

FINAL REPORT

Perchlorate and Halogen-Free High Energy Dense Oxidizers (HEDO)

SERDP Project WP-1765

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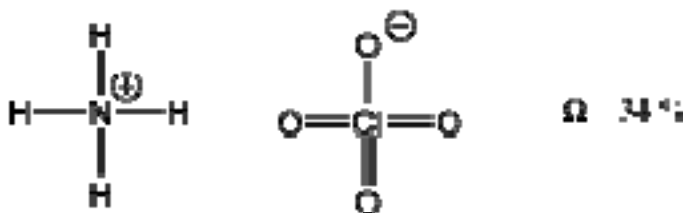
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Abstract:

Several new CHNO compounds with a positive oxygen balance were synthesized and fully characterized. In addition poorly described and characterized compounds from literature proceedings were repeated, fully characterized and evaluated whether they can be used as oxidizer. Most of the derivatives described in this report are based on the trinitro(m)ethyl moiety. Full characterization includes X-ray diffraction, multinuclear NMR spectroscopy, mass spectrometry, vibrational (IR and Raman) spectroscopy, elemental analysis and differential scanning calorimetry. Sensitivities towards impact, friction and electrostatic discharge were measured by BAM methods and a small-scale electrostatic discharge device. Heats of formations were computed by the atomization method (CBS-4M enthalpy based). With these values and the X-ray densities several combustion and detonation parameters were calculated from pure and composited oxidizers. The specific impulses have been compared to this of an ammonium perchlorate / aluminum mixture.

Objective:

The objectives of this project are to explore the chemical synthesis of possible replacements for AP as oxidizer in tactical missile rocket motors. We propose to investigate the synthesis, sensitivities, thermal stability, binder compatibility and decomposition pathways of these new high oxygen materials.



Traditional representatives of high oxygen explosives have been reported in the public literature as research reports and patents, however, often without giving information about

synthetic procedures or specifying the physicochemical characteristics of the compounds obtained.[1] Some of the most promising materials initially considered were polynitroaliphatic compounds containing the dinitromethyl, fluorodinitromethyl and trinitromethyl groups.[2] Among them, the trinitroethyl compounds were found to have the most favorable heats of detonation and oxygen balance values. However, the thermal stability was reported to be generally limited to 150 °C when solid and 100 °C when molten reversing further investigation into trinitroethyl substituted compounds.[3] We have recently investigated compounds mentioned in literature and have developed and tested novel compounds with the trinitroethyl functionality in order to explore its potential for the design of next generation energetic materials trying to enhance the thermal stability of this class of compounds.

In the course of the global emerging interest in high-energetic, dense materials (HEDM) [4] we are currently developing new energetic materials preferentially containing both high oxygen and nitrogen content with the trinitroethyl group contributing to a positive oxygen balance value. Oxygen balance (Ω) is defined as the ratio of the oxygen content of a compound to the total oxygen required for the complete oxidation of all carbon, hydrogen and other elements. These elements are oxidized to form CO₂, H₂O, etc. and is used to classify energetic materials as either oxygen deficient or oxygen rich.

Based on crystal structures we found that trinitroethyl mediated intermolecular interactions like dipolar nitro group interactions and hydrogen bonding of the acidified methylene-type protons. These interactions govern mainly the molecular packing of these compounds yielding high-crystal-density polymorphs with promising energetic performance parameters.[5] Different new high explosive compounds have been introduced belonging to a new class of energetic materials preferentially containing both high-nitrogen and high-oxygen content. Compounds abbreviated with BTDD and BTAT display superior performance properties to RDX. BTAT for example is at the same time less sensitive and displays a better oxygen balance value yielding smokeless combustion and less toxic fumes on decomposition. The compounds are water insoluble in contrast to energetic salts, a prerequisite to protect the ground and one important environmental advantage amongst the qualification criteria for new HEDM. It is shown that temperature stability can be higher than 140 °C for solid and liquid compounds carrying the trinitroethyl moiety not only as far as decomposition temperatures but also as far as chemical long term stabilities are concerned. In our research group we also studied the structures of 2,2,2-trinitroethanol (TNE) [6] as one of the relevant precursors and that of bis(2,2,2-trinitroethyl) carbonate.[7] Within this project we extended our investigations from initially looking at explosive properties to also including the suitability of related but different compounds as potential oxidizers and replacements for AP. In particular, we try to synthesize oxygen-rich trinitroethyl derivatives which are high-oxygen compounds (oxidizers) but not necessarily high-nitrogen species (explosives).

Background:

Ammonium perchlorate (AP) has applications in munitions, primarily as an oxidizer for solid rocket and missile propellants. It is also used as an air-bag inflator in the automotive industry, in fireworks, and as a component of agricultural fertilizers. Because of these uses and AP's high solubility, chemical stability, and persistence, it has become widely distributed in surface

and ground water systems particularly in the south-western United States. There is little information about the effects of perchlorate in these systems on the aquatic life that inhabits them. However, it is known that perchlorate is an endocrine disrupting chemical that interferes with normal thyroid function and that, in vertebrates, thyroid dysfunction impacts both growth and development. Because perchlorate competes for iodine binding sites in the thyroid, the addition of iodine to culture water was examined to determine if perchlorate effects can be mitigated. Finally, perchlorate is known to affect normal pigmentation of amphibian embryos.

Materials and Methods:

In order to ensure the scientific results, complete chemical and physical characterization, determination of sensitivities, calculation and measurement of detonation parameters the following facilities have been used:

- Oxford X-ray diffractometer with CCD detector
- JEOL NMR machines (270 MHz and 400 MHz)
- Mass spectrometer
- UV/VIS spectrometer
- Perkin Elmer FT-IR spectrometer
- Bruker Raman spectrometer
- CHN Netsch Simultaneous Thermal Analyzer STA 429
- Quantachrome Pycnometer
- Büchi B-540 melting point apparatus
- 2 Differential scanning calorimeters (Linseis PT10 and OZM DTA 551-EX)
- BAM drophammer
- BAM friction tester
- OZM small scale electrostatic discharge device
- Koenen Test
- Optical fiber detonation velocity test setup
- 2 ram compactors
- Small-scale-reactivity test
- High-speed camera (4000 fps), VHS camera and digital cameras
- Bomb-chamber
- 2 Microscopes
- Dry-box (Braun)
- Centrifuge
- Rotary evaporator, vacuum lines and pumps
- Cluster for quantum chemical calculations

- o For calculation of the heat of formation the atomization method based on CBS-4M enthalpies was used. This has been described in detail in a recently published paper.[8] All quantum chemical calculations were done with the Gaussian09 program package.[9]
- o The impact sensitivity tests were carried out according to STANAG 4489 [10] modified instruction [11] using a BAM (*Bundesanstalt für Materialforschung*) drophammer.[12] The friction sensitivity tests were carried out according to STANAG 4487 [13] modified instruction [14] using a BAM friction tester. The classification of the tested compounds results from the “UN Recommendations on the Transport of Dangerous Goods”. [15] Additionally all compounds were tested upon the sensitivity towards electrical discharge using the Electric Spark Tester ESD 2010 EN [16].

Results and Discussion:

In our proposal the following experimental milestones were described:

Month	Synthesis
1 – 3	1) synthesis, spectroscopic, structural and energetic characterization of BTNA; 2) exploration of nitroalkyl borate chemistry
4 – 6	3) synthesis, spectroscopic, structural and energetic characterization of TAF; 4) synthesis, spectroscopic, structural and energetic characterization of 1,1,1,6,6,6-hexanitro-hex-3-ine; 5) nitration of H ₂ BTA
7 – 9	6) synthesis, spectroscopic, structural and energetic characterization of B(OCH ₂ -C(NO ₂) ₃) ₃ ; 7) oxidation of H ₂ BTA (N oxide); 8) synthesis of nitro triazole derivatives
10 – 15	9) synthesis, spectroscopic, structural and energetic characterization of C(-O-CH ₂ -C(NO ₂) ₃) ₄ ; 10) up-scaling of the most promising two compounds to 10 g scale for further testing; final report preparation; publication

In the following all of the proposed points are described in detail (if successful). In addition we synthesized several other trinitromethyl based compounds, which are described below.

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1. BIS(2,2,2-TRINITROETHYL) AMINE (BTNA)

BTNA is a high oxygen explosive (oxygen balance $\Omega = +7.0$) and a valuable intermediate in the preparation of energetic materials. However, the structure had not been reported previously. The structure of BTNA at 200 K displays orthorhombic symmetry, space group *Pbca*. The asymmetric unit consists of one bis(2,2,2-trinitroethyl) amine molecule.

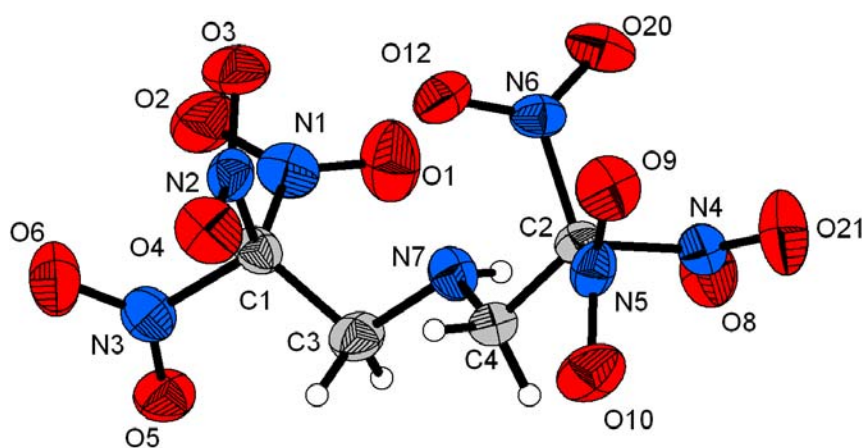


Figure 1. ORTEP representation of the molecular structure of BTNA in the crystalline state. Displacement ellipsoids are shown at the 50 % probability level. Selected bond lengths [Å] and angles [°]: C1–N1 1.524(2), N1–O1 1.206(2), N1–O2 1.215(2), C1–C2 1.521(2), C2–N7 1.457(2), O1–N1–O2 127.31(16), N1–C1–N2 107.57(12), N1–C1–C2 114.24 (14), C1–C2–N7 109.28(13), C2–N7–C4 113.54(14).

The two trinitroethyl moieties display a very similar molecular geometry with a propeller-type orientation of the nitro groups bonded to the β carbon atom. In both moieties the conformation of the substituents of the α - as well as the β carbon atom is found to be staggered. The length of the C–N bonds joining the three nitro groups to the β carbon atom (range 1.513 (2) – 1.530 (2) Å) are significantly longer than the C–N bond distances joining the trinitroethyl moieties to the secondary amine that lie in the normal range of 1.47 Å as observed in the determination of the crystal structures of 2,2,2-trinitroethanol (see below,) bis(2,2,2-trinitroethyl)carbonate, [17] and *N,N'*-bis(2,2,2-trinitroethyl) urea.[18] The independent N–C–N bond angles of the trinitromethyl group are less (range 104.9 (1) – 108.2 (1)°) than the tetrahedral value whereas the corresponding N–C–C bond angles are close to or greater (range 109.5 (1) – 114.2 (1)°) than the tetrahedral value. The six independent nitro groups of each molecule are identical in structure within the limits of error and display common geometry parameters. In turn, the arrangement of the C–N and N–O bonds is coplanar with the sums of the three bond angles around one nitrogen atom being 360° within the limits of error. The extended structure of BTNA involves secondary interactions in terms of intermolecular C–H...O hydrogen bonding as well as dipolar nitro group interactions. The amine proton is

involved in one intermolecular N–H···O hydrogen bond (N7–H7···O10, symmetry code: $x-1/2, -y+1/2, -z+1$) and two intramolecular hydrogen bonds (N7–H7···O1 and N7–H7···O8). Figure 2 displays the unit cell packing of BTNA together with trinitroethyl mediated intermolecular interactions. A color code was chosen in order to more clearly reveal the packing mode of the crystal structure of BTNA when comparing the two different views of the unit cell in Figure 2. Grey denoting all the molecules the unit cell is comprised of whereas the colors blue, orange, red and light blue were used in order to highlight the underlying packing motive. The wave like pattern present in the view along the crystallographic *b* axis turns out to be comprised of molecules of two different layers when looking at the structure along the crystallographic *a* axis. The view along the crystallographic *b* axis reveals two dipolar nitro group interactions (green dashed lines) connecting the molecules along the crystallographic *a* and *c* axis (left picture). Intermolecular C–H···O hydrogen bonding (yellow dashed lines) between two BTNA molecules results in two membered, infinite chains oriented along the crystallographic *b* axis (right picture).

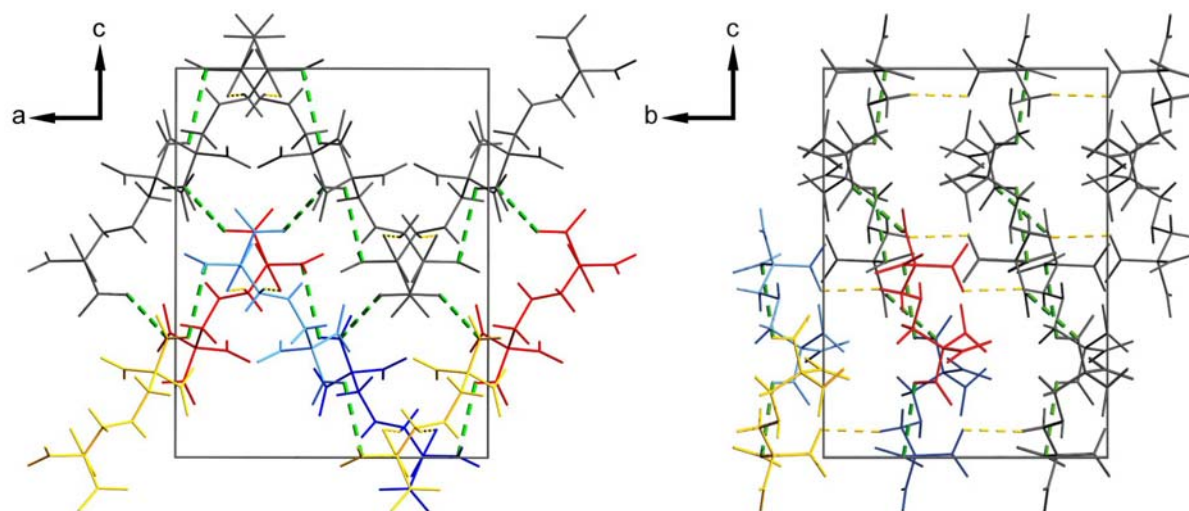


Figure 2. Unit cell packing of BTNA. Yellow dashed lines indicate trinitroethyl mediated intermolecular hydrogen bonding. Green dashed lines indicate dipolar nitro group interactions. Two dipolar nitro group interactions were found with the N3/O5/O6 nitro group interacting with the N4/O7/O8 nitro group (contact distances: 3.174(2) Å [N3···O8(ii)]; 3.039(2) Å [O6···O8(ii)]) and the N5/O9/O10 nitro group (contact distance: 3.1468(2) Å [N5···O5(iii)]; Symmetry code: (i) $3/2-x, 1/2+y, z$; (ii) $x, 1/2-y, -1/2+z$; (iii) $1/2+x, y, 1/2-z$.

