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Bis(1,3-dinitratoprop-2-yl) Nitramine, a New Sensitive Explosive Combining a Nitrate Ester with a NitramineThomas M. Klapötke,^{*[a]} Burkhard Krumm,^[a] F. Xaver Steemann,^[a] and Klaus-Daniel Umland^[a]*In memory of Herbert Schumann, an outstanding chemist and great friend***Keywords:** Explosives; Nitramines; Nitrate ester

Abstract. Nitro functionalized compounds comprise a large substance class and are the most popular explosive materials. Recent research furnished a solid energetic nitrate ester of potential interest. This work is concerned with the synthesis and characterization of novel aliphatic nitramine compounds with similar features.

* Prof. Dr. T. M. Klapötke

Fax: +49(0)89-2180-77492

E-mail tmk@cup.uni-muenchen.de

[a] Department of Chemistry,

Energetic Materials Research,

Ludwig-Maximilian University Munich (LMU),

Butenandtstrasse 5-13 (D), 

81377 Munich, Germany

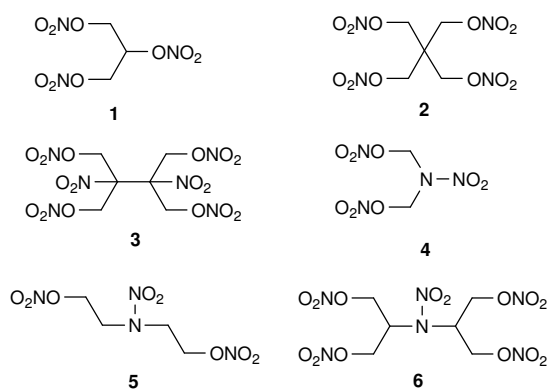
Introduction

Ever since the discovery of nitroglycerine (**1** in Scheme 1) by Ascanio Sobrero in 1846 [1], chemists have investigated nitrated and nitro functionalized compounds for the use as energetic substances. These endeavours furnished *e.g.* pentaerythritol tetranitrate (PETN, **2** in Scheme 1), a very powerful aliphatic nitrate compound, which is not as easy to detonate by means of shock or friction as is nitroglycerine. Recent research led to the synthesis of 2,3-bis(hydroxymethyl)-2,3-dinitrobutane-1,4-diol tetranitrate (NEST-1, **3** in Scheme 1) [2].

Whereas nitroglycerine becomes handy only when mixed with desensitizing agents such as cellite in the composition dynamite, other aliphatic nitrates, *e.g.* PETN and NEST-1, display sensitivities against mechanical stress that allow safe use of the pure compounds.

With remarkable structural similarity to nitroglycerine, the nitramine **4** is reported to be explosive as well. Literature about this compound is rather scarce, despite the huge amount of data available on ethyl analogon **5** and on other nitramine compounds [3].

In this paper, the new nitro-aliphatic nitramine bis(1,3-dinitratoprop-2-yl) nitramine (**6** in Scheme 1) is presented as the most recent outcome of the quest for highly energetic compounds of reduced sensitivity and **4** is investigated more closely.



Scheme 1. Investigated nitro compounds.

Results and Discussion

The synthesis of bis(1,3-dinitratoprop-2-yl) nitramine (**6**) was performed via nitration of the hydroxy-amine bis-(1,3-dihydroxyprop-2-yl)-amine, which in turn can be obtained from 1,3-dihydroxyacetone as reported [4]. Bis-(nitratomethyl)-nitramine (**4**) was obtained from the reaction of bis-(chloromethyl)-nitramine [5] with silver nitrate. Compound **4** decomposes upon longer exposure to humidity.

The respond of the compounds to stress was tested in form of impact by a drop hammer and friction imposed by a friction tester apparatus. The test procedures detailed in EC 440/2008 [6] were used for the determination of sensitivities. In case of **1**, **3** and **5**, the literature values [1,2,7] are given in Table 1.

Table 1. Mechanic sensitivities.

