Energetic Materials

A Study of the 3,3,3-Trinitropropyl Unit as a Potential Energetic Building Block

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In memory of Professor Dr. mult. Heinrich Nöth

Abstract: Compared with the well-established 2,2,2-trinitroethyl group in the chemistry of energetic materials, the 3,3,3-trinitropropyl group is less investigated regarding its chemical and energetic properties. Thus, investigations on the syntheses of several compounds containing the 3,3,3-trinitropropyl group were performed and their properties compared with the 2,2,2-trinitroethyl group. All materials were thoroughly characterized, including single-crystal X-ray dif-

Introduction

The 2,2,2-trinitroethyl group is a central building block in the synthesis of energetic materials, especially in the subgroup of high-energy dense oxidizers (HEDOs). This unit can readily be obtained by reacting trinitromethane and formaldehyde in a Henry reaction or by a Mannich condensation of an amine, formaldehyde, and trinitromethane.^[1] Many compounds with this moiety have been synthesized and characterized in the recent years.^[2,3] Unfortunately, the trinitroethyl moiety is unstable towards bases and nucleophiles and decomposes into their precursors.^[4] In contrast, the 3,3,3-trinitropropyl moiety shows a higher chemical stability because such reverse Henry or Mannich reactions are not possible.^[5] A disadvantage of the 3,3,3trinitropropyl group is its quite complex synthesis and the lower oxygen content.^[6] Although some compounds with a 3,3,3-trinitropropyl moiety have been reported, nothing is known about the energetic properties, the molecular structure, and the stability of such materials.

High-energy dense oxidizers (HEDOs) are energetic compounds that are based on CHNO and release the excess of included oxygen when ignited.^[1b] These oxidizers are, in addition to further components such as binders and fuel, the main part (>70%) in solid rocket propellants.^[7] The released oxygen

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fraction studies. The thermal stabilities were examined using differential thermal analysis (DSC) and the sensitivities towards impact, friction, and electrostatic discharge were tested using a drop hammer, a friction tester, and an electrical discharge device. The energies of formation were calculated and several detonation parameters such as the velocity of detonation and the propulsion performance were estimated with the program package EXPLO5.

reacts with the fuel, such as carbon backbones or aluminum, and produces plenty of hot gases, which are used for the impulsion of rockets.^[8] Presently, ammonium perchlorate (AP), with a high oxygen content and a low price, is the most commonly used oxidizer in composite propellants. Unfortunately, the combustion of AP releases large amounts of toxic gases such as hydrogen chloride, which causes environmental problems.^[9] In addition, use of AP causes pollution of the groundwater in large areas throughout the world.^[10] There is also proof that the perchlorate anion has negative health effects, particularly on the hormonal balance of humans and amphibians.^[11] For these reasons, new halogen-free propellants with high performance and good stability are desirable.

Results and Discussion

Synthesis

The central precursor for this work (Scheme 1) is the reactive isocyanate 1,1,1-trinitropropan-3-isocyanate (1), which is available from a multistep synthesis, starting from a Michael addition of trinitromethane with acrylamide.^[12] The salt 3,3,3-trinitropropan-1-amine hydrochloride (2) was obtained by controlled hydrolysis of 1 in hydrochloric acid. The amine was further converted into the corresponding alcohol 3,3,3-trinitropropanol (3) by a Sandmeyer-type reaction.^[13] In this reaction, a diazonium salt is generated by in situ formed nitrous acid, which is subsequently displaced by a nucleophilic substitution with water. The urea derivative 4 is obtained by the reaction of two molecules of 1 by partial hydrolysis.^[6b] For the synthesis of bis(3,3,3-trinitropropyl) oxalamide (5), the free amine generated from the hydrochloride salt 2 was reacted with oxalyl chloride.^[14] The oxalate derivative bis(3,3,3-trinitropropyl) oxalate

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Scheme 1. Overview of 3,3,3-trinitropropyl-based compounds.

(6) was synthesized by the reaction of oxalyl chloride and the alcohol 3. The conversion of the alcohol into 3,3,3-trinitropropyl carbamate (7) was first mentioned in the 1990s and was realized by a two-step synthesis. At that time, phosgene was reacted with 3 to form the chloroformate, which was further converted with aqueous ammonia to obtain the carbamate 7.^[15] Now, a one-step synthesis was achieved by using the reagent chlorosulfonyl isocyanate (CSI). The advantages of CSI are much shorter reaction times, easier handling of the starting materials, and trouble-free work up.^[16] The carbamate 7 was obtained as a colorless, pure product in higher yield compared with the previous route.^[15] The nitration of **7** resulted in the 3,3,3-trinitropropyl nitrocarbamate (8), which was performed in a mixture of concentrated sulfuric and nitric acid.^[3c, 16c] Mannich condensations between an organic nitro compound, an aldehyde, and an amine are very useful reactions.^[17] The condensation of the amine 2 with formaldehyde and trinitromethane produced the secondary amine 3,3,3-trinitropropyl-N-(2,2,2-trinitroethyl) propan-1-amine (9) as a solid with a limited stability.^[6a] Upon nitration of **9** in a mixture of acetic anhydride and anhydrous nitric acid, the highly energetic nitramine, N-(2,2,2trinitroethyl)-N-(3,3,3-trinitropropyl) nitramine (10) was obtained.^[6a] The nitramine **10** is air and moisture stable, has an oxygen and nitrogen content of 84%, and has a very high oxygen balance $\Omega_{\rm CO}$ of +23.9%.

NMR spectroscopy

The ¹H, ¹³C and ¹⁴N NMR spectra were recorded in CDCl₃ (1, 3, 4, 9), $[D_3]$ acetonitrile (2, 9), and $[D_6]$ acetone (5–8). In the ¹H NMR spectra, the two CH_2 groups are within the range 4.84–3.14 ppm. The methylene unit next to the trinitromethyl moiety is shifted to higher field values compared with the CH_2 groups next to nitrogen or oxygen. The vicinal coupling constants of the hydrogen atoms in the ethylene group are not equal owing to the rotation around the C–C bond, causing a AA'XX' spin system.^[18]

In the ¹³C NMR spectra, the carbon resonances of the two CH_2 groups are found near 58 and 33 ppm. As expected, the same effect as in the proton NMR spectra is also observed in the ¹³C NMR. The carbon resonances next to the trinitromethyl unit are always upfield shifted compared with those connected to the electron-withdrawing elements nitrogen and oxygen. The carbon resonance of the trinitromethyl moiety is observed as a broadened signal; in the case of 3,3,3-trinitropropyl, it is always located around 130 ppm. By comparing this signal with that of the 2,2,2-trinitroethyl unit in **9** and **10**, a significant upfield shift to approximately 125 ppm occurs; and the two groups can thus, be clearly distinguished.

In the ¹⁴N NMR spectra, the resonances for the nitro groups of the trinitromethyl moieties are all quite sharp and found in the range of -29 to -32 ppm. For the nitramine **10**, a typical ¹⁵N NMR spectrum is shown in Figure 1, with full assignment of all nitrogen atoms. The nitrogen resonances of the trinitromethyl moieties were observed at -31.0 ppm for the 3,3,3-trinitropropyl unit and at -34.5 ppm for the 2,2,2-trinitroethyl unit. For both resonances, a triplet caused by coupling with the two neighboring methylene hydrogen atoms is present, with coupling constants of ³J(¹⁵N,¹H)=2.8 Hz and ³J(¹⁵N,¹H)=



Figure 1. ¹⁵N NMR spectrum of *N*-(2,2,2-trinitroethyl)-*N*-(3,3,3-trinitropropyl) nitramine (**10**) in CD₃CN.

