



RESEARCH ARTICLE

Trinitroethyl hydrazides of dicarbonic acids – Energetic compounds with high oxygen and nitrogen content

Thomas M. Klapötke | Burkhard Krumm | Christian Riedelsheimer

Department of Chemistry, Ludwig-Maximilian University Munich, Butenandtstr. 5–13(D), Munich, Germany

Correspondence

Thomas M. Klapötke and Burkhard Krumm, Department of Chemistry, Ludwig-Maximilian University Munich, Butenandtstr. 5–13(D), 81377 Munich, Germany.
Email: tmk@cup.uni-muenchen.de and bkr@cup.uni-muenchen.de

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Abstract

Many currently used energetic materials need to be replaced with new compounds due to toxicity or other drawbacks. Among these is the oxidizer ammonium perchlorate, often used in solid state propellants, which itself, as well as its combustion products, poses health and environmental issues. Herein, three new polynitro energetic compounds are presented containing trinitroethyl moieties. Starting from easily available starting materials, such as malonic acid ethylester, diglycolic and diaminodiacetic acid, simple and straightforward syntheses were performed to obtain first the corresponding hydrazides and subsequently the trinitroethyl hydrazides in good yields and high purity. These compounds have a positive oxygen balance (assuming to the formation of CO), a high oxygen and nitrogen content and moderate densities. Full characterization was performed by NMR spectroscopy, vibrational analysis and elemental analysis. By using the Gaussian program package, the heats of formation were calculated and the energetic parameters were estimated utilizing the EXPLO5 computer code.

KEYWORDS

energetic materials, hydrazides, NMR spectroscopy, synthesis, trinitroethanol

1 | INTRODUCTION

In the field of energetic materials, there are up to now many different bridging units that have been used as the backbone unit for new energetic compounds. These range from pure alkylene to oxygen or nitrogen containing alkylene bridges, or combinations of these [1–4]. By adding reactive terminal functional groups, such as acid groups to these bridges, a variety of compounds can be produced. A well-known example of a hydrocarbon moiety is malonic acid, which can be further modified at the acid position to introduce energetic groups such as azido, nitro or trinitroethyl groups, or to use the acid group for ring closure, such as triazoles [5–7]. Further units like the oxapropyl and nitrazapropyl units are more and more used for energetic compounds, because they contain additional oxygen as well as nitrogen for the

nitrazapropyl unit and therefore can increase the energetic performance [8–9].

In the current research for high-energy dense oxidizers, the goal is to find an alternative to the current most commonly used oxidizer ammonium perchlorate (AP), which exhibits very good properties for oxidizers [10]. The oxygen balance indicates whether there is an excess of oxygen or a deficit after combustion. Ammonium perchlorate shows an extremely high value of +34% in respect to the formation of CO as well as CO₂ [11]. Furthermore, a high thermal stability as well as an easy and economic synthesis favors the ongoing use of AP, although it also has many disadvantages. A major disadvantage is the toxicity of the perchlorate ion, as well as of some decomposition products, which are released into the atmosphere and thus harm the environment. Another disadvantage is obvious at slow cook-off tests, which

show the formation of acidic side-products leading to cracks and cavities in the composite. This can lead to negative effects in terms of the rocket propellant performance [10].

For potential replacements of ammonium perchlorate, several requirements have to be fulfilled, such as a high and positive oxygen balance, an economic synthesis, high density, high thermal stability and a specific impulse in the range of AP [10]. 2,2,2-Trinitroethanol (TNE) has a suitable oxygen balance ($\Omega_{\text{CO}}=31\%$), is readily synthesized, and is accordingly well qualified as starting material for syntheses for potential oxidizers. Furthermore, the trinitroethyl moiety can be incorporated quite easily as the last step of a multistep synthesis, even though 2,2,2-trinitroethanol already has some energetic properties. 2,2,2-Trinitroethyl *N*-nitrocarbamate (TNENC), tris(2,2,2-trinitroethyl) orthoformate (TNEF) and bis(2,2,2-trinitroethyl) oxalate (BTNEO) are TNE-based compounds, which, besides the oxygen balance, show good decomposition temperature, performance and chemical reliability [12–14].