Compd.	E_{dr} / J	F_r / N
1	0.2	353
2	3	60
3	2.7	74.5
4	2	56
5	6	n.d.
6	0.5	353

Formal substitution of the central HCONO₂ moiety in **1** with the nitramino moiety NNO₂ leads to the nitramine **4**. Its impact sensitivity was found to be significantly lower.

Possibly, the sensitizing interaction of adjacent H₂CONO₂ moieties is stronger than the interaction between a H₂CONO₂ moiety and a neighboring nitramino functionality. It cannot be excluded that a sensitizing interaction between both terminal nitrate carbon centers in **1** is blocked by the nitramino “insert” in **4**. If the carbon centered nitrate groups are even farther from the nitramine center, and thus from each other as well, apart, as in the nitramine dioxyethylnitramine dinitrate (DINA, **5**), a further decrease in impact sensitivity is observed in accordance with the expectation.

Compounds **3** and **6** resemble more complex molecules. Compound **3** can be seen as dimer of nitroglycerine (**1**) derived by C-C linkage. The sensitivities of **3** are comparable to PETN (**2**). If the central nitrate functionality in **1** was omitted and a nitramine-linked dimer formed, compound **6** would formally be obtained. As Table 1 indicates, compound **6** is only slightly less sensitive towards impact as **1**. Because the introduction of a nitramine moiety into an energetic alkyl nitrate compound (e.g. **4** and **5**) should result in a significant decrease in sensitivity, the steric effects of the linkage of two 1,3-dinitratoprop-2-yl moieties seem to almost compensate the de-sensitizing effect. For compound **3**, where the linkage is a simple C-C single bond, this effect obviously is stronger as for the nitramine-linked dimer **6**. From this, substitution of nitrate functionalities by C-linked nitro groups seem to de-sensitize even more than does the introduction of a nitramine functionality.

The friction sensitivity should be mostly influenced by the mechanical properties of the substance such as its hardness. Therefore, much more force would be necessary to

successfully initiate decomposition of a soft energetic material. This explains nicely the high friction values for the oils **1** and **6** and lower values for the other (solid) compounds. Friction sensitivities of **2** and **4** are comparable, and both compounds are found roughly by 15 N more sensitive towards friction than **3**. However, the discrepancies between the friction sensitivities of compounds **2**, **3** and **4** cannot be explained satisfactorily by a look at the molecular structures. For the liquid DINA (**5**) no friction value is reported in literature, the measurement of friction sensitivities of liquids is rarely performed.

The melting point of **6** was determined to 23–25 °C and under cool conditions, the compound can be obtained as solid substance. Crystals of **6** were obtained by slow diffusion of n-hexane into a saturated solution of **6** in dichloromethane. The crystal structure of the new nitratealkyl nitramine **6** was solved in the orthorhombic space group $P2_12_12_1$ with four formula units per unit cell. The asymmetric unit represents one formula moiety (Fig. 1).

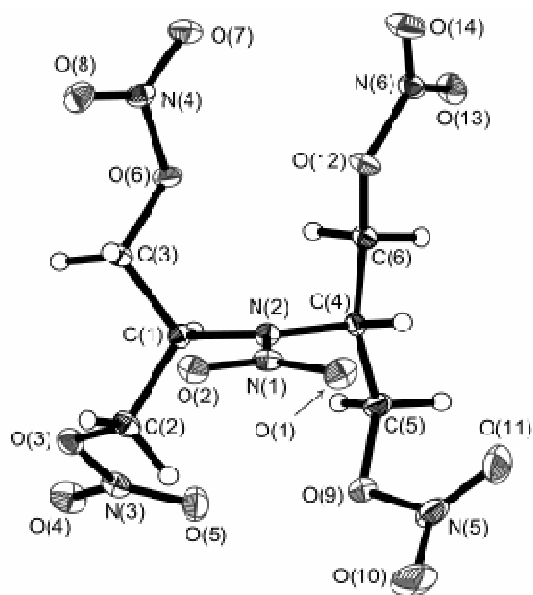


Figure 1. Asymmetric unit of **6**. Crystal data: $C_6H_{10}N_6O_{14}$, $M = 390.18$, $a = 6.1227(2)$ Å, $b = 10.4051(2)$ Å, $c = 22.3943(2)$ Å, $U = 1426.67(6)$ Å³, $T = 100$ K, 8282 reflections measured, 2410 unique ($R_{int} = 0.031$) which were used in calculations. The final $wR(F_2)$ was 0.067 (all data).

