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New Energetic Materials featuring Tetrazoles and Nitramines – Synthesis, Characterization and Properties

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Dedicated to Dr. Klaus Römer on the Occasion of His 70th Birthday

Keywords: Energetic materials; Tetrazoles; X-ray diffraction; Detonation parameters; Sensitivities; NMR spectroscopy

Abstract. The alkylation of 2-nitro-2-azapropyl chloride (**2**) and deprotonated 5-amino-1*H*-tetrazole (**3**), 1*H*-tetrazole (**4**), 5-nitrimino-1,4*H*-tetrazole (**5**), 1-methyl-5-nitrimino-4*H*-tetrazole (**6**) and 2-methyl-5-nitraminotetrazole (**7**) afforded the products 1-(2-nitro-2-azapropyl)-5-aminotetrazole (**8**), 1-(2-nitro-2-azapropyl)-5*H*-tetrazole (**9**), 1-(2-nitro-2-azapropyl)-5-nitriminotetrazole·H_2O (**10a**), 1-(2-nitro-2-azapropyl)-5-nitriminotetrazole·EtOH (**10b**) 1,5-*bis*(2-nitro-2-azapropyl)-5-nitraminotetrazole (**11**), 1-methyl-5-(2-nitro-2-azapropyl)-5-nitraminotetrazole (**12**), 1-methyl-4-(2-nitro-2-azapropyl)-5-nitraminotetrazole (**13**), 1-methyl-5-(2-nitro-2-azapropyl)-5-aminotetrazole (**14**) and 2-methyl-5-(2-nitro-2-azapropyl)-5-nitraminotetrazole (**15**). In addition, the reaction of potassium 1-methyl-5-nitriminotetrazolate with dimethyl sulfate was investigated yielding 1,4-dimethyl-5-nitriminotetrazole (**16**). All products (**8**–**16**) were determined by low temperature single X-ray diffraction. A comprehensive characterization and description of the chemical properties (IR, Raman, and multinuclear (^{1}H, ^{13}C and ^{15}N) NMR spectroscopy, mass spectrometry, elemental analysis and differential scanning calorimetry) is given. The heats of formation were calculated by heats of combustion measured using bomb calorimetry. With these values and the X-ray densities, several detonation parameters (e.g. detonation pressure, detonation velocity, heat of explosion) were computed by the EXPLO5 software. In addition, the sensitivities towards impact, friction and electrical discharge were determined.

Introduction

The synthesis of energetic, non-nuclear materials [1] for possible military or civil application has been a long term goal in our research group [2]. The standards for new energetic materials are high positive heat of formation, high detonation velocity and pressure, high thermal stability and low sensitivity towards external forces like impact, friction or electrostatic discharge. Of particular interest are high-nitrogen compounds (e.g. tetrazoles) in combination with energetic substituents such as nitro groups (R–NO_2) [3, 4], nitrate esters (R–O–NO_2) [5], azide groups (R–N_3) [6] or nitramine functionalities (R_2N–NO_2) [7, 8]. Also the formation of tetrazolium salts with oxygen rich counter anions such as NO_3^- [9, 10] or $N(NO_2)_2^-$ [11, 12] are in the focus of our research, since these compounds have balanced oxygen contents. We recently reported on the synthesis and characterization of 2-(2-nitro-2-azapropyl)-5-nitrotetrazole [13], which has an appropriate oxygen balance similar to that of RDX (hexogen). The oxygen balance indicates the relative amount of oxygen available for the following ideal combustion reactions without adding *outer* oxygen: carbon to carbon dioxide, hydrogen to water, nitrogen to dinitrogen and sulfur to sulfur dioxide. The oxygen balance of CHNSO compounds can be easily calculated by the equation: Ω /% = (wO – 2xC – 1/2yH – 2zS)·1600/M. (w: number of oxygen atoms, x: number of carbon atoms, y: number of hydrogen atoms, z: number of sulfur atoms, M: molecular weight). In this work, we report on the synthesis of new neutral energetic materials combining tetrazole moieties with the 2-nitro-2-azapropyl substituent.

Results and Discussion

The preparative route to 2-nitro-2-azapropyl chloride (**2**) [14] is divided into two steps, shown in Scheme 1. The first step is the nitration of 1,3,5-trimethylhexahydro-1,3,5-triazine forming 2-nitro-2-azapropyl acetate (**1**) [15]. To a mixture of fuming nitric acid and acetic anhydride, 1,3,5-trimethylhexahydro-1,3,5-triazine, dissolved in glacial acetic acid, is added. Because of the strong exothermicity of the reaction it is necessary to control the temperature (70–75 °C) vigilantly. Otherwise, the reaction may run out of control resulting in further rise of the temperature and formation of highly explosive undesirable nitration products.

Compound **1** has to be converted into the 2-nitro-2-azapropyl chloride (**2**) since a leaving group is desired. Therefore, 2-nitro-2-azapropyl acetate is heated under reflux with thionyl

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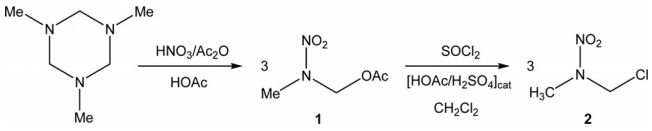


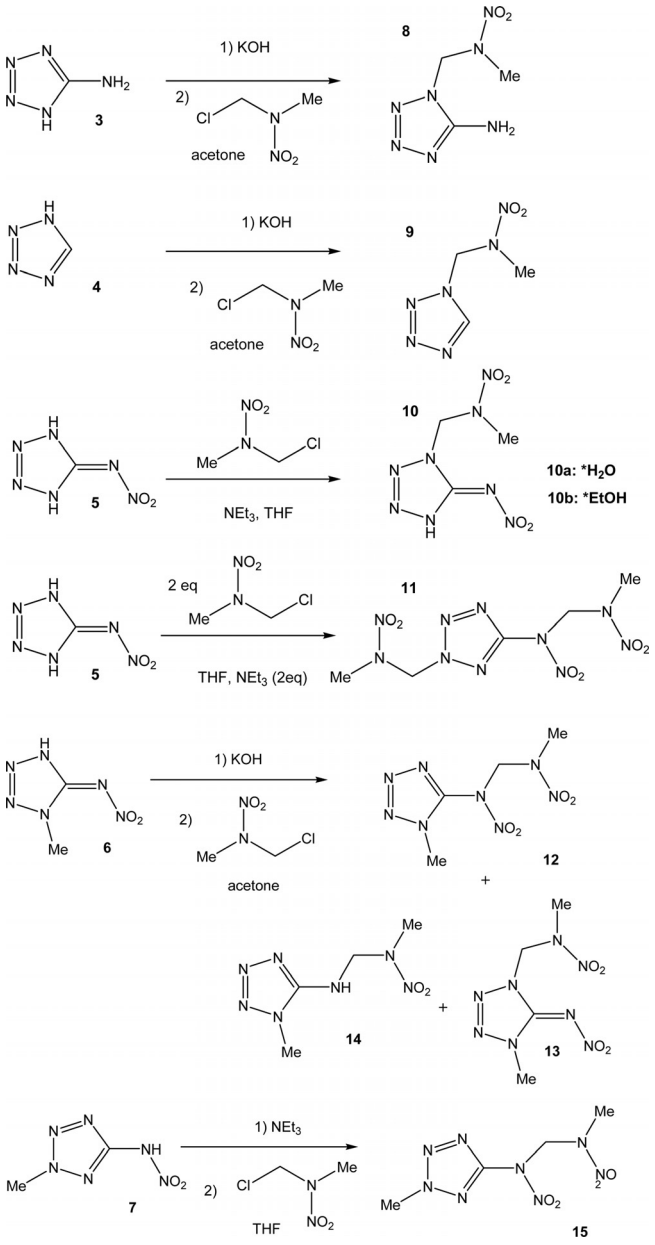
Scheme 1. Synthesis of 2-nitro-2-azapropane chloride (**2**).

chloride in dichloromethane (DCM). Small amounts of acetic acid and sulfuric acid are used as catalysts.

The tetrazole derivatives **8**–**15** were synthesized according to Scheme 2. The starting tetrazoles were either purchased commercially [5-amino-1*H*-tetrazole (**3**)] or synthesized according to procedures described in literature (1*H*-tetrazole (**4**) [16, 5-nitriminotetrazole (**5**), 1-methyl-5-nitrimino-tetrazole (**6**), 2-methyl-5-nitraminotetrazole (**7**) 7a]. For the S_N1-like mechanism, one nitrogen atom of the tetrazole moiety serves as nucleophile, which can be either the nitrogen atoms N1 and N2 or the nitrogen atom N5 of 5-aminotetrazole or different 5-nitriminotetrazoles. For increasing the nucleophilicity of the tetrazole moiety, it has to be activated, which is achieved by deprotonation of the tetrazole or the nitriminotetrazole, respectively, either with alkali metal bases or triethylamine. Polar and aprotic solvents such as acetone and tetrahydrofurane are favored. In case of using an alkali metal salt as starting material, the reaction has to be carried out in suspension. The advantage of carrying out the reaction with the help of triethylamine is the low solubility of the formed triethylammonium chloride in acetone and THF, so that the chloride is removed from the reaction mixture and the progress of the reaction can be observed with the formation of a white precipitate.

1-(2-Nitro-2-azapropyl)-5-aminotetrazole (**8**) was synthesized by stirring a mixture of potassium 5-aminotetrazolate and 2-nitro-2-azapropyl chloride in acetone overnight. The potassium salt of 5-aminotetrazole was synthesized according to literature [17] using aqueous KOH solution and recrystallized from pure ethanol. 1-(2-Nitro-2-azapropyl)-5*H*-tetrazole (**9**) was prepared analogously to **8** by using potassium tetrazolate [16]. 1-(2-Nitro-2-azapropyl)-5-nitriminotetrazole (**10**) could successfully be synthesized by using the monodeprotonated potassium salt of 5-nitriminotetrazole as suspension in acetone or neutral **5** with NEt_3 in THF. After the addition of **2**, the mixture was stirred at room temperature overnight without being refluxed. It is important, that the potassium salt is used in more than double excess. In any case the potassium salt and the 2-nitro-2-azapropyl chloride were used in equimolar amounts, it was not possible to isolate one single product, but always a mixture of **10** and 2,5-*bis*(2-nitro-2-azapropyl)-nitriminotetrazole (**11**). Compound **10** could not be obtained crystalline without inclusion of any solvent. Recrystallization from water or wet methanol afforded the monohydrate **10a**, recrystallization from ethanol afforded the inclusion of one molecule ethanol (**10b**). Compound **11** is synthesized best by stirring two equivalents of **2** with **5**, which was deprotonated in situ by two equivalents of triethylamine.

The reaction of potassium 1-methyl-5-nitriminotetrazolate [18] with **2** ended in three products. The main product 1-methyl-5-(2-nitro-2-azapropyl)-nitraminotetrazole (**12**) was



Scheme 2. Synthesis of 2-nitro-2-azapropyl-tetrazoles **8**–**15**.

obtained in ~60 % yield. The isomer 1-methyl-4-(2-nitro-2-azapropyl)-5-nitriminotetrazole (**13**) was obtained only in very low yields and was detected due to its different crystal shape, while crystal picking of **12**. A third product (~12 %) 1-methyl-5-(2-nitro-2-azapropyl)-5-aminotetrazole (**14**) was obtained as colorless crystals by allowing the mother liquor to stand for a few days. The mechanism of the formation of **14** has not been clarified yet. The coupling reaction of **2** and **7** was carried out as suspension reaction with THF as solvent and one equivalent of triethylamine as base. After filtration and evaporation 2-methyl-5-(2-nitro-2-azapropyl)-nitramino-tetrazole (**15**) was obtained in 94 % yield. The synthesis using the potassium salt of 2-methyl-5-nitraminotetrazole yielded a yellow oil, which could not be recrystallized.

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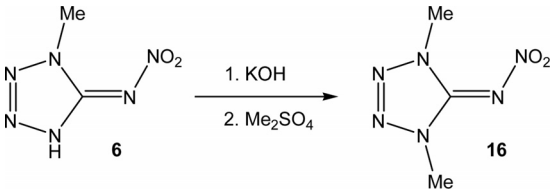
As previously described, alkylation of compound **6** with 2-nitro-2-azapropyl chloride gave three different products. Therefore the alkylation of deprotonated **6** was investigated additionally by the reaction of potassium 1-methyl-5-nitraminotetrazolate and dimethyl sulfate (Scheme 3) In contrast to the previously described alkylation of **6**, only one product [1,4-dimethyl-5-nitriminotetrazole (**16**)] could be isolated in high yields (~85 %).



Scheme 3. Synthesis of 1,4-dimethyl-5-nitriminotetrazole (**16**).

