

# 2-Hydrazonyl-Propandihydrazide – A Versatile Precursor for High-Energy Materials

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In this work, 2-hydrazonyl-propandihydrazide (**2**), a new precursor for energetic materials based on diethyl 2,2-diazo-malonate (**1**) was investigated. Therefore, its versatility was shown by various secondary reactions, including formation of energetic salts (**3–5**), the synthesis of a nitrogen-rich bistriazole (**10**) and a highly instable diazido derivative (**6**). In addition, a Curtius degradation could be observed in detail. When possible, the compounds were analyzed by low temperature X-ray diffraction. All measurable compounds were analyzed by <sup>1</sup>H and

<sup>13</sup>C NMR spectroscopy, elemental analysis, differential thermal analysis (DTA) and regarding their sensitivity towards impact and friction according to BAM standard techniques. All promising compounds were evaluated regarding their energetic behavior using the EXPLO5 code (V6.05) and compared to RDX and CL-20. In addition, compound **2** was investigated towards its aquatic toxicity, using the bioluminescent bacteria *vibrio fischeri*.

## Introduction

Due to the wide spread use of energetic materials in both civilian and military applications, there is a constant need for improvement of known compounds, as well as the development of new energetic materials, exceeding their predecessors in regard to their performance, cost effectiveness and eco-friendliness.<sup>[1–3]</sup> Countless discoveries of the last decade have proven nitrogen rich heterocycles like oxadiazoles, triazoles and tetrazoles to be promising backbones in high-energy material (HEM) synthesis.<sup>[4–6]</sup> Compounds based on these systems often possess the desired properties like high density and detonation performance, good thermal stabilities and low sensitivities.<sup>[7,8]</sup> By the formation of nitrogen rich salts these properties can be further improved.<sup>[9]</sup> One of the most prominent examples for this class of molecules is TKX-50, surpassing commonly used energetic materials like RDX in almost all relevant properties.<sup>[10–12]</sup>

It is synthesized from glyoxal, which is an excellent example for a versatile precursor in the field of HEMs. Numerous compounds including K<sub>2</sub>DNABT, CL-20, TKX-50, bisfuroxanes and furazanes can be prepared starting from glyoxal.<sup>[13–15]</sup> Another well-known example is nitroacetonitrile, which is commonly used to synthesize annulated 1,2,4-triazines.<sup>[16]</sup> Some

examples for energetic precursors are summarized in Figure 1. But the way to these promising energetic compounds often consists of long synthetic routes including numerous steps and complicated reaction paths, some examples of these are shown in Figure 2. It is therefore of high importance to develop new precursor molecules, which are cheap and easy to synthesize and provide various possibilities for functionalization in order to obtain HEMs. In addition, it would be ideal if they possess low sensitivities and no toxicity. Therefore, this work focuses on the synthesis of energetic materials, based on 2-Hydrazonyl-propandihydrazide (**2**), a new energetic precursor. Those new compounds are extensively characterized in regard to their energetic and structural properties.

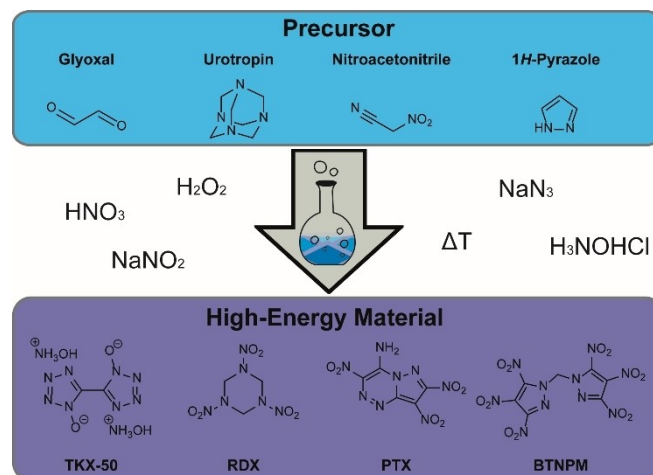
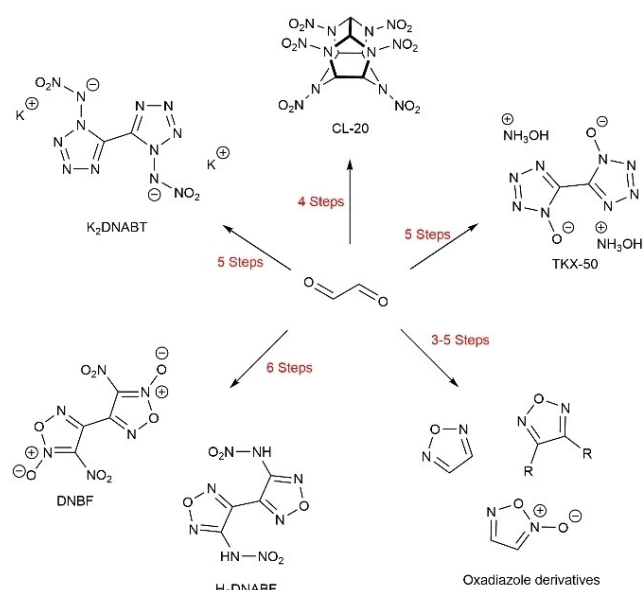


Figure 1. A selection of commonly used precursor molecules and their respective HEMs.

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**Figure 2.** Glyoxal as a precursor for various energetic materials like CL-20,  $K_2$ DNABT, TKX-50, furazane and furoxane derivatives.

## Results and Discussion

### Synthesis

Diethyl 2,2-diazidomalonate (**1**) was synthesized according to literature procedure.<sup>[17]</sup> 2-Hydrazonyl-propandihydrazide (**2**) was obtained by substitution of the azide groups and the ethoxy groups using an excess of hydrazinium hydroxide. Two ethanol molecules are cleaved by the nucleophilic attack of the hydrazine on the carboxyl carbon atom. The ionic compounds **3–5** are synthesized by Brønsted acid-base chemistry when reacting compound **2** with nitric, hydrochloric and perchloric acid, respectively. Hereby, compound **2** is protonated twice and the double salts of the 2-hydrazonemalonohydrazinium cation are formed. After diazotation of compound **6** a Curtius degradation starting from compound **6** can be observed. Hereby, 3-carbonylazido-1H-1,2,4-triazol-5-one (**7**) is formed

almost instantly over the isocyanate intermediate, which reacts further to compound **8**, when exposed to ambient humidity. Additionally, compound **2** was reacted with N-methyl-N-nitroso-N'-nitroguanidine in order to form compound **9**, which was followed by a triazole ring closure, performed under basic conditions and subsequent acidification yielding the neutral compound **10** (Scheme 1). All compounds were fully characterized by IR and multinuclear NMR spectroscopy, mass spectrometry and differential thermal analysis. Further, selected compounds were analyzed using low-temperature single-crystal X-ray measurements.

