmeyer reaction *via* diazotization in sulfuric acid and subsequent reaction with sodium nitrite. As shown in Scheme 1, one nitro group of 3,3′-dinitro-5,5′-bis(1*H*-1,2,4-triazole) was successfully reduced to 5-(5-amino-1*H*-1,2,4-triazol-3-yl)-3-nitro-1*H*-1,2,4-triazole (**1**), similar to the selective reduction of the mono-heterocycle-3,5-dinitro-1*H*-1,2,4-triazole.[13]

The amine group of 5-(5-amino-1*H*-1,2,4-triazol-3-yl)-3-nitro-1*H*-1,2,4-triazole (**1**) was further converted to a nitrimino and an azido moiety (Scheme 2). The treatment of **1** with a mixture of sulfuric acid–nitric acid (6 : 1) leads to the formation of 5-(5-nitrimino-1,3*H*-1,2,4-triazol-3-yl)-3-nitro-1*H*-1,2,4-triazole (NNBT, **2**). The azido compound 5-(5-azido-1*H*-1,2,4-triazol-3-yl)-3-nitro-1*H*-1,2,4-triazole (AzNBT, **3**) was synthesized *via* diazotization in sulfuric acid and subsequent reaction with an excess of sodium azide.

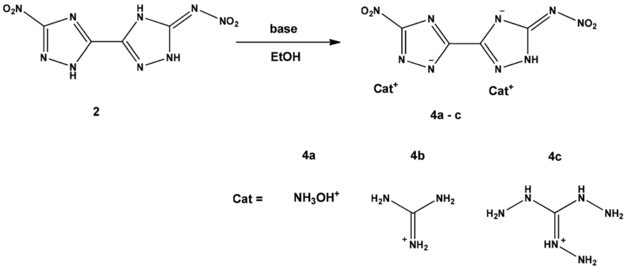
Additionally, selected nitrogen-rich ionic derivatives based on compound **2** have been prepared in order to increase both performance and stability. The formation of the nitrogen-rich salts (**4a–c**) is straightforward. An ethanolic solution of compound **2** was prepared and two equivalents of the corresponding nitrogen-rich bases were added (Scheme 3). Due to the high solubility of compound **2** and the low solubility of compounds **4a–c** in ethanol, all ionic compounds could be isolated in excellent yields and high purity.



Scheme 1 Synthesis of 5-(5-amino-1*H*-1,2,4-triazol-3-yl)-3-nitro-1*H*-1,2,4-triazole (ANBT, **1**).



Scheme 2 Synthesis of 5-(5-nitrimino-1,3*H*-1,2,4-triazol-3-yl)-3-nitro-1*H*-1,2,4-triazole (NNBT, **2**) and 5-(5-azido-1*H*-1,2,4-triazol-3-yl)-3-nitro-1*H*-1,2,4-triazole (AzNBT, **3**).



Scheme 3 Synthetic pathway towards the formation of nitrogen-rich salts of **2** using the corresponding bases.

All energetic compounds were fully characterized by IR and Raman as well as multinuclear NMR spectroscopy, mass spectrometry and differential scanning calorimetry. Selected compounds were additionally characterized by low temperature single crystal X-ray diffractometry.

Spectroscopy characterization

Vibrational spectroscopy. IR and Raman spectra of all compounds were recorded and the frequencies were assigned according to the literature.[28,29]

The Raman spectrum of compound **1** is dominated by the deformation mode of the amino groups at 1629 cm^{-1}. The valence stretching mode of the N–H bond is observed in the range of 3224–3402 cm^{-1}. The vibrational frequencies for the asymmetric stretching mode of the nitro group are observed at 1397 cm^{-1} (IR) and 1434 cm^{-1} (Raman). The symmetric stretching modes are located at lower energy at 1308 cm^{-1} (IR) and 1396 cm^{-1} (Raman). After nitration of the amino group, the deformation modes of the amine group disappear. Instead, the asymmetric valence stretching mode of the nitrimino moiety of compound **2** can be observed at 1581 cm^{-1}. In the case of compound **3**, a signal for the asymmetric stretching modes of the azide group can be observed at 2160 cm^{-1} in the Raman spectrum and at 2143 cm^{-1} in the IR spectrum. The vibrational frequencies for the ν_{as} stretching mode of the nitro group are as well observed at 1540 cm^{-1} (IR) and 1505 cm^{-1} (Raman), and the ν_s stretching modes are located at 1393 cm^{-1} (IR) and 1389 cm^{-1} (Raman).

The nitrogen-rich salts **4a–c** show additional absorption bands in the region between 3100 cm^{-1} and 3500 cm^{-1} as expected for N–H valence stretching modes of the cations (hydroxylammonium and guanidine derivatives).

Multinuclear NMR spectroscopy. All compounds were investigated using ^1H, ^{13}C and ^{14}N NMR spectroscopy. Additionally, ^{15}N NMR spectra were recorded for compounds **1–3**.

All compounds show four signals in the ^{13}C NMR spectrum for the 1,2,4-triazole carbon atoms in the expected range. One singlet for the bridging carbon atom can be found at chemical shifts of 142.9 (**2**) to 150.6 ppm (**1**). The signal of the carbon atom connected to the variable energetic moieties is shifted in all cases to lower fields in comparison to compound **1** (153.1

Table 1 NMR signals of compounds **2**, **3a–f** in DMSO-d$_6$

	δ [ppm]				
	$^{13}C\{^1H\}$				
	C–NO$_2$	C–X^a	C–C	$^{14}N\{^1H\}$	^1H
1	163.5	158.3	150.6, 149.1	−23	6.41
2	163.1	153.1	146.6, 142.9	−23	12.39
3	163.0	155.5	147.3, 146.8	−30, −146	6.11

^{a} X = NH$_2$ (1), =N–NO$_2$ (2), N$_3$ (3).

