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Synthesis and Characterization of 3,5-Diamino-1,2,4-triazolium Dinitramide

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3,5-Diamino-1,2,4-triazole (**1**, guanozol) was protonated with diluted hydrochloric acid, nitric acid, as well as perchloric acid forming 3,5-diamino-1,2,4-triazolium chloride hemihydrate (**2**), 3,5-diamino-1,2,4-triazolium nitrate (**3**) and 3,5-diamino-1,2,4-triazolium perchlorate (**4**), respectively. In a second step **4** was reacted with potassium dinitramide forming 3,5-diamino-1,2,4-triazolium dinitramide (**5**) and low soluble potassium perchlorate. **2**–**5** were characterized by low temperature single X-ray diffraction, IR and Raman as well as multinuclear NMR spectroscopy, mass spectrometry and differential scanning calorimetry. The heat of formation of **1**–**5** were calculated by the CBS-4M method to be 81.1 (**1**), 124.7 (**2**), -76.1 (**3**), -25.2 (**4**) and 138.7 (**5**) kJ mol^{-1}. With these values as well as the X-ray densities several detonation parameters were calculated using both computer codes EXPLO5.03 and EXPLO5.04. In addition, the sensitivities of **1**–**5** were determined by the BAM drophammer and friction tester as well as a small scale electrical discharge device.

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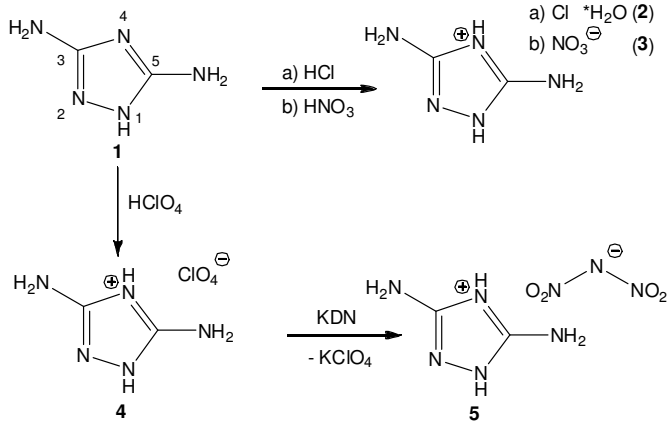
Introduction

The development of azole based new energetic materials [1] for civil and military applications is of great interest in many research programs worldwide due to their unique properties: shock waves producing pressure up to 500,000 times that of Earth's atmosphere, detonation waves travelling at 10 kilometers per second, temperatures soaring to 5500 Kelvin, and power approaching 20 billion watts per square centimetre. Advances in energetic materials, which include high explosives, propellants and pyrotechnics have been gained on nitrogen- and oxygen rich materials.[2] Especially energetic ionic salts of tri- and tetrazoles have been utilized in energetic roles owing to their higher heats of formation, density and oxygen balance compared to those of their carbocyclic analogues. Azolium cations paired with nitrate, perchlorate, dinitramide, or picrate anions form highly energetic salts with mostly good thermal stabilities. With the exception of perchlorate they and their decomposition products are often environmentally benign. Probably most suitable as high explosives, gas generators or components in propellants or propellant charges [3-6] are azolium salts containing the dinitramide anion, $N(NO_2)_2^-$ (DN).[7] They often show excellent oxygen balances by combining both the fuel (tetrazole heterocycle) and the oxidizer (dinitramide). Many N-rich dinitramides like guanidinium dinitramide,[8] aminoguanidinium dinitromide, [9] bisguanidinium dinitramide [10], guanylurea dinitramide (FOX-12) [11] and triaminoguanidinium dinitramide [4,12] were synthesized and characterized as energetic materials. Also tetrazolium derivatives, e.g. 5-aminotetrazolium dinitramide,[13] 1,5-diaminotetrazolium dinitramide [14] 1,4-dimethyl-5-aminotetrazolium dinitramide,[15] 1,5-diamino-4-methyltetrazolium dinitramide [16] are described as energetic materials in literature.[17] In this work we present the synthesis and characterization of the new energetic compound 3,5-diamino-1,2,4-triazolium dinitramide (**5**) which is based on the commercially available guanozol (**1**).

Results and Discussion

Synthesis

3,5-Diamino-1,2,4-triazole (**1**) was protonated with diluted hydrochloric and nitric acid, forming the compounds 3,5-diamino-1,2,4-triazolium chloride hemihydrate (**2**) and 3,5-diamino-1,2,4-triazolium nitrate (**3**). **2** was then recrystallized from water and **3** from an ethanolic solution (water/ethanol: 1:1). The synthesis of 3,5-diamino-1,2,4-triazolium dinitramide (**5**) was performed according to Scheme 1 by the reaction of 3,5-diamino-1,2,4-triazolium perchlorate (**4**) with potassium dinitramide (**KDN**). Compound **4** was synthesized by protonation of **1** with an equimolar amount of 1N perchloric acid. After removing the solvent, single crystals of **4** were obtained by recrystallization from hot ethanol. Compound **4** is readily soluble in water, slightly soluble in MeOH, DMSO as well as DMF and slightly soluble in cold EtOH, acetone, diethyl ether or THF. In the second step, aqueous solutions of **4** and potassium dinitramide were combined forming **5** under precipitation of potassium perchlorate. The suspension was evaporated to dryness and extracted with ethanol yielding clean **5** after evaporation of the solvent. The solubility of **5** is comparable to that of **4**. Single crystals were obtained from a wet ethanolic solution.



Scheme 1 Protocol of the syntheses of 3,5-diamino-1,2,4-triazolium nitrate (**2**), chloride (**3**), perchlorate (**4**) and dinitramide (**5**).

NMR spectroscopy

The formation of the 3,5-diamino-1,2,4-1*H*-triazolium ions can easily be monitored and observed due to the differences in the NMR spectra. The neutral compound **1** shows two unique peaks for each of the amine groups at chemical shifts of 5.56 ppm and 4.68 ppm and one broad peak at a chemical shift of 10.68 ppm for the nitrogen bonded hydrogen atom (N1, heterocyclic ring). This can be explained with the slow exchange of the N-H hydrogen atom between nitrogen atoms N1 and N2 in DMSO-*d6* which generates two different chemical surroundings for each amine group. The same is observed for the carbon atoms. In the ^{13}C-{^{1}H} NMR spectra we observed two peaks at chemical shifts of 161.8 ppm and 156.4 ppm, respectively.

