



Tetranitratoethane†

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Tetranitratoethane (C₂H₂N₄O₁₂), which has an oxygen content of 70.1% was synthesized by nitration of monomeric glyoxal using N₂O₅ and purified by sublimation. Single crystals could be grown from CH₂Cl₂/pentane and were used to determine the structure by X-ray diffraction. Several energetic parameters and values were also established.

In the continuous worldwide quest for new oxidizers in order to replace ammonium perchlorate due to its toxicity for humans' thyroids a few derivatives with a sufficiently high oxygen balance were published during the last years. A few of them are displayed in Fig. 1: (A) tetranitroacetimidic acid,¹ (B) nitryl cyanide,² (C) trinitramine³ and fluorodinitramine,⁴ and (D) 2,2,2-trinitroethyl nitrocarbamate.⁵

In general an oxidizer is a material with a positive oxygen balance Ω , having the ability to form additional O₂ besides H₂O, N₂, CO/CO₂ during its combustion. The absolute oxygen balance Ω , is the ratio between the amount of active available oxygen divided by the overall mass of oxidizer material. Ω is usually given in % w/w and can be calculated assuming different combustion products *e.g.* CO₂ or CO (see footnote Table 1). In this contribution we report on tetranitratoethane, a new solid state oxidizer, which has a higher oxygen content than prominent solid examples such as ADN (ammonium dinitramide), KClO₄, NH₄ClO₄, tetranitroacetimidic acid and even tetranitromethane. Compound **1** is a geminal dinitrato alkane. While nitrate esters such as nitroglycerin (NG) and pentaerythritoltetranitrate (PETN) (Fig. 2A and B) are well known only very few examples of geminal C-nitrato compounds are known. The simplest one, dinitratomethane (Fig. 2C) is a liquid which is obtained from nitration of 1,3,5-trioxane in a HNO₃/H₂SO₄ mixture.⁶

Geminal dinitrate esters form during the nitration of the geminal diol form of aldehydes. They can be also obtained *via*

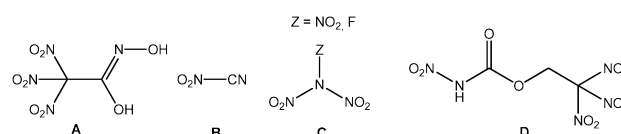


Fig. 1 Structural formula of tetranitroacetimidic acid (A), nitryl cyanide (B), trinitramine and fluoronitramine (C) as well as 2,2,2-trinitroethyl nitrocarbamate (D).

the addition of N₂O₅ to the double bond of aldehydes like **1** is obtained from monomeric glyoxal.‡ A stream of monomeric glyoxal was introduced into a solution of N₂O₅ in acetonitrile at ice bath temperature (Scheme 1). After a few minutes the reaction was poured on ice and crude **1** separated as an oily liquid. The mixture was extracted with CH₂Cl₂. After removing the solvent crude **1** was obtained as an oil which solidified on standing. The material was purified by sublimation at 70 °C under high vacuum against dry ice. The crystals of the crude material melt at 62 °C before sublimation takes place.

The purified material is stable at room temperature under a dry atmosphere. In air it slowly hydrolyses forming nitric acid and glyoxal again. The hydrolysis however is slow enough to prevent the material from being hydrolyzed in ice water after quenching the reaction. The pure material was slowly crystallized from a dry mixture of CH₂Cl₂/pentane in a stream of dry nitrogen. Among others one big (*ca.* 0.4 × 1.0 × 1.0 cm) crystal of **1** was formed over night. The X-ray structure§ reveals the material crystallizing in the orthorhombic space group *P2₁/c* with a density of 1.991 g cm⁻³ at 173 K (Fig. 3). A DSC with a heating rate of 5 °C indicates the material starting to decompose at 90 °C. NMR spectroscopy in CDCl₃ revealed a singlet ¹³C{¹H} resonance at 91.3 ppm and a ¹H proton resonance at 7.21 ppm.

Compound **1**, which has a higher oxygen content and balance than ammonium perchlorate (Table 1) is very sensitive toward friction (5 N) and impact (2 J). In terms of sensitivity it is comparable to nitroglycerin and more sensitive than PETN (Table 1). The heat of formation of -385 kJ mol⁻¹ was calculated using the atomization method based on CBS-4M electronic enthalpies (see ESI†).

