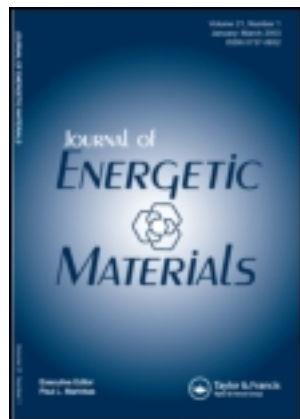


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### Oxalylhydrazinium Nitrate and Dinitrate—Efficiency Meets Performance

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# Oxalyldiazinium Nitrate and Dinitrate— Efficiency Meets Performance

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*Oxalyldiazinium nitrate (OHN) and dinitrate (OHDN) were synthesized by protonation of oxalyldihydrazide with nitric acid. The synthesis is extremely cost effective (~\$40/kg at the lab scale) and can be carried out in large scales and very good yields. OHN and OHDN were intensively characterized by low-temperature X-ray diffraction (XRD), nuclear magnetic resonance (NMR) and vibrational spectroscopy. These new organic nitrate salts could be used as powerful ingredients in energetic formulations due to their low sensitivities (measured by Bundesanstalt für Materialforschung und Prüfung methods). Their thermal stability was investigated by differential scanning calorimetry (DSC) measurements. Further thermal studies of OHN showed compatibility with TNT (2,4,6-trinitrotoluene), DNAN (2,4-dinitroanisole), and RDX (1,3,5-trinitro-1,3,5-triazinane). The theoretical detonation and propulsion parameters of OHN and OHDN were calculated with the EXPLO5.5 code and compared to well-known insensitive explosives. The aquatic toxicity of OHN was determined by the luminescent bacteria inhibition test, yielding a much lower toxicity than RDX.*

**Keywords** compatibility; crystal structure; explosives; nitrates; sensitivity

## Introduction

In the last decade, efforts to improve munitions safety and survivability led to the concept of *insensitive munitions*. These munitions must withstand accidents, fires, or enemy attack. Therefore, there is a great demand for new insensitive explosives that also meet military performance criteria. Many examples of low-sensitivity secondary explosives have been described in the literature [1]. Prominent examples of pure compounds are TATB (1,3,5-triamino-2,4,6-trinitrobenzene) [2], ANTA (3-amino-5-nitrotriazole) [3], DINGU (dinitroglycoluryl) [4], TNGU (tetranitroglycoluryl) [5], DNI (2,4-dinitroimidazole) [6], FOX-7 (1,1-dinitro-2,2-diaminoethene) [7], FOX-12 (guanylurea dinitramide) [8], NTO (nitro-triazolone) [9], and LLM-105 (3,5-dinitro-2,6-pyrazinediamine 1-oxide) [10]. Another explosive of interest is DAAF (diaminoazoxyfurazan), which has been intensively investigated by many research groups [11]. However, most of the compounds have lower

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performances than RDX (1,3,5-trinitro-1,3,5-triazinane, hexogen) and high melting explosive (HMX; octogen) or show extensive preparative routes.

In this article, we present the new weakly sensitive compounds oxalyldihydrazinium nitrate (OHN, **2**) and oxalyldihydrazinium dinitrate (OHDN, **3**) which are characterized by good oxygen balances, promising calculated detonation performance, and an astonishingly facile and low-cost synthesis.

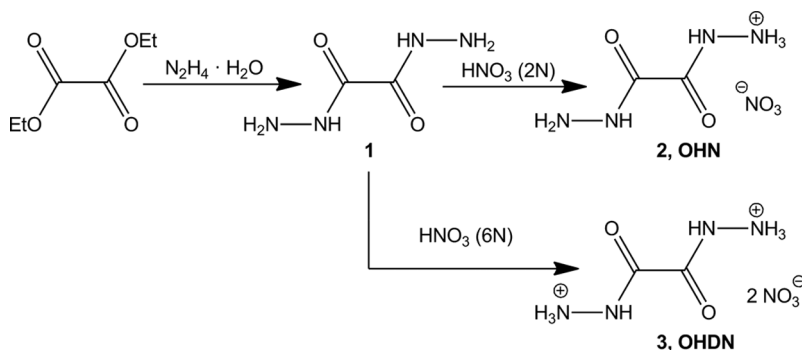
## Results and Discussion

The precursor of OHN and OHDN is oxalyldihydrazide (**1**), which was synthesized from diethyl oxalate and hydrazine hydrate [12] by simple dropwise addition of diethyl oxalate to an ethanolic solution of hydrazine hydrate. The product precipitates instantly and therefore the reaction takes only a few minutes, yielding **1** in high purity and almost 100% yield. The nitrate salt **2** can be prepared by dissolving **1** in a slight excess of hot 0.5 M HNO<sub>3</sub>. **2** Precipitates almost quantitatively by the addition of cold ethanol and can be collected easily by filtration. The dinitrate salt **3** was prepared in 100% yield similar to **2** but using an excess of 30% hot nitric acid. The synthesis of **2** and **3** is figured in Scheme 1.

