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Diaminouronium Nitrimitotetrazolates – Thermally Stable Explosives

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and Jörg Stierstorfer^[a]

In memory of Herbert Schumann, an outstanding chemist and great friend

Keywords: Crystal Structure; Detonation Parameters; Energetic Materials; Sensitivities; Tetrazoles;

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Abstract:

Diaminouronium 5-nitrimitotetrazolate (**1**) and diaminouronium 1-methyl-5-nitrimitotetrazolate (**2**) were synthesized by the reaction of diaminourea with 5-nitrimitotetrazole (**3**) and 1-methyl-5-nitrimitotetrazole (**4**), respectively. The energetic compounds **1** and **2** were fully characterized by single crystal X-ray diffraction, NMR spectroscopy, IR- and Raman spectroscopy as well as DSC measurements. The sensitivities towards impact, friction and electrical discharge were determined. Several detonation parameters (e.g. heat of explosion, detonation velocity) were computed by the EXPLO5 computer code based on calculated (CBS-4M) heats of formation and X-ray densities. In addition, the detonation velocity of **1** was experimentally determined and compared to the computed values.

Keywords: Crystal Structure, Energetic Materials, Sensitivities, Tetrazoles.

Introduction

Nitrogen rich materials play an important role in the design of new energetic materials for use in propellants, explosives, and pyrotechnics [1]. For a nitrogen rich material to find practical application as a high explosive it needs to possess high thermal and mechanical stabilities, while at the same time satisfying the increasing demand for higher performing (high detonation velocity, pressure and heat of explosion) materials. Unfortunately, in many cases high performance and low sensitivity appear to be mutually exclusive; many high performing materials are not stable enough to find practical use [2] and many materials with the desired sensitivity do not possess the performance requirements of a material to replace a commonly-used explosive [3]. This trend is exemplified in the range of 5-membered azoles from pyrazole to pentazole, where pyrazole is not used in energetics due to low performance, and

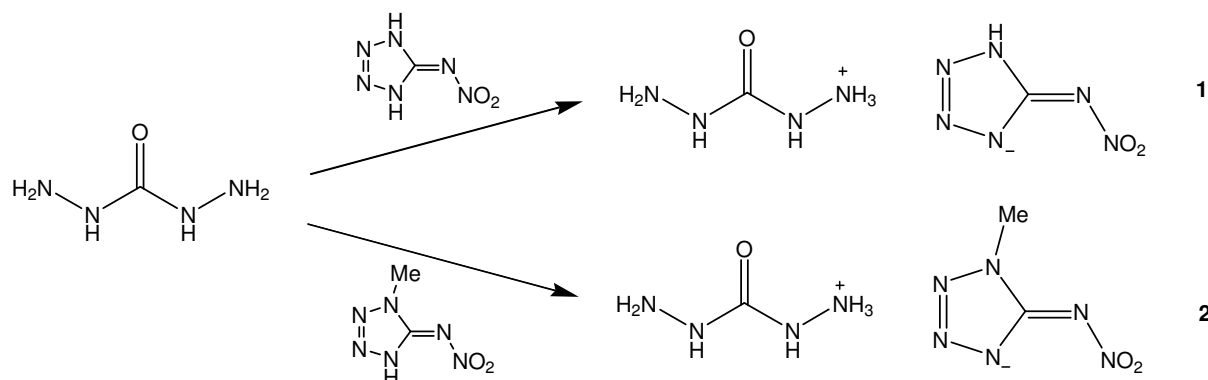
the few pentazole derivatives known are highly unstable [4]. One of the most promising heterocyclic backbones for the preparation of high-performing energetics is the tetrazole ring. Possessing high heats of formation resulting from the nitrogen-nitrogen bonds, ring strain, and high density, the tetrazole ring has allowed the preparation of high performing primary [5] and secondary [6] explosives, illustrating the dynamic nature of the tetrazole ring; depending on the ring substituents and anion/cation pairing, tetrazole based energetics can span the spectrum of sensitivity from insensitive to highly sensitive (primary explosives). Additionally, due to their aromatic ring, tetrazoles are generally thermally stable. Of the tetrazoles suitable for use in secondary explosives, nitriminotetrazoles are one of the most promising due to high thermal stability [7].

Apart from the high heats of formation, for a molecule or salt to be a high-performing energetic, a high oxygen balance is required. The oxygen balance is given in percent and represents the amount of oxygen with respect to the molar mass of the molecule, which is necessary to convert all of its non-oxidizing content to their respective oxides and is easily calculated by the equation $\Omega (\%) = (wO - 2xC - 1/2yH - 2zS) \cdot 1600/M$ (w : number of oxygen atoms, x : number of carbon atoms, y : number of hydrogen atoms, z : number of sulfur atoms). Previous work with nitriminotetrazoles and especially alkylated nitriminotetrazoles [7], has led to compounds with high performance despite negative oxygen balances. The use of oxygen-containing cations with nitriminotetrazoles to improve the oxygen balance of the final nitriminotetrazolate salts is a previously unexplored field. In this work we describe the synthesis and properties of two new energetic nitriminotetrazoles containing the diaminourea cation.