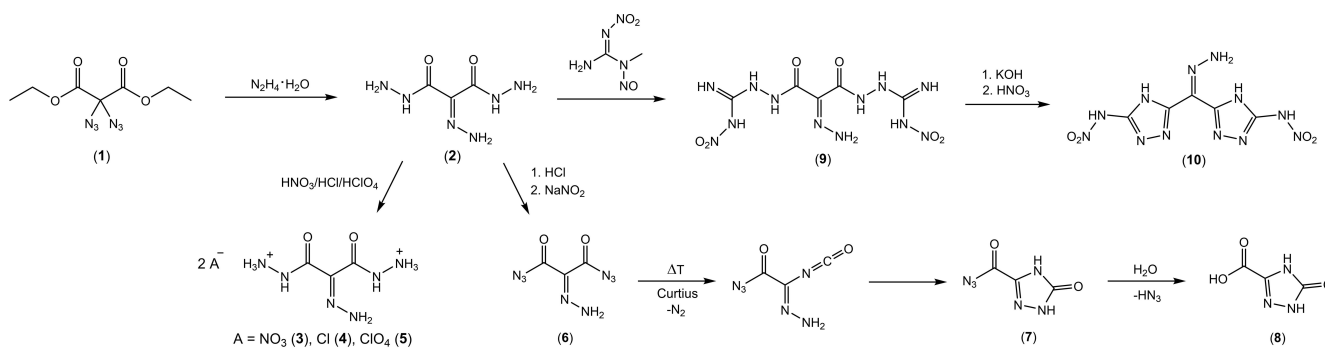
### Crystal Structures

Measurable crystals could be obtained for the compounds **2–5**, **7** and **8**, either directly from the reaction mixture (**7**, **8**) or by recrystallization from water (**2–5**).

General information on the X-ray measurements and refinements are given in the SI. Structures were deposited with the CCDC database under the following numbers (**2**: 2149590, **3**: 2149591, **4**: 2149592, **5**: 2149593, **7**: 2149594, **8**: 2149595).

2-Hydrazonyl-propandihydrazide (**2**) crystallizes in the monoclinic space group  $P2_1/c$  with a density of  $1.601 \text{ g cm}^{-3}$  at 113 K (Figure 3). For all structures, thermal ellipsoids of non-hydrogen atoms are drawn at the 50% probability level and hydrogen atoms are shown as small spheres of arbitrary radius. The cell volume is  $664.35(9) \text{ \AA}^3$  with four formula units per cell. The molecule is highly planar, shown by the torsion angles, which are very close to  $0^\circ$  or  $180^\circ$ . ( $N6-N5-C3-C2$   $173.8^\circ$ ,  $N4-N3-C2-C1$   $0.3^\circ$ ,  $N2-N1-C1-C2$   $178.9^\circ$ ). Both, intramolecular and intermolecular hydrogen bonds can be observed. ( $N4-H4B \cdots O1$ ,  $N5-H5 \cdots N3$ ,  $N1-H1 \cdots O2$ ,  $N2-H2A \cdots O1$ ,  $N4-H4B \cdots O2$ ) The bond lengths confirm the mesomeric system, with values between single and double bonds for  $C1-N1$  ( $1.333 \text{ \AA}$ ),  $C2-N3$  ( $1.314 \text{ \AA}$ ),  $N3-N4$  ( $1.309 \text{ \AA}$ ) and  $C3-N5$  ( $1.336 \text{ \AA}$ ).<sup>[18,19]</sup>

2-Hydrazonyl-propandihydrazidum dinitrate-0.25  $H_2O$  (**3**) crystallizes in the monoclinic space group  $P2_1/c$  with a density of  $1.743 \text{ g cm}^{-3}$  at 107 K (Figure 4). The cell volume is  $1107.53(10) \text{ \AA}^3$  with one formula unit per cell. The torsion angles



**Scheme 1.** Synthesis of compound **2** as a versatile precursor for energetic compounds **3**, **4**, **5**, **9** and **10**, as well as the Curtius degradation from compound **6** to **8**.

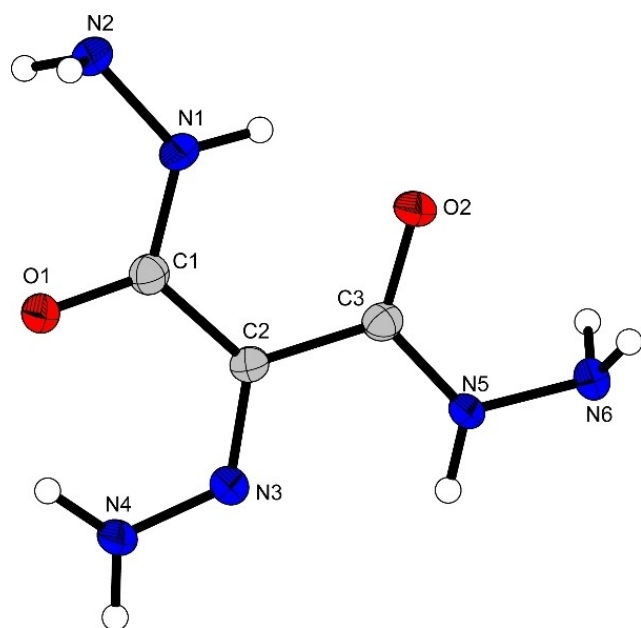


Figure 3. Molecular unit of 2-hydrazoneyl-propandihydrazide (2).