In summary, the overall synthesis of **2** and **3** is fast, facile, cost-efficient, and almost quantitative. For the lab scale (up to 1 kg), we estimate the total cost of commercially purchased chemicals and solvents needed for the synthesis of 1 kg OHN to be less than €30 (\$40). Considering that lab chemicals are always more expensive than chemicals used at an industrial scale, the material costs for OHN on a large scale are much lower, for example, than the costs for RDX.

Compounds **1–3** can be easily identified by nuclear magnetic resonance (NMR) spectroscopy. The <sup>1</sup>H-NMR spectrum of **1** shows two singlets at 9.93 and 4.47 ppm for the NH and NH<sub>2</sub> protons, respectively. A signal at 158.4 ppm can be observed in the <sup>13</sup>C-NMR spectrum, which is shifted to 157.7 and 157.3 ppm when the compound is protonated with HNO<sub>3</sub> once or twice, respectively. In the <sup>1</sup>H-NMR, **2** shows only one broad singlet at 8.28 ppm and **3** shows a broad singlet at 10.58 ppm.

Crystals of **2** and **3** suitable for X-ray analysis (see Experimental section) were obtained from water and dilute nitric acid, respectively. Both salts crystallize in monoclinic space groups (**2**: C2/c, **3**: P2<sub>1</sub>/c). The most important crystallographic data are listed in Table 1. The molecular units are shown in Figs. 1 and 2. The



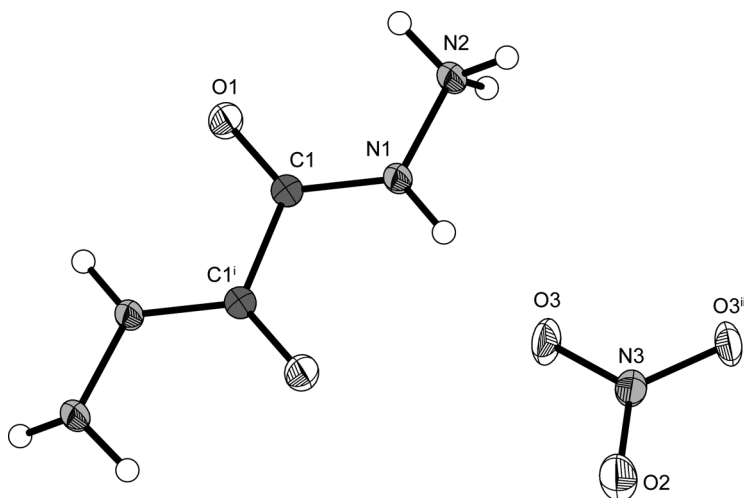
**Scheme 1.** Synthesis of oxalyldihydrazide and its nitrate salts **2** and **3**.

**Table 1** X-ray data and parameters

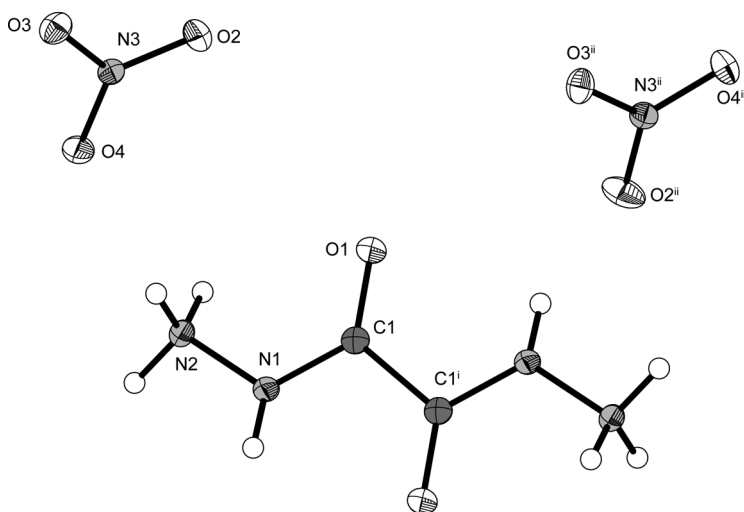
Compound	<b>2</b>	<b>3</b>
Formula	C <sub>2</sub> H <sub>7</sub> N <sub>4</sub> O <sub>5</sub>	C <sub>2</sub> H <sub>8</sub> N <sub>6</sub> O <sub>8</sub>
Form. weight (g mol <sup>-1</sup> )	181.13	244.14
Crystal system	Monoclinic	Monoclinic
Space group	C2/c	P2 <sub>1</sub> /c
Color/habit	Colorless block	Colorless block
Size (mm)	0.11 × 0.15 × 0.20	0.13 × 0.22 × 0.30
<i>a</i> (Å)	10.2076(12)	5.7999(2)
<i>b</i> (Å)	11.0956(9)	7.9900(3)
<i>c</i> (Å)	6.3591(8)	9.0753(3)
α (°)	90	90
β (°)	114.793(14)	97.585(4)
γ (°)	90	90
<i>V</i> (Å <sup>3</sup> )	653.84(14)	416.88(3)
<i>Z</i>	4	2
ρ <sub>calc.</sub> (g cm <sup>-3</sup> )	1.840	1.945
μ (mm <sup>-1</sup> )	0.176	0.195
<i>F</i> (000)	376	252
Theta min–max (°)	4.4, 27.0	4.5, 27.0
Data set	–12:11; –9:14; –8:8	–7:7; –10:10; –11:11
Reflections collected	1,796	4,331
Independent reflections	712	913
<i>R</i> <sub>int</sub>	0.029	0.027
Observed reflections	512	827
No. parameters	72	90
<i>R</i> <sub>1</sub> (obs)	0.0320	0.0269
w <i>R</i> <sub>2</sub> (all data)	0.0793	0.0739
<i>S</i>	0.92	1.08
Resd. Dens. (e Å <sup>-3</sup> )	–0.28, 0.18	–0.27, 0.40
Solution	SIR-92	SIR-92
Refinement	SHELXL-97	SHELXL-97
Absorption correction	Multiscan	Multiscan
CCDC	864719	902480

