Investigation and Characterization of Nitrazapropane-, Oxapropane- and Trinitrazaheptane-Bridged Nitro Esters

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In this work, 1,3-dinitroxy-2-nitrazapropane and 1,7-dinitroxy-2,4,6-trinitrazaheptane were synthesized and investigated. Starting from hexamine, the open-chain compounds were prepared by a modified Bachmann procedure which is commonly used for the synthesis of hexogen (RDX) and octogen (HMX). All new compounds were characterized by NMR spectroscopy, X-ray diffraction, vibrational analysis and elemental analysis. Their thermal behavior was studied by differential thermal analysis (DTA) and thermogravimetric analysis (TGA). The sensitivities towards impact (IS) and friction (FS) were determined according to the BAM (Bundesanstalt für Materialforschung und -prüfung) standard method. Their energetic properties, which were determined from the energies of formation at the CBS-4 M level, were calculated using the EXPLO5 computer code. Moreover, 1,3-dinitroxy-2-oxapropane was synthesized and investigated. The various compounds were compared with each other and with the commonly used explosives in terms of their physicochemical properties and detonation behavior.

Introduction

RDX, also known as hexogen, is one of the best-researched and most-used secondary explosives.[1] It has several applications in the civilian as well as military sector, for example in combination with a binder used as plastic-bonded explosives (PBX).[1–3] With a moderate sensitivity towards external stimuli and high detonation performance RDX (1,3,5-trinitro-1,3,5-triazinane) is a popular energetic material. In addition, the preparation is quite facile. Nowadays, there are many procedures known for RDX synthesis.[1,4]

Two of the most studied and in industry used synthesis are the Woolwich process and the Bachmann process.[1,4–6] In the Woolwich synthesis, RDX is obtained using hexamine as starting material and only nitric acid as the nitration agent.[1,6] In the Bachmann process a mixture of nitric acid, ammonium nitrate and acetic anhydride is used as a nitration mixture.[4,7] The Bachmann process, however, allows not only the targeted production of RDX starting from hexamine, but also its eight-membered ring derivative HMX (1,3,5,7-tetranitro-1,3,5,7-tetrazocane), by adjusting the reaction conditions.[8–9] As can be seen from Figure 1, a lower reaction temperature during nitration is more suitable to obtain HMX as the main product. In addition, the preferred synthesis of HMX uses a lower acidity and a smaller amount of ammonium nitrate.[1,9–11]

This modification of the reaction conditions is especially advantageous because two different products can be produced at the same industrial plant using the same chemicals just by changing a few conditions. As shown in Figure 1, the conditions can also be changed in such a way that the open-chain nitramines 1,3-diacetoxy-2-nitrazapropane and 1,7-diacetoxy-2,4,6-trinitrazaheptane are formed preferentially.[12–13] Here the reaction temperature is significantly lower than the temperature of the other two reactions. In addition, no ammonium nitrate is required, but reaction time necessitates 18 hours, while the synthesis of RDX and HMX is finished after only one hour.[12–13]

In this work, attempts were made to synthesize new energetic materials based on these open-chain nitramines, displayed in Figure 1. From these precursors, further promising derivatives could be produced at existing Bachmann plants and

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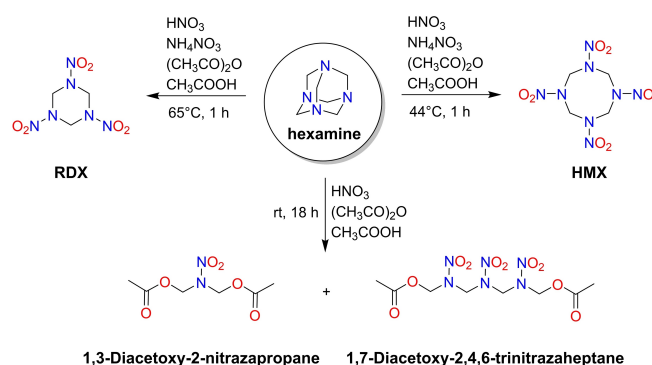
Figure 1. Products obtained from the nitration of hexamine with different reaction conditions.