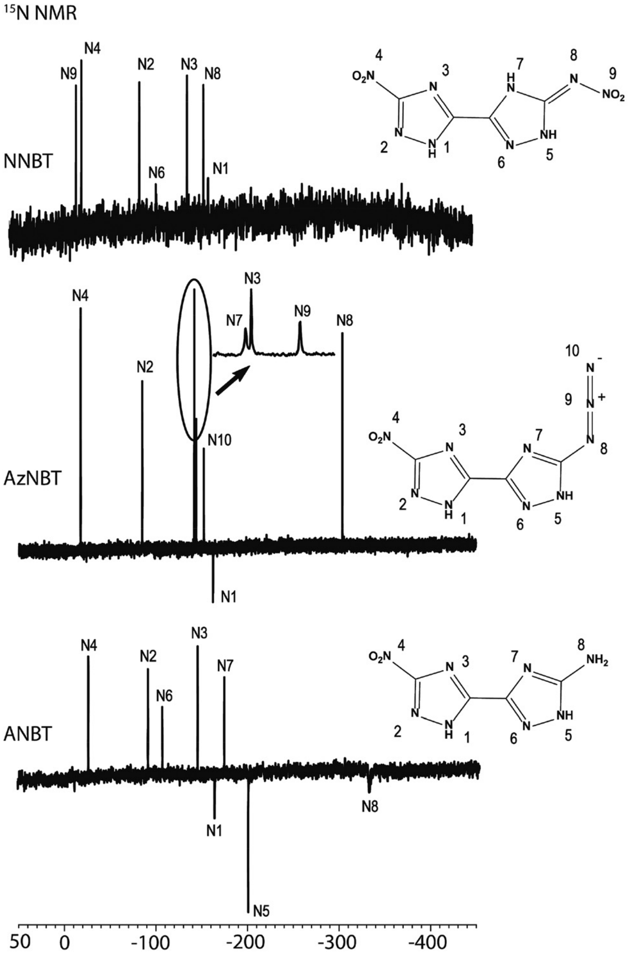


Fig. 1 ^{15}N NMR spectra of 5-(5-nitrimino-1,3*H*-1,2,4-triazol-3-yl)-3-nitro-1*H*-1,2,4-triazole (**2**, top), 5-(5-azido-1*H*-1,2,4-triazol-3-yl)-3-nitro-1*H*-1,2,4-triazole (**3**, middle) and 5-(5-amino-1*H*-1,2,4-triazol-3-yl)-3-nitro-1*H*-1,2,4-triazole (**1**, bottom) recorded in DMSO-d$_6$; *x*-axis represents the chemical shift δ in ppm.

(**2**) to 155.5 ppm (**3**)), the signal for the carbon atom connected to the nitro group remains almost constant in all cases similar to the symmetric 3,3′-dinitro-5,5′-bis(1*H*-1,2,4-triazole).[27]

In the ^{14}N NMR spectra, the nitro group of compounds **1–3** can be identified by a broad singlet at −23 (**1**, **2**) to −30 ppm (**3**). The azido moiety in compound **3** can be observed as a broad singlet at −146 ppm in the ^{14}N NMR spectrum. Well resolved resonances could only be observed in the ^{15}N NMR spectrum (as discussed below). The NMR signals of all compounds are summarized in Table 1.

The deprotonation of compound **2** with nitrogen-rich bases shifts the signals in the $^{13}C\{^1H\}$ NMR spectra to lower fields. The carbon atom connected to the nitro group is located in the range of 164.1–165.6 ppm, whereas the carbon atom connected to the nitrimino moiety can be found at 157.3–159.2 ppm. The nitro group signal in the $^{14}N\{^1H\}$ NMR spectra could be observed for all ionic compounds at −17 ppm. The $^{14}N\{^1H\}$ NMR spectra of **3b–c** additionally show the signal of the corresponding cation at −359 ppm.

The assignments in the ^{15}N NMR spectra are based on the comparison with the symmetric bistriazoles[27] and additional theoretical calculations using Gaussian 09 (MPW1PW91/aug-cc-pVDZ).[30] In all cases, four well resolved resonances are observed in the ^{15}N NMR spectrum for the four nitrogen atoms of the nitrotriazole moiety in the expected range (Fig. 1). In the case of compound **1**, the signals of the amino-triazole moiety are located at −106.5 ppm (N6), −173.8 ppm (N7), −199.7 ppm (N5) and −330.9 ppm (N8). The two signals of the nitrogen atoms N5 and N6 in the spectrum of compound **3** could not be observed, as it is often the case for 5-azidotriazoles due to a fast proton exchange.[31] All other signals of the azido-triazole moiety could be observed in the same range compared to 3,3′-diazido-5,5′-bis(1*H*-1,2,4-triazole).[27] The three signals of the azido moiety are well resolved and can be found in the expected range with N4 being shifted to the highest field with a chemical shift of −295.4 ppm. Compound **2** exhibits only the signals of the nitrogen atoms N6 (−108.4 ppm) and N8 (−159.7 ppm) of the triazole ring as well as the additional nitro group (N9, −22.1 ppm). Similar to compound **3**, the signals for N5 and N7 are not visible.

Single crystal X-ray structure analysis

Single crystal X-ray diffraction studies were undertaken for compounds **2** and **3**, both compounds were recrystallized from water to obtain crystals suitable for X-ray analysis. In the following, the structural characteristics of these compounds will be discussed in detail in comparison to the recently published symmetric bistriazoles.[27]

5-(5-Nitrimino-1,3*H*-1,2,4-triazol-3-yl)-3-nitro-1*H*-1,2,4-triazole (**2**) crystallizes as tetrahydrate in the triclinic space group $P\bar{1}$ with a cell volume of 629.3(2) Å^3 and two molecular moieties in the unit cell. The calculated density at 173 K is 1.653 g cm^{-3} and hence well below the corresponding symmetric dinitro- (1.902 Å^3)[27] and dinitrimino (1.772 Å^3)[23] compound. As expected, the bistriazole moiety shows a completely planar assembly due to the electron delocalization in the molecule, the nitrimino moiety is pointing towards the nitrogen atom N5 and participates in an intramolecular hydrogen bond N5–H5⋯O3 with a D⋯A length of 2.619(3) Å and a D–H⋯A angle of 103(2)°. The asymmetric unit of compound **2** together with the atom labeling is presented in Fig. 2.

The structure is built up by several intermolecular hydrogen bonds towards the surrounding water molecules. As shown in Fig. 3, the dominating structures are infinite chains along the

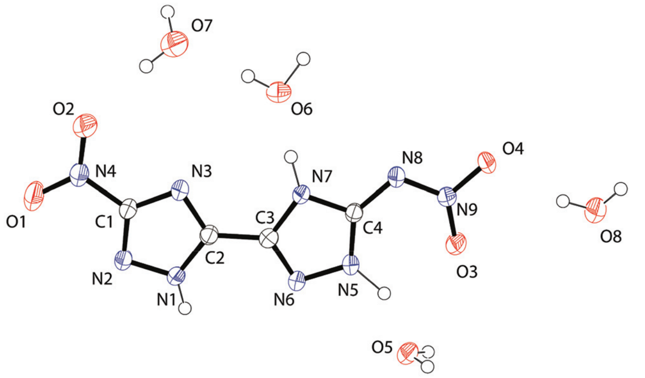


Fig. 2 Asymmetric unit within the crystal structure of **2**. Thermal ellipsoids are set to 50% probability; selected bond lengths [Å]: N7–C4 1.360(3), N7–C3 1.364(3), N7–H7 0.97(4), O4–N9 1.273(3), N3–C2 1.320(3), N3–C1 1.350(3), N2–C1 1.313(3), N2–N1 1.348(3), N1–C2 1.347(3), N1–H1 0.85(3), N8–N9 1.324(3), N8–C4 1.356(3), N9–O3 1.232(3), N6–C3 1.300(3), N6–N5 1.378(3), C4–N5 1.333(3), C2–C3 1.452(4), O2–N4 1.228(3), N5–H5 1.10(3), C1–N4 1.441(4), O1–N4 1.234(3).

b-axis. The chains are connected by water molecules to a two dimensional network in the *bc*-plane, the layers are stacked above each other along the *a*-axis. The two dimensional network built up by strong hydrogen bonds is displayed in Fig. 3 (Table 2).

