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Full Paper

Explosives Based on Diaminourea

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Abstract

Diaminourea (DAU, **1**) is synthesized by the reaction of dimethylcarbonate with hydrazine hydrate. DAU was protonated using nitric as well as perchloric acid yielding diaminouronium nitrate (**2**), diaminouronium dinitrate monohydrate (**3**) and diaminouronium perchlorate (**4**). The bis-perchlorate salt could not be isolated due to its high hygroscopicity. Explosives **2**–**4** were fully characterized using X-ray diffraction, NMR and vibrational spectroscopy, mass spectrometry and elemental analysis. The thermal properties were determined by differential scanning calorimetry (DSC). The sensitivities towards impact (**2**: 9 J, **3**: >40 J, **4**: 2 J), friction (**2**: 288 N, **3**: >360 N, **4**: 5 N) and electrical discharge (**2**: 0.60 J, **3**: 0.50 J, **4**: 0.30 J) were investigated using Bundesanstalt für Materialforschung (BAM) methods and a small scale electrostatic discharge device. The detonation parameters of **2** and **3** were computed using the EXPLO5.04 code with the X-ray densities as well as calculated (CBS-4 M) energies of formation as input values.

Keywords: Crystal Structures, Detonation Parameters, Explosives, Nitrates

1 Introduction

More than 2000 years after first making an appearance, energetic materials continue to expand their scope of application, based on continuous improvement in the underlying chemistry [1]. Energetic materials cover the whole range of explosives, propellants and pyrotechnics, which release their stored energy either by combustion, deflagration or detonation. The ongoing search for new insensitive and environmentally benign but also powerful replacements for secondary explosives such as hexogen (RDX) is exciting on the one hand and very challenging on the other hand [2]. In this work, we report on the mono- and bis-protonated diaminouronium nitrate as well as the perchlorate salt of diaminourea, their synthesis and full characterization. Surprisingly, in contrast to urea- and guanidine chemistry which are rampant in energetic materials' literature [3], diaminourea is rarely described [4].

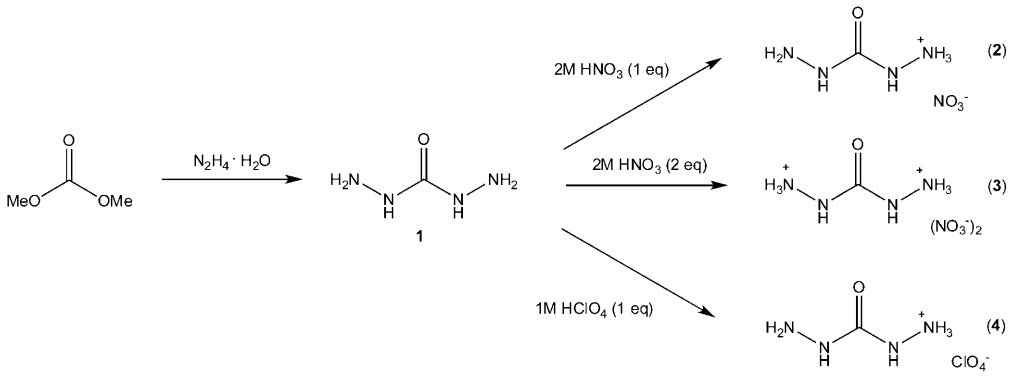
2 Results and Discussion

2.1 Synthesis

Diaminouronium nitrate (**2**), diaminouronium dinitrate monohydrate (**3**) and diaminouronium perchlorate (**4**) can be synthesized by facile acid–base reaction in aqueous media starting from the base diaminourea. The synthetic routes to **2**–**4** are shown in Scheme 1.

Diaminourea is synthesized according to literature [5] starting from dimethyl carbonate and hydrazine hydrate in a two step reaction, where both hydrazine moieties are introduced successively. Since the water solubility of diaminourea is very good and it is a fairly strong base, it can be solubilized and protonated by dilute acids such as 2 M nitric or 1 M perchloric acid. After the removal of the water in vacuo, only the perchlorate salt remains as a colourless solid, which can easily be recrystallized. Both nitrate salts, especially the monodeprotonated salt **2**, cause major problems during their isolation since both remain as colourless liquids after the water has been evaporated. **3** crystallizes after the liquid has been taken up in methanol and slowly been evaporated again, whereas **2** solidified after the liquid was taken up in methanol and chilled to −20 °C for several days. Scratching the flask with a glass rod after the mixture was allowed to come to room temperature resulted in the crystallization of the product. Regarding the easy synthesis of these compounds it has to be pointed out, that the comparatively cheap starting materials dimethyl carbonate, hydrazine hydrate and dilute nitric acid make compound **2** a very attractive candidate as a replacement for common secondary explosives.