Results and Discussion

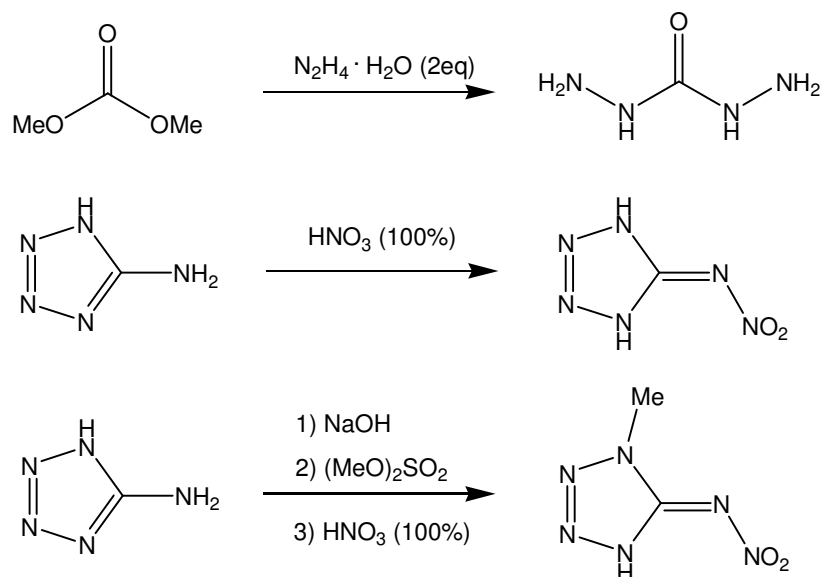
Synthesis

The synthetic routes to compounds **1** and **2** are depicted in Scheme 1. As they are both ionic species, they are accessible by facile Brønsted acid base chemistry. An aqueous solution of diaminourea, which is readily soluble in water, is reacted with an equimolar amount of 5-nitriminotetrazole and 1-methyl-5-nitriminotetrazole respectively, which also were dissolved in warm water prior to addition.



Scheme 1. Synthesis of **1** and **2** via Brønsted acid base chemistry

1
2
3 Diaminourea as well as 5-nitriminotetrazole and 1-methyl-5-nitriminotetrazole were
4 synthesized according to literature procedure [8, 9] which can be seen in Scheme 2.
5 Hydrazinolysis of dimethylcarbonate in aqueous solution leads to diaminourea, whereas the
6 acidic methylated and unmethylated nitriminotetrazoles are obtained by methylation of 5-
7 aminotetrazole using sodium hydroxide and dimethyl sulphate and following nitration with
8 fuming nitric acid or direct nitration of 5-aminotetrazole respectively.
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Scheme 2. Synthesis of the starting materials.

Crystal Structures

The single crystal X-ray diffraction data was 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 CRYSA LIS CCD software [10] and the data reduction was performed with the CRYSA LIS RED software [10]. The structure was solved with SIR-92 [11] and refined with SHELXL-97 [12] implemented in the program package WinGX [13] and finally checked using PLATON [14]. Due to the chiral space groups in both structure, the *Friedel pairs* were merged. In all structures potential hydrogen atoms have been observed and freely refined. Selected data and parameters from the X-ray data collection and refinement are given in Table 1. Further information regarding the crystal-structure determination have been deposited with the Cambridge Crystallographic Data Centre [15] as supplementary publication Nos XXX (1) and XXX (2).

Table 1. X-ray data and parameters

	1	2
Formula	C ₂ H ₈ N ₁₀ O ₃	C ₃ H ₁₀ N ₁₀ O ₃
Form. weight [g mol ⁻¹]	220.18	234.12
Crystal system	Monoclinic	Orthorhombic
Space group	<i>Pn</i> (No. 7)	<i>P2₁2₁2₁</i> (No. 19)
Color / Habit	Colorless rods	Colorless plates

Size, mm	0.08 x 0.26 x 0.28	0.06 x 0.18 x 0.20
a [Å]	3.7569(2)	4.9434(2)
b [Å]	12.3854(6)	13.6462(6)
c [Å]	8.7087(5)	14.5469(6)
α [°]	90	90
β [°]	92.106(5)	90
γ [°]	90	90
V [Å ³]	404.95(4)	981.21(7)
Z	2	4
$\rho_{\text{calc.}}$ [g cm ⁻³]	1.806	1.585
μ [mm ⁻¹]	0.159	0.136
$F(000)$	228	488
$\lambda_{\text{MoK}\alpha}$ [Å]	0.71073	0.71073
T [K]	173	173
Theta Min-Max [°]	4.7, 26.0	4.3, 25.5
Dataset	-5:4; -18:15; -9:13	-6:5; -18:16; -19:18
Reflections collected	2072	5910
Independent reflections	1095	1807
R_{int}	0.0244	0.0374
Observed reflections	995	1354
No. parameters	168	185
R_1 (obs)	0.0265	0.0311
wR_2 (all data)	0.0548	0.0526
S	0.965	0.840
Resd. dens. [e Å ⁻³]	-0.18, 0.15	-0.19, 0.15
Device type	Oxford Xcalibur3 CCD	Oxford Xcalibur3 CCD
Solution	SIR-92	SIR-92
Refinement	SHELXL-97	SHELXL-97
Absorption correction	multi-scan	multi-scan
CCDC	---	---

Diaminouronium 5-nitriminotetrazolate (**1**) crystallizes in the monoclinic chiral space group Pn . Its density of 1.806 g cm⁻³ is quite high in comparison with other tetrazolate salts [16]. The molecular unit is shown in Figure 1. The structure of the 5-nitriminotetrazolate anion is comparable to that found in corresponding copper(II) salts [17]. Bond lengths are given in Table 2. The diaminouronium cation follows the structure described e.g. for diaminouronium 5-(4-amino-1,2,5-oxadiazol-3-yl)tetrazolate [18].

