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Making a Big Bang

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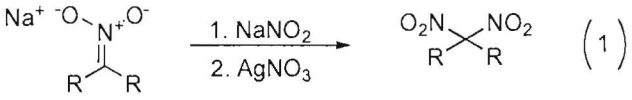
Synthesis of a New Energetic Nitrate Ester

David E. Chavez, Michael A. Hiskey, Darren L. Naud and Damon Parrish*

((Dedication----optional))

Nitrate esters have been known as useful energetic materials since the discovery of nitroglycerin by Ascanio Sobrero in 1846.[1] The development of methods to increase the safety and utility of nitroglycerin by Alfred Nobel led to the revolutionary improvement in the utility of nitroglycerin in explosive applications in the form of dynamite. Since then, many nitrate esters have been prepared and incorporated into military applications such as double-based propellants, detonators and as energetic plasticizers.[2-4] Nitrate ester have also been shown to have vasodilatory effects in humans and thus have been studied and used for treatments of ailments such as angina. The mechanism of the biological response towards nitrate esters has been elucidated recently.[5] Interestingly, many of the nitrate esters used for military purposes are liquids (ethylene glycol dinitrate, propylene glycol dintrate, etc). Pentaerythritol tetranitrate(PETN) is one of the only solid nitrate ester, besides nitrocellulose, that is used in any application. Unfortunately, PETN melting point is above 100 °C, and thus must be pressed as a solid for detonator applications. A more practical material would be a melt-castable explosive, for potential simplification of manufacturing processes Herein we describe the synthesis of a new energetic nitrate ester (**1**) that is a solid at ambient temperatures, has a melting point of 85-86 °C and has the highest density of any known nitrate ester composed only of carbon, hydrogen, nitrogen and oxygen. We also describe the chemical, thermal and sensitivity properties of **1** as well as some preliminary explosive performance data.

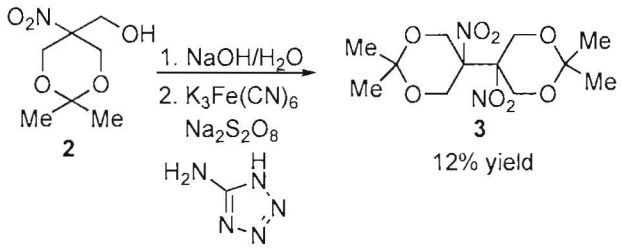
As part of our efforts to develope new energetic materials, we became interested in employing the Kaplan-Shechter[6-8] reaction to construct new energetic gem-substituted nitro-nucleophile moieties. The Kaplan-Shechter reaction is one of the most convenient methods for installing gem-dinitro substituents, and involves the treatment of a nitronate salt with nitrite in the presence of an oxidant, such as silver nitrate (eq 1).



(1)

Our original goal was to use nitro compound **2** as a substrate for an oxidative coupling reactions with heterocyclic nucleophiles, such as 5-amino-tetrazole (Scheme 1). We investigated the modified Kaplan-Shechter reaction as a method to obtain this goal. The reaction conditions involve deformylation of **2** by treament with hydroxide in the presence of potassium ferricyanide and sodium persulfate, followed by addition of 5-aminotetrazole. The overall result was the production of a small yield of a white precipitate being formed. Upon ^{1}H NMR analysis, it was determined that no coupling had occurred between **2** and 5-aminotetrazole. Instead, homocoupling of the nitronate salt of **2** appeared to have taken place, albeit in an inefficient process (12% yield) to provide **3**. Homocoupling of nitronate salts has been reported in the literature.[9] although the use of **3** as a homocoupling substrate under the modified Kaplan-Schechter conditions has not been reported.

Scheme 1. Attempted oxidative coupling reaction



Alternate methods for the synthesis of **3** have been reported and include, homocoupling of the 5-bromo-5-nitro derivative of **2** in the presence of *tert*-butyl thiol, [10] and the use of an $S_{RN}1$ substitution reaction to provide the product in 30-50% yield.[11-13] Other methods have been reported as well.[14,16]

In the examination of the homocoupled product, we reasoned that it would be possible to hydrolyze the dimethyl ketal protecting group to access the tetraol product **4**, which has not been reported in the literature. Further, exhaustive nitration of the tetraol **4** would lead to a novel nitrate ester molecule **1**. However, in order for the method to be practical, the yield of the oxidative coupling step would need to be improved dramatically.