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Scheme 1. Synthetic routes to compounds **2**–**4**.

2.2 Crystal Structures

To determine the molecular structures of **2**–**4** in the crystalline state an Oxford Xcalibur3 diffractometer with a Spellman generator (voltage 50 kV, current 40 mA) and a KappaCCD detector was used. The data collection was performed using the CrysAlis CCD software [6], the data reduction with the CrysAlis RED software [7]. The solution and refinement of all structures were performed using the programs SIR-92 [8], SHELXS-97 [9] and SHELXL-97 [10] implemented in the WinGX software package [11] and finally checked with the PLATON software [12]. In all crystal structures the hydrogen atoms were located and refined. The absorptions were corrected with the SCALE3 ABSPACK multi-scan method [13].

Selected data and parameter of the X-ray determinations are given in Table 1.

The structure of neutral DAU is known in literature and has been even determined at different temperatures [14]. Diaminouronium nitrate (**2**) crystallizes in the monoclinic space group $P2_1/c$ with four molecular moieties in the unit cell. Its density of 1.782 g cm^{-3} is higher than in most other CHNO nitrates in literature, e.g. morpholinium nitrate (1.444 g cm^{-3}) and glycylglycine nitrate (1.63 g cm^{-3}) [15]. The structure of the DAU cation is in agreement to that of its 5-(4-amino-oxadiazolyl)-tetrazolide salt in the literature [16]. The nitrate anion shows regular D_{3h} symmetry with N–O bond lengths of 125 pm.

The high density can be explained by having a look at the hydrogen bonds within the structure of **2**. Its packing is strongly influenced by an intense hydrogen-bond network within discrete layers but also between them. Selected intermolecular and intramolecular H-bonds within a layer are shown in Figure 1. Various graph sets [17] such as the intramolecular S(1,1)5 as well as ring (R) and chain (C) motives can be detected and are partly drawn.

Diaminouronium dinitrate (**3**) could only be obtained crystalline as its monohydrate, which crystallizes in the orthorhombic space group *Pbca* with eight cation/anion pairs in the unit cell. The molecular structure is shown in Figure 2. The density of 1.785 g cm^{-3} is slightly higher than that of **2**, however, would be even higher without inclusion of crystal water. The structure of the cation is comparable to that of diaminouronium sulphate described in literature [18].

Figure 3 shows the molecular structure of diaminouronium perchlorate (**4**), which crystallizes in the monoclinic space group $P2_1/c$. In contrast to the structure of **2**, the DAU cation is bent over (C1–N3–N4) forming two intramolecular S(1,1)5 hydrogen bonds. The perchlorate anion shows regular T_d symmetry with Cl–O bond lengths of 143 pm.

2.3 Spectroscopy

2.3.1 NMR spectroscopy

All compounds were investigated using proton and carbon NMR spectroscopy. For the dinitrate salt **3**, also a ^{14}N NMR spectrum was recorded. Due to very fast proton exchange for the protonated diaminouronium cation in solution, only a very broad signal at 7.94 ppm (**2**), 9.79 ppm (**3**) and 7.59 ppm (**4**) can be observed. The ^{13}C NMR spectra reveal a singlet at 159.2 ppm for both monoprotonated species **2** and **4** and a singlet, which is slightly shifted upfield to 157.2 ppm for the bis-protonated species **3**. This trend is reconfirmed looking at the NMR data of unprotonated diaminourea, where the carbon signal is found at 162.0 ppm. Only for the bis-protonated salt **3** it was worthwhile running a ^{14}N NMR spectrum, because in addition to the nitrate anion at −4.5 ppm, there was a second relatively sharp signal visible at −359.5 ppm belonging to the protonated nitrogen atoms N2 and N4 (see Figure 2) with their comparatively symmetric environment.

2.3.2 Vibrational Spectroscopy

IR as well as Raman spectroscopy were employed for the characterization of **2**–**4**. The most remarkable IR bands and Raman lines respectively belong to the inorganic anions NO_3^- and ClO_4^-. The Raman spectra show lines for the symmetric stretching vibration of the nitrate anion at 1055 cm^{-1} (**2**) and 1049 cm^{-1} (**3**) and the symmetric stretching vibration of the perchlorate anion at 939 cm^{-1}

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Table 1. X-ray data and parameters.