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| Table 1. Selected IR and Raman bands for 3–10. ^[a] | | | | | | | | | | | | |
|--|----------|-----------|----------|-----------|----------|-----------|----------|-----------|----------|-----------|--|--|
| | 1 | | 2 | | : | 3 | 4 | 4 | 5 | | | |
| | IR | Raman | IR Raman | | IR | Raman | IR | Raman | IR | Raman | | |
| νCO | - | - | - | - | - | - | 1642 (m) | 1644 (12) | 1659 (m) | 1694 (41) | | |
| $v_{as}NO_2$ | 1586 (s) | 1610 (24) | 1597 (s) | 1606 (45) | 1581 (s) | 1608 (19) | 1587 (m) | 1593 (28) | 1583 (s) | 1607 (22) | | |
| $\nu_{s}NO_{2}$ | 1298 (m) | 1304 (30) | 1303 (m) | 1312 (26) | 1296 (s) | 1306 (25) | 1298 (m) | 1309 (33) | 1297 (m) | 1299 (40) | | |
| | 6 | | 7 | | 8 | | | 9 | 10 | | | |
| | IR | Raman | | |
| νCO | 1764 (m) | 1769 (51) | 1704 (m) | 1699 (15) | 1758 (m) | 1760 (41) | - | - | - | - | | |
| $v_{as}NO_2$ | 1600 (s) | 1615 (25) | 1583 (s) | 1617 (36) | 1590 (s) | 1617 (32) | 1581 (s) | 1604 (21) | 1599 (s) | 1613 (35) | | |
| | | | | | | | | | 1555 (s) | | | |
| $v_{s}NO_{2}$ | 1296 (m) | 1292 (29) | 1298 (m) | 1299 (25) | 1291 (m) | 1307 (30) | 1302 (s) | 1309 (27) | 1285 (s) | 1294 (23) | | |
| | | | | | | 1290 (31) | | | 1268 (s) | 1270 (25) | | |
| [a] Frequencies in cm^{-1} . IR intensities: $vs = verv$ strong $s = strong$ $m = medium$ $w = weak$. Raman intensities in brackets | | | | | | | | | | | | |

1.9 Hz. The two nitrogen resonances of the nitramine moiety are observed as multiplets, as expected. The nitro group is located between the two triplets of the trinitromethyl groups at -32.9 ppm, and that of the amine, upfield at -213.7 ppm.

Vibrational spectroscopy

All compounds were also characterized by their molecular vibration frequencies by IR and Raman spectroscopy. The most characteristic frequencies in the compounds are those of the carbonyl and nitro groups, which are summarized in Table 1. For the trinitromethyl units, both the asymmetric $v_{as}(NO_2)$ in the range 1600–1581 cm⁻¹ and the symmetric stretching vibrations $v_s(NO_2)$ at 1285–1307 cm⁻¹ are observed. For **8** and **10**, additional NNO₂ groups are included and also additional $v_{as}(NO_2)$ and $v_s(NO_2)$ vibrations appear at slightly higher wavenumbers.^[19] Furthermore, the $\nu_{\rm as}({\rm NO_2})$ vibration is shifted to higher wavenumbers when connected to electron-withdrawing moieties; such as the carboxylate moiety in 6 (1600 cm⁻¹) compared with the carbamate moiety in **7** (1583 cm^{-1}). The same effect influences the C=O stretching vibrations ν (C=O). An example is the urea derivative 4, where the ν (C=O) is located at 1642 cm⁻¹, whereas in the carbamate **7** (1704 cm⁻¹) and in the nitrocarbamate 8 (1758 cm⁻¹) significant shifts to higher energies are observed.

Single-crystal X-ray diffraction

Single-crystals suitable for X-ray diffraction studies were obtained by crystallization at room temperature from dichloromethane (6, 8, 10), chloroform (9), or acetonitrile (5, 7). A full list of the crystallographic refinement parameters and structural data for compounds 4–10 is shown in the Supporting Information. To our knowledge, no molecular structure with a 3,3,3-trinitropropyl moiety is presently known.

The urea compound **4** crystallizes in the orthorhombic space group *Pccn* in a large unit cell containing twelve molecules. The asymmetric unit consists of one and a half molecules. The full molecule is shown in Figure 2. The C–N bond lengths in the trinitromethyl moiety are in the range of 1.53 Å, which is



Figure 2. Molecular structure of bis(3,3,3-trinitropropyl) urea (4). Selected bond lengths [Å] and angles [°]: C1–C2 1.49 5(7), C1–N1 1.519(6), C1–N2 1.539(6), C1–N3 1.526(6), C2–C3 1.535(7), C3–N4 1.447(7), C4–N4 1.352(7), C4–N5 1.343(7), C4–O7 1.233(5); C5-N5-C4 123.0(5), O7-C4-N4 121.9(5), C4-N4-H5 120(4), H5-N4-C3 118(4), C3-N4-C4-O7 –6.5(8), H5-N4-C4-O7 –175(5), O7-C4-N5-C5 3.3(8).

significantly longer than a regular C–N bond (1.47 Å) and results from steric repulsion from the three relatively large nitro groups around one carbon atom.^[3c] The three nitro groups are organized around the carbon in a propeller-like geometry to optimize the non-bonded N···O intramolecular attractions. This results in an intramolecular interaction between the partially positively charged nitrogen atom and the negatively charged oxygen atom in the nitro groups.^[3c]

These N···O attractions are found to have distances in the range 2.41–2.63 Å, which are much shorter than the sum of the van der Waals radii of nitrogen and oxygen (3.07 Å).^[3c,20] This steric arrangement of the nitro groups was also observed in the half molecule of the asymmetric unit, which is completed by a proper two-fold rotation axis. Furthermore, a disorder of the trinitromethyl group is observed. Two different positions can be identified with a nearly equivalent proportion. In the disorder, the nitro groups always share an oxygen atom that is fully occupied, whereas the other oxygen atom and the nitrogen atom are independent (see Supporting Information, Fig-



ure S2). Another consequence of the trinitromethyl group's presence, with the quite strong electron-withdrawing effect of the nitro groups, is the reduced bond length of the neighboring carbon–carbon bond (C1–C2 1.485 Å).^[2] As expected, the urea unit is nearly planar and shows typical bond geometry.

The oxalamide **5** and the oxalate **6** both crystallize in the monoclinic space group $P2_1/c$ and show the propeller-like steric geometry of the trinitromethyl group. In **5**, the asymmetric unit consists of two half independent molecules that are almost equal. An inversion center in the center of the carbon-carbon bond of the oxalamide moiety completes the molecule (Figure 3). The length of this bond (1.54 Å) is rather long for a sp² carbon bond, but is common for an oxalamide structure.^[21] The same was observed in the structure of oxalate **6** (Figure 4). The unique unit is here only one half of the molecule. The 3,3,3-trinitropropyl arm is nipped of to the oxygen O2 atom of the oxalate unit. This causes an additional N···O intramolecular attraction between the partially positively charged nitrogen N3 and O2, which is confirmed by the short distance (2.80 Å).

The carbamate **7** crystallizes in the orthorhombic space group *Pbca* with eight molecules in the unit cell and one molecule as the asymmetric unit (Figure 5). The carbamate moiety, the C2 carbon atom inclusive, shows a nearly planar arrange-



Figure 3. Molecular structure of bis(3,3,3-trinitropropyl) oxalamide (5). Selected bond lengths [Å] and angles [°]: C2–C1 1.506(2), C3–C2 1.531(3), C4–C4' 1.538(2), N4–C3 1.449(2), N4–C4 1.320(2); C3-N4-C4 121.8(2), H5-N4-C4 120(1), O7-C4-N4 125.0(2), O7-C4-C4 121.6(1), N4-C4-C4 113.4(1), C3-N4-C4-C4 178.3(1), N4-C4-C4-N4 –180.0(2), H5-N4-C4-O7 172(2).



Figure 4. Molecular structure of bis(3,3,3-trinitropropyl) oxalate (**6**). Selected bond lengths [Å] and angles [°]: C1–O1 1.198(2), C1–O2 1.325(2), C1–C1′ 1.540(2), C2–C3 1.513(2), C2–O2 1.454(2), C3–C4 1.504(2), N2–O4 2.535(2), N1–O7 2.632(2), N3–O6 2.554(2), N3–O2 2.800(2); O1-C1-O2 126.2(1), C3-C2-O2 107.6(1), O1-C1-O2-C2 4.0(2), C1-O2-C2-C3 173.3(1).