BTNA was found to be only moderate sensitive towards impact (15 J) and not sensitive towards friction (> 360 N). Using a loading density of 1.881 g cm⁻³ and a calculated heat of formation of -138 kJ kg⁻¹ the following detonation values were computed: $Q_{CJ} = -6010$ kJ kg⁻¹, $T_{ex} = 4733$ K, $V_o = 705$ L kg⁻¹, $p_{CJ} = 343$ kbar and $D = 8815$ m s⁻¹.

Table 1: Energetic Properties of Bis-(2,2,2-trinitroethyl) amine (**BTNA**)

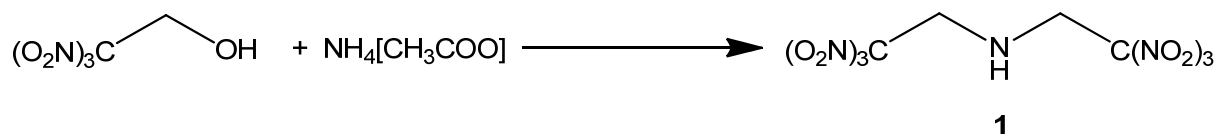
	BTNA	AP	RDX
Formula	C ₄ H ₅ N ₇ O ₁₂	NH ₄ ClO ₄	C ₃ H ₆ N ₆ O ₇
FW / g mol ⁻¹	343.12	117.5	222.12
IS / J	15 (100–500 μm)	15	7.5
FS / N	>360 (100–500 μm)		120
ESD / J			0.1–0.2
N / %	28.57	11.04	37.8
Ω / %	7.0	34.04	–21.6
T _{Dec.} / °C	112	130 [19]	210
ρ / g cm ⁻³	1.881	1.95	1.80
Δ _f H _m ^o / kJ mol ⁻¹	–47	–296	70
Δ _f U ^o / kJ kg ⁻¹	–50.29	–2412	417
EXPLO5.04 values:			
–Δ _{Ex} U ^o / kJ kg ⁻¹	6010		6125
T _{det} / K	4733		4236
P _{CJ} / kbar	343		349
V _{Det.} / m s ⁻¹	8815		8748
V _o / L kg ⁻¹	705		739
I _s / s (20 % Al, 70.0 bar)		243	---

Though Murray and Sauer claim [20] that the condensation of nitroform with hexamethylenetetramine would afford bis(2,2,2-trinitroethyl) amine we were not successful using this strategy or confirm it.

Potassium nitroformate (0.8849 g, 4.47 mmol) was suspended in water (1 mL) and hydrochloric acid was added (1 M) until the pH value of one was achieved. Hexamethylenetetramine (0.1026 g, 0.731 mmol) was dissolved in water (1 mL) and added to the solution of potassium nitroformate using a syringe while stirring the reaction mixture at 20 °C (water bath). In order to keep the pH value below one, a further amount of hydrochloric acid (1 M, 2.5 mL) was added in small portions. The reaction mixture was allowed to stir at room temperature for twelve hours. The yellow precipitate formed was filtered and identified as potassium nitroformate using Raman spectroscopy. The solution was evaporated and the yellow solid shown to be potassium nitroformate according to the intensities obtained from Raman spectroscopy.

Bis(2,2,2-trinitroethyl) amine was successfully prepared from the reaction of 2,2,2-trinitroethanol with ammonium acetate.[21] 2,2,2-Trinitroethanol (2.5 g, 1.38 mmol) is dissolved in water (1 mL). To this is added a solution of ammonium acetate (0.525 g, 0.68 mmol) dissolved in water (4 mL) at room temperature. The solution turned orange after a few seconds and a white precipitate formed on stirring the solution at room temperature after

five minutes. Stirring was continued for further 30 minutes. The precipitate was filtered and washed with cold water (3 times, each 2 mL). The white solid obtained was air dried (oven, 40 °C, 30 min). The crystal growth was accomplished by storing a saturated carbon tetrachloride solution in the refrigerator (7 °C), yielding colorless single crystals of needle like habit.

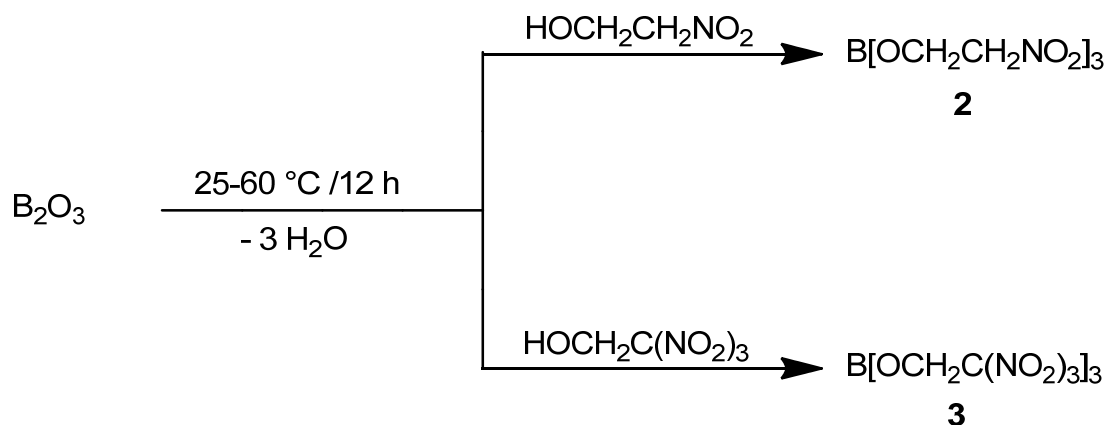


Scheme 1: Formation of Bis(2,2,2-trinitroethyl) amine (BTNA, **1**).

DSC (Linseis, 5 K min⁻¹): 112 °C (onset, decomp.); **IR** (KBr disk) $\tilde{\nu}$ = 3406 (w), 3370 (m), 2987 (w), 2946 (w), 2894 (w), 1582 (vs), 1478 (s), 1442 (s), 1431(m), 1408 (w), 1397 (w), 1376 (m), 1350 (w), 1339 (w), 1307 (vs), 1298 (vs), 1258 (s), 1243 (m), 1156 (m), 1133 (m), 1089 (m), 1059 (w), 1049 (m), 1020 (w), 1008 (w), 883 (m), 873 (m), 854 (s), 803 (vs), 791 (vs), 781 (vs), 751 (w), 740 (m), 712 (w), 660 (m), 642 (s) cm⁻¹; **Raman** $\tilde{\nu}$ = 3011 (8), 2982(13), 2949(24), 1607(27), 1445 (20), 1431 (11), 1398 (16), 1377 (15), 1354 (43), 1311 (41), 1260 (8), 859 (100), 809 (8), 782 (8), 663 (8), 644 (10), 562 (9), 536 (11), 423 (47), 397 (50), 376 (90), 299 (19), 280 (22), 213 (24) cm⁻¹; **Mass spectrometry** (DEI, 70 eV): 343 [m⁺].

2. EXPLORATION OF NITROALKYLBORATE CHEMISTRY

The nitro compounds based on boron esters presented in this project are suitable candidates for high energy density oxidizers and for smoke-free, green coloring agents in pyrotechnic compositions. In literature, only little is known about tris(2-nitroethyl) borate.[22] Further compounds of this substance class haven't been fully described at all, to the best of our knowledge. In this contribution, a detailed study of the synthesis and characterization of the nitroethyl borates tris(2-nitroethyl) borate and tris(2,2,2-trinitroethyl) borate is presented. Tris(2-nitroethyl) borate and tris(2,2,2-trinitroethyl) borate can be obtained from boron oxide with 2-nitroethanol and 2,2,2-trinitroethanol, respectively (Scheme 2).



Scheme 2: Synthesis of tris(2-nitroethyl) borate (**2**) and tris(2,2,2-trinitroethyl) borate (**3**).

The advantages of this synthesis are the easy preparation method, the cheap reagent boron oxide and the high yields. Furthermore, up-scaling in an easy and safe way is possible with this synthesis method, even quantities of more than 12 g were synthesized without any problems. The synthesis of the starting material 2,2,2-trinitroethanol for the synthesis of **2** was carried out, according to literature, in high quantities with high yields. The characterization of **2** and **3** was performed by multinuclear NMR, IR and Raman spectroscopy as well as mass spectrometry and elemental analysis. All analytical data show the expected results. Data from mass spectrometry for **2** was not easy to obtain, because the compound easily fragments during the measurement and therefore no molecule peak or bigger molecule fragments could be detected. The oxygen balance of **2** is -59.70% and of **3** is $+13.07\%$. The density for **3** was determined to 1.982 g cm^{-3} , which is a quite high value. DSC measurements revealed an exothermic decomposition at $216\text{ }^{\circ}\text{C}$ for **2** and $161\text{ }^{\circ}\text{C}$ for **3**. In the flame of a Bunsen burner, **2** and **3** show a green flame and smoke-free combustion, the burn rate of **3** is faster. The sensitivity data for **3** is given in Table 2.

Table 2: Sensitivity data for **3**.

Grain size	< 100 μm
Impact sensitivity	15 J
Friction sensitivity	144 N
Electrostatic sensitivity	0.5 J

Compound **2** crystallizes in the monoclinic space group $P2_1/c$ with four formula units per unit cell and a density of 1.524 g cm^{-3} . All bond lengths and angles of **2** were found as expected. Many $\text{N}\cdots\text{O}$ interactions between the nitro groups of adjacent molecules are present in the crystal structure, with the shortest $\text{N}\cdots\text{O}$ interaction of $2.94\text{ \AA}$. Furthermore, hydrogen bonds between the nitro groups and the hydrogen atoms of the methylene groups could be observed in the crystal. Energies of formation, calculated on the CBS-4M level of theory, are -1100.471996 H for **2** and -2326.133067 H for **3**. Therefore, the theoretic values for the standard enthalpy of formation are determined to $\Delta_f H^\circ(298.15\text{ K}) = -1126.7\text{ kJ/mol}$ for **2** and -913.9 kJ/mol for **3**.

Tris(2-nitroethyl) borate (**2**)

In a nitrogen flushed flask $0.62\text{ g B}_2\text{O}_3$ (8.9 mmol) was reacted with $4.86\text{ g 2-nitroethanol}$ (53.4 mmol) at elevated temperature in dry carbon tetrachloride. Crystallization of the product and removing of the solvent yielded a colorless powder. Yield: $3.65\text{ g (73 \%)}$. **DSC**: $216\text{ }^\circ\text{C}$ (exothermic decomposition).

Raman $\tilde{\nu} = 3031$ (16), 2971 (100), 2909 (20), 1558 (12), 1472 (12), 1423 (18), 1395 (19), 1370 (45), 1274 (14), 1219 (9), 1148 (4), 1100 (12), 1068 (8), 992 (10), 921 (5), 898 (9), 876 (61), 740 (9), 617 (14), 482 (6), 376 (5), 288 (6), 225 (7) cm^{-1} . **IR** $\tilde{\nu} = 3554$ (w), 2964 (w), 1548 (vs), 1473 (m), 1413 (s), 1382 (s), 1346 (s), 1319 (vs), 1269 (m), 1216 (m), 1148 (w), 1101 (m), 1064 (s), 991 (w), 894 (m), 874 (m), 793 (w), 718 (w), 651 (w) cm^{-1} . **$^1\text{H NMR}$** (CDCl_3): $\delta = 4.92$ (s, CH_2 , 2H) ppm. **$^{11}\text{B NMR}$** (CDCl_3): $\delta = 17.1$ (s) ppm. **$^{13}\text{C}\{^1\text{H}\}$ NMR** (CDCl_3): $\delta = 76.0$ (s, CH_2NO_2), 59.7 (s, CH_2) ppm. **$^{14}\text{N NMR}$** (CDCl_3): $\delta = -0.5$ (s, NO_2) ppm. **Mass spectrometry** (DCI+) m/z (%): 281 (1) [M^+], 221 (2) [$\text{M}^+ - \text{CH}_2\text{NO}_2$], 191 (94) [$\text{M}^+ - \text{OCH}_2\text{CH}_2\text{NO}_2$], 74 (18) [$\text{CH}_2\text{CH}_2\text{NO}_2^+$]. **Elemental analysis** for $\text{C}_6\text{H}_{12}\text{BN}_3\text{O}_9$: C, 14.95; H, 4.30; N, 25.65. Found: C, 14.42; H, 4.47; N, 24.91.

Tris(2,2,2-trinitroethyl) borate (**3**)

In a nitrogen flushed flask $13.16\text{ g 2,2,2-trinitroethanol}$ (72.7 mmol) is reacted with $1.27\text{ g B}_2\text{O}_3$ (18.2 mmol) in dry acetonitrile at ambient temperature, unreacted boron oxide is removed by filtration and the solution is evaporated. Yield: $12.71\text{ g (95 \%)}$.

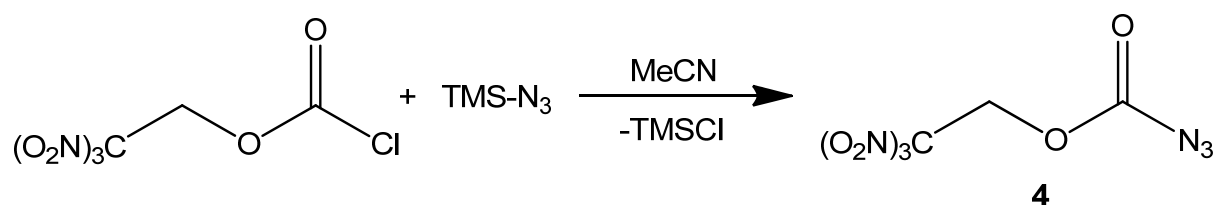
DSC: $161\text{ }^\circ\text{C}$ (exothermic decomposition); **Raman** $\tilde{\nu} = 3009$ (20), 2970 (37), 1613 (24), 1599 (25), 1456 (9), 1445 (9), 1427 (5), 1395 (17), 1375 (8), 1355 (45), 1310 (36), 1278 (16), 1181 (3), 1149 (6), 1096 (6), 1076 (9), 1019 (6), 1006 (7), 887 (10), 858 (100), 824 (5), 809 (8), 782 (8), 763 (5), 722 (5), 653 (6), 600 (4), 565 (4), 542 (17), 523 (5), 418 (47), 402 (53), 379 (71), 341 (11), 306 (18), 261 (18), 234 (13), 205 (27) cm^{-1} . **IR** $\tilde{\nu} = 3217$ (m), 3008 (w), 2970 (w), 2894 (w), 1585 (vs), 1475 (m), 1456 (m), 1444 (m), 1420 (s), 1374 (m), 1332 (s), 1298 (s), 1274 (m), 1198 (w), 1149 (w), 1100 (m), 1075 (m), 1006 (w), 882 (m),

856 (m), 804 (m), 780 (m), 761 (w), 719 (w), 649 (w), 624 (m) cm^{-1} . ^1H NMR (acetone- D_6): $\delta = 5.19$ (s, CH_2 , 2H) ppm. ^{11}B NMR (acetone- D_6): $\delta = 19.3$ (s) ppm. $^{13}\text{C}\{^1\text{H}\}$ NMR (acetone- D_6): $\delta = 128.1$ (s, $\text{C}(\text{NO}_2)_3$), 63.7 (s, CH_2) ppm. ^{14}N NMR (acetone- D_6): $\delta = -31$ (s, NO_2) ppm. **Elemental analysis** for $\text{C}_6\text{H}_6\text{BN}_9\text{O}_{21}$: C, 13.08; H, 1.10; N, 22.88. Found: C, 12.09; H, 1.54; N, 19.41.