	2	**3**	**4**
Formula	$CH_7N_5O_4$	$CH_9N_6O_8$	$CH_7ClN_4O_5$
Form. Weight (g mol^{-1})	153.12	234.15	190.56
Crystal System	Monoclinic	Orthorhombic	Monoclinic
Space Group	$P2_1/c$ (14)	*Pbca* (61)	$P2_1/c$ (14)
Colour/Habit	Colourless Block	Colourless Block	Colourless Plate
Size (mm)	$0.14\times0.15\times0.17$	$0.13\times0.15\times0.17$	$0.03\times0.15\times0.20$
a (pm)	688.79(3)	799.3(5)	109.47(1)
b (pm)	957.01(4)	878.2(5)	712.49(5)
c (pm)	899.32(4)	248.31(5)	909.38(9)
α (°)	90	90	90
β (°)	105.723(5)	90	110.827(11) 90
γ (°)	90	90	90
V (pm^3)	5706300(500)	17430000(1500)	6629400(1100)
Z	4	8	4
$\rho_{calc.}$ (g cm^{-3})	1.782	1.785	1.909
μ (mm^{-1})	0.171	0.181	0.564
F(000)	320	976	392
$\lambda_{MoK\alpha}$ (pm)	71.073	71.073	71.073
T (K)	173	173	173
θ Min–Max (°)	4.3, 26.7	4.2, 26.5	4.5, 26.0
Dataset	−8:8; −12:12; −11:11	−10:10; −11:11; −31:31	−13:13; −6:8; −9:11
Reflections Collected	8632	25007	3339
Independent Reflections	1206	1794	1297
*R*int	0.023	0.030	0.039
Observed Reflections	1031	1452	946
Parameters	119	176	128
R_1 (obs)	0.0257	0.0267	0.0328
wR_2 (All Data)	0.0707	0.0779	0.0746
S	1.04	1.05	0.91
Resd. Dens. (e pm^{-3})	-0.23×10^{-6}, 0.20×10^{-6}	-0.19×10^{-6}, 0.19×10^{-6}	-0.43×10^{-6}, 0.25×10^{-6}
Device Type	Oxford Xcalibur3 CCD	Oxford Xcalibur3 CCD	Oxford Xcalibur3 CCD
Solution	SIR-92	SIR-92	SHELXS-97
Refinement	SHELXL-97	SHELXL-97	SHELXL-97
Absorption Correction	Multi-scan	Multi-scan	Multi-scan
CCDC	805986	805987	805985

(**4**). The respective asymmetric stretching vibrations can be observed in the IR spectra at 1385 cm^{-1} (**2**), 1384 cm^{-1} (**3**) and 1063 cm^{-1} (**4**). Additionally, the IR spectra show bands for the C=O stretching vibration of the cation in the region of 1630 to 1730 cm^{-1}. Also the N–N-stretching vibration of the hydrazine moiety of the cation is visible in bands which are scattered around 1500 cm^{-1}. The N–H

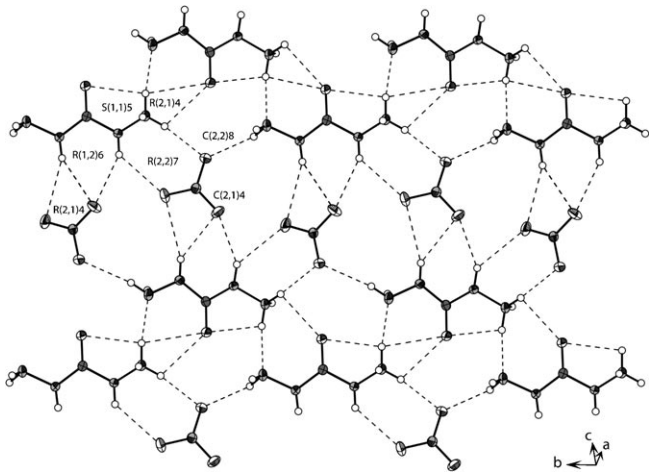


Figure 1. View on selected hydrogen bonds in the structure of **2**.

