

Nitraza-/Oxa-Propylene- and Hydrazonemethylene-Bridged 1,2,4-Nitraminotriazoles and Selected Salts

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Dedicated to Prof. Jean'ne M. Shreeve on the occasion of her 90th Birthday

Two new bridged nitraminotriazoles with bridging oxapropylene and nitrazapropylene moieties were synthesized, and converted into several salts, as well as from the hydrazonemethylene bridged nitraminotriazole. All compounds were fully characterized by NMR and IR spectroscopy, elemental analysis as well as differential thermal analysis. The sensitivity towards friction and impact were determined according to BAM

standard technics and the energetic properties were calculated by using the EXPLO5 computer code. The neutral compounds as well as the various salts were examined in terms of their physicochemical properties and detonation performance to each other and compared to the commonly used secondary explosive RDX.

Introduction

Energetic materials are widely used in both civilian and military applications. For this reason, there is a constant search for production improvements of already known compounds, but there is also research on new energetic compounds exhibiting better properties, such as easier synthesis, or more environmentally friendly production.^[1–3] Current research shows that nitrogen-rich heterocycles such as triazoles, tetrazoles or oxadiazoles are promising units for new high-energy materials (HEMs), because of their high heat of formation, good densities, high thermal stability, good detonation performance and low sensitivities.^[4–7] In addition, these HEMs mainly decompose into non-toxic nitrogen gas, which is very important in terms of green chemistry.^[7]

HEMs based on 1,2,4-triazoles are of interest for new potential secondary explosives. Their main advantages stem from typically low sensitivity towards heat or mechanical stimuli.^[7] One of the best known and studied examples is nitrotriazolone (NTO), which exhibits low sensitivity as well as high thermal stability, and further can be used as a stabilizer for more sensitive and thermally labile compounds.^[8] Other exam-

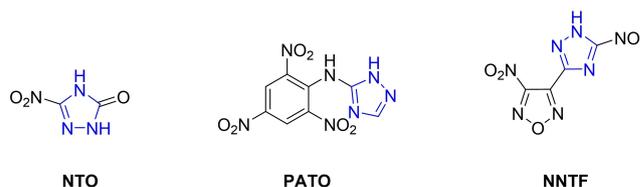


Figure 1. Examples of 1,2,5-triazole based secondary explosives.

ples are PATO (3-picrylamino-1,2,5-triazoles) and NNTF (3-nitro-4-(5-nitro-1,2,4-triazol-3-yl)furan), which show potential for use as secondary explosives (Figure 1).^[9–10]

In order to further improve specific properties, bridged azoles became of more interest. By variation of azoles and bridging moieties, a wide selection of new energetic molecules is possible with varying properties.^[11–13] Azo bridges for example increase the nitrogen content and energy of the molecule, but can lead on the other hand to an increased sensitivity compared to the azole itself.^[14] In contrast, short alkyl bridges can increase thermal stability, but could decrease the sensitivity.^[15] A selection of various bridging moieties are shown in Figure 2, such as the methylene, azo, oxapentylene and nitrazapropylene bridging unit.

By using different bridges with the same azole moiety, the properties of the new compounds may vary. Since 1,2,4-triazoles have good properties, such as low sensitivity and high thermal stability, this work aims to synthesize and characterize new bridged nitramino-1,2,4-triazoles and compare their properties with each other. The bridging units were selected to vary the oxygen and nitrogen content for a comparison in terms of thermal stability, sensitivities and energetic performance. In addition, several salts could be accessible via the acidic hydrogen of the nitramine moiety and their properties discussed.

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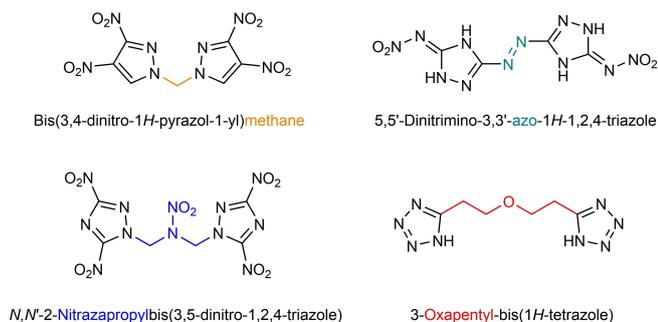


Figure 2. A selection of various bridged azoles.^[15–18]