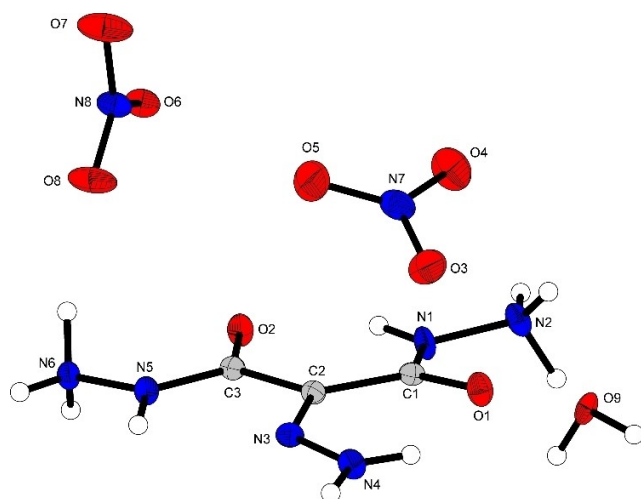


Figure 4. Molecular unit of 2-hydrazoneyl-propandihydrazidium dinitrate · 0.25 H<sub>2</sub>O (3).

show a planar molecule, similar to compound 2 (N6–N5–C3–C2 –174.9°, N4–N3–C2–C1 0.7°, N2–N1–C1–C2 176.4°). The compound crystallizes with one water per four product molecules.

Compound 4 crystallizes in the triclinic space group *P*-1 with a density of 1.657 g cm<sup>-3</sup> at 100 K and two formula units per unit cell (Figure 5). The cell volume is 503.15(6) Å<sup>3</sup>. The structure shows high similarities to the previously described compounds 2 and 3 in regard to its planarity (N6–N5–C3–C2 –172.7°, N4–N3–C2–C1 176.2°, N2–N1–C1–C2 178.3°). The crystal structure contains one water per unit cell. All bond lengths comply with the described values for compound 2.<sup>[18,19]</sup>

Compound 5 crystallizes in the monoclinic space group *P*<sub>2</sub>/*n* with a density of 1.991 g cm<sup>-3</sup> at 105 K and four formula units

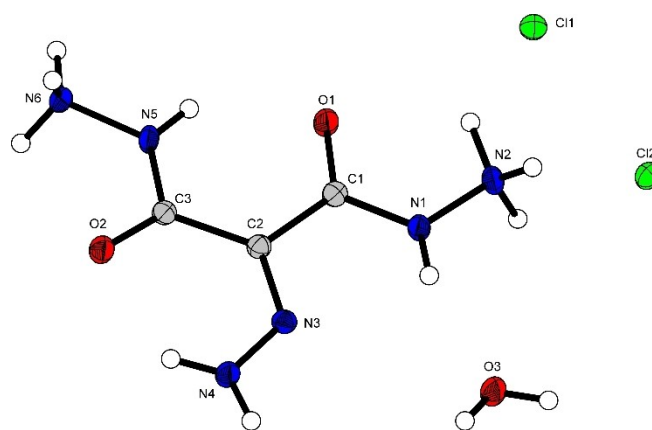


Figure 5. Molecular unit of 2-hydrazoneyl-propandihydrazidium dichloride monohydrate (4).

per unit cell (Figure 6). The cell volume is 1264.94(13) Å<sup>3</sup>. The structure fits the expectations in regard to the torsion angles, being slightly less planar than the previous described structures (N6–N5–C3–C2 –171.0°, N4–N3–C2–C1 178.5°, N2–N1–C1–C2 –168.8°). The crystal structure contains one water per unit cell. All bond lengths comply with the described values for compound 2.<sup>[18,19]</sup>

Compound 7 crystallizes in the monoclinic space group *P*<sub>2</sub>/*c* with a density of 1.797 g cm<sup>-3</sup> at 105 K and four formula units per unit cell (Figure 7). The cell volume is 569.48(17) Å<sup>3</sup>. Based on the torsion angles the structure can also be described as planar (C1–N1–N2–C2 –0.4°, N2–C2–C3–N4 2.7°, N5–N4–C3–O2 2.3°). All bond lengths comply with the expected values for C–C, C–N, C–O and N–N single and double bonds (C2–C3 1.49 Å, N1–N2 1.38 Å, N4–C3 1.40 Å, C1–O1 1.25 Å).<sup>[18,19]</sup>

Compound 8 crystallizes in the monoclinic space group *P*<sub>2</sub>/*c* with a density of 1.766 g cm<sup>-3</sup> at 102 K and four formula units per unit cell (Figure 8). The cell volume is 553.20(4) Å<sup>3</sup>. Similar to compound 7 the torsion angles describe a planar structure (C2–N1–C1–N2 –0.4°, N1–C2–C3–O3 0.8°, N3–N2–C1–O1 –177.6°). The compound crystallizes with one water molecule per unit cell. All bond lengths comply with the expected values

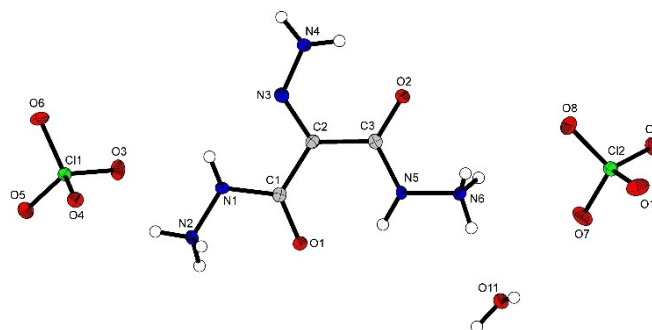


Figure 6. Molecular unit of 2-hydrazoneyl-propandihydrazidium diperchlorate monohydrate (5).

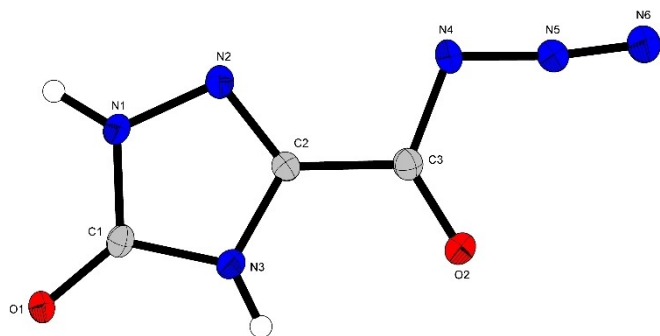


Figure 7. Molecular unit of 3-carbonylazido-1H-1,2,4-triazol-5-one (7).