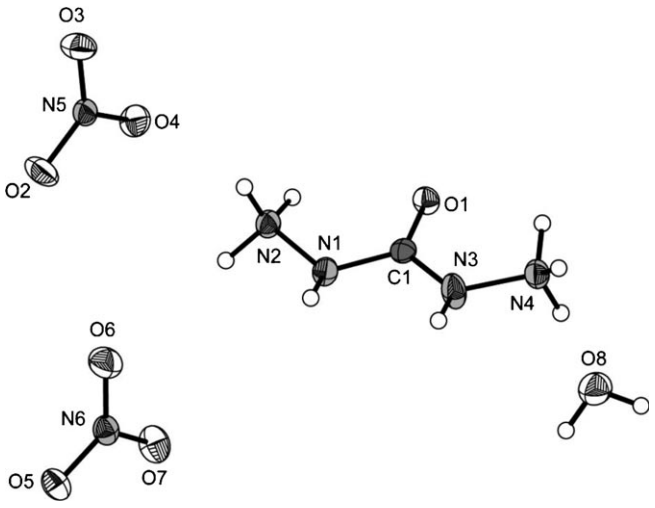


Figure 2. Molecular unit of **3***H_2O. Hydrogen atoms shown as spheres of arbitrary radius and thermal displacements set at 50 % probability.

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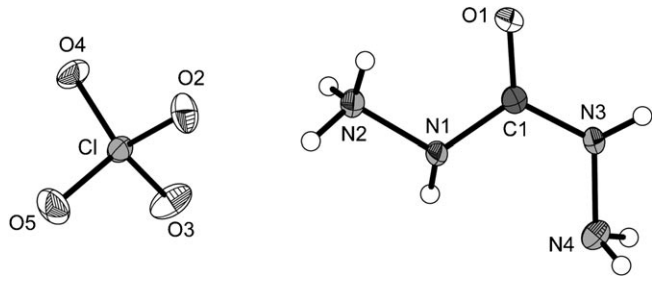


Figure 3. Molecular unit of **4**. Hydrogen atoms shown as spheres of arbitrary radius and thermal displacements set at 50% probability. Selected geometries: bond lengths (pm) N1–C1 136.5(3), N1–N2 142.2(3), N3–C1 133.4(3), N3–N4 140.8(3), O1–C1 123.7(3); bond angles (°) C1–N1–N2 113.8(2), C1–N3–N4 120.5(2), N3–C1–N1 115.5(2), O1–C1–N1 120.7(2), O1–C1–N3 123.8(2).

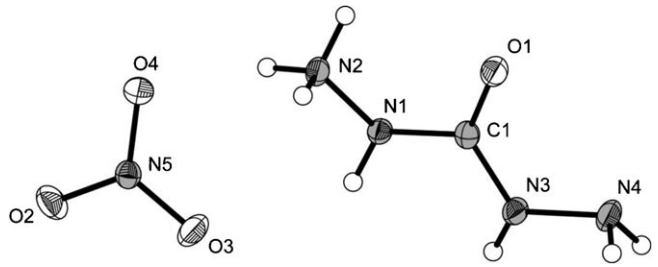


Figure 4. Molecular unit of **2**. Hydrogen atoms shown as spheres of arbitrary radius and thermal displacements set at 50% probability. Selected geometries: bond lengths (pm) N1–C1 139.89(13), N1–N2 142.69(12), N3–C1 134.11(13), N3–N4 141.35(13), O1–C1 122.12(13); bond angles (°) C1–N1–N2 112.75(9), C1–N3–N4 118.01(9), N3–C1–N1 113.67(9), O1–C1–N1 120.68(9), O1–C1–N3 125.63(10).

stretching vibrations at 3300–3440 cm^{-1} are visible in all spectra.

2.3.3 Mass Spectrometry

For detection of the different ions via mass spectrometry, the FAB technique was used. The spectra were recorded using either glycerin (**3**) or 3-nitrobenzyl alcohol (**2**,**4**) as liquid matrix. In the FAB-spectra the perchlorate (*m*/*z* 98.9) as well as the nitrate anion (*m*/*z* 62.0) could be detected. Also the mono-protonated DAU $CH_7N_4O^+$ is detected in the FAB+ in all cases (*m*/*z* 91.1), whereas the bis-protonated DAU was also detected in the FAB-spectrum of **3** as $CH_8N_5O_4^-$ (*m*/*z* 154.0), which would correspond to an addition species of $CH_8N_4O^{2+}$ and NO_3^-.