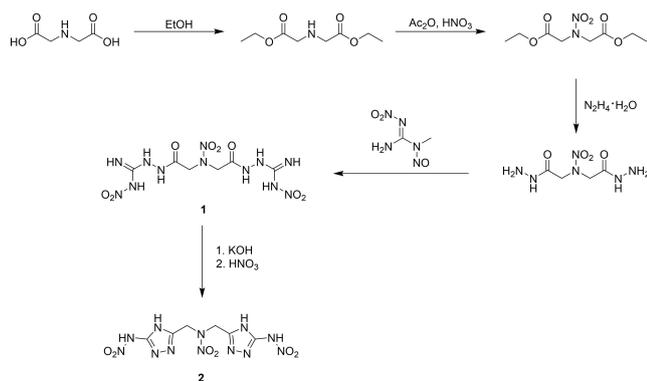
Results and Discussion

Synthesis

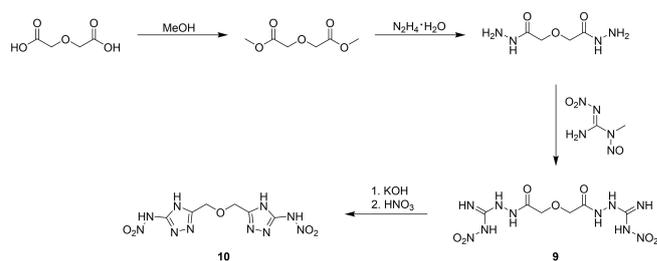
Via a three-step procedure as shown in Scheme 1, starting from easily available iminodiacetic acid, diacetylnitramino dihydrazide was prepared.^[19] Subsequent reaction with freshly synthesized *N*-methyl-*N*-nitroso-*N'*-nitro-guanidine^[20] resulted in the formation of diacetylnitramino-bis-*N*-amino-nitroguanidine (1). The cyclization to the nitrazapropylene bridged triazole was accomplished under basic conditions, followed by nitration to the nitraminotriazole 1,3-bis(3-nitramino-4H-1,2,4-triazol-5-yl) 2-nitrazapropene (2, BNATNP) (Scheme 1).

The acidic hydrogen atoms of the nitraminotriazole 2 can be deprotonated with selected organic and inorganic bases to form the corresponding salts 3–8 (Scheme 3). The salts were obtained pure and in quantitative yield, except for the hydroxylammonium salt, because here a mixture was obtained, which could not be further purified.

Diglycolic acid is converted into the corresponding dihydrazide in two steps.^[21–22] In a similar fashion as described before, subsequent reaction with *N*-methyl-*N*-nitroso-*N'*-nitro-guanidine furnished diacetyloxa-bis-*N*-amino-nitroguanidine (9). Similarly, the cyclization to the nitraminotriazole was performed



Scheme 1. Synthetic route towards 1,3-bis(3-nitramino-4H-1,2,4-triazol-5-yl) 2-nitrazapropene (2, BNATNP) starting from iminodiacetic acid.



Scheme 2. Synthetic pathway towards 1,3-bis(3-nitramino-4H-1,2,4-triazol-5-yl) 2-oxapropane (10, BNATOP) starting from diglycolic acid.

to give 1,3-bis(3-nitramino-4H-1,2,4-triazol-5-yl) 2-oxapropane (10, BNATOP) (Scheme 2).

The nitraminotriazole 10 is converted into salts 11–17 with same bases (Scheme 3).

Finally, the hydrazono bridged nitraminotriazole, 1,3-bis(3-nitramino-4H-1,2,4-triazol-5-yl) hydrazonemethane (BNATHM), available in three steps from diethyl 2,2-diazidomalonate,^[23] was converted into four salts 18–21 as shown in Scheme 3. The reaction with the other bases as applied before, did not result in uniform products.

NMR Spectroscopy

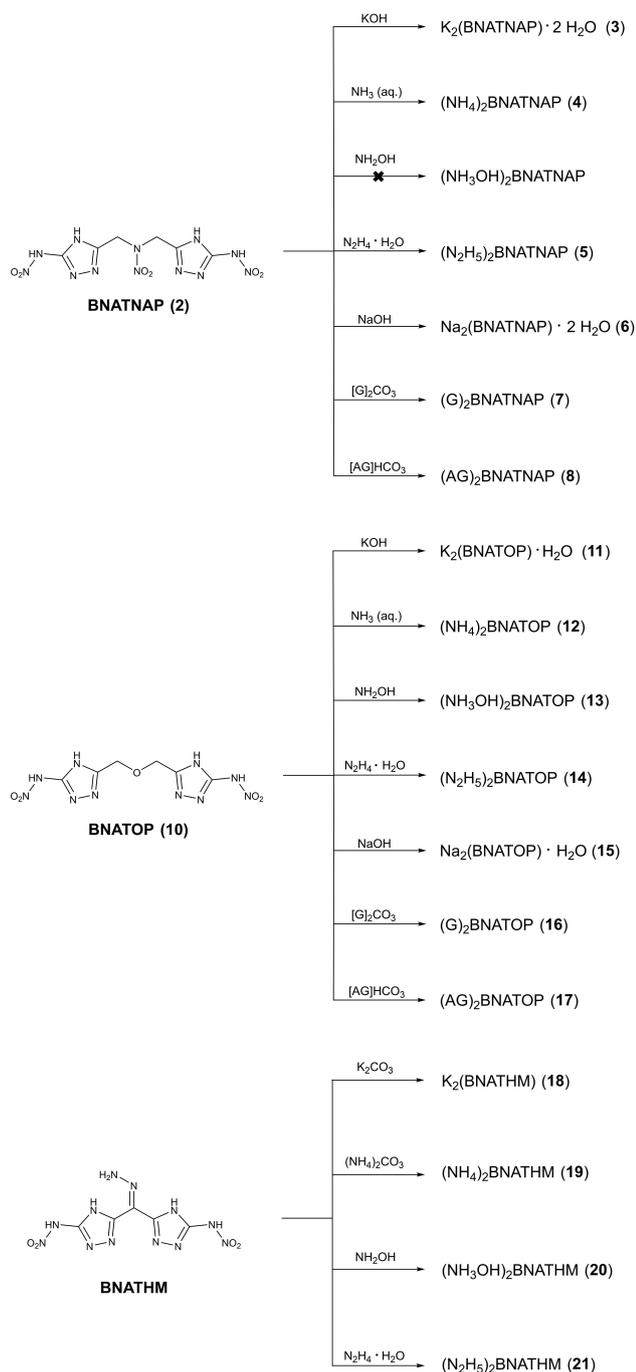
The characterization was performed by ¹H and ¹³C{¹H} NMR spectroscopy in DMSO-*d*₆, however the restricted solubility prevented the detection of the ¹⁴N resonances of the nitro groups.