The azido-compound **3** also crystallizes in the triclinic space group $P\bar{1}$ with a cell volume of 1013.55(18) $Å^3$ and two molecular moieties in the asymmetric unit, the calculated density for the dihydrate is 1.692 g cm^{-3}. As shown in Fig. 4, the proton is located at the nitrogen atom N5 next to the azido group and not next to the C–C bond as is the case for the nitrotriazole. Both heterocycles are now twisted by 180° around the C2–C3 bond, the three nitrogen atoms of the azido group exhibit a slightly bent arrangement with an N_8–N_9–N_{10} angle of 170.4(3)°.

The crystal structure of compound **3** is built up by the formation of pairs *via* the strong hydrogen bond including oxygen atoms O5 and O7 of the water molecules. As shown in Table 3, the D–H⋯A angle is close to 180° and the D⋯A length is considerably shorter than the sum of van der Waals radii ($r_w(O) + r_w(N) = 3.07$ Å).[32] The pairs of AzNBT molecules are further connected to a two dimensional network by several hydrogen bonds towards the surrounding water molecules (Table 3). The azido moieties do not participate in any hydrogen bond but are connected *via* a short contact N_{10}⋯N_{20} (distance d = 3.011(4) Å) towards each other and towards the oxygen atom O3 of the nitro group (N_{20}⋯O_3, distance d = 2.903(3) Å) (Fig. 5).

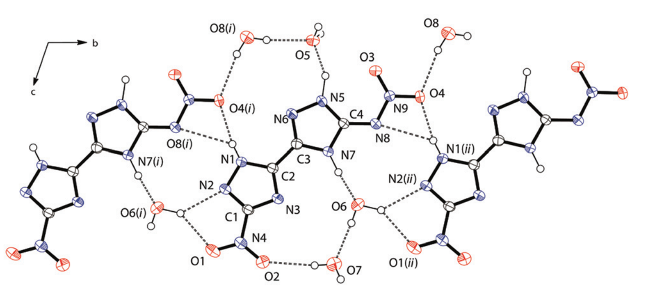


Fig. 3 Hydrogen bonding scheme in the crystal structure of **2** forming chains along the *b*-axis. Thermal ellipsoids are set to 50% probability. Symmetry operators: (i) *x*, −1 + *y*, *z*; (ii) *x*, 1 + *y*, *z*.

Table 2 Hydrogen bonds present in the crystal structure of **2**

D–H⋯A	d (D–H) [Å]	d (H⋯A) [Å]	d (D–H⋯A) [Å]	<(D–H⋯A) [°]
N1–H1⋯$O4^i$	0.86(3)	1.94(4)	2.786(3)	168(3)
N1–H1⋯$O8^i$	0.86(3)	2.54(4)	3.189(4)	134(3)
N5–H5⋯$O5^i$	1.10(4)	1.62(4)	2.647(3)	152(3)
N7–H7⋯O6	0.98(4)	1.61(4)	2.583(3)	174(3)
O5–H5a⋯O7	0.84(4)	2.07(4)	2.835(4)	151(4)
O5–H5b⋯O8	0.88(5)	1.95(5)	2.807(3)	167(5)
O6–H6a⋯O7	0.84(2)	1.91(2)	2.746(3)	176(3)
O6–H6b⋯$O1^{ii}$	1.02(3)	2.10(3)	2.988(4)	144(2)
O6–H6b⋯$N2^{ii}$	1.02(3)	2.17(3)	3.008(4)	138(2)
O7–H7a⋯$O8^{iii}$	0.84(6)	1.96(6)	2.785(3)	167(6)
O7–H7b⋯O2	0.84(3)	2.23(3)	3.036(4)	160(5)
O8–H8a⋯O4	0.84(3)	2.11(3)	2.942(3)	169(4)
$O8^i$–H8b⋯O5	0.85(6)	1.97(6)	2.809(4)	167(6)

Symmetry operators: (i) x, $-1 + y$, z; (ii) x, $1 + y$, z; (iii) $1 - x$, $1 - y$, $-z$.

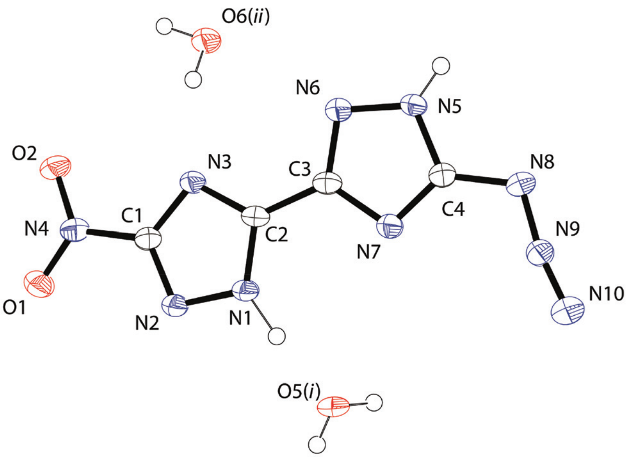


Fig. 4 Crystal structure of **3**. Thermal ellipsoids are set to 50% probability; symmetry operators: (i) 1 − *x*, 1 − *y*, −*z*; (ii) −*x*, 1 − *y*, 1 − *z*; selected bond lengths [Å]: O1–N4 1.220(3), O2–N4 1.238(3), N1–C2 1.350(4), N1–N2 1.356(3), N1–H1 1.01(3), N2–C1 1.325(4), N3–C1 1.335(4), N3–C2 1.339(4), N4–C1 1.451(4), N5–C4 1.353(4), N5–N6 1.354(4), N5–H5 0.84(4), N6–C3 1.332(4), N7–C4 1.313(4), N7–C3 1.368(4), N8–N9 1.255(4), N8–C4 1.398(4), N9–N10 1.129(3), C2–C3 1.451(4).