Crystal Structures

Suitable single crystals of **8**–**16** were picked from the crystallization mixture, mounted in Kel-F oil and transferred to the N_2 stream of an Oxford Xcalibur3 diffractometer with a Spellman generator (voltage 50 kV, current 40 mA) and a KappaCCD detector. The data collection was performed using the CrysAlis CCD software [19], the data reduction with the CrysAlis RED software [20]. The structures were solved with SIR-92 (**8**–**12**, **14**, **15**) [21], and SHELXS-97 (**13**, **16**) [22], refined with SHELXL-97 [23] and finally checked using the PLATON software [24], integrated in the WINGX software suite [25]. The non-hydrogen atoms were refined anisotropically and the hydrogen atoms were located and freely refined. In the case of the chiral space groups in **9** and **11**, the "Friedel" pairs were merged. The absorptions were corrected by a SCALE3 ABSPACK multi-scan method [26]. All relevant data and parameters of the X-ray measurements and refinements are given in Table 1 and Table 2. Further information on the crystal-structure determinations have been deposited with the Cambridge Crystallographic Data Centre [27] as supplementary publication No. 652906 (**8**), 703983 (**9**), 703979 (**10a**), 703978 (**10b**), 703984 (**11**), 652908 (**12**), 652907 (**13**), 703982 (**14**), 703980 (**15**) and 703981(**16**).

1-(2-Nitro-2-azapropyl)-5-aminotetrazole (**8**) crystallizes in the monoclinic space group $P2_1/c$ with four molecules in the unit cell. The molecular moiety is depicted in Figure 1. The density of 1.628 g·cm^{-3} is higher than that of 5-aminotetrazole

Table 1. Crystallographic data and parameters of compounds **8**–**11**.

	8	**9**	**10a**	**10b**	**11**
Formula	$C_3H_7N_7O_2$	$C_3H_6N_6O_2$	$C_3H_8N_8O_5$	$C_5H_{12}N_8O_5$	$C_5H_{10}N_{10}O_6$
FW /g·mol^{-1}	173.16	158.14	236.17	264.20	306.23
Crystal system	monoclinic	monoclinic	monoclinic	monoclinic	monoclinic
Space Group	$P2_1/c$ (No. 14)	$P2_1$ (No. 4)	$P2_1/c$ (No. 14)	$P2_1/c$ (No. 14)	$P2_1$ (No. 4)
Color / Habit	colorless rods	colorless plates	colorless rods	colorless rods	colorless needles
Size /mm	0.04 × 0.12 × 0.14	0.06 × 0.10 × 0.15	0.16 × 0.18 × 0.25	0.09 × 0.13 × 0.14	0.05 × 0.06 × 0.14
a /Å	8.6244(4)	6.0193(3)	6.3626(3)	5.6304(4)	9.175(1)
b /Å	6.8715(4)	6.4786(3)	22.1364(8)	24.810(2)	6.177(1)
c /Å	12.0481(6)	8.4598(4)	6.9804(3)	8.5116(6)	11.171(2)
α /°	90	90	90	90	90
β /°	98.263(4)	98.952(5)	13.982(6)	109.103(6)	90.38(1)
γ /°	90	90	90	90	90
V /Å^3	706.59(6)	325.89(3)	898.28(8)	1123.52(14)	633.09(17)
Z	4	2	4	4	2
$\rho_{calcd.}$ /g·cm^{-3}	1.628	1.612	1.746	1.562	1.606
μ /mm^{-1}	0.136	0.136	0.160	0.137	0.144
F(000)	360	164	488	552	316
$\lambda_{Mo-K\alpha}$ /Å	0.71073	0.71073	0.71073	0.71073	0.71073
T /K	200	200	200	200	200
τ min–max /°	3.9, 26.0	3.9, 32.4	4.0, 26.2	3.8, 25.3	3.8, 30.1
Dataset h; k; l	–10:10; –8:7; –11:14	–8:9; –9:9; –12:12	–7:7; –26:27; –8:3	–6:6; –29:29; –10:10	–12:12; –8:8; –15:15
Reflect. coll.	3508	4877	4690	10537	8408
Independ. refl.	1379	1206	1792	2032	2007
R_{int}	0.049	0.021	0.018	0.036	0.050
Reflection obs.	743	1042	1343	1398	1034
No. parameters	137	124	177	193	208
R_1 (obs)	0.0323	0.0251	0.0371	0.0487	0.0318
wR_2 (all data)	0.0742	0.0656	0.1057	0.1557	0.0698
S	0.82	1.08	1.09	1.07	0.91
Resd. Dens. /e·Å^{-3}	–0.16, 0.18	–0.19, 0.24	–0.43, 0.41	–0.39, 0.91	–0.17, 0.18
Device type	Oxford Xcalibur3 CCD	Oxford Xcalibur3 CCD	Oxford Xcalibur3 CCD	Oxford Xcalibur3 CCD	Oxford Xcalibur3 CCD
Solution	SIR-92	SIR-92	SIR-92	SIR-92	SIR-92
Refinement	SHELXL-97	SHELXL-97	SHELXL-97	SHELXL-97	SHELXL-97
Absorpt. corr.	multi-scan	multi-scan	multi-scan	multi-scan	multi-scan
CCDC	652906	703983	703979	703978	703984

Table 2. Crystallographic data and parameters of compounds **12**–**16**.

	12	**13**	**14**	**15**	**16**
Formula	$C_4H_8N_8O_4$	$C_4H_8N_8O_4$	$C_4H_9N_7O_2$	$C_4H_8N_8O_4$	$C_3H_6N_6O_2$
FW /g·mol^{-1}	232.18	232.18	187.18	232.18	158.12
Crystal system	monoclinic	orthorhombic	monoclinic	monoclinic	orthorhombic
Space Group	$P2_1/c$ (No. 14)	*Pbca* (No. 61)	$P2_1/c$ (No. 14)	$P2_1/c$ (No. 14)	*Pbca* (No. 61)
Color / Habit	colorless rods	colorless blocks	colorless rods	colorless rods	colorless blocks
Size /mm	0.06 × 0.15 × 0.20	0.05 × 0.05 × 0.07	0.09 × 0.13 × 0.16	0.08 × 0.11 × 0.12	0.03 × 0.14 × 0.15
a /Å	11.1953(6)	9.413(2)	5.8461(3)	9.2526(5)	14.2278(5)
b /Å	9.3248(4)	9.225(2)	18.4860(7)	11.3617(6)	6.1607(2)
c /Å	9.9411(4)	21.355(4)	8.0667(4)	9.5915(6)	31.200(1)
α /°	90	90	90	90	90
β /°	111.217(5)	90	110.769(5)	106.156(6)	90
γ /°	90	90	90	90	90
V /Å^3	967.45(8)	1854.5(6)	815.13(7)	968.49(10)	2734.81(16)
Z	4	8	4	4	16
$\rho_{calcd.}$ /g·cm^{-3}	1.594	1.663	1.525	1.592	1.536
μ /mm^{-1}	0.140	0.146	0.125	0.140	0.129
F(000)	480	960	392	480	1312
$\lambda_{Mo-K\alpha}$ /Å	0.71073	0.71073	0.71073	0.71073	0.71073
T /K	200	200	200	200	100
τ min–max /°	3.9, 26.0	3.6, 26.0	3.9, 26.0	4.0, 26.0	3.8, 26.0
Dataset *h*; *k*; *l*	–8:13; –7:11; –12:12	–11:8; –10:11; –26:18	–7:6; –21:22; –8:9	–10:11; –14:10; –11:10	–17:17; –7:7; –38:38
Reflect. coll.	4064	8975	4004	4883	25785
Independ. refl.	1890	1814	1580	1890	2676
R_{int}	0.026	0.147	0.041	0.027	0.080
Reflection obs.	1125	643	1085	1146	1386
No. parameters	177	177	154	177	247
R_1 (obs)	0.0342	0.0415	0.043	0.0349	0.0369
wR_2 (all data)	0.0757	0.0917	0.0884	0.0904	0.0893
S	0.89	0.78	1.01	0.94	0.98
Resd. Dens. /e·Å^{-3}	–0.24, 0.20	–0.29, 0.24	–0.20, 0.21	–0.22, 0.22	–0.25, 0.17
Device type	Oxford Xcalibur3 CCD	Oxford Xcalibur3 CCD	Oxford Xcalibur3 CCD	Oxford Xcalibur3 CCD	Oxford Xcalibur3 CCD
Solution	SIR-92	SHELXS-97	SIR-92	SIR-92	SHELXS-97
Refinement	SHELXL-97	SHELXL-97	SHELXL-97	SHELXL-97	SHELXL-97
Absorpt. corr.	multi-scan	multi-scan	multi-scan	multi-scan	multi-scan
CCDC	652908	652907	703982	703980	703981

monohydrate (**3**·H_2O) [31]. Bond lengths can be found in Table 3 and are similar to those of **3**·H_2O. As a matter of course, the tetrazole ring is planar, (as observed in all structures in this work) building an aromatic 6π ring system. The distance C1–N5 [1.341(2) Å] is significantly shorter than that of a typical C–N single bond. The protons at the primary amine N5 are twisted only slightly (15–20 °) out of the ring plane. The N1–C2 bond length of 1.459(2) Å follows exactly the distance of C–N single bonds. The nitrogen atom N6 is surrounded nearly trigonal planar, whereby also the nitro oxygen atoms lay in this plane. A weak intramolecular hydrogen bond is found between the atoms N5 and O1 [N5–H5B···O1: 0.89(2), 2.49(2), 3.165(2) Å, 134(3)°].

The packing of **8** is characterized by a wave like pattern, which can be seen in Figure 2. This motif is fixed by the strong hydrogen bond N5–H5a···N4^{i} [0.90(2), 2.10(2), 2.987(2) Å, 169(2)°; (i) = 2–*x*, –*y*, 2–*z*].

1-(2-Nitro-2-azapropyl)-tetrazole (**9**) crystallizes in the chiral monoclinic space group $P2_1$ with two molecules in the unit cell. The density of 1.612 g·cm^{-3} is only slightly lower than that of **8**, although no classical hydrogen bonds can be formed. However, the proton located at the carbon atom C1 is forming a weak non-classical hydrogen bond [C1–H1···N4^{i}: 0.92(2), 2.66(2), 3.534(2) Å, 160(2)°; (i) 1–*x*, 0.5+*y*, 1–*z*]. The molecular structure (Figure 3) is similar to that of **8**. Again, the nitrogen atom N5 is enclosed trigonal planar [torsion angle C2–N5–N6–O2 = 178.6(1)°].

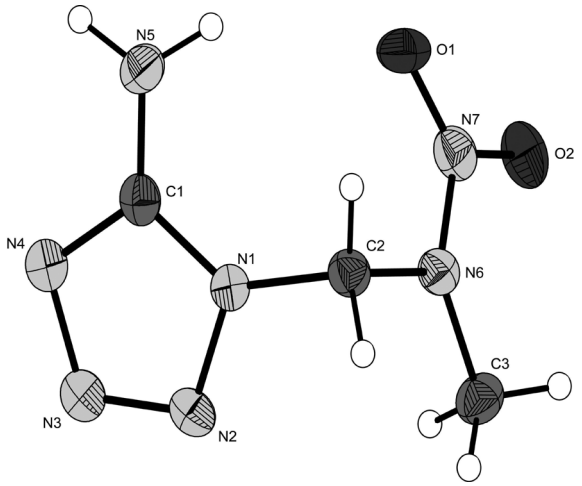


Figure 1. Molecular moiety of **8**. Ellipsoids of non-hydrogen atoms are drawn at the 50 % probability level.

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Table 3. Bond lengths /Å of compounds **8**–**16**.