In order to further increase the energetic performance, it would be desirable to perform a Mannich reaction of hydrazides with TNE. Here, the TNE group provides a high oxygen content and the hydrazide group can further increase the nitrogen content, producing a more energetic compound overall [15–16].

In this contribution three different backbones were converted into their corresponding hydrazides and then reacted with TNE *via* a Mannich reaction. The economic and readily available starting materials, malonic acid diethyl ester, diglycolic acid and iminodiacetic acid, have major differences in carbon, nitrogen and oxygen contents, which means that the target molecules could exhibit different properties.

2 | EXPERIMENTAL SECTION

Solvents, deuterated solvents and all further chemicals were used as received from suppliers, without further purification. NMR spectra were recorded with a Bruker 400 MHz spectrometer at ambient temperature. The chemical shifts were referenced with respect to external Me_4Si (^1H 399.8 MHz; ^{13}C 100.5 MHz) and MeNO_2 (^{14}N 28.9 MHz).

Infrared spectra were recorded at ambient temperature in the range 4000–400 cm^{-1} on a Perkin-Elmer Perkin-Elmer BXII FT-IR system with a Smith DuraSampler IR II diamond ATR.

Analyses of C/H/N contents were performed with an Elementar vario EL or Elementar vario micro cube. Melting and decomposition temperatures of the

described compounds were measured through differential thermal analysis (DTA) with an OZM Research DTA 552-Ex instrument. The samples were measured in a range of 25–400 °C at a heating rate of 5 °C min^{-1} .

The sensitivities towards impact and friction were determined with a BAM drop hammer [17] and a BAM friction tester [18].

All quantum chemical calculations were carried out using the Gaussian 16 program package [19]. The enthalpies (H) and free energies (G) were calculated using the complete basis set (CBS) method of Petersson and co-workers in order to obtain very accurate energies. The CBS models are using 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 starts 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. A MP4(SDQ)/6-31+(d,p) calculation is used to approximate higher order contributions. In this study, we applied the modified CBS-4 M [20–21].

Caution: The compounds discussed here are sensitive materials. Therefore, it is recommended to carry out all reactions on a small scale, using the proper safety equipment, including ear, hand and body protection.

N,N-bis(2,2,2-trinitroethyl)malonic acid dihydrazide (1)

2,2,2-Trinitroethanol (1.37 g, 7.56 mmol, 2 eq.) was dissolved in methanol (4 mL). Malonic acid dihydrazide [22] (500 mg, 3.78 mmol, 1 eq.) was also solved in methanol (10 mL) and further added dropwise. A yellow precipitate was formed immediately. The mixture was stirred until the precipitate fully dissolved. After adding water (50 mL), a precipitate was formed again, which was filtered and washed with water. The product (**1**, 820 mg, 46%) was obtained as a yellow powder.

^1H NMR (400 MHz, CD_3CN , ppm) $\delta=8.44$ (d, 2H, $^3J_{\text{H,H}}=5.7$ Hz, CONH), 5.26 (td, 2H, $^3J_{\text{H,H}}=6.1$, 5.7 Hz, NHCH₂), 4.54 (d, 4H, $^3J_{\text{H,H}}=6.1$ Hz, CH₂C(NO₂)₃), 3.03 (s, 2H, COCH₂). $^{13}\text{C}\{^1\text{H}\}$ NMR (101 MHz, CD_3CN , ppm) $\delta=168.0$ (CO), 137.6 (br, C(NO₂)₃), 55.8, 55.6 (CH₂). ^{14}N NMR (29 MHz, CD_3CN , ppm) $\delta=-30$ (NO₂). **Elemental Analysis:** C₇H₁₀N₁₀O₁₄ (458.21): calc. C 18.35, H 2.20, N 30.57%; found C 18.24, H 2.12, N 30.29%. **IR:** (ATR): $\tilde{\nu}$ [cm^{-1}]=2983 (w), 2893 (w), 2315 (w), 2240 (w), 2204 (w), 2176 (w), 2166 (w), 2144 (w), 2092 (w), 2042 (w), 2016 (w), 2000 (w), 1924 (w), 1691 (s), 1588 (vs), 1552 (s), 1507 (m), 1469 (m), 1423 (m), 1370 (m), 1336 (m), 1305 (s), 1255 (m), 1255 (m), 1236 (m), 1225