Physicochemical properties: heats of formation, detonation parameters and thermal stabilities

The heats of formation of **1–3** and **4a–c** have been calculated on the CBS-4M level of theory using the atomization energy method and utilizing experimental data (for further details and results refer to the ESI†). All compounds show highly endothermic enthalpies of formation with 267 kJ mol^{-1} (**1**), 360 kJ mol^{-1} (**2**) and 635 kJ mol^{-1} (**3**), all by far outperforming RDX (85 kJ mol^{-1}). The enthalpies of the ionic derivatives **4a**

Table 3 Hydrogen bonds present in the crystal structure of **3**

D–H···A	*d* (D–H) [Å]	*d* (H···A) [Å]	*d* (D–H···A) [Å]	<(D–H···A) [°]
$N1^{i}$–H1···$O5^{ii}$	1.01(4)	1.62(4)	2.631(3)	175(3)
$N5^{v}$–H5···$O8^{i}$	0.85(4)	2.08(3)	2.842(3)	149(3)
N11–H11···$O7^{iii}$	0.94(4)	1.70(4)	2.627(4)	166(3)
N15–H15···$N6^{v}$	0.89(4)	2.41(4)	3.048(4)	129(3)
N15–H15···$O6^{iv}$	0.89(4)	2.21(4)	2.906(3)	135(3)
$O5^{ii}$–H5b···N12	0.78(5)	2.27(5)	3.025(3)	165(5)
$O6^{iv}$–H6a···$N3^{v}$	0.83(4)	2.07(4)	2.871(3)	163(4)
$O7^{iii}$–H7a···$N2^{i}$	0.85(4)	2.12(3)	2.945(3)	162(3)
O8–H8a···N13	0.81(5)	2.03(5)	2.796(3)	157(4)

Symmetry operators: (i) *x*, *y*, 1 + *z*, (ii) 1 − *x*, 1 − *y*, 1 − *z*, (iii) −*x*, 1 − *y*, 1 − *z*, (iv) −*x*, −*y*, 1 − *z*, (v) *x*, −1 + *y*, *z*, (vi) 1 + *x*, *y*, *z*.

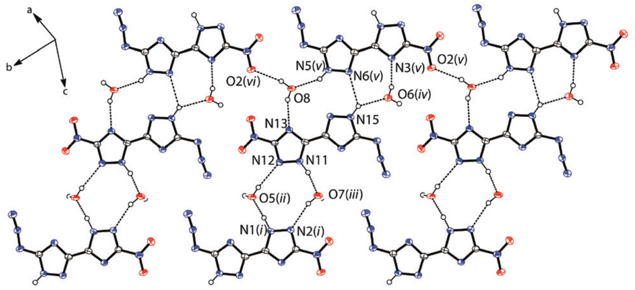


Fig. 5 Hydrogen bonding scheme in the crystal structure of **3**; thermal ellipsoids are set to 50% probability. Symmetry operators: (i) *x*, *y*, 1 + *z*; (ii) 1 − *x*, 1 − *y*, 1 − *z*, (iii) −*x*, 1 − *y*, 1 − *z*, (iv) −*x*, −*y*, 1 − *z*, (v) *x*, −1 + *y*, *z*, (vi) 1 + *x*, *y*, *z*.

and **4b** are in the same range (243 kJ mol^{-1} (**4a**), 129 kJ mol^{-1} (**4b**)), the very high nitrogen content of compound **4c** (65.5%) leads to the highest value of 834 kJ mol^{-1}. To estimate the detonation performances of the prepared compounds selected key parameters were calculated with EXPLO5 (version 5.05)[33] and compared to RDX. The calculated detonation parameters using experimentally determined densities (gas pycnometry at 25 °C with dried compounds) and heats of formation are summarized in Table 4.

The starting material 5-(5-amino-1*H*-1,2,4-triazol-3-yl)-3-nitro-1*H*-1,2,4-triazole (**1**) is insensitive towards friction and impact and shows a decomposition temperature of 255 °C similar to the precursor 3,3′-dinitro-5,5′-bis(1*H*-1,2,4-triazole) (251 °C).[27] As shown in Fig. 6, the introduction of energetic moieties dramatically decreases the thermal stability to 150 °C (**2**) and 181 °C (**3**). In comparison to the symmetric bistriazole compounds, the decomposition temperatures of all compounds are significantly lower, emphasizing the unique stability of bistriazoles.

The sensitivities towards impact (8 J) were found to be in the range of RDX, surprisingly higher in comparison to the symmetric nitrimino- and azido-triazoles. The same trend could be observed for the friction sensitivity, which was found to be very low (360 N). Again, the symmetrically substituted bistriazoles are far more sensitive. Both compounds **2** and **3** show lower detonation velocities and pressures than RDX, although all have higher heats of formation and comparable densities. The calculated detonation velocities of both compounds (7925 ms^{-1} (**2**), 7823 ms^{-1} (**3**)) are in the same range and well below the commonly used explosive RDX. In contrast to compound **2**, the ionic derivatives **4a–c** are insensitive towards friction and impact, only the hydroxylammonium salt is slightly sensitive towards impact (15 J).

As expected, the combination with nitrogen-rich cations increases both thermal stability and performance (Fig. 7). The ionic derivatives show higher decomposition temperatures (174 °C (**4a**), 230 °C (**4b**), 193 °C (**4c**)) and enhanced detonation parameters. The detonation velocities were calculated in the range of 7611 m s^{-1} (**4b**) to 8707 m s^{-1} (**4c**). The best

Table 4 Physico-chemical properties of compounds **1–3** and **4a–c** in comparison to hexogen (RDX)