Atoms	**8**	**9**	**10**·H_2O	**10**·EtOH	**11**	**12**	**13**	**14**	**15**	**16**
N1–N2	1.371(2)	1.351(2)	1.370(2)	1.364(3)	1.331(3)	1.345(2)	1.363(3)	1.365(2)	1.326(2)	1.358(2)
N2–N3	1.294(2)	1.295(2)	1.268(2)	1.279(3)	1.318(3)	1.311(2)	1.285(3)	1.292(2)	1.311(2)	1.282(2)
N3–N4	1.360(2)	1.373(2)	1.360(2)	1.355(3)	1.319(3)	1.362(2)	1.365(3)	1.366(2)	1.320(2)	1.354(2)
N5–N6			1.350(2)	1.358(3)	1.381(3)	1.395(2)	1.371(3)		1.403(2)	1.350(2)
N6–O1			1.243(2)	1.247(3)	1.219(3)	1.220(2)	1.252(3)		1.216(2)	1.241(2)
N6–O2			1.220(2)	1.225(3)	1.219(3)	1.223(2)	1.236(3)		1.214(2)	1.236(2)
N1–C1	1.339(2)	1.335(2)	1.356(2)	1.348(3)	1.320(3)	1.334(2)	1.354(4)	1.336(2)	1.318(2)	1.337(3)
N4–C1	1.330(2)	1.317(2)	1.335(2)	1.344(4)	1.334(3)	1.315(2)	1.348(4)	1.333(2)	1.336(2)	1.340(2)
N5–C1	1.341(2)		1.341(2)	1.341(3)	1.392(3)	1.399(2)	1.327(4)	1.353(2)	1.399(2)	1.347(3)
N1(4,5)–C2(3)	1.459(2)	1.464(2)	1.461(2)	1.463(3)	1.457(3)	1.458(2)	1.479(4)	1.436(3)	1.459(2)	1.454(3)
N1–Me						1.460(2)	1.464(5)	1.455(3)	1.456(2)	1.458(3)
C2(3)–N(NO_2)Me	1.445(2)	1.442(2)	1.438(2)	1.435(3)	1.439(3)	1.448(2)	1.434(4)	1.462(3)	1.440(2)	
N–NO_2	1.358(2)	1.340(1)	1.355(2)	1.355(3)	1.337(3)	1.347(2)	1.365(4)	1.344(2)	1.348(2)	
N(NO_2)–Me	1.468(2)	1.458(2)	1.457(2)	1.457(4)	1.457(3)	1.458(2)	1.460(5)	1.454(2)	1.446(3)	
N(Me)–O1(3)	1.233(2)	1.241(1)	1.229(2)	1.227(3)	1.230(2)	1.240(2)	1.239(3)	1.243(2)	1.234(2)	
N(Me)–O2(4)	1.231(2)	1.233(1)	1.228(2)	1.229(3)	1.236(2)	1.233(2)	1.230(3)	1.236(2)	1.218(2)	

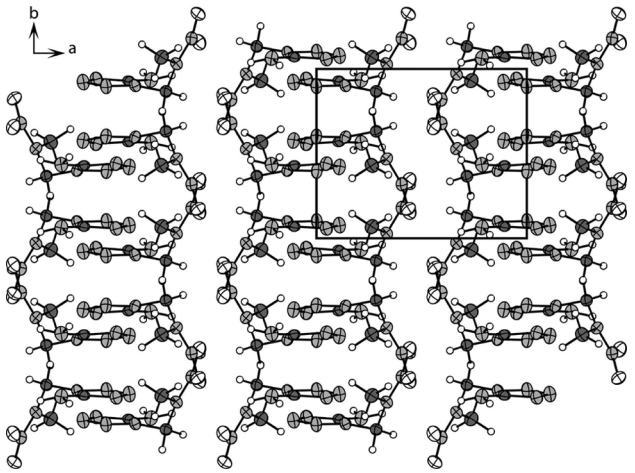

Figure 2. View on the packing of **8** along the *b* axis. One unit cell is marked.

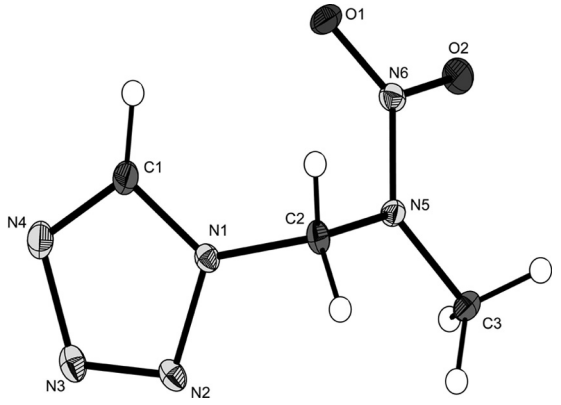

Figure 3. Molecular moiety of **9**. Ellipsoids of non-hydrogen atoms are drawn at the 50 % probability level.

1-(2-Nitro-2-azapropyl)-5-nitrimino-1*H*-tetrazole (**10**) was only obtained crystalline with one molecule of water or ethanol, as shown in Figure 4 and Figure 5. Both crystallize with densities of 1.746 g·cm^{-3} (**10**·H_2O) and 1.562 g·cm^{-3} (**10**·EtOH) in the space group $P2_1/c$ with four molecules in the unit cell. The molecular structures are very similar and in good agreement to those of other 1-substituted 5-nitrimino-tetrazoles, e.g. 1-methyl-5-nitriminotetrazole. The 2-nitro-2-azapropyl substituent follows the structure found in **8** and **9**. The remaining ring proton forms a very strong hydrogen bond to the crystal water ([N4–H4···O5: 0.90(3), 1.77(3), 2.673(2) Å, 168(3)°] and also to the ethanol oxygen atom [N4–H4···O5: 0.89(4), 1.79(4), 2.648(3) Å, 161(4)°], respectively. This may explain that the solvent free compound was only obtained as colorless oil. The hydroxyl group of the ethanol forms on his part a strong hydrogen bond to one of the nitro oxygen atoms of a neighbored molecule [O5–H5···O1^{i}: 0.93(5), 2.01(5), 2.930(3) Å, 168(4)°; (i) 1–*x*, 1–*y*, 1–*z*]. Also the water hydrogen atoms form strong hydrogen bonds to the atoms O2 and N5 of different neighbored molecules, which is a reason for the relatively high density observed for this compound.

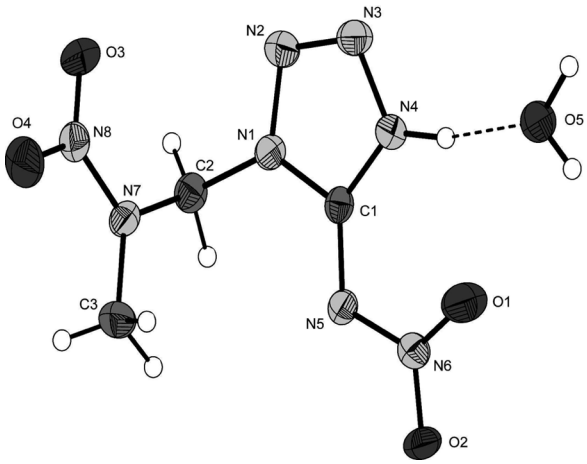

Figure 4. Molecular moiety of **10**·H_2O. Ellipsoids of non-hydrogen atoms are drawn at the 50 % probability level. Marked hydrogen bond: N4–H4···O5: 0.94(3), 1.77(3), 2.691(2) Å, 166(2)°.

2,5-Bis(2-nitro-2-azapropyl)-5-nitraminotetrazole (**11**) crystallizes in the monoclinic space group $P2_1$ with two molecules

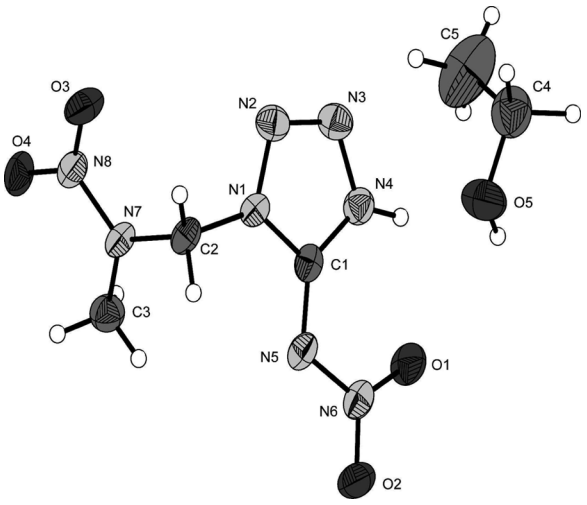

Figure 5. Molecular moiety of **10**·EtOH. Ellipsoids of non-hydrogen atoms are drawn at the 50 % probability level.

in the unit cell. No classical or non-classical hydrogen bonds can be found in the packing of **11**. However, the resulting density of 1.606 g·cm^{-3} is in the range of the other structures discussed in this work. The molecular moiety is shown in Figure 6. Interestingly, alkylation takes place at the nitrogen atoms N2 and N5. The structure of both 2-nitro-2-aza-propyl chains is nearly the same.

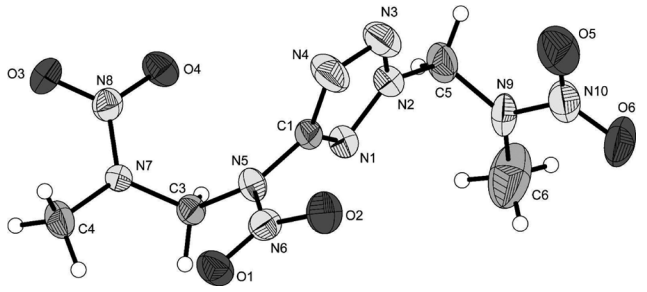

Figure 6. Molecular moiety of **11**. Ellipsoids of non-hydrogen atoms are drawn at the 50 % probability level. Selected distances not given in Table 3: N9–N10 = 1.353(3), N9–C4 = 1.424(4), N9–C5 = 1.435(4), N10–O5 = 1.213(3), N10–O6 = 1.220(3), C4–N2 = 1.455(4).

The alkylation products of 1-methyl-5-nitriminotetrazole **12** and **13** crystallize in common space groups (**12**: $P2_1/c$, **13**: *Pbca*). The molecular structures (Figure 7 and Figure 8) show significant differences. Whereas in **12** the nitro group is strongly twisted out of the ring plane [torsion angle N1–C1–N5–N6 = –75.6(2)°] it is less twisted [N1–C1–N5–N6 = 39.3(6)°] in **13**. Also the C1–N5 bond lengths differ obviously. In the structure of **12** this bond of 1.399(2) Å is closer to a C–N single bond, whereas in **13** a distance [1.327(4) Å] closer to a C=N double bond is observed. The density of **13** (1.663 g·cm^{-3}) is significantly higher than that of **12** (1.594 g·cm^{-3}). It might be a general trend that 1,4-substituted nitriminotetrazoles have higher densities than 1,5-substituted ones, which also can be observed by comparing 1,4-dimethyl-5-nitriminotetrazole (**15**, 1.536 g·cm^{-3}) with 1,5-dimethyl-5-nitriminotetrazole ([7c, 1.522 g·cm^{-3}).

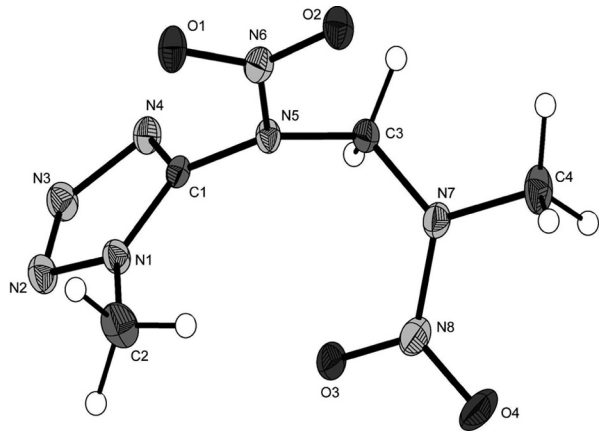

Figure 7. Molecular moiety of **12**. Ellipsoids of non-hydrogen atoms are drawn at the 50 % probability level.

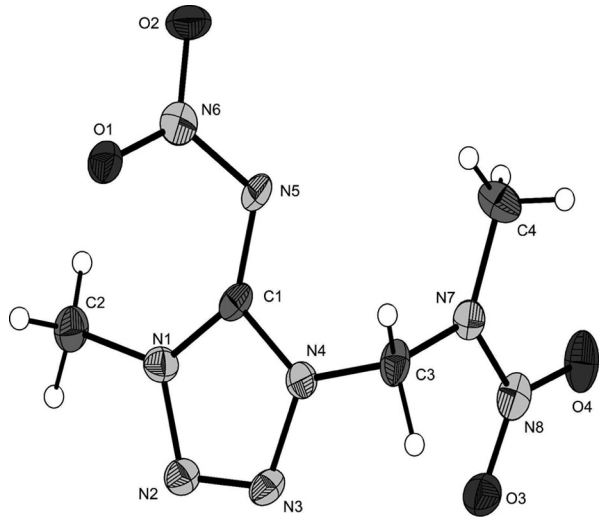

Figure 8. Molecular moiety of **13**. Ellipsoids of non-hydrogen atoms are drawn at the 50 % probability level.

The lowest density observed in this work was calculated for 1-methyl-5-(2-nitro-2-azapropyl)-5-aminotetrazole (**14**) (1.525 g·cm^{-3}), which crystallizes in the monoclinic space group $P2_1/c$ with four molecules in the unit cell. The 2-nitro-2-azapropyl unit bonded [N5–C3 = 1.454(3) Å] at nitrogen atom N5 follows the constitution observed for the other structures discussed in this work. The tetrazole part in Figure 9 resembles the structure of 1-methyl-5-aminotetrazole and its salts. The C1–N5 bond length of 1.347(3) Å is similar to this observed for **8**.

2-Methyl-5-(2-nitro-2-azapropyl)-5-nitraminotetrazole (**15**) crystallizes in the monoclinic space group $P2_1/c$ with four molecules in the unit cell. The density of 1.592 g·cm^{-3} is similar to that observed for the corresponding 1-methyl compound **12** (1.596 g·cm^{-3}). The molecular moiety is shown in Figure 10. The left part is in agreement to the structure observed for

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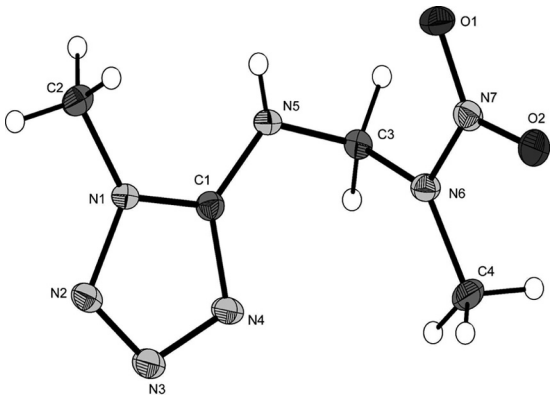

Figure 9. Molecular moiety of **14**. Ellipsoids of non-hydrogen atoms are drawn at the 50 % probability level.