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thus, may find versatile applications. Already known from the literature are the corresponding diazido derivatives, which are, however, difficult for a possible application due to their very high sensitivity.[12] The goal in this work, was to look for a route to the corresponding nitro esters, which are very similar to nitroxyethylnitramine (NENA) compounds and could represent promising energetic materials by combining both nitro ester and nitramine moiety in one compound.[14–15] 1,3-Dinitroxy-2-nitrazapropane is mentioned once in literature but apparently was impossible to isolate due to its instability.[16] Furthermore, attempts were made to synthesize the corresponding oxapropane-bridged dinitroxy compound which is also only mentioned once in literature without analysis or further characterization.[16] Due to its similar structure to the widely used plasticizers EGDN (ethylene glycol dinitrate), DEGDN (diethylene glycol dinitrate), and TEGDN (triethylene glycol dinitrate), this could be a potential application area for 1,3-dinitroxy-2-oxapropane.[17–18] In addition, compounds with oxapropane bridges should show better thermal stability compared to nitrazapropane bridged compounds, which would make them even more promising for a potential application in safety concerns.[19]

Results and Discussion

Synthesis

1,3-Diacetoxy-2-nitrazapropane (**1**) and 1,7-diacetoxy-2,4,6-trinitrazaheptane (**2**) were prepared by a modified literature procedure.[12–13] Starting from hexamine, the Bachmann nitration reaction was modified to give the open-chain nitramines as the main products. After 18 hours according to Scheme 1, **2** can be easily separated by filtration. From the remaining filtrate, **1** is obtained by vacuum distillation at elevated temperatures of around 170 °C. Afterward, both acetoxy functionalized **1** and **2** were chlorinated using hydrogen chloride to obtain 1,3-dichloro-2-nitrazapropane (**3**) and 1,7-dichloro-2,4,6-trinitrazaheptane (**4**).

In order to obtain the corresponding nitro esters **5** and **6** starting from **3** and **4**, different approaches were attempted for the nitrazapropane and trinitrazaheptane compounds. First, a classical nitration reaction using fuming nitric acid as nitration
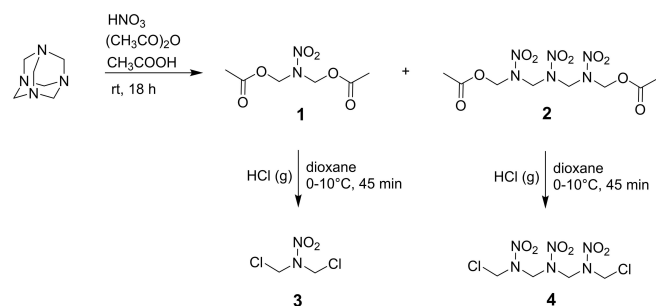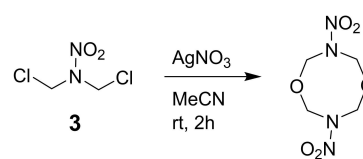
agent was attempted in each case, shown in Scheme 2. This was successful for both, the nitrazapropane and the trinitrazaheptane derivatives and **5** and **6** were obtained through a nucleophilic substitution reaction. In both cases, however, it should be noted that a short reaction time in nitric acid is crucial, and that even after separation of the products it is essential to ensure extensive washing with water, until free of acid to avoid decomposition. As known from literature, accidents have occurred because residual acid in nitro esters has led to uncontrolled autocatalytic decomposition reactions.[18,20–21] As shown in Scheme 2 for reaction pathway II, alternatively the chloromethyl groups can be converted into the nitro esters (nitroxy or nitratomethyl groups) by reaction with silver nitrate in acetonitrile. In this so-called Victor-Meyer reaction,[22] it was taken advantage of the poor solubility of silver chloride in organic solvents. The reaction mechanism here also follows an S_N2 mechanism and **5** and **6** were obtained pure after filtration and extraction.