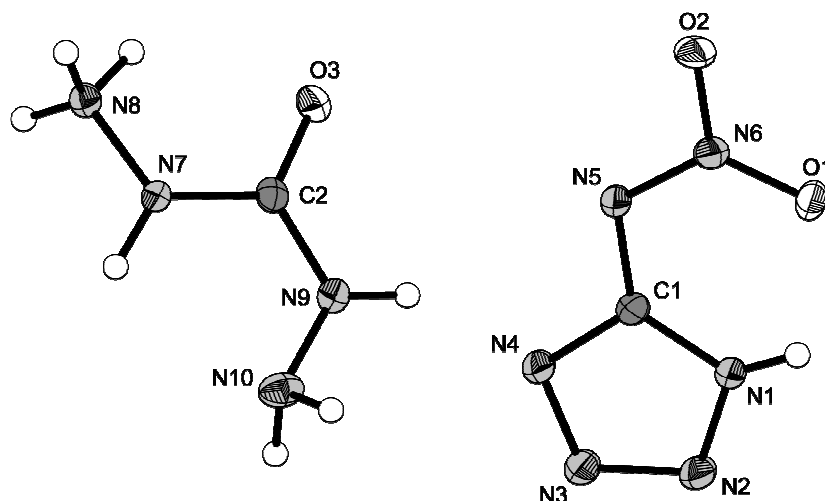


Figure 1. Molecular unit of diamouronium 5-nitriminotetrazolate (**1**). Ellipsoids of non-hydrogen atoms are drawn at the 50 % probability level.

The packing is strongly influenced by an intense hydrogen-bond network. The formation of all intramolecular (graph sets [19] DAU^+ : 2 x $S(1,1(5))$; graph set HAtNO_2^- : $S(1,1(6))$) as well as of selected intermolecular H-bonds is shown in Figure 2.

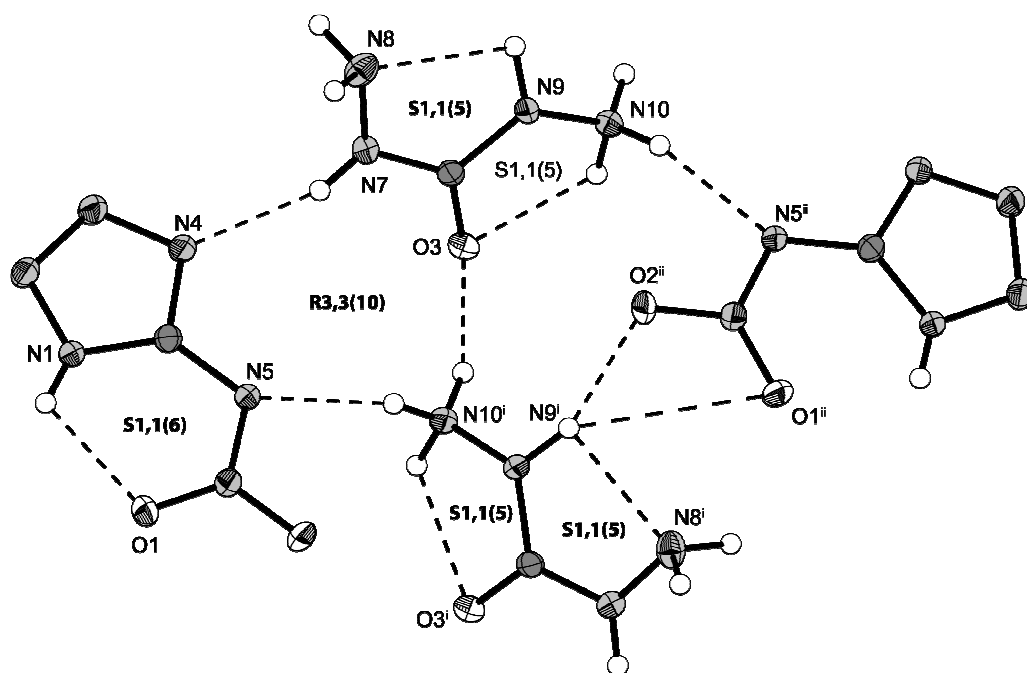


Figure 2. View on selected hydrogen bonds in the structure of **1**. Symmetry codes (i) $-0.5+x, 1-y, 0.5+z$; (ii) $0.5+x, 1-y, -0.5+z$

Diaminouronium 1-methyl-5-nitriminotetrazolate (**2**) crystallizes in the orthorhombic chiral space group $P2_12_12_1$. Its density of 1.585 g cm^{-3} is significantly lower than that of **1**, however, it is in the range of other 1-methyl-5-nitriminotetrazolate salts with nitrogen-rich counter cations [7]. The anions are planar ($\angle(\text{O1-N6-C1-N4}) = 1.22(2)^\circ$) and show comparable bond lengths and angles to copper(II) 1-methyl-5-nitriminotetrazolates in the literature [20].

