Energetic Materials Based on the 5-Azido-3-nitro-1,2,4-triazolate Anion

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Abstract. This study presents the preparation of 5-azido-3-nitro-1H-1,2,4-triazole (1) in both good yield and high purity, starting from commercially available chemicals in a three step synthesis. Furthermore, several metal and nitrogen-rich salts with sodium (3), potassium (4), cesium (5), silver (6), lead (7), ammonium (8), guanidinium (9), and aminoguanidinium (10) were prepared by simple acid-base reactions. All compounds were well characterized by various means, in-

Introduction

Many research groups world-wide are focusing on the development of new nitrogen-rich energetic materials.^[1] The currently deployed energetic materials, be it primary (lead azide, lead styphnate) or secondary explosives (RDX, HMX) all contain toxic or polluting components like heavy metals, nitramines, etc. Lead containing compounds were recently discussed in the news.^[2] New materials should therefore fulfil several criteria like high performance, a good thermal stability (at least 180 °C, better over 200 °C), low sensitivities (for primaries: as low as possible but still sensitive enough for initiation by impact, electric, etc. stimuli) and a low toxicity (no cadmium, mercury, lead, perchlorate, etc.). Primary explosives further need to show a fast deflagration-to-detonation transition (DDT), i.e. the transition from a sub-sonic heat-based energy transport to a shockwave upon ignition.^[3] A possibility for achieving these goals is the use of nitrogen-rich heterocycles, especially tetrazoles and 1,2,4-triazoles $[\Delta_f H^{\circ}(CH_2N_4) =$ +237 kJ·mol⁻¹; $\Delta_{\rm f} H^{\circ}({\rm C}_{2}{\rm H}_{3}{\rm N}_{3}) = +109 \text{ kJ·mol}^{-1}$.^[4,5] Both are in the focus of extended research due to their combination of several energetic factors (ring strain, N-N single and double bonds), often combined with high thermal stabilities (resulting from the aromatic π system), and the formation of molecular dinitrogen as the main detonation product. Especially 5-nitrotetrazole derivatives were extensively studied in the past years as potential lead azide replacements, for example the outdated mercury salt,^[6a] the novel "green" copper(I) salt (DBX-1),^[6b]

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cluding vibrational (IR, Raman) and multinuclear (¹H, ¹³C, ¹⁴N, ¹⁵N) NMR spectroscopy, mass spectrometry, and DSC. Additionally the structure of 7 was determined by single-crystal X-ray diffraction. The sensitivities towards various outer stimuli (impact, friction, electrostatic discharge) were determined according to BAM standards. The metal salts were tested as potential primary explosives utilizing various preliminary tests.

and the laser ignitable tetraammine-cis-bis(5-nitrotetrazolato- N^2)cobalt(III) perchlorate (BNCP).^[6c] Although the triazole moiety is less energetic than the tetrazole one it shows often a higher thermal stability due to the less catenated nitrogen atoms in one row and features two carbon atoms for the introduction of energetic groups to tailor the characteristics for the desired needs.^[1,7]

A possibility to even further increase the heat of formation for various agoles is the introduction of the agide group, often resulting in primary explosives when salts with various metals are formed. Also several metal-free primary explosives incorporating the azide moiety have been reported in the past years,^[8] including multiple binary C-N compounds like 2,4,6triazido-1,3,5-triazine (TTA), which is stable up to 187 °C but suffers from a low density of 1.56 g·cm⁻³, reducing its use as a transfer charge in detonators. Due to the difficult functionalization of 5-azido-1H-tetrazole,^[9] often furnishing some extremely sensitive compounds,^[10] the 1,2,4-triazole moiety was our choice for further investigation. Several derivatives of 3azido-1H-1,2,4-triazole have been reported in the past years,^[11] including the extremely sensitive 3,5-diazido-1H-1,2,4-triazole. After evaluation of the already reported derivatives, 5-azido-3-nitro-1H-1,2,4-triazole (1) caught our attention. While most other (reported) derivatives are quite difficult to prepare or have low reaction yields, 1 seemed interesting due to the facile preparation of the possible starting material, which is 5-amino-3-nitro-1H-1,2,4-triazole (ANTA).^[1f] Intensively described ANTA is thermally stable up to 220 °C. Although the title compound **1** is already literature known at least since 1974,^[12] we were not able to find reliable data on its preparation and characterization. Though two publications mention its potential use as an energetic material,^[13] no characterization or data was given.

The goal of this study is therefore the complete characterization of 5-azido-3-nitro-1H-1,2,4-triazole, including the formation of less-toxic metal and nitrogen-rich salts and investiga-

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tion of the potential as eco-friendly new primary and secondary explosives.

Results and Discussion

Syntheses

The synthesis starts with commercially available 3,5-diamino-1*H*-1,2,4-triazole, which is diazotized with a tenfold excess of sodium nitrite in diluted sulfuric acid, leading to the substitution of both amino groups with nitro groups. The highly hygroscopic 3,5-dinitro-1*H*-1,2,4-triazole can be isolated as its ammonium salt (ADNT) upon treatment with aqueous ammonia solution in about 88% yield.^[14] Refluxing with five equivalents hydrazine monohydrate reduces selectively one nitro group and furnishes 5-amino-3-nitro-1*H*-1,2,4-triazole (ANTA) in about 72% yield.^[14]

According to the previously published procedure,^[15] diazotization of ANTA with sodium nitrite in 25% sulfuric acid and subsequent reaction with sodium azide finally gives 5-azido-3-nitro-1*H*-1,2,4-triazole (1) with a yield of ca. 88%. Further reaction with dimethyl sulfate in aqueous sodium hydroxide solution yielded the methyl derivative **2** in a low yield of 18%,^[15] due to its high solubility in the reaction medium (Scheme 1 and Scheme 2).



Scheme 1. Synthesis of 5-azido-3-nitro-1*H*-1,2,4-triazole (1) from its precursors ADNT and ANTA.



Scheme 2. Synthesis of 5-azido-1-methyl-3-nitro-1,2,4-triazole (2) from 1.

The alkali metal salts with sodium (3), potassium (4),^[15] cesium (5), as well as the nitrogen-rich salts with ammonium (8), guanidinium (9), and aminoguanidinium (10) were prepared according to Scheme 3 in ethanolic solution using 1 and the respective carbonates, bicarbonates, or free bases and subsequent removal of the solvent under reduced pressure. The silver salt (6) was prepared by the reaction of 1 with silver nitrate in the dark. The lead salt (7) was prepared by the reaction of lead nitrate with in situ prepared 3 in water.