(m), 1194 (m), 1142 (m), 1113 (m), 1084 (w), 1034 (m), 990 (m), 956 (m), 868 (m), 856 (m), 807 (s), 786 (s), 729 (m), 711 (m), 688 (m), 672 (m), 650 (m), 627 (m), 552 (m). **DTA** ($5^{\circ}\text{C min}^{-1}$): 115°C (dec.). **Sensitivities** (BAM): impact 4 J; friction 192 N (grain size 100–500 μm).

N,N-bis(2,2,2-trinitroethyl)diglycolic acid dihydrazide (**2**)

2,2,2-Trinitroethanol (1.12 g, 6.16 mmol, 2 eq.) was dissolved in methanol (3 mL) and diglycolic acid dihydrazide [23] (500 mg, 3.98 mmol, 1 eq.) in methanol (10 mL). The diglycolic acid dihydrazide solution was added to the other solution. The combined solution was stirred for 2 h at room temperature. After adding water (50 mL) to the solution, a yellow precipitate was formed, which was filtered and washed with water. The product (**2**, 1.03 g, 51%) was obtained as a yellow solid.

^1H NMR (400 MHz, CD_3CN , ppm) δ =8.61 (d, 2H, $^3J_{\text{H,H}}=4.4$ Hz, NH), 5.23 (td, 2H, $^3J_{\text{H,H}}=6.2$, 4.4 Hz, NH), 4.58 (d, 4H, $^3J_{\text{H,H}}=6.2$ Hz, $\text{CH}_2\text{C}(\text{NO}_2)_3$), 4.04 (s, 4H, OCH_2). **$^{13}\text{C}\{^1\text{H}\}$ NMR** (101 MHz, CD_3CN , ppm) δ =170.5 (CO), 128.8 (br, $\text{C}(\text{NO}_2)_3$), 71.0 (OCH_2), 55.7 (NCH_2). **^{14}N NMR** (29 MHz, CD_3CN , ppm) δ =−30 (NO_2). **Elemental Analysis:** $\text{C}_8\text{H}_{12}\text{N}_{10}\text{O}_{15}$ (488.24): calc. C 19.68, H 2.48, N 28.69%; found C 19.90, H 2.43, N 28.32%. **IR:** (ATR): ν [cm $^{-1}$]=3280 (m), 3271 (m), 1698 (m), 1654 (m), 1579 (vs), 1517 (m), 1493 (s), 1454 (m), 1434 (w), 1412 (w), 1397 (w), 1336 (m), 1305 (s), 1246 (w), 1237 (w), 1133 (s), 1113 (m), 1048 (m), 998 (m), 977 (w), 962 (w), 878 (m), 856 (m), 856 (m), 794 (s), 779 (s), 756 (m), 722 (m), 713 (m), 670 (w), 651 (w), 628 (w), 592 (m), 552 (m). **DTA** ($5^{\circ}\text{C min}^{-1}$): 128°C (dec.). **Sensitivities** (BAM): impact 3 J; friction 192 N.

N,N-bis(2,2,2-trinitroethyl)nitraminodiacetic acid dihydrazide (**3**)

2,2,2-Trinitroethanol (0.508 g, 2.81 mmol, 2.3 eq.) was dissolved in methanol (3 mL). Nitraminodiacetic acid dihydrazide [22] (250 mg, 1.21 mmol, 1.0 eq.) was dissolved in methanol (10 mL) and added to the first solution. The combined solution was stirred for 2 h at room temperature. Adding water (50 mL) to the solution, resulted in the formation of a yellow precipitate, which was filtered and washed with water. The product (**3**, 316 mg, 49%) was obtained as a yellow solid.

