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Synthesis of 1,3-Dinitrohexahydropyrimidine via Ring Contraction of Ether-Linked Nitramines

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14. ABSTRACT

Two ether-linked nitramine explosives have been synthesized. The reactivity of ether-linked nitramines has been probed and it was found that with heating, it is possible to perform a ring contraction to a methylene-linked nitramine that may be suitable for melt-cast applications.

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TNT, melt cast, ring contraction, DHP, ether-linked nitramines

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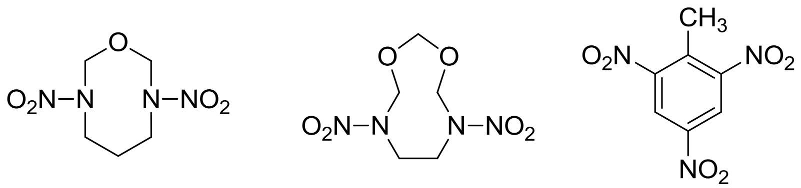
1. Introduction

Trinitrotoluene (TNT) **3** is a widely used energetic material and was first reported in 1863. By the First World War, all major combatants employed TNT as their most heavily used explosive due to its low melting point, stability, noncorrosive properties, and good performance. Its use predominated in the Second World War in spite of the development of materials such as pentaerythritol tetranitrate, 1,3,5-Trinitroperhydro-1,3,5-triazine, and octahydro-1,3,5,7-tetranitro-1,3,5,7-tetrazocine (better known, respectively, as PETN, RDX, and HMX) due to TNT's high productivity. Its use continued through the Vietnam conflict but due to numerous accidents experienced by both the US Navy at sea and the US Air Force in Thailand, alternate binders were sought. The most notable examples were cast-cure, nitramine-based plastic-bonded explosive (PBXs), developed in the 1970s. Cast-cure PBXs, however, are difficult to produce because of incompatibility with existing plants, due to the requirement for high-shear mixers and elevated temperature. Modern alternatives to TNT include eutectic mixtures such as the insensitive munitions explosive IMX-101 and eutectic salts such as DEMN that either have toxicity issues or are difficult to process and incorporate into formulations. Therefore, because of its high productivity, low cost, and favorable processing, the use of TNT is still widespread in military applications around the globe. The search for replacements, however, is ongoing. A series of compounds has been discovered: 3,7-dinitro-1,3,7-oxadiazocane **1** and 5,8-dinitro-1,3,5,8-dioxadiazonane **2** composed of ether-linked nitramines, which are predicted to exhibit explosive properties similar to TNT and have not been described in the literature.



1 **2** **3**

Fig. 1 Structures of Compounds 1–3

Compound **1** is an immediate precursor to melt-castable material 1,3-dinitrohexahydropyrimidine (DHP) **5**, as depicted in Fig. 2, which has TNT's performance and similar physical properties. Furthermore, these compounds undergo a ring-contraction reaction when heated to form either a smaller ether-linked nitramine or a methylene-linked nitramine.

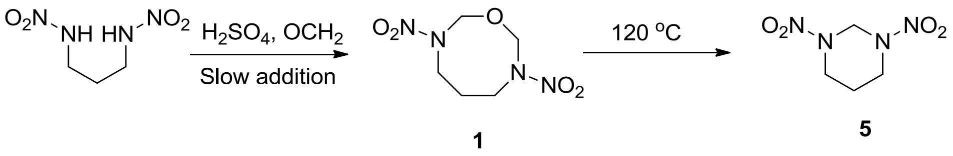


Fig. 2 Ring contraction

Due to their usefulness as synthetic intermediates—and the fact they are not well described in the literature—these ether-linked nitramines warranted further investigation.

2. Computational Analysis and Sensitivity

Compounds **1** and **2** were evaluated using quantum mechanical-modeling codes developed at the US Army Research Laboratory.[1–5] Using these codes, it becomes possible to accurately predict the heat of formation and density of novel energetic materials. With this information in hand, the compounds can then be evaluated using the Cheetah thermochemical codes to give a theoretical detonation performance. The results of these calculations are listed in the Table below.