Both routes work different for **5** and **6**; whereas **5** is obtained in larger yields *via* nitration with AgNO$_3$ (60% *vs.* 30%), **6** is the opposite *via* nitration with HNO$_3$ (75% *vs.* 34%).
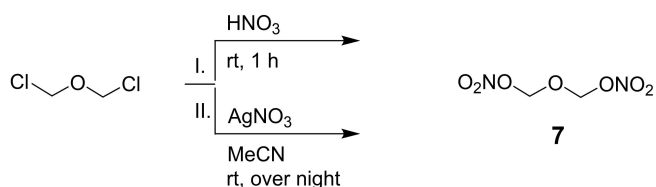
For the nitration of **3** *via* pathway II different reaction times were tested to determine the best conditions. It was found that if **3** is stirred with silver nitrate for only 2 hours, an inseparable mixture is observed and not only the desired product. In this mixture, a cyclized product is formed in very small amounts identified by X-ray diffraction as 3,7-dinitro-1,5,3,7-dioxadiazocane, shown in Scheme 3 and Figure 7. However, it was not possible to specifically prepare and isolate the compound, therefore it was treated as a by-product with no further analysis possible. Thus, to obtain pure **6**, a reaction time of at least 12 h is necessary.
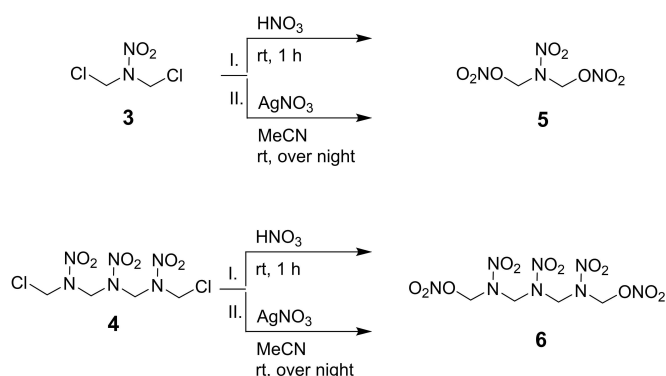
Scheme 2. Conversion of **3** and **4** into the nitro esters **5** and **6**.

Scheme 1. Synthetic route to the chloromethyl substituted nitramines **3** and **4**.

Scheme 3. 3,7-Dinitro-1,5,3,7-dioxadiazocane as a product of nitration after short reaction time.

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Scheme 4. Nitration of bis-chloromethyl ether to form the corresponding nitrate **7**.

Figure 3. ^{15}N NMR spectrum of 1,7-dinitroxy-2,4,6-trinitrazaheptane (**6**) in acetone-d_6.
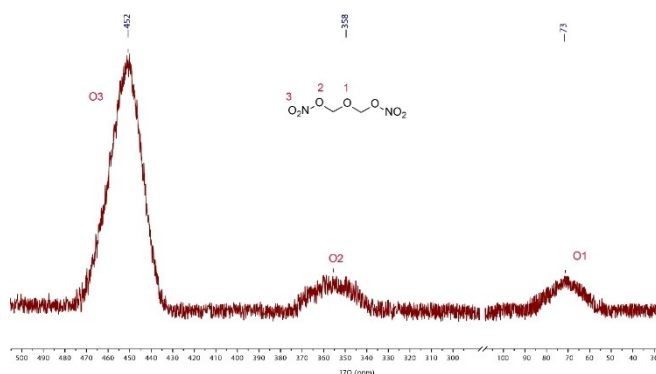
Figure 4. ^{17}O NMR spectrum of 1,3-dinitroxy-2-oxapropane (**7**) as a neat liquid.

1,3-Dichloro-2-oxapropane (bischloromethyl ether) was prepared according to a literature procedure.[23] Here as well, the nitration of the chloromethyl group was attempted via two different pathways as shown in Scheme 4.

A comparison of both options shows that nitration with silver nitrate is preferable. While the nitration with fuming nitric acid results in only low yields of an impure product, the Victor-Meyer reaction[22] with silver nitrate furnished in good yields (82 %) the pure nitro ester 1,3-dinitroxy-2-oxapropane **7**.

Characterization

All synthesized compounds were characterized by ^{1}H, $^{13}C\{^{1}H\}$ and ^{14}N NMR spectroscopy in acetone-d_6. In addition, ^{15}N NMR spectra of **5** and **6** as well as a ^{17}O NMR spectrum of **7** were recorded, and are shown and discussed in more detail in the following. All other spectra and assignments can be found in the Experimental Section and in the Supporting Information.