In contradiction to the neutral compound the triazolium ions always show a different pattern in the NMR spectra. When protonated, only one signal is observed for the two amine groups, shifted well to lower field, at a chemical shift of 7.07 ppm (**2**), 6.97 ppm (**3**), 6.94 ppm (**4**) and 6.94 ppm (**5**), respectively. The two hydrogen atoms located on the heterocyclic ring show only one broad singulet signal at chemical shifts of 12.03 ppm (**2**), 12.08 ppm (**3**), 11.93 ppm (**4**) and 12.13 ppm (**5**). The same is observed in the $^{13}C\{^{1}H\}$ NMR spectra where we observe only one signal for the two equivalent carbon atoms of the heterocyclic ring at a chemical shift of 151.4 ppm (**2**), 151.8 ppm (**3**), 151.8 ppm (**4**) and 152.0 ppm (**5**), shifted to higher fields compared with **1**.

In addition unique peaks for the nitrate and dinitramide anions are observed in the ^{14}N NMR spectra of compounds **3** and **5** at chemical shifts of -4 ppm for compound **3** and -10 ppm for compound **5**, respectively.

Structures

The single crystal X-ray diffraction data of **1**–**5** were collected using an Oxford Xcalibur3 diffractometer with a Spellman generator (voltage 50 kV, current 40 mA) and a KappaCCD detector. The data collection was undertaken using the CRYSALIS CCD software [18] and the data reduction was performed with the CRYSALIS RED software.[19] The structures were solved with SIR-92 [20] and refined with SHELXL-97 [21] implemented in the program package WinGX [22] and finally checked using PLATON.[23] Further information regarding the crystal-structure determination have been deposited with the Cambridge Crystallographic Data Centre [24] as supplementary publication Nos. 784960 (**1**), 784963 (**2**), 784962 (**3**), 784959 (**4**) and 784961 (**5**).

The structure of guanozol (**1**) was redetermined, since the solution published by G. L. Starova *et al.* [25] (i) has been measured at room temperature and (ii) was published in the non standard space group $P2_1/b$. The asymmetric unit is shown in Figure 1. The bond distances, angles and torsion angles agree with the previously measured structure.

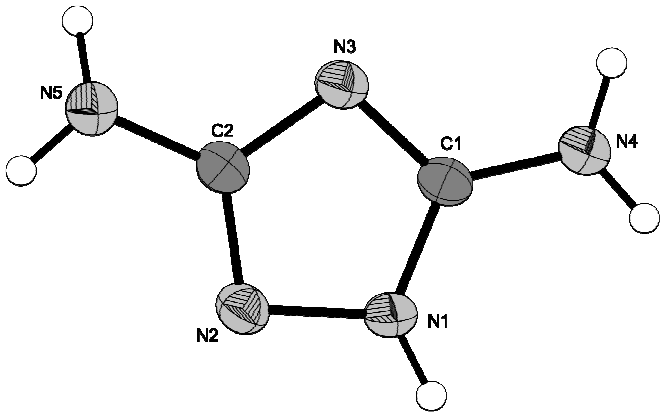


Figure 1 Molecular moiety of **1**. Thermal ellipsoids represent the 50% probability level. Selected bond lengths (Å): N5–C2 1.375(2), N3–C1 1.334(3), N3–C2 1.354(2), N2–C2 1.324(6), N4–C1 1.350(3), N2–N1 1.395(3), N1–C1 1.336(4); selected bond angles (°): N3–C1–N1 110.27(11), C2–N2–N1 101.28(11), N3–C1–N4 125.44(12), C1–N1–N2 109.67(12), N1–C1–N4 124.18(14), N2–C2–N3 115.76(13), N2–C2–N5 122.62(12), C1–N3–C2 103.02(11), N3–C2–N5 121.44(13).

Protonation of **1** using diluted hydrochloric acid yields 3,5-diamino-1,2,4-triazolium chloride as its semihydrate, which crystallizes in the monoclinic space group $P2_1/c$. The asymmetric unit, four times in a unit cell, includes two moieties of cations and anions resulting in a density of 1.584 g cm^{-3}. The chlorides participate in a strong hydrogen bond network interacting with all of the existing hydrogen atoms. The structure of the cation is influenced only very marginal by protonation at the nitrogen atom N3. With this, the angle C1–N3–C2 is slightly elongated to 106.6° (C3–N8–C4 106.4°; **1**: C1–N3–C2 103.02(11)°).

3,5-Diamino-1,2,4-triazolium chloride hemihydrate (**2**) crystallizes in the monoclinic space group $P2_1/n$ with eight molecular moieties in the unit cell. The asymmetric unit (Figure 2) consists of two anion/cation pairs and one crystal water. The density of 1.584 g cm^{-3} is in the range of other azole chlorides, e.g. 5-azido-3-amino-1,2,4-triazolium hydrochloride mono-hydrate (1.572 g cm^{-3}).[26] The two independent chloride ligands are coordinated by six (Cl1) as well s four (Cl2) hydrogen atoms forming no regular polyhedron.

Table 1 Crystallographic data and parameters.

	1	**2**	**3**	**4**	**5**
Formula	$C_2H_5N_5$	$C_4H_{14}N_{10}Cl_2O$	$C_2H_6N_6O_3$	$C_2H_6N_5ClO_4$	$C_2H_6N_8O_4$
FW [g mol^{-1}]	99.11	289.15	162.13	199.57	206.15
Crystal system	monoclinic	monoclinic	monoclinic	triclinic	monoclinic
Space Group	$P2_1/c$ (No. 14)	$P2_1/n$ (No. 14)	$P2_1/c$ (No. 14)	P-1 (No. 2)	$P2_1/n$ (No. 14)
Color / Habit	colorless rods	colorless plates	colorless rods	colorless prismn	colorless rods
Size [mm]	0.13 x 0.14 x 0.16	0.05 x 0.17 x 0.18	0.13 x 0.15 x 0.30	0.14 x 0.17 x 0.18	0.12 x 0.14 x 0.20
a [Å]	10.6366(6)	6.0570(5)	9.5615(7)	5.3035(5)	13.0772(7)
b [Å]	4.3042(2)	24.662(2)	9.1082(6)	7.6267(7)	17.4883(5)
c [Å]	10.8114(6)	8.1341(6)	7.4390(6)	9.2813(8)	14.1722(5)
α [°]	90	90	90	74.399(8)	90
β [°]	118.784(7)	93.516(7)	96.362(8)	84.825(7)	107.678(4)
γ [°]	90	90	90	83.683(8)	90
V [Å^3]	433.81(5)	1212.78(16)	643.86(8)	358.67(6)	3088.1(2)
Z	4	4	4	2	16
$\rho_{calc.}$ [g cm^{-3}]	1.518	1.584	1.673	1.848	1.774
μ [mm^{-1}]	0.114	0.541	0.150	0.520	0.162
F(000)	208	600	336	204	1696
$\lambda_{MoK\alpha}$ [Å]	0.71073	0.71073	0.71073	0.71073	0.71073
T [K]	200	200	200	200	200
Theta Min-Max [°]	3.8, 26.0	4.2, 26.0	4.3, 26.0	3.9, 26.0	3.7, 26.0
Dataset	-12:13; -5:5; -13:8	-7:4; -30:26; -9:10	-11:11; -11:7; -9:9	-6:6; -9:9; -11:11	-16:16; -21:21; -17:17
Reflections collected	2134	4625	3272	3539	30659
Independent reflections	852	2375	1264	1419	6040
R_{int}	0.019	0.038	0.033	0.023	0.026
Observed reflections	677	1518	1264	1011	4065
No. parameters	84	106	124	133	602
R_1 (obs)	0.0315	0.0350	0.0276	0.0327	0.0319
wR_2 (all data)	0.0862	0.0623	0.0639	0.0885	0.0984
S	1.04	0.82	0.92	1.00	1.03
Resd. Dens. [e Å^{-3}]	-0.22, 0.14	-0.29, 0.31	-0.16, 0.15	-0.28, 0.27	-0.31, 0.40
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
Absorption correction	multi-scan	multi-scan	multi-scan	multi-scan	multi-scan
CCDC	784960	784963	784962	784959	784961