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Figure 5. Molecular structure of two molecules of 3,3,3-trinitropropyl carbamate (7). Selected bond lengths [Å] and angles [°]: C1–N1 1.325(2), C1–O1 1.224(1), C1–O2 1.355(1), C2–C3 1.515(2), C2–O2 1.440(2), C3–C4 1.510(2), N1–H1 0.86(1), N1–H2 0.85(2), O2–N4 2.946(1), N4–O6 2.526(1), O7–N2 2.565(1), O3–N3 2.541(2); N1-C1-O1 125.9(1), N1-C1-O2 111.3(1), O1-C1-O2 122.7(1), C3-C2-O2 109.6(1), C2-C3-C4 117.4(1), H2-N1-C1-O1 –175(1), N1-C1-O2-C2 –179.1(1).

ment. The bond lengths of the C1–N1 (1.33 Å) and the two N1–H bonds (0.85 and 0.86 Å) in the carbamate part are shortened, which is typical for such moieties.^[3c] The conformations of the substituents at C2, C3, and C4 are all almost perfectly staggered. The extended structure involves secondary interactions in terms of classical intermolecular N–H···O hydrogen bonding and unusual hydrogen bonding with carbon as donor (C–H···O) (for further information, see the Supporting Information). The carbamate unit forms a nearly perfect planar eightmembered ring with another unit (Figure 5).

The crystal growing, data collection, solution and refinement of the 3,3,3-trinitropropyl nitrocarbamate (8) was difficult, as illustrated by the quite high refinement values. The data collection also had to be performed at ambient temperature owing to a phase transition at lower temperature. This is particularly interesting, as the related compound, 2,2,2-trinitroethyl nitrocarbamate, shows the same behavior.^[3c] Compound 8 crystallizes in the orthorhombic space group Pccn with one molecule as an asymmetric unit (Figure 6). The nitrocarbamate moiety is in a perfect plane that includes the carbon atom C2. The N1-N2 bond length of the nitramine is 1.37 Å, which indicates a significant double bond character, which is achieved by delocalization of the nitrogen lone pair on N2. Compared with the carbamate structure of 7, the carbonyl group (C1-O3) shows a slight shortening as a result of the electron-withdrawing nitro group.

The Mannich condensation product **9** crystallizes in the monoclinic space group $P_{2_1/c}$ with two formula units per unit cell. The asymmetric unit consists of one and a half molecules, which is only possible through a disorder in the half molecule (Figure 7). This interesting disorder shows a statistical occupation of nitrogen and oxygen atoms (1:1) at the same position (see the Supporting Information, Figure S8). This disorder occurs as a result of an inversion center that is located on the *b* axis of the cell.^[3a] The average of the N–O and C–NO₂ bond lengths of the trinitromethyl units in the ethyl and propyl moiety are all in the same range, which is about 1.21 Å for N–O and 1.52 Å for C–NO₂. Also, both trinitromethyl groups independently show propeller-like orientation of the nitro groups. Additionally, the carbon–carbon bonds are virtually identical, falling within the range 1.50–1.52 Å. The geometry around the

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Figure 6. Molecular structure of 3,3,3-trinitropropyl nitrocarbamate (8). Selected bond lengths [Å] and angles [°]: O4–C1 1.329(5), O4–C2 1.430(6), O3–C1 1.182(4), C1–N2 1.367(5), N2–N1 1.367(6), C2–C3 1.491(8), C3–C4 1.501(8); C2-O4-C1 115.8(3), N2-C1-O4 107.0(4), N1-N2-C1 124.0(4), O1-N1-N2-C1 176.4(4), O2-N1-N2-H1 –176(3), H1-N2-C1-O3 172(3), N2-C1-O4-C2 177.3(3).



Figure 7. Molecular structure of 3,3,3-trinitro-*N*-(2,2,2-trinitroethyl) propan-1amine (9). Selected bond lengths [Å] and angles [°]: N4–C2 1.467(3), N4–C3 1.451(3), N4–H3 0.92(2), C1–C2 1.513(3), C3–C4 1.515(3), C4–C5 1.503(3); C2-C1-N1 112.0(2), C2-C1-N2 110.5(2), C2-C1-N3 114.5(2), C4-C5-N5 111.7(2), C4-C5-N6 113.3(2), C4-C5-N7 114.5(2), C3-N4-H3 109(2), H3-N4-C2 111(2), C3-N4-C2 111.6(2).

nitrogen atom of the secondary amine is nearly tetrahedral with angles of 108.7, 111.6, and 111.6°.

The nitramine 10 crystallizes in the monoclinic space group Pc with glide planes as the only symmetry operation. In the unit cell there are two identical formula units (Figure 8). The geometric environment of the nitramine shows a more planar structure around the nitrogen atom N4, which is demonstrated by the guite high angle values of 115.6, 116.5, and 122.0°. This is achieved by the delocalization of the electron lone pair of the N4 nitrogen atom and is affected by the strong electronwithdrawing effect of the nitro group. Otherwise, the distances, angles, and the propeller-like structure are very identical to 9. One very striking parameter for this structure is the high density of 1.902 g cm⁻³ at 173 K. This is even more remarkable because of the impossibility of forming classical hydrogen bonds. However, for each hydrogen atom, a so-called non-classical hydrogen bond of the type C-H-O is found, the majority of which are classified as quite strong.^[22]



Figure 8. Molecular structure of *N*-(2,2,2-trinitroethyl)-*N*-(3,3,3-trinitropropyl) nitramine (**10**). Selected bond lengths [Å] and angles [°]: O8–N5 1.219(3), O7–N5 1.234(2), N5–N4 1.370(3), N4–C2 1.447(3), N4–C3 1.469(3), C1–C2 1.527(3), C3–C4 1.540(3), C5–C4 1.509(3); C2-N4-N5 115.6(2), N5-N4-C3 116.5(2), C2-N4-C3 122.0(2), C2-N4-N5-O8 –159.3(2), O7-N5-N4-C3 175.8(2), C5-C4-C3-N4 –179.6(2), N2-C1-C2-N4 176.8(2).

Thermal and energetic properties

Compounds 4-10 are possible energetic materials and, therefore, potential HEDOs. All molecules are stable when exposed to air and or moisture. Table 2 summarizes the physical and thermal properties. Melting points and thermal stabilities were investigated by differential scanning calorimetry (DSC) with a heating rate of 5°C per minute. Quite high and satisfying melting and decomposition points were observed. For example, the oxalamide 5 shows the highest decomposition point at 181 °C. A clear trend in which the 3,3,3-trinitropropyl group shows higher thermal stability than the 2,2,2-trinitroethyl group, as anticipated, could not be confirmed. However, in the case of the nitramine 10, the exchange of one ethyl for a propyl group leads to a tremendous difference and gives a 57°C higher decomposition point than the corresponding ethyl derivative, bis(2,2,2-trinitroethyl) nitramine.[23] A comparison with the corresponding 2,2,2-trinitroethyl derivatives and common explosives is illustrated in Table 2.

For the manipulation of energetic materials, the sensitivity toward impact, friction, and electrostatic discharge is especially important. The sensitiveness towards impact (IS) of a compound is tested by the action of a dropping weight on a sample. The friction sensitivity (FS) is determined by rubbing a small amount between a porcelain plate and a pin with different contact pressures.^[24] Some compounds can be classified as sensitive toward friction (≥360 N insensitive, 360-80 N sensitive, 80–10 N very sensitive, \leq 10 N extremely sensitive), and some are sensitive to impact (\geq 40 J insensitive, 40–35 J less sensitive, 35–4 J sensitive, \leq 3 J very sensitive).^[1b,25] The compounds 9 and 10 take a special position owing to their high sensitiveness to impact and are in the range of the well-known explosive Hexogen (RDX). The relative electrostatic discharge (ESD) sensitivity of an explosive is tested with an apparatus, whereby variable capacitive resistances and loading voltages



Table 2. Comparison of physical and chemical properties of materials containing the 3,3,3-trinitropropyl and 2,2,2-trinitroethyl groups and with common explosives AP, TNT, and RDX.