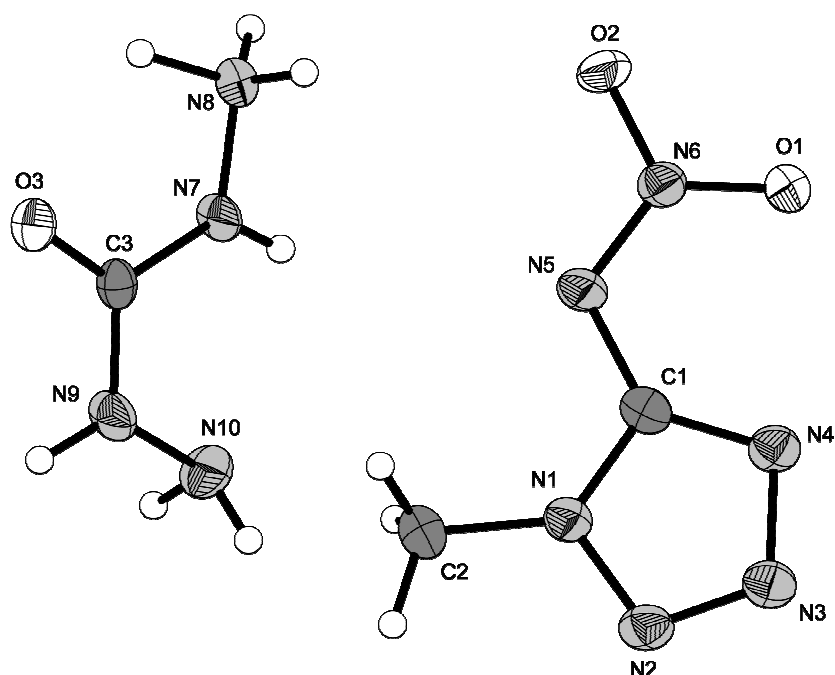


Figure 3. Molecular unit of diamouronium 1-methyl-5-nitriminotetrazolate (**2**). Ellipsoids of non-hydrogen atoms are drawn at the 50 % probability level.

The structure of **2** also shows an intense hydrogen-bond network. All of the hydrogen atoms of the diaminouonium cations are involved in hydrogen bridges, which are shown in Figure 4.

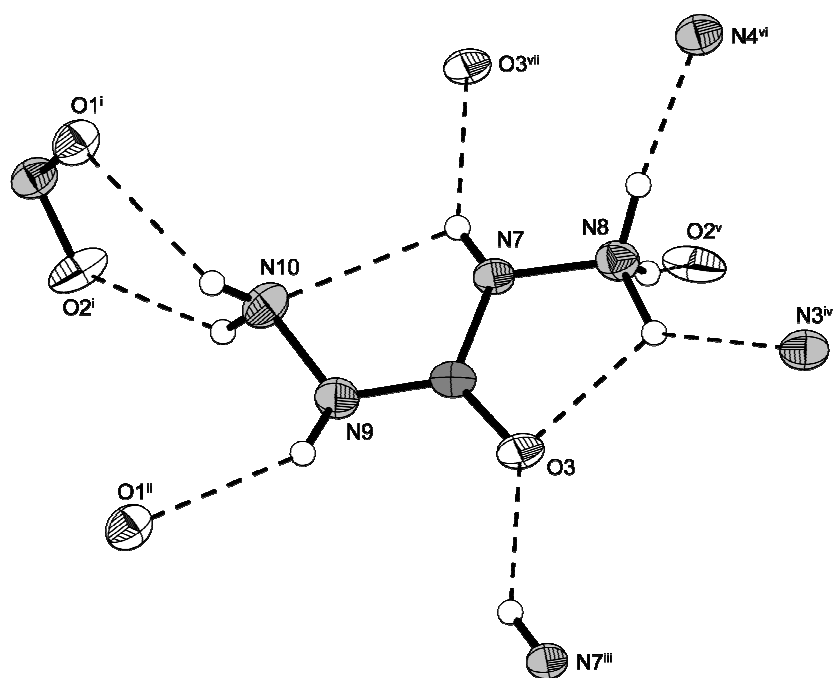


Figure 4. View on the hydrogen bridges of one diaminouonium cation in the structure of **2**. Symmetry codes (i) $2-x, 0.5+y, 0.5-z$; (ii) $1-x, 0.5+y, 0.5-z$; (iii) $-1+x, y, z$; (iv) $0.5-x, -y, 0.5+z$; (v) $-1+x, y, z$; (vi) $1.5-x, -y, 0.5+z$ (vii) $1+x, y, z$

Table 2. Bond lengths and bond angles of **1** and **2**.

atoms	1	2
O1–N6	1.240(2)	1.249(2)
O2–N6	1.269(2)	1.276(2)
N5–N6	1.313(2)	1.315(2)
N5–C1	1.377(3)	1.372(3)
N1–C1	1.338(3)	1.346(3)
N4–C1	1.330(3)	1.341(3)
N1–N2	1.347(3)	1.347(2)
N2–N3	1.298(2)	1.297(3)
N3–N4	1.355(3)	1.370(2)
N1–C2		1.459(3)
O3–C2(3)	1.244(2)	1.235(3)
N7–N8	1.419(2)	1.407(3)
N7–C2(3)	1.386(2)	1.346(3)
N9–N10	1.417(3)	1.422(3)
N9–C2(3)	1.331(3)	1.338(3)

Spectroscopy

Both compounds described were investigated using ^1H and ^{13}C NMR spectroscopy. For better comparison with literature values, all spectra were measured using d_6 -DMSO as solvent and all chemical shifts are given with respect to TMS (^1H , ^{13}C).