2.4 Thermal Analysis

Differential scanning calorimetry (DSC) measurements to determine the melt- and decomposition temperatures of **2**–**4** (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 min^{-1} on a Linseis PT 10 DSC [19] calibrated by standard pure indium and zinc at a heating rate of 5 °C min^{-1}. The decomposition temperatures are given as onset temperatures. The DSC curves of the compounds show endothermic peaks at 53 °C (**3**), 86 °C (**2**) and 158 °C (**4**), which can be assigned to their melting points. The melting temperatures were additionally determined and confirmed to be correct on a Büchi B-540 melting point apparatus to exclude the possibility of the loss of eventually contained residual solvent. A second endothermic peak in the DSC curve of **3** at 106 °C indicates the loss of the water molecule, which is included in the molecular unit. The lowest decomposition temperature – indicated by an exothermic peak – is observed at 115 °C for **3**, the bis-protonated diaminourea compound, which is right after the loss of the water molecule. Both mono-protonated compounds **2** and **4** show very similar decomposition temperatures of 242 °C (**2**) and 244 °C (**4**). Therefore, diaminouronium nitrate has a remarkably high liquidity range of 156 °C, making it a possible candidate for a future melt-cast explosive.

2.5 Energy of Formation

All calculations were carried out using the Gaussian G09 program package [20]. 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 CBS limit. CBS-4 begins with an HF/3-21G(d) geometry optimization; the zero point energy is computed at the same level. It then uses a large basis set SCF calculation as a base energy, and an MP2/6-31+G calculation with a CBS extrapolation to correct the energy through second order. An MP4(SDQ)/6-31+(d,p) calculation is used to approximate higher order contributions. In this study, we applied the modified CBS-

Table 2. Enthalpies of the gas-phase species M.

M	$-H^{298}$ (a.u.)	$\Delta_f H^o$(g,M) (kJ mol^{-1})	V_M (nm^3)
DAU^+	335.781212	+1644	0.079
DAU^{++}	335.970629	+1726	0.076
NO_3^-	280.080446	−314	0.064
ClO_4^-	760.171182	−276	0.087
H_2O	76.346181	+534	0.014

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Table 3. Explosive and detonation parameters.

	2	**3**	**4**	RDX
Formula	$CH_7N_5O_4$	$CH_{10}N_6O_8$	$CH_7ClN_4O_5$	$C_3H_6N_6O_6$
FW (g mol^{-1})	153.12	234.15	190.56	222.12
IS (J)	9	>40	2	7.5
FS (N)	288	>360	5	120
ESD (J)	0.60	0.50	0.30	0.1–0.2
N (%)	45.74	35.90	29.40	37.84
Ω (%)	−15.7	10.3	0.0	−21.6
$T_{Dec.}$ (°C)	242	115	244	210
ρ (g cm^{-3})	1.782	1.785	1.909	1.80
$\Delta_f H^o_m$ (kJ mol^{-1})	−180	−876	−122	70
$\Delta_f U^o$ (kJ kg^{-1})	−1048	−3613	−538	417
EXPLO5 values				
$-\Delta_{Ex}U^o$ (kJ kg^{-1})	5048	2718	–	6125
T_{det} (K)	3391	2390	–	4236
P_{CJ} (Pa)	3.35×10^{10}	2.29×10^{10}	–	3.49×10^{10}
$V_{Det.}$ (m s^{-1})	8903	7577	–	8748
V_o (L kg^{-1})	910	889	–	739

4 M 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 [21]. The enthalpies of the gas-phase species M (Table 2) were computed according to the atomization energy method (Eq. 1) [22] described circumstantially in the literature [23].

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

Using calculated lattice enthalpies (Table 2) the gas-phase enthalpies of formation (Table 2) were converted into the solid state (standard conditions) enthalpy of formation $\Delta_f H^o_m$ (Table 3). Lattice energies (U_L) and lattice enthalpies (ΔH_L) were calculated from the corresponding molecular volumes according to Jenkin's equations [24].

Lastly, the molar standard enthalpies of formation (ΔH_m) were used to calculate the molar solid state energies of formation (ΔU_m) according to Eq. (2) (Table 3).

$$\Delta U_m = \Delta H_m - \Delta nRT \quad (2)$$

(Δn being the change of moles of gaseous components)

2.6 Detonation Parameters

The calculation of the detonation parameters was performed with the program package EXPLO5 (version 5.04) [25]. 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 [26]:

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

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

The detonation parameters calculated with the EXPLO5 program (V5.04) of compounds **2** and **3** using the experimentally determined densities (X-ray) are summarized in Table 3 and compared to the values calculated for commonly used RDX.