| | 4 | | 5 | | 6 | | 7 | | 8 | | 9 | | 10 | | AP | TNT | RDX |
|---|--------|-------|--------|--------|--------|--------|--------|-------|--------|-------|--------|-------|--------|-------|-------|-------|-------|
| propyl vs ethyl | propyl | ethyl | propyl | ethyl | propyl | ethyl | propyl | ethyl | propyl | ethyl | propyl | ethyl | propyl | ethyl | | | |
| T _m [°C] (onset) ^[a] | - | 185 | - | n.a. | 121 | 115 | 78 | 91 | 68 | 109 | 65 | 114 | 141 | 94 | - | 81 | 204 |
| T _{dec} [°C] (onset) ^[b] | 160 | 187 | 181 | n.a | 170 | 201 | 152 | 169 | 134 | 153 | 96 | 114 | 153 | 96 | 240 | 248 | 228 |
| IS [J] ^[c] | 20 | 3 | 10 | n.a. | >40 | 10 | >40 | 40 | >30 | 10 | 7 | 5 | 7 | 2 | 20 | 15 | 7 |
| FS [N] ^[d] | 120 | 160 | 160 | n.a | > 360 | > 360 | > 360 | 64 | >288 | 96 | 120 | 120 | 160 | 64 | 360 | 360 | 120 |
| ESD [J] ^[e] | 0.40 | n.a. | 0.50 | n.a. | 0.40 | n.a. | 0.30 | n.a. | 0.20 | n.a. | 0.20 | n.a. | 0.15 | n.a. | 0.50 | 0.45 | 0.20 |
| N [%] ^[f] | 27.1 | 29.0 | 25.3 | 27.1 | 18.9 | 20.2 | 23.5 | 25.0 | 24.7 | 26.0 | 27.5 | 28.6 | 27.9 | 28.9 | 11.9 | 18.5 | 37.8 |
| O [%] ^[g] | 50.2 | 53.9 | 50.7 | 54.1 | 57.6 | 61.5 | 53.8 | 57.1 | 56.5 | 59.5 | 53.8 | 56.0 | 55.7 | 57.7 | 54.5 | 42.3 | 43.2 |
| N+O [%] ^[h] | 77.3 | 82.9 | 76.0 | 81.2 | 76.5 | 81.7 | 77.3 | 82.1 | 81.2 | 85.5 | 81.3 | 84.6 | 83.6 | 86.6 | 66.4 | 60.8 | 81.0 |
| $arOmega_{ m CO}$ [%] ^[i] | + 3.9 | +20.7 | +3.6 | + 19.3 | +14.4 | + 30.8 | +6.7 | +21.4 | +19.8 | +32.7 | +15.7 | +25.7 | +23.9 | +33.0 | +34.0 | -24.7 | 0 |
| $arOmega_{	ext{CO}_2}$ [%] $^{[j]}$ | -20.2 | +0.0 | -20.3 | -3.9 | -14.4 | +7.7 | -20.2 | 0 | -2.8 | +14.9 | -6.7 | +7.0 | +4.0 | +16.5 | +34.0 | -74.0 | -21.6 |
| [a] Onset melting $T_{\rm m}$ and [b] onset decomposition point $T_{\rm dec}$ from DSC measurement carried out at a heating rate of 5°C min ⁻¹ . [c] Impact sensitivity. | | | | | | | | | | | | | | | | | |

[i] Oxygen balance assuming the formation of CO, respectively. [j] CO₂.

generate different spark energies. The electric discharge was determined which is needed to initiate a decomposition or an explosion. The lowest value for an initialization was found for the nitramine **10**, with an energy of 0.15 J, which is in the range of secondary explosives such as pentareythritol tetranitrate (PETN) and RDX.^[24]

The main performance criteria of energetic materials are the heat of explosion, Q_v the detonation velocity, $V_{\text{Det}v}$ and the detonation pressure, P_{CI} . All these detonation and combustion parameters are summarized in Table 3 (for further values, see the Supporting Information). The performance data were calculated by the computer code EXPLO5 (V.6.02)^[26] and based on the calculated energy of formation using CBS-4M ab initio calculations. The nitramine **10** has the highest energy of formation $\Delta_f U^\circ$, with a value of -79.7 kJ kg^{-1} , which indicates a high energy content in the molecule. This and the high density are reflected by the very high detonation velocity, $v_{\text{Det}v}$ of 9119 ms⁻¹ compared with RDX (8838 ms⁻¹). The other compounds also show quite high detonation velocities, $v_{\text{Det}v}$ in the

range 7732–8713 $m\,s^{-1}$ and these values are in the range of well-known explosives such as PETN (8403 $m\,s^{-1}$) and trinitroto-luene (TNT; 7241 $m\,s^{-1}$).

Another very important value, especially for high-energy dense oxidizers, is the specific impulse, Is. Oxidizers are the main component in composite propellants and are the compounds that release the excess of included oxygen when ignited. This oxygen is used for the oxidation of further added fuel to generate a lot of heat and gases for the propulsion. As an effective fuel, aluminum is often used, which has a very high heat of combustion and thereby produces a very hot burning temperature.^[8] Other advantages of aluminum are its low price, the low atomic weight, and its non-hazardous combustion product (Al₂O₃). The so-generated high burning temperature is important because the specific impulse, I_{s} , is proportional to the square root of the temperature.^[1b] A further important factor is the molecular weight of the gaseous products at the nozzle exit of the rocket chamber, which is inversely proportional to the square root of the specific impulse.^[1b] This means

| Table 3. Calculated heats of formation, predicted detonation and combustion parameters (using the EXPLO5V6.02 code) for 4-10 compared with AP. | | | | | | | | | | | |
|--|---|---|--|----------------|-------------------|-------------------|-------------------|----------------------------------|--|--|--|
| | 4 | 5 | 6 | 7 | 8 | 9 | 10 | AP | | | |
| formula | C ₇ H ₁₀ N ₈ O ₁₃ | C ₈ H ₁₀ N ₈ O ₁₄ | C ₈ H ₈ N ₆ O ₁₆ | $C_4H_6N_4O_8$ | $C_4H_5N_5O_{10}$ | $C_5H_7N_7O_{12}$ | $C_5H_6N_8O_{14}$ | NH ₄ ClO ₄ | | | |
| density RT ^[a] | 1.75 | 1.71 | 1.67 | 1.73 | 1.70 | 1.78 | 1.89 | 1.95 | | | |
| $\Delta_{\rm f} H_m^{\circ} [{\rm kJmol^{-1}}]^{\rm [b]}$ | -359.1 | -522.3 | -789.4 | -503.5 | -401.7 | -86.4 | -66.8 | -295.8 | | | |
| $\Delta_{\rm f} U^\circ [{ m kJkg^{-1}}]^{[c]}$ | -774.1 | -1091.5 | -1693.5 | -2021.0 | -1331.3 | -151.7 | -79.7 | -2623.2 | | | |
| $Q_{\rm v} [{\rm kJ} {\rm kg}^{-1}]^{\rm [d]}$ | -5385 | -5095 | -5126 | -4662 | -5809 | -6565 | -6377 | -1422 | | | |
| $T_{\rm ex} \left[{\rm K} \right]^{[{\rm e}]}$ | 3692 | 3605 | 3808 | 3328 | 4175 | 4445 | 4420 | 1735 | | | |
| $V_0 [{\rm L}{\rm kg}^{-1}]^{\rm [f]}$ | 739 | 732 | 724 | 724 | 755 | 738 | 756 | 885 | | | |
| P _{CJ} [kbar] ^[g] | 294 | 268 | 256 | 265 | 269 | 330 | 367 | 158 | | | |
| $V_{\rm Det} [{\rm ms^{-1}}]^{\rm [h]}$ | 8227 | 7937 | 7732 | 7896 | 8134 | 8713 | 9119 | 6368 | | | |
| <i>I</i> _s [s] ^[1] | 254 | 245 | 250 | 237 | 256 | 272 | 264 | 157 | | | |
| <i>I</i> _s [s] (15% AI) ^[j] | 267 | 263 | 259 | 256 | 261 | 274 | 269 | 235 | | | |
| <i>I</i> _s [s] (15% Al, 14% binder) ^[k] | 251 | 245 | 246 | 240 | 253 | 261 | 267 | 261 | | | |

[a] RT densities are recalculated from X-ray densities. [b] Enthalpy and [c] energy of formation calculated by the CBS-4M method using Gaussian 09. [d] Heat of explosion. [e] Explosion temperature. [f] Volume of gaseous products. [g] Detonation pressure and [h] detonation velocity calculated by using the EXPLO5 (Version 6.02) program package.^[26] [i] Specific impulse of the neat compound using the EXPLO5 (Version 6.02) program package at 70.0 bar chamber pressure.^[26] [j] Specific impulse for compositions with 85% oxidizer/compound and 15% aluminum. [k] Specific impulse for compositions with 71% oxidizer/compound, 15% aluminum, and 14% binder (6% polybutadiene acrylic acid, 6% polybutadiene acrylonitrile, and 2% bisphenol A ether.