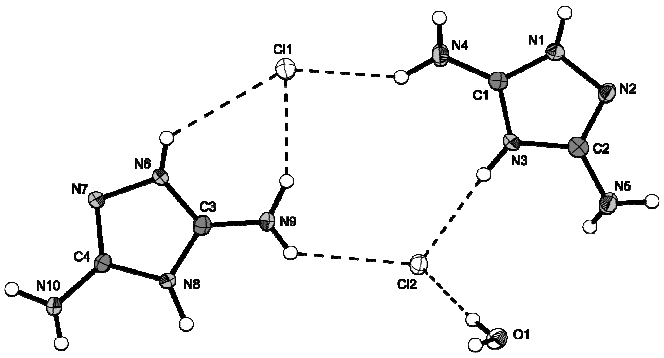


Figure 2 Molecular moiety of **2**. Thermal ellipsoids represent the 50% probability level. Selected bond lengths (Å): N1–C1 1.3173, N1–N2 1.3966, N2–C2 1.3074, N3–C1 1.3545, N3–C2 1.3725, N4–C1 1.3229, N5–C2 1.3532, N6–C3 1.3187, N6–N7 1.3948, N7–C4 1.3131, N8–C3 1.3445, N8–C4 1.3781, N9–C3 1.3326, N10–C4 1.3351.

3,5-Diamino-1,2,4-triazolium nitrate (**3**) crystallizes in the monoclinic space group $P2_1/c$ with four molecular moieties in the unit cell. The density of 1.672 g cm^{-3} is in the range of other azole nitrate derivatives, e.g. 5-aminotetrazolium nitrate.[27]

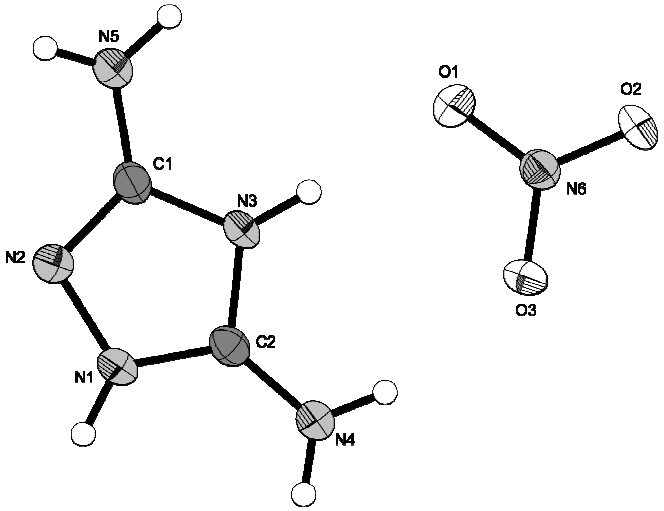


Figure 3 Molecular moiety of **3**. Thermal ellipsoids represent the 50% probability level. Selected bond lengths (Å): N1–C2 1.317(2), N1–N2 1.401(6), N5–C1 1.338(5), N2–C1 1.305(2), N3–C2 1.348(4), N3–C1 1.375(4), O1–N6 1.257(5), O2–N6 1.240(2), N4–C2 1.318(5), O3–N6 1.257(3); selected bond angles (°): C2–N1–N2 111.75(11), N2–C1–N5 125.99(13), C1–N2–N1 103.49(11), N2–C1–N3 111.23(12), N4–C2–N3 124.93(12), O2–N6–O1 120.92(11), O2–N6–O3 120.13(11), O1–N6–O3 118.95(10).

In the structure of **3** layers are formed, which are formed by a strong hydrogen-bond network. All of the oxygen atoms of the nitrate anions participate in strong hydrogen bonds listed in Table 2.

Table 2 Hydrogen bonds based on the nitrate anions in the structure of **3**.

Atoms D,H,A	Dist. D,H [Å]	Dist. H,A [Å]	Dist. D,A [Å]	Angle D,H,A [°]
N3–H3–O1^{i}	0.891(15)	1.945(16)	2.8362(15)	178.1(12)
N4–H4A–O3^{i}	0.869(18)	2.123(18)	2.9549(17)	159.9(14)
N5–H5B–O1^{iii}	0.843(18)	2.094(19)	2.9350(18)	175.9(16)
N4–H4B–O3^{iv}	0.867(17)	2.057(17)	2.9038(17)	165.3(15)
N4–H4B–O2^{iv}	0.867(17)	2.643(16)	3.0789(16)	112.3(13)
N1–H1–O2^{v}	0.874(17)	2.048(17)	2.9190(16)	175.3(15)

(i) x, 0.5-y, 0.5+z; (ii) -x, -0.5+y, 0.5-z; (iii) -x, 1-y, -z; (iv) 1-x, 1-y, 1-z; (v) x, 1.5-y, 0.5+z.

By analyzing the graph sets [28] with the software RPLUTO [29] several chain (**C1,1(6)**, **C1,1(4)** and **C2,2(5)**) and ring motifs (e.g. **R2,2(8)**) can be found within the layers, which are illustrated in Figure 4.

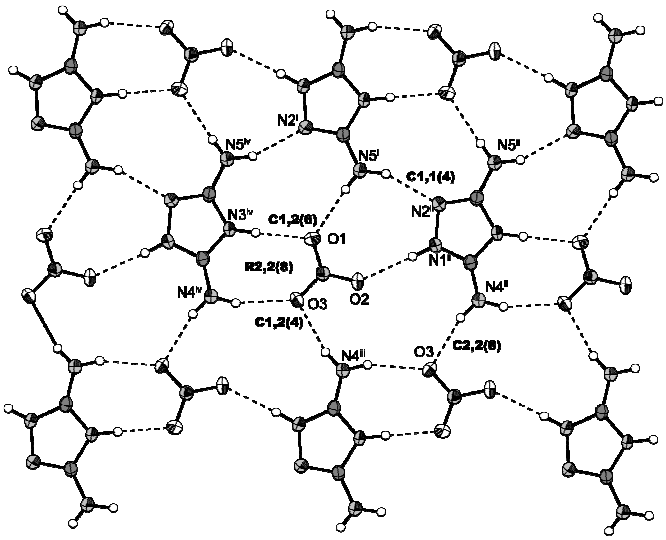


Figure 4 Hydrogen bonding within the layers in the structure of **3**. Symmetry codes: (i) -x, 1-y, -z; (ii) x, 1.5-y, -0.5+z; (iii) 1-x, 1-y, 1-z; (iv) x, 0.5-y, -0.5+z.