2-methyl-5-aminotetrazole described by *Bryden* [31]. The N5–C1 bond length of 1.399(2) Å is also comparable to that of **12**. Therefore, compound **15** should be described as a "5-nitr*a*minotetrazole".

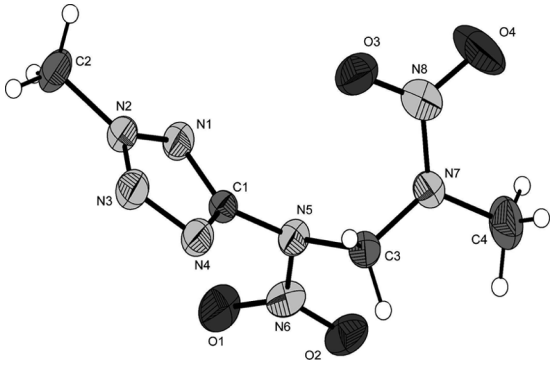

Figure 10. Molecular moiety of **15**. Ellipsoids of non-hydrogen atoms are drawn at the 50 % probability level.

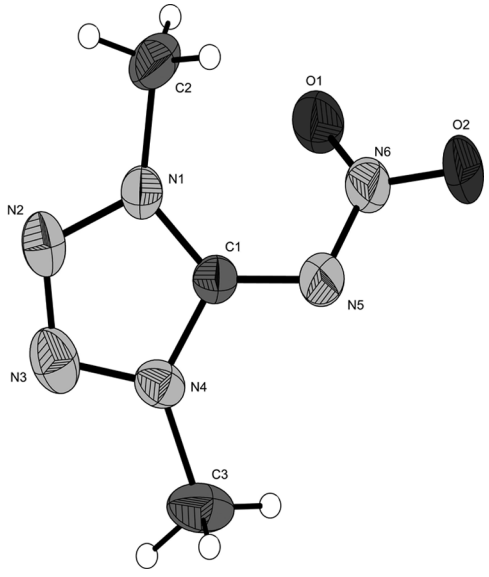

Figure 11. Molecular moiety of **16**. Ellipsoids of non-hydrogen atoms are drawn at the 50 % probability level.

1,4-Dimethyl-5-nitriminotetrazole (**16**) crystallizes in the orthorhombic space group *Pbca* with 16 molecules in the unit cell. In Figure 11 only one molecular moiety is shown.

Both methyl groups are bonded with the same distance of 1.458(3) Å (N1–C2) and 1.454(3) Å (N4–C3) to the tetrazole nitrogen atoms. The C1–N5 bond length of 1.341(2) Å is closer to a C=N double bond, which legitimates the nomenclature "nitrimine". The nitrimine group is strongly twisted out of the ring plane forming a torsion angle N4–C1–N5–N6 of 142.9(2)°. Since no hydrogen bonds can be formed the observed density of 1.536 g·cm^{-3} is low in comparison with other 5-nitriminotetrazoles. For comparison, 5-nitriminotetrazole and 1-methyl-5-nitrimino-tetrazole show densities of 1.894 g·cm^{-3} and 1.716 g·cm^{-3}, respectively.

Spectroscopy

Multinuclear NMR Spectroscopy

Compounds **8**–**12** as well as **14** and **15** were investigated by using ^{1}H, ^{13}C{^{1}H}, and ^{15}N or ^{15}N{^{1}H} NMR spectroscopy. The chemical shifts are given with respect to TMS (^{1}H, ^{13}C) as well as $MeNO_2$ (^{14}N, ^{15}N) as external standards. All spectra were measured in *[D$_6$]DMSO*.

^{1}H NMR: Compared to the starting material **2**, all proton signals of the methylene group of **8**–**15** are strongly shifted downfield because of the coordination of the 2-nitro-2-azapropyl moiety to the electron withdrawing tetrazole ring system. They exhibit values of 6.06 (**12**) to 6.81 ppm (**11**). Compound **11** contains two of the 2-nitro-2-azapropyl groups attached to the tetrazole ring. One exception from that rule is **14**, in which the 2-nitro-2-azapropyl moiety is attached to the 5-amino group of 1-methyl-5-aminotetrazole with a chemical shift of 5.21 ppm for CH_2 protons and a C–H coupling constant of 6.3 Hz. The same applies for the methyl group of the 2-nitro-2-azapropyl moiety with chemical shifts of 3.47 ppm to 3.55 ppm for **9**–**15**. The methyl group of **8** is shifted upfield to 3.13 ppm. The aromatic proton of **9** (9.58 ppm) is slightly shifted downfield compared to 1*H*-tetrazole. The methyl protons directly attached to the tetrazole ring in **12**, **14** and **15** exhibit chemical shifts of 4.03 ppm, 3.71 ppm and 4.49 ppm, which is downfield of the chemical shifts for 1-methyl-5-aminotetrazole (3.69 ppm) and 2-methyl-5-aminotetrazole (4.07 ppm) respectively. In addition, for **10**·H_2O and **10**·EtOH the signals of water and ethanol can be seen with chemical shifts according to those for H_2O and EtOH as residual solvents in DMSO.

^{13}C NMR: The aromatic tetrazole carbon atoms exhibits chemical shifts between 145.2 (**9**) and 159.5 ppm (**11**), with the trend to downfield shifted signals for the 2-substituted tetrazoles **11** and **15** of 159.5 and 159.1 ppm, respectively, and upfield shifted signals for the 1-sustituted compounds **12** and **14** of 150.6 and 155.7 ppm as well as for the unsubstituted compound **9** (145.2 ppm). Comparison of **8** and **10** allows the conclusion, that nitration of the 5-amino group at the tetrazole results in a significant upfield shift of the cyclic carbon atom (**8**: 156.2 ppm, **10**: 151.4 ppm). The chemical shifts for the methyl-

ene and the methyl group of the 2-nitro-2-azapropyl moiety are in the expected range of 59.6 to 67.4 ppm for the methylene group and 39.0 to 39.9 ppm for the methyl group, which are almost identical to the chemical shifts observed for the starting material, however slightly shifted downfield.

^{15}N NMR spectra of compounds **8**–**12**, as well as **14** and **15** can be seen in Figure 12. Although the ^{15}N NMR spectrum of **8** was measured proton decoupled, all seven nitrogen atoms of **8** could clearly be assigned according to the ^{15}N NMR of 1-methyl-5-aminotetrazole 32]. Nitrogen atoms N3 (6.9 ppm) and N2 (–26.6 ppm) are shifted most to lower field because of two neighboring nitrogen atoms in the tetrazole ring. Atom N4 with one neighboring nitrogen atom and one carbon atom is shifted to –94.7 ppm, whereas the two nitrogen atoms neighbored by two carbon atoms, N1 and N6, are shifted to –176.2 ppm and –205.3 ppm with the higher shift for the nitramine nitrogen. The electron rich 5-amino-group is found at –335.9 ppm and the nitro group of the nitramine at –30.0 ppm.

A similar explanation also applies to the ^{15}N NMR spectra of **9**–**12** and **14** as well as **15**. Proton coupled ^{15}N NMR spec-

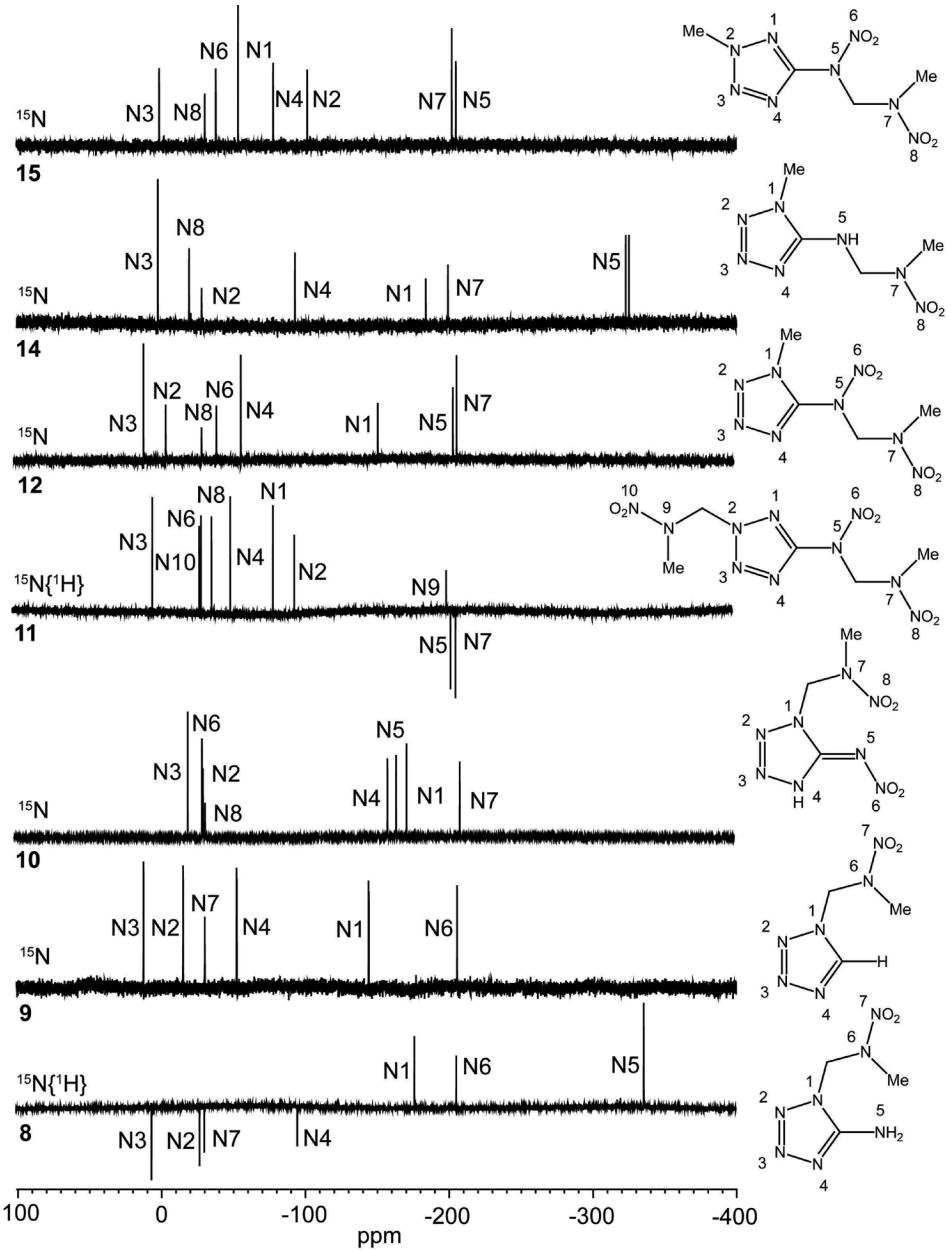

Figure 12. ^{15}N NMR spectra of **8**, **9**, **10**·H_2O, **11**, **12**, **14** and **15** measured in *[D_6]DMSO*. δ: **8** = 6.9 (N3), –26.6 (N2), –30.0 (N7), –94.7 (N4), –176.2 (N1), –205.3 (N6), –333.9 (N5); **9** = 12.2 (N3), –15.3 (N2), –30.4 (N7), –52.6 (N4), –144.3 (N1), –205.9 (N6); **10**·H_2O = –20.2 (N3), –30.1 (N6), –30.8 (N2), –32.2 (N8), –159.1 (N4), –165.1 (N5), –172.4 (N1), –209.4 (N7); **11** = 2.9 (N3), –29.7 (N10), –30.9 (N6), –38.2 (N8), –51.2 (N4), –80.9 (N1), –95.7 (N2), –201.3 (N9), –204.2 (N5), –207.8 (N7); **12** = 9.9 (N3), –5.5 (N2), –30.4 (N8), –40.8 (N6), –57.8 (N4), –152.7 (N1), –205.0 (N7), –207.5 (N5); **14** = 1.3 (N3), –20.3 (N2), –29.0 (N8), –93.8 (N4), –184.5 (N4), –199.9 (N1), –324.4 (N5); **15** = 1.4 (N3), –30.4 (N8), –37.9 (N6), –53.4 (N4), –77.9 (N1), –101.6 (N2), –202.1 (N5), –204.9 (N7).

troscopy is more suitable for alkyl-substituted tetrazoles, since the assignments can be performed by evaluating the ^2J and ^3J ^{15}N–^1H coupling constants. Interestingly, in the case of the 2-nitro-2-azapropyl substituent only the ^3J coupling (triplet, ca. 1.5 Hz) can be observed significantly, whereas the ^2J coupling is hard to detect. All spectra are in agreement with similar ones found for 1- and 2-methyl-5-nitraminotetrazole [7a]. There are strong similarities between the NMR spectra of **12**, **14**, and **15**, which only differ in the position of the methyl group (**12** and **15**) or concerning the nitro group at N5 (**12** and **14**). In all spectra, N3 is shifted downfield [9.9 ppm (**12**), 1.3 ppm (**14**), and 1.4 ppm (**15**)]. The resonance of the nitrogen core N2 strongly varies depending on the substitution of the tetrazole ring. It exhibits chemical shifts of –5.5 ppm (**12**) and –20.3 ppm (**14**) for the 1-sustituted tetrazoles and is shifted to –101.6 ppm in the case of **15**, where the tetrazole ring is substituted in position 2. The chemical shifts of nitrogen atom N4 range from –53.4 ppm in **15** to –93.8 ppm in **14**, where it splits up into a doublet with a coupling constant of $^3J_{NH}$ = 2.2 Hz because of the coupling with the remaining proton of the 5-amino group. N4 in **12** can be assigned to the resonance at –57.8 ppm. The resonance of the 5-amino group in compound **14** exhibits a doublet with $^1J_{N–H}$ = 94 Hz at –324.4 ppm.