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that for high performance, a high burning temperature and a low weight of the gaseous products, such as CO, CO₂, H₂O, or H₂, is required. For the following discussion, it is important that the payload of the rocket can be doubled if the specific impulse is increased by 20 s. The specific impulses, I_{s_1} of the compounds 3-10 were calculated as neat samples, with aluminum (15%), and with a binder/aluminum system (16% aluminum, 6% polybutadiene acrylic acid, 6% polybutadiene acrylonitrile, and 2% bisphenol A ether). These impulses were compared with the calculated impulse of ammonium perchlorate (AP) in an analogous composition. The specific impulses, I_s , for the neat compounds show altogether much higher values than AP, which is predictable as the compounds have their own fuel in form of the carbon backbone. The neat compounds 9 and 10 show impulse values of 272 s and 264 s, which are already higher than the optimized composite of AP (261 s). A further advantage of the neat compounds are the burning residues, which are harmless and entirely gaseous products, and make the RADAR detection of such propulsion systems quite complicated.^[1a] The addition of aluminum (15%) as fuel increases the values for all compounds; the carbamate 7 shows the lowest value at 256 s and the amine 9 has the highest specific impulse with 274 s. The optimized standard mixture for AP is composed of 71% oxidizer, 15% aluminium, and 14% binder. In such a system, all impulses decrease, an effect that is caused by the increase of the carbon content. Only the nitramine 10 can outperform AP with a value of 267 s in such a binder mixture. Therefore, smaller amounts of binder are more suitable for this type of CHNO oxidizers. For example, with only half the amount of binder, the value of the specific impulse of 10 can be enhanced to 275 s.

Conclusion

A variety of compounds with energetic properties based on the 3,3,3-trinitropropyl group were synthesized and thoroughly characterized, including X-ray diffraction. The thermal stabilities were measured by different scanning calorimetry (DSC). In general, the expected higher decomposition points compared with the 2,2,2-trinitroethyl group could not be confirmed; however, some higher stabilities were detected. Additionally, this is confirmed by the lower sensitivities of the 3,3,3-trinitropropyl compounds discussed here.

With respect to application as high-energy dense oxidizers in composite solid rocket propellants, several energetic performance data were calculated. The best compound, with excellent detonation parameters, is the nitramine **10**, which has a very high detonation velocity (9119 m s⁻¹) and a strong detonation pressure; both values significantly exceed those of TNT, RDX, and PETN (for details, see Table S10 in Supporting Information). Thus, **10** seems to serve as a good oxidizer candidate for composite rocket propellants. The specific impulse, I_{sr} , reaches 269 s within a mixture of 15% aluminum as fuel, which is a result of the quite high energy of formation and the positive oxygen balance ($\Omega_{co} = + 23.9$). However, the synthesis of such 3,3,3-trinitropropyl-containing materials is more elaborate compared with compounds containing 2,2,2-trinitroethyl groups.

Experimental Section

General information

All chemicals were used as supplied. Raman spectra were recorded in a glass tube with a Bruker MultiRAM FT-Raman spectrometer with Nd:YAG laser with excitation up to 1000 mW at 1064 nm in the range 400-4000 cm⁻¹. Infrared spectra were measured with a PerkinElmer Spectrum BX-FTIR spectrometer equipped with a Smiths DuraSamplIR II ATR device. All spectra were recorded at ambient temperature. NMR spectra were recorded with a JEOL Eclipse 400 instrument and chemical shifts were determined with respect to external standards, Me₄Si (¹H, 399.8 MHz; ¹³C, 100.5 MHz) and MeNO₂ (¹⁵N, 40.6 MHz; ¹⁴N, 28.8 MHz). Mass spectrometric data were obtained with a JEOL MStation JMS 700 spectrometer (DCI+, DEI+). Analysis of C/H/N were performed with an Elemental VarioEL Analyzer. Melting and decomposition points were measured with a PerkinElmer Pyris6 DSC and an OZM Research DTA 552-Ex with a heating rate of $5 \,^{\circ}$ C min⁻¹ in a temperature range $15-400 \,^{\circ}$ C and checked by a Büchi Melting Point B-540 apparatus (not corrected). The sensitivity data were performed by using a BAM drophammer and a BAM friction tester.^[2, 25]

X-ray crystallography

Crystals suitable for X-ray crystallography were selected by means of a polarization microscope and mounted on the tip of a glass fiber. The measurements were investigated with an Oxford XCalibur3 (4, 5, 6, 7, 9, and 10) or a Bruker-Nonius KappaCCD diffractometer (8). The diffractometers are equipped with a generator (voltage 50 kV, current 40 mA) and a KappaCCD detector operating with $Mo_{K\!\alpha}$ radiation ($\lambda\!=\!0.7107$ Å). The solution of the structure was performed by direct methods (SIR97)^[27] and refined by fullmatrix least-squares on F² (SHELXL)^[28] implemented in the WINGX software package^[29] and finally checked with the PLATON software.^[30] All non-hydrogen atoms were refined anisotropically. The hydrogen atom positions were located on a difference Fourier map. ORTEP plots are shown with thermal ellipsoids at the 50% probability level. CCDC-1062382 (4), 1062383 (5), 1062384 (6), 1062385 (7), 1062386 (8), 1062387 (9), and 1062388 (10) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Quantum chemical calculations

All ab initio calculations were carried out by using the program package Gaussian 09 (Rev. A.02)^[31] and visualized by GaussView 5.08.^[32] Structural optimizations and frequency analyses were performed with Becke's B3 three parameter hybrid functional using the LYP correlation functional (B3LYP). For C, H, N, and O, a correlation-consistent polarized double-zeta basis set cc-pVDZ was used. The structures were optimized with symmetry constraints and the energy was corrected with the zero point vibrational energy.^[33] The enthalpies (*H*) and free energies (*G*) were calculated by using the complete basis set (CBS) method in order to obtain accurate values. The CBS models used the known asymptotic convergence of pair natural orbital expressions to extrapolate from calculations using a finite basis set to the estimated complete basis set limit. CBS-4m starts with a HF/3-21G(d) geometry optimization, which is

the initial guess for the following SCF calculation as a base energy and a final MP2/6-31 + G calculation with a CBS extrapolation to correct the energy in second order. The used CBS-4 m method additionally implements a MP4(SDQ)/6-31 + (d,p) calculation to approximate higher order contributions and also includes some additional empirical corrections.^[34] The enthalpies of the gas-phase species were estimated according to the atomization energy method.^[35]

Calculation of energetic performance

All calculations affecting the detonation parameters were carried out by using the program package EXPLO5 V6.02.^[26,36] The detonation parameters were calculated at the Chapman–Jouguet (CJ) point with the aid of the steady-state detonation model using a modified Becker–Kistiakowski–Wilson equation of state for modeling the system. The CJ point is found from the Hugoniot curve of the system by its first derivative. The specific impulses were also calculated with the EXPLO5 V6.02 program, assuming an isobaric combustion of a composition of 70% oxidizer, 16% aluminum as fuel, 6% polybutadiene acrylic acid, 6% polybutadiene acrylonitrile as binder, and 2% bisphenol A ether as epoxy curing agent. A chamber pressure of 70.0 bar and an ambient pressure of 1.0 bar with frozen expansion conditions were assumed for the calculations.

Synthesis

CAUTION! All prepared compounds are energetic materials with sensitivity toward heat, impact, and friction. Although no hazards occurred during preparation and manipulation, additional proper protective precautions (face shield, leather coat, earthened equipment and shoes, Kevlar[®] gloves and ear plugs) should be used when undertaking work with these compounds.