Both bridging units in 2 and 10 contain methylene groups, adjacent to either nitrogen or oxygen. Those in 2 are observed in the range of 5.22–4.60 ppm, whereas those in 10 are detected at 4.62–3.94 ppm. The resonances of the nitramine and triazole hydrogen atoms are found in the region of 14.2–12.7 ppm. The corresponding ¹³C NMR resonances were observed for the CH₂ groups at 53.7–47.2 ppm for the nitrazapropylene units and at 65.3–62.3 ppm for the oxapropylene units. The triazole resonances attached to the nitramine group are detected at 157–147 ppm and those attached to the nitrazapropylene units at 159–153 ppm.

Crystal Structures

Suitable crystals for X-ray determination were obtained for the aminoguanidinium salt 17 by recrystallization from water. The salt crystallizes in the monoclinic space group *C2/c* with a density of 1.60 g cm⁻³ at 174 K. The structure as well as two different views onto the unit cell are shown in Figure 3.

The C–N bond lengths of the triazole are in the range of 1.32–1.36 Å, which is quite exactly in the middle between a C–N single and double bond length.^[24] For the N–N bond of the ring, the bond length is 1.36 Å, which fits perfectly for typical N–N bond length of 1,2,4-triazoles.^[25] The torsions angles



Scheme 3. Salt formation overview for BNATNAP **2** (3–8), BNATOP **10** (11–17) and BNATHM (18–21).

$\text{N3–N1–C2–N3} -0.41^\circ$ and $\text{C3–N2–N1–C2} -0.03^\circ$ demonstrate that the five-membered ring is nearly planar.

For the aminoguanidinium cation, same trends can be observed as for the 1,2,4-triazole ring in terms of C–N bond lengths as well as for the planarity of the molecule. The C–N bond length is between 1.32–1.34 Å, which is again in the middle of a C–N single and double bond length and the torsion angles $\text{N9–N8–C4–N7} 0.0^\circ$ and $\text{N9–N8–C4–N6} -179.73^\circ$ indicate the planarity.

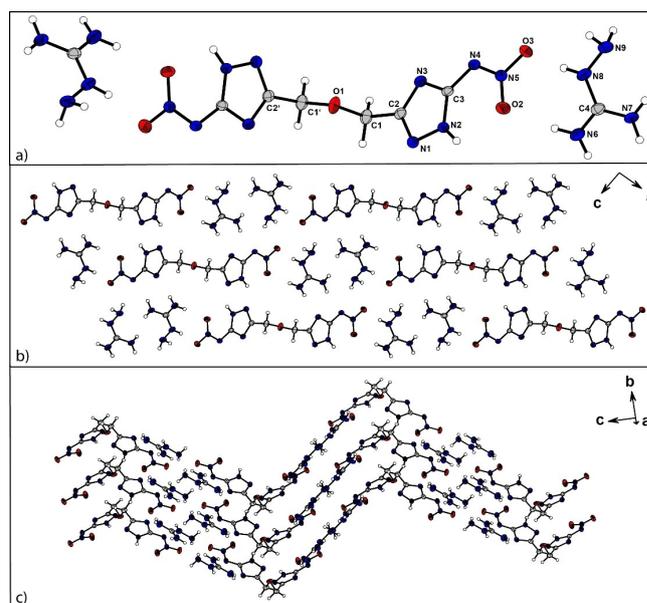


Figure 3. (a) Crystal structure of the aminoguanidinium salt **17**, showing the atom labeling. (b) View of the unit cell along the *b* axis to show the stacking. (c) View of the unit cell slightly shifted from the *a* axis to show the zigzag layers.

Moreover, the unit cell illustrates that along the *b* axis the molecules stack perfectly, and each bridged triazole is surrounded by two aminoguanidinium cations. Furthermore, in Figure 3 on the bottom (c) shows the formation of zigzag layers, in which the oxapropylene bridging units form the corners.