Vibrational Spectroscopy

Also vibrational spectroscopy, such as IR and Raman spectroscopy is adequate to identify substituted 5-amino- as well as 5-nitriminotetrazoles. All absorptions measured were assigned according to commonly observed absorptions described in literature [33–35].

The infrared and Raman spectra of **8**–**15** are mainly determined by the stretching and deformation vibrations of aliphatic methylene and methyl groups, nitro groups and vibrations of the tetrazole ring. The bands of the C–H stretching vibrations are located in the range of 3055–2837 cm^{-1}, whereas, three or four bands can be distinguished in all cases. Stretching and deformation vibrations of the tetrazole ring can be assigned to one distinct band, which is located within the range of 1020–1025 cm^{-1} and two or three further absorptions in the range from 1038 cm^{-1} to 1147 cm^{-1}. Apart from that, a different absorption of the tetrazole moiety is observed between 1265 cm^{-1} and 1320 cm^{-1}. The most characteristic absorptions, however, derive from the nitro groups. Compounds **8**, **9** and **15** exhibit one set of absorptions each, which are located at 1297 cm^{-1} and 1521 cm^{-1} (**8**), 1281 cm^{-1} and 1533 cm^{-1} (**9**) and 1300 cm^{-1} and 1600 cm^{-1} (**15**). Compounds **10**·H_2O, **12** and **14**, having two nitro groups each, exhibit two sets of absorptions: 1265 cm^{-1}, 1525 cm^{-1}, 1295 cm^{-1} and 1577 cm^{-1} (**10**·H_2O), 1266 cm^{-1}, 1530 cm^{-1}, 1288 cm^{-1}, 1584 cm^{-1} (**12**) and 1261 cm^{-1}, 1531 cm^{-1}, 1282 cm^{-1} and 1585 cm^{-1} (**14**). For compound **11**, even three sets of nitro group absorptions can be seen according to the three nitramine units contained in the molecule. The absorptions are located in the same range given for the nitro groups discussed above. For compound **8**, the stretching and deformation vibration of the 5-amino group can be assigned additionally at 3424 cm^{-1} and 1646 cm^{-1}, respectively. The vibrations of the molecular units of **10**·H_2O and **10**·EtOH are almost equal and therefore not discussed separately. The most obvious difference is the O–H stretching vibration of the water molecule in the monohydrate **10**·H_2O at 3484 cm^{-1} and the O–H stretching vibration of the ethanol hydroxy group in **10**·H_2O at 3540 cm^{-1}. Compound **9**, additionally, exhibits absorption bands for the C_{ring}–H stretching and the deformation vibration at 3128 and 1479 cm^{-1}, respectively.

Mass Spectrometry

Mass spectra of the neutral compounds **8**–**15** were measured either in EI, DEI, FAB or ESI technique. All compounds measured could be clearly identified by the molecule peak $[M + H]^+$. Further fragments visible in all mass spectra are the 2-nitro-2-azapropyl fragment at *m*/*z* 89 and the azide moiety resulting from the cleavage of the tetrazole ring at *m*/*z* 43. In the cases of **8**, **12** and **14**, the remaining fragment $[M – NNO_2]^+$ can be seen at *m*/*z* 99.1, 157.2 and 112.1 respectively. The tetrazole ring $[CHN_4]^+$ at *m*/*z* 69.1 can be observed in the spectra of **8**, **9** and **12**. Often, the loss of one or even two nitro groups is observed, which exemplarily is discussed for compound **11**:

The molecule peak $[M + H]^+$ is observed at *m*/*z* 307.2. The successive cleavage of the three bonds, depicted in Figure 13, leads to three fragments at *m*/*z* 260.2 $[M – NO_2]^+$, 215.2 $[M + H – 2NO_2]^+$ and *m*/*z* 186.2 $[M + H – CH_3NNO_2 – NO_2]^+$. Different pathways are shown in the second and third fragmentation (B), (C). The loss of a nitro group and the cleavage of the C–N bond in position 5 of the tetrazole ring leads to the fragments at *m*/*z* 111.1 $[CN_4CH_2NCH_3]^+$ and *m*/*z* 57.1 $[CH_3NCH_2]^+$. Finally, the 2-nitro-2-azapropyl moiety is sepa-

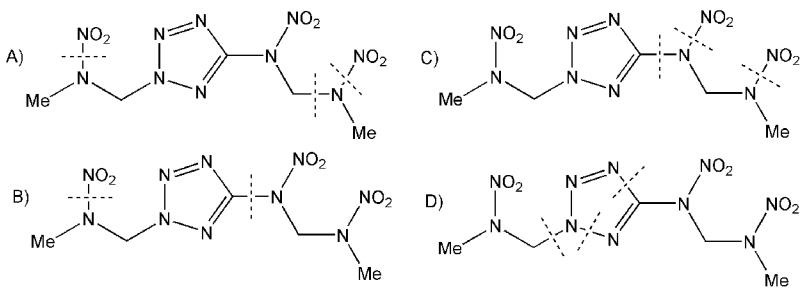

Figure 13. Possible fragmentation pattern of cleaving in the mass spectrum of **11**.

rated and the tetrazole ring is further fragmented (D) to yield the peaks at *m*/*z* 89.1 $[CH_3NNO_2CH_2]^+$ and at *m*/*z* 43.1 $[N_3]^+$.

Energetic Properties

Differential Scanning Calorimetry

Differential scanning calorimetry (DSC) measurements to determine the melting and decomposition temperatures of **8**–**15** (~1.5 mg of each energetic material) were performed in covered aluminum containers containing a hole in the lid with a nitrogen flow of 20 mL·min^{-1} with a Linseis PT10 DSC at a heating rate of 5 °C·min^{-1}. The DSC plots in Figure 14 show the thermal behavior in the 20–400 °C temperature range. Temperatures are given as onset temperatures.

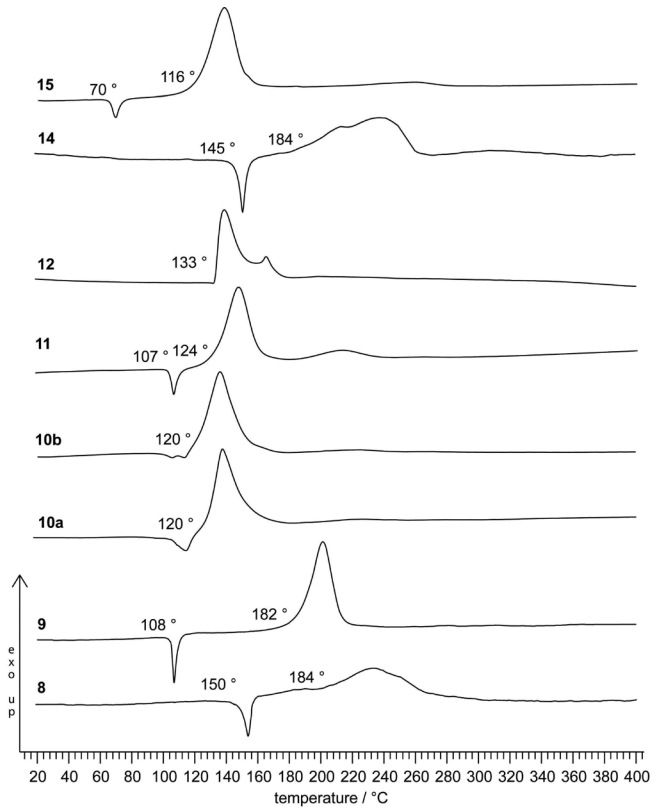

Figure 14. DSC thermograms (*exo*-up) of compounds **8**–**12**, as well as **14** and **15** (heating rates: 5 °C min^{-1}).

The examined samples of **8**–**12**, as well as **14** and **15** exhibit decomposition temperatures between 116 °C and 184 °C. Apart from compound **12**, all compounds melt before decomposition and therefore have a definite liquidity range, which ranges e.g. for **9** more than 70 °C from melting to decomposition. The highest decomposition temperatures of 184 °C belong to **8** and **14**, which are the two 5-aminotetrazole derivatives. The amino group attached to the tetrazole ring stabilizes the compounds relative to those connected to the nitramine unit. All nitriminotetrazole compounds **10**·H_2O, **10**·EtOH **11**, **12**, and **15** have decomposition temperatures, which are far below those of **8**, **9** and **14**. Comparing the two isomers **12** and **15**, the decomposition of **12** at 133 °C starts very precisely, whereas the decomposition peak of molten **15** is observed very broad. Also its melting point is observed much lower at 70 °C, which is the lowest melting point observed in this chapter.

Bomb Calorimetry

The heats of combustion of compounds **8**–**15** were determined experimentally using a Parr 1356 bomb calorimeter. The enthalpy of formation, $\Delta_f H°$, for each of the compounds was calculated at 298.15 K using Hess' law and the following combustion reaction.

$$C_nH_mN_xO_y + (n + \frac{m}{4} - \frac{y}{2})O_2 \rightarrow nCO_2 + \frac{m}{2}H_2O + \frac{x}{2}N_2$$

The heats of formation of the combustion products $H_2O(l)$ (–286 kJ·mol^{-1}) and $CO_2(g)$ (–394 kJ·mol^{-1}) were obtained from the literature [38, 39]. The values for $\Delta_f H°$ as well as those for $\Delta_c H°$ are summarized in Table 4. The heats of formation for the synthesized compounds are in a broad range from even exothermic (–639 kJ·mol^{-1}, **10**·EtOH) to strongly endothermic (+383 kJ·mol^{-1}, **8**). The other tetrazole derivatives are all formed endothermically ($\Delta_f H°$ **9** = 286, **10**·H_2O = 18, **11** = 296, **12** = 254, **14** = 121, **15** = 333 kJ·mol^{-1}).

The difference of isomers **15** and **12** is 81 kJ·mol^{-1}. The values for **10**·H_2O and **10**·EtOH are lower due to water or ethanol solvate molecules contained. Considering the molar heat of formation of gaseous water of 242 kJ·mol^{-1}, the value for **10**·H_2O is in the range of the other compounds. From the experimentally determined heats of formation and X-ray densities, various thermochemical properties have been calculated using the EXPLO5 software (see below) and are summarized in Table 4.

Sensitivities

For initial safety testing, the impact (RDX = 8 J, $Pb(N_3)_2$ = 4 J) and friction sensitivities (RDX = 120 N, $Pb(N_3)_2$ = 1 N) as well as the electrostatic sensitivity were determined.[40–46] The detailed values are summarized in Table 4. The only compound containing three nitramine groups (**11**) stands out with its low impact sensitivity of 2 J. The compounds containing two nitramine groups, one directly connected to the tetrazole ring and a second within the 2-nitro-2-azapropyl moiety fill the range between 5 J and 12 J, which are the methylated isomers **12** (5 J) and **15** (8 J) and on the other hand the unsubstituted homologues **10**·H_2O (12 J) and **10**·EtOH (10 J), which prospectively should be more sensitive, but as they crystallize with one molecule of water and ethanol respectively, the sensitivities are lower. Tetrazole **9** has a moderate sensitivity of 15 J, whereas **8** and **14** are completely insensitive. The friction sensitivities vary from moderately sensitive to insensitive. Again, the molecules containing a nitriminotetrazole moiety are more sensitive. The electrostatic sensitivity tests were carried out using an electric spark tester ESD 2010EN (OZM Research) operating with the "Winspark 1.15 software package" [47]. The electrical spark sensitivities on crystalline material

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Table 4. Physico-chemical properties of compounds **8**–**12** as well as **14** and **15**.