1,1,1-Trinitropropan-3-isocyanate (1): Prepared according to references [5, 12]. ¹H NMR (CDCl₃): δ = 3.90 (m, 2H, *CH*₂), 3.32 ppm (m, 2H, *CH*₂); ¹³C NMR (CDCl₃): δ = 127.4 (*C*(NO₂)₃), 123.6 (NCO), 37.4 (CH₂), 35.0 ppm (CH₂); ¹⁴N NMR (CDCl₃): δ = -31 (*C*(NO₂)₃), -360 ppm (NCO); elemental analysis calcd (%) for C₄H₄N₄O₇ (220.10): C 21.83, H 1.83, N 25.46; found: C 21.31, H 1.80, N 26.07; IR (ATR): ν = 3380 (w), 2956 (w), 2897 (w), 2269 (m, ν (NCO)), 2155 (w), 1721 (m), 1584 (s, ν _{as}(NO₂)), 1423 (m), 1364 (m), 1297 (s, ν _s(NO₂)), 1227 (m), 1195 (m), 1148 (m), 1092 (w), 1065 (w), 980 (w), 897 (w), 854 (m), 811 (m), 798 (s), 754 (m), 667 cm⁻¹ (w); Raman (1000 mW): ν = 2953 (70), 2156 (13), 2147 (13), 1718 (11), 1610 (24, ν _{as}(NO₂)), 1451 (18), 1421 (22), 1363 (37), 1304 (30, ν _s(NO₂)), 1100 (10), 1051 (13), 914 (20), 887 (12), 856 (100), 811 (10), 535 (10), 502 (16), 460 (10), 375 (68), 305 (17), 279 (22), 254 cm⁻¹ (20).

3,3,3-Trinitropropan-1-amine hydrochloride (2): Prepared according to references [6b, 12]. ¹H NMR (CD₃CN): δ = 7.92 (br, NH₃), 3.69 (m, 2 H, CH₂), 3.42 ppm (m, 2 H, CH₂); ¹³C NMR (CD₃CN): δ = 125.7 (C(NO₂)₃), 34.6 (CH₂), 30.8 ppm (CH₂); ¹⁴N NMR (CD₃CN): δ = -31 (C(NO₂)₃), -349 ppm (NH₃); elemental analysis calcd (%) for C₃H₉N₄O₇ (230.56): C 15.63, H 3.06, N 24.30; found: C 15.94, H 3.06, N 24.30; IR (ATR): ν = 3132 (m), 3101 (m), 3035 (m), 2977 (m), 2890 (m), 2833 (m), 2783 (w), 2705 (w), 2655 (w), 2567 (w), 2500 (w), 1597 (s, ν _{as}(NO₂)), 1499 (w), 1478 (w), 1458 (m), 1425 (w), 1303 (m, ν _s(NO₂)), 999 (w), 973 (w), 954 (w), 895 (w), 790 cm⁻¹ (w); Raman (300 mW): ν = 3038 (9), 2993 (18), 2965 (34), 2937 (37), 2850 (6), 2806 (8), 1606 (45, ν _{as}(NO₂)), 1471 (10), 1434 (12), 1370 (52), 1346 (17), 1312 (26, ν _s(NO₂)), 1301 (23, ν _s(NO₂)), 1162 (12), 1147 (14), 1022 (11), 989 (15), 924 (12), 911 (17), 858 (100), 802 (8), 739 (6),

656 (6), 643 (6), 557 (9), 408 (66), 383 (64), 343 (47), 289 (20), 221 cm⁻¹ (7); IS: 20 J (grain size 100–250 μ m); FS: 360 N (grain size 100–250 μ m); ESD: >0.5 J (grain size 100–250 μ m); ESD: >0.4 J (grain size 100–250 μ m); DSC (5 °C min⁻¹, onset): 161 °C (m.p.), 178 °C (dec.).

3,3,3-Trinitropropanol (3): 3,3,3-Trinitropropan-1-amine hydrochloride (2) (1.0 g, 4.3 mmol) was dissolved in water (10 mL) and a solution of NaNO₂ (0.60 g, 8.7 mmol) in water (10 mL) was slowly added at 0°C. The yellow solution was stirred at 0°C for 1 h and at 60°C for 1.5 h. The reaction mixture was extracted three times with dichloromethane (3×25 mL), washed with brine (25 mL), and dried over MgSO₄. After removing the solvent in vacuo, 3,3,3-trinitropropanol (3) was obtained as a slightly yellow oil (0.65 g, 78%). ¹H NMR (CDCl₃): $\delta = 4.12$ (m, 2H, CH₂), 3.33 (m, 2H, CH₂), 1.99 ppm (s, 1 H, OH); ¹³C NMR (CDCl₃): $\delta = 128.1$ (C(NO₂)₃), 56.5 (CH₂OH), 36.6 ppm (CH₂); ¹⁴N NMR (CDCl₃): $\delta = -30$ ppm (NO₂); elemental analysis calcd (%) for $C_3H_5N_3O_7$ (195.09): C 18.47, H 2.58, N 21.54; found: C 18.92, H 2.59, N 21.49; IR (ATR): v = 3599 (w), 3385 (br, w, $\nu({\rm OH})),~2947$ (w), 2904 (w), 1581 (s, $\nu_{\rm as}({\rm NO}_2)),~1473$ (w), 1420 (w), 1368 (m), 1296 (s, v_s(NO₂)), 1223 (w), 1140 (w), 1071 (m), 1035 (m), 984 (w), 924 (w), 854 (m), 842 (m), 811 (m), 798 (s), 771 cm⁻¹ (m); Raman (300 mW): v = 2992 (60), 2984 (60), 2949 (100), 2913 (41), 1608 (19, v_{as}(NO₂)), 1478 (7), 1458 (9), 1425 (15), 1368 (35), 1350 (23), 1306 (25, $\nu_s(NO_2)$), 1082 (8), 926 (7), 857 (57), 472 (6), 375 (23), 336 cm⁻¹ (6); IS: >40 J; FS: >360 N; DSC (5 °C min⁻¹, onset): 141 °C (boil. with dec.).

Bis(3,3,3-trinitropropyl) urea (4): 3,3,3-Trinitropropyl-1-isocyanate (1) (2.20 g, 10 mmol) was dissolved in a mixture of acetone/water (3:1; 12 mL) and heated at reflux for 3 h. After evaporating the solvent in vacuo, a yellow solid was obtained, which was recrystallized from chloroform. Bis(3,3,3-trinitropropyl) urea (4) was obtained as a pure colorless solid (1.82 g, 88%). ¹H NMR (CDCl₃): $\delta =$ 4.58 (br, 2H, NH), 3.64 (m, 4H, CH₂), 3.35 ppm (m, 4H, CH₂); ¹³C NMR ((CD₃)₂CO): $\delta = 158.5$ (CO), 130.8 (C(NO₂)₃), 35.9 (CH₂), 35.0 ppm (CH₂); ¹⁴N NMR (CDCl₃): $\delta = -30$ ppm (NO₂); elemental analysis calcd (%) for C7H10N8O13 (414.20): C 20.30, H 2.43, N 27.05; found: C 20.32, H 2.36, N 26.80; IR (ATR): v = 3345 (w), 2945 (w), 2881 (w), 1642 (m, ν (CO)), 1587 (s, ν_{as} (NO₂)), 1566 (s), 1460 (w), 1442 (w), 1425 (w), 1392 (w), 1365 (w), 1298 (m, v_s(NO₂)), 1262 (m), 1246 (m), 1144 (m), 1101 (w), 1037 (w), 943 (w), 892 (w), 856 (m), 826 (w), 796 (s), 770 cm⁻¹ (w); Raman (1000 mW): $\nu = 2979$ (35), 2944 (53), 1644 (12, v(CO)), 1593 (28, v_{as}(NO₂)), 1443 (19), 1427 (24), 1388 (25), 1367 (50), 1309 (33, v_s(NO₂)), 1147 (16), 1119 (15), 1045 (30), 977 (10), 924 (14), 896 (14), 859 (100), 800 (10), 769 (9), 635 (14), 597 (11), 518 (19), 406 (53), 376 (51), 278 cm^{-1} (34); IS: 20 J (grain size 100-250 µm); FS: 120 N (grain size 100-250 µm); ESD: > 0.4 J (grain size 100–250 µm); DSC (5 °C min⁻¹, onset): 160 °C (dec.).