The nitroethyl boron compounds tris(2-nitroethyl) borate (**2**) and tris(2,2,2-trinitroethyl) borate (**3**) have been prepared by reaction of the corresponding nitroalcohol with boron oxide. The preparation method is very easy to perform with high yields. Furthermore, up-scaling is possible with this synthesis method in an easy and safe way. The nitroethyl compounds were fully characterized using multinuclear NMR, IR and Raman spectroscopy as well as mass spectrometry and elemental analysis. Thermal stability was studied using differential scanning calorimetry. Furthermore, the energies of formation were calculated and the synthesis of the starting material 2,2,2-trinitroethanol is described in detail below.

3. SYNTHESIS, SPECTROSCOPIC, STRUCTURAL AND ENERGETIC CHARACTERIZATION OF 2,2,2-TRINITROMETHYL AZIDOFORMATE (TAF)

In order to study whether the thermal stability could further be enhanced we also developed compounds where we take advantage of the unshared p electron pair of nitrogen trying to impact thermal stability through oxygen-balance neutral introduction of conjugation affording carbamates from the reaction between 2,2,2-trinitroethylchloroformate and a nitrogen nucleophile. 2,2,2-trinitroethyl-azidoformate (**4**, TAF) was obtained from the reaction of 2,2,2-trinitroethylchloroformate and trimethylsilylazide as shown in Scheme 3. [23]



Scheme 3: Synthesis of 2,2,2-trinitroethyl azidoformate.

The synthesis of **TAF** is already known and described in literature. We synthesized the compound again to measure the missing sensitivity and performance data and to get used to this type of reaction. We were successful in producing **TAF** in high yields and high purity. Attempts in replacing the expensive TMS-N₃ with NaN₃ failed. It seems that the improved reactivity of TMS-N₃ is needed for the reaction.

The structure of **TAF** at 100 K has monoclinic symmetry, space group *P*2₁/*c*. The asymmetric unit consists of two molecules (Figure 3).

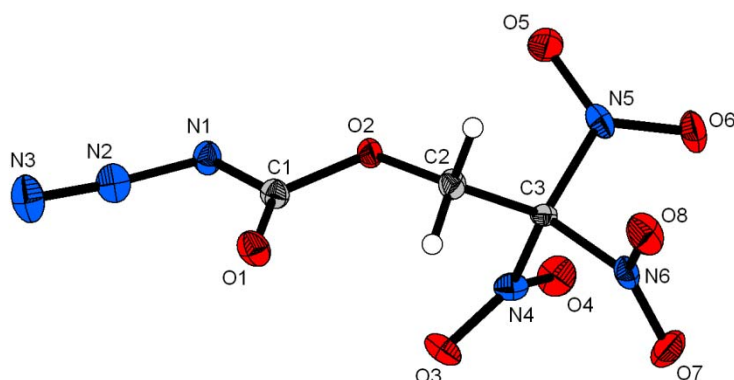


Figure 3: ORTEP representation of the molecular structure of TAF in the crystalline state. Displacement ellipsoids are shown at the 50 % probability level.

The DSC diagram of **TAF** shows that melting of the white solid occurs at 28 °C (onset). A second endothermic signal (96 °C onset) corresponds to boiling with subsequent decomposition (130 °C onset / 158 °C max). A second exothermic signal appears (192 °C onset / 206 °C max) possibly originating from 2,2,2-trinitroethylcarbamate formed during pyrolysis of **TAF** in analogy to the azide pyrolysis of ethyl azidoformate where elimination of molecular N₂ has been reported to occur on thermal decomposition.

Table 3: Energetic Properties of 2,2,2-Trinitromethylazidoformate (**TAF**)

	TAF	AP	RDX
Formula	C ₃ H ₂ N ₆ O ₈	NH ₄ ClO ₄	C ₃ H ₆ N ₆ O ₇
FW / g mol ⁻¹	250.08	117.5	222.12
IS / J	17 (100–500 μm)	15	7.5
FS / N	> 48 (100–500 μm)		120
ESD / J	0.03		0.1–0.2
N / %	33.6	11.04	37.8
Ω / %	+6.40	34.04	–21.6
T _{Dec.} / °C	130	130 [19]	210
ρ / g cm ⁻³	1.85	1.95	1.80
Δ _f H _m ^o / kJ mol ⁻¹	–144	–296	70
Δ _f U ^o / kJ kg ⁻¹	–496	–2412	417
EXPLO5.04 values:			
–Δ _{Ex} U ^o / kJ kg ⁻¹	5186		6125
T _{det} / K	4321		4236
P _{CJ} / kbar	311		349
V _{Det.} / m s ⁻¹	8254		8748
V _o / L kg ⁻¹	671		739
I _s / s (20 % Al, 70.0 bar)	250	243	---

2,2,2-Trinitroethyl azidoformate (4)

Trimethylsilyl azide (0.524 g, 4.55 mmol) was dissolved in acetonitrile (10 mL). 2,2,2-Trinitroethyl chloroformate (0.499 g, 2.04 mmol), dissolved in acetonitrile (1 mL) was added to this solution dropwise at room temperature and kept under a constant stream of nitrogen. The color of the solution changed from colorless to orange and got turbid after a few minutes with the formation of a precipitate. The reaction was allowed to stir for further twelve hours. The solvent was then removed using a high vacuum line affording orange oil together with precipitate. Pure **TAF** was obtained as a white solid on sublimation of the reaction residue using a cold finger (–78 °C).

DSC (5 °C min⁻¹, °C): 142 °C (dec.); **IR** (FT): $\tilde{\nu}$ = 3018 (vs), 2971 (vs), 2893 (s), 2651 (w), 2601 (w), 2399 (w), 2190 (vs), 1751 (s), 1598 (s), 1442 (s), 1386 (s), 1354 (s), 1297 (s), 1236 (s), 1186 (s), 1099 (m), 1049 (m), 1007 (m), 941 (m), 879 (m), 855 (m), 806 (m), 783 (m), 742 (m), 708 (w) cm⁻¹; **Raman** (1064 nm, 300 mW, 25 °C): $\tilde{\nu}$ = 2974 (36), 2170 (11), 1615 (38), 1384 (29), 1357 (43), 1304 (44), 1099 (15), 1009 (22), 942 (27), 894 (19), 857 (83), 734 (21), 531 (20), 408 (61), 375 (73), 292 (53), 256 (41) cm⁻¹; **¹H NMR** (acetone-*D*₆, 25 °C) δ =

5.96 (2H, s, -CH₂-) ppm; ¹³C NMR (acetone-*D*₆, 25 °C) δ = 63.7 (s, -CH₂-), 123.9 (bs, -C(NO₂)₃), 156.1 (s, O₂CN₃) ppm; ¹⁵N NMR (acetone-*D*₆, 25 °C) δ = -34.7 (s, -NO₂), -141.1 (s, N_{beta}), -148.2 (s, N_{gamma}) -266.9 (s, N_{alpha}) ppm; **Mass spectrometry** (EI⁺): 250 [M⁺], 204 [M⁺ - NO₂], 164 [M⁺ - O₂C-N], 158 [M⁺ - 2 NO₂], 118 [M⁺ - (O₂C-N₃, 2 NO₂)], 70 [N₃CO₂], 44 [CO₂]; **Elemental analysis** (C₃H₂N₆O₈): calc.: C 14.4, H 0.80, N 33.6 %; found: C 14.7, H 1.00, N 32.50 %.

4. SYNTHESIS, SPECTROSCOPIC, STRUCTURAL AND ENERGETIC CHARACTERIZATION OF 1,1,1,6,6,6-HEXANITRO-HEX-3-INE

1,1,1,6,6,6-Hexanitrohex-3-ine can be obtained according to the literature [24] from 1,4-dibromobut-2-ine with silver nitroformate (Scheme 4).



Scheme 4: Synthesis of 1,1,1,6,6,6-hexanitrohex-3-ine.

The synthesis and characterization of 1,1,1,6,6,6-hexanitrohex-3-ine was successfully done, but only in low yields, so no sensitivity and performance data could be measured so far. The low yield seems to be due to the non-satisfying *in-situ* preparation of silver nitroformate from silver oxide. Further investigations of the synthetic route with potassium nitroformate as nitroform transfer agent as well as with the new synthetic route of silver nitroformate (see below) are in progress. 1,1,1,6,6,6-Hexanitrohex-3-ine crystallizes in the orthorhombic space group *Pbca* with eight formula units per unit cell and a density of 1.8183 g cm⁻³ (Figure 4).

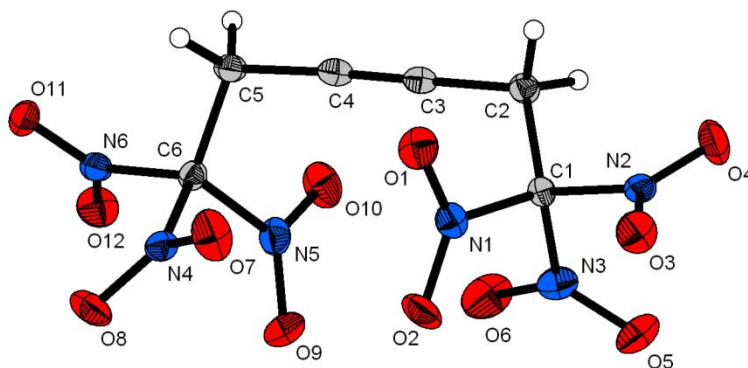


Figure 4: Molecular structure of 1,1,1,6,6,6-hexanitrohex-3-ine. Selected bond lengths [Å] and angles [°]: C1–C2 1.513(2), C2–C3 1.463(2), C3–C4 1.179(2), C4–C5 1.469(2), C5–C6 1.513(2), C1–N1 1.522(2), C1–N2 1.527(2), C1–N3 1.528(2), C6–N4 1.523(2), C6–N5 1.525(2), C6–N6 1.513(2), C1–C2–C3 112.88(14), C2–C3–C4 177.97(17), C3–C4–C5 176.57(17), C4–C5–C6 112.02(13), C2–C1–N1 112.87(13), C2–C1–N2 111.38(12), C2–C1–N3 112.68(12), C5–C6–N4 113.48(12), C5–C6–N5 113.02(13), C5–C6–N6 110.95(12), N1–C1–N2 105.82(11), N1–C1–N3 107.49(12), N2–C1–N3 106.12(12), N4–C6–N5 105.92(12), N4–C6–N6 105.88(12), N5–C6–N6 107.09(11).

All bond lengths and angles of 1,1,1,6,6,6-hexanitrohex-3-ine were found to be expected (Figure 4), with ONO angles between 128.18(14)° (O9–N4–O10) and 127.05(13)° (O7–N4–O8) and CNO angles between 118.69(13)° (C6–N6–O12) and 113.67(12)° (C6–N6–O11).

Surprisingly the cis isomer was found in the crystal arrangement. Possible reasons might be N...O interactions between both nitroform groups. The torsion angle between the C1–C2 and the C5–C6 bond is 31.7(2)°, so the two nitroform groups are twisted according to each other. Many hydrogen bonds between the nitro groups and the hydrogen of the methylene group of different molecules are also present in the crystal structure, with the shortest O–H bond of 2.46 Å (O7...H2A(i)).

DSC measurements revealed a melting point of 126 °C and a exothermic decomposition at temperatures above 193 °C. The energy of formation was calculated on CBS-4M level of theory as $\Delta_f U^\circ = 444.4$ kJ/kg (at 298.15 K) and thus the enthalpy of formation is $\Delta_f H^\circ = 367.0$ kJ/kg (at 298.15 K). The oxygen balance of this compound is –9.1 %. Detonation parameters of 1,1,1,6,6,6-hexanitrohex-3-ine were obtained using the EXPLO5 program (Table 4). The sensitivities were also determined: impact sensitivity 3 J, friction sensitivity 72 N, electrostatic discharge 0.8 J.

Table 4: Energetic Properties of 1,1,1,6,6,6-hexanitrohex-3-ine

	1,1,1,6,6,6-Hexanitrohex-3-ine	AP	RDX
Formula	C ₆ H ₄ N ₆ O ₁₂	NH ₄ ClO ₄	C ₃ H ₆ N ₆ O ₇
FW / g mol ⁻¹	352.13	117.5	222.12
IS / J	3 (500–1000 µm)	15	7.5
FS / N	72 (500–1000 µm)		120
ESD / J	0.80		0.1–0.2
N / %	23.87	11.04	37.8
Ω / %	–9.1	34.04	–21.6
T _{Dec.} / °C	193	130 [19]	210
ρ / g cm ⁻³	1.81	1.95	1.80
Δ _f H _m [°] / kJ mol ⁻¹	367	–296	70
Δ _f U [°] / kJ kg ⁻¹	444	–2412	417
EXPLO5.04 values:			
–Δ _{EX} U [°] / kJ kg ⁻¹	7219		6125
T _{det} / K	5541		4236
P _{CJ} / kbar	349		349
V _{Det.} / m s ⁻¹	8821		8748
V _o / L kg ⁻¹	660		739
I _s / s (20 % Al, 70.0 bar)	263	243	---

1,1,1,6,6,6-hexanitrohex-3-ine

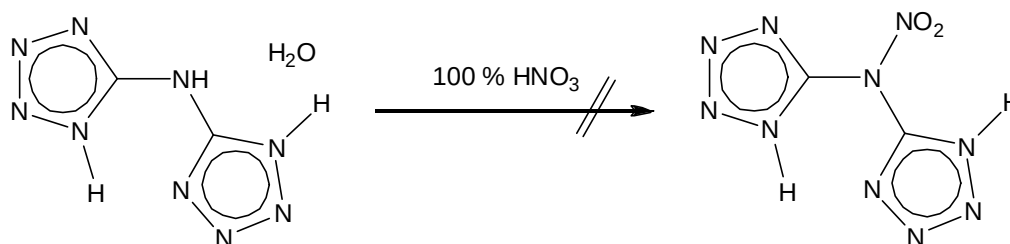
A solution of 1.171 g of nitroform (7.75 mmol) in 10 mL of ethyl acetate is added gradually to a suspension of 898 mg of Ag₂O (7.75 mmol) in 15 mL of ethyl acetate with stirring and cooling in an ice bath. The mixture is stirred for two hours at this temperature and filtered to remove unreacted silver oxide. To the filtrate 151 mg of 1,4-dibromobut-2-ine (0.71 mmol) is

added and the solution is stirred at room temperature for three hours. The precipitated silver bromide is filtered off and the filtrate is partially evaporated in vacuo at room temperature. The residue is poured into water to remove the excess of silver nitroformate and the aqueous mixture is extracted several times with chloroform. The combined organic extracts are evaporated at room temperature to a small volume and crystallized at $-32\text{ }^{\circ}\text{C}$ to give colorless crystals.