Starting with the commercially available dioxane **2**, we studied the effects of concentration, oxidizer, and nitronate formation. Additionally, we varied the amount of the potassium ferricyanide catalyst as well. Interestingly, we found that increasing amounts of potassium ferricyanide led to reduction in the yield of the homocoupled product, whereas the yield of **3** increased in the absence of the catalyst. After optimization of temperature, concentration and number of equivalents of base, we were able to improve the yield of the homocoupled product to 65%.

With an improved method for the preparation of **3** in hand, we turned our attention to the remaining two steps. Ketal deprotection was easily accomplished using HCl in methanol as the solvent.

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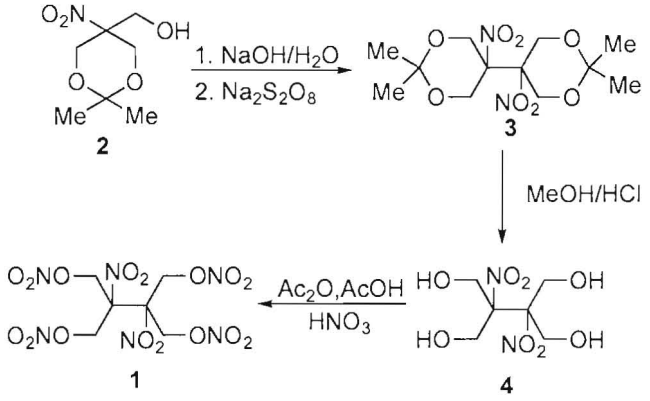
Removal of the solvent provided **4** in good yield. The nitration of the tetraol was found to proceed smoothly in the presence of acetyl nitrate with acetic acid as the solvent providing the corresponding tetranitrate ester **1** in 85% yield.

Scheme 2. Synthesis of **1**.



Compound **1** was characterized spectroscopically and thermally. The material begins to decompose at 141 °C with a decompostion energy release of 1818 J/g. Interestingly, the material has a melting point range of 85-86 °C. This property may allow the material to be melt-castable. The heat of formation was measured to be -371 kJ/mol by combustion calorimetry using a Parr 6300 bomb calorimeter. The tetranitrate ester (**1**) can be recrystallized from a variety of solvents, but large hexagonal crystals can be obtained from ethanol. Figure 1 displays a digital photograph of the crystal morphology.

Figure 1. Photographs of crystals of **1** displaying the crystal morphology of crystal grown from ethanol. The ruler dimensions are in mm.

X-ray crystallography was used to determine the crystal density of **1**.[16] A colorless thin plate of dimensions 0.40 x 0.10 x 0.02 mm^2 was mounted on a MiteGen MicroMesh using a small amount of Exxon Paratone-N Oil. Data were collected on a Bruker three-circle platform diffractometer equipped with a SMART APEX II CCD detector. The crystal structure of **1** is shown in Figure 2. The crystal density was determined to be 1.917 g/cm^3, making **1** the most dense nitrate ester known in the literature (Figure 2). Comparisons of the bond distances and bond angles to PETN[18] show that the C2A-O2A and the O2A-N2A bond distances are slightly longer in **1**. Additionally, the C2-C2A-O2A and the C2A-O2A-N2A angles are smaller than in PETN.

The material was also characterized with respect to its sensitivity to destructive stimuli, such as impact, spark and friction. It was determined that **1** was very similar to pentaerythritol tetranitrate with respect to its sensitivity properties (see table 1).