To identify the specified compounds NMR spectroscopy, especially carbon NMR spectra are a valuable method since the spectra are dominated by only two or three signals respectively. The signals for the ring carbon atoms in **1** and **2** can be found at 158.0 ppm (**1**) and 157.6 ppm (**2**). Hence, no shift of this signal in the anionic species is observed due to the methylation of the tetrazole ring. The signal of the carbon atom of the carbonyl moiety of the cation is observed at around 159.5 ppm. An additional methyl signal at 33.0 ppm for the methylated nitriminotetrazolate can be assigned and its position is in accordance with values found in literature [7].

IR and Raman spectroscopy is also suitable for the identification of the described nitriminotetrazolate salts. IR and Raman spectra of both compounds were measured and the absorptions were assigned according to commonly observed values found in literature [7, 21–23]. The range between 3550 and 3230 cm^{-1} is mainly determined by the N-H stretching vibrations of the diaminouonium cation. For the methylated compound **2** the symmetric C-H stretching vibration of the methyl group can nicely be observed in the Raman spectrum at 2957 cm^{-1} . Another characteristic IR absorption is the C=O-stretching vibration of the cation at 1692 cm^{-1} in both cases. The tetrazole ring system itself exhibits stretching and deformation

vibrations that can be detected as a set of signals lying in the range from 1031 cm⁻¹ to 1637 cm⁻¹ with a C=N-stretching vibration between 1617 and 1637 cm⁻¹.

Sensitivities and thermal behavior

The impact sensitivity tests were carried out according to STANAG 4489 [24] modified instruction [25] using a BAM (Bundesanstalt für Materialforschung) drophammer [26]. The friction sensitivity tests were carried out according to STANAG 4487 [27] modified instruction [28] using the BAM friction tester. The classification of the tested compounds results from the “UN Recommendations on the Transport of Dangerous Goods” [29]. All compounds were tested upon the sensitivity towards electrical discharge using the Electric Spark Tester ESD 2010 EN [30]. The values for the impact sensitivities could be determined to 5 J (2) and 3 J (3) and therefore both compounds have to be classified as sensitive and very sensitive towards impact. The same classification applies to the friction sensitivity. With values of 108 N (1) and 160 N (2) both nitriminotetrazolate salts are sensitive towards friction. Compared to the triaminoguanidinium salt of 1-methyl-5-nitriminotetrazole, which was formerly investigated by our research group [7] and exhibits values of 6 J and 240 N, the diaminouronium salt is more sensitive especially towards friction. The sensitivities towards electrical discharge were determined to be 0.20 J (2) and 0.15 J (3).

Differential scanning calorimetry (DSC) measurements to determine the melt- and decomposition temperatures of **1** and **2** (about 1.5 mg of each energetic material) were performed in covered Al-containers with a hole (0.1 mm) in the lid for gas release and a nitrogen flow of 20 mL per minute on a Linseis PT 10 DSC [31] calibrated by standard pure indium and zinc at a heating rate of 5°C min⁻¹. The decomposition temperatures are given as absolute onset temperatures and both compounds decompose at around 200°C with a slightly higher value for methylated **2** (204°C) compared to 198°C for unmethylated **1**. Compared to triaminoguanidinium (210°C) and diaminoguanidinium 1-methyl-5-nitriminotetrazolate (208°C), where the oxo (=O) moiety of the cation is exchanged by a hydrazo (=NH-NH₂) and an imino (=NH) moiety respectively, there is not a significant difference in thermal stability.

Theoretical Calculations

All calculations were carried out using the Gaussian G03W (revision B.03) program package [32]. 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 [33]. The enthalpies of the gas-phase species M were computed according to the atomization energy method (eq. 1) (Tables 3–5) [34].

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

Table 3. CBS-4M results

	point group	$-H^{298}$ / a.u.	<i>NIMAG</i>
DAU ⁺	C_s	335.795706	0
HAtNO ₂ ⁻	C_s	516.973495	0
1MeAtNO ₂ ⁻	C_1	556.194636	0
H		0.500991	0
C		37.786156	0
N		54.522462	0
O		74.991202	0

Table 4. Literature values for atomic ΔH_f^{298} / kcal mol⁻¹

	NIST [35]
H	52.1
C	171.3
N	113.0
O	59.6

Table 5. Enthalpies of the gas-phase species M.