Figure 2 shows the ^{15}N NMR spectrum of **5**. The singlet at −188.6 ppm can be assigned to the nitramine nitrogen (denoted as N1). The resonances of the nitro groups appear as multiplets due to coupling with the methylene hydrogen atoms in the typical regions at lower field at −39.6 ppm for the nitro group (N2) of the nitramine moiety as a quintet ($^{3}J_{N,H} = 3.4$ Hz), and at −48.5 ppm for the nitro ester nitrogen (N3) as a triplet ($^{3}J_{N,H} = 4.8$ Hz).

The ^{15}N NMR spectrum of **6** is displayed in Figure 3, and shows the five resonances as to be expected due to the
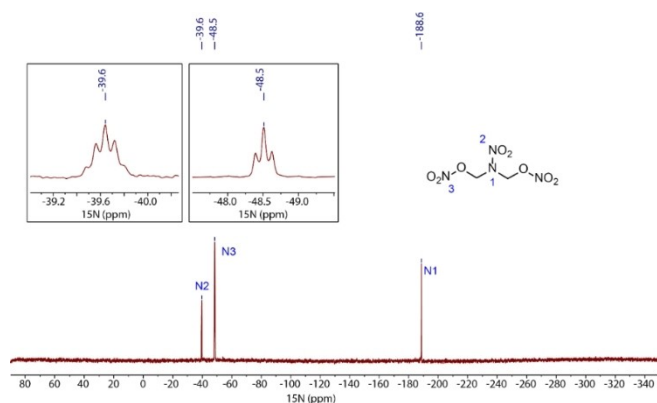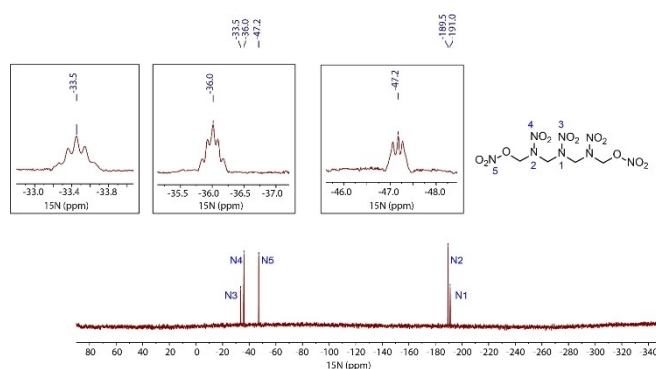
symmetry. The two singlets at −189.5 (denoted as N2) and −191.0 (N1, central nitrogen) ppm are found for the nitramine nitrogen atoms in a 2:1 ratio. Accordingly, the two nitro nitrogen resonances of the nitramine moieties are detected at −33.5 ppm (N3, quintet, $^{3}J_{N,H} = 3.2$ Hz) and at −36.0 ppm (N4, quintet, $^{3}J_{N,H} = 3.1$ Hz), as well with a 1:2 ratio. The triplet (N5, $^{3}J_{N,H} = 4.7$ Hz) at −47.2 ppm is assigned to the nitro ester nitrogen resonances.

Figure 4 shows the ^{17}O NMR spectrum of the nitro ester substituted ether **7**. Since this compound is liquid at ambient temperature, and due to the low abundance of the ^{17}O isotope and the quadrupolar nature (0.037 %, I = −5/2), the spectrum was recorded as neat liquid. Due to the symmetry of the compound, three resonances with significant broadening are detected, as to be expected by the symmetry. The resonance at 73 ppm is assigned to the central ether oxygen atom (denoted as O1), that at 358 ppm corresponds to the ester oxygen (O2). The most intense (four oxygen atoms) resonances at lowest field at 452 ppm is assigned to the nitro oxygen atoms (O3). The shift of the nitro oxygen resonance is in good agreement for that of methyl nitrate.[24]

Figure 2. ^{15}N NMR spectrum of 1,3-dinitrooxy-2-nitrazapropane (**5**) in acetone-d_6.

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X-ray Diffraction

Low temperature single-crystal X-ray diffraction experiments were performed on single crystals of **5**, **6** and the side product 3,7-dinitro-1,5,3,7-dioxadiazocane.[25] The crystal structures with selected bond lengths and angles are shown and discussed in the following, more information about the crystallographic data and structure refinement can be found in the Supporting Information.