3,5-Diamino-1,2,4-triazolium perchlorate (**4**) crystallizes in the triclinic space group *P*-1 with two molecular moieties in the unit cell. The density of 1.848 g cm^{-3} is in the range of other azole perchlorate derivatives, e.g. 5-aminotetrazolium perchlorate.[30] The molecular structure (Figure 5) of the cation is in accordance to that in **2** and **3**. The perchlorate anions show a regular tetrahedral structure (all O–Cl–O angles between 109° and 111°).

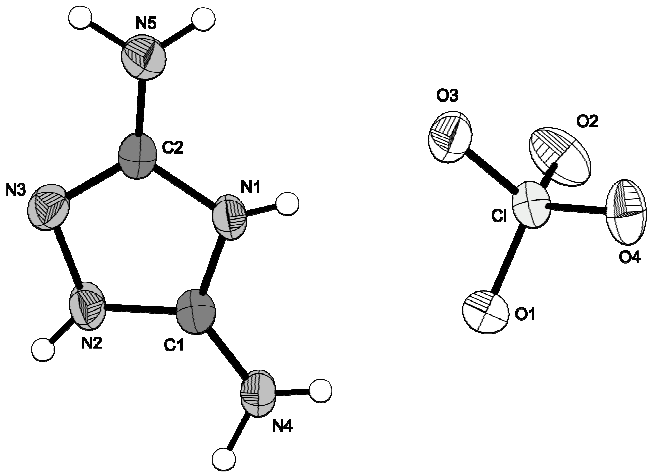


Figure 5 Molecular moiety of **5**. Thermal ellipsoids represent the 50% probability level. Selected bond lengths (Å): Cl–O4 1.431(6), N5–C2 1.354(8), Cl–O2 1.431(6), Cl–O3 1.440(5), Cl–O1 1.440(6), N2–C1 1.318(6), N3–C2 1.296(5), N3–N2 1.399(8), N4–C1 1.329(6), N1–C1 1.341(7), N1–C2 1.380(6); selected bond angles (°): C1–N2–N3 111.81(18), C2–N3–N2 103.62(20), C1–N1–C2 107.48(19), N2–C1–N4 127.29(20), N2–C1–N1 105.98(20), N3–C2–N5 126.72(23), N3–C2–N1 111.10(21).

Again a layer-like structure is formed in which three of the oxygen atoms of the perchlorate anions participate in hydrogen bonds. The fourth oxygen atom is directed alternating to both the upper and lower layers. Analyzing the graph sets yields several chain and ring motives, some of them marked in Figure 6.

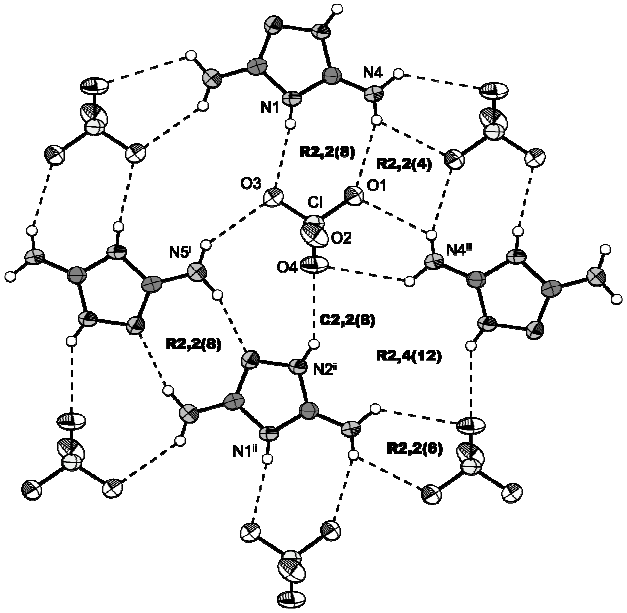


Figure 6 Hydrogen bonding within the layers in the structure of **4**. Symmetry codes: (i) -1-x, -y, 1-z; (ii) -1+x, -1+y, z; (iii) -2-x, 1-y, -z.

3,5-Diamino-1,2,4-triazolium dinitramide (**5**) crystallizes in the monoclinic space group $P2_1/n$ with 16 (!) molecular moieties in the unit cell. For better clearness only one of the four independent molecular units is shown in Figure 7. The density observed is 1.774 g cm^{-3}, which is comparable to that of 1,5-diaminotetrazolium dinitramide (1.771 g cm^{-3}) described in literature.[14]

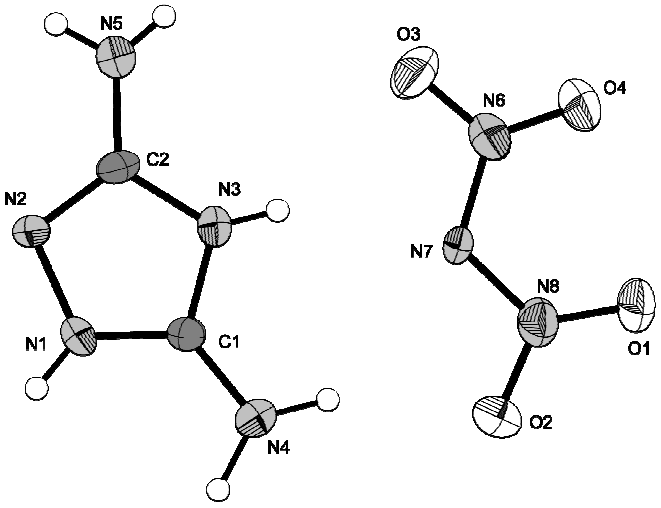


Figure 7 Molecular moiety of **5**. The ellipsoids represent the 50% probability level. Selected bond lengths (Å): O2–N8 1.240(4), O1–N8 1.251(4), N7–N8 1.354(4), N7–N6 1.368(4), O3–N6 1.238(4), O4–N6 1.218(4), N1–C1 1.317(4), N2–C2 1.308(5), N2–N1 1.403(4), N4–C1 1.313(5), C1–N3 1.358(5), N3–C2 1.367(5), C2–N5 1.343(5).

Compound **5** crystallizes in accordance to **3** and **4** forming a layer-like structure. Except for the outer nitrogen atoms in the dinitramide anions all atoms participate in hydrogen bonds, shown in Figure 8. Due to that fact, several remarkable also bifurcated hydrogen-bonds are formed.