Scheme 3. Synthesis of 5-azido-3-nitro-1,2,4-triazolate salts 3-10.

Crystal Structures

The crystal structures of 1, 2, and 4 have already been published by us.^[15] Compound 1 has a quite high calculated density for an azidoazole (1.774 g·cm⁻³), owing to the nitro group. Methylation decreases the density noticeably (2: 1.654 g·cm⁻³). The potassium salt (4) has interestingly only a slightly higher density (1.933 g·cm⁻³) than that reported for potassium 5-azidotetrazolate (1.913 g·cm⁻³),^[9b] although it contains a nitro group. The molecular structures of the three compounds are shown in Figure 1.

Lead bis(5-azido-3-nitro-1,2,4-triazolate) monohydrate (7) crystallizes in the monoclinic space group $P2_1/c$ with a cell volume of 2560.06(10) Å³ and eight molecules in the unit cell. The calculated density at 173 K is 2.768 g·cm⁻³. The asymmetric unit consists of two independent molecular units, one of which is depicted in Figure 2.

The structure is made up by infinite chains along the *b* axis. One such chain is depicted in Figure 3. The chains are parallel along the *b* axis and stacked along the *c* axis. While there are only weak van der Waals interactions to the sides, a weak and mostly electrostatic hydrogen bond (O9–H91···N10ⁱⁱ) is present along the stacking (Table 1, Table 2).

NMR Spectroscopy

Compounds 1–5 and 8–10 were analyzed by ¹H, ¹³C, and ¹⁴N NMR spectroscopy in $[D_6]DMSO$, with 1, 2, and 4 additionally by ¹⁵N NMR spectroscopy.

In the ¹H NMR spectrum, the highly acidic nitrogen bonded proton in **1** is found at $\delta = 9.73$ ppm as a very broad signal. In less basic [D₃]acetonitrile it is located at $\delta = 10.74$ ppm as a narrower, but still broad, signal. ANTA in contrast shows two sharp singlets at 13.14 (ring proton) and 6.80 ppm (NH₂). In **2** the methyl proton shifts are found at $\delta = 3.74$ ppm. While the ammonium cation proton resonances in **8** are located at $\delta =$ 7.14 ppm, the three equivalent amine groups of the guanidinium cation of **9** show a sharp signal at $\delta = 6.92$ ppm. The aminoguanidinium cation of **10** shows four signals, in accordance to the four different types of protons, located at 8.58 (NH–NH₂), 7.27 (NH₂), 6.77 (NH₂) and 4.69 ppm (NH–NH₂).

In all ¹³C NMR spectra both triazole carbon atoms are observed. For the neutral compounds C1 can be observed at $\delta = 160.3$ ppm (1) and 158.7 ppm (2), and C2 at $\delta = 151.8$ ppm (1) and 150.3 ppm (2). Compound 2 additionally shows the resonance of the methyl group C3 at $\delta = 35.4$ ppm. The depro-

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Figure 1. Molecular structures of 1, 2, and 4.^[15] Thermal ellipsoids at 50% probability.



Figure 2. One of the two independent molecular units of 7. Thermal ellipsoids at 50% probability.

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tonation of the ring greatly affects the shifts of both carbon atoms, leading to a down field shift for C1 and a high field shift for C2. The signals of C1 are thus located between 163.6 and 163.9 ppm, while the C2 signals are between 155.7 and 156.2 ppm. The two guanidinium salts (9 and 10) show the signal of the cation at $\delta = 157.9$ and 158.8 ppm, respectively. The ¹⁴N NMR spectrum of all compounds shows the resonance of the nitro group and the azide N_{β} atom. While the former is at -22 ppm in 1 and at -23 ppm in 2 deprotonation results in a down field shift with the signal now being between -12 and -15 ppm. The latter is at -141 and -142 ppm for 1 and 2, respectively, and again down field shifted in the anionic compounds, being between -133 and -134 ppm. Compound 8 also shows the shift of the ammonium nitrogen atom at -354 ppm. Figure 4 shows the ¹⁵N NMR spectra of 1, 2, and 4. In the case of 1 and 2 also the proton de-coupled ¹⁵N{¹H} NMR spectra were recorded. The assignments were based on comparison with theoretical calculations using Gaussian 09 (MPW1PW91/aug-cc-pVDZ).^[16] In the case of 1, seven defi-

nite resonances can be observed at shifts of -20.9 (N4), -91.6 (N2), -137.0 (N7), -139.9 (N6), -154.0 (N3), -172.7 (N1), and -285.9 ppm (N5), with N2 not being visible in the ¹⁵N{¹H} NMR spectrum. A N-H coupling of N1 and N2 is not observable due to the high acidity and therefore fast proton exchange in DMSO. Compound 2 shows signals at -22.6 (N4), -83.3 (N2, q), -137.9 (N7), -141.6 (N6), -153.9 (N3), -184.6 (N1, q), and -288.7 ppm (N5). The methylation at N1 leads to a high field shift for N1 [Δ (N1) = -11.9 ppm] and a similar down field shift for N2 [Δ (N2) = 8.3 ppm], while the shifts of the other nitrogen atoms are only marginally affected. Both cores couple with the hydrogen atoms of the methyl group, leading to a ²J coupling of N1 with a coupling constant of ${}^{2}J_{\rm NH}$ = 2.11 Hz and a ${}^{3}J$ coupling of N2 with a coupling constant of ${}^{3}J_{\rm NH} = 2.03$ Hz. The deprotonation in 4 leads to a large down field shift of N1 to -67.2 ppm [Δ (N1) = 105.5 ppm], a smaller of N2 to -48.5 ppm [$\Delta(N2) = 43.1$ ppm] and also N4 is shifted to $-12.4 \text{ ppm} [\Delta(\text{N4}) = 8.5 \text{ ppm}]$. This is in accordance to 5.5'bis(3-nitro-1*H*-1,2,4-triazole) and its dianion.^[17] Interestingly, N6 is also affected and shifted to $-130.4 \text{ ppm} [\Delta(\text{N6}) =$ 9.5 ppm]. The other shifts are virtually the same as in 1 and 2, leading to the remaining signals being observable at -140.4 (N7), -152.8 (N3), and -288.5 ppm (N5).