Bis(3,3,3-trinitropropyl) oxalamide (5):^[14] 3,3,3-Trinitropropan-1amine hydrochloride (**2**) (1.00 g, 4.3 mmol) was dissolved in water (15 mL). The solution was overlayed with diethyl ether (30 mL) and cooled to 0 °C. Sodium hydrogen carbonate (0.40 g, 4.8 mmol) was added in small portions and the mixture was stirred for 30 min at 0 °C. The organic layer was separated and the aqueous solution was extracted with diethyl ether (2×25 mL). The combined organic phase was dried over MgSO₄ and cooled to 0 °C. Oxalyl chloride (0.20 g, 1.7 mmol) was slowly added to the organic phase. After 20 min, the precipitated solid was filtered off, washed with cooled diethyl ether and dried. Bis(3,3,3-trinitropropyl) oxalamide (**5**) was obtained as a pure colorless solid (0.61, 75%). ¹H NMR ((CD₃)₂CO):

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 $\delta = 8.56$ (br, 2 H, NH), 3.83 (m, 4 H, CH₂), 3.69 ppm (m, 4 H, CH₂); ¹³C NMR ((CD₃)₂CO): $\delta = 160.8$ (C(O)O), 130.4 (C(NO₂)₃), 35.0 (CH₂), 33.8 ppm (CH₂); ¹⁴N NMR ((CD₃)₂CO): $\delta = -29$ ppm (NO₂); elemental analysis calcd (%) for $C_8 H_{10} N_8 O_{14}$ (442.21): C 21.73, H 2.28, N 25.34; found: C 21.63, H 2.29, N 25.26; IR (ATR): v = 3273 (w), 3066 (w), 2949 (w), 2892 (w), 1687 (w), 1659 (m, v(CO)), 1621 (m), 1583 (s, $v_{\rm as}({\rm NO}_2)$), 1521 (s), 1444 (w), 1423 (w), 1376 (w), 1325 (w), 1297 (m, v_s(NO₂)), 1258 (m), 1227 (m), 1147 (w), 1112 (w), 1053 (w), 1029 (w), 939 (w), 857 (w), 825 (m), 798 (m), 781 (m), 751 (w), 725 cm⁻¹ (w); Raman (300 mW): $\nu\!=\!3298$ (7), 3282 (8), 3025 (10), 2985 (24), 2950 (67), 1694 (41, v(CO)), 1607 (22, v_{as}(NO₂)), 1561 (18), 1447 (18), 1430 (19), 1367 (39), 1336 (22), 1299 (40, v_s(NO₂)), 1244 (17), 1117 (10), 1050 (22), 947 (16), 885 (18), 859 (100), 801 (12), 750 (7), 648 (8), 584 (12), 515 (9), 452 (11), 422 (28), 397 (37), 382 (54), 309 (9), 275 (35), 229 cm⁻¹ (14); IS: 10 J (grain size 100–250 μm); FS: 160 N (grain size 100–250 μm); ESD: >0.5 J (grain size 100–250 μm); DSC (5 °C min⁻¹, onset): 181 °C (dec.).

Bis(3,3,3-trinitropropyl) oxalate (6): 3,3,3-Trinitropropanol (3) (0.50 g, 2.6 mmol) was added slowly at 0 $^\circ\text{C}$ to a solution of oxalyl chloride (0.16 g, 1.3 mmol) in THF (10 mL). The reaction mixture was stirred for 1 h at 25 °C and heated at reflux for further 16 h. The reaction mixture was cooled and the solvent was removed in vacuo. The crude solid product was recrystallized from acetone, yielding pure bis(3,3,3-trinitropropyl) oxalate (6) (0.50 g, 87%) as a colorless solid. ¹H NMR ((CD₃)₂CO): δ = 4.83 (m, 2 H, CH₂), 4.02 ppm (m, 2 H, CH₂); ¹³C NMR ((CD₃)₂CO): δ = 156.3 (C(O)O), 129.8 $(C(NO_2)_3)$, 60.6 (CH_2O) , 33.2 ppm (CH_2) ; ¹⁴N NMR $((CD_3)_2CO)$: $\delta =$ -30 ppm (NO₂); elemental analysis calcd (%) for C₈H₈N₆O₁₆ (444.18): C 21.63, H 1.82, N 18.92; found: C 22.01, H 1.91, N 18.62; IR (ATR): v = 2998 (w), 2960 (w), 1764 (m, v(CO)), 1753 (m), 1600 (s, v_{as}(NO₂)), 1580 (s), 1463 (w), 1412 (w), 1387 (w), 1373 (w), 1296 (m, v_s(NO₂)), 1261 (w), 1244 (w), 1193 (s), 1143 (w), 1105 (w), 1043 (m), 922 (w), 854 (w), 832 (w), 801 (m), 792 (m), 765 (m), 660 cm⁻¹ (w); Raman (300 mW): v = 3029 (16), 2998 (46), 2982 (58), 2959 (77), 2905 (11), 1769 (51, v(CO)), 1615 (25, v_{as}(NO₂)), 1597 (22), 1462 (17), 1415 (21), 1377 (32), 1352 (15), 1292 (29, v_s(NO₂)), 1246 (14), 1107 (12), 1053 (23), 938 (22), 923 (24), 855 (100), 821 (10), 801 (8), 767 (7), 632 (8), 510 (11), 466 (15), 416 (41), 391 (64), 368 (58), 323 (8), 258 (18), 230 cm $^{-1}$ (15); IS: >40 J (grain size $<100~\mu m$); FS: > 360 N (grain size < 100 μ m); ESD: > 0.4 J (grain size < 100 μ m); DSC (5 °C min⁻¹, onset): 121 °C (melt.), 170 °C (dec.).

3,3,3-Trinitropropyl carbamate (7): 3,3,3-Trinitropropanol (3) (1.20 g, 6.1 mmol) was dissolved in dry acetonitrile (20 mL) and cooled to 0°C. Chlorosulfonyl isocyanate (CSI, 0.95 g, 6.7 mmol) was added slowly. The ice bath was removed and stirring at room temperature was continued for 1 h. The reaction mixture was again cooled with an ice bath and water (10 mL) was added with caution. The reaction mixture was stirred further 10 min at room temperature to complete hydrolysis. The organic solvent was removed in vacuo and the formed precipitate was filtered. The light yellow precipitate was recrystallized from a mixture of ethanol and water (7:1) and colorless 3,3,3-trinitropropyl carbamate (7) was obtained (1.06 g, 82%). ¹H NMR ((CD₃)₂CO): $\delta = 6.07$ (br, NH₂), 4.51 (m, 2H, CH₂O), 3.78 ppm (m, 2H, CH₂); ¹³C NMR ((CD₃)₂CO): δ = 156.5 (CO), 130.1 (C(NO₂)₃), 58.0 (CH₂O), 34.3 ppm (CH₂); ¹⁴N NMR ((CD₃)₂CO): $\delta = -29$ (NO₂), -311 ppm (NH₂); elemental analysis calcd (%) for C₄H₆N₄O₈ (238.11): C 20.18, H 2.54, N 23.53; found: C 20.10, H 2.63, N 23.22; IR (ATR): v = 3393 (w), 3334 (w), 3275 (w), 3197 (w), 2985 (w), 1751 (w), 1704 (m, v(CO)), 1608 (m), 1583 (s, v_{as}(NO₂)), 1469 (w), 1410 (m), 1371 (w), 1353 (m), 1332 (m), 1298 (m, v_s(NO₂)), 1132 (m), 1103 (m), 1081 (s), 976 (m), 934 (w), 893 (w), 854 (w), 819 (m), 800 (m), 780 (m), 758 (w), 673 cm⁻¹ (w); Raman (500 mW): $\nu = 3264$ (5), 3196 (6), 3021 (15), 2993 (39), 2949 (60), 1699 (15, ν (CO)), 1617 (36, $\nu_{as}(NO_2)$), 1589 (24), 1471 (13), 1414 (20), 1373 (47), 1339 (19), 1299 (25, $\nu_s(NO_2)$), 1282 (24), 1141 (20), 1104 (11), 1018 (11), 978 (23), 936 (25), 895 (24), 855 (100), 820 (12), 802 (11), 758 (11), 670 (10), 654 (10), 633 (12), 542 (19), 508 (21), 475 (23), 416 (55), 396 (68), 373 (83), 291 cm⁻¹ (17); IS: >40 J (grain size 500–1000 µm); FS: >360 N (grain size 500–1000 µm); ESD: >0.3 J (grain size 500–1000 µm); DSC (5 °C min⁻¹, onset): 78 °C (melt.; 82 °C Lit.^[15]), 152 °C (dec.).