^1H NMR (400 MHz, CD_3CN , ppm) δ =9.17 (d, 2H, $^3J_{\text{H,H}}=4.4$ Hz, CONH), 5.32 (td, 2H, $^3J_{\text{H,H}}=6.1$, 4.4 Hz, NHCH_2), 4.56 (d, 4H, $^3J_{\text{H,H}}=6.1$ Hz, $\text{CH}_2\text{C}(\text{NO}_2)_3$), 4.40 (s, 4H, NCH_2). **$^{13}\text{C}\{^1\text{H}\}$ NMR** (101 MHz, CD_3CN , ppm) δ =168.6 (CO), 137.7 (br, $\text{C}(\text{NO}_2)_3$), 55.6, 55.1 (CH_2). **^{14}N NMR** (29 MHz, CD_3CN , ppm) δ =−30 (CNO_2), −31 (NNO_2). **Elemental Analysis:** $\text{C}_8\text{H}_{12}\text{N}_{12}\text{O}_{16}$ (532.25):

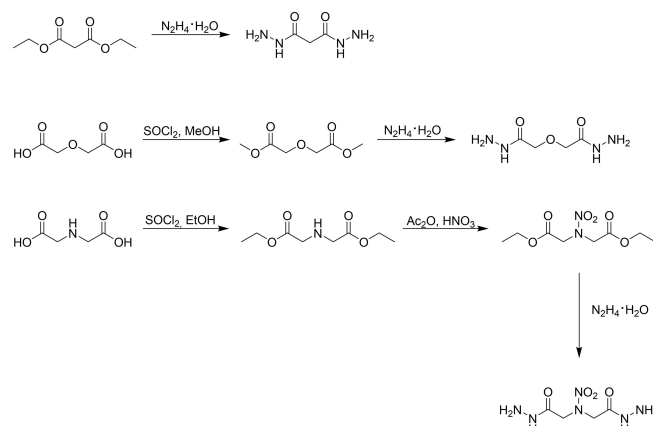
calc. C 18.05, H 2.27, N 31.58%; found C 18.28, H 2.35, N 31.34%. **IR:** (ATR): ν [cm $^{-1}$]=3336 (w), 3279 (w), 3265 (w), 3234 (w), 3226 (w), 3218 (w), 3203 (w), 3188 (w), 3010 (w), 1736 (w), 1682 (m), 1678 (m), 1585 (vs), 1557 (m), 1538 (s), 1532 (s), 1489 (m), 1456 (w), 1439 (m), 1375 (w), 1284 (s), 1149 (w), 1109 (w), 1109 (w), 943 (w), 878 (w), 856 (w), 804 (m), 780 (m), 764 (m), 653 (m), 553 (w), 545 (w). **DTA** ($5^{\circ}\text{C min}^{-1}$): 122°C (dec.). **Sensitivities** (BAM): impact 4 J; friction 120 N.

3 | RESULTS AND DISCUSSION

3.1 | Synthesis

For the synthesis of the three target compounds, the corresponding hydrazides were prepared as reported (Scheme 1) [22–23]. Readily available compounds, malonic acid diethyl ester, diglycolic acid and iminodiacetic acid, were chosen as starting compounds. For the two diacids, the corresponding ester had to be prepared first. For the diglycolic acid the methyl ester and for the iminodiacetic acid the ethyl ester were obtained using thionyl chloride and the corresponding alcohol methanol or ethanol [24–25]. In this process, thionyl chloride activates the acid function by forming the corresponding acid chloride, which immediately reacts further with the alcohol to form the corresponding ester. Due to the formation of only gaseous by-products SO_2 and HCl , very high yields were obtained.