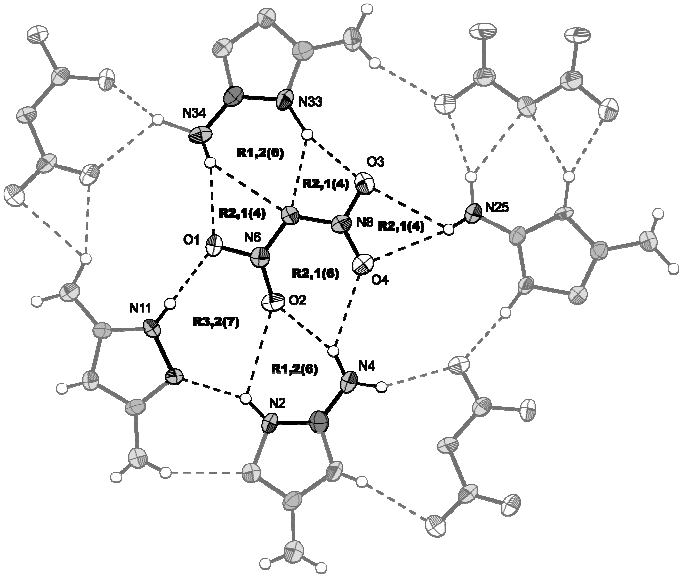


Figure 8 Hydrogen bonding of one dinitramide anion in the structure of **5**.

Heat of Formation

Due to the highly energetic character of **3** and **5**, bomb calorimetric measurements could only performed with small amounts, consequently doubtful combustion energies were obtained. Therefore an extensive computational study was accomplished for **1**–**5**, which is presented in the following.

All calculations were carried out using the Gaussian G03W (revision B.03) program package.[31] The enthalpies (H) and free energies (G) were calculated using the complete basis set (CBS) method of Petersson and coworkers in order to obtain very accurate energies. The CBS models use the known asymptotic convergence of pair natural orbital expressions to extrapolate from calculations using a finite basis set to the estimated complete basis set limit. CBS-4 begins with a HF/3-21G(d) geometry optimization; the zero point energy is computed at the same level. It then uses a large basis set SCF calculation as a base energy, and a MP2/6-31+G calculation with a CBS extrapolation to correct the energy through second order. A MP4(SDQ)/6-31+(d,p) calculation is used to approximate higher order contributions. In this study we applied the modified CBS-4M method (M referring to the use of Minimal Population localization) which is a re-parametrized version of the original CBS-4 method and also includes some additional empirical corrections.[32] The enthalpies of the gas-phase species M were computed according to the atomization energy method (eq. 1) (Tables 3–5).[33]

$$\Delta_f H^\circ_{(g,\,M,\,298)} = H_{(Molecule,\,298)} - \sum H^\circ_{(Atoms,\,298)} + \sum \Delta_f H^\circ_{(Atoms,\,298)} \quad (1)$$

Table 3. CBS-4M results

	point group	el. state	$-H^{298}$ / a.u.	*NIMAG*
DATr (1)	C_s		352.484409	0
HDATr$^+$	C_s	$^1A_1$	352.839733	0
Cl$^-$	K_h		459.809901	0
NO$_3^-$	D_{3h}	^1A	280.080446	0
ClO$_4^-$	T_d		760.171182	0
DN$^-$	C_2		464.499549	0
H		$^2A_{1g}$	0.500991	0
C			37.786156	0
N		$^4A_{1g}$	54.522462	0
O			74.991202	0
Cl			459.674576	0

Table 4 Literature values for atomic $\Delta H^\circ_f{}^{298}$ / kcal mol^{-1}

	NIST [34]
H	52.1
C	171.3
N	113.0
O	59.6
Cl	29.0

Table 5 Enthalpies of the gas-phase species M.

M	M	$\Delta_f H^\circ$(g,M) / kcal mol^{-1}
DATr (1)	$C_2H_5N_5$	41.8
HDATr$^+$	$C_2H_6N_5^+$	185.3
Cl$^-$	Cl^-	-55.9
NO$_3^-$	NO_3^-	–74.9
ClO$_4^-$	ClO_4^-	-66.1
DN$^-$	$N_3O_4^-$	-29.6

The solid state energy of formation (Table 7) of **DATr** was calculated by subtracting the gas-phase enthalpy with the heat of sublimation (22.5 kcal mol^{-1}) obtained by the TROUTMAN rule (ΔH_{sub} = 188·T$_m$) (T$_m$=204 °C).[35] In the case of **ADNQ**, the lattice energy (U_L) and lattice enthalpy (ΔH_L) were calculated from the corresponding molecular volumes (Table 9) according to the equations provided by Jenkins *et al.*.[36] With the calculated lattice enthalpy (Table 6) the gas-phase enthalpy of formation (Table 5) was converted into the solid state (standard conditions) enthalpy of formation. These molar standard enthalpies of formation (ΔH_m) were used to calculate the molar solid state energies of formation (ΔU_m) according to equation 2 (Table 7).

$$\Delta U_m = \Delta H_m - \Delta n\, RT \quad (2)$$

(Δn being the change of moles of gaseous components)

Table 6 Lattice energies and lattice enthalpies.

	V_{M_3} / nm^3	U_L / kJ mol^{-1}	ΔH_L / kJ mol^{-1}	ΔH_L / kcal mol^{-1}
2	0.151	543.8	545.8	130.3
3	0.161	535.0	538.5	128.6
4	0.179	520.1	523.6	125.0
5	0.193	509.8	513.2	122.6

Table 7 Solid state energies of formation ($\Delta_f U^\circ$)

	$\Delta_f H^\circ$(s) / kcal mol^{-1}	$\Delta_f H^\circ$(s) / kJ mol^{-1}	Δn	$\Delta_f U^\circ$(s) / kJ mol^{-1}	M / g mol^{-1}	$\Delta_f U^\circ$(s) / kJ kg^{-1}
1	19.4	81.1	5	93.4	99.12	942.8
2	-29.8	-124.7	6.5	-108.6	144.57	-751.0
3	–18.2	–76.1	7.5	–57.6	162.14	–354.9
4	–6.0	–25.2	8	–5.4	199.58	–26.8
5	33.1	138.7	9	161.0	206.16	781.1

Detonation parameters

The calculation of the detonation parameters was performed with the program package EXPLO5 (version 5.03 and 5.04).[37] The program is based on the chemical equilibrium, steady-state model of detonation. It uses the Becker-Kistiakowsky-Wilson's equation of state (BKW EOS) for gaseous detonation products and Cowan-Fickett's equation of state for solid carbon. The calculation of the equilibrium composition of the detonation products is done by applying modified White, Johnson and Dantzig's free energy minimization technique. The program is designed to enable the calculation of detonation parameters at the CJ point. The BKW equation in the following form was used with the BKWN set of parameters (α, β, κ, θ) as stated below the equations and X_i being the mol fraction of *i*-th gaseous product, k_i is the molar covolume of the *i*-th gaseous product [38]:

$pV / RT = 1 + xe^{\beta x}$ $x = (\kappa \Sigma X_i k_i) / [V (T + \theta)]^{\alpha}$

$\alpha = 0.5$, $\beta = 0.176$, $\kappa = 14.71$, $\theta = 6620$.