Figure 2. Thermal ellipsoid plot of **1**. The crystals were grown from ethanol by slow evaporation. It was a routine crystal structure with a final R-value of 4.1%. Thermal ellipsoids are shown at the 50% probability level

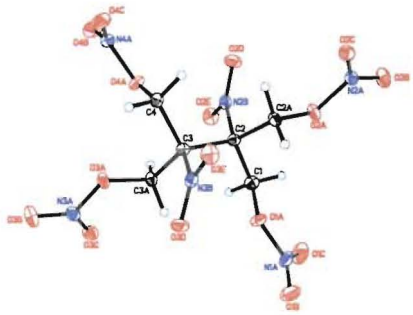


Table 1. Sensitivity properties of 1

	Impact[a]	Spark[b]	Friction[c]	DSC[d]
1	11 cm	0.625 J	7.6 Kg	140 °C
PETN	12 cm	0.625 J	5.8 Kg	160 °C

[a] LANL type 12, 50% drop height, 2.5 Kg [b] ABL spark Threshold Initiation Level (TIL) [c] 50% load Bruceton up/down method [d] 10 °C ramp rate.

Explosive performance calculations were performed with the CHEETAH thermochemical code, using the experimental crystal density and measured heat of formation value as the input data. As displayed in Table 2, **1** is predicted to perform equally as well as HMX , a well characterized high-performance explosive. Unlike HMX however, nitrate ester **1** has a low melting point, which may provide a unique opportunity for melt-castable explosive components. Additionally, **1** offers the possibility of use as a very energetic plasticizer or double base propellant ingredient. Further experimentations are ongoing to fully characterize the explosive performance and properties of this novel nitrate ester. Additionally, compound **4** can serve as a synthon for new energetic materials and we are currently investigating the synthetic utlility of **4** as well.

Table 2. Predicted Performance Properties of 1

	$V_{Det.}$ (Km/s)	P_{CJ} (GPa)
1[a]	9.1	40
HMX[b]	9.1	39

[a] Cheetah 5.0 calculation [b] Livermore Explosives Handbook

Experimental Section

Caution! *Although no problems have occurred during the synthesis and handling of **1**, the material is an explosive. Laboratories and personnel should be properly grounded and safety equipment such as Kevlar gloves, blast shields and ear plugs are necessary, especially when working on large scales.*

2,2,2',2'-tetramethyl-5,5'-dinitro-5,5'-Bi-1,3-dioxane(3): To a solution of sodium hydroxide (32 g, 0.80 mol) in water (1 L) in a jacketed flask was added **2** (76.4 g, 0.40 mol) at 20 °C. The reaction mixture was heated at 60 °C for one hour then cooled to 20 °C. Solid sodium persulfate (190 g, 0.80 mol) was added to the reaction mixture and the mixture allowed to stir for 20 hours while maintaining the reaction at 20 °C. During this time a white precipitate of **3** forms. The reaction mixture was then adjusted to pH > 11, filtered, washed with cold water and air dried to provide 41.6 g of **3** (65 %); The product was identical in all respects to that previously reported in the literature (ref)

2,3-Bis-hydroxymethyl-2,3-dinitro-1,4-butanediol(4): To methanol (240 mL) was added **3** (25.6 g, 0.08 mol). The reaction mixture was stirred while HCl gas was bubbled into the reaction mixture. Upon complete dissolution, the HCl addition was stopped and the reaction mixture stoppered and stirred for 48 hours. After this time, the reaction mixture turns from an amber color to a dark brown. The volatiles are then removed and the remainder is triturated with warm chloroform and filtered to provide 8.1 g of **4** (85%); m. p. 100-102 °C . IR (KBr): ν = 3596, 3284, 2975, 2913, 2888, 1482, 1463, 1408, 1385, 1341, 1303, 1255, 12230, 1159, 1135, 1069, 1035, 994, 930 cm^{-1}; ^1H NMR (300 MHz, deuterioacetonitrile) δ = 3.35 (bs, 4H), 4.22 (m, 8H).; ^{13}C NMR (100 MHz, deuterioacetonitrile) δ = 61.18, 96.38; elemental analysis calc'd for $C_6H_{12}N_2O_8$: C, 30.01; H, 5.04; N, 11.66; found: C, 30.38; H, 5.29; N, 11.35.