In the case of the iminodiacetic acid diethyl ester, nitration of the bridged nitrogen to the corresponding nitramino derivative was performed. This nitration was carried out using acetic anhydride and anhydrous nitric acid and, after quenching on ice, a colorless powder was obtained in 80% yield [22].



SCHEME 1 Syntheses of the hydrazides of malonic acid diethyl ester, diglycolic acid and iminodiacetic acid [22–25].

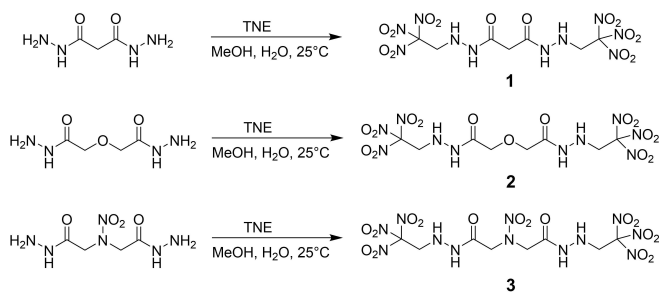
The next step was hydrazinolysis from the various esters with hydrazine monohydrate. This process utilized the insolubility of the hydrazides in ethanol, which precipitated during the reaction and were filtered. As a result, very high up to quantitative yields could be achieved [22–23].

The quick hydrolysis of 2,2,2-trinitroethanol is utilized for the synthesis of the target compounds, resulting in the formation of formaldehyde and trinitromethane. Thus, using a Mannich reaction, the hydrazides can react first with the generated formaldehyde and subsequently with the generated trinitromethane to give the corresponding trinitroethyl hydrazides. The reaction can either be carried out in water, or the reactants are first dissolved in methanol and then water is added [15–16]. For the syntheses of *N,N*-bis(2,2,2-trinitroethyl)malonic acid dihydrazide (**1**), *N,N*-bis(2,2,2-trinitroethyl)diglycolic acid dihydrazide (**2**), *N,N*-bis(2,2,2-trinitroethyl)nitraminodiacetic acid dihydrazide (**3**) it has been shown that performing in methanol and adding water not only improves the purity of the compounds, but also the yield, compared to performing in water only (Scheme 2). As a result, the TNE-hydrazides were obtained as yellow powders with yields of 46% for **1**, 51% for **2** and 49% for **3**.

3.2 | NMR spectroscopy

The characterization of **1**, **2** and **3** was performed by ^1H , ^{13}C and ^{14}N NMR spectroscopy in CD_3CN . All spectra and assignments can be found in the Experimental Section or in the Supporting Information (Figures S1–S3).

For all compounds, four resonances were detected in the ^1H NMR spectrum. The NH resonance adjacent to the carbonyl group is found in the range of 9.17–8.44 ppm as a doublet with a coupling constant of $^3J_{\text{H,H}} = 5.7$ Hz for **1**, respectively 4.4 Hz for **2** and **3**. The other NH resonance, which is connected to the trinitroethyl



SCHEME 2 Syntheses of *N,N*-bis(2,2,2-trinitroethyl)malonic acid dihydrazide (**1**), *N,N*-bis(2,2,2-trinitroethyl)diglycolic acid dihydrazide (**2**), and *N,N*-bis(2,2,2-trinitroethyl)nitraminodiacetic acid dihydrazide (**3**).

group, appears in the range of 5.32–5.23 ppm, which shows a triplet of doublets, due to the coupling with the neighboring hydrogen atoms of the CH_2 and NH groups. The multiplets show two different coupling constants, a larger value of $^3J_{\text{H,H}} = 6.1/6.2$ Hz and a smaller value of $^3J_{\text{H,H}} = 5.7$ Hz for **1** and $^3J_{\text{H,H}} = 4.4$ Hz for **2** and **3**, respectively. The resonance of the methylene group of the trinitroethyl group is detected at 4.58–4.54 ppm as a doublet with a matching coupling constant of $^3J_{\text{H,H}} = 6.1/6.2$ Hz. The resonance of the methylene group of the bridging moieties is found as singlets at 3.03 ppm for **1**, 4.04 ppm for **2**, and 4.40 ppm for **3**.