Physicochemical Properties

A full characterization in regard to the physicochemical properties was performed for all energetic compounds. This includes their sensitivities towards impact and friction, the thermal behavior, heats of formation and detonation parameters. Those were determined and compared to the state-of-the-art secondary explosive in industrial use, RDX, shown in Table 1 and Table 2. The sensitivity values towards impact and friction were determined with the 1 out of 6 method according to BAM standards.^[26] The thermal properties of all compounds were determined by differential thermal analysis (DTA) in the temperature range of 25–400 °C with a heating rate of 5 °C.

The three neutral nitraminotriazoles **2**, **10** and BNATHM differ only in the bridging unit, containing either more or less nitrogen or oxygen. This is reflected in the nitrogen and oxygen content, where it can be seen that BNATHM has the largest content with 78%, closely followed by **2** with 77%. Not surprisingly, **10** shows the lowest value of 73%, since it contains only one oxygen atom in the bridging unit. However, despite the lower oxygen and nitrogen content, **10** shows a very similar sensitivity as the other compounds. All compounds show no sensitivity towards friction, but a high sensitivity towards impact in the range of 2.5–4 J. Thus, these neutral triazoles

Table 1. Physicochemical properties of **2**, **10** and BNATHM compared to RDX.^[24]

Formula	2 C ₆ H ₈ N ₁₂ O ₆	10 C ₆ H ₈ N ₁₀ O ₅	BNATHM C ₅ H ₆ N ₁₂ O ₄	RDX C ₃ H ₆ N ₆ O ₆
<i>M</i> [g·mol ⁻¹]	344.21	300.20	298.18	222.12
<i>I</i> S ^[a] [J]	3	4	2.5	7.5
<i>F</i> S ^[b] [N]	360	360	360	120
<i>N</i> + <i>O</i> ^[c] [%]	76.72	73.31	77.83	81.06
Ω_{CO_2} ^[d] [%]	-46	-59	-34	-22
<i>T</i> _{endo} ^[e] / <i>T</i> _{exo} ^[f] [°C]	-/159	-/187	-/177	203/208
ρ ^[g] [g·cm ⁻³]	1.76	1.73	1.81	1.82
$\Delta_f H^\circ$ ^[h] [kJ·mol ⁻¹]	438	266	541	87
EXPLO5 V6.05				
$-\Delta_c U^\circ$ ^[i] [kJ·kg ⁻¹]	6378	5664	5137	5816
<i>T</i> _{c-j} ^[j] [K]	3295	2987	3624	3758
<i>p</i> _{c-j} ^[k] [GPa]	26.6	23.2	31.0	34.5
<i>D</i> _{c-j} ^[l] [m·s ⁻¹]	8233	7818	8654	8898
<i>V</i> ₀ ^[m] [dm ³ ·kg ⁻¹]	773	767	766	780

[a] Impact sensitivity (BAM drophammer, method 1 of 6); [b] friction sensitivity (BAM friction tester, method 1 of 6); [c] combined nitrogen and oxygen content; [d] oxygen balance toward carbon dioxide ($\Omega_{\text{CO}_2} = (n\text{O} - 2x\text{C} - y\text{H})/2(1600/M)$); [e] endothermic peak (DTA, $\beta = 5^\circ\text{C}\cdot\text{min}^{-1}$); [f] temperature of decomposition (DTA, $\beta = 5^\circ\text{C}\cdot\text{min}^{-1}$); [g] Densities measured by gas pycnometry; [h] standard molar enthalpy of formation; [i] detonation energy; [j] detonation temperature; [k] detonation pressure; [l] detonation velocity; [m] volume of detonation gases at standard temperature and pressure conditions.

have an increased sensitivity compared to RDX, even though RDX has a higher oxygen and nitrogen content.

There were no endothermic events observed in the DTA, which could be assigned to melting points. The highest decomposition temperature shows **10** with 187 °C, followed by BNATHM with 177 °C. The lowest value was observed for **2** (159 °C), which could be due to the nitramino group of the bridging unit, which are often thermally labile.

Regarding the densities, the triazoles show quite similar values of 1.73–1.81 g cm⁻³, which are in the same range as RDX. Based on the densities, obtained by gas pycnometer, and the

heats of formation, obtained by CBS-4M calculations, the energetic properties were calculated with EXPLO5 (V6.05).^[27] The calculated detonation velocities and pressures follow the same trend as the nitrogen and oxygen content. BNATHM shows the highest N+O content (78%) as well as the highest energetic parameters (*D*_{c-j} = 8654 ms⁻¹, *p*_{c-j} = 31.0 GPa), whereas **10** shows the lowest N+O content (73%) and in turn the lowest detonation velocity and pressure (*D*_{c-j} = 7818 ms⁻¹, *p*_{c-j} = 32.2 GPa). In summary, BNATHM shows the best values, which cannot surpass RDX. However, **10** shows higher thermal stability, as well as lower sensitivities than BNATHM, which is also associated with lower energetic properties.