The detonation parameters calculated with the EXPLO5 versions V5.03 and V5.04 using the experimentally determined densities (X-ray) are summarized in Table 8. It is not possible to calculate detonation parameters of compounds containing chlorine; therefore, the corresponding cells have been abandoned.

Table 8 Physico-chemical properties of **1–5** in comparison with trinitrotoluene (**TNT**), nitropenta (**PETN**) and hexogen (**RDX**).

	1	**2**	**3**	**4**	**5**	**TNT***	**PETN***	**RDX***
Formula	$C_2H_5N_5$	$C_2H_7N_5ClO_{1/2}$	$C_2H_6N_6O_3$	$C_2H_6ClN_5O_4$	$C_2H_6N_8O_4$	$C_7H_5N_3O_6$	$C_5H_8N_4O_{12}$	$C_3H_6N_6O_7$
Molecular Mass [g mol^{-1}]	99.12	144.57	162.14	199.58	206.12	227.13	316.14	222.12
Impact sensitivity [J][a]	> 40	> 40	40	25	> 3	15	3	7.5
Friction sensitivity [N][b]	> 360	> 360	288	240	192	353	60	120
ESD–test [J]	> 5	> 10	0.3	0.8	0.3	n.d.	n.d.	0.1 - 0.2
N [%][c]	70.67	48.44	51.84	35.10	54.36	18.50	17.72	37.8
Ω [%][d]	–104.9	–71.91	–39.48	–20.04	–23.28	-73.96	-10.1	–21.6
$T_{dec.}$ [°C][e]	204 (mp)	282	276	252	164	>160	202	210
ρ [g cm^{-3}][f]	1.520	1.584	1.672	1.848	1.774	1.654	1.778	1.800
$\Delta_f H_m°$ [kJ mol^{-1}][g]	81.1	-124.7	–76.1	–25.2	138.7	-59.1	-539.0	70
$\Delta_f U°$ [kJ kg^{-1}][h]	942.8	-751.0	–354.9	–33.1	781.1	-184.9	-1611.7	417
EXPLO5 values: V5.03 (V5.04)								
$-\Delta_E U°$ [kJ kg^{-1}][i]	1853 (1674)	---	4052 (4060)	---	5101 (5157)	5112 (5227)	5979 (6190)	6038 (6125)
T_E [K][j]	1152 (1561)	---	3104 (2996)	---	3810 (3705)	3756 (3657)	4423 (4306)	4368 (4236)
p_{C-J} [kbar][k]	113 (134)	---	233 (246)	---	302 (321)	205 (216)	321 (320)	341 (349)
$V_{Det.}$ [m s^{-1}][l]	6058 (6516)	---	7789 (7927)	---	8624 (8681)	7178 (7253)	8665 (8320)	8906 (8748)
Gas vol. [L kg^{-1}][m]	847 (758)	---	833 (826)	---	833 (810)	617 (574)	765 (688)	793 (739)

[a] BAM drophammer, grain size (75–150 µm); [b] BAM friction tester, grain size (75–150 µm); [c] Nitrogen content; [d] Oxygen balance [39]; [e] Temperature of decomposition by DSC (β = 5 °C); [f] X-ray structure; [g] Molar enthalpy of formation; [h] Energy of formation; [i] Energy of Explosion; [j] Explosion temperature; [k] Detonation pressure; [l] Detonation velocity; [m] Assuming only gaseous products; * values based on Ref. [40] and the EXPLO5 database; n.d.: not determined.

Especially the detonation parameters of compound **5** show promising values, higher than those of trinitrotoluene (**TNT**) and in the range of those of pentaerythrityl tetranitrate (**PETN**). Also compound **3** exceeds the values of TNT in addition to its great thermal stability of 276 °C and low sensitivities (Table 8). The most important criteria of high explosives are the detonation velocity ($V_{Det.}$= **3**: 7927, **5**: 8681, TNT: 7253, PETN: 8320, RDX: 8748 m s^{-1}), the detonation pressure ($p_{det.}$ = **3**: 246, **5**: 321, TNT: 216, PETN: 320, RDX: 349 kbar) and the energy of explosion ($\Delta_E U°$ = **3**: -4060, **5**: -5157, TNT: 5227, PETN: 6190, RDX: 6125 kJ kg^{-1}).

For application of new energetic compounds important values for safety, handling and processing are the sensitivity data. All values were determined according to BAM standard methods described in the NATO STANAG 4487, 4489 and 4490 specifications for energetic materials.[41-47]

Unfortunately, well performing **5** is very sensitive towards impact (> 3 J) which is slightly below the commercial available PETN (3 J) and RDX (7.5 J). However, it is not as sensitive in terms of friction (**5**: > 192 N, RDX: > 120 N) and electrostatic discharge (**5**: > 0.3 J, RDX: > 0.1-0.2 J). The latter values are most important for handling and processing on an industrial scale and therefore compound **5** could be considered for application.

The most promising compound regarding to the sensitivity data is compound **3** which shows rather low sensitivity to friction (288 N), to impact (40 J) and to electrostatic discharge (0.3 J). According to the UN Recommendations on the Transport of Dangerous Goods compound **3** is regarded insensitive.[48,49]

Thermostability of energetic compounds is considered important especially in processing and storing the material. Because of the diverse use of energetic materials e.g. under extreme climatic conditions like in desserts, for oil drilling or military ammunition high temperature stability is desired. The introduced compounds **3** and **5** display good values for melting (**3**: 159 °C, **5**: 155 °C) and decomposition (**3**: 276 °C, **5**: 164 °C). Compound **5** melts at 155 °C and decomposes subsequently at 164 °C, whereas compound **3** shows a melting point at 159 °C followed by a wide liquid range of 110 °C and decomposes finally at 276 °C. The high difference between melting and decomposition point leaves compound **3** very suitable as melt cast explosive. Comparing compounds **3** and **5** to common explosives, they exceed both TNT (m.p. 80 °C, $T_{dec.}$ >160 °C) and compound **3** passes even RDX (m.p./ $T_{dec.}$ 210 °C) and PETN (m.p. 140 °C, $T_{dec.}$200 °C), regarding the thermal stability against decomposition.