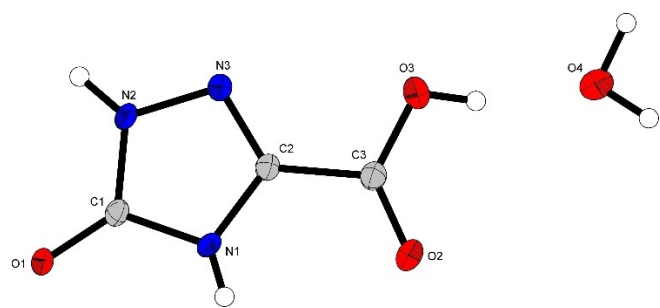


Figure 8. Molecular unit of 3-carboxyl-1H-1,2,4-triazol-5-one monohydrate (8).

for C–C, C–N, C–O and N–N single and double bonds (C2–C3 1.49 Å, N2–N3 1.37 Å, N3–C2 1.30 Å, C1–O1 1.25 Å).<sup>[18,19]</sup>

### NMR and Vibrational Spectroscopy

All <sup>1</sup>H and <sup>13</sup>C NMR measurements were performed in DMSO-*d*<sub>6</sub>.

The proton NMR of compound **2** shows five signals. This is due to the *E/Z*-isomerism caused by the inflexible hydrazone moiety, building intramolecular hydrogen bridges with one side of the otherwise symmetrical molecule. The two signals at 4.26 and 4.46 ppm belong to the NH<sub>2</sub> - groups of the hydrazides. The two signals at 8.88 and 10.20 ppm are the NH groups, which are shifted more due to a higher influence of the described effect on those protons. The same effect can be observed in the corresponding <sup>13</sup>C spectrum, which shows three signals. The two signals at 162.9 and 164.9 ppm belong to the unsymmetrical carbohydrazides, and the signal at 119.0 ppm represents the hydrazone group. Compounds **3**, **5** and **9** behave in a similar manner, as it would be expected. Although compound **10** also has the intermediate hydrazone group, it shows symmetric signals in the <sup>1</sup>H and <sup>13</sup>C spectra, which are caused by the mesomerism of the ring system. The IR spectrum of **6** was measured in chloroform, since this compound decomposes as soon as it is isolated. The hydrazone moiety can be identified by the two broad bands at 3313 and 3163 cm<sup>-1</sup>, as well as the band at 1574 cm<sup>-1</sup>. The band at 2129 cm<sup>-1</sup> corresponds to the azide groups and the carbonyl vibration is found at 1675 cm<sup>-1</sup>.<sup>[20,21]</sup>

### Physicochemical Properties

All energetic compounds were characterized regarding their physicochemical properties. This includes their sensitivities towards impact, friction and electrostatic discharge, the thermal behavior, heats of formation and detonation parameters. Those were determined experimentally or computationally and compared to RDX, being the state-of-the-art secondary explosive in industrial use, and CL-20, which is one of the best performing compounds in terms of detonation properties, shown in Table 1. The sensitivity values towards impact and friction were determined according to the BAM standards.<sup>[22]</sup>

Table 1. Physicochemical properties of compounds **2**, **3**, **5**, **9**, **10**, RDX, and CL-20.<sup>[24]</sup>

|   | <b>2</b>  | <b>3</b>  | <b>5</b>  | <b>9</b>  | <b>10</b>  | RDX   | CL-20   |
|---|---|---|---|---|--|---|---|
| Formula   | C <sub>3</sub> H <sub>8</sub> N <sub>6</sub> O <sub>2</sub> | C <sub>3</sub> H <sub>10.5</sub> N <sub>8</sub> O <sub>8.25</sub> | C <sub>3</sub> H <sub>12</sub> N <sub>6</sub> O <sub>11</sub> Cl <sub>2</sub> | C <sub>5</sub> H <sub>10</sub> N <sub>12</sub> O <sub>6</sub> | C <sub>5</sub> H <sub>6</sub> N <sub>12</sub> O <sub>4</sub> | C <sub>3</sub> H <sub>6</sub> N <sub>6</sub> O <sub>6</sub> | C <sub>3</sub> H <sub>6</sub> N <sub>6</sub> O <sub>6</sub> |
| <i>M</i> [g mol <sup>-1</sup> ]   | 160.14  | 290.56  | 379.06  | 334.21  | 298.18   | 222.12  | 438.19  |
| <i>I</i> S <sup>[a]</sup> [J]   | > 40  | 30  | > 40  | > 40  | 2.5  | 7.5   | 3   |
| <i>F</i> S <sup>[b]</sup> [N]   | > 360   | > 360   | > 360   | > 360   | 360  | 120   | 96  |
| <i>N</i> + <i>O</i> <sup>[c]</sup> [%]  | 72.46   | 83.89   | 68.60   | 79.01   | 77.83  | 81.06   | 82.17   |
| <i>Ω</i> <sub>CO<sub>2</sub></sub> <sup>[d]</sup> [%]                                 | -80   | -17   | 0   | -43   | -34  | -22   | -11   |
| <i>T</i> <sub>endo</sub> <sup>[e]</sup> / <i>T</i> <sub>exo</sub> <sup>[f]</sup> [°C] | -178  | -167  | -124  | -209  | -177   | 203/208   | -224  |
| <i>ρ</i> <sup>[g]</sup> [g cm <sup>-3</sup> ]   | 1.56  | 1.70  | 1.94  | 1.73  | 1.81   | 1.82  | 2.08  |
| <i>Δ</i> <sub>f</sub> <i>H</i> <sup>[h]</sup> [kJ mol <sup>-1</sup> ]                 | -21   | 224   | -239  | 184   | 541  | 87  | 365   |
| <b>EXPLO5 V6.05</b>   |   |   |   |   |  |   |   |
| - <i>Δ</i> <sub>E</sub> <i>U</i> <sup>[i]</sup> [kJ kg <sup>-1</sup> ]                | 2851  | 6552  | 5993  | 4327  | 5137   | 5807  | 6160  |
| <i>T</i> <sub>C-J</sub> <sup>[j]</sup> [K]  | 2096  | 4073  | 4080  | 3023  | 3624   | 3800  | 4071  |
| <i>p</i> <sub>C-J</sub> <sup>[k]</sup> [GPa]  | 19.3  | 34.2  | 36.9  | 25.9  | 31.0   | 34.0  | 44.5  |
| <i>D</i> <sub>C-J</sub> <sup>[l]</sup> [m s <sup>-1</sup> ]                           | 7610  | 8920  | 9082  | 8228  | 8654   | 8882  | 9778  |
| <i>V</i> <sub>0</sub> <sup>[m]</sup> [dm <sup>3</sup> kg <sup>-1</sup> ]              | 885   | 859   | 837   | 829   | 766  | 793   | 720   |