Thermal Stabilities

Differential scanning calorimetry measurements were undertaken in order to determine the thermal behavior of the synthesized compounds (Table 3). The decomposition temperatures of the investigated compounds, given as the extrapolated onset temperatures, range from 143 °C (8) up to 199 °C (5). The neutral compound 1 as well as the methyl derivative 2 both show distinct melting points (117 and 122 °C, respectively). The ammonium (8) and aminoguanidinium (10) salts melt under decomposition (143 and 145 °C, respectively). Although the sodium salt (3) has a difference of 80 °C between loss of crystal water and decomposition it is not possible to dehydrate



Figure 3. View on the chains present in the crystal structure of 7. Thermal ellipsoids at 50% probability.

Table 1.	Hydrogen	bonds	present	in	7.
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D–H•••A	D–H /Å	H•••A /Å	D•••A /Å	D–H•••A /°
O9-H91N5	0.90(3)	2.00(4)	2.773(6)	143(4)
O9-H92···N12	0.89(6)	2.01(6)	2.823(7)	152(5)
O9-H92-O4i	0.89(6)	2.54(6)	3.094(5)	121(4)
O9-H91N10 ⁱⁱ	0.90(3)	2.63(6)	3.179(5)	121(4)
Symmetry codes	: (i) $x, y-1,$	<i>z</i> ; (ii) – <i>x</i> +1,	<i>−y</i> +1, <i>−z</i> .	. ,

Table 2. Crystallographic data for 7.

	7		
Formula	C ₄ H ₂ N ₁₄ O ₅ Pb		
$M / \text{g·mol}^{-1}$	533.39		
Color	yellow		
Habit	block		
Crystal size /mm	$0.20 \times 0.20 \times 0.05$		
Crystal system	monoclinic		
Space group	$P2_1/c$ (14)		
a /Å	19.4348(4)		
b /Å	8.7495(2)		
c /Å	15.6181(4)		
a /°	90		
β /°	105.429(2)		
γ /°	90		
$V/Å^3$	2560.06(10)		
Z	8		
$\rho_{\rm calcd.}$ /g·cm ⁻³	2.768		
Т /К	173(2)		
<i>F</i> (000)	1968		
μ /mm ⁻¹	13.245		
Absorption correction	multi-scan		
Dataset $(h; k; l)$	-22:23; -10:10; -19:19		
θ range /°	4.32-26.00		
Reflections collected	24771		
Independent reflections	4996		
Observed reflections	4357		
R _{int.}	0.0539		
Restraints	4		
Parameters	449		
R_1 (obs.)	0.0251		
wR_2 (all data)	0.0595		
S	1.115		
Res. dens. /e•Å ⁻³	-1.188 / 2.462		
Solution	SIR97		
Refinement	SHELXL-97		

it completely, as evidenced by IR spectroscopy and DSC. The lead salt (7) also cannot be dehydrated, as there is no sign of water loss before decomposition. The most stable compounds



Figure 4. ¹⁵N and ¹⁵N{¹H} NMR spectra of (from top to bottom): 5-azido-3-nitro-1*H*-1,2,4-triazole (1), 5-azido-1-methyl-3-nitro-1,2,4-triazole (2), and potassium 5-azido-3-nitro-1,2,4-triazolate (4).

are the salts with guanidinium (9) and cesium (5), showing decomposition at 180 and 199 °C, respectively. Compound 1 itself and the promising potassium salt (4) show similar decomposition points with 174 and 175 °C, respectively. Furthermore both 1 and 4 are thermally stable for at least 48 h at 75 °C in an open glass vessel, as shown by isoperibolic long term measurements, which resulted in neither any signals, nor a weight loss or color change of the samples after the measurement. Usually the deprotonation of nitroazoles raises the stability of the system by overcompensation of the electron-withdrawing nitro group (besides higher lattice energy in the crystalline state due to the ionic nature). However, in the investigated system it mostly decreases the thermal stability, e.g. the

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benefits of deprotonation can hardly compensate for the negative effect of the higher electron density of the system. 5-Nitramino-3-nitro-1*H*-1,2,4-triazole for example has a decomposition temperature of 135 °C, while the respective ammonium salt is stable until 205 °C and the guanidinium salt even 220 °C, with the bis(guanidinium) salt decomposing at 225 °C.^[7b] Also 5-nitrimino-3-azido-1,4*H*-1,2,4-triazole is reported with a decomposition temperature of 143 °C, while all nitrogen-rich salts show higher thermal stabilities,^[11c] especially the guanidinium salt (198 °C). Although the neutral compound is less thermally stable than **1** its nitramine is seemingly better suited for the raised electron density and compensation of its own lower stability, when compared to the nitro group of **1**, concerning this special case with an azide as the second functional group.

Table 3. Thermal behavior of compounds 1–10. Temperatures are given as onset temperatures, as determined by DSC ($\beta = 5 \text{ °C-min}^{-1}$).

Compound	$T_{\rm dh.}$ /°C ^{a)}	$T_{\rm m}$ /°C	$T_{\rm d}$ /°C
1	_	117	174
2	_	122	161
3	96	_	177
4	_	_	175
5	_	-	199
6	_	-	171
7	_	_	149
8	_	143	143
9	_	-	180
10	-	145	145

a) Dehydration temperature.

Toxicity Assessment

To assess the toxicity of **1** and its anion to aquatic life, diluted aqueous solutions of the compounds were subjected to the luminescent marine bacterium *Aliivibrio fischeri*, a representative species for other aquatic life, using the Microtox[®] method^[18] with the commercially available bioassay system Lange LUMIStox. Being the most important toxicological parameter, the EC₅₀ value of the sample was determined. EC₅₀ is the effective concentration of the examined compound, at which the bioluminescence of the strain *Aliivibrio fischeri* is decreased by 50% after a defined period of exposure when compared to the original bioluminescence of the sample before being treated with the differently diluted solutions of the test compound.