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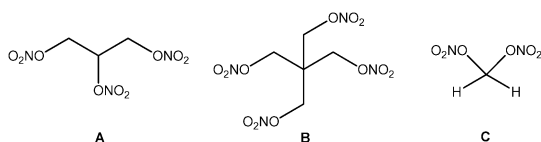
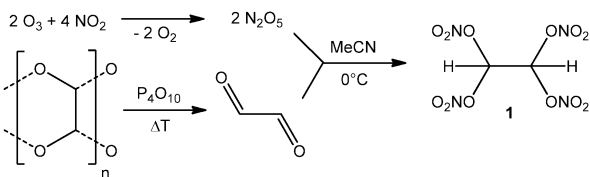
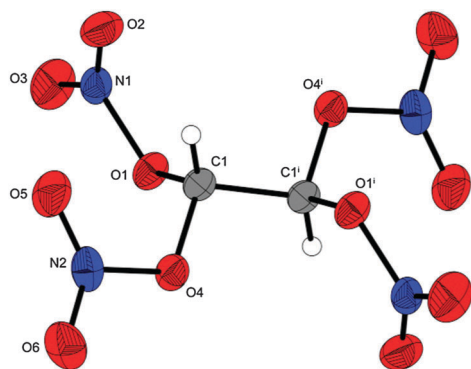
† Electronic supplementary information (ESI) available: (1) X-ray parameters, (2) heat of formation calculation, (3) experimental. CCDC 1420413. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/c5cc09010e



Table 1 Selected physicochemical values of **1**, ammonium perchlorate (AP), nitroglycerine (NG) and pentaerythritol tetranitrate (PETN)

| | 1 | AP | NG | PETN |
|--|--|----------------------------------|---|--|
| Formula | C ₂ H ₂ N ₄ O ₁₂ | NH ₄ ClO ₄ | C ₃ H ₅ N ₃ O ₉ | C ₅ H ₈ N ₄ O ₁₂ |
| FW/g mol ⁻¹ | 274.06 | 117.49 | 227.09 | 316.14 |
| IS/J ^a | 2 | 20 | 0.2 | 3 |
| FS/N ^b | 5 | > 360 | > 360 | 60 |
| N, O% ^c | 20.44, 70.06 | 11.92, 54.47 | 18.5, 63.41 | 17.72, 60.73 |
| Ω _{CO} , Ω _{CO₂} /% ^d | +52.54, +40.87 | 34.04, 34.04 | 3.5, 24.66 | -10.12, 15.18 |
| T _m , T _{dec} /°C ^e | 62, 90 | —, 240 | 13, 185 | 141, 202 |
| ρ/g cm ⁻³ (RT) ^f | 1.954 | 1.95 | 1.595* | 1.75* |
| Δ _f H _m ^g /kJ mol ⁻¹ | -384.6 | -295.8 | -311.3 | -479.7 |
| Δ _f U ^h /kJ kg ⁻¹ | -1321.9 | -2623.2 | -1278.1 | -1423.3 |
| I _{sp} /s ⁱ | 272.3 | 263.8 | 263.8 | 256.6 |
| I _{sp} /s ^j | 265.1 | 255.9 | 257.6 | 241.3 |
| Ox/Al/% w/w ^k | 65.44/19.56 | 65.85/19.15 | 70.83/14.17 | 69.83/15.62 |

^a Impact sensitivity according to BAM drophammer (1 of 6). ^b Friction sensitivity according to BAM friction tester (1 of 6). ^c Nitrogen and oxygen content. ^d Oxygen balance toward carbon monoxide (Ω_{CO} = nO - xC - yH/2(1600/FW)) and carbon dioxide (Ω_{CO₂} = nO - 2xC - yH/2(1600/FW)). ^e Melting and decomposition temperature (DSC, 5 deg min⁻¹). ^f Density at 298 K (for **1** calculated with: ρ_{x-ray-100K}/1.0297). ^g Heat of formation (calculated using the atomization method and CBS-4M enthalpies). ^h Energy of formation. ⁱ Optimized specific impulse (Cheetah 6.0, shifting equilibrium, 15% w/w HTPB). ^j Optimized specific impulse (Cheetah 6.0, frozen equilibrium, 15% w/w HTPB). ^k Optimized amounts of oxidizer and aluminum.