[a] Impact sensitivity (BAM drophammer, method 1 of 6); [b] friction sensitivity (BAM friction tester, method 1 of 6); [c] combined nitrogen and oxygen content; [d] oxygen balance toward carbon dioxide ( $\Omega_{CO_2} = (nO - 2xC - yH/2)/(1600/M)$ ); [e] endothermic peak (DTA,  $\beta = 5^\circ C min^{-1}$ ); [f] temperature of decomposition (DTA,  $\beta = 5^\circ C min^{-1}$ ); [g] X-ray densities recalculated to 298 K; compounds **9** and **10** measured by gas pycnometry; [h] standard molar enthalpy of formation; [i] detonation energy; [j] detonation temperature; [k] detonation pressure; [l] detonation velocity; [m] volume of detonation gases at standard temperature and pressure conditions.

When looking at compound **2** and the energetic salts **3** and **5**, it was observed, that they are insensitive towards friction, with values above 360 N. In regard to the impact values only compound **3** shows a slight sensitivity of 30 J. For compound **3** and **5** the insensitivity can be explained by the crystal water, generally reducing those values. Compound **9** also shows no sensitivity towards impact and friction with values of above 40 J and 360 N. Compound **10** exhibits interesting properties, possessing a high impact sensitivity of 2.5 J, which is close to the range of primary explosives, while at the same time being almost insensitive towards friction stimuli with a value of 360 N. When compared to RDX and CL-20, all compounds are less sensitive, with the exception of compound **10** showing a higher impact sensitivity. It was attempted to measure the friction sensitivity of compound **6** directly after separating it from the reaction mixture, which resulted in positive tests at 1 N. But it has to be mentioned that the *Curtius* degradation visibly took place, as the product turned yellow during the measurement and therefore no certain values could be obtained.

The thermal properties of all compounds were determined by differential thermal analysis. None of the measured compounds show endothermic events, which could be assigned to melting points. In terms of decomposition temperatures, the range starts at a rather low value 124 °C for the perchlorate salt **5** and ends at 209 °C for compound **9**. The remaining three compounds **2**, **3** and **10** show decent decomposition temperatures slightly below 180 °C. The DTA plots of compounds **2**, **9** and **10** are depicted in Figure 9. With the exception of Compound **9**, all measured compounds are less stable towards thermal influences than RDX. The investigated compounds exhibit very high combined nitrogen and oxygen contents up to 84% for compound **3**. Based on the densities, obtained by gas pycnometry or from the crystal structures the energetic properties were calculated with EXPLO5 (V6.05).<sup>[23]</sup> The heats of formation were obtained by CBS-4 M calculations. The densities of compound **2** and its salts **3** and **5** range from 1.56 g cm<sup>-3</sup> to 1.94 g cm<sup>-3</sup> with the neutral compound showing the lowest value, the perchlorate salt the highest value and the nitrate salt a moderate value of 1.70 g cm<sup>-3</sup>, which is in line with the expectations. The densities of compounds **9** and **10** were determined by gas pycnometry, since no crystal structures

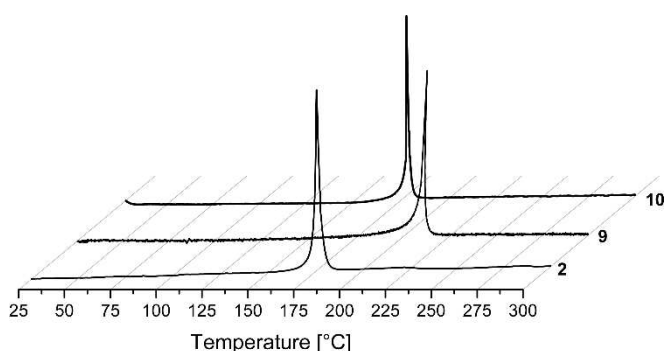


Figure 9. DTA plots of compound **2**, **9** and **10** measured with a heating rate of 5 K·min<sup>-1</sup>.

could be obtained. Compound **9** shows a lower density of 1.73 g cm<sup>-3</sup>, when compared to compound **10**, which was to be expected due to the large size of the molecule. With 1.81 g cm<sup>-3</sup> compound **10** is in the same density range of RDX, which is a promising starting condition for the detonation properties. When looking at the detonation velocities and pressures, the values of the measured compounds range from 7610 ms<sup>-1</sup> and 19.3 GPa for compound **2**, up to 9082 ms<sup>-1</sup> and 36.9 GPa for compound **5**. Therefore, compounds **3** and **5** are able to surpass RDX in terms of their detonation properties, exhibiting detonation velocities around 9000 ms<sup>-1</sup>. Compound **10** still shows decent values which are only slightly below RDX with a detonation velocity of 8654 ms<sup>-1</sup> and a pressure of 31.0 GPa. It was expected, that compounds **2** and **9** are the least well performing, since they lack structural energetic properties. This was confirmed by the calculations, with values of 7610 ms<sup>-1</sup> and 19.3 GPa for compound **2** and 8228 ms<sup>-1</sup> and 25.9 GPa for compound **9**. CL-20 surpasses all synthesized compounds in terms of thermal stability and detonation performance, which was to be expected. But due to much simpler and more cost-efficient syntheses, as well as lower sensitivities, the presented compounds are still a valuable addition to the roster of secondary explosives and prove the worth of compound **2** as an energetic precursor.