For the common secondary explosive RDX (1,3,5-trinitro-1,3,5-triazacyclohexane) a value of 322 μ g·mL⁻¹ is observed after an incubation time of 15 min and 266 μ g·mL⁻¹ after 30 min.^[18c] While **1** has EC₅₀ values of 421 μ g·mL⁻¹ (15 min) and 362 μ g·mL⁻¹ (30 min), compound **4** was determined with 2283 μ g·mL⁻¹ (15 min) and 1065 μ g·mL⁻¹ (30 min), making both compounds slightly less toxic than RDX to *Aliivibrio fischeri*. The values are comparable to 1,4-dimethyl-5-aminotetrazolium azide (512 μ g·mL⁻¹ for 15 min and 435 μ g·mL⁻¹ for 30 min) or guanidinium 5-nitrotetarzolate (1383 μ g·mL⁻¹ for 15 min and 784 μ g·mL⁻¹ for 30 min) and much less toxic than bis(tetrazol-5-yl)amine for example (14 μ g·mL⁻¹ for 15 min and 15 μ g·mL⁻¹ for 30 min).^[18c]

Sensitivities

For initial safety testing the impact and friction sensitivities as well as the electrostatic sensitivities were determined and assigned according to the UN recommendations on the transport of dangerous goods.^[19]

The parent compound **1** is less sensitive towards impact (5 J) than expected due to the fact that it is an azole based compound incorporating an azide besides a nitro group, although it still has to be qualified as sensitive. The friction sensitivity is noticeable higher (42 N) and should therefore only be handled with care. Methylation vielding 2 drastically lowers the sensitivities (> 40 J, 288 N). While the monohydrated sodium salt (3) is "only" sensitive (3 J, 144 N), the other metal salts are very sensitive primary explosives, both concerning their nature and their sensitivities. All show impact sensitivities of <1 J and can already be detonated by a hit with a small hammer. The friction sensitivities are similarly high with <5 N, except for the monohydrate 7 (7 N). While the ammonium (8) and aminoguanidinium (10) salts are also rather sensitive against impact with 3 and 7 J, respectively, the guanidinium salt (9) is almost insensitive (30 J). Compound 8 also has the highest friction sensitivity of the three nitrogen-rich salts (144 N), with 9 and 10 being comparably rather low sensitive (288 and 240 N, respectively). The commonly used secondary explosive RDX is also classified as sensitive against both impact and friction (7.4 J, 120 N). Concerning the sensitivity against electrostatic discharge, compound 1 has the highest of the neutral and nitrogen-rich compounds (50 mJ). The others range between 200 mJ (2) and 500 mJ (8 and 9), including the sodium salt (3). These findings are in agreement to those observed for RDX (200 mJ) and other nitramine compounds.^[20] The metal salts 4, 5, and 6 are far more sensitive, being between 3 mJ (6) and 15 mJ (4) and therefore in the range of primary explosives like Pb(N3)2 (5 mJ). Furthermore, compounds 4, 5, 6, and 7 are the only ones to always detonate (impact, friction and electrostatic discharge), while the other compounds merely only vanish without sound.

Energetic Properties

The metal salts containing the cations sodium (3), potassium (4), cesium (5), silver (6), and lead (7) were the main focus of this study and were tested for their potential of being primary explosives. Compounds 6 and 7 have only comparative character, due to silver salts being (a) expensive, (b) often light sensitive and (c) extremely toxic to aquatic life and microorganisms,^[21] and 7 due to the obvious lead content, which negates its use as a lead azide replacement. The main reason for 6 was the ease of preparation and the often high sensitivity of silver salts of azole compounds, revealing the potential of the anion to form primary explosives. Compound 7 was prepared for thermal characterization. As already mentioned, a true primary explosive is characterized by a fast deflagration-to-detonation

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Figure 5. Hot plate test of 4 (200 mg) on a copper plate, heated with a Bunsen burner. A deep dent is visible in the former place of the substance.

transition (DDT) when subjected to heat or flame. Therefore a small amount (approx. 5 mg) of 3-7 was heated on a spatula using a lighter, without direct flame contact. Except for the hydrated 3 all compounds detonated upon reaching their respective ignition temperatures. Compound 4 was further tested with the hot plate test, where 200 mg were placed on a 2 mm thick copper plate and heated with a Bunsen burner from below (again without direct flame contact). Upon reaching its ignition temperature the compound detonated violently, leaving no solid residues (see Figure 5). Secondary explosives like RDX only deflagrate under these conditions. Next, a small sample (again approx. 5 mg) of 4-6 was fixed to a surface with a bit of transparent tape and poked with a pre-heated needle. Sadly, in this case the DDT was not fast enough to achieve a detonation, the compounds were merely only deflagrating, although very fast. Nevertheless, the potassium salt (4) was tested for its ability to initiate a commonly used secondary



Figure 6. Copper tube test of 4 (400 mg RDX, 10 mg 4). Left: test setup; right: collected fragments after detonation.

explosive, like RDX. Thus about 400 mg of RDX were loaded in a copper tube (6.50 mm \times 57.70 mm), layered with a varying amount of **4** (10, 25, 50, 75, or 100 mg) and slightly pressed. For the ignition a commercial type A electrical igniter was used on top.^[22] Figure 6 shows the copper tube before and after the experiment with 10 mg of **4** as the primary explosive. Initiation of RDX without the primary explosive, using only the igniter, is not possible. The results reveal **4** and the similarly performing cesium salt (**5**) as interesting materials for further testing.

An application of the anion in nitrogen-rich ionic secondary explosives is unlikely due to low densities (9: $1.50 \text{ g} \cdot \text{cm}^{-3}$), which should be at least $1.78 \text{ g} \cdot \text{cm}^{-3}$ to be able to compete with RDX, and especially due to the low thermal stabilities of the presented salts 8–10. More energetic cations like hydroxylammonium or triaminoguanidinium have always lower stabilities than ammonium (8) or aminoguanidinium (10), thus far below the requirement of 180 °C.

Conclusions

The goal of the presented study was the preparation and full characterization of 5-azido-3-nitro-1*H*-1,2,4-triazole (1) and selected metal and nitrogen-rich salts with sodium (3), potassium (4), cesium (5), silver (6), lead (7), ammonium (8), guanidinium (9), and aminoguanidinium (10). The thermal stabilities of the compounds are rather low between 143 °C (8) and 199 °C (5). The toxicity of 1 and 4 was assessed with the Microtox[®] method, revealing both as less toxic than RDX to *Aliivibrio fischeri*. The salts with potassium (4) and cesium (5) were identified as interesting new primary explosives. Both are able to undergo a deflagration-to-detonation transition upon heating on a spatula, with 4 additionally tested by heating on a copper plate with a Bunsen burner. The initiation ability of **4** was tested with RDX, with even as low as 10 mg of substance being able to initiate the secondary explosive.