formation of intense networks of hydrogen bonds (Fig. 3) yields high (**2**: 1.840 g cm<sup>-3</sup>) to very high densities (**3**: 1.945 g cm<sup>-3</sup>). Due to the center of inversion in the cation of **2**, one position of the hydrazinium protons is half-occupied. Therefore, the planar structure of the non-hydrogen atoms within the cations is not affected by the second protonation. The N1–N2 bonds are slightly shorter than N–N single bonds. Further information regarding the crystal structure determination has been deposited as a Crystallographic Information File with the Cambridge Crystallographic Data Centre as supplementary publication Nos. 864719 and 902480.

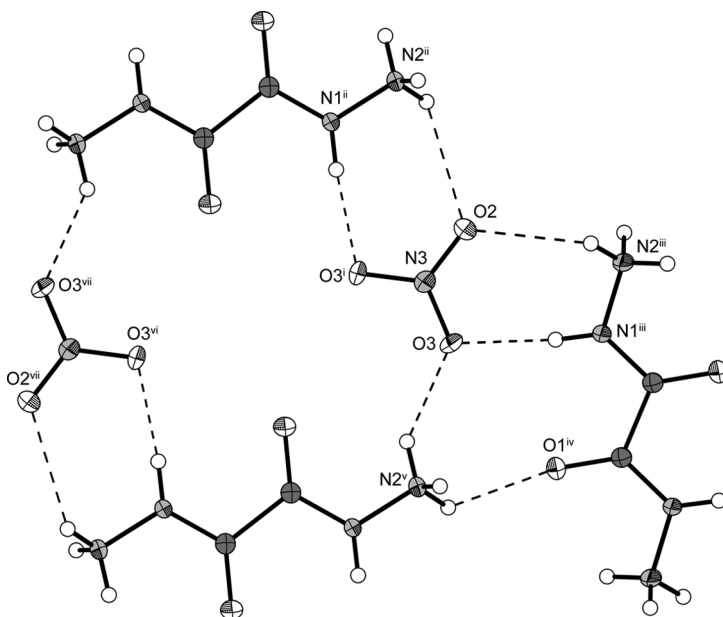
DSC thermographs of **2**, **3** and their precursor **1** are shown in Fig. 4. All temperatures are given as onset temperature using heating rates of 5° min<sup>-1</sup>. **1** Melts at 236°C and decomposes subsequently at 245°C, whereas **2** shows a sharp decomposition peak at 273°C. **2** Shows an endothermic signal at 180°C. This could be caused



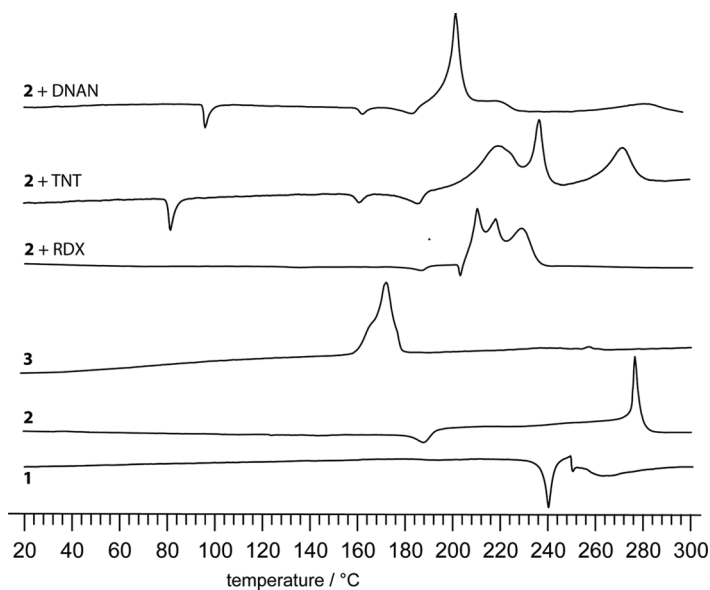
**Figure 1.** Molecular moiety of oxalylhydrazinium nitrate (**2**). Ellipsoids are drawn at the 50% probability level. (i)  $-x, -y, 1 - z$ ; (ii)  $1 - x, y, 0.5 - z$ . Selected bond lengths (Å): O1–C1 1.2278(17), N1–C1 1.3219(19), N1–N2 1.4128(18), O2–N3 1.229(2), O3–N3 1.2534(14), C1–C1<sup>i</sup> 1.532(2); selected bond angles (°): C1–N1–N2 118.37(13), O1–C1–N1 125.11(13), O1–C1–C1<sup>i</sup> 122.41(16), N1–C1–C1<sup>i</sup> 112.45(15), O2–N3–O3 119.79(9), O2–N3–O3 119.79(9), O3–N3–O3<sup>ii</sup> 120.41(18).