The crystal structures of 1,3-dinitroxy-2-nitrazapropane (**5**, left) and 1,7-dinitroxy-2,4,6-trinitrazaheptane (**6**, right) are shown in Figure 5.

The azapropane **5** was recrystallized from acetonitrile and crystallizes as colorless plates in the orthorhombic space group *Pbcn* with a recalculated density of 1.874 g cm^{-3} at 298 K and four molecules per unit cell. The azaheptane **6** crystallizes as colorless plates in the orthorhombic space group *P*2$_1$2$_1$2$_1$ with a recalculated density of 1.578 g cm^{-3} at 298 K. Moreover, it crystallizes with a propionitrile solvate and two different molecules in its unit cell. Both structures, **5** and **6**, show a noticeable twisted character, due to the repulsion of the nitro groups. For **5** both nitro groups are arranged *trans* to each other to keep a maximum distance. Nevertheless, the structure is symmetrical when viewed from the nitrogen (N2) in the center, and the twisting of the two nitrato groups occurs with the same angle (N1–O1–C1–N2 −73.53(14)). In Figure 6 the unit cell of compound **5** along the *b* axis is shown.
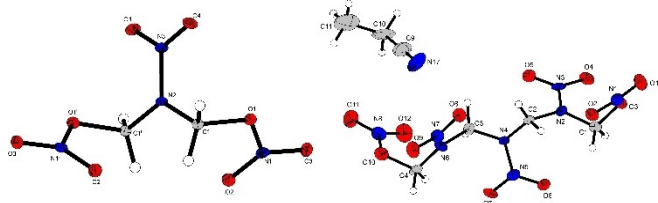

Figure 5. Crystal structure of **5** and **6** with selected bond lengths (Å): **5** O2–N1 1.2104(15), O1–N1 1.4100(15), O3–N1 1.1989(15); **6** O1–N1 1.201(9), O2–N1 1.214(10), O3–N1 1.413(10), O11–N8 1.199(9), O12–N8 1.219(10), O10–N8 1.403(10) (For compound **6**, selected values of one of the two independent molecules in the unit cell are given).
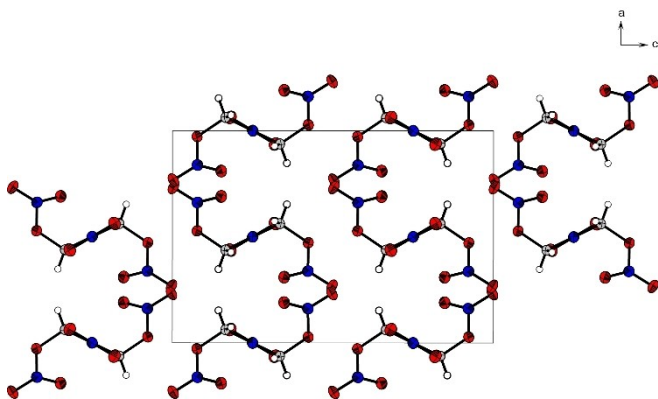

Figure 6. Molecular structure of compound **5** along the *b* axis with selected angles (°): N1–O1–C1–N2 −73.53(14), N3–N2–C1–O1 −68.68(11).
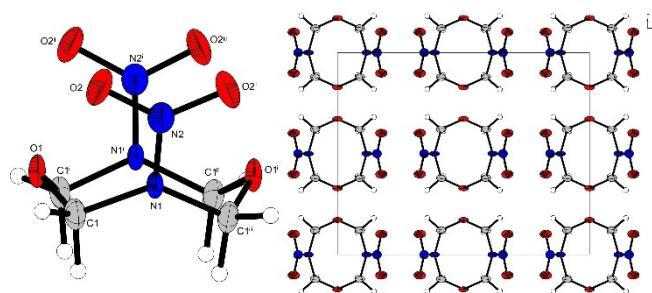

Figure 7. Crystal structure of 3,7-dinitro-1,5,3,7-dioxadiazocane (left) and molecular structure of its unit cell along the *c* axis (right) with selected values: bond lengths (Å): N2–N1 1.349(8), O2–N2 1.236(4); angles (°): O2–N2–N1 118.2(3), N2–N1–C1 117.3(3), C1–N1–C1 124.8(6).