M	Formula	$\Delta_f H^\circ(\text{g}, \text{M})$ / kcal mol ⁻¹
DAU ⁺	CH ₇ N ₄ O	155.6
HAtNO ₂ ⁻	CHN ₆ O ₂	35.9
1MeAtNO ₂ ⁻	C ₂ H ₃ N ₆ O ₂	166.3

The solid state energy of formations (Table 8) of **1** and **2**, the lattice energy (U_L) and lattice enthalpy (ΔH_L) (Table 7) were calculated from the corresponding molecular volumes (Table 6) according to the equations provided by Jenkins [36]. With the calculated lattice enthalpy (Table 7) the gas-phase enthalpy of formation (Table 5) was converted into the solid state (standard conditions) enthalpy of formation (Table 8). 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 8).

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

(Δn being the change of moles of gaseous components)

Table 6. Molecular volumes.

	$V_M / \text{\AA}^3$	V_M / nm^3
DAU ⁺	81	0.081
HAtNO ₂ ⁻	121	0.121
1MeAtNO ₂ ⁻	164	0.164

Table 7. Lattice energies and lattice enthalpies.

	V_M / nm^3	$U_L / \text{kJ mol}^{-1}$	$\Delta H_L / \text{kJ mol}^{-1}$	$\Delta H_L / \text{kcal mol}^{-1}$
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1	0.202	503.6	507.1	121.1
2	0.245	478.7	482.2	115.2

Table 8. Solid state enthalpies and energies of formation ($\Delta_f U^\circ$)

	$\Delta_f H^\circ(\text{s}) /$ kcal mol ⁻¹	$\Delta_f H^\circ(\text{s}) /$ kJ mol ⁻¹	Δn	$\Delta_f U^\circ(\text{s}) /$ kJ mol ⁻¹	M / g mol ⁻¹	$\Delta_f U^\circ(\text{s}) /$ kJ kg ⁻¹
1	70.4	294.6	10.5	320.7	220.20	1456.3
2	80.1	335.4	11.5	363.9	234.23	1553.7

Detonation parameters

The calculation of the detonation parameters was performed with the program package EXPLO5 (version 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]:

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

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

The detonation parameters calculated with the EXPLO5 program (V5.04) of compounds **1** and **2** using the experimentally determined densities (X-ray) are summarized in Table 9 and compared to the values calculated for the triaminoguanidinium 1-methyl-5-nitriminotetrazolate and commonly used RDX.

Table 9. Detonation parameters

	1	2	TAG-1- MeATNO₂	RDX
$\rho / \text{g cm}^{-3}$ [a]	1.81	1.59	1.57	1.80
$\Omega / \%$ [b]	-36.3	-54.7	-64.5	-21.6
$\Delta_{\text{Ex}} U^\circ / \text{kJ kg}^{-1}$ [c]	-4848	-4850	-4781	-6125
$T_{\text{det}} / \text{K}$ [d]	3335	3246	3091	4236
$P_{\text{CJ}} / \text{kbar}$ [e]	337	252	255	349
$V_{\text{Det.}} / \text{m s}^{-1}$ [f]	8979	8172	8309	8748
$V_o / \text{L kg}^{-1}$ [g]	848	832	847	739

[a] X-ray density. [b] Oxygen balance. [c] Energy of explosion. [d] Detonation temperature. [e] Detonation pressure.

[f] Detonation velocity. [g] Volume of explosion gases assuming only gaseous products.

1
2
3 Due to the much higher crystal density, the value for the detonation velocity for the parent
4 compound **1** (8979 m s^{-1}) exceeds the one of methylated **2** (8127 m s^{-1}) by far and is even
5 slightly higher when compared to RDX. The detonation pressures, however, only differ
6 slightly. Again, a comparison of **2** to the triaminoguanidinium salt of 1-methyl-5-
7 nitriminotetrazole seems to be appropriate since both compounds only differ by one isolobal
8 moiety which is the hydrazo ($=\text{NH-NH}_2$) moiety in the case of the triaminoguanidinium salt
9 and the oxo ($=\text{O}$) moiety in **2**. There is only one value, which is in the same range for both
10 compounds, which is the explosion energy (-4895 kJ kg^{-1} (**2**), -4888 kJ kg^{-1} (TAG-1-
11 MeATNO₂)). Not only the detonation velocity, but also the detonation pressure of the
12 triaminoguanidinium salt is substantially higher than for the diaminouronium salt **2**, even
13 though having a slightly lower crystal density and a lower oxygen balance. In summary, the 5-
14 nitriminotetrazolate salt **1** shows much better performance than its methylated sister
15 compound **2**. Further, the exchange of the triaminoguanidinium cation by the diaminouronium
16 cation does not improve the detonation performance in case of the 1-methyl-5-
17 nitriminotetrazolate anion, although one would expect a higher performance for oxygen
18 containing cations such as the diaminouronium cation. The reason, why we observe inverse
19 behaviour might be the connectivity of the oxygen in the cation. In the case of diaminourea, it
20 is connected to a carbon atom, which therefore is already partially oxidized and does not
21 release as much energy as a carbon atom with a lower oxidation state. Probably, oxygen
22 containing cations involving a nitro functionality such as the aminonitroguanidinium cation
23 lead to a better performance of the materials containing the respective anions investigated in
24 this work.