	8	**9**	**10**·H_2O	**10**·EtOH	**11**	**12**	**14**	**15**
Formula	$C_3H_7N_7O_2$	$C_3H_6N_6O_2$	$C_3H_8N_8O_5$	$C_5H_{12}N_8O_5$	$C_5H_{10}N_{10}O_6$	$C_4H_8N_8O_4$	$C_4H_9N_7O_2$	$C_4H_8N_8O_4$
Mol. Mass /g·mol^{-1}	173.13	158.14	236.15	264.20	306.20	232.16	187.16	232.16
Impact sensitivity /J[a)]	> 100	15	12	10	2	5	40	8
Friction sensitivity /N[b)]	120	128	144	84	108	240	120	96
ESD–test /J	0.22	1.45	1.04	0.75	0.50	0.20	0.60	0.065
N /%[c)]	56.63	53.15	47.45	42.41	45.74	48.27	52.39	48.27
Ω /%[d)]	–69.3	–70.8	–33.8	–66.6	–47.0	–55.1	–89.8	–55.1
$T_{dec.}$ /K[e)]	457	467	393	393	397	406	465	389
Density /g·cm^{-3} f)	1.628	1.612	1.746	1.562	1.606	1.663	1.525	1.592
$-\Delta U_{comb.}$ /cal·g^{-1} g)	3547	3520	2380	2760	2892	3068	3812	3149
$-\Delta H_{comb.}$ /kJ·mol^{-1} h)	2564	2324	2342	3044	3694	2972	2982	3051
$\Delta_f H_m$ /kJ·mol^{-1} i)	383	286	18	–639	296	254	121	333
$-\Delta_E U$ /kJ·kg^{-1} j)	5368	5341	4971	2374	5470	5285	3775	5569
T_E /K[k)]	3554	3494	3594	2025	3905	3695	2644	3882
p_{C-J} /kbar[l)]	273	247	281	138	245	254	194	243
$V_{Det.}$ /m·s^{-1} m)	8467	8085	8311	6408	7936	7977	7542	7902
Gas vol. /L·kg^{-1} n)	802	776	822	804	791	780	798	783

a) BAM drophammer [Ref. 40–44], grain size (75–150 μm); b) BAM friction tester [Ref. 40, 43–46], grain size (75–150 μm); c) Nitrogen content; d) Oxygen balance; e) Temperature of decomposition by DSC (β = 5 K); f) estimated from a structure determination; g) Experimental (constant volume) combustion energy; h) Experimental molar enthalpy of combustion; i) Molar enthalpy of formation; j) Energy of Explosion; k) Explosion temperature; l) Detonation pressure. m) Detonation velocity; n) Assuming only gaseous products.

were determined to be 0.22 J (**8**), 1.45 J (**9**), 1.04 J (**10**·H_2O), 0.75 J (**10**·EtOH), 0.50 J (**11**), 0.20 J (**12**), 0.60 J (**14**) and 0.07 J (**15**). Except for the methyl-substituted compounds **12** and **15**, all have values lower than commonly primary explosives ($Pb(N_3)_2$: 0.005 J) and secondary explosives (RDX: 0.2 J). It should be mentioned that the test towards electrical discharge strongly depends on the particle size and shape. Although we tried to use fine crystalline materials (75–125 μm) a guarantee for the determined values (especially value of **15**) cannot be given.

Detonation Parameters

The calculation of the detonation parameters was performed with the program package EXPLO5 (version 5.02) [48, 49, 50]. Among the investigated compounds **8**, **9** and **10**·H_2O reveal detonation velocities significantly higher than 8000 m·s^{-1}. Although showing detonation pressures of p_{C-J} = 273 (**8**), 247 (**9**), and 281 kbar (**10**·H_2O) and an explosion temperature of more than 3500 K, the performance data are lower than those of RDX (p_{C-J} = 346 kbar, $V_{Det.}$ = 8936 m·s^{-1}, $\Delta_E U$ = –6043 kJ·kg^{-1}). The detonation velocities of **10**·EtOH, **11**, **12**, **14**, and **15** are below $V_{Det.}$ = 8000 m·s^{-1}, but, however, succeeding easily the detonation parameter of TNT. A reason for the lower p_{C-J} and $V_{Det.}$, in comparison to those of RDX, are the low densities observed for **8**–**15**. The explosion temperatures seem to be associated with the amount of nitramine moieties contained in the molecule. The explosion temperature of **11**, containing three nitramine units almost reaches 4000 K (3905 K). The value of the highest explosion temperature is also associated with a very high explosion energy of 5470 kJ·kg^{-1}. The explosion temperature of **14**, which is the methylated 5-aminotetrazole derivative is low (2644 K). The remaining values are spread over the range between 2700 K and 3700 K (except from **10**·EtOH) with the trend to higher temperatures for nitriminotetrazole derivatives (**12**: 3695 K; **15**: 3664 K).

Conclusions

From this experimental study the following conclusions can be drawn:

1-(2-Nitro-2-azapropyl)-5-aminotetrazole (**8**), 1-(2-nitro-2-azapropyl)-5*H*-tetrazole (**9**), 1-(2-nitro-2-azapropyl)-5-nitriminotetrazole (**10**·H_2O, **10**·EtOH), 2,5-bis(2-nitro-2-azapropyl)-5-nitraminotetrazole (**11**), 1-methyl-5-(2-nitro-2-azapropyl)-5-nitraminotetrazole (**12**), 1-methyl-4-(2-nitro-2-azapropyl)-5-nitriminotetrazole (**13**), 1-methyl-5-(2-nitro-2-azapropyl)-5-aminotetrazole (**14**) and 2-methyl-5-(2-nitro-2-azapropyl)-nitraminotetrazole (**15**) could be synthesized, mostly in good yields from deprotonated 5-amino-1*H*-tetrazole (**3**), 1*H*-tetrazole (**4**), 5-nitriminotetrazole (**5**), 1-methyl-5-nitriminotetrazole (**6**) and 2-methyl-5-nitramino-tetrazole (**7**), respectively.

1,4-Dimethyl-5-nitriminotetrazole (**16**) was synthesized by methylation of potassium 1-methyl-5-nitriminotetrazolate with dimethyl sulfate.

The crystal structures of **8**–**16** were determined by low-temperature single-crystal X-ray diffraction. The compounds crystallize in common space groups ($P2_1/c$: **8**, **10**·H_2O, **10**·EtOH, **12**, **14** and **15**; $P2_1$: **9** and **11**; *Pbca*: **13** and **16**) with densities between 1.52 and 1.75 g·cm^{-3}. In addition **8**–**15** were characterized comprehensively by vibrational spectroscopy (IR and Raman), multinuclear (^{1}H, ^{13}C, ^{14}N and ^{15}N) NMR spectroscopy, mass spectrometry, elemental analysis and differential scanning calorimetry.

The thermal behavior of **8**–**15** was investigated by DSC measurements. The decomposition temperatures reach from 116 °C (**15**) to 184 °C (**8**, **14**).

The sensitivities towards impact, friction and electrical discharge of compounds **8**–**16** were determined by using the

BAM drophammer and friction tester as well as a small scale electrical discharge tester. The values are mostly lower than those of commonly used secondary explosives such as RDX or HMX. The most sensitive compound is **11**. The impact sensitivities range from 2 to 100 J. Most of the compounds are only moderately sensitive towards friction. The sensitivity towards electrical discharge, of course, strongly depends on the particle sizes and range from 0.07–1.45 J.

The heats of formation $\Delta_f H°$ were calculated using heats of combustion obtained from bomb calorimetric measurements. All compounds, except for **10**·EtOH (–639 kJ·mol^{-1}) are formed endothermically with values between 18 kJ·mol^{-1} (**10**·H_2O) and 383 kJ·mol^{-1} (**8**).

By using $\Delta_f H°$ and the maximum densities obtained from XRD several detonation parameter (heat of explosion, explosion temperature, detonation pressure and velocity) were computed with the EXPLO5 software. The highest detonation pressures (273 and 281 kbar) as well as velocities (8467 and 8311 m·s^{-1}) were calculated for compounds **8** as well as **10**·H_2O.

Experimental Section

CAUTION! The prepared tetrazoles **8**–**16** and their starting materials are energetic compounds with increased sensitivities against heat, impact and friction. Although we had no problems in synthesis, proper protective measures (safety glasses, face shield, leather coat, earthened equipment and shoes, Kevlar® gloves and ear plugs) should be used during work on **8**–**16**.

2-Nitro-2-azapropyl acetate (1): The reaction was carried out according to modified procedure described in the literature [15]. A 500 mL three-necked reaction flask equipped with a thermometer and a dropping funnel was charged with acetic anhydride (88 mL, 936 mmol) and cooled to 0 °C with an ice bath. Fuming nitric acid (28 mL, 666 mmol) was slowly added taking care, that the temperature did not exceed 5 °C for the reaction is somewhat exothermic. To the reaction mixture a solution of 1,3,5-trimethylhexahydro-1,3,5-triazine (25.2 mL, 184 mmol) in glacial acetic acid (25 mL, 436 mmol) was added drop wise within 1 hour before it was heated under reflux to 70–75 °C for 1 hour. The mixture was allowed to cool down to room temperature, water (100 mL) was added and it was extracted with dichloromethane (8 × 25 mL). Either the organic or the aqueous phase was nearly neutralized (pH 6) with ammonium carbonate, the organic phase was washed with water (100 mL) and the combined aqueous phases were again extracted with dichloromethane (4 × 25 mL). The organic phases were dried with magnesium sulfate, the solvent was removed in a rotary evaporator and the crude product was distilled under reduced pressure (3 mbar, 89 °C) to give 50.20 g (61 % yield) of 2-nitro-2-azapropyl acetate as a colorless liquid. **IR** (KBr): $\tilde{\nu}$ = 3482 (w), 2996 (m), 2955 (m), 1751 (vs), 1547 (vs), 1470 (s), 1431 (s), 1630 (s), 1393 (s), 1369 (s), 1301 (s), 1214 (s), 1126 (m), 1017 (s), 958 (s), 857 (m), 829 (m), 770 (m), 681 (m), 647 (w), 603 (m), 495 (m) cm^{-1}. **^{1}H NMR** ($CDCl_3$, 25 °C): δ = 5.68 (s, CH_2), 3.41 (s, H_3C–$N(NO_2)$), 2.09 (s, H_3C–C(O)O). **^{13}C NMR** ($CDCl_3$, 25 °C): δ = 170.6($C(O)CH_3$), 72.8 (CH_2), 38.6 (H_3C–$N(NO_2)$), 20.6 ($C(O)CH_3$).

2-Nitro-2-azapropyl chloride (2): The reaction was carried out according to modified procedure described in the literature [15]. A 250 mL reaction flask was charged with 2-nitro-2-azapropyl acetate (24.7 g, 167 mmol), glacial acetic acid (0.7 mL, 12.3 mmol), conc. H_2SO_4 (2 drops), and dichloromethane (35 mL). Thionyl chloride (23.4 g, 334 mmol) was added dropwise over a period of 90 minutes. Afterwards, the mixture was heated to 40–45 °C under reflux for 1 hour, before the solvent was removed under reduced pressure. For purification the pale yellow oil was distilled in vacuo (2 mbar, 48 °C) to give 2-nitro-2-azapropyl chloride (18.14 g, 87 % yield) as a colorless liquid. **^{1}H NMR** ($CDCl_3$, 25 °C): δ = 5.60 (s, CH_2), 3.38 (s, H_3C–$N(NO_2)$). **^{13}C NMR** ($CDCl_3$, 25 °C): δ = 60.4(CH_2Cl), 37.6 (CH_3).

1-(2-Nitro-2-azapropyl)-5-aminotetrazole (8): 5-Amino-tetrazole (17.0 g, 200 mmol) was suspended in a solution of water (100 mL) and KOH (13.2 g, 200 mmol, 85 %). The suspension was heated to 50 °C and 5-aminotetrazole dissolved. Evaporation of the solvent gave potassium-5-aminotetrazolate in quantitative yields. The pale yellow solid can be recrystallized from water/ethanol with 92 % yield (22.7 g). Potassium 5-aminotetrazolate (7.39 g, 60 mmol) was suspended in acetone (50 mL) and the 2-nitro-2-azapropyl chloride (8.22 g, 66 mmol) was slowly added through a dropping funnel. The suspension was stirred overnight, filtered off and the solid was washed with warm acetone. The solvent was removed in a rotary evaporator and a yellowish solid remained, which was recrystallized from hot ethanol to give 6.02 g of **8** (58 % yield). ($C_3H_7N_7O_2$, 173.13) calcd.: C 20.81, H 4.08, N 56.63 %; found: C 22.14, H 4.25, N 55.09 %; **DSC** (T_{onset}, 5 °C·min^{-1}): 147–153 °C (mp.), 184 °C (dec.). **IR** (KBr): $\tilde{\nu}$ = 3424 (s), 3300 (m), 3134 (m), 3097 (m), 2721 (s), 1646 (s), 1579 (s), 1521 (vs), 1472 (m), 1446 (m), 1424 (m), 1387 (w), 1354 (m), 1297 (s), 1261 (s), 1206 (s), 1116 (m), 1074 (m), 1021 (m), 992 (m), 927 (w), 846 (w), 795 (m), 764 (m), 740 (w), 719 (w), 680 (m), 654 (m), 604 (w), 485 (w) cm^{-1}; **Raman** (1064 nm, 400 mW, 25 °C): $\tilde{\nu}$ = 3038 (36), 2995 (42), 2964 (36), 1648 (10), 1582 (14), 1529 (10), 1443 (27), 1424 (21), 1356 (23), 1318 (29), 1262 (50), 1128 (18), 1094 (14), 1070 (14), 1021 (15), 928 (17), 849 (100), 793 (57), 655 (14), 603 (22), 445 (27), 398 (23), 304 (19), 235 (27) cm^{-1}. **^{1}H NMR** (*[D$_6$]DMSO*, 25 °C): δ = 6.98 (s, NH_2), 6.14 (s, CH_2), 3.13 (s, CH_3). **^{13}C NMR** (*[D$_6$]DMSO*, 25 °C): δ = 156.2 (CN_4), 59.6 (CH_2), 39.4 (s, CH_3). **^{15}N NMR** (*[D$_6$]DMSO*, 25 °C): δ = 6.9 (N3), –26.6 (N2), –30.0 (N7), –94.7 (N4), –176.2 (N1), –205.3 (N6), –333.9 (N5); **MS:** *m*/*z* (DEI): 173.1 $[M]^+$; **impact sensitivity:** > 100 J (neg.); **friction sensitivity:** > 120 N; **ESD:** > 0.22 J; **RADEX** (130 °C, 50 h): no decomposition.