For **6** also a noticeable twist is obvious. A view at the nitro groups reveals a slight twist away from each other due to repulsion. Thus, viewed from left to right, the first nitro group is oriented backward, the second forward, then the third in the center upward, the fourth backward again, and the last again forward. As a result, a *zigzag*-type structure of the C–N backbone is formed.

The crystal structure of the unexpected side product 3,7-dinitro-1,5,3,7-dioxadiazocane is shown in Figure 7. Crystallization was obtained from ethyl acetate as a colorless plate in the orthorhombic space group *Fmm*2 with a recalculated density of 1.679 g cm^{-3} at 298 K and four molecules per unit cell, which can be seen in Figure 7 on the right.

On the left in Figure 7, the chair-chair (CC) structure of the diazocane backbone of 3,7-dinitro-1,5,3,7-dioxadiazocanes can be seen. The two nitro groups, which are attached to the ring nitrogen atoms, are aligned *cis* to each other in the same axial direction.

Thermal Analyses

Thermal characterization of **5**, **6** and **7** was performed using differential thermal analysis (DTA) and thermogravimetric analysis (TGA) with a heating rate of 5 °C min^{-1}. Because of the liquid character and high vapor pressure of **7** it was necessary to increase the heating rate up to 20 °C min^{-1} for the determination of the decomposition temperature. The melting and decomposition points are shown explicitly in Table 1.

Table 1. Melting and decomposition temperatures of **5**, **6** and **7**.

	5	6	7
T$_{melt}$ [°C]	44[a]	150[a]	−23[c]
T$_{dec}$ [°C]	117[b]	155[b]	177[d]

[a] Onset point of the endothermic event of the DTA measurement with a heating rate of 5 °C/min. [b] Onset point of the exothermic event of the DTA measurement with a heating rate of 5 °C/min. [c] Measured with a low-temperature thermometer. [d] Decomposition temperature from the TGA measurement with a heating rate of 20 °C/min.

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In addition, the DTA plot in combination with the TGA plot of 1,3-dinitroxy-2-nitrazapropane (5) is shown in Figure 8. A comparison of the two nitraza bridged 5 and 6 show that the melting point of 5 is significantly lower than the melting point of 6 with a difference of more than 100 °C. However, the decomposition temperatures differ by only 33 °C. While 5 does not decompose until 117 °C, 6 melts at 150 °C and then decomposes immediately. Thus, it can be assumed that the endothermic event initiates the exothermic decomposition of the compound.

In addition, Figure 9 shows the TGA measurement of 7 at different heating rates. On the left, at a heating rate of 10 °C min^{-1} or less, the compound evaporates and therefore does not decompose, which can be seen from the permanent loss of mass starting already at the beginning of the measurement. However, if heated fast enough, the decomposition temperature can be reached before the complete sample is evaporated. In Figure 9 on the right, at a heating rate of 20 °C min^{-1}, the decomposition temperature of 7 is at 177 °C.
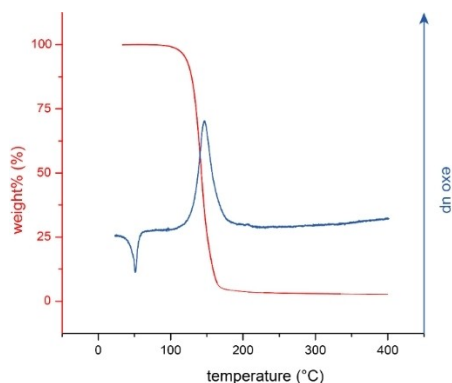

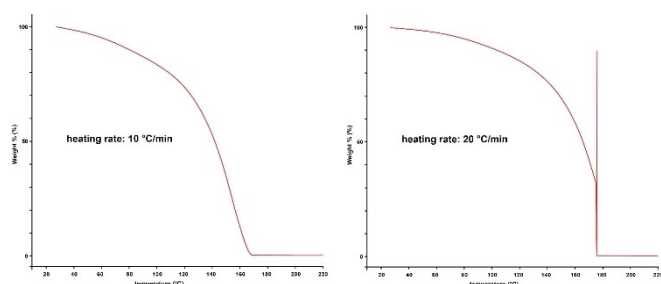**Figure 8.** DTA and TGA measurement of 1,3-dinitroxy-2-nitrazapropane (5).