Conclusions

From this combined experimental and theoretical study the following conclusions have been drawn:

- 3,5-Diamino-1,2,4-triazole (**1**) can be protonated using diluted mineralic acids such as hydrochloric, nitric and perchloric acid. The hydrodinitramide salt (**5**) of **1** can be synthesized by metathesis reaction of the perchlorate salt (**4**) with potassium dinitramide. The obtained compounds 3,5-diamino-1,2,4-triazolium chloride hemihydrate (**2**), 3,5-diamino-1,2,4-triazolium nitrate (**3**) and 3,5-diamino-1,2,4-triazolium perchlorate (**4**), and 3,5-diamino-1,2,4-triazolium dinitramide (**5**) are air-stable, not hygroscopic colorless solids.

- All salts were recrystallized from ethanol/water mixtures yielding single crystals, which were analyzed by X-ray diffraction. The salts crystallizes in common space groups (**2**, **5**: $P2_1/n$, **3**: $P2_1/c$, **4**: $P\bar{1}$). All structures are dominated by a strong hydrogen-bond network.

- The energetic properties of **1**–**5** were determined and compared with trinitrotoluene (TNT), pentaerythrityl tetranitrate (PETN) and hexogen (RDX). The sensitivities towards impact, friction and electrostatic discharge were measured. The sensitivities escalate from **1** to **5**. The dinitramide salt **5** is very sensitive towards impact (3 J) and moderately towards friction (192 N).

- The detonation parameters of **1**, **3**, and **5** were calculated with the computer codes EXPLO5.03 and EXPLO5.04, respectively. The detonation velocities and pressures of **3** and **5** are greater than those of TNT and in the case of **5** in the range of PETN.

Experimental Part

Caution: Although all 3,5-diamino-1,2,4-triazolium salts reported in this publication are rather stable against friction, impact and electric discharge, proper safety precautions should be taken when handling dinitramide salts. The derivatives are energetic materials and tend to explode under certain conditions, especially under physical stress. Laboratories and personnel should be properly grounded, and safety equipment such as Kevlar gloves, leather coats, face shields nd ear plugs are recommended.

General. All chemical reagents, except 3,5-diamino-1,2,4-1*H*-triazole and ammonium dinitramide, and solvents were obtained from Sigma-Aldrich Inc. or Acros Organics (analytical grade) and were used as supplied. 3,5-diamino-1,2,4-1*H*-triazole was obtained from ABCR and ammonium dinitramide was supplied by EURENCO Bofors AB. Potassium dinitramide was prepared from ammonium dinitramide following known literature procedures[**Error! Bookmark not defined.**a]. ^{1}H, ^{13}C{^{1}H}, and ^{14}N NMR spectra were recorded on a JEOL Eclipse 400 instrument in DMSO-d_6 at or near 25 °C. The chemical shifts are given relative to tetramethylsilane (^{1}H, ^{13}C) or nitromethane (^{14}N) as external standards and coupling constants are given in Hertz (Hz). Infrared (IR) spectra were recorded on a Perkin-Elmer Spectrum BX FT-IR instrument equipped with an ATR unit at 25 °C. Transmittance values are qualitatively described as "very strong" (vs), "strong" (s), "medium" (m) and "weak" (w). Raman spectra were recorded on a Bruker RAM II spectrometer equipped with a Nd:YAG laser (1064 nm) and a reflection angle of 180°. The intensities are reported as percentages of the most intense peak and are given in parentheses. Elemental analyses were performed with a Netsch Simultaneous Thermal Analyzer STA 429. Melting points were determined by differential scanning calorimetry (Setaram DSC141 instrument, calibrated with standard pure indium and zinc). Measurements were performed at a heating rate of 5 °C min^{-1} in closed aluminum sample pans with a 1 µm hole in the top for gas release under a nitrogen flow of 20 mL/min with an empty identical aluminum sample pan as a reference. For initial safety testing, the impact and friction sensitivities as well as the electrostatic sensitivity were determined.[48] The impact sensitivity tests were carried out according to STANAG 4489 [41] modified according to instruction [44] using a BAM [46] drophammer. The friction sensitivity tests were carried out according to STANAG 4487 [42] modified according to instruction [45] using the BAM friction tester. The electrostatic sensitivity tests were carried according to STANAG 4490 [43] out using an electric spark testing device ESD 2010EN (OZM Research) operating with the "Winspark 1.15 software package".[48]

3,5-Diamino-1,2,4-triazole (**1**)

As obtained from ABCR.
DSC (5 °C min^{-1}): 205 °C (mp., onset); **^{1}H NMR**: δ (ppm) = 10.68 (s, 1H, NH), 5.56 (s, 2H, NH_2), 4.68 (s, 2H, NH_2); **^{13}C{^{1}H} NMR** (D_6-DMSO): δ (ppm) = 161.8, 156.4; ***m/z*** (DEI) = 99.09 ([M]$^{+}$); **IS**: > 40 J; **FS**: > 360 N; **ESD**: >1.5 J.

3,5-Diamino-1,2,4-triazolium chloride hemihydrate (**2**)

0.99 g (10 mmol) of 3,5-diamino-1,2,4-1*H*-triazole was added with stirring to 10 mL (10 mmol) of 1 *M* hydrochloric acid solution. The

resulting solution was heated slightly to 50 °C and was kept at this temperature for 10 minutes. After cooling to room temperature the solvent was evaporated completely and the white residue was recrystallized from water, yielding 1.34 g (99%) of pure **2** as white crystalline needles.
DSC (5 °C min^{-1}): 105 °C (mp., onset), 145 °C (-H_2O, onset), 282 °C (dec., onset); **IR** (ATR): 3328 (s), 3224 (s), 3157 (vs), 2899 (m), 2651 (m), 1690 (m), 1657 (s), 1651 (ms), 1646 (m), 1635 (m), 1352 (w), 1297 (w), 1160 (w), 1059 (w), 1011 (w), 794 (w), 711(w); **Raman** (1064 nm, 25 °C): 3322 (17), 3229 (24), 3181 (22), 1688 (75), 1657 (31), 1593 (15), 1568 (18), 1540 (12), 1455 (36), 1333 (26), 1305 (17), 1166 (28), 1071 (100), 1051 (65), 797 (50), 724 (16), 664 (74), 500 (33), 355 (42); **^{1}H NMR**: δ (ppm) = 12.03 (s, br, 2H, NH), 7.07 (s, 4H, NH_2); **^{13}C{^{1}H} NMR**: δ (ppm) = 151.4; **MS**: FAB^+ = 100.12 ($[M]^+$), FAB^- = 34.95 ($[Cl]^-$); **EA**: calcd.: C 16.62, H 4.88, N 48.45; found: C 16.74, H 4.58, N 48.21; **IS**: > 40 J; **FS**: 360 N; **ESD**: > 1.5 J.