25 26 27 28 29 30 31 32 33 34 35 **Velocity of detonation test**

36
37 In order to evaluate the detonation velocity of **1** experimentally, compound **1** was prepared on
38 a 50 g scale. The detonation velocity tests were performed in an OZM laboratory detonation
39 chamber (model KV-250). The measurement of the detonation velocity was performed using
40 the OZM detonating velocity measuring system EXPLOMET-FO-2000. The use of the fiber
41 optic technique ensures excellent electrical noise immunity. For the detonation velocity
42 measurement a PE tube with an inner diameter of 14 mm was used, which was equipped with
43 three optical fibers with a distance of 17 mm between them. The amount of compound **1** used
44 for the test was 11.6 g resulting in a density of 0.699 g cm^{-3} . The compound was loaded into
45 the PE tube and manually compressed with a force of ca. 30 N. As a booster charge 0.30 g of
46 nitropenta (PETN) were added on top and carefully compressed manually using ca. 20 N
47 force. Initiation was achieved with an electrically ignited detonator containing PETN and
48 RDX (ORICA, DYNADET C2-25MS). To evaluate the used method, the same setup was
49 employed for measuring the detonation velocity of RDX under the same conditions. 14.4 g of
50 RDX were filled into the tube ($\rho = 0.869 \text{ g cm}^{-3}$) and for best comparison of the measured
51 values, also 0.30 g of PETN were added on top of the RDX. The results of the measurement
52 can be seen in Table 10. The measured values between fiber 1 and 2 and between 2 and 3
53 were averaged and compared to the values computed with the EXPLO5 (version 5.04)
54 software [37]. The recorded values for both measurements (RDX as well as compound **1**) are
55 in surprisingly good agreement with the computed values and differ by less than 200 m s^{-1} for
56 compound **1** and only 41 m s^{-1} for RDX.
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Table 10. Calculated and measured detonation velocities of **1** and RDX

	1	RDX
mass (g)	11.6	14.4
density (g cm ⁻³)	0.699	0.869
V _{det, exp.} (m s ⁻¹)	4384	5339
V _{det, theor.} (m s ⁻¹)	4568	5370

Conclusion

From this combined theoretical and experimental study the following conclusions can be drawn:

- Diaminouronium nitriminotetrazolate (**1**) and diaminouronium 1-methyl nitriminotetrazolate (**2**) were prepared in high yield and purity from the corresponding nitriminotetrazole and diaminourea.
- The crystal structures of **1** and **2** were determined by low-temperature single-crystal X-ray diffraction. The compounds crystallize in the space groups *Pn* and *P2₁2₁2₁* with densities of 1.806 and 1.585 gcm⁻³ respectively. Additionally both compounds were fully characterized by vibrational spectroscopy (IR and Raman) ¹H and ¹³C NMR, mass spectroscopy, and elemental analysis.
- Thermal stabilities of **1** and **2** were investigated by DSC and decompose at 198 and 204 °C respectively.
- The sensitivities of towards friction, impact and electrostatic discharge were investigated by BAM methods. **1** and **2** were found to have impact sensitivities of 5 J and 3 J respectively, friction sensitivities of 108 N and 160 N respectively, and ESD sensitivities of 0.2 J and 0.15 J respectively. These are within the range of commonly-used high explosives such as RDX.
- Using calculated heats of formation and experimentally obtained crystal densities the detonation parameters (heat of explosion, explosion temperature, detonation pressure and velocity) were calculated. **1** has a detonation velocity of 8979 m s⁻¹ and a detonation pressure of 337 kbar. **2** has a detonation velocity of 8172 m s⁻¹ and a detonation pressure of 252 kbar.

Experimental Part

Caution! Methylated and unmethylated 5-nitriminotetrazole and their salts are energetic materials with increased sensitivities towards shock and friction. Therefore, proper safety precautions (safety glass, face shield, earthened equipment and shoes, Kevlar[®] gloves and ear plugs) have to applied while synthesizing and handling the described compounds.

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3 All chemicals and solvents were employed as received (Sigma-Aldrich, Fluka, Acros). ^1H and
4 ^{13}C spectra were recorded using a JEOL Eclipse 270, JEOL EX 400 or a JEOL Eclipse 400
5 instrument. The chemical shifts quoted in ppm in the text refer to typical standards such as
6 tetramethylsilane (^1H , ^{13}C). To determine the melting and decomposition temperatures of the
7 described compounds a Linseis PT 10 DSC (heating rate 5°C min^{-1}) was used. Infrared
8 spectra were measured using a Perkin Elmer Spectrum One FT-IR spectrometer as KBr
9 pellets. Raman spectra were recorded on a Bruker MultiRAM Raman Sample Compartment
10 D418 equipped with a Nd-YAG-Laser (1064 nm) and a LN-Ge diode as detector. Mass
11 spectra of the described compounds were measured at a JEOL MStation JMS 700 using FAB
12 technique. To measure elemental analyses a Netsch STA 429 simultaneous thermal analyzer
13 was employed.
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19 **Diaminouronium 5-nitriminotetrazolate (1)**