2,3-Bis-hydroxymethyl-2,3-dinitro-1,4-butanediol tetranitrate (1): To a 200 mL jacketed flask was added acetic acid (50 mL) and acetic anhydride (50 mL). The solution was then cooled to 0 °C and HNO_3 (34 g, 98%) was added dropwise while maintaining the reaction temperature below 5 °C. The reaction was allowed to stir for 20 min. and **4** (12 g, 0.05 mol) was added portionwise. After stirring for 2 hours at 0 °C, the temperature was raised to 20 °C over one hour and then stirred at 20 °C for one hour The reaction mixture was then poured into 200 mL of ice water and stirred. The white solid was filtered, washed with water and air dried to give 20 g of crude **1**. This material was then recrystallized from isopropanol to give 18 g (85%). m. p. 85-86 °C. IR (KBr): ν = 3045, 3028, 2982, 2927, 1658, 1583, 1491, 1465, 1450, 1390, 1371, 1334, 1287, 1156, 1099, 1056, 1022, 995, 898, 854cm^{-1}; ^1H NMR (300 MHz, deuterioacetone) δ = 5.6 (s, 8H); ^{13}C NMR (100 MHz, deuterioacetone) δ = 68.57, 90.73; elemental analysis calc'd for $C_6H_8N_6O_{16}$: C, 17.15; H, 1.92; N, 20.00; found: C, 17.48; H, 2.20; N, 19.86.

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[16] Crystal data for **1** ($C_6H_8N_6O_{16}$): $C_6H_8N_6O_{16}$, FW = 420.18, Monoclinic, $P2_1/n$, a = 8.1228(6) Å, b= 23.0560(16) Å, c = 8.5072(6) Å, α = 90°, β = 113.9530(10)°, γ = 90°, V = 1456.01(18) Å^3, Z = 4, ρ_{calc} = 1.917 Mg/m^3, μ = 0.195 mm^{-1}, $F(000)$ = 856, R_1 = 0.0412 for 2382 observed ($I > 2\sigma I$) reflections and 0.0743 for all 3593 reflections, Goodness-of-fit = 0.977, 253 parameters. The crystals were irradiated using a graphite monochromated MoK_α radiation (λ = 0.71073). An MSC X-Stream low temperature device was used to keep the crystals at a constant -170°C during data collection. Data collection was performed and the unit cell was initially refined using *SMART* [v5.625](Bruker (2001a). SMART v5.625. Bruker AXS Inc., Madison, Wisconsin, USA) .Data Reduction was performed using *SAINT* [v6.36A] (Bruker (2002). SAINT v6.36A. Bruker AXS Inc., Madison, Wisconsin, USA) and *XPREP* [v6.12] (Bruker (2001b). XPREP v6.12. Bruker AXS Inc., Madison, Wisconsin, USA). Corrections were applied for Lorentz, polarization, and absorption effects using *SADABS* [v2.03] (Bruker (2000). SADABS v2.03, Bruker AXS Inc., Madison, Wisconsin, USA). The structure was solved and refined with the aid of the programs in the *SHELXTL-plus* [v6.10] system of programs (Bruker (2000). SHELXTL v6.10. Bruker AXS Inc., Madison, Wisconsin, USA). The full-matrix least-squares refinement on F^2 included atomic coordinates and anisotropic thermal parameters for all non-H atoms. The H atoms were included using a riding model. Crystallographic data (excluding structure factors) for the structure reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-694822. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambrudge, CB21EZ, UK (fax: (+44)1223-336-033: email: deposit@ccdc.cam.ac.uk; web: www.ccdc.cam.ac.uk/data_request/cif.
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Making a Big Bang

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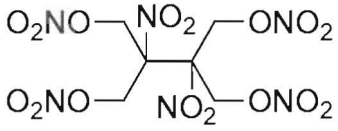

1

The synthesis of a new high energy-density nitrate ester with unique properties is described. Nitrate ester **1** has a density of 1.917 g/cm^3 and a melting point of 85-86 °C. These properties may lead to high performance melt castable applications.