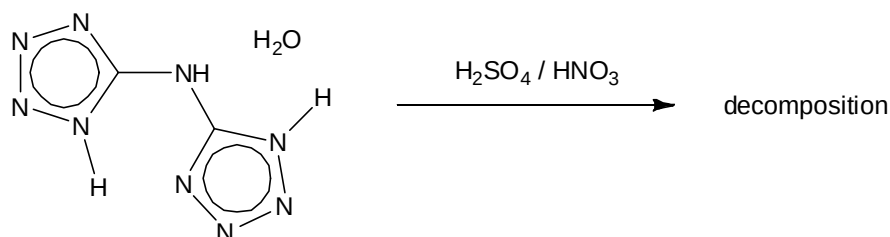
Raman $\tilde{\nu} = 2972$ (42), 2938 (100), 2341 (9), 2305 (15), 2264 (38), 1613 (20), 1597 (22), 1407 (35), 1365 (52), 1324 (27), 1307 (41), 1250 (8), 1170 (4), 1142 (6), 1002 (18), 859 (80), 831 (5), 806 (8), 773 (7), 723 (7), 642 (7), 546 (16), 406 (56), 371 (72), 310 (21), 289 (44), 234 (15) cm^{-1} . **IR** $\tilde{\nu} = 2970$ (m), 2936 (m), 2892 (w), 1581 (vs), 1404 (m), 1365 (m), 1300 (s), 1249 (m), 1214 (w), 1169 (w), 1140 (w), 1128 (w), 1021 (w), 863 (m), 857 (m), 829 (w), 804 (s), 772 (m), 720 (w), 668 (w), 640 (w) cm^{-1} . **^1H NMR** (CDCl_3): $\delta = 3.99$ (s, CH_2 , 4H) ppm. **$^{13}\text{C}\{^1\text{H}\}$ NMR** (CDCl_3): $\delta = 124.8$ (s, $\text{C}(\text{NO}_2)_3$), 74.3 (s, $\text{CH}_2\text{--C}\equiv\text{C--CH}_2$), 26.8 (s, CH_2) ppm. **^{14}N NMR** (CDCl_3): $\delta = -34$ (s, NO_2) ppm. **Elemental analysis** for $\text{C}_6\text{H}_4\text{N}_6\text{O}_{12}$: C, 20.47; H, 1.14; N, 23.87. Found: C, 20.48; H, 1.23; N, 22.99.

5. NITRATION OF H₂BTA

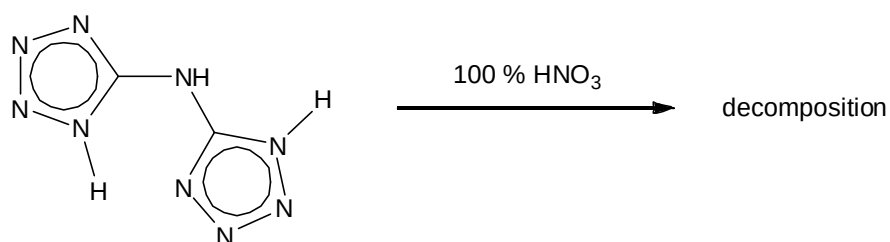
5,5'-Bis(tetrazolyl) amine (H₂bta) is a promising energetic material due to its great thermal stability, low sensitivities and facile synthetic procedure. Therefore, it would be of great interest to introduce oxidizing groups such as –NO₂ or C(NO₂)₃. However, all attempts nitrating H₂bta failed as depicted in Schemes 5–8.



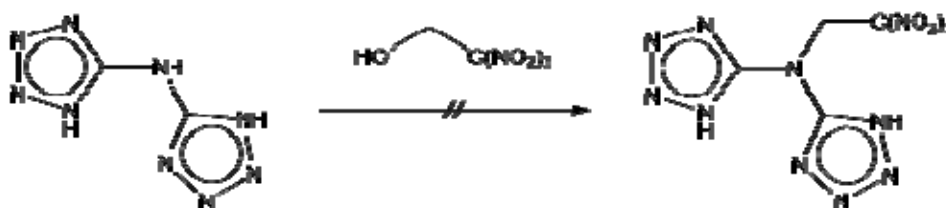
Scheme 5: Attempted Nitration of H₂bta*H₂O with HNO₃ (100%).



Scheme 6: Attempted Nitration of H₂bta*H₂O with H₂SO₄/HNO₃ (100%).



Scheme 7: Attempted Nitration of H₂bta with HNO₃ (100%).



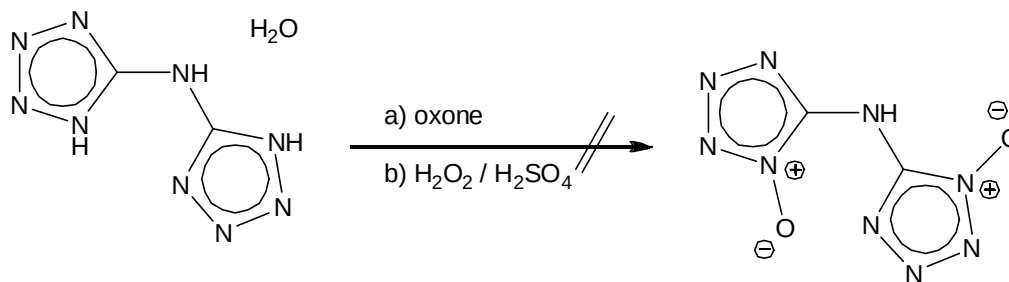
Scheme 8: Reaction of H₂bta with 2,2,2-trinitroethanol.

6. OXIDATION OF H₂BTA (N OXIDE)

We suggested to combine the advantageous properties of the tetrazole moiety with that of an N-oxide group compound. This was successfully approved recently with the 5-nitrotetrazole-2N-oxide system.[25] N-oxides have the following advantages:

- better oxygen balance
- higher density
- better performance
- reduced sensitivity

That H₂bta is a promising energetic compound was already mentioned before. The introduction of two N-oxide moieties on the tetrazole ring would increase the oxygen balance on the one hand but also the density, thermal stability and sensitivities on the other hand. Unfortunately, our reactions using different conditions (see Scheme 9) were unsuccessfully and mostly starting material could only be retrieved.



Scheme 9: Failed N-oxidations of H₂bta.

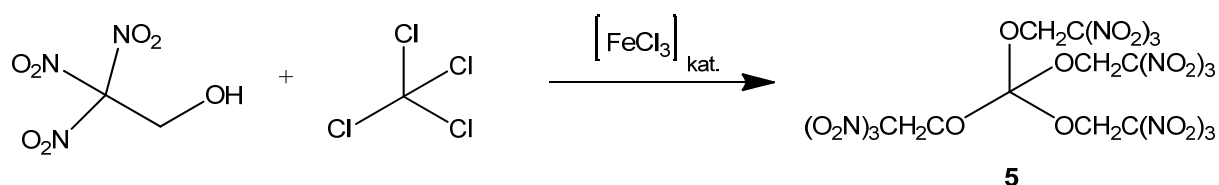
7. SYNTHESIS OF NITRO TRIAZOLE DERIVATIVES

Usually triazoles are declared to have great nitrogen content. For this project it is hard to synthesize triazoles with balanced oxygen contents. Even 3,5-dinitrotriazole has an oxygen balance below 0 %. Up to now, we failed in synthesis of C-connected trinitromethyl triazoles derivatives.

8. SYNTHESIS, SPECTROSCOPIC, STRUCTURAL AND ENERGETIC CHARACTERIZATION OF C(-O-CH₂-C(NO₂)₃)₄

Tetrakis(2,2,2-trinitroethyl) orthocarbonate (**5**, TNEOC) was synthesized by the reaction of carbon tetrachloride with four equivalents of 2,2,2-trinitroethanol and catalytic amounts of iron trichloride (FeCl₃). Compound **5** was fully characterized by single crystal X-ray diffraction, vibrational spectroscopy (IR and Raman), multinuclear NMR spectroscopy, elemental analysis and multi-temperature DSC measurement. Due to the positive oxygen balance, the suitability of **5** as a potential oxidizer in energetic formulations has been investigated and discussed. In addition, the heat of formation of **5** was calculated using the atomization method based on CBS-4M enthalpies. With this value and the experimental (X-ray) density, several detonation parameters such as the detonation pressure, velocity, energy and temperature were computed using the EXPLO5 code. In addition, the sensitivity towards impact, friction and electrical discharge was tested using the BAM drop hammer, a friction tester as well as a small scale electrical discharge device.

2,2,2-Trinitroethyl orthocarbonate (**5**, TNEOC) can be obtained according to [26] from carbon tetrachloride with 2,2,2-trinitroethanol (Scheme 10) under inert gas conditions. Compound **5** was prepared by the reaction of 2,2,2-trinitroethanol with carbon tetrachloride and a catalytic amount of dry iron(III) chloride under careful exclusion of moisture to avoid significant amounts of bis(2,2,2-trinitroethyl) carbonate as main by-product.



Scheme 10: Synthesis of tetrakis(2,2,2-trinitroethyl) orthocarbonate.

The product is insoluble in water and CCl₄. At the end of the reaction the colorless crude product can be filtered off and recrystallized from chloroform, ether or methanol. The compound is unstable towards bases, in accordance to 2,2,2-trinitroethanol.

Despite the fact that **5** has to be synthesized under inert gas conditions, the compound is stable when exposed to air. DSC measurements showed that the product melts at a temperature of 159 °C. The decomposition starts at 170 °C. The compound is stable in vacuum (0.85 cm³ of gas g⁻¹) [26] for six days at 100 °C.

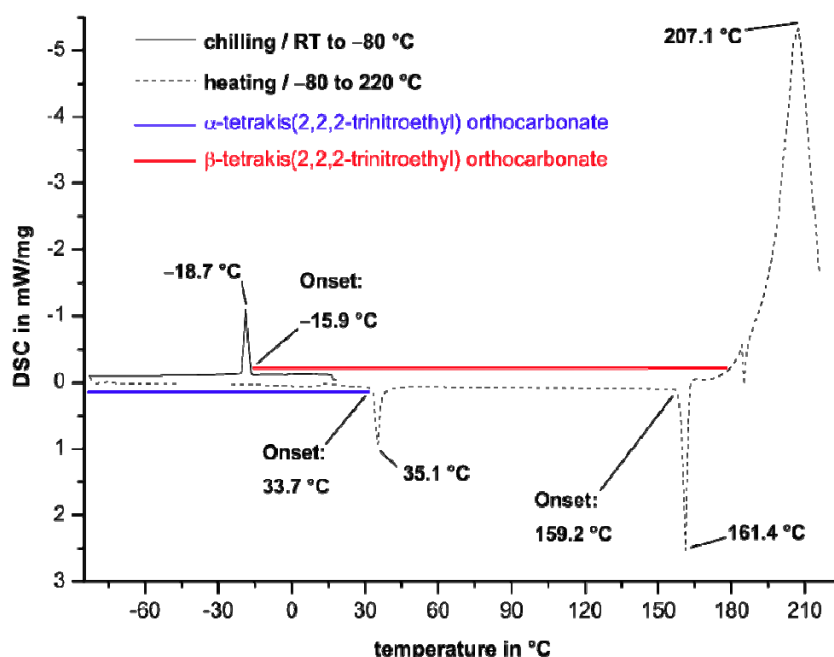


Figure 5: DSC measurement of TNEOC.

Single crystal X-ray diffraction experiments showed a reaction at low temperatures. The colorless crystals began to crack and turned yellow. Recent observed reflections disappeared while cooling the sample. The DSC measurements showed a phase transition state (exothermic peak) between the α - and β -configuration of **5** starting at -16 °C during chilling the compound to -80 °C. Reheating the same sample provided an endothermic signal at 34 °C (onset) which indicates the phase transition reversionary. The rate of heating was ± 5 °C. The α -configuration of **5** is metastable up to 33 °C. Above this temperature β -**5** could be obtained. *FOX-7* shows a comparable transition state at a temperature of 116 °C.^[17] We observed crystal structures of both polymorphs. α -Tetrakis(2,2,2-trinitroethyl) orthocarbonate crystallizes in the orthorhombic space group *F2dd* with eight formula units per cell and a density of 1.938 cm^{-3} . The crystals were measured at 173 K . This configuration is metastable up to 33 °C. The C–N bonds of the trinitromethyl groups show bond lengths of ~ 1.53 Å, slightly longer than those of trinitromethane ($1.497(3)$ Å [27]).

All bond lengths and angles of α -**5** were found to be expected. Improper H $\cdots$ O hydrogen bonds with bond lengths of 2.518 Å and 2.412 Å, which connect two nearby molecules with each other have been obtained within the structure of α -**5** (Figure 6). These contacts are a reason for the increased crystal density of α -**5** comparing to β -**5**.