Formula	ANBT (**1**) $C_4H_4N_8O_2$	NNBT (**2**) $C_4H_3N_9O_4$	AzNBT (**3**) $C_4H_2N_{10}O_2$	Hx- NNBT (**4a**) $C_4H_9N_{11}O_6$	G- NNBT (**4b**) $C_6H_{13}N_{15}O_4$	TAG- NNBT (**4c**) $C_6H_{19}N_{21}O_4$	RDX[n] $C_3H_6N_6O_6$
Molecular mass [g mol^{-1}]	196.1	241.1	222.1	307.2	359.3	449.4	222.1
Impact sensitivity[a] [J]	40	8	8	15	40	40	7
Friction sensitivity[b] [N]	360	360	360	360	360	360	120
ESD-test [J]	1.5	0.5	0.3	0.25	0.5	0.35	—
N[c] [%]	57.1	45.5	63.1	50.2	58.5	65.5	37.8
Ω[d] [%]	−65.3	−36.4	−50.4	−33.8	−64.5	−62.3	−21.6
$T_{dec.}$[e] [°C]	255	150	181	174	230	193	210
ρ[f] [g cm^{-3}]	1.61	1.70	1.68	1.80	1.75	1.75	1.80
$\Delta_f H_m°$[g] [kJ mol^{-1}]	267	360	635	243	129	834	85
$\Delta_f U°$[h] [kJ kg^{-1}]	1451	1577	2934	896	469	1976	417
EXPLO5 values: V5.05							
$-\Delta_E U°$[i] [kJ kg^{-1}]	3853	4965	4798	5287	3332	4432	6125
T_E[j] [K]	3061	3967	3880	3699	2542	2971	4236
$p_{C\text{-}J}$[k] [kbar]	194	261	246	326	242	303	349
$V_{Det.}$[l] [m s^{-1}]	7216	7925	7823	8706	7911	8707	8748
Gas vol.[m] [L kg^{-1}]	684	678	663	778	770	817	739

[a] BAM drop hammer. [b] BAM friction tester. [c] Nitrogen content. [d] Oxygen balance. [e] Temperature of decomposition by DSC (*β* = 5 °C, onset values). [f] Density values derived from gas-pycnometer measurements of anhydrous compounds at 25 °C. [g] Molar enthalpy of formation. [h] Energy of formation. [i] Energy of explosion. [j] Explosion temperature. [k] Detonation pressure. [l] Detonation velocity. [m] Assuming only gaseous products. [n] Values based on ref. 34 and the EXPLO5.5 database.

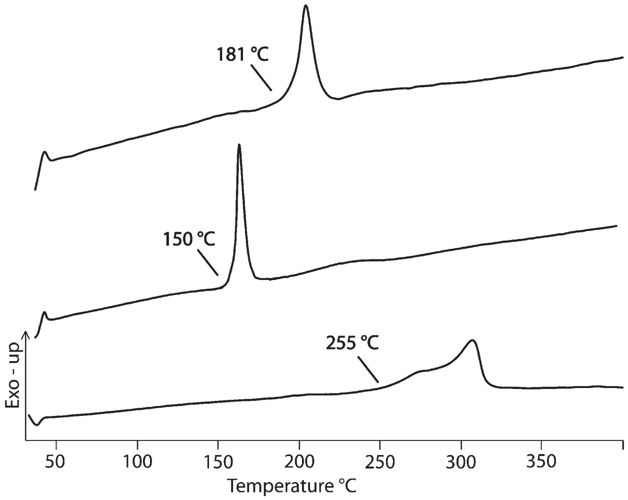


Fig. 6 DSC plots of ANBT (**1**), NNBT (**2**) and AzNBT (**3**); DSC plots were recorded with a heating rate of 5 °C min^{-1}.

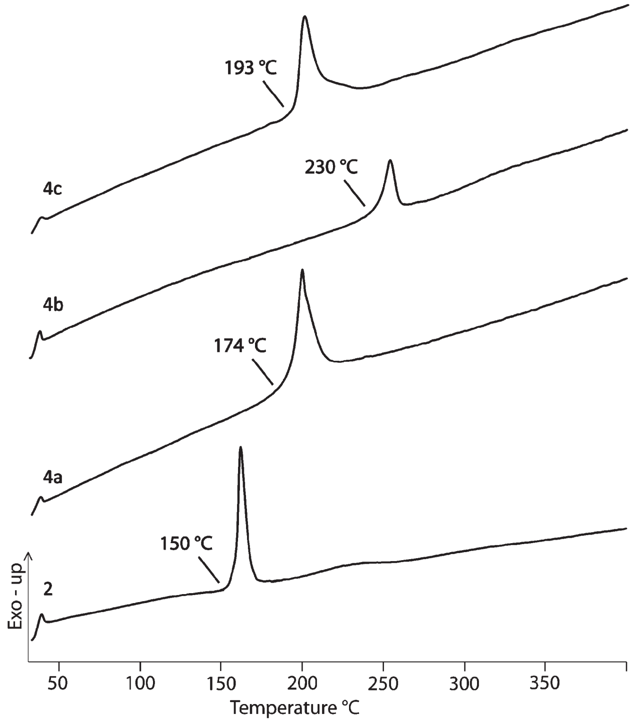


Fig. 7 DSC plots of NNBT (**2**) and ionic derivatives **4a–c**; DSC plots were recorded with a heating rate of 5 °C min^{-1}.

performances were calculated for the triaminoguanidinium salt (**4c**) with a detonation velocity of 8707 m s^{-1} and the hydroxylammonium salt (**3a**) with a detonation velocity of 8706 m s^{-1}, which is in the same range compared to RDX. Taking into account the high nitrogen content (50.2% (**4a**), 58.5% (**4b**), 65.5% (**4c**)), those compounds could be of interest as secondary explosive or burn rate modifiers.

Conclusions

The starting material 3,3′-dinitro-5,5′-bis(1*H*-1,2,4-triazole) was successfully reduced to 5-(5-amino-1*H*-1,2,4-triazol-3-yl)-3-nitro-1*H*-1,2,4-triazole (**1**). The amine group of **1** was further converted to energetic moieties (nitrimino (**2**) and azido(**3**)), which leads to the previously unknown asymmetric energetic bistriazole compounds. All compounds have been fully characterized by means of vibrational and multinuclear NMR spectroscopy, mass spectrometry and differential scanning calorimetry. Single crystal X-ray measurements were accomplished for compounds **2** and **3** and provide insight into structural characteristics as well as inter- and intramolecular interactions. Regarding the stability values and energetic parameters, the nitrimino compound (**2**) and the azido compound (**3**) are sensitive towards impact sensitivity (8 J) but insensitive towards friction (360 N). With detonation velocities below 8000 ms^{-1}, compounds **2** and **3** are able to compete with commonly used TNT, however, the performance data for RDX are not reached. Energetic ionic compounds were synthesized from **2** using nitrogen-rich cations, all reactions were carried out using the free bases or their corresponding carbonates. All energetic, ionic compounds (**4a–c**) were characterized by the same techniques as described for the uncharged compounds. All ionic compounds reveal positive heats of formation in the range of 129 kJ mol^{-1} (**4b**) to 834 kJ mol^{-1} (**4c**). The most interesting compounds regarding the energetic properties are the hydroxylammonium and triaminoguanidinium compounds (**4a** and **4c**). Those compounds exhibit decomposition temperatures above 200 °C and performance values in the range of RDX (8706 m s^{-1} (**4a**) and 8707 m s^{-1} (**4c**)).

