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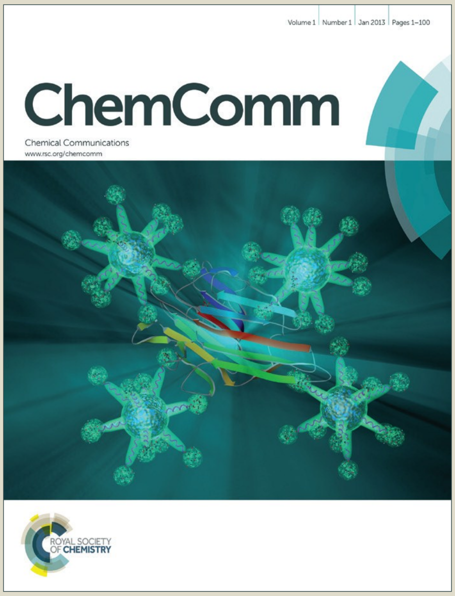

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Tetranitratoethane

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Tetranitratoethane ($C_2H_2N_4O_{12}$), which has an oxygen content of 70.1% was synthesized by nitration of monomeric glyoxal using N_2O_5 and purified by sublimation. Single crystals could be grown from CH_2Cl_2/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 figure 1: A) tetranitroacetimidic acid [1], B) nitryl cyanide [2], C) trinitramine [3] and fluorodinitramine [4], and D) 2,2,2-trinitroethyl nitrocarbamate [5].

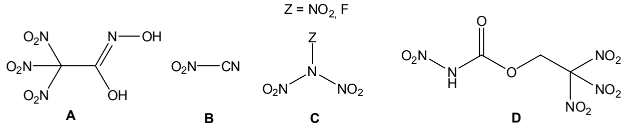


Figure 1. Structural formula of tetranitroacetimidic acid (A), nitryl cyanide (B), trinitramine and fluoronitramine (C) as well as 2,2,2-trinitroethyl nitrocarbamate (D).

In general an oxidizer is a material with a positive oxygen balance *Ω*, having the ability to form additional O_2 besides H_2O, N_2, CO/CO_2 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. CO_2 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), $KClO_4$, NH_4ClO_4, tetranitroacetimidic acid and even tetranitromethane. Compound **1** is a geminal dinitrato alkane. While nitrate esters such as nitroglycerin (NG) and pentaerythritoltetranitrate (PETN) (Figure 2a and b) are well known only very few examples of germinal C-nitrato compounds are known. The simplest one, dinitratomethane (Figure 2c) is a liquid which is obtained from nitration of 1,3,5-trioxane in a HNO_3/H_2SO_4 mixture[6].

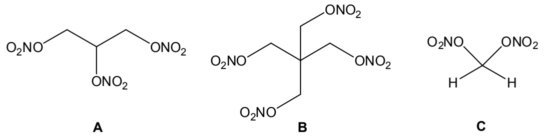
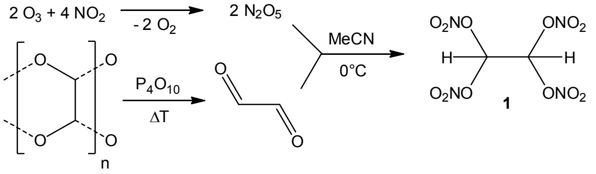


Figure 2. Structural formula of nitroglycerin (A), PETN (B), and dinitratomethane (C).

Gemial dinitrate esters form during the nitration of the geminal diol form of aldehydes. They can be also obtained via the addition of N_2O_5 to the double bond of aldehydes like **1** is obtained from monomeric glyoxal.§ A stream of monomeric glyoxal was introduced into a solution of N_2O_5 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 CH_2Cl_2. 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.



Scheme 1. Formation of **1** from glyoxal and N_2O_5.

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 CH_2Cl_2/pentane in a stream of dry nitrogen. Among others one big (ca. 0.4 x 1.0 x 1.0 cm) crystal of **1** was formed over night (Figure 3). The X-ray structure§§ reveals the material crystallizing in the orthorhombic space group $P2_1/c$ with a density of 1.991 g cm^{-3}

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† Footnotes relating to the title and/or authors should appear here.

Electronic Supplementary Information (ESI) available: [1) X-ray parameters, 2) Heat of formation Calculation, 3) Experimental]. See DOI: 10.1039/x0xx00000x at 173 K. A DSC with a heating rate of 5°C indicates the material starting to decompose at 90 °C. NMR spectroscopy in $CDCl_3$ revealed a singlet $^{13}C\{^1H\}$ resonance at 91.3 ppm and a ^1H proton resonance at 7.21 ppm.

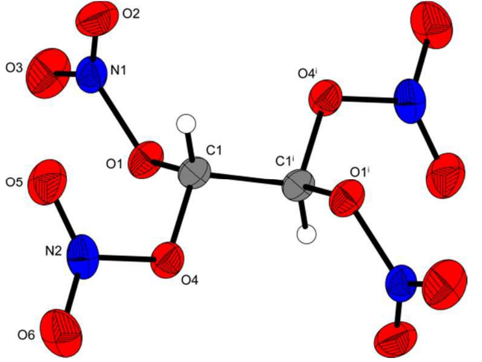

Figure 3. Molecular structure of **1**. Thermal ellipsoids represent the 50% probability level. Selected bond distances [Å]: O1–C1 1.421(1), O1–N1 1.443(1), O4–C1 1.410(1), O4–N2 1.449(1), O5–N2 1.193(1) O2–N1 1.190(1), O6–N2 1.191(1), N1–O3 1.193(1), C1–C1^i 1.526(2). Symmetry Code: (i) 1−x, −y, 1−z.

Compound **1**, which has a higher oxygen content and balance than ammonium perchlorate (Table 1) is very sensitive toward friction (5N) and impact (2J). 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).

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

	1	**AP**	**NG**	**PETN**
Formula	$C_2H_2N_4O_{12}$	NH_4ClO_4	$C_3H_5N_3O_9$	$C_5H_8N_4O_{12}$
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*
$\Delta_fH_m°$ / kJ mol^{-1} ^{g}	–384.6	–295.8	−311.3	−479.7
$\Delta_fU°$ / kJ kg^{-1} ^{h}	–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); f Density at 298K (for **1** calculated with: $\rho_{Xray\text{-}100K}$/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.

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 P_4O_{10} and slowly heated in an oil bath to 200°C in a 50 mL flask until the material turned black. The green vapors were introduced into an ice cooled solution of 15 g N_2O_5 in 50 mL CH_2Cl_2 or CH_3CN. Then the reaction was poured on 100 mL ice water and immediately exctracted with four times 50 mL CH_2Cl_2. The organic phase was washed with 1 % $NaHCO_3$ until neutral and dried over $MgSO_4$. 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}): $\tilde{\nu}$ = 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}): $\tilde{\nu}$ = 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); **^{1}H NMR** (400 MHz, $CDCl_3$, 25 °C, ppm): δ= 7.21; **^{13}C NMR{^{1}H}** (400 MHz, $CDCl_3$, 25 °C, ppm) δ= 91.3; **^{14}N NMR** (400 MHz, $CDCl_3$, 25 °C, ppm) δ= -62.3; **EA** ($C_2H_2N_4O_{12}$, 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, $P2_1/c$, 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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