The detonation velocity and detonation pressure of **2** both ($V_{Det.} = 8903$ m s^{-1}, $P_{CJ} = 3.35\times10^{10}$ Pa) are comparable to the values calculated for RDX ($V_{Det.} = 8748$ m s^{-1}, $P_{CJ} = 3.49\times10^{10}$ Pa) with the velocity being slightly higher and the pressure being slightly lower, whereas the values for bis-protonated **3** drop rapidly ($V_{Det.} = 7577$ m s^{-1}, $P_{CJ} = 2.29\times10^{10}$ Pa) compared to mono-protonated **2**. Since the density of both, **2** and **3**, is almost similar (**2**: $\rho = 1.782$ g cm^{-3}, **3**: $\rho = 1.785$ g cm^{-3}) and the density of a compound is the most determining factor for the performance data, the influence of other input data e.g. the energy of formation can be discussed very easily. The energy of formation for **3** ($\Delta_f U^o = -3613$ kJ kg^{-1}) is much more negative than it is for **2** ($\Delta_f U^o = -1048$ kJ kg^{-1}) resulting in a lower detonation energy and, therefore a much lower detonation temperature. The reason for the lower enthalpy of formation is not only the higher lattice enthalpy but also the inclusion of the water molecule into the crystal structure. For the perchlorate salt **4**, no detonation parameters can be determined, since EXPLO5 (V5.04) does not include heteroatoms such as chlorine for the calculation of the performance data as discussed above.

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2.7 Sensitivities

The impact sensitivity tests were carried out according to STANAG 4489 [27] modified instruction [28] using a Bundesanstalt für Materialforschung (BAM) drophammer [29]. The friction sensitivity tests were carried out according to STANAG 4487 [30] modified instruction [31] using the BAM friction tester. The classification of the tested compounds results from the 'UN Recommendations on the Transport of Dangerous Goods' [32]. All compounds were tested upon the sensitivity towards electrical discharge using the Electric Spark Tester ESD 2010 EN [33]. Looking at the impact and friction sensitivity of the investigated compounds, a strong differentiation can be observed. Whereas the diaminouronium dinitrate monohydrate (**3**) is insensitive towards impact and friction [>40 J (IS), >360 N(FS)], the diaminouronium nitrate (**2**) is sensitive towards friction and impact with values of 9 J (IS) and 288 N (FS), however being still less sensitive than commonly used RDX [1,3,5-trinitrohexahydro-1,3,5-triazin; 7.5 J (IS), 120 N(FS)]. The perchlorate salt **4** reveals values for the impact sensitivity of 2 J and 5 N for the friction sensitivity and therefore has to be considered as very sensitive towards impact and extremely sensitive towards friction, which is in the expected range for water-free perchlorates. The insensitivity of **3** can be ascribed to the fact that it crystallizes as a monohydrate. The sensitivities towards electrical discharge are in more or less close range. The determined values are 0.60 J (**2**), 0.50 J (**3**) and 0.30 J (**4**). Again the perchlorate salt is most sensitive, whereas the both nitrate salts are very similar in their sensitivity.

3 Experimental Part

All chemicals and solvents were employed as received (Sigma-Aldrich, Fluka, Acros). ^{1}H and ^{13}C spectra were recorded using a JEOL Eclipse 270, JEOL EX 400 or a JEOL Eclipse 400 instrument. The chemical shifts quoted in ppm in the text refer to typical standards such as tetramethylsilane (^{1}H, ^{13}C). To determine the melting and decomposition temperatures of the described compounds a Linseis PT 10 DSC (heating rate 5 °C min^{-1}) and a Büchi Melting Point B-540 apparatus was used. Infrared spectra were measured using a Perkin Elmer Spectrum One FT-IR spectrometer as KBr pellets. Raman spectra were recorded on a Bruker MultiRAM Raman Sample Compartment D418 equipped with an Nd-YAG-Laser (1064 nm) and an LN-Ge diode as detector. Mass spectra of the described compounds were measured at a JEOL MStation JMS 700 using FAB technique. To measure elemental analyses a Netsch STA 429 simultaneous thermal analyzer was employed.