Because the present study is focussed on nitrate ester compounds, energetic properties have to be discussed. In order to predict energy release as well as detonation characteristics (pressure, temperature and velocity), the enthalpies of formation and densities can be used in conjunction with the EXPLO5 thermodynamic code [8].

A simple estimation of the enthalpies of formation can be done by increment calculations using average increment enthalpy values from the literature [9]. Intramolecular interactions between nitro or nitrate functionalities can be taken into account. Table 2 lists the calculation results as well as values obtained by bomb calorimetric measurements resp. quantum chemical calculations (CBS-4M) [10].

Table 2. Enthalpies of formation (in kJ/mol).

	Calculated (group additivity)	Measured / Calculated ^a
1	-371	-371 [7]
2	-532	-593 [7]
3	-674	-469 (CBS-4M)
4	-102	-108
5	-279	-276 [7]
6	-379	-1055 / -1068 (CBS-4M)

a) values from bomb calorimetric measurements unless noted otherwise

For substances **1**, **2**, **4**, and **5** good agreement between calculated and measured enthalpies is observed. For the more heavily branched nitrate alkyls **3** and **6**, measurement and increment calculation widely disagree. Obviously, the intramolecular interactions in these molecules are not adequately represented by the increment values from literature. For compound **6**, calorimetric measurements confirm the CBS-4M result.

Using the measured and reported enthalpies of formation, the EXPLO5 computer code [8] calculates the detonation parameters of the compound at the CJ point with the aid of the steady-state detonation model. A modified

Becker-Kistiakowski-Wilson equation of state is used to model the system. The CJ point is found from the Hugoniot curve of the system by its first derivative [11]. The resulting heats of detonation (Q_v), detonation temperatures (T), pressures (p) and velocities (D) are shown in Table 3, as are the oxygen balances (Ω).

Table 3. Detonation parameters.

	ρ (g/cm ³)	Ω (%)	Q_v (kJ/kg)	T (K)	p (kbar)	D (m/s)	$D_{\text{meas.}}$ (m/s) ^b
1	1.591	+3.52	-6037	4629	236	7752	7600 (1.59)[1]
2	1.760	-10.12	-5923	4423	318	8652	8400 (1.7) [1]
3	1.917	0	-6569	4814	367	9023 ^a	9100[2]
4	1.860	+15.09	-5426	4303	315	8525	
5	1.488	-21.65	-5473	4057	217	7645	7580 (1.47) [1]
6	1.817	-12.30	-4683	3650	285	8245 ^a	

a) EXPLO5 values based on CBS-4M results; b) For **3** the reported value was calculated theoretically

With high detonation velocity and pressure, the nitrate ester **3** turns out to be the most promising energetic substance, comparable to PETN (**2**), the nitrate nitramines **4** and KBX (**6**) display slightly lower detonation values. The lowest values are observed for nitroglycerine (**1**) and DINA (**5**), both in the same range.

Conclusions

The new nitramine **6** might have some advantages in comparison to NEST-1 (**3**) and the well-established PETN (**2**), e.g. its very low friction sensitivity, a low melting point and a decomposition temperature of 166 °C (**2**: ca. 185 °C [1], **3**: 141 °C [2]). Unfortunately, the impact sensitivity of **6** is only slightly lower than for nitroglycerine (**1**), therefore only applications of **6** in desensitized mixtures seem reasonable.

Experimental Section

Synthesis of bis(1,3-dinitratoprop-2-yl) nitramine (**6**, KBX)

Nitric acid (100 %, 1.8 mL, 41 mmol) was cooled to 10 °C and dissolved in glacial acetic acid (4.4 mL, 46 mmol). Upon slow addition of bis(1,3-dihydroxyprop-2-yl) amine (0.96 g, 5.8 mmol) in acetic acid (2.3 mL, 41 mmol), the ice bath was removed and the solution stirred for 72 hours at ambient temperature.