For the total of 17 new salts, there is a clear trend towards increased thermal stability, with the exception of salts **18–21** based on BNATHM, which decompose in the same range as the neutral compound. The highest decomposition temperature was observed for guanidinium salt **16** with 268 °C followed by ammonium salt **12** with 225 °C. All salts containing crystal water (**3**, **6**, **11**, **15**) and the ammonium salt **12** also show an endothermic event.

For all salts, the sensitivities towards impact and friction were measured. It was found that most salts are not sensitive towards friction, except for the ammonium, hydrazinium and hydroxylammonium salts (**4–5**, **12–14**, **19–21**), which show low sensitivities in the range of 240–290 N. The hydrazinium salt **5** is the only salt to show a higher sensitivity towards friction with a value of 160 N. For the sensitivity towards impact, the same trend was observed. The metal, guanidinium and aminoguanidinium salts (**7–8**, **16–17**, **18**) show a moderate sensitivity towards impact in the range of 10–40 J. The ammonium, hydrazinium and hydroxylammonium salts (**4–5**, **12–14**, **19–21**) are very sensitive towards impact with values of 2–5 J, which are in the range of primary explosives.

For the salts without crystal water, the densities were determined using a gas pycnometer, except for **16**. The density of aminoguanidinium salt **16** was recalculated to room temper-

Table 2. Physical and energetic properties of **3–21**.

	<i>T</i> _{endo} ^[a] [°C]	<i>T</i> _{exo} ^[b] [°C]	ρ ^[c] [g·cm ⁻³]	<i>D</i> _{c-j} ^[d] [m·s ⁻¹]	<i>p</i> _{c-j} ^[k] [GPa]	<i>I</i> S ^[d] [J]	<i>F</i> S ^[e] [N]	$\Delta_f H^\circ$ ^[h] [kJ·mol ⁻¹]
3 ·2H ₂ O	64	207	–	–	–	20	> 360	–
4	–	176	1.73	8467	26.7	6	288	312
5	–	181	1.74	8663	27.4	3	160	618
6 ·2H ₂ O	123, 132	193	–	–	–	40	> 360	–
7	–	182	1.56	7460	19.1	40	> 360	260
8	–	212	1.60	7903	21.7	20	> 360	447
11 ·H ₂ O	143	195	–	–	–	15	> 360	–
12	181	225	1.72	8263	24.4	5	280	63
13	–	191	1.72	8400	26.7	3	288	188
14	–	195	1.68	8502	25.9	5	240	358
15 ·H ₂ O	155	208	–	–	–	40	> 360	–
16	–	268	1.57	7367	18.1	40	> 360	41
17	–	220	1.57 ^{X-ray}	7704	20.0	25	> 360	279
18	–	205	1.93	7271	20.2	10	> 360	106
19	–	175	1.69	8355	25.2	2	252	399
20	–	170	1.73	8701	29.1	5	288	567
21	–	181	1.75	9197	31.4	3	252	702

[a] endothermic peak (DTA, $\beta = 5^\circ\text{C}\cdot\text{min}^{-1}$); [b] temperature of decomposition (DTA, $\beta = 5^\circ\text{C}\cdot\text{min}^{-1}$); [c] Densities measured by gas pycnometer if not otherwise noted; [d] detonation velocity; [e] detonation pressure; [f] Impact sensitivity (BAM drophammer, method 1 of 6); [g] friction sensitivity (BAM friction tester, method 1 of 6); [h] standard molar enthalpy of formation.

ature from the crystal structure. For the salts of **2** and **10**, the densities of the ammonium, hydrazinium and hydroxylammonium salts (**4–5**, **12–14**) are in the same range as the neutral compounds and for the guanidinium and aminoguanidinium salts (**7–8**, **16–17**), the densities are slightly lower. The densities of the salts of BNATHM (**18–21**) are lower compared to the neutral compound, except for the potassium salt **18**, which shows the highest value of all new compounds with 1.92 g cm^{-3} .

After determining the densities and calculating the heat of formation, the different energetic parameters were calculated for the various salts. The highest values were obtained again for the ammonium, hydroxylammonium and hydrazinium salts (**4–5**, **12–14**, **19–21**) with values above 8200 ms^{-1} . Overall, the hydrazinium salts (**5**, **14** and **21**) show the highest values from 8500 ms^{-1} for **14** to 9200 ms^{-1} for **21**. The guanidinium and aminoguanidinium salts (**7–8**, **16–17**) show the lowest values from $7200\text{--}7900 \text{ ms}^{-1}$, which are even lower compared to their neutral compounds.

In summary, the hydrazinium salts show the best overall properties in terms of thermal stability and energetic parameters. However, these compounds are also very sensitive to impact.