### Toxicity Assessment

In order to determine the ecotoxicological impact of the presented precursor, EC<sub>50</sub> measurements based on the bioluminescent *vibrio fischeri* NRRL-B-11177 marine bacteria strain were performed. Therefore, the EC<sub>50</sub> values of compound **2** were measured after 15 and 30 minutes and compared to the measured values of oxalyldihydrazide and glyoxal. The first one was chosen, based on the structural similarities of oxalyldihydrazide to compound **2**. While glyoxal was picked as it is one of the most common precursors in energetic synthesis. The EC<sub>50</sub> value refers to the concentration of a toxicant which induces a response of 50% after a specific exposure time. In this case the EC<sub>50</sub> value is determined by inhibition of the luminescence by 50%, when exposed to the toxicant.<sup>[25]</sup> Based on the resulting effective concentration the measured substances were classified as nontoxic (> 1.00 g L<sup>-1</sup>), toxic (0.10–1.00 g L<sup>-1</sup>), and very toxic (< 0.10 g L<sup>-1</sup>).<sup>[26]</sup> The measured values are shown in Table 2. Compound **2** can be described as nontoxic toward aquatic organisms, since its EC<sub>50</sub> value is above 1 g L<sup>-1</sup>. Oxalyldihydrazide is also categorized as nontoxic, with even higher values, which indicates a slightly increased toxicity of compound **2** due to the hydrazone moiety. Glyoxal is classified as toxic with values of 0.43 g L<sup>-1</sup> and 0.33 g L<sup>-1</sup> after 15 min and 30 min,

| Table 2. EC50 values of <b>2</b> , oxalyldihydrazide and glyoxal. |          |                   |         |
|---|----------|-------------------|---------|
| Incubation  | <b>2</b> | Oxalyldihydrazide | Glyoxal |
| 15 min  | 4.62     | 19.65             | 0.43    |
| 30 min  | 2.61     | 12.99             | 0.33    |

respectively. In summary the hydrazide moiety does not seem to have a negative impact on the toxicity towards aquatic life. Therefore, compound **2** can be described as an ecofriendly precursor for energetic material synthesis.

## Conclusion

In this work, we present 2-hydrazonyl-propandihydrazide (**2**) as a new precursor in energetic material synthesis. Therefore, the energetic salts **3** and **5**, as well as a bridged nitraminobistriazole (**10**) were synthesized deriving from compound **2** by straightforward and short methods. Additionally, a Curtius degradation of 2-hydrazonyl-propandihydrazide (**6**) was observed including the intermediate (**7**) and final product (**8**). Crystal structures of compounds **2–5**, **7** and **8** were determined. The densities range from 1.56 g cm<sup>-3</sup> of the precursor (**2**) to 1.94 g cm<sup>-3</sup> of the perchlorate salt (**5**). All compounds were characterized by NMR, and IR as well as regarding their physicochemical properties, including thermal behavior and sensitivity towards impact and friction. Due to its very unstable character towards various stimuli, compound **6** was only analyzed by IR spectroscopy. For compound **7**, only the crystal structure could be obtained due to the short lifespan of this intermediate at standard conditions. The compounds investigated towards their energetic behavior show almost no friction and impact sensitivities, with the exception of compound **10** (3 J, 360 N) and compound **3** (30 J, > 360 N). The compounds **2**, **3**, **5**, **9**, and **10** were investigated in regard to their detonation parameters, which were calculated with the EXPLO5 code. Compounds **3** and **5** exceed RDX in terms of all calculated values with detonation velocities of 8920 m s<sup>-1</sup> and 9082 m s<sup>-1</sup>, respectively. Compounds **9** and **10** are still in the same range of RDX with values of 8228 m s<sup>-1</sup> and 8654 m s<sup>-1</sup>. Finally, the new precursor was evaluated by the luminous bacteria inhibition test in order to investigate its ecotoxicological impact. It was compared to glyoxal to provide a well-known precursor as reference. 2-hydrazonyl-propandihydrazide (**2**) is categorized as nontoxic, while the measurements show a toxic classification for glyoxal towards aqueous organisms. Future work might involve upscaling, compatibility testing and additional safety evaluation.

## Experimental Section

All chemicals and solvents were purchased from Sigma Aldrich and used without further purification. The general information about analytical devices including NMR, X-ray crystallography, IR, DTA, as well as information about the calculation of the energetic properties can be found in the SI. Compound (**1**) and *N*-methyl-*N*-nitroso-*N'*-nitroguanidine were synthesized according to literature procedures.<sup>[17,27]</sup>

**Caution:** The investigated compounds are potentially toxic and explosive. Therefore, it is recommended to carry out all reactions in a small scale, in addition to using the proper safety equipment, including ear, hand and body protection.

**2-Hydrazonyl-propandihydrazide (2):** Diethyl 2,2-diazidomalonate (**1**) (1.00 g, 4.13 mmol, 1.0 eq) was dissolved in water (5 mL) and

hydrazine hydrate (1.2 mL, 24.77 mmol, 6.0 eq) was added. Afterwards it was stirred for 24 h at room temperature. The precipitate was filtered and washed with cold water. The filtrate was concentrated in vacuo in order to obtain an additional amount of product. Compound (**2**) was obtained as colorless solid (452 mg, 2.82 mmol, 68%). <sup>1</sup>H NMR (400 MHz, DMSO-d<sub>6</sub>) δ (ppm) = 10.52 (s, 2H, NH<sub>2</sub>), 10.20 (s, 1H, NH), 8.88 (s, 1H, NH), 4.47 (s, 2H, NH<sub>2</sub>), 4.24 (s, 2H, NH<sub>2</sub>); <sup>13</sup>C NMR (101 MHz, DMSO-d<sub>6</sub>) δ (ppm) = 165.4, 163.3, 119.5; IR (ATR, rel. int.):  $\tilde{\nu}$  (cm<sup>-1</sup>) = 3386 (m), 3305 (m), 3195 (m), 2170 (w), 2137 (w), 2007 (w), 1992 (w), 1635 (m), 1601 (m), 1552 (m), 1488 (s), 1325 (m), 1279 (m), 1219 (m), 1137 (m), 1090 (m), 990 (m), 962 (s), 815 (m), 794 (m), 721 (s), 633 (m), 555 (s), 488 (m), 407 (s); **Elemental analysis:** calcd. (%) for C<sub>3</sub>H<sub>8</sub>N<sub>6</sub>O<sub>2</sub> (M = 160.14 g mol<sup>-1</sup>): C 22.50, H 5.04, N 52.48; found: C 22.62, H 5.08, N 52.16; **Sensitivities** (grain size: 100–500 μm): BAM impact: > 40 J, BAM friction: > 360 N; **DTA** (5 °C min<sup>-1</sup>): T<sub>exo</sub> = 178 °C.