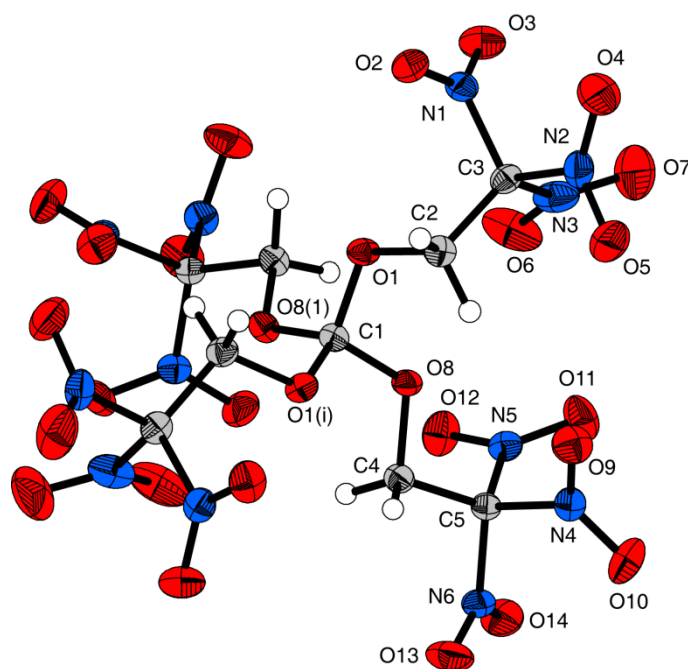


Figure 6: Crystal structure of α -tetrakis(2,2,2-trinitroethyl) orthocarbonate (**5**) at 173 K. Displacement vectors are given at 50% probability. Selected distances [Å] and angles [°]: C1–O1 1.388(2), C1–O2 1.376(2), O1–C2 1.425(2), O2–C4 1.425(2), C2–C3 1.513(3), C4–C5 1.513(3), C3–N1 1.519(2), C3–N2 1.528(3), C3–N3 1.513(3), C5–N4 1.533(2), C5–N5 1.517(2), C5–N6 1.521(2), N1–O3 1.218(2), N1–O4 1.206(3), N2–O5 1.199(3), N2–O6 1.218(3), N3–O7 1.205(3), N3–O8 1.215(3), N4–O9 1.212(2), N4–O10 1.202 (2), N5–O11 1.204(2), N5–O12 1.208(2), N6–O13 1.213(2), N6–O14 1.205(2); O2–C1–O1 107.4(2), C1–O1–C2 114.7(2), C1–O2–C4 117.6(2), C2–C3–N1 112.7(1), C2–C3–N2 108.2(2), C2–C3–N3 116.5(2), C4–C5–N4 114.5(1), C4–C5–N5 110.9(1), C4–C5–N6 110.2(1), C3–N1–O3 114.6(1), C3–N2–O5 118.1(2), C3–N3–O7 116.1(2), C5–N4–O9 116.2(1), C5–N5–O11 117.9(2), C5–N6–O13 113.7(2), O3–N1–O4 127.7(2), O5–N2–O6 128.1(2), O7–N3–O8 127.3(2), O9–N4–O10 127.2(2), O11–N5–O12 127.6(2), O13–N6–O14 129.0(2). $i = 1-x, 1-y, z$; $ii = 1.25-x, -0.25+y, y-0.25+z$.

β -**5** crystallizes in the tetragonal space group $I\bar{4}2d$ with four formula units per cell and a density of 1.808 cm^{-3} . The crystals were measured at 258 K. Below this temperature they began to crack, went along with a color change from colorless to yellow and previous observed reflections disappeared. All bond lengths and angles of β -**5** were found as expected. As a result of the measurement temperature, O–N–O angles differ between $132.4(10)^\circ$ (O1–N1–O2) and $118.8(16)^\circ$ (O4–N2–O3) and CNO between $106.1(11)^\circ$ (O2–N1–C3) and $123.6(11)^\circ$ (O4–N2–C3). Therefore the $R1$ (0.2025) and the $\omega R2$ (0.2722) values are quite high and the displacement vectors in Figure 7 are shown at only 30 %. The structure does not display intermolecular interactions.

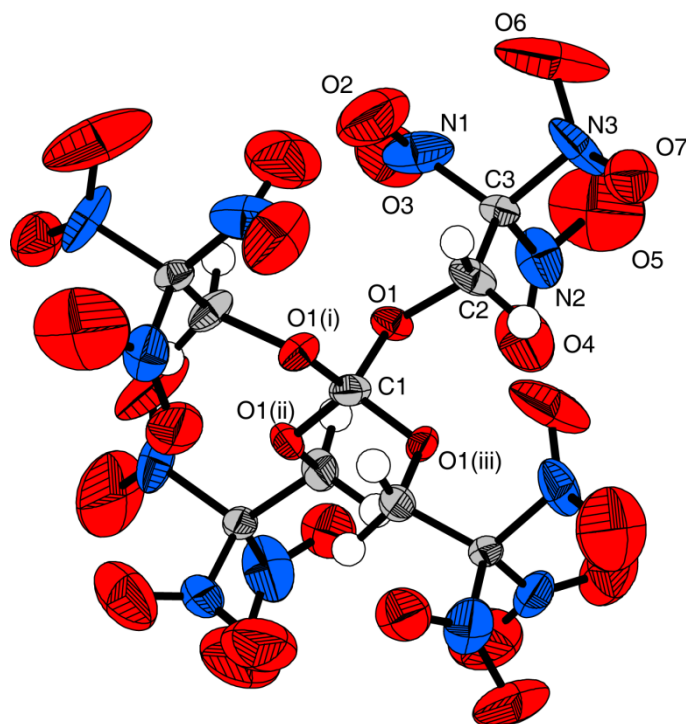


Figure 7: The molecular structure of β -2,2,2-trinitroethyl orthocarbonate. Displacement vectors are given at 30 % probability. Selected distances [Å] and angles [°]: C4–O7 1.394(4), O7–C2 1.417(9), C2–C3 1.480(11), N1–C3 1.498(10), N2–C3 1.511(14), N3–C3 1.520(11), O7–C4–O7 107.32(18), C4–O7–C2 116.5(4), O7–C2–C3 104.6(6), C2–C3–N1 111.1(7), C2–C3–N2 112.1(7), C2–C3–N3 114.3(6), N1–C3–N2 109.1(8), N1–C3–N3 105.3(7). $i = 1.5-x, -0.5+y, 1.5-z$; $ii = -0.5+x, 1.5-y, 1.5-z$; $iii = 1-x, 2-y, z$.

Energetic Properties

The accomplished sensitivity tests towards impact, friction and electrostatic discharge provided the following results given in Table 5. **5** is very sensitive towards impact and sensitive towards friction and electrostatic discharge. Calculations of the detonation parameters using the EXPLO5 code have been done. As a result, the detonation velocity of α -**5** (8487 m s⁻¹) is slightly greater than the value for PETN (8400 m s⁻¹). Due to the different densities of α -**5** and β -**5** the velocity decreases to 8053 m s⁻¹ for β -**5**. The values for the detonation pressure show the same behavior.

Table 5: Energetic Properties of Tetrakis(2,2,2-trinitroethyl) orthocarbonate (**TNEOC**)

	α -TNEOC	β -TNEOC	AP	RDX
Formula	C ₉ H ₈ N ₁₂ O ₂₈	C ₉ H ₈ N ₁₂ O ₂₈	NH ₄ ClO ₄	C ₃ H ₆ N ₆ O ₇
FW / g mol ⁻¹	732.22	732.22	117.5	222.12
IS / J	1 (250–500 μ m)	1	15	7.5
FS / N	> 96 (250–500 μ m)	> 96		120
ESD / J	0.2	0.2		0.1–0.2
N / %	22.95	22.95	11.04	37.8
Ω / %	13.11	13.11	34.04	–21.6
T _{Dec.} / °C	34	191	130 [19]	210
ρ / g cm ⁻³	1.938	1.808	1.95	1.80
$\Delta_f H_m^\circ$ / kJ mol ⁻¹	–1021	–1021	–296	70
$\Delta_f U^\circ$ / kJ kg ⁻¹	–940	–940	–2412	417
EXPLO5.04 values:				
– $\Delta_{Ex} U^\circ$ / kJ kg ⁻¹	5092	5074		6125
T _{det} / K	4208	4279		4236
P _{CJ} / kbar	316	272		349
V _{Det.} / m s ⁻¹	8419	8148		8748
V _o / L kg ⁻¹	674	674		739
I _s / s (20 % Al, 70.0 bar)	249	249	243	---

Tetrakis(2,2,2-trinitroethyl) orthocarbonate

Tetrakis(2,2,2-trinitroethyl) orthocarbonate was prepared according to example 1 in [26]. 2,2,2-Trinitroethanol (TNE) (1.8 g, 10.0 mmol) and dry iron(III) chloride (0.2 g, 1.23 mmol) were diluted in carbon tetrachloride (6.7 mL, 69.4 mmol) in a 25 mL flask with careful exclusion of moisture. The mixture was heated up in an oil bath (85 °C) and refluxed for 24 h. The chilled carbon tetrachloride solution has been decanted from the product and iron(III) chloride. The solvent was removed in vacuum. To dissolve the remaining iron(III) chloride the residue was washed with iced dilute hydrochloric acid (20 mL, 6M). The crude product was dissolved in dichloromethane (30 mL) and extracted three times with iced dilute hydrochloric acid (20 mL, 6M) to remove the last amounts of iron(III) chloride. Removing the solvent gave 1.0 g of crude product. By recrystallization of the crude product from chloroform (35 mL/g) 1.5 g of 5 (83 % yield) were obtained.

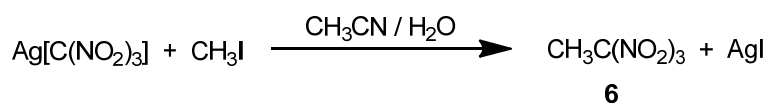
DSC (T_{melt}, 5 °C min⁻¹): 159–161 °C (mp.), 191 °C (dec.); **IR** $\tilde{\nu}$ = 3008 (w), 2959 (w), 2888 (w), 2356 (vw), 1594 (vs, ν_{as} NO₂), 1449 (w), 1395 (w), 1349 (vw), 1290 (m), 1261 (w), 1191 (m), 1144 (s), 1120 (m), 1091 (m), 1069 (m), 884 (w), 856 (m), 806 (m), 784 (m), 742 (w), 677 (w), 651 (w), 614 (w) cm⁻¹; **Raman** (1064 nm, 300 mW, 25 °C): $\tilde{\nu}$ = 3009 (17), 2960 (35), 2885 (8), 1597 (25) (ν_{as} NO₂), 1454 (17), 1435 (9), 1389 (16), 1350 (41), 1305 (30) (ν_s NO₂), 1261 (16), 1171 (10), 1147 (7), 1094 (12), 1068 (12), 1019 (9), 994 (11), 885 (17), 859 (100), 809 (9), 782 (12), 746 (6), 640 (9), 622 (9), 555 (15), 474 (9), 415 (44), 404 (42), 377 (80), 313 (17), 270 (26), 201 (27) cm⁻¹; **¹H NMR** (acetone-D₆): δ = 5.60 (s, 8, CH₂) ppm; **¹³C**

NMR (acetone- D_6): δ = 124.4 (s, br, $C(NO_2)_3$); 119.4 (s, $C(OCH_2)_4$), 63.9 (OCH_2) ppm; ^{14}N
NMR (acetone- D_6): δ = -35 (s, $C(NO_2)_3$) ppm; **Mass spectrometry** (DEI $^+$): 552
[$M-OCH_2C(NO_2)_3$] $^+$, 164 [$CH_2C(NO_2)_3$] $^+$, 118 [$CH_2C(NO_2)_2$] $^+$, 46 [NO_2] $^+$, 30 [NO] $^+$;
Elemental analysis ($C_9H_8N_{12}O_{28}$) calcd.: C 14.75 %, H 1.10 %, N 22.95 %, O 61.18 %;
found: C 14.75 %, H 1.23 %, N 22.95 %, O 61.44 %.

9. INVESTIGATION OF 1,1,1-TRINITROETHANE

1,1,1-Trinitroethane (**6**) compound is already described in literature, but only the melting point and elemental analysis is known so far.[28] Also different preparation methods are reported in literature,[29] including the preparation from silver nitroformate with methyl iodide. The reaction could be done either in water or in acetonitrile, whereas acetonitrile is the preferred choice.

1,1,1-Trinitroethane can be obtained from silver nitroformate with methyl iodide. The starting material silver nitroformate was freshly prepared in a previous step and reacted immediately with methyl iodide, to avoid some decomposition of silver nitroformate. The synthesis furnished a pure, crystalline and stable compound, which is not soluble in water.



Scheme 11: Synthesis of 1,1,1-trinitroethane.

Synthetic Procedure I using pure nitroform:

Due to the light sensitivity of silver salts, the following reaction was performed under absence of light. Into a colorless solution of 415 mg of nitroform (2.75 mmol) in 5 mL of dry acetonitrile 477 mg of Ag₂O (2.06 mmol) is added with stirring at 0 °C. After addition of 1 mL of water, the mixture is stirred for 40 min at ambient temperature following by filtration to remove unreacted silver oxide. To the filtrate 780 mg of methyl iodide (5.50 mmol) is added and the solution is stirred at ambient temperature for 24 h. The precipitated silver iodide is filtered off and the solvent of the remaining solution is evaporated in vacuo. The remaining light yellow solid is dissolved in dry pentane and the insoluble yellow component is filtered off. Crystallization from pentane yielded colorless crystals.

Synthetic Procedure II using aqueous nitroform solution:

Due to the light sensitivity of silver salts, the following reaction was performed under absence of light. Into the yellow turbid solution of 1.193 g of Ag₂CO₃ (4.33 mmol) in 10 mL of acetonitrile 1.308 g of nitroform (8.66 mmol; 30 % solution of nitroform in water (stabilized with urea)) is added with stirring. After stirring the mixture for 2 h at ambient temperature 1.229 g of methyl iodide (8.66 mmol) is added and the solution is stirred at ambient temperature for 24 h. The precipitated silver iodide is filtered off and the yellow-orange solution is extracted three times with each 50 mL of pentane. The combined organic layers are dried over anhydrous magnesium sulfate and the solvent is concentrated to a small amount. Crystallization at 10 °C yielded colorless crystals (Yield: 0.439 g (60 %)).

Characterization

A full characterization of 1,1,1-trinitroethane, including the crystal structure, was achieved. 1,1,1-Trinitroethane crystallizes in the cubic space group *I*-43*d* with sixteen formula units per unit cell and a density of 1.7366 g cm⁻³. All bond lengths and angles of 1,1,1-trinitroethane were found as expected (Figure 8). The molecule itself is highly symmetric with a 3-fold axis

along the C1–C2 bond. Many hydrogen bonds between the nitro groups and the hydrogen of the methyl group of different molecules are present in the crystal structure, resulting in a dense hydrogen bonding network. Each hydrogen of the methyl group is involved in two hydrogen bonds, whereas altogether six hydrogen bonds per molecule are present, with the shortest O $\cdots$ H bond of 2.585(18) Å.