Conclusions

Two new nitrazapropylene and oxapropylene bridged nitraminotriazoles, as well as the hydrazonemethylene bridged derivative, along with some of their salts were prepared and characterized. From easily available starting materials iminodiacetic and diglycolic acids, via the corresponding nitroguanidines, the triazoles are accessible. Furthermore, a detailed investigation on their physicochemical and energetic properties was performed. As a result from the comparison of the bridging units, the nitrazapropylene bridge has the lowest thermal stability, probably due to the thermally labile nitramino group, though improving the energetic parameters. The oxapropylene bridge prevents an increase in the energetic properties, but increases the thermal stability. The overall most balanced nitraminotriazole is BNATHM, with moderate thermal stability and the best energetic properties.

The salts confirm the same trends but with increased thermal stability; for those with nitrogen-rich cations, the energetic properties are also further enhanced. However, the triazoles and salts with a detonation velocity exceeding 8000 ms^{-1} are very sensitive towards impact in the range of primary explosives.

Experimental Section

Solvents, deuterated solvents and all further chemicals were used as received from suppliers, without further purification. The hydrazide precursors for **1** and **9** were synthesized according to literature procedures.^[19,21–22]

^1H and $^{13}\text{C}\{\text{H}\}$ NMR spectra were recorded with a Bruker 400 MHz spectrometer at ambient temperature. The chemical shifts were referenced with respect to external Me_4Si (^1H 399.8 MHz; ^{13}C 100.5 MHz).

Infrared spectra were recorded at ambient temperature in the range $4000\text{--}400 \text{ cm}^{-1}$ on a Perkin-Elmer Perkin-Elmer BXII FTIR system with a Smith DuraSampler IR II diamond ATR.

Analyses of C/H/N contents were performed with an Elementar vario EL or Elementar vario micro cube. Melting and decomposition temperatures of the described compounds were measured through differential thermal analysis (DTA) with an OZM Research DTA 552-Ex instrument. The samples were measured in a range of $25\text{--}400 \text{ }^\circ\text{C}$ at a heating rate of $5 \text{ }^\circ\text{C min}^{-1}$.

The sensitivities towards impact and friction were determined with a BAM drop hammer^[28] and a BAM friction tester.^[29]

Single crystal X-ray diffraction study was performed on an Oxford Diffraction Xcalibur3 diffractometer with a generator (voltage 50 kV, current 40 mA) and a KappaCCD area detector operating with $\text{Mo-K}\alpha$ radiation ($\lambda = 0.7107 \text{ \AA}$). The data collection was performed using the CRYSTALIS RED software.^[30] The solution of the structure was performed by direct methods and refined by full-matrix least-squares on F2 (SHELXT)^[31] implemented in the OLEX2 software suite.^[32] All non-hydrogen atoms were refined anisotropically and the hydrogen atoms were located and freely refined. DIAMOND plots are shown with thermal ellipsoids at the 50% probability level and the hydrogen atoms are shown as small spheres of arbitrary radius.

Information on the X-ray measurements and refinements are given in the Supporting Information. Deposition Number 2247722 (for **17**) contains the supplementary crystallographic data for this paper. These data are provided free of charge by the joint Cambridge Crystallographic Data Centre and Fachinformationszentrum Karlsruhe Access Structures service.

All quantum chemical calculations were carried out using the Gaussian G09 program package.^[33] The enthalpies (H) and free energies (G) were calculated using the complete basis set (CBS) method of Petersson and co-workers in order to obtain very accurate energies. The CBS models are using the known asymptotic convergence of pair natural orbital expressions to extrapolate from calculations using a finite basis set to the estimated CBS limit. CBS-4 starts with an HF/3-21G(d) geometry optimization; the zero-point energy is computed at the same level. It then uses a large basis set SCF calculation as a base energy, and an MP2/6-31+G calculation with a CBS extrapolation to correct the energy through second order. A MP4(SDQ)/6-31+(d,p) calculation is used to approximate higher order contributions. In this study, we applied the modified CBS-4M.^[34–35]

Caution: The compounds discussed here are sensitive materials. Therefore, it is recommended to carry out all reactions on a small scale, using the proper safety equipment, including ear, hand and body protection.

Diacetylnitramino-bis-N-amino-nitroguanidine (1): A suspension of *N*-methyl-*N*-nitroso-nitroguanidine (720 mg, 7.06 mmol, 2.1 equiv.) in 10 mL of water was added to a solution of diacetylnitramino dihydrazide (693 mg, 3.36 mg, 1 equiv.) in 10 mL of water and heated to $55 \text{ }^\circ\text{C}$ for 2 h during which a grey precipitate formed. Cooling to room temperature, filtration and washing with water yielded **1** as an off-white solid (1.03 g, 79%). $^1\text{H NMR}$ (400 MHz, $\text{DMSO-}d_6$): δ (ppm) = 10.37 (s, 2H, NH), 9.77 (s, 2H, NH), 8.76 (s, 2H, NH), 8.17 (s, 2H, NH), 4.60 (s, 4H, CH_2); $^{13}\text{C}\{\text{H}\}$ NMR (101 MHz, $\text{DMSO-}d_6$): δ (ppm) = 166.4 (CO), 160.9 (C(NH)), 53.7 (CH); IR (ATR, rel. int.): $\tilde{\nu}$ (cm^{-1}) = 3963 (w), 3909 (w), 3826 (w), 3783 (w),