Experimental section

Caution: Due to the fact that energetic triazole compounds are to some extent unstable against outer stimuli, proper safety precautions should be taken when handling the materials. Especially dry samples are able to explode under the influence of impact or friction. Lab personnel and the equipment should be properly grounded and protective equipment like earthed shoes, leather coat, Kevlar® gloves, ear protection and face shield is recommended for the handling of any energetic material.

General

All chemical reagents and solvents were obtained from Sigma-Aldrich Inc. or Acros Organics (analytical grade) and were used as supplied without further purification. ^{1}H, $^{13}C\{1H\}$, $^{14}N\{1H\}$ and ^{15}N NMR spectra were recorded on a JEOL Eclipse 400 instrument in DMSO-d_6 at 25 °C. The chemical shifts are given relative to tetramethylsilane (^{1}H, ^{13}C) or nitro methane (^{14}N, ^{15}N) as external standards and coupling constants are given in Hertz (Hz). Infrared (IR) spectra were recorded on a Perkin-Elmer Spectrum BX FT-IR instrument equipped with an ATR unit at 25 °C. Transmittance values are qualitatively described as "very strong" (vs), "strong" (s), "medium" (m), "weak" (w) and "very weak" (vw). Raman spectra were recorded on a Bruker RAM II spectrometer equipped with a Nd:YAG laser (200 mW) operating at 1064 nm and a reflection angle of 180°. The intensities are reported as percentages of the most intense peak and are given in parentheses. Elemental analyses (CHNO) were performed with a Netzsch Simultaneous Thermal Analyzer STA 429. (The N microanalysis values are all lower than the calculated values. This is common with high N compounds and cannot be avoided.) Melting and decomposition points were determined by differential scanning calorimetry (Linseis PT 10 DSC calibrated with standard pure indium and zinc). Measurements were performed at a heating rate of 5 °C min^{-1} in closed aluminum sample pans with a 1 μm hole in the lid for gas release to avoid an unsafe increase in pressure under a nitrogen flow of 20 mL min^{-1} with an empty identical aluminum sample pan as a reference.

For initial safety testing, the impact and friction sensitivities as well as the electrostatic sensitivities were determined. The impact sensitivity tests were carried out according to STANAG 4489,[35] modified according to WIWeB instruction 4-5.1.02[36] using a BAM[37] drop hammer. The friction sensitivity tests were carried out according to STANAG 4487[38] and modified according to WIWeB instruction 4-5.1.03[39] using the BAM friction tester. The electrostatic sensitivity tests were accomplished according to STANAG 4490[40] using an electric spark testing device ESD 2010 EN (OZM Research).

The single-crystal X-ray diffraction data of **2** and **3** were collected using an Oxford Xcalibur3 diffractometer equipped with a Spellman generator (voltage 50 kV, current 40 mA), an enhanced molybdenum Kα radiation source (λ = 71.073 pm), an Oxford Cryosystems Cryostream cooling unit, a four circle kappa platform and a Sapphire CCD detector. Data collection and reduction were performed with CrysAlisPro.[41] The structures were solved with SIR97,[42] refined with full-matrix least-squares procedures using SHELXL-97,[43] and checked with PLATON,[44] all integrated into the WinGX software suite.[45] The finalized CIF files were checked with checkCIF.[46] Intra- and intermolecular contacts were analyzed with Mercury.[47] CCDC 935564 (**2**) and 935565 (**3**) contain the supplementary crystallographic data for this paper.

3,3′-Diamino-5,5′-bis(1*H*-1,2,4-triazole) and 3,3′-dinitro-5,5′-bis(1*H*-1,2,4-triazole) were synthesized according to the literature.[27]

5-(5-Amino-1*H*-1,2,4-triazol-3-yl)-3-nitro-1*H*-1,2,4-triazole (ANBT, 1). 3,3′-Dinitro-5,5′-bis(1*H*-1,2,4-triazole) dihydrate (13.0 g, 49.6 mmol) was suspended in hydrazine (50 wt% in water, 105 mL) and stirred at 80 °C for 16 h. 50% Hydrochloric acid (500 mL) was added to the mixture resulting in a color change from red to colorless. The solution was extracted with ethyl acetate to remove unreacted 3,3′-dinitro-5,5′-bis(1*H*-1,2,4-triazole) (regained after evaporation of the solvent: 4.1 g, 18 mmol). The aqueous phase was brought to pH = 3 by adding a saturated solution of sodium acetate. The occurring precipitate was collected by filtration and resuspended in 0.25 M hydrochloric acid (400 mL). Filtration and washing with water, ethanol and diethyl ether yielded 5-(5-amino-1*H*-1,2,4-triazol-3-yl)-3-nitro-1*H*-1,2,4-triazole (4.00 g, 20.4 mmol, 41%) as a colorless solid.

^{1}H NMR (DMSO-d$_6$): δ = 6.41 (s, 2H, $-NH_2$) ppm; **^{13}C NMR** (DMSO-d$_6$): δ = 163.5, 158.3, 150.6, 149.1 ppm; **^{14}N NMR** (DMSO-d$_6$): δ = −23 ($-NO_2$) ppm. **IR:** ν (cm^{-1}) (rel. int.) = 3578(w), 3402(m), 3320(m), 3224(m), 3155(m), 2922(w), 2709(m), 2584(m), 1699(vs), 1660(m), 1550(s), 1533(m), 1522(s), 1476(m), 1463(m), 1446(m), 1430(m), 1397(s), 1333(m), 1308(s), 1241(w), 1183(w), 1123(m), 1123(m), 1079(w), 1067(m), 1023(w), 978(s), 890(m), 838(vs), 751(w), 713(m), 654(w). **Raman** (200 mW): ν (cm^{-1}) (rel. int.) = 1709(4), 1660(7), 1629(79), 1549(8), 1530(10), 1471(8), 1434(36), 1420(32), 1396(100), 1334(54), 1311(14), 1252(3), 1180(3), 1124(89), 1093(9), 1072(13), 1036(22), 952(4), 843(14), 770(6), 754(7), 747(5), 591(2), 591(2), 497(3), 400(9), 332(6), 318(7), 299(3), 243(4), 222(9). **Elemental analysis ($C_4H_4N_8O_2$):** calc.: C 24.50, H 2.06, N 57.13; found: C 24.20, H 2.39, N 55.02. **Mass spectrometry**: *m*/*z* (DEI$^+$) 196.1 [M$^+$].