**Figure 2.** Molecular moiety of oxalylhydrazinium dinitrate (**3**). Ellipsoids are drawn at the 50% probability level. (i)  $2 - x, -y, -z$ ; (ii)  $1 - x, -0.5 + y, -0.5 - z$ . Selected bond lengths (Å): O1–C1 1.2273(14), N1–C1 1.3306(15), N1–N2 1.4162(13), C1–C1<sup>i</sup> 1.531(2), O2–N3 1.2502(13), O3–N3 1.2739(13), O4–N3 1.2381(12); selected bond angles (°): C1–N1–N2 118.03(9), O1–C1–N1 125.35(11), O1–C1–C1<sup>i</sup> 122.88(13), N1–C1–C1<sup>i</sup> 111.77(12), O2–N3–O3, O2–N3–O3 119.83(10), O3–N3–O5 121.05(10), O3–N3–O5 119.12(9); torsion angle (°): N2–N1–C1–O1  $-0.19(17)$ , N2–N1–C1–C1<sup>i</sup>  $-179.95(11)$ .



**Figure 3.** Hydrogen bonding in the structure of **2**. Ellipsoids are drawn at the 50% probability level. Selected hydrogen bonds (D–H···A:  $d(\text{D–H})$  (Å),  $d(\text{H···A})$  (Å),  $d(\text{D···A})$  (Å),  $\angle(\text{D–H···A})$  (°)):  $\text{N2}^{\text{v}}\text{–H2A}^{\text{v}}\ \text{O3}$  0.89(2), 2.125(19), 2.8924(18), 144.3(16);  $\text{N2}^{\text{v}}\text{–H2B}^{\text{v}}\ \text{O1}^{\text{iv}}$  0.90(2), 2.18(2), 2.8087(18), 126.6(16);  $\text{N2}^{\text{ii}}\text{–H2B}^{\text{ii}}\ \cdots\ \text{O2}$  0.90(2), 2.569(19), 3.0226(18), 112.1(14);  $\text{N1}^{\text{ii}}\text{–H1}^{\text{ii}}\ \text{O3}^{\text{i}}$  0.88(2), 1.95(2), 2.8302(18), 174.6(18);  $\text{N1}^{\text{iii}}\text{–H1}^{\text{iii}}\ \cdots\ \text{O2}$  0.88(2), 2.629(18), 3.1783(13), 121.3(16); symmetry codes (i)  $1 -x, y, 0.5 -z$ ; (ii)  $1 -x, -y, 1 -z$ ; (iii)  $x, -y, -0.5 +z$ ; (iv)  $-x, y, 0.5 -z$ ; (v)  $0.5 -x, 0.5 -y, 1 -z$ ; (vi)  $0.5 +x, 0.5 -y, 0.5 +z$ ; (vii)  $1.5 -x, 0.5 -y, 1 -z$ .



**Figure 4.** DSC thermographs of **1** and its nitrate salts **2** and **3** (pure) as well as mixtures of **2** with 1:1 mixtures with DNAN, TNT and RDX.

by a possible phase transition. Melting of **2** could not be observed and was proven by heating in a melting apparatus. The dinitrate salt is less stable toward temperature. Exothermic decomposition was observed above 155°C. Both compounds are compatible with aluminum.

We also looked for compatibilities of **2** in 1:1 mixtures with DNAN (2,4-dinitroanisole), TNT (2,4,6-trinitrotoluene) and RDX. In the case of the RDX mixture, only the decomposition point of RDX can be observed at >205°C. In the thermo plots of the TNT and DNAN mixtures, the corresponding melting points of TNT (78–80°C) and DNAN (94–96°C) can be observed. Decomposition could not be observed below temperatures of 190°C.

In the following, the energetic properties of **2** and **3** are described. The impact and friction sensitivities were measured using a BAM drop hammer [13] and BAM friction tester [13], respectively. A comparison of their energetic properties with those of the compounds presented in Fig. 5 is shown in Tables 2 and 3.

For better comparison, all heats of formation were calculated with the atomization method using CBS-4M-based electronic enthalpies. The gas-phase enthalpies of formation were either converted to the solid-state enthalpies by Trouton's rule [14] or by subtracting the lattice enthalpies theoretically calculated by Jenkins' equations [15]. All densities were adopted from X-ray measurements at low temperatures.