Experimental Section

General: All chemicals were used as supplied (ABCR, Acros Organics, AppliChem, Sigma-Aldrich, VWR), if not stated otherwise.

NMR spectra were recorded with the spectrometers JEOL Eclipse 270, Eclipse 400 and JEOL ECX 400. The measurements were conducted in regular glass NMR tubes (Ø 5 mm) and, if not stated otherwise, at

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25 °C. Tetramethylsilane (¹H, ¹³C) and nitromethane (¹⁴N) were used as external standards. As additional internal standard the reference values of the partially deuterated solvent impurity (¹H) and the fully deuterated solvent (¹³C) were used.^[23] IR spectra were recorded with a Perkin-Elmer BX FT IR spectrometer on a Smiths DuraSamplIR II diamond ATR unit with pure samples. Low resolution mass spectra were recorded with a JEOL MStation JMS-700. The determination of the carbon, hydrogen, and nitrogen contents was carried out by combustion analysis with an Elementar Vario EL. Differential scanning calorimetry was conducted with a Linseis DSC-PT10 in closed aluminum pans, equipped with a hole (Ø 0.1 mm) for gas release, and a heating rate of 5 °C·min⁻¹. Melting points were checked with a Büchi Melting Point B-540 in open glass capillaries. Densities were determined by gas pycnometry at room temperature using a Quantachrome Ultrapyc 1200e.

The sensitivities against impact (IS) and friction (FS) were determined according to $BAM^{[24]}$ standards using a BAM drop hammer and a BAM friction apparatus.^[25]

Crystal Structure Determination: The crystal structure of **7** was determined by single-crystal X-ray diffraction with an Oxford Diffraction Xcalibur 3 diffractometer with a Sapphire CCD detector, four circle kappa platform, Enhance molybdenum K_{α} radiation source ($\lambda = 71.073 \text{ pm}$) and Oxford Cryosystems Cryostream cooling unit. Data collection and reduction were performed with CrysAlisPro.^[26] The structure was solved with SIR97,^[27] refined with SHELXL-97,^[28] and checked with PLATON,^[29] all integrated into the WinGX software suite.^[30] The finalized CIF file was checked with checkCIF.^[31] Intra-and intermolecular contacts were analyzed with Mercury.^[32] Illustrations of molecular structure refinement results for compound **7** are summarized in Table 2

Crystallographic data (excluding structure factors) for the structure in this paper have been deposited with the Cambridge Crystallographic Data Centre, CCDC, 12 Union Road, Cambridge CB21EZ, UK. Copies of the data can be obtained free of charge on quoting the depository number CCDC-917586 (7) (Fax: +44-1223-336-033; E-Mail: deposit@ccdc.cam.ac.uk, http://www.ccdc.cam.ac.uk)

Caution! Most compounds prepared herein are energetic compounds sensitive towards impact, friction, and electric discharge. Although we had no problems handling the compounds, proper protective measures (ear protection, Kevlar[®] gloves, face shield, body armor and earthed equipment) should be used, especially when working with the primary explosives **4**, **5**, **6**, and **7**.

Ammonium 3,5-Dinitro-1,2,4-triazolate (ADNT): According to modified literature procedures,^[14] a dropping funnel without pressureequalizer was charged with a solution of 3,5-diamino-1H-1,2,4-triazole (10.0 g, 100 mmol) in sulfuric acid (0.75 m, 310 mL), which was slowly added drop wise to an ice cooled and vigorously stirred solution of sodium nitrite (69.0 g, 1.00 mol) in water (300 mL) in a 2 L three necked round flask. After the addition, which should take about 2 h, the resulting orange suspension was heated to 70 $^{\circ}\mathrm{C}$ until a clear orange to red solution was formed. It was cooled again with an ice bath and sulfuric acid (30%, 150 mL) was added, followed by the addition of urea (3 g) in small portions. After stirring overnight at room temperature, the mixture was extracted with ethyl acetate $(6 \times 200 \text{ mL})$. The combined organic phases were dried with magnesium sulfate and concentrated under reduced pressure to a viscous yellow oil. It was dissolved in water (10 mL), basified with aqueous ammonia solution (12.5%, 22 mL), layered with diethyl ether, and stored overnight at 4 °C. The resulting precipitate was filtered off, washed with a small amount of water and ethanol, and finally dried in air to yield yellow to orange crystals (17.1 g, 88.1 mmol, 88%). EA (C₂H₆N₆O₅): calcd. C 12.38, H 3.12, N 43.30%; found C 11.78, H 3.27, N 39.51%. ¹H NMR ([D₆]DMSO): δ = 7.09 (br., NH₄⁺), 3.38 (br., H₂O). ¹³C NMR ([D₆]DMSO): δ = 162.9. ¹⁴N NMR ([D₆]DMSO): δ = 162.9. (w), 1370 (m), 3044 (m), 2854 (m), 2465 (w), 2363 (w), 1636 (w), 1536 (s), 1496 (s), 1449 (vs), 1389 (vs), 1352 (vs), 1300 (vs), 1110 (m), 1049 (m), 844 (vs), 832 (s), 768 (w), 684 (m), 645 (s) cm⁻¹.

5-Amino-3-nitro-1*H***-1,2,4-triazole (ANTA):** According to modified literature procedures,^[14] ADNT (19.4 g, 100 mmol) was stirred in hydrazine monohydrate (26 mL, 0.54 mol) for 3 h at 80 °C. The cooled down orange solution was mixed with water (37 mL) and acidified with hydrochloric acid (37 %, 37 mL). After stirring the yellow solution overnight at room temperature the resulting precipitate was filtered off, washed with a very small amount of water, and dried overnight at 70 °C to yield a yellow powder (9.26 g, 71.7 mmol, 72 %). **EA** (C₂H₃N₅O₂): calcd. C 18.61, H 2.34, N 54.26 %; found C 18.85, H 2.28, N 54.21 %. ¹**H** NMR ([D₆]DMSO): δ = 13.14 (s, 1 H, NH), 6.80 (s, 2 H, NH₂). ¹³C NMR ([D₆]DMSO): δ = 160.9 (C1), 157.4 (C2). ¹⁴N NMR ([D₆]DMSO): δ = -18 (NO₂). **IR** (ATR): \tilde{v} = 3434 (m), 3323 (m), 3164 (m), 3005 (m), 1629 (vs), 1572 (m), 1507 (vs), 1383 (s), 1300 (vs), 1143 (m), 1078 (m), 1036 (m), 1013 (s), 957 (w), 838 (s), 801 (w), 756 (m), 721 (m) cm⁻¹.