1-(2-Nitro-2-azapropyl)-tetrazole (9): 1*H*-Tetrazole (701 mg, 10 mmol) was suspended in a solution of KOH (85 %, 660 mg, 10 mmol) in water (15 mL). Tetrazole dissolved and after evaporation of the water under reduced pressure, the potassium tetrazolate formed as a colorless solid. Potassium tetrazolate was directly suspended in acetone (20 mL) without being recrystallized. To this suspension 2-nitro-2-azapropyl chloride (1.245 g, 10 mmol), which was previously dissolved in acetone (few milliliters) was added drop wise. After being stirred overnight, the suspension was heated to reflux for 1 hour and filtered off afterwards. Acetone was removed under reduced pressure and the remaining solid was recrystallized from ethanol to give 1.17 g (74 % yield) **9** as colorless crystals. ($C_3H_6N_6O_2$, 158.12) calcd.: C 22.79, H 3.82, N 53.15 %; found: C 22.71, H 3.57, N 52.47 %; **DSC** (T_{onset}, 5 °C·min^{-1}): 108 °C (mp.), 182 °C (dec.). **IR** (KBr): $\tilde{\nu}$ = 3450 (vs), 3128 (m), 3051 (w), 1634 (m), 1533 (m), 1479 (m), 1383 (w), 1341 (w), 1303 (m), 1281 (m), 1168 (m), 1096 (m), 1038 (w), 959 (w), 885 (w), 854 (w), 766 (m), 750 (m), 718 (w), 672 (m), 614 (m) cm^{-1}; **Raman** (1064 nm, 350 mW, 25 °C): $\tilde{\nu}$ = 3127 (33), 3050 (37), 3003 (65), 2959 (36), 1529 (22), 1478 (26), 1448 (33), 1428 (35), 1410 (37), 1374 (27), 1335 (31), 1294 (53), 1264 (34), 1169 (36), 1095 (36), 1038 (29), 1012 (61), 852 (100), 750 (33), 641 (27), 613 (38), 444 (31), 407 (24), 352 (24), 265 (24), 209 (19) cm^{-1}. **^{1}H NMR** (*[D$_6$]DMSO*, 25 °C): δ = 9.58 (s, N_4CH), 6.46 (s, CH_2), 3.52 (s, CH_3).

^{13}C NMR (*[D$_6$]DMSO*, 25 °C): δ = 145.2 (CN_4), 61.9 (CH_2), 39.5 (CH_3). **^{15}N NMR** (*[D$_6$]DMSO*, 25 °C): δ = 12.2 (N3), –15.3 (N2), –30.4 (N6), –52.6 (N4), –144.3 (N1), –205.9 (N5); **MS:** *m*/*z* (FAB^+): 159.2 $[M + H]^+$; **impact sensitivity:** > 15 J; **friction sensitivity:** > 128 N; **ESD:** > 1.45 J.

1-(2-Nitro-2-azapropyl)-5-nitriminotetrazole monohydrate (10·H$_2$O): 5-Nitrimino-1,4*H*-tetrazole (4.43 g, 34 mmol) was suspended in an ethanol solution of KOH (85 %, 2.25 g, 34 mmol) and stirred for 15 minutes. The suspension was filtered off, the solid dried to give 5.27 g (31.5 mmol, 92 %) of potassium 5-nitriminotetrazolate. The salt was suspended in THF (50 mL) and 2-nitro-2-azapropyl chloride (1.87 g, 15 mmol), previously dissolved in THF (25 mL), was added drop wise. The suspension was stirred at room temperature overnight and the remaining solid, consisting of potassium 5-nitriminotetrazolate and potassium chloride, was filtered off. THF was removed from the filtrate under reduced pressure, the remaining colorless oil was dissolved in a small amount of water/ethanol for recrystallization to give **10**·H_2O as colorless crystals in 22 % yield (783 mg, 3.3 mmol). ($C_3H_8N_8O_5$, 236.15) calcd.: C 15.26, H 3.41, N 47.45 %; found: C 15.74, H 3.67, N 47.59 %; **DSC** (T_{onset}, 5 °C·min^{-1}): 112–118 °C (mp.), 120 °C (dec.). **IR** (KBr): $\tilde{\nu}$ = 3484 (m), 3049 (w), 1577 (vs), 1554 (s), 1525 (m), 1450 (m), 1408 (m), 1337 (m), 1295 (s), 1265 (s), 1201 (m), 1135 (m), 1113 (w), 1083 (m), 1022 (m), 1007 (m), 916 (m), 799 (m), 765 (m), 746 (m), 686 (w), 673 (w), 643 (m), 607 (m) cm^{-1}; **Raman** (1064 nm, 300 mW, 25 °C): $\tilde{\nu}$ = 3051 (37), 2995 (66), 2962 (43), 1585 (58), 1560 (22), 1526 (55), 1441 (31), 1424 (45), 1400 (42), 1293 (49), 1264 (100), 1133 (11), 1059 (28), 1009 (40), 987 (46), 883 (24), 869 (41), 850 (68), 758 (50), 748 (36), 707 (28), 604 (34), 496 (33), 421 (22), 394 (24), 318 (25), 257 (46), 239 (28) cm^{-1}. **^{1}H NMR** (*[D$_6$]DMSO*, 25 °C): δ = 9.78 (s, NH), 6.12 (s, CH_2), 3.50 (s, CH_3), 3.43 (s, H_2O). **^{13}C NMR** (*[D$_6$]DMSO*, 25 °C): δ = 151.4 (CN_4), 61.2 (CH_2), 39.8 (CH_3). **^{15}N NMR** (*[D$_6$]DMSO*, 25 °C): δ = –20.2 (N3), –30.1 (NO_2, N6), –30.8 (N2, t, $^3J_{N–H}$ = 1.5 Hz), –32.2 (NO_2, N8, m), –159.1 (N4), –165.1 (N5), –172.4 (N1), –209.4 (N7); **MS:** *m*/*z* (FAB^+): 219.2 $[M + H]^+$; **impact sensitivity:** > 12 J; **friction sensitivity:** > 144 N; **ESD:** > 1.04 J.

1-(2-Nitro-2-azapropyl)-5-nitriminotetrazole·EtOH (10·EtOH): 5-Nitrimino-1,4*H*-tetrazole (3.96 g, 30.5 mmol) was dissolved in THF (50 mL) and triethylamine (3.08 g, 30.5 mmol) was slowly added to the solution. A colorless precipitate, which immediately formed, disappeared after a few seconds. 2-Nitro-2-azapropyl chloride (1.87 g, 15 mmol) was dissolved in THF (25 mL) and slowly added through a dropping funnel over a period of 1 hour. A colorless, crystalline precipitate of triethylammonium chloride formed. The reaction was stirred overnight, the precipitate was filtered off and the solvent was removed from the filtrate. A pale yellow oil remained, which was dried under vacuum and taken up in ethanol for recrystallization to give 1.76 g of **10**·EtOH as colorless crystals (22 % yield). The product achieved from the reaction crystallizes with one equivalent of ethanol as solvate as X-ray single crystal structure studies showed. ($C_5H_{12}N_8O_5$, 264.20) calcd.: C 22.73, H 4.58, N 42.41 %; found: C 20.32, H 4.13, N 43.79 %; **DSC** (T_{onset}, 5 °C·min^{-1}): 112–118 °C (mp.), 120 °C (dec.). **IR** (KBr): $\tilde{\nu}$ = 3540 (s), 3488 (s), 3051 (m), 2826 (m), 2737 (m), 2663 (m), 1634 (m), 1586 (vs), 1525 (vs), 1442 (m), 1497 (vs), 1439 (s), 1397 (m), 1356 (s), 1311 (s), 1283 (s), 1260 (s), 1207 (s), 1108 (w), 1057 (m), 1007 (s), 927 (m), 884 (w), 777 (m), 761 (m), 748 (m), 705 (m), 602 (m), 576 (m), 475 (w) cm^{-1}; **Raman** (1064 nm, 300 mW, 25 °C): $\tilde{\nu}$ = 3072 (14), 3005 (37), 2970 (36), 2927 (30), 1571 (100), 1453 (37), 1416 (48), 1260 (80), 1056 (30), 1035 (32), 1064 (100), 984 (44), 876 (32), 850 (61), 757 (71), 709 (24), 604 (14), 487 (25), 252 (32) cm^{-1}. **^{1}H NMR** (*[D$_6$]DMSO*, 25 °C): δ = 9.78 (s, NH), 6.12 (s, CH_2), 3.50 (s, CH_3), 3.44 (q, J = 6.8 Hz, CH_2OH), 1.05 (t, J = 6.8 Hz, CH_3). **^{13}C NMR** (*[D$_6$]DMSO*, 25 °C): δ = 151.4 (CN_4), 61.2 (CH_2), 56.6 (CH_2OH), 39.8 (CH_3), 19.0 (CH_3CH_2OH); **MS:** *m*/*z* (FAB^+): 219.2 $[M + H]^+$; **impact sensitivity:** > 10 J; **friction sensitivity:** > 84 N; **ESD:** > 0.75 J.

2,5-(Bis(2-nitro-2-azapropyl)-nitriminotetrazole (11): 5-Nitrimino-1,4*H*-tetrazole (1.30 g, 10 mmol) was dissolved in THF (40 mL) and triethylamine (2.02 g, 20 mmol) was added dropwise. A colorless precipitate, which formed at first, dissolved again after a few seconds. 2-Nitro-2-azapropyl chloride was dissolved in THF (10 mL) and slowly added to the reaction mixture through a dropping funnel. A colorless precipitate of triethylammonium chloride started to form. The mixture was further stirred overnight, the precipitate was filtered off and the solvent was evaporated from the filtrate to give a yellow, viscous oil. After a few hours, in the oil, the product started to crystallize. The oil/crystal-mixture was vigorously stirred with a small amount of ethanol for 2 hours and a colorless crystalline product could be filtered off. It was recrystallized from ethanol to give 1.27 g (42 % yield) of **11**. ($C_5H_{10}N_{10}O_6$, 306.20) calcd.: C 19.61, H 3.29, N 45.74 %; found: C 19.81, H 3.26, N 46.85 %; **DSC** (T_{onset}, 5 °C·min^{-1}): 107 °C (mp.), 124 °C (dec.). **IR** (KBr): $\tilde{\nu}$ = 3448 (m), 3048 (m), 2999 (w), 2960 (w), 1577 (vs), 1553 (vs), 1449 (s), 1408 (s), 1295 (vs), 1267 (vs), 1201 (s), 1135 (s), 1114 (m), 1083 (s), 1023 (s), 943 (m), 917 (s), 852 (w), 799 (s), 766 (s), 746 (s), 686 (m), 674 (m), 643 (s), 608 (s), 460 (w), 419 (m) cm^{-1}; **Raman** (1064 nm, 350 mW, 25 °C): $\tilde{\nu}$ = 3050 (52), 3000 (57), 2962 (44), 2900 (13), 1588 (14), 1559 (20), 1526 (78), 1449 (29), 1401 (34), 1345 (24), 1294 (64), 1269 (33), 1010 (50), 943 (17), 919 (18), 869 (85), 855 (100), 606 (29), 460 (19), 422 (18), 385 (14), 316 (19), 239 (30) cm^{-1}. **^{1}H NMR** (*[D$_6$]DMSO*, 25 °C): δ = 6.81 (s, 2–CH_2), 6.10 (s, 5–CH_2), 3.55 (s, 5–$H_3CN(NO_2)$), 3.47 (s, 2–$H_3CN(NO_2)$). **^{13}C NMR** (*[D$_6$]DMSO*, 25 °C): δ = 159.5 (CN_4), 67.4 (5–CH_2), 67.0 (2–CH_2), 39.8 (5–$H_3CN(NO_2)$), 39.4 (2–$H_3CN(NO_2)$). **^{15}N NMR** (*[D$_6$]DMSO*, 25 °C): δ = 2.9 (N3), –29.7 (NO_2, N10), –30.9 (NO_2, N6), –38.2 (NO_2, N8), –51.2 (N4), –80.9 (N1), –95.7 (N2), –201.3 (NNO_2(9)), –204.2 (NNO_2, N5), –207.8 (NNO_2, N7); **MS:** *m*/*z* (FAB^+): 307.2 $[M + H]^+$; **impact sensitivity:** > 2 J; **friction sensitivity:** > 108 N; **ESD:** > 0.50 J.