**2-Hydrazonyl-propandihydrazidum dinitrate·0.25 H<sub>2</sub>O (3):** 2-Hydrazineylidenemalonohydrazide (**2**) (250 mg, 1.56 mmol, 1.0 eq.) was mixed with nitric acid (5 ml, 65%) and stirred at 50 °C for 1 h. Compound (**3**) (310 mg, 1.08 mmol, 69%) was obtained as pale-yellow crystals. <sup>1</sup>H NMR (400 MHz, DMSO-d<sub>6</sub>) δ (ppm) = 11.5–9.0 (broad), 10.53; <sup>13</sup>C NMR (101 MHz, DMSO-d<sub>6</sub>) δ (ppm) = 164.7, 161.3, 115.4; <sup>14</sup>N NMR (27 MHz, DMSO-d<sub>6</sub>) δ (ppm) = -4, -359; IR (ATR, rel. int.):  $\tilde{\nu}$  (cm<sup>-1</sup>) = 3230 (m), 2151 (m), 2010 (m), 1997 (w), 1891 (w), 1646 (m), 1550 (m), 1495 (m), 1417 (m), 1309 (s), 1272 (s), 1186 (s), 1157 (s), 1104 (m), 1043 (m), 1010 (m), 985 (m), 824 (m), 788 (m), 688 (s), 577 (s), 491 (s), 471 (s), 436 (s), 425 (s), 410 (s), 401 (s); **Elemental analysis:** calcd. (%) for C<sub>3</sub>H<sub>10</sub>N<sub>8</sub>O<sub>8</sub>·0.25 H<sub>2</sub>O (290.56 g mol<sup>-1</sup>): C 12.40, H 3.64, N 38.55; found: C 12.05, H 3.40, N 38.29; **Sensitivities** (grain size: 100–300 μm): BAM impact: 30 J, BAM friction: > 360 N; **DTA** (5 °C min<sup>-1</sup>): T<sub>exo</sub> = 167 °C.

**2-Hydrazonyl-propandihydrazidum dichloride monohydrate (4):** 2-Hydrazineylidenemalonohydrazide (**1**) (250 mg, 1.56 mmol, 1.0 eq.) was mixed with hydrochloric acid (5 ml, 30%) and 5 ml water and stirred at room temperature for 1 h. Compound (**4**) (360 mg, 1.54 mmol, 99%) was obtained as pale-yellow crystals. <sup>1</sup>H NMR (400 MHz, DMSO-d<sub>6</sub>) δ (ppm) = 12.0–9.5 (broad), 10.64, 10.56; <sup>13</sup>C NMR (101 MHz, DMSO-d<sub>6</sub>) δ (ppm) = 164.6, 161.2, 115.2; IR (ATR, rel. int.):  $\tilde{\nu}$  (cm<sup>-1</sup>) = 3338 (w), 3185 (w), 2758 (w), 2669 (w), 1983 (w), 1948 (w), 1670 (w), 1648 (w), 1616 (w), 1470 (m), 1335 (w), 1296 (w), 1253 (w), 1213 (w), 1175 (w), 1136 (m), 1066 (w), 1009 (w), 879 (w), 806 (w), 738 (w), 681 (w), 590 (m), 529 (m), 478 (w), 420 (m); **Elemental analysis:** calcd. (%) for C<sub>3</sub>H<sub>10</sub>Cl<sub>2</sub>N<sub>6</sub>O<sub>2</sub>·H<sub>2</sub>O (251.06 g mol<sup>-1</sup>): C 14.35, H 4.82, N 33.47; found: C 14.40, H 4.57, N 33.65; **Sensitivities** (grain size: 100–300 μm): BAM impact: > 40 J, BAM friction: > 360 N; **DTA** (5 °C min<sup>-1</sup>): T<sub>exo</sub> = 191 °C.

**2-Hydrazonyl-propandihydrazidum diperchlorate monohydrate (5):** 2-Hydrazineylidenemalonohydrazide (**2**) (250 mg, 1.56 mmol, 1.0 eq.) was mixed with perchloric acid (0.5 ml, 60%) and 5 ml water and stirred at room temperature for 1 h. Compound (**5**) (130 mg, 0.36 mmol, 23%) was obtained as pale-yellow crystals. <sup>1</sup>H NMR (400 MHz, DMSO-d<sub>6</sub>) δ (ppm) = 10.63, 10.59, 4.98, 4.63; <sup>13</sup>C NMR (101 MHz, DMSO-d<sub>6</sub>) δ (ppm) = 164.7, 161.3, 115.2; IR (ATR, rel. int.):  $\tilde{\nu}$  (cm<sup>-1</sup>) = 3543 (w), 3423 (w), 3149 (w), 1676 (w), 1580 (w), 1494 (m), 1310 (w), 1109 (m), 1041 (m), 929 (w), 807 (w), 619 (m), 585 (m), 484 (m), 417 (m); **Elemental analysis:** calcd. (%) for C<sub>3</sub>H<sub>10</sub>N<sub>6</sub>O<sub>10</sub>Cl<sub>2</sub>·H<sub>2</sub>O (379.06 g mol<sup>-1</sup>): C 9.51, H 3.19, N 22.17; found: C 9.46, H 3.00, N 21.99; **Sensitivities** (grain size: 100–500 μm): BAM impact: > 40 J, BAM friction: > 360 N; **DTA** (5 °C min<sup>-1</sup>): T<sub>exo</sub> = 124 °C.

**2-Hydrazonemalonaldiazide (6):** 2-Hydrazonyl-propandihydrazide (**2**) (500 mg, 3.12 mmol, 1.0 eq.) was dissolved in concentrated hydrochloric acid (10 ml, 32%). Chloroform (40 mL) was added, and the solution was cooled below 0 °C. Sodium nitrite (450 mg, 6.52 mmol, 2.1 eq.), dissolved in water (2 mL), was added dropwise

under heavy stirring, while the temperature was kept below 0 °C. The organic phase was washed with ice water and filtered through a magnesium sulfate layer into a crystallizing bowl. The residue was left for crystallization and compound (5) was obtained as colorless highly hygroscopic crystals (290 mg, 1.59 mmol, 51%). IR (ATR, rel. int.):  $\tilde{\nu}$  (cm<sup>-1</sup>) = 3312 (w), 3162 (w), 2985 (w), 2128 (w), 1978 (w), 1756 (w), 1674 (w), 1573 (w), 1467 (w), 1297 (w), 1235 (w), 1154 (w), 1046 (w), 960 (w), 854 (w), 828 (w), 753 (w), 669 (w), 588 (w), 548 (w), 470 (w), 416 (w).