Table Performance predictions from Cheetah 7.0

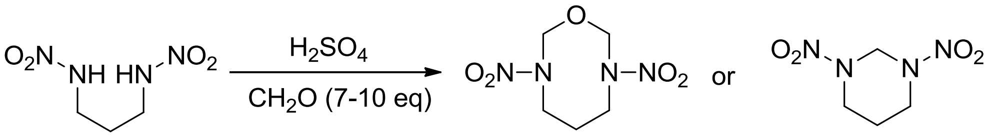
Compound	1	2	TNT[c]
ρ[a]	1.60 [1.57]	1.62 [1.61]	1.65
ΔH_f (kJ/mol)	–177.5[b]	–323.0[b]	–63.2
P_{cj} (GPa)	21.416	21.328	20.022
D_v (km/s)	7.301	7.491	7.180
ΔH_d (kJ/mL)	7.03	7.19	7.00
OB (%)	–77.61	–58.29	–73.96
Impact (cm)	>152.4	>152.4	>152.4
Friction (N)	>360	>360	>360
ESD (J)	>6.25	>6.25	0.625

[a] Experimentally determined values theoretical in brackets.
[b] Predicted using the methods of Rice.[2]
[c] Heat of formation and density numbers obtained from Cheetah 7.0 database. Density, ρ; heat of formation, ΔH_f; Chapman–Jouguet pressure, P_{cj}; detonation velocity, D_v; heat of detonation, ΔH_d; oxygen balance, OB; electrostatic discharge, ESD.

Using the experimentally determined density with the predicted heat of formation, the results of the Cheetah 7.0 calculations on Compounds **1** and **2** indicate the expected performance of these compounds to be approximately 5% greater than TNT's. Interestingly, both **1** and **2** are quite insensitive; this results in no-go's on small-scale impact tests at heights greater than 152.4 cm. Both compounds were also insensitive to friction stimuli beyond 360 N as well as electrostatic stimuli of greater than 6.25 J (as shown in the Table above).

3. Synthesis Discussion

During this investigation it was discovered that the method of addition of 1,3-dinitramopropane **4** to an acidic formaldehyde solution results either in the direct formation of ether-linked dinitramine **1** or mixtures of **1** and 6-membered dinitramine **5.** (See Fig. 3.)

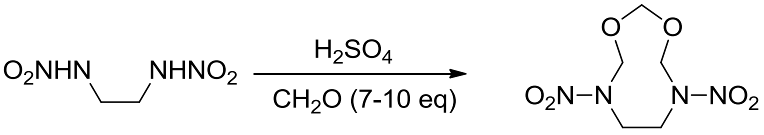


4 **1** **5**

Fig. 3 Synthesis of Compound 1

When **4** is added to the reaction mixture as a solution in various solvents, primarily Compound **1** is formed. However, when **4** is added as a pure solid, a mixture of **1** and an impurity that is most likely **5** can be obtained. The best results were produced from very slow addition of **4** dissolved in water, which produced **1** in good yield.

Similarly, when ethylenedinitramine **6** is used in place of **4**, 9-membered heterocycle **2** is obtained (Fig. 4).



6 **2**

Fig. 4 Synthesis of Compound 2

Both reactions have been performed on up to the 1-g scale. Thermal analysis of both compounds indicates that a decomposition reaction is taking place over a broad range of temperatures starting at 100 °C, which warrants further investigation into the nature of this reaction. The decomposition is accompanied with gas evolution and phase change and is endothermic, according to analysis with differential scanning calorimetry.

4. Results and Experimental Section

The values for the drop-weight experiments were determined using the Langlie one-shot method on an apparatus employing a 2-kg weight from a maximum height of 152.4 cm.[6] Friction sensitivity measurements were determined on a BAM friction apparatus and ESD was determined using an Allegheny Ballistics Laboratory ESD apparatus (Table). Nuclear magnetic resonance (NMR) experiments were accomplished using an Anasazi Instruments 90-megaherz (MHz) NMR device. Fourier transform infrared spectroscopy (FTIR) was obtained from a Brüker Alpha-T fitted with a 5-cm path length gas-flow cell in the transmission module, or a diamond-attenuated total-reflectance (DATR) module. Differential scanning calorimetry was conducted on a TA instruments Q10 or Q20 calorimeter. All chemicals were obtained from Sigma-Aldrich, St Louis, Missouri, and were used as received. Values for pH were determined using colorpHast pH-indicator strips (pH 0–14) from EMD Chemicals Inc.

Note: While these compounds were prepared without incident according to the following procedures, these materials are energetic and should be prepared and handled cautiously only by trained personnel.

4.1 Synthetic Procedures

The 2-imidazolidone, available from Sigma-Aldrich, is used to prepare ethylene dinitramine **6** according to the literature method.[3]

1,3-dinitrotetrahydropyrimidin-2(1H)-one: Was prepared according to a modified literature procedure[9] in which 1.00 g (10.0 mmole) of N,N' trimethylene urea is added to 3.0 mL of acetic anhydride while stirring in an ice bath. Then, 100% nitric acid (1.5 mL) was slowly added drop-wise over approximately 10 min as to maintain the solution's temperature below 25 °C. Upon addition of 1 mL of the nitric acid, the suspension turned into a solution whereupon the product crashed out as a yellow solid by the time all of the nitric acid was added. Upon completion of nitric-acid addition, the thick suspension was stirred for an additional 20 min, then drowned in ice water. The yellow solid was filtered by vacuum filtration, rinsed with copious amounts of water, and dried under vacuum—or carried immediately to the next step. A typical procedure yields 1.69 g of product (8.85 mmole, 89% yield) after drying in vacuum. (See Fig. 5.)