1-Methyl-5-(2-nitro-2-azapropyl)-nitriminotetrazole (12): 1-Methyl-5-nitrimino-4*H*-tetrazole (4.32 g, 30 mmol) was dissolved in a KOH solution (prepared from 1.98 g KOH (85 %) and 50 mL of water), the water was evaporated and potassium 1-methyl-5-nitriminotetrazolate (5.47 g, 30 mmol) was used for the coupling reaction with 2-nitro-2-azapropyl chloride without recrystallization. The potassium salt was suspended in acetone (25 mL) and 2-nitro-2-azapropyl chloride (4.11 g, 33 mmol), dissolved in acetone (10 mL), was added drop wise to the suspension. The mixture was stirred overnight, heated under reflux for 90 minutes and filtered off. The solvent was removed from the filtrate in vacuo which afforded more than 7 g of a yellow oil. The oil was taken up in hot ethanol and recrystallized, which yielded 4.18 g (60 % yield) of **12** as colorless crystals. In the crystallization mixture also a few crystals of **13** were detected. ($C_4H_8N_8O_4$, 232.16) calcd.: C 20.69, H 3.47, N 48.27 %; found: C 20.23, H 2.86, N 47.62 %; **DSC** (T_{onset}, 5 °C·min^{-1}): 133 °C (dec.). **IR** (KBr): $\tilde{\nu}$ = 3432 (m), 3051 (w), 3034 (w), 1584 (vs), 1530 (s), 1480 (m), 1449 (m), 1408 (m), 1390 (m), 1288 (vs), 1266 (s), 1123 (m), 1092 (m), 1015 (m), 913 (m), 855 (w), 766 (m), 748 (m), 700 (m), 659 (w), 643 (m), 604 (m) cm^{-1}; **Raman** (1064 nm, 350 mW, 25 °C): $\tilde{\nu}$ = 3035 (21), 2970 (45), 1545 (39), 1449 (14), 1414 (23), 1309 (23), 1264 (23), 988 (12), 916 (12), 857 (93), 799 (20), 700 (37), 660 (16), 644 (10), 606 (26), 491 (20), 474 (24), 388 (12), 303 (13), 176 (12) cm^{-1}. **^{1}H NMR** (*[D$_6$]DMSO*, 25 °C): δ = 6.06 (s, CH_2), 4.03 (s, $H_3CN(NO_2)$), 3.51 (s, CH_3).

^{13}C NMR (*[D$_6$]DMSO*, 25 °C): δ = 150.6 (CN_4), 67.6 (CH_2), 39.9 ($H_3CN(NO_2)$), 34.7 (CH_3). **^{15}N NMR** (*[D$_6$]DMSO*, 25 °C): δ = 9.9 (N3), –5.5 (N2, q, $^3J_{N–H}$ = 1.9 Hz), –30.4 (N8, NO_2), –40.8 (N6, NO_2), –57.8 (N4), –152.7 (N1, q, $^2J_{N–H}$ = 2.3 Hz), –295.0 (N7), –207.5 (N5); **MS:** *m/z* (DEI^+): 233.3 $[M + H]^+$; **impact sensitivity:** > 5 J; **friction sensitivity:** > 240 N; **ESD:** > 0.20 J.

1-Methyl-4-(2-nitro-2-azapropyl)-aminotetrazole (14): The coupling reaction of potassium 1-methyl-5-nitriminotetrazolate and **2** in acetone (described above) delivered 1-methyl-5-NAP-nitriminotetrazole (**12**), but also 1-methyl-5-NAP-aminotetrazole. It could be separated from **12** due to its different solubility in ethanol. **14** was obtained from the mother liquor in 12 % yield (0.68 g). ($C_4H_9N_7O_2$, 187.16) calcd.: C 25.67, H 4.85, N 52.39 %; found: C 25.71, H 4.84, N 52.51 %; **DSC** (T_{onset}, 5 °C·min^{-1}): 142–147 °C (mp.), 184 °C (dec.). **IR** (KBr): $\tilde{\nu}$ = 3262 (m), 3122 (m), 3040 (m), 1617 (vs), 1500 (vs), 1450 (s), 1343 (m), 1300 (vs), 1288 (s), 1248 (vs), 1226 (m), 1082 (m), 1041 (m), 1021 (m), 1002 (m), 843 (w), 768 (m), 742 (w), 668 (m), 653 (m), 619 (w), 562 (m) cm^{-1}; **Raman** (1064 nm, 350 mW, 25 °C): $\tilde{\nu}$ = 3055 (30), 3027 (30), 2952 (65), 1605 (39), 1467 (31), 1450 (39), 1342 (21), 1306 (54), 1244 (35), 1116 (33), 1081 (18), 1000 (61), 843 (90), 780 (100), 664 (23), 620 (16), 563 (13), 423 (21), 253 (36), 181 (21) cm^{-1}. **^{1}H NMR** (*[D$_6$]DMSO*, 25 °C): δ = 8.09 (t, *J* = 6.3 Hz, NH), 5.21 (d, *J* = 6.3 Hz, CH_2), 3.71 (s, CH_3), 3.53 (s, $H_3CN(NO_2)$). **^{13}C NMR** (*[D$_6$]DMSO*, 25 °C): δ = 155.7 (CN_4), 60.8 (CH_2), 39.0 ($H_3CN(NO_2)$), 32.4 (CH_3). **^{15}N NMR** (*[D$_6$]DMSO*, 25 °C): δ = 1.3 (s, N3), –20.3 (s, N2), –29.0 (m, $^3J_{NH}$ = 2.5 Hz, NO_2), –93.8 (d, $^3J_{NH}$ = 2.2 Hz, N4), –184.5 (t, $^2J_{NH}$ = 2.2 Hz, N1), –199.9 (s, NNO_2), –324.4 (d, $^1J_{NH}$ = 94 Hz, NH); **MS:** *m/z* (FAB^+): 188.2 $[M + H]^+$; **impact sensitivity:** > 40 J; **friction sensitivity:** > 120 N; **ESD:** 0.60 J.

2-Methyl-5-(2-nitro-2-azapropyl)-nitriminotetrazole (15): 2-Methyl-5-nitraminotetrazolate (4.32 g, 30 mmol) was suspended in THF (25 mL) and triethylamine (3.04 g, 30 mmol) was added. A colorless precipitate, which first was formed, disappeared within half a minute. 2-nitro-2-azapropyl chloride (3.74 g, 30 mmol), dissolved in THF (10 mL), was added drop wise. The mixture was stirred at room temperature overnight, filtered off and the solvent was removed from the filtrate. The remaining yellow oil was suspended in pentane (30 mL) and stirred vigorously. After a few minutes all the oil was converted into fine, crystalline material, which was filtered off (6.55 g, 94 % yield) and recrystallized from ethanol/methanol. ($C_2H_3KN_6O_2$, 182.18) calcd.: C 20.69, H 3.47, N 48.27 %; found: C 21.71, H 3.81, N 47.08 %; **DSC** (T_{onset}, 5 °C·min^{-1}): 68–78 °C (mp.), 116 °C (dec.). **IR** (KBr): $\tilde{\nu}$ = 3435 (m), 3043 (m), 1585 (vs), 1531 (vs), 1467 (s), 1458 (s), 1441 (m), 1412 (m), 1397 (s), 1365 (w), 1304 (s), 1282 (s), 1261 (s), 1214 (m), 1195 (m), 1147 (m), 1066 (m), 1048 (m), 1025 (m), 911 (m), 855 (w), 800 (m), 769 (m), 749 (m), 704 (w), 663 (m), 649 (m), 602 (m), 494 (w), 453 (w) cm^{-1}; **Raman** (1064 nm, 350 mW, 25 °C): $\tilde{\nu}$ = 3043 (30), 2994 (43), 2969 (91), 2875 (15), 2837 (9), 1592 (15), 1517 (59), 1457 (20), 1402 (25), 1366 (23), 1337 (18), 1291 (68), 1214 (10), 1197 (15), 1146 (6), 1067 (8), 1046 (26), 1018 (73), 915 (16), 857 (100), 799 (13), 751 (5), 704 (28), 763 (12), 751 (12), 603 (23), 495 (11), 464 (32), 394 (30), 374 (11), 327 (13), 308 (22), 243 (13), 221 (14) cm^{-1}. **^{1}H NMR** (*[D$_6$]DMSO*, 25 °C): δ = 6.09 (s, CH_2), 4.49 (s, CH_3), 3.47 (s, CH_3NNO_2). **^{13}C NMR** (*[D$_6$]DMSO*, 25 °C): δ = 159.1 (CN_4), 67.1 (CH_2), 41.2 (CH_3), 39.7 (CH_3NNO_2). **^{15}N NMR** (*[D$_6$]DMSO*, 25 °C): δ = 1.4 (N3, q, $^3J_{N–H}$ = 1.5 Hz), –30.4 (N8), –37.9 (N6), –53.4 (N4), –77.9 (N1, q, $^3J_{N–H}$ = 1.8 Hz), –101.6 (N2, q, $^2J_{N–H}$ = 2.4 Hz), –202.1 (N5, t, $^2J_{N–H}$ = 1.9 Hz), –204.9 (N7); **MS:** *m/z* (DEI^+): 233.3 $[M + H]^+$; **impact sensitivity:** > 8 J; **friction sensitivity:** > 96 N; **ESD:** > 0.07 J.

1,4-Dimethyl-5-nitriminotetrazole (16): 1-Methyl-5-nitriminotetrazole (1.44 g, 10 mmol) was deprotonated using an aqueous KOH solution (40 mL, 570 mg, 10 mmol). To this, dimethyl sulfate was added drop wise at 60 °C and the mixture was heated under reflux for three hours. Afterwards, the solvent was reduced by half and the product was extracted using CH_2Cl_2 (2 × 30 mL). After evaporating the solvent, the crude product was recrystallized from hot water yielding 1.34 g colorless crystals (85 % yield). ($C_3H_6N_6O_2$, 158.12) calcd.: C 22.79, H 3.82, N 53.15 %; found: C 23.10, H 3.84, N 52.99 %; **DSC** (T_{onset}, 5 °C·min^{-1}): 85 °C (mp.), 200 °C (dec.). **IR** (KBr): $\tilde{\nu}$ = 3029 (w), 2442 (w), 2265 (w), 2115 (w), 1685 (w), 1664 (s), 1495 (m), 1436 (s), 1412 (m), 1376 (s), 1352 (m), 1258 (vs, br), 1229 (vs), 1115 (m), 1049 (m), 1007 (s), 918 (w), 874 (w), 791 (s), 774 (s), 750 (m), 676 (s) cm^{-1}; **Raman**: (1064 nm, 200 mW, 25 °C): $\tilde{\nu}$ = 3032 (31), 2964 (93), 1568 (81), 1467 (26), 1439 (27), 1415 (46), 1378 (38), 1353 (41), 1278 (17), 1232 (15), 1050 (18), 1010 (62), 876 (11), 796 (31), 775 (11), 752 (38), 621 (100), 522 (7), 482 (29), 349 (10), 283 (33), 209 (13), 161 (15) cm^{-1}. **^{1}H NMR** (*[D$_6$]DMSO*, 25 °C): δ = 3.78 (s, 3 H, CH_3). **^{13}C NMR** (*[D$_6$]DMSO*, 25 °C): δ = 39.7 (CH_3), 168.0 (CN_4). **^{14}N NMR** (*[D$_6$]DMSO*, 25 °C): δ = –19.6 (NO_2). **^{15}N NMR** (*[D$_6$]DMSO*, 25 °C): δ = –359.4 (N7, NH_4^+), –149.3 (N5), –111.8 (C2, ^2J(N–H) = 2.1 Hz), –93.8 (N1, ^{3}J(N–H) = 1.8 Hz), –63.9 (N4), –15.4 (N6, NO_2), –6.4 (N3, ^3J(N–H) = 1.8 Hz); **MS:** *m/z* (DEI): 158(34) $[M]^+$, 112(58) $[M – NO_2]^+$, 89(10), 83 (6) $[M – NO_2 – 2CH_3]^+$, 70(5), 69(10), 57(8), 56(20), 55(12), 53(7), 46 (6) $[NO_2]^+$, 45(24), 43 (100) $[HN_3]^+$, 42 (12) $[N_3]^+$, 41(11), 28(35) $[N_2]^+$, 18(23), 15(34) $[CH_3]^+$; **impact sensitivity:** > 30 J; **friction sensitivity:** > 360 N.

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