The detonation parameters were calculated with the EXPLO5.05 computer code [16] using the calculated heats of formation and the crystal densities.

Compared to other low-sensitivity explosives, **2** shows a great thermal stability of 276°C. Its impact sensitivity (plate shaped crystals, 100- to 500- $\mu\text{m}$  grain size) of 11 J is lower than that of RDX and slightly higher than that of the other compounds listed in Table 2. However, no experiments regarding the crystal morphology have been performed. **2** is insensitive toward friction (360 N). Except for FOX-7, TNGU, and RDX, **2** has the highest calculated detonation velocity (8,655  $\text{m s}^{-1}$ ) of the compounds shown in Scheme 2. We also tried to measure the experimental detonation velocity of **2** using the optical fiber method [17]. Loading densities between 1.3 and 1.5  $\text{g cm}^{-3}$  could be achieved. The obtained velocities of detonation initiated by a commercially available detonator (DYNADET C2-25MS, Orica, Victoria, Australia) were between 6,877 and 7,401  $\text{m s}^{-1}$ , which were also calculated to be in the expected range (for these loading densities) by the EXPLO5 code [17]. The explosiveness of **2** has also been evaluated using a small-scale shock reactivity test [18], which was introduced by researchers at Indian Head Division, Naval Surface Warfare Center. **2** could be initiated using a commercially available detonator (DYNADET C2-25MS). The dent obtained was slightly smaller than that of RDX. **3** is more sensitive than **2** and has an impact sensitivity of 7 J and a friction sensitivity of 200 N. Looking at the calculated performance of **3**, the compound had a  $V_{\text{det}}$  of 8,594  $\text{m s}^{-1}$  and a detonation pressure of 331 kbar, comparable to **2**, despite having a much higher density of 1.945  $\text{g cm}^{-3}$  and a better oxygen balance of 0%. This can be explained by the lack in heat of formation, which is caused by the additional mass of a nitrate ion and the additional lattice enthalpy caused by it.

In addition to low cost and high thermal stability, **2** and **3** show another outstanding property. The compounds burn completely smokeless and are therefore suitable as ingredients in smokeless gun or rocket propellants. The specific impulse assuming a chamber pressure of 60 bar of **2** and **3** calculated with EXPLO5.05 was 230 and 220 s, respectively. Mixtures with aluminum showed even higher calculated specific impulses.

**Table 2** Results of heat of formation calculation (based on CBS-4M values)

Compound	Formula	FW (g mol <sup>-1</sup> )	-E (H)	T <sub>m</sub> (°)	T <sub>dec</sub> (°)	Δ <sub>f</sub> H(g) (kJ mol <sup>-1</sup> )	Δ <sub>sub</sub> H/Δ <sub>L</sub> H <sup>a</sup> (kJ mol <sup>-1</sup> )	Δ <sub>f</sub> H <sub>m</sub> <sup>o</sup> (kJ mol <sup>-1</sup> )	dn	Δ <sub>f</sub> U <sup>o</sup> (kJ kg <sup>-1</sup> )
TATB	C <sub>6</sub> H <sub>6</sub> N <sub>6</sub> O <sub>6</sub>	258.15	1,010.586919	350	350	11.4	117.2	-105.7	9	-323.1
ANTA	C <sub>2</sub> H <sub>3</sub> N <sub>5</sub> O <sub>2</sub>	129.08	501.483526	238 [28]	241	188.8	96.1	92.7	5	814.2
DINGU	C <sub>4</sub> H <sub>4</sub> N <sub>6</sub> O <sub>6</sub>	232.11	933.376594	—	225 [29]	-188.2	93.7	-281.9	8	-1,128.9
TNGU	C <sub>4</sub> H <sub>2</sub> N <sub>8</sub> O <sub>10</sub>	321.99	1,341.868154	200	>200	48.8	89.0	-40.2	10	-47.8
2,4-DNI	C <sub>3</sub> H <sub>2</sub> N <sub>4</sub> O <sub>4</sub>	158.07	634.459216	264	270	108.0	100.9	7.1	5	123.0
FOX-7	C <sub>2</sub> H <sub>4</sub> N <sub>4</sub> O <sub>4</sub>	148.08	597.604182	—	235	13.3	95.6	-82.3	6	-455.1
FOX-12	C <sub>2</sub> H <sub>7</sub> N <sub>7</sub> O <sub>5</sub>	209.12	—	—	215	254.4 <sup>b</sup>	511.4 <sup>a</sup>	-257.1	9.5	-1,116.5
NTO	C <sub>2</sub> H <sub>2</sub> N <sub>4</sub> O <sub>3</sub>	130.06	521.361307	265 [30]	270 [31]	-16.5	101.2	-117.7	4.5	-819.1
LLM-105	C <sub>4</sub> H <sub>4</sub> N <sub>6</sub> O <sub>5</sub>	216.11	858.170558	—	342	126.7	115.6	11.1	7.5	137.0
<b>2</b>	C <sub>2</sub> H <sub>7</sub> N <sub>5</sub> O <sub>5</sub>	181.11	—	—	273	236.9 <sup>b</sup>	536.4 <sup>a</sup>	-299	8.5	-1,537
<b>3</b>	C <sub>2</sub> H <sub>8</sub> N <sub>6</sub> O <sub>8</sub>	244.12	—	—	155	925.9 <sup>b</sup>	1724.3	-798.4	11	-3,158.2
RDX	C <sub>3</sub> H <sub>6</sub> N <sub>6</sub> O <sub>6</sub>	222.12	896.346781	205 [32]	210 [32]	176.2	89.9	86.3	9	489.0