The ^{13}C NMR spectra also exhibit four signals for each of the three compounds. The carbonyl resonances were detected in the region of 170.5–168.0 ppm. The resonance of the trinitromethyl carbon atom is found typically as broadened signals at 137.6(**1**)/137.7(**3**) and 128.8 (**2**) ppm. Interestingly, that of the oxygen-bridged derivative **2** shows a significant difference of 9 ppm compared to those of **1** and **3**. Similarly, the resonances of the two methylene groups are found very close to each other for **1** and **3** in the region of 55.8–55.1 ppm, whereas for **2** the signal of the methylene group next to the oxygen is shifted to 71.0 ppm and the CH_2 group of the trinitroethyl group is located in the same region at 55.7 ppm as found for **1** and **3**.

The ^{14}N NMR resonances of the nitro groups for **1**, **2** and **3** were detected at -30 ppm with an additional shoulder at -31 ppm for the NNO_2 resonance of **3**, whereas those of the hydrazide moieties are not visible due to the large linewidth.

In addition, characterization of **1–3** was performed with IR spectroscopy (Supporting Information, Figure S4).

3.3 | Physicochemical properties

The physical properties as well as the energetic parameters of the trinitroethyl hydrazides **1–3** were determined, calculated and summarized in Table 1. The thermal stability was determined by differential thermal analysis (DTA) measurements in the temperature range of 25–400 °C with a heating rate of 5 °C min^{-1} (Supporting Information, Figure S5). The onset decomposition temperatures are in the same range of 115–128 °C, whereas the highest value shows **2** and the lowest value **1** and **3** is in between. Compared to ammonium perchlorate (240 °C), all compounds show a significantly lower thermal stability.

Regarding the sensitivities, which were performed according to the BAM standards [17–18], **1–3** show again quite similar values. They show moderate friction

TABLE 1 Physical and energetic properties of **1–3** compared to ammonium perchlorate (AP).

	1	2	3	AP [11]
Formula	C ₇ H ₁₀ N ₁₀ O ₁₄	C ₈ H ₁₂ N ₁₀ O ₁₅	C ₈ H ₁₂ N ₁₂ O ₁₆	NH ₄ ClO ₄
<i>M</i> [g mol ⁻¹]	458.21	488.24	532.25	117.49
<i>T</i> _{dec} [°C] ^[a]	115	128	122	240
<i>IS</i> [J] ^[b]	4	3	4	20
<i>FS</i> [N] ^[b]	192	192	120	360
ρ [g cm ⁻³] ^[c]	1.77	1.66	1.72	1.95
<i>O</i> [%] ^[d]	48.9	49.2	48.1	54.5
<i>N + O</i> [%] ^[d]	79.5	77.8	79.7	66.4
Ω_{CO} [%] ^[e]	7	3	6	34
Ω_{CO_2} [%] ^[e]	-17	-23	-18	34
$\Delta H_{\text{m}}^{\circ}$ [kJ mol ⁻¹] ^[f]	-255.6	-373.8	-171.1	-295.8
EXPLO5 V6.05				
<i>V</i> _{det} [m s ⁻¹] ^[g]	8383	7931	8292	6855
<i>p</i> _{det} [MPa] ^[g]	30.7	26.3	29.5	18.0
<i>I</i> _{sp} [s] ^[h]	254	252	258	154
<i>I</i> _{sp} [s] ^[h] (15% Al)	266	265	268	234
<i>I</i> _{sp} [s] ^[h] (15% Al, 14% bind.)	237	234	240	257

^[a] Onset decomposition point *T*_{dec} from DTA measurements, heating rate 5 °C min⁻¹.

^[b] Sensitivity towards impact *IS* and friction *FS*.

^[c] Densities measured by gas pycnometer.

^[d] Oxygen and nitrogen content.

^[e] Oxygen balance assuming either the formation of CO or CO₂.