5-Azido-3-nitro-1H-1,2,4-triazole (1): Sodium nitrite (379 mg, 5.50 mmol) was added to a stirred suspension of ANTA (645 mg, 5.00 mmol) in sulfuric acid (25%, 30 mL) at 0 to 5 °C in small portions and the resulting yellow solution was stirred for 1 h at room temperature. After the addition of a small portion of urea, sodium azide (390 mg, 6.00 mmol) was added in small portions, followed by stirring for further 30 min. The reaction mixture was extracted with ethyl acetate $(3 \times 20 \text{ mL})$, the combined organic phases were dried with magnesium sulfate and the solvents evaporated to dryness at reduced pressure. The residue was stirred in n-pentane overnight, filtered, and washed with n-pentane to yield a colorless powder (685 mg, 4.42 mmol, 88%). EA (C₂HN₇O₂): calcd. C 15.49, H 0.65, N 63.23%; found C 15.37, H 0.90, N 59.98 %. ¹H NMR (CD₃CN): δ = 10.74 (br). ¹**H** NMR ([D₆]DMSO): δ = 9.73 (br). ¹³**C** NMR ([D₆]DMSO): δ = 160.3 (C1), 151.8 (C2). ¹⁴N NMR ([D₆]DMSO): $\delta = -22$ (N4), -141 (N6). ¹⁵N NMR ([D₆]DMSO): $\delta = -20.9$ (N4), -91.6 (N2), -137.0 (N7), -139.9 (N6), -154.0 (N3), -172.7 (N1), -285.9 (N7). **IR** (ATR): $\tilde{v} = 3198$ (m), 2367 (w), 2219 (w), 2148 (s), 1670 (w), 1630 (w), 1569 (m), 1525 (vs), 1489 (vs), 1443 (s), 1417 (s), 1378 (s), 1294 (s), 1187 (vs), 1165 (s), 1053 (m), 1035 (s), 1010 (m), 843 (vs), 787 (vs), 766 (s), 706 (vs) cm⁻¹. **Raman** (300 mW): $\tilde{v} = 2159$ (9), 1543 (16), 1492 (100), 1422 (17), 1384 (25), 1369 (9), 1320 (6), 1299 (10), 1169 (17), 1037 (14), 1012 (5) cm⁻¹. **MS** (DEI+): m/z = 155.1 ([C₂HN₇O₂]⁺). **DSC** (5 °C·min⁻¹): $T_{\rm m} = 117$ °C, $T_{\rm d} = 174$ °C. Sensitivities (grain size < 100 µm): IS 5 J, FS 42 N, ESD 50 mJ.

5-Azido-1-methyl-3-nitro-1,2,4-triazole (2): Dimethyl sulfate (1.26 g, 10.0 mmol) was added drop wise to a solution of **1** (1.55 g, 10.0 mmol) and sodium hydroxide (800 mg, 20.0 mmol) in water (10 mL). The reaction mixture was stirred overnight at 105 °C. The precipitate obtained after cooling to room temperature was filtered off, washed with a small amount of water, and dried in air to yield fine colorless needles suitable for X-ray diffraction (270 mg, 1.60 mmol, 16%). EA (C₃H₃N₇O₂): calcd. C 21.31, H 1.79, N 57.98%; found C 21.58, H 1.80, N 56.59%. ¹H NMR ([D₆]DMSO): δ = 3.74 (s, CH₃). ¹³C NMR ([D₆]DMSO): δ = 158.7 (C1), 150.3 (C2), 35.4 (C3).

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NMR ([D₆]DMSO): $\delta = -23$ (N4), -142 (N6). ¹⁵N NMR ([D₆]DMSO): $\delta = -22.6$ (N4), -83.3 (q, ³*J*_{NH} = 2.03 Hz, N2), -137.9 (N7), -141.6 (N6), -153.9 (N3), -184.6 (q, ²*J*_{NH} = 2.11 Hz, N1), -288.7 (N7). **IR** (ATR): $\tilde{v} = 2394$ (w), 2294 (w), 2166 (s), 1551 (s), 1502 (vs), 1449 (s), 1398 (s), 1311 (vs), 1266 (s), 1252 (vs), 1044 (m), 1020 (m), 875 (s), 811 (s), 708 (s), 683 (s), 642 (m) cm⁻¹. **Raman** (300 mW): $\tilde{v} = 2960$ (28), 2160 (11), 1551 (12), 1535 (52), 1499 (54), 1453 (39), 1398 (100), 1303 (32), 1271 (13), 1253 (28), 1046 (24), 1023 (12), 769 (6), 683 (13) cm⁻¹. **MS** (DEI+): *m/z* = 169.0 ([C₃H₃N₇O₂]⁺). **DSC** (5 °C·min⁻¹): *T*_m = 122 °C, *T*_d = 161 °C. Sensitivities (grain size 100 to 500 µm): IS > 40 J, FS 288 N, ESD 200 mJ.

Sodium 5-Azido-3-nitro-1,2,4-triazolate Monohydrate (3): Sodium carbonate (265 mg, 2.50 mmol) and 1 (853 mg, 5.50 mmol) were refluxed in ethanol (60 mL) until a clear yellow solution was obtained. The solvent was removed under reduced pressure and the residue was stirred in diethyl ether to remove excess 1, filtered off, and washed with diethyl ether to yield a yellow powder (885 mg, 4.45 mmol, 91%). EA (C₂H₂N₇NaO₃): calcd. C 12.31, H 1.03, N 50.26%; found C 12.82, H 0.96, N 49.96 %. ¹H NMR ([D₆]DMSO): δ = 3.46 (H₂O). ¹³C NMR ([D₆]DMSO): δ = 163.8 (C1), 155.9 (C2). ¹⁴N NMR $([D_6]DMSO): \delta = -14 \text{ (N4)}, -133 \text{ (N6)}. IR (ATR): \tilde{v} = 3497 \text{ (w)}, 3299$ (w), 2423 (w), 2270 (w), 2150 (s), 1680 (w), 1545 (s), 1496 (m), 1451 (vs), 1395 (s), 1340 (vs), 1295 (s), 1217 (s), 1096 (s), 1055 (w), 1026 (w), 850 (s), 804 (m), 729 (m), 656 (s) cm⁻¹. Raman (300 mW): $\tilde{v} =$ 2158 (15), 1539 (11), 1459 (45), 1395 (94), 1339 (100), 1297 (10), 1220 (7), 1099 (97), 1028 (13) cm⁻¹. **MS** (FAB+): m/z = 23.0 ([Na]⁺); (FAB-): m/z = 154.0 ([C₂N₇O₂]⁻). **DSC** (5 °C·min⁻¹): $T_d = 177$ °C. Sensitivities (grain size $<100~\mu\text{m}$): IS 3 J, FS 144 N, ESD 300 mJ.