<sup>a</sup>Lattice enthalpy.<sup>b</sup>Gas phase enthalpies of formation of the ionic compounds are taken as the respective sums of the noninteracting component ions.



**Table 3** Energetic properties of **2** and **3** in comparison with prominent low sensitive explosives

Compound	IS (J) <sup>a</sup>	FS (N) <sup>b</sup>	$\Omega$ (%) <sup>c</sup>	$\rho$ (g cm <sup>-3</sup> ) <sup>d</sup>	$-\Delta_{\text{Ex}}U^{\circ}$ (kJ kg <sup>-1</sup> ) <sup>e</sup>	$T_{\text{det}}$ (K) <sup>f</sup>	$P_{\text{CJ}}$ (kbar) <sup>g</sup>	$V_{\text{Det.}}$ (m s <sup>-1</sup> ) <sup>h</sup>	$V_o$ (L kg <sup>-1</sup> ) <sup>i</sup>
TATB	50 [32]	>360 [32]	-55.78	1.93 [2]	4,625	3,297	312	8,335	640
ANTA	35 [32]	>360	-43.38	1.819 [3]	4,313	3273	287	8,281	736
DINGU	18 [29]	250 [29]	-27.57	1.992 [4]	4,206	3,306	331	8,364	661
TNGU	25 [5]	194 [5]	4.97	2.00 [5]	5,482	4,474	378	8,779	659
2,4-DNI	>25 [33]	140	-30.36	1.77 [6]	5,183	4,021	279	7,938	635
FOX-7	12–14	340 [34]	-21.61	1.907 [7]	5,306	3,758	363	8,827	741
FOX-12	>30	>360	-22.08	1.775* [35]	5,067	3,471	316	8,591	827
NTO	71	>360	-24.60	1.926 [36]	3,967	3,237	301	8,167	683
LLM-105	18–30	>360	-37.01	1.92 [37]	4,935	3,676	333	8,482	660
<b>2</b>	11	>360	-22.08	1.84	4,661	3,275	325	8,655	827
<b>3</b>	7	200	0	1.945	3,978	3,042	331	8,594	825
RDX	7.4 [32]	120 [32]	-21.61	1.858 [38]	6,190	4,232	380	8,983	734

<sup>a</sup>Impact sensitivity (BAM drop hammer; one of six).

<sup>b</sup>Friction sensitivity (BAM friction tester; one of six).

<sup>c</sup>Oxygen balance related to CO<sub>2</sub> [ $\Omega = (xO - 2yC - 1/2zH)M/1600$ ].

<sup>d</sup>Density from X-ray diffraction.

<sup>e</sup>Energy of explosion.

<sup>f</sup>Explosion temperature.

<sup>g</sup>Detonation pressure.

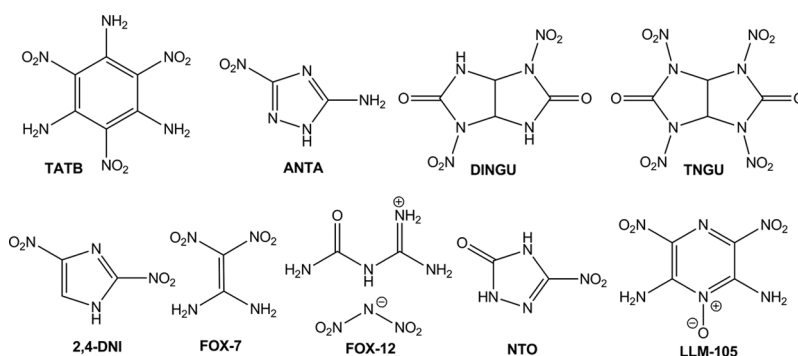
<sup>h</sup>Detonation velocity.

<sup>i</sup>Volume of detonation gases (assuming only gaseous products).

<sup>e-i</sup>Calculated with EXPLO5.05 [16].

\*U. Bemm (personal communication) and CCDC (Cambridge Crystallographic Data Centre) No. 143181.