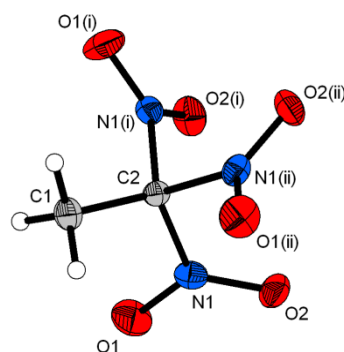


Figure 8: Molecular structure of 1,1,1-trinitroethane. Selected bond lengths [Å] and angles [°]: C1–C2 1.485(5), C2–N1 1.529(2), N1–O1 1.213(2), N1–O2 1.221(2), C1–C2–N1 113.21(12), C2–N1–O1 115.35(16), C2–N1–O2 117.75(16), O1–N1–O2 126.90(17). $i = y, z$, x ; $ii = z, x, y$.

The theoretic value for the standard enthalpy of formation was calculated to ΔH_f° (CBS-4M) = –120.59 kJ/mol (at 298.15 K) and the energy of formation to ΔU_f° (CBS-4M) = –105.71 kJ/mol (at 298.15 K). The oxygen balance of 1,1,1-trinitroethane is +4.85 %. Detonation parameters (e.g. Q_{ex} = –6078 kJ/kg, V_{det} = 8384 m/s, P_{CJ} = 294 m/s) of this compound were obtained using the EXPLO5 program. DSC measurements revealed a melting point of 53 °C and a decomposition at temperatures above 194 °C. In the flame of a Bunsen burner, 1,1,1-trinitroethane shows a smokeless combustion without a sound. The sensitivity data for 1,1,1-trinitroethane are: Impact sensitivity = 8 J, Friction sensitivity = 96 N, Electrostatic sensitivity = 0.1 J.

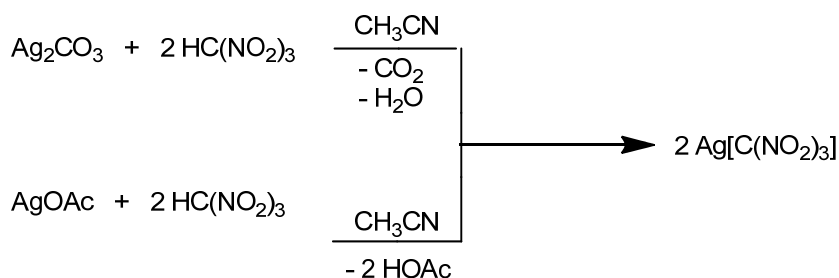
Melting point: 54 °C; **DSC:** 53 °C (melting point), 194 °C (boiling point); **Raman** $\tilde{\nu}$ = 3032 (35), 2957 (68), 1613 (10), 1600 (37), 1436 (13), 1395 (30), 1359 (34), 1313 (24), 1177 (7), 1133 (10), 885 (20), 858 (100), 784 (14), 713 (5), 643 (14), 530 (34), 412 (62), 383 (73), 319 (28) cm^{–1}. **IR** $\tilde{\nu}$ = 3032 (m), 2956 (w), 2900 (w), 1587 (vs), 1434 (m), 1392 (s), 1307 (s), 1266 (m), 1176 (m), 1131 (s), 881 (s), 858 (m), 782 (vs), 711 (w) cm^{–1}. **¹H NMR** (CDCl₃): δ = 2.77 (s, CH₃, 3H) ppm. **¹³C{¹H} NMR** (CDCl₃): δ = 128.0 (s, C(NO₂)₃), 21.3 (s, CH₃) ppm. **¹⁴N NMR** (CDCl₃): δ = –30 (s, NO₂) ppm. **Mass spectrometry** (DCI+) m/z (%): 166 (2) [M⁺], 120 (2) [M⁺ – NO₂], 73 (0.4) [M⁺ – 2 NO₂], 46 (20) [NO₂], 27 (39) [M⁺ – 3 NO₂]. **Elemental analysis** for C₂H₃N₃O₆: Anal. Calcd.: C, 14.55; H, 1.83; N, 25.46. Found: C, 14.51; H, 1.88; N, 25.04.

Table 6: Energetic Properties of 1,1,1-trinitroethane

	1,1,1-trinitroethane	AP	RDX
Formula	$C_3H_3N_5O_{10}$	NH_4ClO_4	$C_3H_6N_6O_7$
FW / g mol ⁻¹	269.09	117.5	222.12
IS / J	10 (500–1000 μ m)	15	7.5
FS / N	96 (500–1000 μ m)		120
ESD / J	0.10		0.1–0.2
N / %	26.03	11.04	37.8
Ω / %	14.9	34.04	–21.6
$T_{Dec.}$ / °C	153	130 [19]	210
ρ / g cm ⁻³	1.725	1.95	1.80
$\Delta_f H_m^\circ$ / kJ mol ⁻¹	–366	–296	70
$\Delta_f U^\circ$ / kJ kg ⁻¹	–1278	–2412	417
EXPLO5.04 values:			
$-\Delta_{Ex} U^\circ$ / kJ kg ⁻¹	4438		6125
T_{det} / K	3855		4236
P_{CJ} / kbar	244		349
$V_{Det.}$ / m s ⁻¹	7571		8748
V_o / L kg ⁻¹	687		739
I_s / s (20 % Al, 70.0 bar)	245	243	---

10. SILVER TRINITROMETHANIDE (7)

Silver nitroformate (7) is a valuable transfer agent for the trinitromethyl group in the research for new oxidizers. The synthesis of 7 described in literature is needlessly complicated [30], therefore focusing on new synthesis methods of high quantities in an easy and safe way seems to be justified. Silver nitroformate (7) can be obtained from either silver carbonate or silver acetate and nitroform (Scheme 12).



Scheme 12: Synthesis of silver nitroformate (7) from selected silver salts with nitroform.

Both preparation methods are best performed in acetonitrile as solvent. It is worth to mention that it is recommended to use a slight amount of water in these syntheses. Water-free silver nitroformate is not stable, neither as solid nor in solution and decomposes quite fast to form AgNO_3 , CO_2 , NO , and N_2 . Therefore, only the monohydrate and hemihydrate are already known in literature [31]. The advantages of this synthesis method compared to the described in literature are the easy preparation method and the high yields. Silver nitroformate was found to serve as a suitable transfer agent of the trinitromethyl group, which could be widely used as a reagent for the synthesis for new high energy dense oxidizers.]

Preparation method using silver carbonate

In a nitrogen flushed flask 1.19 g Ag_2CO_3 (4.3 mmol) is reacted with 1.30 g nitroform (8.6 mmol) in dry acetonitrile at 0 °C. The addition of water stabilizes the formed silver nitroformate. After stirring for several minutes at ambient temperature, the reaction mixture can be used for further reactions. **Warning:** *Evaporation of the solvent resulted repeatedly in an explosive decomposition. Therefore it is not recommended to isolate 7 from this method.*

Preparation method using silver acetate

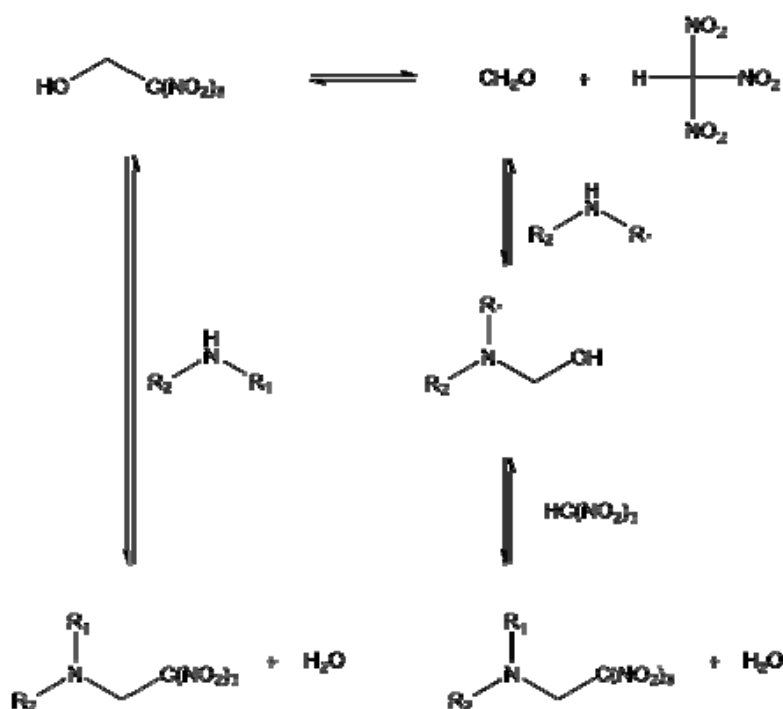
In a nitrogen flushed flask 484 mg AgOAc (2.9 mmol) is reacted with 438 g nitroform (2.9 mmol) in dry acetonitrile at 0 °C. The addition of water stabilizes the formed silver nitroformate. After stirring for several minutes at ambient temperature, the reaction mixture can be used for further reactions. Evaporation of the solvent yields a yellow powder.

Raman $\tilde{\nu} = 1614$ (s), 1563 (19), 1551 (16), 1522 (7), 1370 (38), 1353 (51), 1306 (25), 1296 (29), 1044 (100), 977 (9), 943 (14), 853 (23), 787 (8), 719 (8), 667 (5), 428 (18), 421 (16), 387 (35), 291 (6), 232 (17), 124 (78), 103 (57), 86 (51) cm^{-1} . **IR** $\tilde{\nu} = 1558$ (s), 1541 (vs), 1516 (vs), 1365 (m), 1351 (s), 1328 (s), 1299 (vs), 1145 (m), 1033 (m), 976 (m), 942 (w), 865 (m), 808 (m), 786 (s), 683 (m), 666 (m) cm^{-1} . **$^{13}\text{C}\{^1\text{H}\}$ NMR** ($\text{DMSO}-d_6$):

$\delta = 150.2$ (s, $C(NO_2)_3$); (acetone- D_6): $\delta = 152.5$ (s, $C(NO_2)_3$) ppm. ^{14}N NMR (DMSO- D_6): $\delta = -30$ (s, NO_2); (acetone- D_6): $\delta = -20$ (s, NO_2) ppm. ^{109}Ag NMR (DMSO- D_6): $\delta = 181$ (s); (acetone- D_6): $\delta = 108$ (s) ppm. **Mass spectrometry** (FAB+) m/z (%): 109 (93) / 107 (100) [Ag^+]; (FAB-) m/z (%): 150 (100) [$C(NO_2)_3^-$], 46 (15) [NO_2]. **DSC**: 88 °C (exothermic decomposition).

11. 2,2,2-TRINITROETHANOL (8)

The chemistry of 2,2,2-trinitroethanol (**8**) is different to that of other alcohols owing to the electron withdrawing inductive effect of the trinitromethyl group ($\sigma^* = 4.54$) [32] decreasing the oxygen basicity of the hydroxyl group. The alcohol becomes acidic ($pK_a = 6.1$) and at pH values greater than 6, the equilibrium lies in the direction of the trinitromethanide anion and formaldehyde.[33]



Scheme 13: 2,2,2-Trinitroethanol equilibrium and reaction with secondary amines.

Due to the equilibrium position of the reaction forming 2,2,2-trinitroethanol being dependent on the pH value, two pathways are possible for the MANNICH reaction to occur with either the trinitromethane or 2,2,2-trinitroethanol as the active hydrogen component. To study the behavior of various heterocyclic amines in the MANNICH reaction, we prepared a variety of amines of the tetrazole series and screen their properties in order to be able to judge which compounds would show promising properties in terms of fulfilling the desired criteria a new energetic material has to meet. We were interested in determining the possibility of condensing these amines with formaldehyde and trinitromethane or directly with 2,2,2-trinitroethanol and establishing the conditions of this reaction.

The structure of 2,2,2-trinitroethanol, $\text{C}_2\text{H}_3\text{N}_3\text{O}_7$, at 100(2) K has monoclinic ($P2_1/c$) symmetry with eight formula units in the unit cell whereby the asymmetric unit consists of two molecules. The compound is of interest with respect to energetic materials. The structure displays intramolecular $\text{O}-\text{H}\cdots\text{O}$ as well as intermolecular $\text{O}-\text{H}\cdots\text{O}$ and $\text{C}-\text{H}\cdots\text{O}$ hydrogen bonding, directed four-membered $\text{OH}\cdots\text{OH}\cdots\text{OH}$ rings and dipolar nitro group interactions that account for the high density of 1.839 g cm^{-3} . 2,2,2-Trinitroethanol with three nitro groups bonded to the same carbon atom is a valuable intermediate in the preparation of energetic

materials. However, the structure of 2,2,2-trinitroethanol in the solid state has not been investigated. Only a hypothesis about intramolecular as well as intermolecular hydrogen bonding, based on IR spectroscopy data, has been made.[34] Our X-ray investigation shows intra- as well as intermolecular O–H···O hydrogen bonding next to non-classical C–H···O hydrogen bonding. The asymmetric unit of TNE (Figure 9) consists of two crystallographically independent 2,2,2-trinitroethanol molecules.

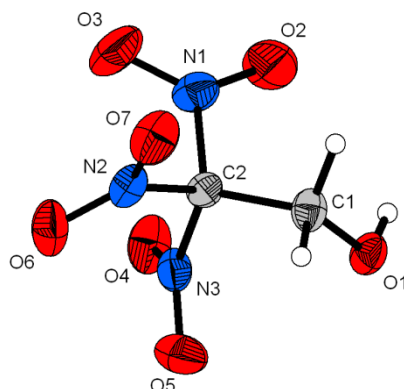
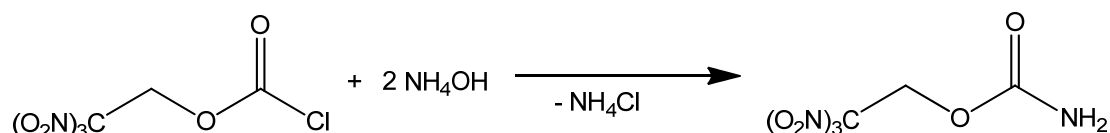


Figure 9: ORTEP representation of the molecular structure of 2,2,2-trinitroethanol in the crystalline state. Only one of the two molecules of the asymmetric unit is shown. Displacement ellipsoids are shown at the 50 % probability level. Selected bond lengths [Å] and angles [°]: C1–C2 1.5352(19), C1–O1 1.4050(17), C2–N1 1.5197(18), C2–N2 1.5155(17), C2–N3 1.5159(17), N1–O2 1.2094(18), N1–O3 1.2130(18), O2–N1–O3 126.98(14), N1–C2–N2 106.24(11), N1–C2–N3 105.90(10), N2–C2–N3 108.43(10), N1–C2–C1 113.42(12), C2–C1–O1 110.77(11), N2–C2–C1–O1 –34.29(16).