3692 (w), 3468 (m), 3393 (w), 3297 (w), 3198 (w), 3069 (w), 2988 (w), 2952 (w), 2617 (w), 2486 (w), 2432 (w), 2336 (w), 2228 (w), 2173 (w), 2126 (w), 2095 (w), 2044 (w), 1993 (w), 1880 (w), 1845 (s), 1714 (s), 1629 (s), 1516 (s), 1420 (s), 1380 (s), 1348 (s), 1286 (m), 1244 (m), 1152 (m), 1083 (s), 1025 (s), 970 (s), 812 (s), 774 (s), 703 (s), 646 (s), 558 (s), 493 (s); **Elemental analysis:** calcd. (%) for $C_6H_{18}N_{12}O_{11}$ (380.24 $g\ mol^{-1}$): C 16.59, H 4.18, N 38.70; found C 16.80, H 4.09, N 38.40; **DTA** ($5^\circ C\ min^{-1}$): $T_{endo} = 111^\circ C$, $T_{exo} = 154^\circ C$.

1,3-Bis(3-nitramino-4H-1,2,4-triazol-5-yl) 2-nitrazapropane (2): A suspension of **1** (937 mg, 2.40 mmol, 1 equiv.) in 10 mL of water was added to a solution of potassium hydroxide (345 mg, 6.10 mmol, 3 equiv.) in 10 mL of water. The resulting crimson solution was stirred at room temperature for 24 h. Afterwards the solution was cooled to $0^\circ C$ and brought to pH 4 using nitric acid (65%) during which a crimson precipitate formed. The solution was immediately filtered and the filtrate was stirred at room temperature for 1 h during which an off-white precipitate formed. Filtration and washing with water and cold ethanol yielded an off-white solid. The crude product was recrystallized from methanol to yield **2** as an off-white powder (232 mg, 28%). $^1H\ NMR$ (400 MHz, $DMSO-d_6$): δ (ppm) = 14.21 (s, 2H, NH), 5.22 (s, 4H, CH_2); $^{13}C\ \{^1H\}\ NMR$ (101 MHz, $DMSO-d_6$): δ (ppm) = 153.1 (C- CH_2), 146.0 (C-NH), 47.2 (CH_2); **IR** (ATR, rel. int.): $\tilde{\nu}$ (cm^{-1}) = 3587 (m), 3536 (m), 3363 (m), 3202 (m), 3145 (m), 3038 (m), 2962 (m), 2825 (s), 2719 (s), 2583 (m), 2183 (m), 2129 (m), 2095 (w), 2008 (w), 1973 (w), 1863 (w), 1721 (w), 1604 (w), 1544 (w), 1505 (w), 1417 (w), 1323 (w), 1228 (w), 1092 (w), 1017 (w), 990 (w), 937 (w), 849 (w), 762 (w), 707 (w), 655 (w), 616 (w), 449 (w); **Elemental analysis:** calcd. (%) for $C_6H_8N_{12}O_6$ (344.21 $g\ mol^{-1}$): C 20.94, H 2.34, N 48.83; found C 21.17, H 2.25, N 48.55; **Sensitivities** (grain size 100–500 μm): impact 3 J, friction 360 N; **DTA** ($5^\circ C\ min^{-1}$): $T_{exo} = 164^\circ C$.

Salt formation of 2 – General Procedure

The bis-triazole **2** (0.500 g, 1.45 mmol) was suspended in 5 mL water and two equivalents of various bases (potassium/sodium hydroxide, 2 M ammonia solution, hydrazine monohydrate, guanidinium carbonate and aminoguanidinium bicarbonate) were added. The mixtures were stirred until the liquid turned clear. Afterwards, the solvent was removed at $80^\circ C$ overnight to obtain the desired salt in 94% for **5** (562 mg), and quantitative yield for **3**·2H₂O (662 mg), **4** (548 mg), **6**·2H₂O (615 mg), **7** (670 mg), **8** (714 mg).