Figure 9. TGA measurements of 1,3-dinitroxy-2-oxapropane (7) with a heating rate of 10 °C min^{-1} (left) and 20 °C min^{-1} (right).

Upon comparison of the thermal stabilities of 5 and 7, which differ only in the different bridging unit, the oxapropane-bridged compounds are shown to be more stable, as already described.[17]

Sensitivities and Energetic Properties

The sensitivities towards impact and friction of 5, 6 and 7 were measured, the determined values are shown in Table 2 compared to prominent examples of the group of nitro esters (NG, EGDN and PETN).

When considering impact sensitivities, 5 and 6 show a value of 2 J, whereas a value lower than 1 J was observed for 7. According to the UN Recommendations on the Transport of Dangerous Goods[26], these compounds are classified as very sensitive. The friction sensitivity value of 6 is 120 N and is therefore classified as sensitive, whereas 5 and 7 with a friction sensitivity of 20 N are classified as very sensitive.[26]

In addition, the energetic properties of 5, 6, and 7 were calculated using the EXPLO5 code version 6.06.01.[27] The calculated EXPLO5 values are based on the density of the compounds and their enthalpy of formation. All relevant values are shown in Table 3 compared to pentaerythritol tetranitrate (PETN), nitroglycerine (NG), and ethylene glycol dinitrate (EGDN), three well-known and widely applied examples of the group of nitro esters.[28–29]

A closer look at the values in Table 3 reveals a similarity of 6 with PETN, while the values of 5 are between PETN and NG. The combined nitrogen and oxygen contents of 5, 6 and 7 are higher compared to those of PETN, NG, and EGDN. As well, the values of the oxygen balance assuming the formation of CO and CO$_2$ are clearly positive for 5 and 7 and even slightly better than NG. The oxygen balance of 6 is slightly lower but with Ω_{CO_2} of 0 % better than the oxygen balance of PETN.

Considering the detonation parameters, the velocity of detonation of 6 is 341 m s^{-1} higher than the value of PETN. The value of 5 is around 8500 m s^{-1}, which is in the same range as PETN, but still significantly better than NG. Due to the low heat of formation, the detonation velocity of 7 unfortunately cannot exceed the values of NG and EGDN.

Conclusions

In this work, the three energetic materials 1,3-dinitroxy-2-nitrazapropane (5), 1,7-dinitroxy-2,4,6-trinitrazaheptane (6) and 1,3-dinitroxy-2-oxapropane (7) were synthesized and fully characterized. Importantly, that the precursor acetates 1 and 2 are obtained by a reaction condition modification of the Bachmann process and thus can be synthesized in already existing plants. The two new nitro esters 5 and 6 can be obtained in a simple two-step synthesis via the corresponding chloromethyl derivatives 3 and 4. For the synthesis of the nitrazapropane-bridged 5 the route via a Viktor-Meyer reaction and for the trinitrazaheptane-bridged 6 the nitration by using fuming nitric acid is preferable in terms of better yields. Both

Table 2. Sensitivities towards impact and friction of 5, 6 and 7.

	5	6	7	PETN[26,27]	NG[26,27]	EGDN[18]
IS[a] [J]	2	2	<1	3	<1	5
FS[b] [N]	20	120	20	60	>360	>360

[a] Impact sensitivity according to the BAM drop hammer (method 1 of 6).
[b] Friction sensitivity according to the BAM friction tester (method 1 of 6).

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Table 3. Energetic properties of **5**, **6** and **7** compared to PETN, NG and EGDN.