2,2,2-Trinitroethanol [35] was prepared from the reaction of trinitromethane with formaldehyde. [36] The crude product can be distilled (Caution: potential risk of explosion!). Suitable conditions for distillation have been found to be: pressure: 36 mbar / oil bath temperature: 135 °C / 2,2,2-trinitroethanol fraction temperature: 115 °C, *or*: pressure: 22 mbar / oil bath temperature: 127 °C / 2,2,2-trinitroethanol fraction temperature: 112 °C. Multinuclear NMR spectroscopy data confirm the structure of the compound: ^1H NMR (acetone- D_6) δ = 5.17 (2H, d, $^3J=5.6$ Hz), 6.32 (1H, t, $^3J= 5.6$ Hz) ppm; ^{13}C NMR (acetone- D_6) δ = 63.1 (d, -CH₂), 127.5 (bs, -C(NO₂)₃) ppm; ^{14}N NMR (acetone- D_6) δ = –30.8 (-NO₂) ppm; impact sensitivity (50 %, 2.5 kg weight) [37]: 11 cm (pure crystals), 22 cm (monohydrate), 25 cm (wet with CCl₄), 86–101cm (crude oil); m.p. 73.5–74 °C, sublimes easily under reduced pressure. The crystal growth was accomplished by sublimation of the solid at 298 K applying static low pressure (0.1 mbar), yielding colorless single crystals of rectangular habitus.

12. 2,2,2-TRINITROETHYL CARBAMATE (TNC, 9)

2,2,2-Trinitroethyl carbamate (TNC) was synthesized *via* the reaction of 2,2,2-trinitroethyl chloroformate and an aqueous solution of ammonia. It is used only as a reaction intermediate. The oxygen balance of **TNC** is 0%. The synthesis of TNC can be done with water as solvent. The yields of pure product are about 60 %.



Scheme 14: Synthesis of 2,2,2-trinitroethyl carbamate.

TNC was fully characterized by NMR, IR and Raman spectroscopy, as well as with elemental analysis and mass spectrometry and shows promising as a new and quite stable potential precursor for high energetic oxidizing materials. **9** crystallizes in the monoclinic space group $P2_1/c$ with four formula units per unit cell and a density of 1.839 g cm^{-3} . The single crystal structure has also been determined completely.

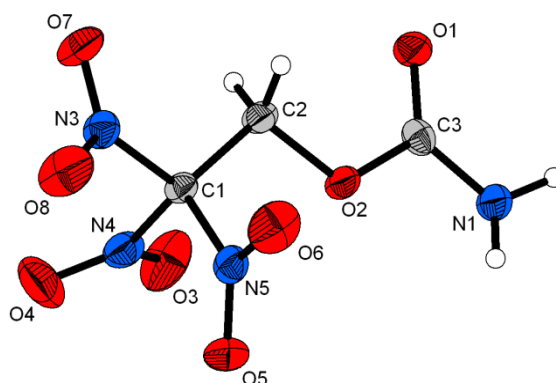


Figure 10: Molecular structure of TNC.

TNC is insensitive towards impact and it is stable up to 165°C . These facts would make it a great potential precursor for unknown HEDOs. The compound is soluble in polar organic solvents, but badly soluble in water. Long-term stability and compatibility tests have not been done, yet. The compound is stable towards bases. Acids may cause decomposition.

Table 7: Energetic Properties of 2,2,2-Trinitroethyl carbamate (**TNC, 9**)

	TNC	AP	RDX
Formula	C ₃ H ₄ N ₄ O ₈	NH ₄ ClO ₄	C ₃ H ₆ N ₆ O ₇
FW / g mol ⁻¹	224.10	117.5	222.12
IS / J	> 40 (< 100 μm)	15	7.5
FS / N	64 (< 100 μm)		120
ESD / J	0.15		0.1–0.2
N / %	25.00	11.04	37.8
Ω / %	0	34.04	–21.6
T _{Dec.} / °C	165	130 [19]	210
ρ / g cm ⁻³	1.84	1.95	1.80
Δ _f H _m [°] / kJ mol ⁻¹	–459	–296	70
Δ _f U [°] / kJ kg ⁻¹	–1960	–2412	417
EXPLO5.04 values:			
–Δ _{Ex} U [°] / kJ kg ⁻¹	5269		6125
T _{det} / K	4051		4236
P _{CJ} / kbar	316		349
V _{Det.} / m s ⁻¹	8284		8748
V _o / L kg ⁻¹	696		739
I _s / s (20 % Al, 70.0 bar)	248	243	---

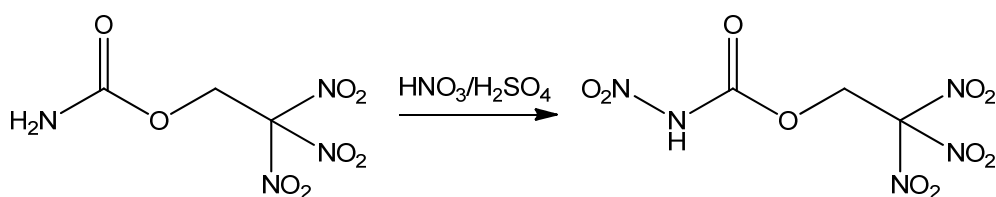
2,2,2-Trinitroethyl carbamate

A solution of 2,2,2-trinitroethyl chloroformate (0.50 g, 2.05 mmol) in dichlormethane (5 mL) was stirred at –30 °C and concentrated aqueous ammonia (0.5 mL) was added slowly over a period of five minutes. The reaction mixture was stirred for one hour at –30 °C. The colorless precipitate was filtered off and recrystallized in water to obtain 0.28 g (63 %) colorless needles.

DSC (5 °C min⁻¹, °C): 90 °C (mp.), 142 °C (dec.); **IR** (FT): $\tilde{\nu}$ = 3447 (w), 3352 (w), 3302 (w), 2962 (m), 1729 (m), 1590 (m), 1441 (w), 1399 (m), 1367 (w), 1325 (m), 1300 (m), 1248 (w), 1167 (w), 1138 (w), 1105 (m), 1027 (w), 910 (w), 873 (w), 858 (w), 804 (m), 784 (m), 772 (m), 741 (w), 673 (w), 646 (w), 606 (w), 546 (m), 527 (m) cm⁻¹ **Raman** (1064 nm, 200 mW, 25 °C): $\tilde{\nu}$ = 3300 (4), 3004 (23), 2964 (51), 2828 (3), 1721 (17), 1622 (31), 1608 (28), 1587 (18), 1445 (17), 1404 (8), 1369 (54), 1304 (31), 1250 (15), 1171 (10), 1145 (10), 1112 (9), 1091 (9), 1027 (17), 910 (19), 878 (10), 859 (100), 802 (14), 786 (12), 745 (10), 674 (10), 647 (12), 549 (18), 524 (9), 426 (55), 397 (46), 377 (72), 305 (53), 265 (17), 212 (30) cm⁻¹; **¹H NMR** (acetone-*D*₆, 25 °C) δ = 5.68 (s, 2, CH₂), 6.49 (s, 1, NH₂), 6.77 (s, 1, NH₂) ppm; **¹³C NMR** (acetone-*D*₆, 25 °C) δ = 154.5 (s, C–NH₂); 125.7 (s, C(NO₂)₃), 61.8 (s, C–C(NO₂)₃) ppm; **¹⁴N NMR** (acetone-*D*₆, 25 °C) δ = –310 (NH₂), –33 (s, C(NO₂)₃) ppm; **Elemental analysis** (C₃H₄N₄O₈): calc.: C 16.08, H 1.80, N 25.00 %; found: C 15.89, H 1.78, N 24.50 %; **BAM drophammer**: > 40 J; **friction tester**: 64 N; **ESD** 0.15 J.

13. 2,2,2-TRINITROETHYL NITROCARBAMATE (TNC-NO₂, **10**)

2,2,2-Trinitroethyl nitrocarbamate (**10**, TNC-NO₂) is a new and quite stable potential high energetic oxidizer. With regards to possible applications, it is the most promising compound within this work. Therefore, the compound has been upscaled in the 10 g scale. The nitration of 2,2,2-trinitroethyl carbamate can be done with a mixture of concentrated sulfuric and fuming nitric acid. The compound has been fully characterized by NMR, IR and Raman spectroscopy, as well as with elemental analysis, mass spectrometry and single crystal X-ray diffraction.



Scheme 15: Synthesis of 2,2,2-trinitroethyl nitrocarbamate.

The synthesis of **10** was carried out directly in nitro-sulfuric acid. The reaction leads to almost essential pure product. **10** crystallizes in the monoclinic space group $P2_1/c$ with four formula units per unit cell and a density of 1.725 g cm^{-3} (Figure 11). The sensitivities towards impact, friction and electrostatic discharge of **10** have been determined. They are comparable to RDX (Table 8). The compound melts at $109 \text{ }^\circ\text{C}$ (onset) and is stable up to $153 \text{ }^\circ\text{C}$ (onset). **10** is compatible with fine aluminium powder. Long-term stability test have not been done, yet.

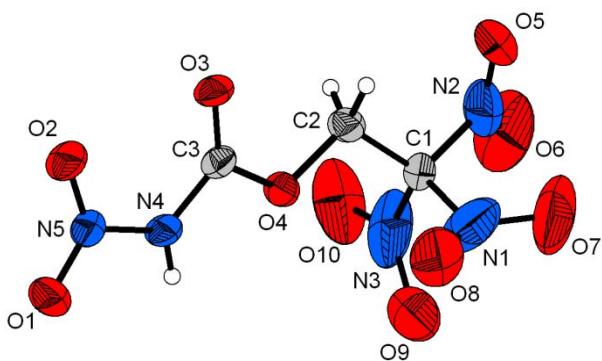


Figure 11: Crystal structure of TNC-NO₂.

Table 8: Energetic Properties of 2,2,2-Trinitroethyl nitrocarbamate (TNC-NO₂)

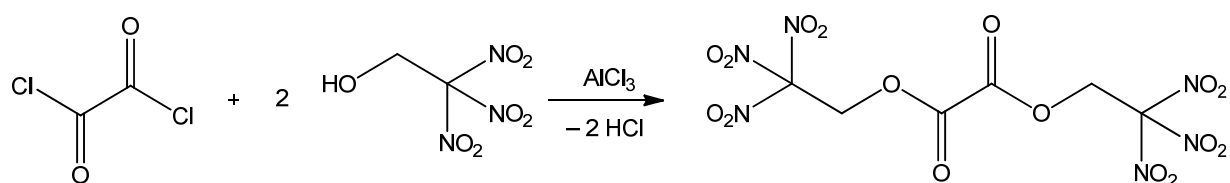
	TNC-NO ₂	AP	RDX
Formula	C ₃ H ₃ N ₅ O ₁₀	NH ₄ ClO ₄	C ₃ H ₆ N ₆ O ₇
FW / g mol ⁻¹	269.09	117.5	222.12
IS / J	10 (500–1000 μm)	15	7.5
FS / N	96 (500–1000 μm)		120
ESD / J	0.10		0.1–0.2
N / %	26.03	11.04	37.8
Ω / %	14.9	34.04	–21.6
T _{Dec.} / °C	153	130 [19]	210
ρ / g cm ⁻³	1.725	1.95	1.80
Δ _f H _m ^o / kJ mol ⁻¹	–366	–296	70
Δ _f U ^o / kJ kg ⁻¹	–1278	–2412	417
EXPLO5.04 values:			
–Δ _{Ex} U ^o / kJ kg ⁻¹	4438		6125
T _{det} / K	3855		4236
P _{CJ} / kbar	244		349
V _{Det.} / m s ⁻¹	7571		8748
V _o / L kg ⁻¹	687		739
I _s / s (20 % Al, 70.0 bar)	245	243	---

A mixture of 1 mL fuming nitric acid and 1 mL sulfuric acid was placed in a flask with a mechanical stirrer. The flask was cooled in an ice bath and 2,2,2-trinitroethyl carbamate (0.25 g, 1.12 mmol) was added slowly. The solution was stirred 2 h at 0 °C and 2 h at room temperature. The solution was poured into 200 mL ice water, which was extracted with ethyl acetate (3 × 50 mL). The organic phases were combined and dried over magnesium sulphate. The solvent was removed under reduced pressure. The crude product was recrystallized from carbon tetrachloride to obtain 0.30 g (99 %) colourless needles.

DSC (5 °C min⁻¹, °C): 109 °C (mp.), 153 °C (dec.); **IR** (FT): $\tilde{\nu}$ = 3168 (w), 3062 (w), 3013 (w), 2900 (w), 1772 (m), 1588 (s), 1466 (m), 1444 (w), 1390 (w), 1351 (w), 1326 (m), 1398 (s), 1271 (w), 1170 (s), 990 (m), 972 (s), 882 (w), 856 (w), 826 (m), 792 (m), 777 (m), 760 (m), 745 (m), 710 (w) 668 (w) cm⁻¹ **Raman** (1064 nm, 300 mW, 25 °C): $\tilde{\nu}$ = 3170 (9), 3013 (33), 2966 (48), 2868 (9), 1768 (49), 1609 (46), 1468 (23), 1442 (23), 1393 (32), 1353 (46), 1324 (75), 1303 (55), 1272 (26), 1183 (19), 1095 (16), 1050 (51), 998 (62), 883 (21), 859 (100), 794 (17), 781 (18), 761 (19), 657 (18), 542 (25), 461 (58), 377 (72), 407 (85), 376 (92), 271 (69) cm⁻¹; **¹H NMR** (chloroform-*D*, 25 °C) δ = 5.53 (s, 2, CH₂), 10.70 (s, 1, NH) ppm; **¹³C NMR** (chloroform-*D*, 25 °C) δ = 145.2 (s, C–NH₂); 12.2 (s, C(NO₂)₃), 62.1 (s, C–C(NO₂)₃) ppm; **¹⁴N NMR** (chloroform-*D*, 25 °C) δ = –55 (N–NO₂), –36 (s, C(NO₂)₃); **Elemental analysis** (C₃H₃N₄O₁₀): calc.: C 13.39, H 1.12, N 26.03 %; found: C 13.54, H 1.09, N 25.70 %.

14. BIS(2,2,2-TRINITROETHYL) OXALATE (BTNEO)

Another interesting oxidizer is bis(2,2,2-trinitroethyl) oxalate (BTNEO). It can be obtained from the reaction of oxalyl dichloride with 2,2,2-trinitroethanol. The synthesis and characterization was successfully done in acceptable yields. Bis(2,2,2-trinitroethyl) oxalate (BTNEO) can be obtained referring to [38] from oxalyl dichloride with 2,2,2-trinitroethanol dichloride and a catalytic amount of dry aluminum(III) chloride (Scheme 16).



Scheme 16: Synthesis of bis(2,2,2-trinitroethyl) oxalate.