**3-Carbonylazido-1H-1,2,4-triazol-5-one (7):** 2-Hydrazone-malonyldiazide (6) was stored in the freezer for 2 days at -20 °C. Colorless crystals were obtained from the stored compound, which turned out to be 3-carbonylazido-1H-1,2,4-triazol-5-one (6), shown by X-ray measurements.

**3-Carboxyl-1H-1,2,4-triazol-5-one monohydrate (8):** 2-Hydrazone-malonyldiazide (6) was stored in the refrigerator for 7 days at 3 °C. Yellow crystals were obtained from the stored compound, which turned out to be 3-carboxyl-1H-1,2,4-triazol-5-one (7), shown by X-ray measurements <sup>1</sup>H NMR (400 MHz, DMSO-d<sub>6</sub>):  $\delta$  (ppm) = 12.54 (s, 1H), 12.43 (s, 1H); <sup>13</sup>C NMR (101 MHz, DMSO-d<sub>6</sub>):  $\delta$  (ppm) = 162.5, 155.8, 139.5.

**2-Hydrazonyl malono-di-N-amino-nitroguanidine (9):** 2-Hydrazonylidenemalonohydrazide (2) (725 mg, 4.53 mmol, 1.0 eq.) was dissolved in H<sub>2</sub>O (15 ml) and N-methyl-N-nitroso-N'-nitroguanidine (1.33 g, 9.05 mmol, 2.0 eq.) dissolved in H<sub>2</sub>O (50 ml) was added. The reaction mixture was stirred for 50 min at 95 °C. The precipitate was collected by filtration, washed with cold H<sub>2</sub>O and cold EtOH and dried at rt to yield compound 8 (1.32 g, 3.95 mmol, 87%) as a yellow solid. <sup>1</sup>H NMR (400 MHz, DMSO-d<sub>6</sub>):  $\delta$  (ppm) = 10.70, 10.40, 9.90, 9.84–9.48, 8.66, 7.99; <sup>13</sup>C NMR (101 MHz, DMSO-d<sub>6</sub>):  $\delta$  (ppm) = 165.5, 163.2, 161.4, 161.2, 118.5; IR (ATR, rel. int.):  $\tilde{\nu}$  (cm<sup>-1</sup>) = 3387 (vw), 3293 (vw), 3191 (w), 2971 (vw), 1739 (s), 1669 (vw), 1652 (vw), 1610 (m), 1567 (s), 1505 (m), 1476 (w), 1429 (s), 1376 (s), 1345 (s), 1261 (s), 1230 (vs), 1217 (vs), 1189 (vs), 1116 (m), 1058 (s), 954 (vw), 923 (vw), 836 (vw), 779 (vw), 739 (vw), 563 (vs), 517 (vs), 486 (vs), 473 (vs), 412 (vs); **Elemental analysis:** calcd. (%) for C<sub>5</sub>H<sub>10</sub>N<sub>12</sub>O<sub>6</sub> (334.21 g mol<sup>-1</sup>): C 17.97, H 3.02, N 50.29; found: C 18.08, H 3.04, N 50.43; **Sensitivities** (grain size: 100–500  $\mu$ m): BAM impact: > 40 J, BAM friction: > 360 N; **DTA** (5 °C min<sup>-1</sup>): T<sub>exo</sub> = 209 °C.

**Bis(dinitramino-1H-1,3,4-bis-triazol-5-yl) methylhydrazone (10):** Bis(nitroguanidiny)-2-hydrazone-malonohydrazide (9) (3.40 g, 10.2 mmol, 1.0 eq.) was dissolved in H<sub>2</sub>O (80 ml) and KOH (1.71 g, 30.5 mmol, 3.0 eq.) dissolved in H<sub>2</sub>O (65 ml) was added. The reaction mixture was stirred over night at 80 °C, cooled to 50 °C and conc. HNO<sub>3</sub> (65%) was added until pH = 3. The precipitate was collected by filtration, washed with cold H<sub>2</sub>O and dried for two days at 100 °C to yield compound 10 (1.53 g, 5.13 mmol, 50%) as a beige solid. <sup>1</sup>H NMR (400 MHz, DMSO-d<sub>6</sub>):  $\delta$  (ppm) = 14.17 (bs, 2H, ring-NH), 10.30–9.00 (m, 4H, N-NH<sub>2</sub>, NH); <sup>13</sup>C NMR (101 MHz, DMSO-d<sub>6</sub>):  $\delta$  (ppm) = 152.79, 152.11, 112.03; MS: m/z (ESI<sup>-</sup>) = 297.1 [C<sub>5</sub>H<sub>6</sub>N<sub>12</sub>O<sub>4</sub>]; IR (ATR):  $\tilde{\nu}$  = 3181 (vw), 1560 (m), 1483 (w), 1401 (w), 1225 (s), 1144 (m), 1044 (m), 988 (m), 913 (m), 871 (m), 771 (s), 731 (s), 707 (s), 614 (s), 492 (vs), 419 (vs); **Elemental analysis:** calcd. (%) for C<sub>5</sub>H<sub>6</sub>N<sub>12</sub>O<sub>4</sub>: C 20.14, H 2.03, N 56.37; found: C 19.79, H 2.23, N 53.88; **Sensitivities** (grain size: 300–1000  $\mu$ m): BAM impact: 2.5 J, BAM friction: 360 N; **DTA** (onset, 5 °C min<sup>-1</sup>): T<sub>exo</sub> = 177 °C.

Deposition Numbers 2149590 (for 2) 2149591 (for 3), 2149592 (for 4) 2149593 (5) 2149594 (for 7), and 2149595 (for 8) contain the supplementary crystallographic data for this paper. These data are provided free of charge by the joint Cambridge Crystallographic Data Centre and Fachinformationszentrum Karlsruhe Access Structures service www.ccdc.cam.ac.uk/structures.

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## Conflict of Interest

The authors declare no conflict of interest.

## Data Availability Statement

The data that support the findings of this study are available from the corresponding author upon reasonable request.

**Keywords:** Energetic materials · Precursors · Structure elucidation · Triazole · Toxicity assessment

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