Lastly, the aquatic toxicity of **2** was investigated by the luminescent bacteria inhibition test. Many explosives such as TNT, CL-20 (2,4,6,8,10,12-hexanitro-2,4,6,8,10,12-hexaazaisowurtzitane) [19], and RDX have been shown to be toxic [20] to vital organisms at the base of the food chain. In addition, RDX is a probable human carcinogen [21]. To assess the toxicity of OHN to aquatic life, diluted aqueous solutions of the explosive were subjected to the luminescent marine bacterium *Vibrio fischeri* using the commercially available bioassay system LANGE LUMISTox [22]. *Vibrio fischeri* is a representative species for other aquatic life and therefore is a useful indicator when it comes to groundwater pollution. As the most important toxicological parameter, the EC<sub>50</sub> value of the sample was determined. EC<sub>50</sub> is the effective concentration of the examined compound, at which the bioluminescence of the strain *Vibrio fischeri* is decreased by 50% after a defined period of exposure compared to the original bioluminescence of the sample



**Scheme 2.** Prominent low-sensitivity explosives: TATB (1,3,5-triamino-2,4,6-trinitrobenzene), ANTA (3-amino-5-nitrotriazole), DINGU (1,4-dinitrotetrahydroimidazo[4,5-d]imidazole-2,5-(1H,3H)-dione), TNGU (tetranitroglycoluril), DNI (2,4-dinitroimidazole), FOX-7 (1,1-dinitro-2,2-diaminoethene), FOX-12 (guanylurea dinitramide), NTO (nitro-triazolone), and LLM-105 (3,5-dinitro-2,6-pyrazinediamine 1-oxide).

before being treated with the differently diluted solutions of the test compound. For RDX we observed an  $EC_{50}$  value of 91 ppm. The  $EC_{50}$  value after an incubation time of 30 min of OHN was determined to be 1,240 ppm. This was much lower than the  $EC_{50}$  value found for RDX, indicating a lower toxicity toward aquatic life.

## Experimental Part

The crystal structure was determined on an Oxford Diffraction (Abingdon, UK) Xcalibur3 diffractometer with a Spellman generator (voltage 50 kV, current 40 mA) and a KappaCCD detector using a  $\lambda_{MoK\alpha}$  radiation wavelength of 0.71073 Å at  $-100^\circ\text{C}$ . Data collection and data reduction were carried out using CrysAlisPro software [23]. The structure was solved with SIR-92 [24] refined with SHELXL-97 [25] and finally checked using the PLATON software [26] integrated in the WINGX software suite [27]. The non-hydrogen atoms were refined anisotropically and the hydrogen atoms were located and freely refined. The absorption was corrected by a SCALE3 ABSPACK multiscan method (empirical absorption correction using spherical harmonics, implemented in SCALE3 ABSPACK scaling algorithm) [23].

All reagents and solvents were used as received (Sigma-Aldrich, Munich, Germany; Fluka, Munich, Germany; Acros Organics, Geel, Belgium) if not stated otherwise. Melting and decomposition points were measured with a Linseis PT10 DSC (Selb, Germany) using heating rates of  $5^\circ\text{C min}^{-1}$ , which were checked with a Büchi (Essen, Germany) melting point B-450 apparatus.  $^1\text{H}$ -,  $^{13}\text{C}$ -, and  $^{15}\text{N}$ -NMR spectra were measured with a JEOL 400 MHz instrument (Tokyo, Japan). All chemical shifts are provided in parts per million relative to tetramethylsilane (TMS) ( $^1\text{H}$ ,  $^{13}\text{C}$ ) or nitromethane ( $^{15}\text{N}$ ). Infrared spectra were measured with a Perkin-Elmer Spektrum One FT-IR instrument (Waltham, MA, USA). Raman spectra were measured with a Perkin-Elmer Spektrum 2000 R NIR FT-Raman instrument equipped with an Nd:YAG laser (1,064 nm). Elemental analyses were performed with a Netsch STA 429 simultaneous thermal analyzer (Selb, Germany).

### ***Oxalyldihydrazide (1)***

To a solution of 6 mL (124 mmol) hydrazine hydrate in 100 mL ethanol, 7.31 g (50 mmol) of diethyl oxalate was added dropwise. The precipitate was isolated by filtration, washed with ethanol, and dried in air, yielding 5.73 g (97%) of colorless product. DSC ( $5^{\circ}\text{C min}^{-1}$ ):  $236^{\circ}\text{C}$  (mp),  $245^{\circ}\text{C}$  (dec.); IR (atr,  $\text{cm}^{-1}$ ):  $\tilde{\nu} = 3284$  (m), 3180 (w), 1646 (m), 1579 (m), 1531 (s), 1421 (w), 1319 (w), 1293 (w), 1255 (s), 1124 (s), 952 (vs), 828 (s), 718 (vs); Raman (1,064 nm, 300 mW,  $25^{\circ}\text{C}$ ,  $\text{cm}^{-1}$ ):  $\tilde{\nu} = 1770$  (6), 1572 (5), 1472 (8), 1357 (4), 1279 (18), 1124 (4), 1098 (3), 1024 (4), 935 (100), 793 (49), 638 (24), 627 (12), 473 (17), 458 (14);  $^1\text{H-NMR}$  ( $\text{DMSO-}d_6$ ,  $25^{\circ}\text{C}$ , ppm)  $\delta$ : 9.93 (2H), 4.47 (4H);  $^{13}\text{C-NMR}$  ( $\text{DMSO-}d_6$ ,  $25^{\circ}\text{C}$ , ppm)  $\delta$ : 158.4; EA ( $\text{C}_2\text{H}_6\text{N}_4\text{O}_2$ , 118.09). Calc.: C, 20.34; H, 5.12; N, 47.44%; found: C, 20.59; H, 4.90; N, 47.53%.