3.1 Diaminouronium Nitrate (2)

Diaminourea (0.90 g, 10 mmol) is dissolved in nitric acid (2 M, 5 mL, 10 mmol) at room temperature. The solvent is removed from the clear solution resulting in a colourless oil. Recrystallization from ethanol/water yields **2** as colourless solid (after long standing). Alternatively the compound was crystallized after storage at -20 °C under methanol for several days and scratching the flask with a glass rod after the mixture was allowed to come to room temperature. Yield: 1.48 g, 9.7 mmol, 97 %.

DSC (5 °C min^{-1}): 242 °C (dec.); IR (KBr, cm^{-1}): $\tilde{\nu}=$ 3304 (s), 3227 (s), 3194 (s), 2977 (s), 2914 (s), 2698 (m), 2401 (m), 1764 (w), 1697 (s), 1589 (s), 1544 (s), 1504 (s), 1385 (vs), 1272 (s), 1216 (m), 1101 (m), 1021 (m), 983 (w), 825 (w), 787 (w), 750 (m), 584 (m), 508 (w), 472 (w); Raman (1064 nm, 300 mW, 25 °C, cm^{-1}): $\tilde{\nu}=$3336 (6), 3228 (1), 1704 (6), 1647 (2), 1592 (3), 1537 (2), 1488 (1), 1370 (2), 1303 (1), 1268 (3), 1191 (1), 1170 (3), 1055 (100), 984 (7), 726 (4), 714 (5), 520 (4), 378 (2); ^{1}H NMR (d_6-DMSO, 25 °C): δ(ppm) = 7.94 (s, 7H, H_2N–N*H*–CO–N*H*–NH_3^+); ^{13}C NMR (d_6-DMSO, 25 °C): δ(ppm) = 159.2 (*C*=O); *m*/*z* (FAB$^+$): 91.0 ($CH_7N_4O^+$); *m*/*z* (FAB$^-$): 62.0 (NO_3^-); EA ($CH_7N_5O_4$, 153.1) calcd.: C 7.85, H 4.61, N 48.74 %; Found: C 7.60, H 4.46, N 48.14 %; impact sensitivity: 9 J; friction sensitivity: 288 N; ESD: 0.60 J (at grain size 500–1000 μm).

3.2 Diaminouronium Dinitrate Monohydrate (3)

Diaminourea (1.00 g, 11.1 mmol) is dissolved in nitric acid (2 M, 11.1 mL, 22.2 mmol) at room temperature. The solvent is removed from the clear solution in vacuo resulting in a colourless oil, which can easily be recrystallized from methanol. **3** crystallizes in colourless blocks in 78 % yield (2.03 g, 8.67 mmol).

DSC (5 °C min^{-1}): 40 °C (m. p.), 115 °C (dec.); IR (KBr, cm^{-1}): $\tilde{\nu}=$3440 (m), 2961 (m), 2682 (m), 2426 (w), 1767 (w), 1729 (m), 1541 (m), 1384 (s), 1188 (m), 1091 (m), 1047 (m), 833 (w), 748 (w), 597 (w); Raman (1064 nm, 300 mW, 25 °C, cm^{-1}): $\tilde{\nu}=$1701 (3), 1588 (3), 1509 (2), 1400 (1), 1269 (1), 1220 (3), 1049 (100), 980 (12), 722 (9), 506 (4); ^{1}H NMR (d_6-DMSO, 25 °C: δ(ppm) = 9.79 (s, 7H, H_2N–N*H*–CO–N*H*–$N*H*_3^+$); ^{13}C NMR (d_6-DMSO, 25 °C): δ(ppm) = 157.2 (*C*=O); ^{14}N NMR (d_6-DMSO, 25 °C): δ(ppm) = -4.5 (NO_3^-), -359.5 (–NH_3^+); *m*/*z* (FAB$^+$): 91.1 ($CH_7N_4O^+$); *m*/*z* (FAB$^-$): 62.0 (NO_3^-), 154.0 ($CH_8N_5O_4^-$); EA ($CH_{10}N_6O_8$, 234.13) Calcd.: C 5.13, H 4.31, N 35.90 %; Found: C 5.63, H 3.93, N 37.12 %; impact sensitivity: >40 J; friction sensitivity: >360 N; ESD: 0.50 J (at grain size 500–1000 μm).

3.3 Diaminouronium Perchlorate (4)

Diaminourea (1.70 g, 18.9 mmol) is dissolved in 18.9 mL of 1 M perchloric acid at room temperature. The solvent of the clear solution is removed in vacuo and the white solid residue was recrystallized from an ethanol/water mixture to yield **4** almost quantitatively. (3.50 g, 18.4 mmol, 97 %).