Water (25 mL) was added and the solution extracted with dichloromethane (8 × 25 mL). Aqueous and organic layers were saturated with sodium carbonate and the aqueous layer was again extracted with dichloromethane (4 × 25 mL). The united organic layers were washed with water (25 mL), dried over magnesium sulfate and evaporated. Column chromatography (dichloromethane, silica gel) furnished 1.6 g (72 %) KBX (**6**) as pale yellow oil. Single crystals were obtained from a saturated solution in dichloromethane by slow diffusion into *n*-hexane.

6: ¹H NMR (RT, CDCl₃): δ = 5.52 (m, 1 H; CH), 4.82 (m, 2 H; CH₂), 4.66 (m, 2 H; CH₂) ppm. ¹³C NMR (RT, CDCl₃): δ = 74.7 (CH), 68.0 (CH₂) ppm. ¹⁵N NMR (RT, CDCl₃): δ = -49.1 (NO₂), -49.2 (ONO₂) ppm. IR: ν (cm⁻¹) = 3025 w, 2965 w, 2914 w, 2852 w, 1631 vs, 1526 w, 1292 m, 1267 vs, 1086 w, 1015 m, 896 w, 824 s, 751 m, 699 w, 625 w. Raman (400 mW): ν (cm⁻¹) = 2986 (100), 2774 (13), 1647 (18), 1457 (17), 1292 (56), 857 (41), 555 (17). Elemental analysis: Calcd. (C₆H₁₀N₆O₁₄), found (%): C 18.5, 18.7; H 2.6, 2.7; N 21.5, 20.7. DSC (crystals): mp: ~25 °C, decomposition > 165 °C. K_{ow} = 172.4. E_{dr} < 0.5 J (liquid). F_r < 353 N.

Structure Determination

The single crystal X-ray diffraction data of **6** were collected using an Oxford Xcalibur3 diffractometer with a Spellman generator (voltage 50 kV, current 40 mA) and a KappaCCD detector. The data collection was undertaken using the CrysAlis CCD software

[12] and the data reduction was performed with the CrysAlis Red software [13]. The structure was solved with Sir-92 [14] and refined with Shelxl-97 [15] implemented in the program package WinGX [16] and finally checked using Platon [17]. Selected data and parameters from the X-ray data collection and refinement are given in Table X. The crystallographic informations file (cif) on 6 has been deposited with the Cambridge Crystallographic Data Centre under the depository number CCDC-775656. Copies of the data can be obtained free of charge on application to The Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (Fax: int. code + (1223)336-033; e-mail for inquiry: fileserv@ccdc.cam.ac.uk; e-mail for deposition: deposit@ccdc.cam.ac.uk).

Table 4. Crystallographic data of **6**.

formula	C ₆ H ₁₀ N ₆ O ₁₄
molecular weight / g/mol	390.18
temperature / K	100
crystal dimensions / mm	0.11 × 0.15 × 0.29
crystal system	orthorhombic
space group	P2 ₁ 2 ₁ 2 ₁
a / Å	6.1227(2)
b / Å	10.4051(2)
c / Å	22.3943(2)
V / Å ³	1426.67(6)
Z	4
ρ _{calc} / g/cm ³	1.8166
μ / mm ⁻¹	0.182
F(000)	800
θ range / °	3.79–30.09
index ranges	–8 ≤ h ≤ 8 –13 ≤ k ≤ 14 –19 ≤ l ≤ 31
reflections, measured	8282
reflections, unique	2410 (R _{int} = 3.1 %)
R1, wR2 (2σ)	0.0291 / 0.0590
R1, wR2 (all)	0.0448 / 0.0656
data/restraints/parameters	2410 / 0 / 235
GOOF of F ²	0.984
residual densities / e/Å ³	0.229 / –0.240

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