3,5-Diamino-1,2,4-triazolium nitrate (**3**)

0.99 g (10 mmol) of 3,5-diamino-1,2,4-1*H*-triazole was added with stirring to 5 mL (10 mmol) of 2 *M* nitric acid solution. The resulting solution was heated slightly to 50 °C and was kept at this temperature for 10 minutes. After cooling to room temperature the solvent was reduced to about one third of its original volume and the slightly yellow solution was left standing for crystallization. **3** separated from the solution over the course of one week, left standing on air, yielding 1.46 g (91%). Crystals of **3** suitable for X-ray diffraction measurements were obtained by recrystallization from a water/ethanol mixture (1:1).
DSC (5 °C min^{-1}): 159 °C (mp., onset), 276 °C (dec., onset); **IR** (ATR): 3792 (vw), 3423 (m), 3326 (m), 3282 (m), 3166 (m), 2936 (m), 2792 (m), 2688 (m), 1680 (s), 1662 (vs), 1612 (m), 1537 (w), 1425 (m), 1321 (s), 1297 (s),1040 (w), 1010 (w), 812 (w), 794 (w), 716 (w), 657 (w); **Raman** (1064 nm, 25 °C): 3274 (7), 3175 (14), 1705 (20), 1689 (37), 1660 (22), 1601 (20), 1551 (7), 1468 (18), 1418 (11), 1354 (8), 1172 (16), 1076 (77), 1053 (100), 1042 (95), 1016 (51), 796 (32), 718 (26), 665 (65), 499 (15), 347 (26); **^{1}H NMR**: δ (ppm) = 12.08 (s, br, 2H, NH), 6.97 (s, 4H, NH_2); **^{13}C{^{1}H} NMR**: δ (ppm) = 151.8; **^{14}N NMR**: δ (ppm) = -4 (NO_3^-); **MS**: FAB^+ = 100.09 ($[M]^+$), FAB^- = 62.01 ($[NO_3]^-$); **EA**: calcd.: C 14.82, H 3.73, N 51.84; found: C 15.07, H 3.57, N 51.64; **IS**: 40 J; **FS**: 288 N; **ESD**: 0.3 J.

3,5-Diamino-1,2,4-triazolium perchlorate (**4**)

0.99 g (10 mmol) of 3,5-diamino-1,2,4-1*H*-triazole was added with stirring to 10 mL (10 mmol) of 1 *M* perchloric acid solution. After complete dissolution of **1**, the solvent was evaporated to dryness and the remaining white residue was recrystallized from hot ethanol, yielding 1.95 g (98%) of pure **4**. Crystals suitable for X-ray diffraction measurements were also obtained from hot ethanol.
DSC (5 °C min^{-1}): 185 °C (mp., onset), 252 °C, 294°C, 335 °C (dec., onset); **IR** (ATR): 3561 (w), 3468 (m), 3455 (m), 3408 (s), 3366 (s), 3276 (m), 3216 (s), 3178 (s), 1672 (s), 1601 (m), 1541 (m), 1456 (m), 1344 (w), 1079 (s), 1050 (s), 1011 (m), 932 (w), 667 (w), 621 (w); **Raman** (1064 nm, 25 °C): 3460 (2), 3414 (4), 3369 (5), 3217 (6), 3176 (5), 1698 (18), 1664 (13), 1600 (14), 1458 (18), 1342 (7), 1170 (11), 1063 (26),1016 (10), 935 (100), 797 (20), 667 (30), 630 (23), 491 (14), 470 (17), 453 (24), 343 (16); **^{1}H NMR**: δ (ppm) = 11.93 (s, br, 2H, NH), 6.94 (s, 4H, NH_2); **^{13}C{^{1}H} NMR**: δ (ppm) = 151.8; **MS**: FAB^+ = 100.10 ($[M]^+$), FAB^- = 99.00 ($[ClO_4]^-$); **EA**: calcd.: C 12.04, H 3.03, N 35.10; found: C 12.00, H 3.13, N 35.34; **IS**: 25 J; **FS**: 240 N; **ESD**: 0.8 J.

3,5-Diamino-1,2,4-triazolium dinitramide (**5**)

Aqueous solutions of 0.997 g (5 mmol) of **4** in 3 mL of water and 0.725 g (5 mmol) potassium dinitramide in 3 mL of water were combined under stirring, resulting in the formation of a yellow precipitate. The suspension was then stirred for an additional 15 minutes and the solvent was evaporated completely afterwards. The remaining yellow (slightly wet) residue was extracted with 40 mL of ethanol. The ethanolic solution was concentrated to one fourth of its original volume and left for crystallization, yielding 0.86g (83%) of clean **5**. Crystals suitable for X-ray diffraction measurements were obtained from a wet ethanolic solution.
DSC (5 °C min^{-1}): 155 °C (mp., onset), 164 °C (dec., onset); **IR** (ATR): 3788 (vw), 3460 (w), 3425 (w), 3397 (m), 3319 (w), 3269 (m), 3180 (m), 3114 (m), 1707 (m), 1691 (m), 1652 (s), 1512 (s), 1469 (m), 1429 (m), 1342 (m), 1173 (vs), 1150 (s), 1054 (w), 1034 (m), 1004 (s), 960 (m), 815 (w), 799 (w), 761 (m), 723 (w), 688 (m), 673 (m); **Raman** (1064 nm, 25 °C): 3408 (3), 3346 (7), 3323 (6), 3284 (6), 3224 (5), 1699 (23), 1659 (19), 1607 (8),1589 (9), 1544 (10), 1527 (9), 1470 (22),1435 (13), 1326 (100), 1285 (20), 1213 (7), 1182 (17),1151 (21), 1050 (51), 963 (27), 819 (53), 802 (22), 767 (7), 670 (30), 499 (35), 486 (18), 452 (10), 352 (25), 306 (23); **^{1}H NMR**: δ (ppm) = 12.13 (s, br, 2H, NH), 6.94 (s, 4H, NH_2); **^{13}C{^{1}H} NMR**: δ (ppm) = 152.0; **^{14}N NMR**: δ (ppm) = -10 ($N_3O_4^-$); **MS**: FAB^+ = 100.10 ($[M]^+$), FAB^- = 106.00 ($[N_3O_4]^-$); **EA**: calcd.: C 11.65, H 2.93, N 54.36; found: C 11.46, H 2.80, N 53.93; **IS**: > 3 J; **FS**: 192 N; **ESD**: 0.3 J.

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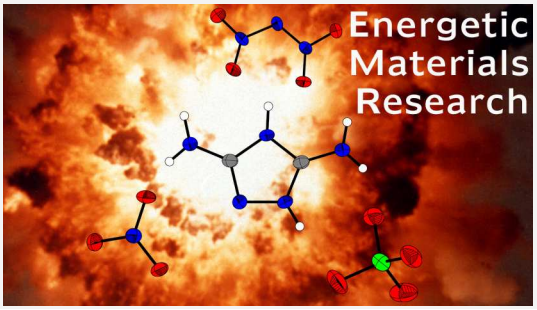

Thomas M. Klapötke,* Franz A. Martin, Norbert T. Mayr and Jörg Stierstorfer

…….. Page No. – Page No.

Synthesis and Characterization of 3,5-Diamino-1,2,4-triazolium Dinitramide