DSC (5 °C min^{-1}): 158 °C (m.p.), 244 °C (dec.); IR (ATR, cm^{-1}): $\tilde{\nu}=$3556 (w), 3342 (m), 3200 (m), 3122 (m), 2773 (w), 1701 (m), 1637 (m), 1598 (m), 1572 (m), 1487 (m), 1427 (m), 1353 (w), 1293 (w), 1154 (m), 1063 (vs),

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1005 (s), 933 (m), 758 (m), 714 (m); Raman (1064 nm, 400 mW, 25 °C, cm^{-1}): $\tilde{\nu}$ = 3345 (5), 3102 (2), 1687 (2), 1640 (2), 1592 (3), 1424 (7), 1365 (2), 1165 (4), 1123 (8), 939 (100), 681 (2), 630 (19), 583 (7), 470 (15), 453 (24), 259 (2); ^{1}H NMR (DMSO-d_6, 25 °C): δ(ppm) = 7.59 (s, br, 7H, H_2N–N*H*–CO–N*H*–NH_3^+); ^{13}C NMR (DMSO-d_6, 25 °C): δ(ppm) = 159.2 (*C*=O); *m*/*z* (FAB^+): 91.1 $[C(O)(NH)_2(NH_2)(NH_3)^+]$; *m*/*z* ($FAB^-$): 98.9 $[ClO_4^-]$; EA ($CH_7ClN_4O_5$, 190.54): Calc.: C 6.30, H 3.70, N 29.40 %; Found: C 6.25, H 3.68, N 29.42 %; impact sensitivity: 2 J; friction sensitivity: 5 N; ESD: 0.30 J (at grain size 100–500 μm).

4 Conclusion

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

(i) Mono-protonated (**2**) and bis-protonated (**3**) diaminouronium nitrate as well as the mono-protonated perchlorate salt (**4**) could be synthesized in good yields and high purity from the corresponding acids and diaminourea.

(ii) The crystal structures of **2**–**4** were determined by low-temperature single-crystal X-ray diffraction. The compounds crystallize in the space groups $P2_1/c$ (**2**, **4**) and *Pbca* (**3**) with densities of 1.782 (**2**) 1.785 (**3**) and 1.909 g cm^{-3} (**4**), respectively. Additionally all compounds were fully characterized by vibrational spectroscopy (IR and Raman) ^{1}H and ^{13}C NMR, mass spectroscopy, and elemental analysis.

(iii) Thermal stabilities and melting points of **2**–**4** were investigated by DSC and a melting point apparatus. They melt at 53 °C (**3**), 86 °C (**2**) and 158 °C (**4**) and decompose at 115 °C (**3**), 242 °C (**2**) and 244 °C (**4**), respectively.

(iv) The sensitivities towards friction, impact and electrostatic discharge were investigated by BAM methods. **2**–**4** were found to have impact sensitivities of 9 J, > 40 J and 2 J respectively, friction sensitivities of 288 N, > 360 N and 5 N respectively, and ESD sensitivities of 0.60 J, 0.50 J and 0.30 J, respectively. These are in a range from very sensitive (**4**) to insensitive (**3**).

(v) Using calculated heats of formation and experimentally obtained crystal densities the detonation parameters (heat of explosion, explosion temperature, detonation pressure and velocity) were calculated. **2** has a detonation velocity of 8903 m s^{-1} and a detonation pressure of 33.5 GPa. **3** has a detonation velocity of 7577 m s^{-1} and a detonation pressure of 22.9 GPa.

Symbols and Abbreviations

FW	formula weight (g mol^{-1})
IS	impact sensitivity (J)
FS	friction sensitivity (N)
ESD	electrostatic discharge (J)
N	nitrogen content (%)
Ω	oxygen balance (%)
$T_{Dec.}$	decomposition temperature (°C)
ρ	density (g cm^{-3})
$\Delta_f H^o_m$	heat of formation (kJ mol^{-1})
$\Delta_f U^o$	energy of formation (kJ kg^{-1})
$\Delta_{Ex} U^o$	energy of explosion (kJ kg^{-1})
$T_{det.}$	detonation temperature (K)
P_{CJ}	detonation pressure at Chapman Jouguet Point (Pa)
$V_{Det.}$	detonation velocity (m s^{-1})
V_o	volume of detonation gases (L kg^{-1})

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