	5	6	7	PETN[25,26]	NG[25,26]	EGDN[18]
Formula	$C_2H_4N_4O_8$	$C_4H_8N_8O_{12}$	$C_2H_4N_2O_7$	$C_5H_8N_4O_{12}$	$C_3H_5N_3O_9$	$C_2H_4N_2O_6$
FW [g mol^{-1}]	212.08	360.16	168.06	316.14	227.09	152.06
$\rho_{calc.}$ (298 K) [g cm^{-3}]	1.87[a]	1.75[b]	1.52[c]	1.78	1.60	1.49
N+O [%][d]	86.77	84.42	83.31	78.45	81.91	81.55
Ω_{CO} [%][e]	+30	+18	+29	+15	+25	+21
Ω_{CO2} [%][e]	+15	0	+10	−10	+4	0
$T_{dec.}$ [°C][f]	117	155	177	180	143	190
$\Delta_fH°(s/l)$ [kJ mol^{-1}][g]	−194.5 (s)	+21.2 (s)	−367.6 (l)	−533.7 (s)	−370.8 (l)	−241.0 (l)
EXPLO5 V6.06.01						
P_{CJ} [GPa][h]	31	33	19	31	23	21
V_{det} [m s^{-1}][i]	8494	8753	7167	8412	7694	7519
$-\Delta_{ex}U°$ [kJ kg^{-1}][j]	6799	6531	5206	5962	5911	6426
T_{det} [K][k]	3583	4431	3869	3941	4225	4441
V_0 [dm^3 kg^{-1}][l]	782	805	796	742	779	810

[a] determined by gas-pycnometer; [b] recalculated from X-Ray density; [c] liquid at room temperature, therefore determined experimentally through the formula ρ=m/V; [d] Combined nitrogen and oxygen content; [e] oxygen balance assuming the formation of CO or CO₂; [f] temperature of decomposition (at a heating rate of 5 °C min^{-1} for **5** and **6** and 20 °C min^{-1} for **7**); [g] calculated (CBS-4 M) heat of formation; [h] detonation pressure; [i] detonation velocity; [j] energy of explosion; [k] explosion temperature; [l] volume of detonation gases at standard temperature and pressure condition.

compounds are classified as sensitive due to their sensitivities towards impact and friction and also show only moderate thermal stability of 117 °C (**5**) and 155 °C (**6**). These properties are very similar to the explosive PETN, which is widely used as a booster and obtains its energetic character also through functionalization with nitro ester groups. If the energetic parameters of these three compounds are compared, it can be seen that both 1,3-dinitroxy-2-nitrazapropane (**5**) and 1,7-dinitroxy-2,4,6-trinitrazaheptane (**6**) show higher values, such as a higher detonation velocity than PETN. A possible application of **5** and **6** as booster explosives in booster charges would be therefore conceivable. Furthermore, 1,3-dinitroxy-2-oxapropane (**7**), which is liquid at room temperature and melts at −23 °C, can be obtained in a simple two-step synthesis from formaldehyde in good yields. As in the case of **5**, nitration with silver nitrate (Viktor-Meyer reaction) leads to better yields. This route represents an advantage over nitration with nitric acid, since no acidic conditions are used here. In the past, accidents have occurred because residual acid in nitro esters has led to uncontrolled autocatalytic decomposition. The synthesis of **5** and **7** via pathway II would avoid this risk. The properties of **7** show a strong similarity to nitroglycerin, which is still used today in double-base and triple-base propellants. A comparison of both compounds reveal, that the oxygen balance of **7** exceeds that of NG but due to its lower heat of formation shows a lower detonation velocity. Nevertheless, a possible application or 1,3-dinitroxy-2-oxapropane (**7**), in propellant mixtures or as an energetic plasticizer such as EGDN would be conceivable.

Experimental Section

CAUTION! All investigated compounds are potentially explosive energetic materials, which show partly (especially **5** and **7**) increased sensitivities towards various stimuli (e.g. elevated temperatures, impact or friction). Therefore, proper security precautions (safety glass, face shield, earthed equipment and shoes, leather coat, Kevlar gloves, Kevlar sleeves, and ear plugs) have to be applied while synthesizing and handling the described compounds. The synthesis procedure and analytics can be found in the Supporting Information.

Supporting Information

The authors have cited additional references within the Supporting Information.[30–48] The Supporting Information includes General Experimental Information, NMR Spectroscopy, IR Spectroscopy, DTA Measurement, TGA Measurement, X-Ray Diffraction, Heat of Formation Calculations and Calculation of Energetic Performance Parameters.

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Conflict of Interests

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.

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