5-(5-Nitrimino-1,3*H*-1,2,4-triazol-3-yl)-3-nitro-1*H*-1,2,4-triazole (NNBT, 2). 5-(5-Amino-1*H*-1,2,4-triazol-3-yl)-3-nitro-1*H*-1,2,4-triazole (2.4 g, 12 mmol) was dissolved in concentrated sulfuric acid (24 mL) and cooled to 0 °C. Concentrated nitric acid (4.8 mL) was added dropwise and the mixture was stirred at room temperature for 1 h. The solution was poured on ice and the resulting precipitate collected by filtration. 5-(5-Nitrimino-1,3*H*-1,2,4-triazol-3-yl)-3-nitro-1*H*-1,2,4-triazole (2.7 g, 11 mmol, 92%) was yielded as a colorless solid.

^{1}H NMR (DMSO-d$_6$): δ = 12.39 ppm; **^{13}C NMR** (DMSO-d$_6$): δ = 163.1, 153.1, 146.6, 142.9 ppm; **^{14}N NMR** (DMSO-d$_6$): δ = −23 ppm. **IR:** ν (cm^{-1}) (rel. int.) = 3564(w), 3461(w), 3295(w), 2715(w), 1651(w), 1581(s), 1558(m), 1554(m), 1524(w), 1462(s), 1408(m), 1383(m), 1350(m), 1312(vs), 1264(s), 1220(m), 1159(w), 1119(w), 1096(w), 1037(w), 1001(vw), 951(vs), 879(m), 879(m), 842(m), 774(w), 756(w), 751(w), 735(w), 709(s). **Raman** (200 mW): ν (cm^{-1}) (rel. int.) = 1652(77), 1610(8), 1581(100), 1561(20), 1523(24), 1502(40), 1457(12), 1430(18), 1385(10), 1353(6), 1318(15), 1224(3), 1161(6), 1122(22), 1099(3), 1016(23), 1004(27), 854(6), 844(4), 775(2), 759(20), 662(1), 596(1), 596(1), 550(1), 501(2), 469(1), 422(4), 252(5), 229(2). **Elemental analysis ($C_4H_3N_9O_4$):** calc.: C 19.92, H 1.25, N 52.28; found: C 22.26, H 1.60, N 50.20. **Mass spectrometry**: *m*/*z* (FAB$^-$) 240.3 [$C_4H_2N_9O_4^-$]. **Sensitivities** (grain size: <100 μm): friction: 360 N; impact: 8 J; ESD: 0.5 J. **DSC** (onset 5 °C min^{-1}): T_{Dec}: 150 °C.

5-(5-Azido-1*H*-1,2,4-triazol-3-yl)-3-nitro-1*H*-1,2,4-triazole (AzNBT, 3). 3-Amino-3′-nitro-5,5′-bis(1*H*-1,2,4-triazole) (1.04 g, 5.30 mmol) was dissolved in 20% sulfuric acid (60 mL) and cooled to −5 °C. Sodium nitrite (0.37 g, 5.37 mmol) was dissolved in water (20 mL) and added dropwise. The solution was stirred for 3 h at room temperature. Sodium azide (1.72 g, 26.5 mmol, 5 eq.) was dissolved in water (10 mL) and added dropwise (**Danger**: evolution of HN_3!). After stirring overnight, the solution was extracted with ethyl acetate and the combined organic phases dried over magnesium sulfate. The solvent was removed in a vacuum yielding 3-azido-3′-nitro-5,5′-bis(1*H*-1,2,4-triazole) (0.89 g, 3.99 mmol, 75%) as a colorless solid.

^{1}H NMR (DMSO-d$_6$): δ = 6.11 (s, 2H, H$_{triazole}$) ppm; **^{13}C NMR** (DMSO-d$_6$): δ = 163.0, 155.5, 147.3, 146.8 ppm; **^{14}N NMR** (DMSO-d$_6$): δ = −30 (–NO$_2$), −146 (–N$_3$) ppm. **IR**: ν (cm^{-1}) (rel. int.) = 3231(w), 3150(w), 3044(w), 2944(w), 2830(w), 2221(vw), 2143(s), 2139(s), 1614(w), 1541(vs), 1496(m), 1466(m), 1443(m), 1411(s), 1393(s), 1307(vs), 1190(m), 1048(m), 1031(m), 968(m), 836(s), 800(m), 707(m), 707(m). **Raman** (200 mW): ν (cm^{-1}) (rel. int.) = 2160(11), 1617(100), 1548(33), 1505(55), 1452(5), 1417(46), 1389(52), 1331(3), 1319(9), 1294(2), 1266(3), 1179(20), 1120(4), 1066(3), 1048(3), 1033(8), 1020(19), 841(5), 804(3), 764(6), 717(1), 550(2), 500(1), 500(1), 414(3), 391(13), 318(5), 210(4). **Elemental analysis ($C_4H_2N_{10}O_2$)**: calc.: C 21.63, H 0.91, N 63.06; found: C 21.74, H 1.06, N 61.47. **Mass spectrometry**: *m*/*z* (DEI$^+$) 222.0 [$C_4H_2N_{10}O_2{}^+$]. **Sensitivities** (grain size: <100 μm): friction: 360 N; impact: 8 J; ESD: 0.3 J. **DSC** (onset 5 °C min^{-1}): T_{Dec}: 181 °C.

Dihydroxylammonium 5-(5-nitrimino-1*H*-1,2,4-triazolate-3-yl)-3-nitro-1,2,4-triazolate (4a). 5-(5-Nitrimino-1,3*H*-1,2,4-triazol-3-yl)-3-nitro-1*H*-1,2,4-triazole (526 mg, 2.18 mmol) was dissolved in ethanol (50 mL) and hydroxylamine (50% in H$_2$O, 0.27 mL, 4.36 mmol, 2.2 eq.) was added. The resulting precipitate was collected by filtration and yielded hydroxylammonium 5-(5-nitrimino-1,2,4-triazol-3-yl)-3-nitro-1*H*-1,2,4-triazolate (540 mg, 1.76 mmol, 81%) as a colorless solid.