3,3,3-Trinitropropyl nitrocarbamate (8): Nitric acid (100%, 2 mL) was dropped into concentrated sulfuric acid (2 mL) at 0 °C. Into this nitration mixture, chilled in an ice bath, 7 (0.48 g, 2.0 mmol) was added in small portions. The suspension was stirred for 10 min at 0°C and one hour at ambient temperature. The nitration mixture was poured onto ice-water (200 mL), extracted with ethyl acetate (3×50 mL), and the combined organic phases were dried over magnesium sulfate. The solvent was removed under reduced pressure and the crude solid product was recrystallized from carbon tetrachloride to obtain colorless 3,3,3-trinitropropyl nitrocarbamate (8, 0.37 g, 65%). ¹H NMR ((CD₃)₂CO): $\delta = 13.6$ (br, NH), 4.80 (m, 2 H, CH₂O), 3.98 ppm (m, 2 H, CH₂); ¹³C NMR ((CD₃)₂CO): δ = 148.7 (CO), 129.9 (br, C(NO₂)₃), 60.3 (CH₂O), 33.6 ppm (CH₂); ¹⁴N NMR ((CD₃)₂CO): $\delta = -29$ (NO₂), -46 ppm (NO₂); elemental analysis calcd (%) for $C_4H_5N_5O_{10}$ (283.11): C 16.97, H 1.78, N 24.74; found: C 16.89, H 1.87, N 24.33; IR (ATR): $\nu = 3134$ (w), 3037 (w), 2895 (w), 1758 (m, $\nu(\text{CO})),\;1590$ (s, $\nu_{as}(\text{NO}_2)),\;1458$ (m), 1410 (w), 1390 (w), 1367 (w), 1334 (m), 1291 (m, v_s(NO₂)), 1255 (m), 1175 (s), 1099 (m), 1046 (m), 1001 (m), 921 (m), 851 (m), 798 (s), 749 (m), 736 cm⁻¹ (m); Raman (500 mW): $\nu = 3149$ (6), 2994 (35), 2958 (55), 1760 (41, ν (CO)), 1617 (32, v_{as}(NO₂)), 1455 (24), 1413 (24), 1370 (43), 1330 (49), 1307 (30, v_s(NO₂)), 1290 (31, v_s(NO₂)), 1255 (11), 1182 (12), 1152 (6), 1103 (13), 1049 (35), 996 (50), 935 (25), 855 (100), 802 (10), 765 (8), 738 (11), 659 (8), 633 (8), 529 (17), 484 (20), 459 (30), 425 (33), 383 (62), 307 (17), 250 (23), 206 cm^{-1} (32); IS: 30 J (grain size $\,<$ 100 $\mu m);$ FS: 288 N (grain size $<100~\mu m$); ESD: >0.2~J (grain size $<100~\mu m$); DSC (5 °C min⁻¹, onset): 68 °C (melt.), 134 °C (dec.).

3,3,3-Trinitro-N-(2,2,2-trinitroethyl)propan-1-amine (9):^[5,6] 2,2,2-Trinitroethanol (0.41 g, 2.2 mmol) was dissolved in water (20 mL) and added to a solution of 2 (0.50 g, 2.2 mmol) in water (5 mL). A solution of sodium hydroxide (1 mL, 2 M) was added and the reaction mixture was stirred at 25 °C for 1 h. The precipitated solid was filtered off, washed with small portions of cold water, dried, and stored in a desiccator. 3,3,3-Trinitro-N-(2,2,2-trinitroethyl)propan-1amine (9) was obtained as a yellow solid (0.49 g, 63%). ¹H NMR (CDCl₃): $\delta = 4.15$ (m, 2H, CH₂), 3.24 (m, 2H, CH₂), 3.15 (m, 2H, CH₂), 2.16 ppm (m, 1 H, NH); 13 C NMR (CDCl₃): $\delta = 128.0$ (C(NO₂)₃), 126.9 $(C(NO_2)_3)$, 52.6, 44.5, 34.9 ppm; ¹⁴N NMR $(CDCI_3)$: $\delta = -31 (NO_2)$, -32 ppm (NO₂); elemental analysis calcd (%) for C₅H₇N₇O₁₂ (357.15): C 16.82, H 1.98, N 27.45; found: C 16.68, H 2.12, N 27.08; IR (ATR): $\nu = 3366$ (w), 2945 (w), 2880 (w), 1581 (s, $\nu_{as}(NO_2)$), 1479 (w), 1416 (w), 1367 (w), 1302 (s, $\nu_s(NO_2)$), 1236 (w), 1185 (w), 1132 (m), 1039 (w), 901 (w), 878 (w), 856 (w), 829 (w), 800 (s), 766 (m), 655 cm⁻¹ (w); Raman (700 mW): v = 2983 (17), 2952 (31), 2881 (12), 1604 (21, $\nu_{\rm as}(\rm NO_2)$), 1474 (11), 1420 (9), 1373 (29), 1348 (16), 1309 (27, $\nu_{\rm s}({\rm NO}_2)$), 1151 (10), 1001 (6), 933 (6), 859 (87), 800 (5), 646 (10), 543 (13), 405 (47), 376 (62), 313 (9), 273 (5), 244 cm^{-1} (7); IS: 7 J (grain size 100-250 µm); FS: 120 N (grain size 100-250 µm); ESD: > 0.4 J (grain size 100–250 μ m); DSC (5 $^{\circ}$ C min⁻¹, onset): 44 $^{\circ}$ C (phase trans.), 65 °C (melt.), 96 °C (dec.).

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N-(2,2,2-Trinitroethyl)-N-(3,3,3-trinitropropyl) nitramine (10): The synthesis was performed according to the literature procedure^[5] with minor changes. Acetic anhydride (1.4 mL, 14.8 mmol) was added to nitric acid (100%, 1.4 mL, 33.6 mmol) at 0°C. Amine 9 (240 mg, 0.7 mmol) was added and the mixture was allowed to warm to 30 °C until 9 was completely dissolved (1.5 h). After 15 h at 25 °C, the reaction mixture was poured onto ice-water (25 mL). The precipitated solid was filtered, washed with water, and dried. N-(2,2,2-Trinitroethyl)-N-(3,3,3-trinitropropyl) nitramine (10) was obtained as a colorless solid (204 mg, 75%). ¹H NMR (CD₃CN: δ = 5.59 (s, 2H, CH₂), 4.27 (m, 2H, CH₂), 3.65 ppm (m, 2H, CH₂); ¹³C NMR (CD₃CN): $\delta = 129.4$ (C(NO₂)₃), 124.2 (C(NO₂)₃), 55.2, 49.5, 31.6 ppm; ¹⁵N NMR (CD₃CN): $\delta = -31.0$ (t, ³J = 2.8 Hz, C(NO₂)₃), -32.9 (m, NNO₂), -34.5 (t, ${}^{3}J = 1.9$ Hz, C(NO₂)₃), -213.7 ppm (m, NNO₂); elemental analysis calcd (%) for C₅H₆N₈O₁₄ (402.15): C 14.93, H 1.50, N 27.86; found: C 15.02, H 1.55, N 27.58; IR (ATR): v = 3020 (w), 1599 (s, v_{as}(NO₂)), 1555 (s, v_{as}(NO₂)), 1454 (w), 1412 (w), 1395 (w), 1342 (w), 1285 (s, v_s(NO₂)), 1268 (s, v_s(NO₂)), 1208 (w), 1138 (w), 1062 (w), 1007 (w), 876 (w), 858 (m), 799 (s), 780 (m), 763 (m), 662 cm⁻¹ (w); Raman (300 mW): $\nu = 3046$ (11), 3020 (15), 3000 (19), 2977 (36), 2958 (41), 1613 (35, $\nu_{as}(NO_2)$), 1456 (9), 1429 (7), 1413 (10), 1396 (15), 1386 (18), 1367 (20), 1345 (40), 1294 (23, $\nu_s(NO_2)$), 1270 (25, $\nu_{\rm s}({\rm NO}_2)),\;1063$ (9), 1049 (12), 989 (7), 919 (12), 877 (26), 858 (100), 640 (10), 599 (7), 549 (9), 452 (8), 428 (16), 408 (41), 391 (37), 375 (34), 364 (40), 294 (25), 235 cm⁻¹ (11); IS: 7 J (grain size 100-250 μm); FS: 160 N (grain size 100-250 μm); ESD: > 0.4 J (grain size 100–250 μm); DSC (5 °C min⁻¹, onset): 141 °C (melt.), 153 °C (dec.).

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