^[f] Heat of formation calculated at CBS-4 M level using GAUSSIAN16 [20].

^[g] Predicted detonation velocity and detonation pressure.

^[h] Specific impulse *I*_{sp} of the neat compound and compositions with aluminum or aluminum and binder (6% polybutadiene acrylic acid, 6% polybutadiene acrylonitrile and 2% bisphenol A ether) using EXPLO5 (Version 6.05) program package (chamber pressure 7 MPa, nozzle pressure 0.1 MPa, isobaric combustion, equilibrium to throat and frozen to exit) [26].

sensitivities in the range of 120–192 N and quite high impact sensitivity of 3–4 J. Therefore, the compounds are more sensitive than ammonium perchlorate, but still in a region in which safe working can be ensured.

The oxygen content of the trinitroethyl hydrazides are slightly below 50%, which is only slightly lower than AP. But in case of the total oxygen and nitrogen content, the values are almost 80% for **1** and **3** and slightly below 78% for **2**, whereas AP shows only a value of around 66%. Regarding the oxygen balance, the three new compounds show a positive value assuming the formation of CO, but in case of the formation of CO₂ the values are negative. Since the oxygen balance is mainly dependent on the oxygen content, they are slightly inferior compared to AP, but still show moderate values.

Since it was not possible to obtain crystal structures, the density was determined experimentally by gas pycnometer. The highest value was obtained of **1** with 1.77 g cm⁻³ and the lowest value for **2** with 1.66 g cm⁻³, whereas **3** is with 1.72 g cm⁻³ again in between.

By using the densities and the calculated heat of formation values, which were calculated on CBS-4 M level,

the energetic parameters were calculated with EXPLO5 code [26]. For the detonation velocity, **1** shows the highest value with almost 8400 ms⁻¹ followed by **3** with 8300 ms⁻¹ and the lowest value shows **2** with around 7900 ms⁻¹. These values are much higher compared to the one of AP (6855 ms⁻¹), which is due to, among other factors, the much higher oxygen and nitrogen content.

The values for the specific impulse *I*_{sp} of the neat compounds **1–3** are in the range of 252–258 s and are therefore much higher compared to AP with 154 s. The same applies to the values in combination with 15% aluminum, which range from 265 to 268 s, whereas AP shows a value of 234 s. However, the values in combination with 15% aluminum and 14% binder are lower compared to AP (234–240 s vs. 257 s).

In summary, the trinitroethyl hydrazides **1–3** show interesting energetic properties. However, they exhibit drawbacks especially with respect to their thermal stability. Nevertheless, **1** is the best compound overall, especially in terms of oxygen balance and energetic properties.

4 | CONCLUSION

In this study, new trinitroethyl hydrazides of dicarbonic acids were synthesized and fully characterized by NMR spectroscopy, thermal stability, sensitivities and energetic parameters. Readily available acids or esters were converted into the corresponding hydrazides and via Mannich reaction with 2,2,2-trinitroethanol into the trinitroethyl substituted hydrazides **1**, **2** and **3** in high purity without further purification. The compounds show a positive oxygen balance regarding the formation of CO and have relatively high oxygen and nitrogen contents. The energetic parameters showed that the malonic, glycolic and iminodiacetic acid derivatives **1–3** have a much higher detonation velocity and specific impulse of the neat compounds, as well as together with 15% aluminum compared to ammonium perchlorate. However, the compounds are disadvantageous in terms of thermal stability, as well as a lower specific impulse together with aluminum and binder than ammonium perchlorate. Overall, the malonic acid dihydrazide **1** exhibits the best physical and energetic properties among the three, due to the best detonation velocity and moderate sensitivity, as well as its oxygen balance.

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DATA AVAILABILITY STATEMENT

The data that supports the findings of this study are available in the supplementary material of this article.

ORCID

Thomas M. Klapötke  <http://orcid.org/0000-0003-3276-1157>

Burkhard Krumm  <http://orcid.org/0000-0002-2100-4540>

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