BTNEO crystallizes in the monoclinic space group $P2_1/c$ with four formula units per unit cell and a density of 1.884 cm^{-3} (Figure 13). All bond lengths and angles of bis(2,2,2-trinitroethyl) oxalate were found as expected.[39]

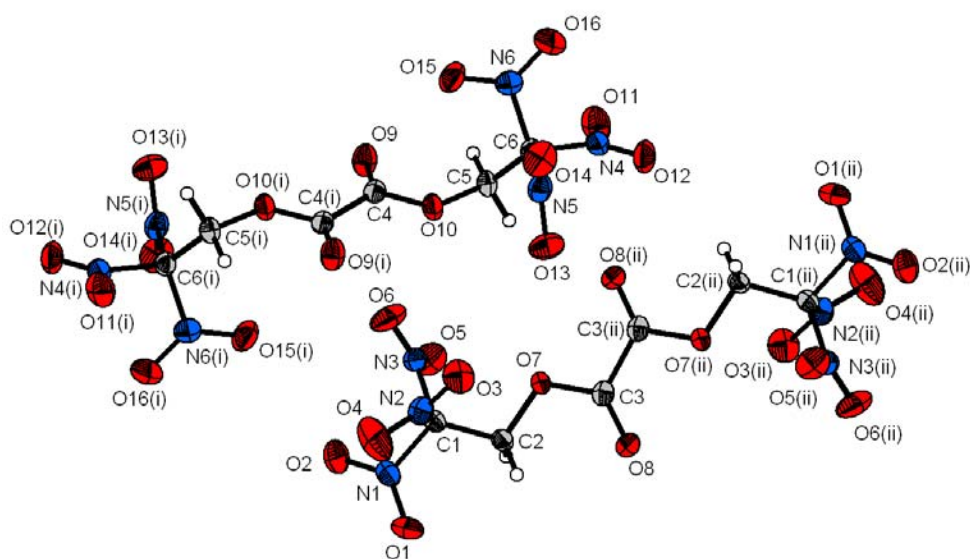


Figure 12: The molecular structure of bis(2,2,2-trinitroethyl) oxalate (BTNEO). Selected bond lengths [$\text{\AA}$] and angles [$^\circ$]: C1–C2 1.507(2), C2–O7 1.431(1), O7–C3 1.338(1), C3–O8 1.187(1), C1–N1 1.517(1), C4–O9 1.188(1), C4–O10 1.337(1), O10–C5 1.433(1), C5–C6 1.502(2), C6–N4 1.518(1), N1–C1–C2 110.4(1), C1–C2–O7 106.5(1), C2–O7–C3 115.1(1), O7–C3–O8 125.5(1), O1–N1–C1 117.5(1), O1–N1–O2 127.1(1), N4–C6–C5 109.5(1), C6–C5–O10 108.1(1), C5–O10–C4 115.6(1), O10–C4–O9 126.7(1), O11–N4–C6 113.8(1), O11–N4–O12 128.1(1) O10–C4–C4i–O9i 0.8(1), O8–C3–C3ii–O7ii 0.1(2). $i = 1-x, -y, 1-z$; $ii = 2-x, -y, -z$.

Sensitivity data were measured and performance data calculated. Despite the fact that bis(2,2,2-trinitroethyl) oxalate has to be synthesized under inert gas conditions, the compound is stable when exposed to air. It melts at a temperature of 116 °C and it decomposes exothermically at about 150 °C. The results of the accomplished sensitivity tests as well as the detonation parameters calculated using the EXPLO5 code are shown in Table 9. The detonation parameters have been calculated using the EXPLO5 code. The detonation velocity is comparable with nitroguanidine $D_{NQ} = 8200 \text{ ms}^{-1}$.

Table 9: Energetic Properties of bis(2,2,2-trinitroethyl) oxalate (**BTNEO**)

	BTNEO	AP	RDX
Formula	$\text{C}_6\text{H}_4\text{N}_6\text{O}_{16}$	NH_4ClO_4	$\text{C}_3\text{H}_6\text{N}_6\text{O}_7$
FW / g mol^{-1}	416.13	117.5	222.12
IS / J	5 ($> 1000 \mu\text{m}$)	15	7.5
FS / N	96 ($> 1000 \mu\text{m}$)		120
ESD / J	0.15		0.1–0.2
$N / \%$	19.54	11.04	37.8
$\Omega / \%$	7.69	34.04	–21.6
$T_{\text{Dec.}} / ^\circ\text{C}$	150	130 [19]	210
$\rho / \text{g cm}^{-3}$	1.884	1.95	1.80
$\Delta_f H_m^\circ / \text{kJ mol}^{-1}$	–366	–296	70
$\Delta_f U^\circ / \text{kJ kg}^{-1}$	–1668	–2412	417
EXPLO5.04 values:			
$-\Delta_{\text{Ex}} U^\circ / \text{kJ kg}^{-1}$	5163		6125
$T_{\text{det}} / \text{K}$	4214		4236
$P_{\text{CJ}} / \text{kbar}$	307		349
$D / \text{m s}^{-1}$	8123		8748
$V_o / \text{L kg}^{-1}$	645		739
I_s / s (20 % Al, 70.0 bar)	245	243	---

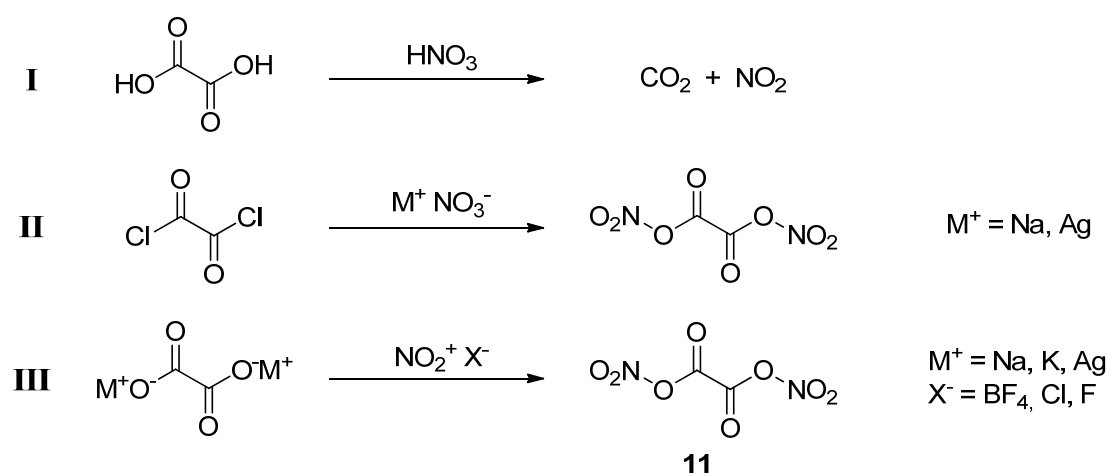
In contrast to [38] 2,2,2-trinitroethanol (0.98 g, 5.4 mmol) was dissolved in dry carbon tetrachloride (7 mL) in a 20 mL flask under careful exclusion of moisture. Oxalyl dichloride (0.34 g, 2.68 mmol) and dry aluminum(III) chloride (0.2 g, 1.5 mmol) were added. The mixture was heated up in an oil bath (85 °C) and refluxed for 2 h. The obtained solid was washed with iced dilute hydrochloric acid (30 mL, 2M) and water (30 mL) to remove 2,2,2-trinitroethanol and aluminum(III) chloride. By recrystallization of the dried crude product from diethyl ether (20 mL/g) 0.71 g of **BTNEO** (63 % yield) were obtained.

^1H NMR: (chloroform- D): $\delta = 5.55$ (s, 4, CH_2) ppm; **^{13}C NMR:** (acetone- D_6): $\delta = 152.3$ (s, OCO); 121.7 (s, $\text{C}(\text{NO}_2)_3$), 62.4 (OCH_2) ppm; **^{14}N NMR:** (acetone- D_6): $\delta = -37$ (s, $\text{C}(\text{NO}_2)_3$) ppm; **IR:** $\tilde{\nu} = 3016$ (w), 2966 (w), 2891 (w), 1790 (vw), 1772 (m, $\nu \text{ CO}$), 1601 (m), 1590 (vs, $\nu_{\text{as}} \text{ NO}_2$), 1435 (w), 1394 (w), 1351 (vw), 1295 (m), 1282 (w), 1268 (m), 1236 (s), 1171 (m), 1155 (m), 1094 (w), 1030 (vw), 966 (vw), 884 (vw), 855 (w), 824 (w), 806 (w), 790 (m), 776 (w), 765 (8w), 715 (vw), 661 (vw) cm^{-1} ; **Raman:** (300 mW): $\tilde{\nu} = 3018$ (17), 2969 (36), 1795

(49, ν CO), 1622 (20), 1614 (20), 1605 (23), 1595 (18) (ν_{as} NO₂), 1439 (12), 1397 (33), 1357 (33), 1305 (32), 1267 (12), 1167 (8), 1105 (5), 1093 (6), 1056 (20), 1012 (9), 911 (23), 858 (100), 801 (13), 778 (8), 643 (10), 545 (14), 441 (24), 409 (70), 377 (73), 326 (28), 305 (24), 274 (36), 236 (40), 193 (42) cm⁻¹; **Elemental analysis** (C₆H₄N₆O₁₆): calc.: C 17.32, H 0.97, N 20.20 %; found: C 17.12, H 1.08, N 19.70 %.

15. NITRATION OF OXALIC ACID

We started to investigate hydrogen-free oxidizers based on nitrated oxalic acids. Recent theoretical calculations on the mixed anhydride of oxalic and nitric acid indicate that the covalent oxalic acid dinitrate ester should be more stable than the ionic dinitronium oxalate. The following three synthetic strategies were developed to generate compound **11** (Scheme 17). Strategy **I** is the nitration of anhydrous oxalic acid with nitric acid (100 %) under argon atmosphere. The reaction was performed in various dry solvents and in a temperature range from room temperature to $-30\text{ }^{\circ}\text{C}$. The synthetic approach following strategy **I** did not yield the desired compound **11**, however, the predicted decomposition products CO_2 and NO_2 could be detected at all temperatures (25 to $-30\text{ }^{\circ}\text{C}$) and in all dry solvents used.



Scheme 17: Synthetic strategies for the production of oxalic acid dinitrate ester (**11**).

Strategy **II** is the reaction of oxalyl chloride with nitrates in dry solvents. This reaction route, indicates that the desired molecule **11** is formed as an intermediate before the subsequent dissociation, because the C–O Bond has to be formed before if yielding CO_2 and NO_2 . However, for the dissociation into CO_2 and NO_2 the N–O bond must be cleaved. Strategy **II** reactions were performed directly in the NMR tubes under argon atmosphere and at temperatures lower than $-50\text{ }^{\circ}\text{C}$. The following ^{13}C and ^{14}N NMR spectra were obtained from the reactions of oxalyl chloride with AgNO_3 in acetone. In the ^{13}C NMR the signals of CO , CO_2 and unreacted oxalyl chloride were observed. Two signals (at 155.5 and 163.1 ppm) could not be assigned to any predicted species.

The nitration strategy **III** is the exchange of the metal cations in metal oxalates with the nitronium cation by different NO_2^+ sources. The formation of insoluble metal salts (e.g. KCl or AgCl) would be favorable in this reaction pathway. For an absolute water-free working the use of SO_2 as solvent could be useful, in particular for the reaction of sodium or potassium oxalate with NO_2BF_4 . In the ^{14}N NMR next to the signal of N_2 (-71.3 ppm) two signals in the range of N_2O_5 and one very intensive signal in the range of nitrate groups (-37.8 ppm) could be observed. The signal -23.3 ppm could be assigned to be N_2O_4 , the dimer of predicted NO_2 .

Unexpected was a very low field signal at +203.8 ppm. It could be assigned to HNO_2 or NO_2^- . This is due to the reducing nature of the oxalyl chloride that acted on the nitrate.

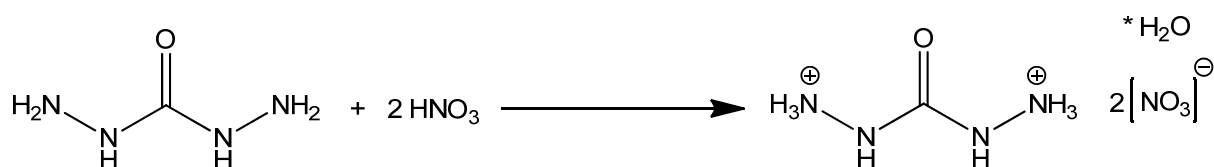
A similar reaction of oxalyl chloride with AgNO_3 was performed in THF. At $-70\text{ }^\circ\text{C}$. No reaction could be observed. As a consequence, the NMR spectrometer was warmed up to $-50\text{ }^\circ\text{C}$. The ^{13}C NMR spectrum revealed comparable signals as for the reaction in acetone. However the ^{14}N NMR spectrum shows another pattern: there was no signal observed for the N_2O_4 . The low field signal for HNO_2 or its anion NO_2^- was found to be less intensive (+219.1 ppm). In the range of nitrato groups two signals (-43.5 and -39.2 ppm) were observed in THF and just next to the signal of N_2 (-71.1 ppm) a very intensive signal was observed that could not be assigned yet

The reaction of oxalyl chloride with nitrates (synthetic strategy **II**) requires accurate calculations of the ^{14}N -shifts of relevant decomposition products for the assignment of the obtained signals. Furthermore it might be useful to variegate the cation of the nitrates, e. g. tetraalkylamonium, in order to obtain an increased solubility for the starting materials at these low temperatures. Then the reaction of sodium and potassium oxalate with NO_2BF_4 (synthetic strategy **III**) is still under investigation. The reactions will first be performed in sealed NMR tubes in order to measure the ^{13}C and ^{14}N NMR spectra at various temperatures starting from $-70\text{ }^\circ\text{C}$.

Additionally live IR and Raman monitoring of strategy **I** and **II** will be performed.

16. DIAMINOURENIUM DINITRATE

We recently investigated diaminouronium nitrate, which is a new secondary explosive. With regard to development of new high-oxidizers the double-protonated compound diaminouronium dinitrate (DAU_2NO₃) was synthesized starting from cheap available diaminourea, which is protonated with two equivalents of dilute nitric acid according to Scheme 18.



Scheme 18: Synthesis of diaminouronium dinitrate monohydrate.

The water is removed in vacuo and the product is isolated as a colorless solid after addition of methanol to the evaporated residue. The compound crystallizes as a monohydrate although showing an oxygen balance of 10.3 %. However, the water can be removed at 75 °C using vacuo. DAU_2NO₃ is completely insensitive towards impact and friction but, unfortunately, decomposing already at 115 °C. Latter property retards probably all possible applications.

17. UP-SCALING OF THE MOST PROMISING TWO COMPOUNDS TO 10-G-SCALE FOR FURTHER TESTING; FINAL REPORT PREPARATION

The most promising compound **10** was synthesized in the 10 g scale and is waiting for shipment to the contract partner for further investigations in oxidizer applications.

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