Potassium 5-Azido-3-nitro-1,2,4-triazolate (4): Potassium carbonate (138 mg, 1.00 mmol) and 1 (341 mg, 2.20 mmol) were refluxed in ethanol (24 mL) until a clear yellow solution was obtained. The solvent was removed under reduced pressure and the residue was stirred in diethyl ether, filtered off, and washed with diethyl ether to yield a yellow powder (315 mg, 1.63 mmol, 82 %). EA (C₂KN₇O₂): calcd. C 12.44, N 50.76%; found C 13.28, N 50.00%. ¹³C NMR ([D₆]DMSO): $\delta = 163.9$ (C1), 156.2 (C2). ¹⁴N NMR ([D₆]DMSO): $\delta = -12$ (N4), -134 (N6). ¹⁵N NMR ([D₆]DMSO): $\delta = -12.4$ (N4), -48.5 (N2), -67.2(N1), -130.4 (N6), -140.4 (N7), -152.8 (N3), -288.5 (N7). IR (ATR): $\tilde{v} = 2444$ (w), 2243 (w), 2142 (s), 1531 (s), 1478 (m), 1441 (vs), 1386 (s), 1324 (vs), 1286 (m), 1226 (m), 1084 (s), 1054 (w), 1018 (w), 843 (m), 796 (w), 731 (m), 656 (m) cm⁻¹. **Raman** (300 mW): $\tilde{v} = 2153$ (4), 1457 (11), 1445 (28), 1387 (44), 1323 (72), 1083 (100), 1019 (5) cm⁻¹. **MS** (FAB+): m/z = 38.9 ([K]⁺); (FAB-): m/z = 154.0($[C_2N_7O_2]^-$). **DSC** (5 °C·min⁻¹): $T_d = 175$ °C. Sensitivities (grain size $<100\,\mu m$): IS <1 J, FS <5 N, ESD 15 mJ.

Cesium 5-Azido-3-nitro-1,2,4-triazolate (5): Cesium carbonate (326 mg, 1.00 mmol) and **1** (341 mg, 2.20 mmol) were refluxed in ethanol (24 mL) and a few drops of water until a clear yellow solution was obtained. A very small amount of water and little more ethanol were added to the residue after removal of the solvent under reduced pressure. The solid was filtered off and washed with diethyl ether to yield a yellow powder (504 mg, 1.76 mmol, 88 %). EA (C₂CsN₇O₂): calcd. C 8.37, N 34.17%; found C 8.66, N 33.73%. ¹³C NMR ([D₆]DMSO): δ = 163.7 (C1), 155.7 (C2). ¹⁴N NMR ([D₆]DMSO): δ = -15 (N4), -134 (N6). IR (ATR): $\tilde{v} = 2446$ (w), 2363 (w), 2339 (w), 2264 (w), 2216 (w), 2150 (m), 2130 (m), 1512 (s), 1474 (vs), 1436 (vs), 1387 (s), 1330 (s), 1292 (m), 1226 (m), 1080 (s), 1036 (w), 844 (m), 782 (w), 727 (m), 660 (w) cm⁻¹. Raman (300 mW): $\tilde{v} = 1435$ (21), 1384 (41), 1330 (77), 1076 (100), 1014 (6) cm⁻¹. MS (FAB+): m/z = 133.0 ([Cs]⁺); (FAB–): m/z = 154.0 ([C₂N₇O₂]⁻). DSC (5 °C·min⁻¹): $T_{\rm d}$ = 199 °C. Sensitivities (grain size < 100 µm): IS < 1 J, FS < 5 N, ESD 7 mJ.

Silver 5-Azido-3-nitro-1,2,4-triazolate (6): A solution of silver nitrate (170 mg, 1.00 mmol) in water (20 mL) was added drop wise to a solution of **1** (155 mg, 1.00 mmol) in water (40 mL). The resulting suspension was stirred in the dark for 30 min, filtered, and washed with water and ethanol to yield a pale yellow powder (174 mg, 664 µmol, 66%). **EA** (C₂AgN₇O₂): calcd. C 9.17, N 37.43%; found C 9.62, N 36.73%. **IR** (ATR): $\tilde{v} = 2429$ (w), 2141 (s), 1553 (m), 1493 (s), 1467 (vs), 1403 (m), 1347 (m), 1307 (s), 1220 (s), 1116 (m), 1104 (m), 846 (m), 798 (m), 718 (w) cm⁻¹. **Raman** (300 mW): $\tilde{v} = 2141$ (7), 1541 (6), 1492 (4), 1460 (57), 1407 (30), 1347 (100), 1310 (5), 1118 (15), 1105 (28), 1046 (7) cm⁻¹. **MS** (DEI+): *m/z* = 106.9 ([Ag]⁺). **DSC** (5 °C·min⁻¹): *T*_d = 171 °C. Sensitivities (grain size < 100 µm): IS < 1 J, FS < 5 N, ESD 3 mJ.

Lead Bis(5-azido-3-nitro-1,2,4-triazolate) Monohydrate (7): A solution of lead nitrate (365 mg, 1.10 mmol) in water (20 mL) was added drop wise to a solution of 1 (310 mg, 2.00 mmol) in hot water (40 mL) and sodium hydroxide solution (2 m, 1.0 mL, 2.0 mmol). Yellow single-crystals precipitated after several weeks. The yield was not determined. EA (C₄H₂N₁₄PbO₅): calcd. C 9.01, H 0.38, N 36.77%; found C 9.25, H 0.43, N 35.66%. IR (ATR): $\tilde{v} = 3297$ (w), 2154 (s), 1530 (m), 1450 (vs), 1386 (s), 1328 (s), 1294 (s), 1223 (m), 1212 (m), 1100 (s), 1064 (m), 1019 (m), 844 (m), 805 (m), 720 (m) cm⁻¹. DSC (5 °C·min⁻¹): $T_d = 149$ °C. Sensitivities (grain size < 100 µm): IS < 1 J, FS 8 N.