Diglycolic acid-bis(N-amino-nitroguanidine) (9): Diglycolic acid dihydrazide (1.62 g, 10.0 mmol, 1 equiv.) was dissolved in water (20 mL) and N-methyl-N-nitroso-N'-nitroguanidine (2.94 g, 20.0 mmol, 2 equiv.), suspended in water (50 mL) was added. The mixture was stirred for 3 h at $95^\circ C$, cooled to $0^\circ C$, the precipitate filtered and washed with cold water and cold EtOH. After drying at room temperature, **9** (2.66 g, 79%) was obtained as a colorless solid. $^1H\ NMR$ (400 MHz, $DMSO-d_6$): δ (ppm) = 10.03 (s, 2H, NH), 9.7 (br, 2H, NH), 8.7 (br, 2H, NH), 8.2 (br, 2H, NH), 4.14 (s, 4H, CH_2); $^{13}C\ \{^1H\}\ NMR$ (101 MHz, $DMSO-d_6$): δ (ppm) = 168.8 (CO), 161.1 (C < C > NH), 69.8 (CH_2); **IR** (ATR, rel. int.): $\tilde{\nu}$ (cm^{-1}) = 3387(m), 3351(w), 3332(w), 3301(m), 3255(w), 3182(m), 3176(m), 3062(m), 2970(w), 2930(w), 1738(w), 1699(s), 1642(s), 1587(s), 1564(m), 1507(m), 1423(m), 1378(s), 1352(s), 1318(vs), 1272(s), 1244(s), 1187(s), 1187(s), 1085(s), 1048(m), 1031(m), 990(w), 923(w), 784(w), 753(s), 616(vs), 564(m), 537(s), 507(m), 481(vs), 437(s); **Elemental analysis:** calcd. (%) for $C_6H_{12}N_{10}O_7$ (336.23 $g\ mol^{-1}$): C 21.43; H 3.60; N 40.80. Found: C 21.49; H 3.84; N 40.80; **DTA** ($5^\circ C\ min^{-1}$): $T_{exo} = 193^\circ C$.

1,3-Bis(3-nitramino-4H-1,2,4-triazol-5-yl) 2-oxapropane (10):

Diglycolic-di-N-amino-nitroguanidine (**9**) (1.00 g, 2.94 mmol, 1 equiv.) was dissolved in water (20 mL) and KOH (500 mg, 8.93 mmol, 3.0 equiv.), dissolved in water (15 mL), was added. The

mixture was stirred overnight at $80^\circ C$. The clear solution was cooled to $50^\circ C$ and acidified to pH 3 with HNO_3 (65%). The resulting suspension was cooled to $0^\circ C$, the precipitate filtered, washed with cold water and dried for two days at $100^\circ C$ to yield **10** (610 mg, 68%) as a beige solid. $^1H\ NMR$ (400 MHz, $DMSO-d_6$): δ (ppm) = 14.2 (br, 2H, NH), 4.62 (s, 4H, CH_2); $^{13}C\ \{^1H\}\ NMR$ (101 MHz, $DMSO-d_6$): δ (ppm) = 153.0 (C- CH_2), 147.5 (C- NO_2), 62.4 (CH_2); **IR** (ATR, rel. int.): $\tilde{\nu}$ (cm^{-1}) = 3341(w), 3223(w), 2665(w), 2578(w), 1607(s), 1567(s), 1501(m), 1447(m), 1427(m), 1412(m), 1309(s), 1234(vs), 1210(s), 1127(s), 1098(s), 1015(m), 995(s), 951(m), 905(m), 870(m), 853(m), 803(w), 774(s), 774(s), 748(w), 713(s), 688(s), 665(m), 655(m), 603(m), 591(m), 575(m), 570(m), 545(m), 528(m), 484(m), 467(s), 444(s), 426(w), 420(w); **Elemental analysis:** calcd. (%) for $C_6H_8N_{10}O_5$ (300.20 $g\ mol^{-1}$): C 24.01; H 2.69; N 46.66; found: C 23.84; H 2.76; N 46.30; **Sensitivities** (grain size 100–500 μm): impact 4 J, friction > 360 N; **DTA** ($5^\circ C\ min^{-1}$): $T_{exo} = 187^\circ C$.

Salt formation of 10 – General Procedure

The bis-triazole **10** (0.500 g, 1.67 mmol) was suspended in 5 mL water and two equivalents of various bases (potassium/sodium hydroxide, 2 M ammonia solution, 50% aqueous hydroxylamine solution, hydrazine monohydrate, guanidinium carbonate and aminoguanidinium bicarbonate) were added. The mixtures were stirred until the liquid turned clear. Afterwards, the solvent was removed at $60^\circ C$ overnight to obtain the desired salt in 73% (**11**·2H₂O, 480 mg), 63% (**12**, 352 mg), 67% (**13**, 410 mg), 72% (**14**, 438 mg), 86% (**15**·H₂O, 520 mg), 89% (**16**, 622 mg) and 91% (**17**, 681 mg) yield.

Salt formation of BNATHM – General Procedure

Bis(3-nitramino-4H-1,2,4-triazol-5-yl) hydrazonemethane (BNATHM, 0.200 g, 0.67 mmol) was suspended in 10 mL water and two equivalents of various bases (potassium hydroxide, ammonium carbonate, 50% aqueous hydroxylamine solution, hydrazine monohydrate) were added. The mixtures were stirred for 1 h at $80^\circ C$. Afterwards, the solvent was removed at $50^\circ C$ overnight to obtain the desired salt in 70% (**18**, 177 mg), 46% (**19**, 102 mg), 68% (**20**, 167 mg), 72% (**21**, 176 mg) yield.

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Conflict of Interests

The authors declare no conflict of interest.

Data Availability Statement

The data that support the findings of this study are available in the supplementary material of this article.

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