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22 5-Nitriminotetrazole (0.89 g, 6.85 mmol) is dissolved in a few milliliters of water and added
23 to a solution of diaminourea (0.62 g, 6.85 mmol). The mixture was warmed, stirred at
24 elevated temperature for ten minutes and the solvent was removed under vacuum. The white
25 solid residue was recrystallized from ethanol to yield 1.96 g (6.10 mmol, 89%) of **2** as a white
26 crystalline material.
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29 DSC (5°C min^{-1} , $^\circ\text{C}$): 180°C (m.p.), 198°C (dec.); IR (KBr, cm^{-1}): $\tilde{\nu} = 3550$ (s), 3414 (vs),
30 3234 (s), 2321 (w), 2024 (w), 1692 (s), 1637 (s), 1617 (vs), 1543 (m), 1512 (s), 1441 (m),
31 1385 (m), 1326 (s), 1229 (m), 1136 (s), 1110 (m), 1089 (m), 1062 (m), 1031 (m), 1006 (w),
32 963 (m), 921 (w), 870 (w), 773 (m), 746 (m), 696 (m), 623 (s), 570 (m), 482 (m); Raman
33 (1064 nm, 250 mW, 25°C , cm^{-1}): $\tilde{\nu} = 1542$ (100), 1447 (4), 1390 (8), 1340 (2), 1327 (32),
34 1232 (4), 1150 (9), 1112 (3), 1081 (7), 1030 (42), 1017 (60), 962 (2), 921 (5), 875 (6), 748
35 (2), 741 (14), 578 (5), 486 (7), 430 (2), 420 (14), 384 (9), 252 (10); ^1H NMR (DMSO- d_6 , 25°C , ppm) δ : 8.56 (s, 8H, -NH -NH $_2$, -NH $_3^+$); ^{13}C NMR (DMSO- d_6 , 25°C , ppm) δ : 159.3
36 (C(O)(NHNH $_2$)(NHNH $_3^+$)), 158.0 (CN $_4$); m/z (FAB $^+$): 91.1 [C(O)(N $_2$ H $_3$) $_2$ +H $^+$]; m/z (FAB $^-$):
37 129.0 [ATNO $_2^-$]; EA (C $_2$ H $_8$ N $_{10}$ O $_3$, 220.15): calc.: C 10.91, H 3.66, N 63.62 %; found: C 11.19,
38 H 3.78, N 63.42 %; BAM drophammer: 5 J; friction tester: 108 N; ESD: 0.20 J (at grain size
39 500 - 1000 μm).
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47 **Diaminouronium 1-methyl-5-nitriminotetrazolate (2)**

48
49 1-Methyl-5-nitriminotetrazole (1.44 g, 10.0 mmol) is dissolved in a few milliliters of warm
50 water and added to a solution of diaminourea (0.90 g, 10.0 mmol). The mixture was heated to
51 reflux for one minute and the solvent was removed under vacuum afterwards. The white solid
52 residue was recrystallized from an ethanol/water mixture. Yield: 2.15 g (9.20 mmol, 92%).
53

54
55 DSC (5°C min^{-1} , $^\circ\text{C}$): 163°C (m.p.), 204°C (dec.); IR (KBr, cm^{-1}): $\tilde{\nu} = 3415$ (s), 3371 (s),
56 3355 (s), 3326 (s), 3306 (s), 3230 (m), 3139 (m), 2956 (m), 2666 (m), 2019 (w), 1692 (s),
57 1619 (s), 1515 (s), 1466 (s), 1425 (m), 1411 (m), 1383 (s), 1324 (vs), 1295 (m), 1279 (m),
58 1240 (m), 1177 (m), 1163 (m), 1117 (m), 1108 (m), 1052 (w), 1032 (m), 989 (w), 960 (w),
59 928 (w), 881 (w), 774 (w), 752 (w), 740 (w), 691 (w), 636 (w), 581 (w); Raman (1064 nm,
60 400 mW, 25°C , cm^{-1}): $\tilde{\nu} = 3326$ (5), 3140 (3), 3008 (2), 2957 (13), 1690 (7), 1636 (2), 1504
(91), 1465 (27), 1411 (12), 1371 (5), 1322 (8), 1301 (36), 1240 (3), 1179 (9), 1109 (29), 1052

(5), 1033 (100), 992 (5), 961 (10), 883 (11), 776 (2), 754 (9), 693 (17), 585 (7), 498 (9), 454 (4), 377 (8), 294 (20), 240 (7), 216 (5); ¹H NMR (DMSO-*d*₆, 25 °C, ppm) δ: 7.79 (s, 7H, -NH -NH₂, -NH₃⁺), 3.67 (s, 3H, -CH₃); ¹³C NMR (DMSO-*d*₆, 25 °C, ppm) δ: 159.6 (C(O)(NHNH₂)(NHNH₃⁺)), 157.6 (CN₄), 33.1 (CH₃); m/z (FAB⁺): 91.1 [C(O)(N₂H₃)₂+H⁺]; m/z (FAB⁻): 143.0 [1-MeATNO₂⁻]; EA (C₃H₁₀N₁₀O₃, 234.18): calc.: C 15.39, H 4.30, N 59.81 %; found: C 15.30, H 4.07, N 59.98 %; BAM drophammer: 3 J; friction tester: 160 N; ESD: 0.15 J (at grain size 100 - 500µm).

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55 friction: Insensitive > 360 N, less sensitive = 360 N, sensitive < 360 N a. > 80 N, very
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3 sensitive ≤ 80 N, extreme sensitive ≤ 10 N; According to the UN Recommendations
4 on the Transport of Dangerous Goods (+) indicates: not safe for transport.
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