Ammonium 5-Azido-3-nitro-1,2,4-triazolate (8): Aqueous ammonia solution (2 m, 3.0 mL, 6.0 mmol) and 1 (853 mg, 5.50 mmol) were stirred in ethanol (40 mL) for 30 min. The solvent was removed under reduced pressure and the residue was stirred in diethyl ether, filtered off, and washed with diethyl ether to yield a yellow powder (695 mg, 4.04 mmol, 74%). EA (C₂H₄N₈O₂): calcd. C 13.96, H 2.34, N 64.11%; found C 14.38, H 2.30, N 64.61%. ¹H NMR ([D₆]DMSO): δ = 7.19 (s, NH₄⁺). $^{13}\mathbf{C}$ NMR ([D₆]DMSO): δ = 163.6 (C1), 155.9 (C2). ¹⁴N NMR ([D₆]DMSO): $\delta = -15$ (N4), -133 (N6), -354 (NH₄⁺). **IR** (ATR): $\tilde{v} = 3333$ (w), 3135 (w), 2948 (w), 2757 (w), 2465 (w), 2135 (s), 1685 (w), 1533 (w), 1486 (m), 1445 (vs), 1423 (vs), 1393 (vs), 1341 (vs), 1297 (s), 1235 (s), 1090 (vs), 1065 (w), 1052 (w), 1029 (w), 842 (s), 801 (m), 726 (m), 655 (s) cm⁻¹. Raman (300 mW): $\tilde{v} = 2139$ (4), 1454 (28), 1395 (38), 1335 (72), 1090 (100), 1031 (7) cm⁻¹. **MS** (FAB+): m/z = 18.1 ([NH₄]⁺); (FAB-): m/z = 154.0([C₂N₇O₂]⁻). **DSC** (5 °C·min⁻¹): $T_m = 143$ °C (equals T_d). Sensitivities (grain size $< 100 \mu m$): IS 3 J, FS 144 N, ESD 500 mJ.

Guanidinium 5-Azido-3-nitro-1,2,4-triazolate (9): Guanidinium carbonate (815 mg, 2.50 mmol) and 1 (853 mg, 5.50 mmol) were refluxed in ethanol (60 mL) and a few drops of water until a clear yellow solution was obtained. The solvent was removed under reduced pressure and the residue was stirred in diethyl ether, filtered off, and washed with diethyl ether to yield a yellow powder (1.03 g, 4.81 mmol, 96%). EA (C₃H₆N₁₀O₂): calcd. C 16.83, H 2.82, N 65.41%; found C 17.18, H 2.73, N 64.77%. ¹H NMR ([D₆]DMSO): $\delta = 6.92$ (s, NH₂). ¹³C NMR ([D₆]DMSO): $\delta = 163.7$ (C1), 157.9 (G⁺), 155.7 (C2). ¹⁴N NMR ([D₆]DMSO): $\delta = -15$ (N4), -133 (N6). **IR** (ATR): $\tilde{v} = 3476$ (m), 3348 (w), 3079 (m), 2440 (w), 2254 (w), 2143 (vs), 1688 (m), 1654 (s), 1574 (w), 1518 (m), 1477 (vs), 1445 (vs), 1396 (s), 1335 (vs), 1300 (m), 1227 (m), 1143 (w), 1087 (vs), 1045 (w), 1027 (w), 1007 (w), 841 (s), 786 (w), 719 (w), 655 (w), 624 (w) cm⁻¹. **Raman** (300 mW): $\tilde{v} = 2154$ (2), 1520 (6), 1483 (5), 1451 (29), 1397 (40), 1337 (78), 1088 (100), 1030 (5), 1009 (11), 843 (13) cm⁻¹. **MS** (FAB+): m/z = 60.0 ([CH₆N₃]⁺); (FAB-): m/z = 154.0

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([$C_2N_7O_2$]⁻). **DSC** (5 °C·min⁻¹): T_d = 180 °C. Sensitivities (grain size < 100 µm): IS 30 J, FS 288 N, ESD 500 mJ.

Aminoguanidinium 5-Azido-3-nitro-1,2,4-triazolate (10): Aminoguanidinium hydrogen carbonate (681 mg, 5.00 mmol) and 1 (853 mg, 5.50 mmol) were refluxed in ethanol (60 mL) until a clear yellow solution was obtained. After filtration the solvent was removed under reduced pressure and the residue was stirred in diethyl ether, filtered off, and washed with diethyl ether to yield a pale yellow powder (1.06 g, 4.62 mmol, 92%). EA (C₃H₇N₁₁O₂): calcd. C 15.72, H 3.08, N 67.23 %; found C 16.19, H 2.92, N 66.75 %. ¹H NMR ([D₆]DMSO): $\delta = 8.58$ (s, 1 H, NH–NH₂), 7.27 (s, 2 H, C–NH₂), 6.77 (s, 2 H, C– NH₂), 4.69 (s, 2 H, NH–NH₂). ¹³C NMR ([D₆]DMSO): δ = 163.7 (C1), 158.8 (AG⁺), 155.8 (C2). ¹⁴N NMR ([D₆]DMSO): $\delta = -15$ (N4), -133 (N6). **IR** (ATR): $\tilde{v} = 3435$ (w), 3326 (w), 3138 (w), 2425 (w), 2128 (s), 1669 (s), 1526 (m), 1479 (s), 1442 (vs), 1397 (m), 1334 (s), 1300 (s), 1222 (m), 1084 (s), 1043 (w), 990 (w), 953 (w), 920 (m), 839 (s), 782 (w), 728 (w), 656 (m), 621 (w) cm⁻¹. Raman (300 mW): $\tilde{v} = 2143$ (4), 1464 (26), 1443 (8), 1397 (42), 1337 (91), 1089 (100), 1024 (8), 842 (5) cm⁻¹. **MS** (FAB+): m/z = 75.0 ([CH₇N₄]⁺); (FAB-): $m/z = 154.0 ([C_2N_7O_2]^-)$. **DSC** (5 °C·min⁻¹): $T_m = 145$ °C (equals T_d). Sensitivities (grain size $< 100 \,\mu$ m): IS 7 J, FS 240 N, ESD 400 mJ.

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