**Fig. 2** Structural formula of nitroglycerin (A), PETN (B), and dinitratomethane (C).**Scheme 1** Formation of **1** from glyoxal and N₂O₅.**Fig. 3** Molecular structure of **1**. Thermal ellipsoids represent the 50% probability level. Selected bond distances [Å]: O1-C1 1.421(1), O1-N1 1.443(1), O4-C1 1.410(1), O4-N2 1.449(1), O5-N2 1.193(1), O2-N1 1.190(1), O6-N2 1.191(1), N1-O3 1.193(1), C1-C1' 1.526(2). Symmetry code: (i) 1 - x, -y, 1 - z.

The specific impulse from isobaric combustion calculations of three component (oxidizer, aluminum and HTPB) mixtures with optimized oxidizer to aluminum ratio was calculated using the Cheetah 6.0 code. The mixtures using **1** perform slightly higher

(8–9 s) than the ammonium perchlorate mixtures and those containing nitroglycerine and PETN (for theoretical comparison). As a general empirical rule, an increase of the value for the specific impulse by 20 s leads to a doubling of the possible payload of a rocket.⁷

Summarizing all the physicochemical properties of **1**, especially the low thermal stability but also the high sensitivities will probably exclude any practical application of **1**. Nevertheless **1** is a solid oxidizer carrying one of the highest oxygen contents which were ever synthesized.

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Notes and references

‡ 5 g of dehydrated and powdered glyoxal were mixed with 15 g of P₄O₁₀ and slowly heated in an oil bath to 200 °C until the material turned black. The green vapors were introduced into an ice cooled solution of 15 g N₂O₅ in 50 mL CH₂Cl₂ or CH₃CN. Then the reaction was poured on 100 mL ice water and immediately extracted with four times 50 mL CH₂Cl₂. The organic phase was washed with 1% NaHCO₃ until neutral and dried over MgSO₄. After carefully (RT) removing the solvent under vacuum the crude material was sublimed at 70 °C under high vacuum against dry ice yielding 7–8 g of a colorless solid. The yield strongly depends on the technique which is used for generating anhydrous glyoxal. Based on monomeric glyoxal the yield is nearly quantitative. DSC (5 °C min⁻¹, °C): 90 °C (dec.); IR (ATR, cm⁻¹): $\bar{\nu}$ = 3000 (w), 2948 (w), 1678 (s), 1664 (s), 1537 (w), 1465 (w), 1342 (w), 1271 (s), 1140 (w), 1048 (m), 989 (s), 821 (m), 771 (vs), 732 (s), 720 (s), 684 (s), 596 (s), 563 (m); Raman (1064 nm, 200 mW, 25 °C, cm⁻¹): $\bar{\nu}$ = 2997 (54), 2859 (6), 1729 (6), 1693 (50), 1671 (10), 1465 (6), 1356 (45), 1306 (90), 1278 (13), 1148 (47), 1074 (10), 1014 (15), 855 (100), 790 (6), 778 (14), 757 (11), 734 (8), 675 (64), 626 (22), 579 (53); ¹H NMR (400 MHz, CDCl₃, 25 °C, ppm): δ = 7.21; ¹³C NMR{¹H} (400 MHz, CDCl₃, 25 °C, ppm) δ = 91.3; ¹⁴N NMR (400 MHz, CDCl₃, 25 °C, ppm) δ = -62.3; EA (C₂H₂N₄O₁₂, 174.06): calc.: C 8.77, H 0.74, N 20.44%; found: C 8.97, H 0.83, N 20.19%; BAM drophammer: 2 J (> 500 μm); friction tester: < 5 N (> 500 μm).

§ Selected X-ray parameters: monoclinic, P2₁/c, a 7.5489(4) Å, b 7.2995(3) Å, c 8.3759(8) Å, γ 97.93(1)°, V 457.12(5), Z 2, ρ 1.991 g cm⁻³, CCDC 1420413.

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