### ***Oxalyldihydrazinium Nitrate (2)***

1.18 g (10 mmol) oxalyldihydrazide was dissolved in a hot mixture of 5.5 mL 2 M  $\text{HNO}_3$  and 10 mL water. The solution was poured into 20 mL of ice-cold ethanol, yielding 1.80 g (99%) of colorless crystalline **2**. DSC ( $5^{\circ}\text{C min}^{-1}$ ):  $273^{\circ}\text{C}$  (dec.); IR (atr,  $\text{cm}^{-1}$ ):  $\tilde{\nu} = 3307$  (w), 3178 (w), 3028 (w), 2775 (w), 1674 (m), 1531 (m), 1326 (s), 1243 (s), 1152 (w), 1088 (w), 995 (m), 802 (m), 709 (m); Raman (1064 nm, 300 mW,  $25^{\circ}\text{C}$ ,  $\text{cm}^{-1}$ ):  $\tilde{\nu} = 3224$  (4), 1735 (9), 1703 (15), 1584 (12), 1553 (28), 1346 (19), 1289 (23), 1206 (9), 1094 (10), 1049 (100), 1003 (4), 938 (15), 812 (2), 719 (7), 510 (5), 400 (5);  $^1\text{H NMR}$  ( $\text{DMSO-}d_6$ ,  $25^{\circ}\text{C}$ , ppm)  $\delta$ : 8.28  $^{13}\text{C}\{^1\text{H}\}$  NMR ( $\text{DMSO-}d_6$ ,  $25^{\circ}\text{C}$ , ppm)  $\delta$ : 157.8; EA ( $\text{C}_2\text{H}_7\text{N}_5\text{O}_5$ , 181.11): calc.: C 13.26, H 3.90, N 38.67%; found: C 13.50, H 3.74, N 38.59%; BAM drophammer: 12 J; friction tester:  $>360$  N; ESD: 0.3 J.

### ***Oxalyldihydrazinium Dinitrate (3)***

Oxalyldihydrazide, 2.36 g (20 mmol), was dissolved in 10 mL of boiling 30% nitric acid. The solution was cooled to room temperature and crystallization was completed by the addition of 20 mL cold ethanol; 4.88 g (100%) of colorless **3** was isolated by filtration. DSC ( $5^{\circ}\text{C min}^{-1}$ ):  $155^{\circ}\text{C}$  (dec.); IR (atr,  $\text{cm}^{-1}$ ):  $\tilde{\nu} = 3052$  (m), 2699 (w), 1687 (s), 1567 (m), 1533 (s), 1340 (vs), 1256 (s), 1202 (s), 1174 (s), 1047 (m), 1026 (w), 815 (s), 729 (w); Raman (1,064 nm, 200 mW,  $25^{\circ}\text{C}$ ,  $\text{cm}^{-1}$ ):  $\tilde{\nu} = 3050$  (18), 1719 (19), 1559 (10), 1214 (9), 1123 (11), 1052 (100), 927 (11), 732 (10);  $^1\text{H-NMR}$  ( $\text{DMSO-}d_6$ ,  $25^{\circ}\text{C}$ , ppm)  $\delta$ : 10.58;  $^{13}\text{C}\{^1\text{H}\}$ -NMR ( $\text{DMSO-}d_6$ ,  $25^{\circ}\text{C}$ , ppm)  $\delta$ : 157.3; EA ( $\text{C}_2\text{H}_8\text{N}_6\text{O}_8$ , 244.12). Calc.: C, 9.84; H, 3.30; N, 34.43%; found: C, 9.76; H, 3.41; N, 33.22%; BAM drop hammer: 7 J; friction tester: 200 N; ESD:  $>1.5$  J.

## **Conclusions**

From this initial study the following conclusions can be drawn:

- Oxalyldihydrazinium nitrate (OHN, **2**) and oxalyldihydrazinium dinitrate (OHDN, **3**) were synthesized and intensively characterized. The crystal structures of OHN and OHDN were determined. Both new organic nitrate salts could be used in high-energy applications and also as ingredients for propellant compositions.
- OHN is less sensitive than RDX and OHDN is of comparable sensitivity to RDX. OHN and OHDN can be easily and cost-effectively synthesized in large scales and excellent yields. The lab-scale costs were calculated to be \$40 per kilogram of OHN.

The thermal stability of OHN is much greater than that of RDX. Thermal studies of mixtures of OHN with TNT, DNAN, and RDX showed compatibility up to 180°C.

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