^{1}H NMR (DMSO-d$_6$): δ = 12.85, 8.69, 4.57 ppm; **^{13}C NMR** (DMSO-d$_6$): δ = 165.7, 159.2, 157.4, 156.9 ppm; **^{14}N NMR** (DMSO-d$_6$): δ = −17 ppm. **IR**: ν (cm^{-1}) (rel. int.) = 3579(w), 3013(w), 2711(m), 1611(w), 1521(m), 1480(w), 1451(s), 1405(m), 1344(m), 1327(m), 1307(m), 1284(s), 1255(vs), 1209(m), 1138(m), 1123(m), 1107(s), 1017(w), 1003(w), 986(s), 867(m), 842(s), 800(w), 800(w), 773(w), 765(m), 749(w), 726(m), 685(vw), 655(vw). **Raman** (200 mW): ν (cm^{-1}) (rel. int.) = 1587(100), 1531(33), 1482(18), 1465(18), 1458(17), 1442(10), 1412(65), 1388(35), 1340(25), 1311(9), 1289(11), 1141(44), 1125(47), 1071(6), 1042(11), 1019(28), 1006(14), 989(11), 871(5), 846(14), 775(2), 765(4), 751(12), 751(12), 728(3), 687(2), 603(2), 437(4), 258(2), 211(3). **Elemental analysis ($C_4H_9N_{11}O_6$)**: calc.: C 15.64, H 2.95, N 50.16; found: C 15.39, H 3.22, N 47.61. **Mass spectrometry**: *m*/*z* (FAB$^+$) 34 [NH_3OH^+] *m*/*z* (FAB$^-$) 240.1 [$C_4H_2N_9O_4{}^-$]. **Sensitivities** (grain size: <100 μm): friction: 360 N; impact: 15 J; ESD: 0.25 J. **DSC** (onset 5 °C min^{-1}): T_{Dec}: 174 °C.

Diguanidinium 5-(5-nitrimino-1*H*-1,2,4-triazolate-3-yl)-3-nitro-1,2,4-triazolate (4b). 5-(5-Nitrimino-1,3*H*-1,2,4-triazol-3-yl)-3-nitro-1*H*-1,2,4-triazole (508 mg, 2.11 mmol) was dissolved in ethanol (50 mL). Guanidinium bicarbonate (380 mg, 2.11 mmol, 1 eq.) was dissolved in water and added to the solution. The mixture was refluxed for 30 min. The formed precipitate was collected by filtration and yielded guanidinium 5-(5-nitrimino-1,2,4-triazol-3-yl)-3-nitro-1*H*-1,2,4-triazolate (655 mg, 1.82 mmol, 86%) as a yellow solid.

^{1}H NMR (DMSO-d$_6$): δ = 13.20, 7.38 ppm; **^{13}C NMR** (DMSO-d$_6$): δ = 165.3, 158.1 (G$^+$), 157.3, 156.0, 152.9 ppm; **^{14}N NMR** (DMSO-d$_6$): δ = −17 ppm. **IR**: ν (cm^{-1}) (rel. int.) = 3604(vw), 3442(m), 3436(m), 3430(m), 3427(m), 3421(m), 3347(w), 3151(m), 3146(m), 1680(s), 1668(s), 1665(s), 1643(s), 1576(w), 1524(m), 1509(m), 1479(m), 1443(s), 1394(s), 1387(s), 1359(vs), 1313(s), 1283(vs), 1283(vs), 1259(m), 1143(w), 1090(s), 1014(w), 983(m), 869(w), 843(m), 774(w), 761(m), 745(w), 726(m), 678(w), 662(w). **Raman** (200 mW): ν (cm^{-1}) (rel. int.) = 1574(100), 1551(9), 1521(24), 1484(41), 1447(3), 1396(65), 1382(50), 1313(11), 1298(13), 1287(6), 1259(3), 1146(21), 1096(64), 1035(14), 1015(41), 985(2), 870(4), 844(14), 764(3), 747(7), 681(1), 604(1), 538(7), 538(7), 533(7), 432(5), 420(6), 310(1), 253(2). **Elemental analysis ($C_6H_{13}N_{15}O_4$)**: calc.: C 20.06, H 3.65, N 58.48; found: C 19.88, H 3.99, N 54.95. **Mass spectrometry**: *m*/*z* (FAB$^+$) 60 [$CH_6N_3{}^+$] *m*/*z* (FAB$^-$) 240.1 [$C_4H_2N_9O_4{}^-$]. **Sensitivities** (grain size: <100 μm): friction: 360 N; impact: 40 J; ESD: 0.5 J. **DSC** (onset 5 °C min^{-1}): T_{Dec}: 230 °C.

Di(triaminoguanidinium) 5-(5-nitrimino-1*H*-1,2,4-triazolate-3-yl)-3-nitro-1,2,4-triazolate (4c). Triaminoguanidine (419 mg, 4.02 mmol, 2 eq.) was added to a solution of 5-(5-nitrimino-1,3*H*-1,2,4-triazol-3-yl)-3-nitro-1*H*-1,2,4-triazole (485 mg, 2.01 mmol) in ethanol (50 mL). Filtration of the precipitate yielded triaminoguanidinium 5-(5-nitrimino-1,2,4-triazol-3-yl)-3-nitro-1*H*-1,2,4-triazolate (762 mg, 1.70 mmol, 85%) as a yellow solid.

^{1}H NMR (DMSO-d$_6$): δ = 9.71 ppm; **^{13}C NMR** (DMSO-d$_6$): δ = 164.9, 157.8, 154.8, 151.4 ppm; **^{14}N NMR** (DMSO-d$_6$): δ = −17 ppm. **IR**: ν (cm^{-1}) (rel. int.) = 3440(w), 3360(m), 3356(m), 3326(m), 3187(m), 1688(vs), 1522(s), 1480(m), 1440(s), 1396(vs), 1376(s), 1352(vs), 1305(m), 1297(m), 1279(s), 1227(w), 1212(m), 1139(m), 1083(m), 1073(m), 1039(m), 1022(m), 979(s), 979(s), 857(w), 839(m), 775(w), 762(w), 704(m), 660(m). **Raman** (200 mW): ν (cm^{-1}) (rel. int.) = 3225(4), 1686(2), 1655(2), 1575(100), 1554(13), 1516(22), 1479(32), 1385(60), 1358(19), 1325(9), 1307(13), 1279(14), 1256(4), 1133(13), 1085(73), 1024(11), 1008(28), 887(7), 861(5), 840(12), 750(6), 420(8), 262(3), 262(3). **Elemental analysis ($C_6H_{19}N_{21}O_4$)**: calc.: C 16.11, H 4.26, N 65.46; found: C 16.11, H 4.48, N 62.55. **Mass spectrometry**: *m*/*z* (FAB+) 105 [$CH_9N_6{}^+$] *m*/*z* (FAB$^-$) 240.2 [$C_4H_2N_9O_4{}^-$]. **Sensitivities** (grain size: <100 μm): friction: 360 N; impact: 40 J; ESD: 0.35 J. **DSC** (onset 5 °C min^{-1}): T_{Dec}: 193 °C.

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