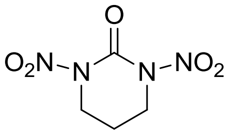


Fig. 5 1,3-dinitrotetrahydropyrimidin-2(1H)-one

N,N'-(propane-1,3-diyl)dinitramide **4:** Was prepared according to the literature procedure[10] in which 1,3-dinitrotetrahydropyrimidin-2(1H)-one is added to water with stirring and reacted with solid pellets of sodium hydroxide until all solid starting material is dissolved and the pH is strongly alkaline (14 as indicated by pH paper). Concentrated aqueous hydrochloric acid was added, at which point a large amount of bubbling occurred as carbon dioxide escapes from the reaction. Acid is added until the pH is strongly acidic (0 as indicated by pH paper) and either extraction with ethyl acetate or overnight crystallization in the freezer yielded the title compound as a white solid. (See Fig. 6.)

Fig. 6 N,N'-(propane-1,3-diyl)dinitramide

3,7-dinitro-1,3,7-oxadiazocane **1**: Was prepared by the dropwise addition of 1.0 g (6.0 mmole) of N,N'-(propane-1,3-diyl)dinitramide in 10 mL of water to 22 mL of a 73% sulfuric-acid–water solution containing 1.4 g (46 mmole) of paraformaldehyde. The addition rate was controlled such as to keep the solution's temperature below 7 °C (addition occurred over 15 min). After the addition was completed the solution was stirred for an additional 5 min whereupon it turned milky with a white precipitate, which was drowned in ice water and filtered to yield 796 mg (3.86 mmole, 64%) of **1** as a white solid after drying under vacuum. **^{1}H NMR** (90.420 MHz, Acetone-D$_6$) δ 5.40 (s, 4H), δ 4.06 (dd, 4H, j = 5.15 Hz, 5.15 Hz), δ 1.98 (m, 2H); **^{13}C NMR** (22.605 MHz, Acetone-D$_6$) δ 81.74 (2C), 52.00 (2C), 24.27 **FTIR** (DATR), ṽ = 3064, 1518, 1386, 1286, 1254, 1234, 995, 959, 874, 762, 583. (See Fig. 7.)

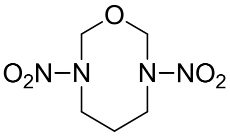


Fig. 7 3,7-dinitro-1,3,7-oxadiazocane

5,8-dinitro-1,3,5,8-dioxadiazonane **2**: Was prepared by the dropwise addition of 1.00 g (6.67 mmole) of N,N'-(ethane-1,2-diyl)dinitramide dissolved in 8.5 mL 1,4-dioxane to 20 mL of a 73% sulfuric-acid–water solution containing 1.40 g (46 mmole) of paraformaldehyde. The nitramine solution was prepared by heating the dioxane until the nitramine dissolved. This solution was allowed to cool but not to the point of precipitation. The warm nitramine solution was added to the acidic formaldehyde solution before precipitation of the nitramine occurred. The sulfuric acid solution was chilled down to below 5 °C prior to addition of the nitramine solution. The addition was completed in about 30 s using a pipet to add the solution nitramine solution to the chilled acidic formaldehyde solution. After the addition was completed the solution was stirred for an additional 5 min whereupon it turned milky with a white precipitate, which was drowned in ice water and filtered to yield

1.05 g (4.77 mmole, 72%) of **1** as a white solid after drying under vacuum. **^{1}H NMR** (90.420 MHz, Acetonitrile-D_3) δ 5.40 (s, 4H), δ 5.03 (s, 2H), δ 4.16 (s, 4H); **^{13}C NMR** (22.605 MHz, Acetonitrile-D_3) δ 99.24, 79.92 (2C), 47.377 (2C); **FTIR** (DATR),$\tilde{\nu}$ = 3040, 2966, 1511, 1458, 1264, 1264, 1101, 1003, 989. (See Fig. 8.)

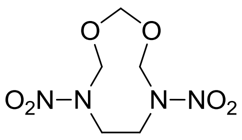


Fig. 8 5,8-dinitro-1,3,5,8-dioxadiazonane

5. Discussion of DHP and Formaldehyde Extrusion from Ether-Linked Nitramines

DHP has been synthesized by a classic ring closure of the primary nitramine precursor (Fig. 9).

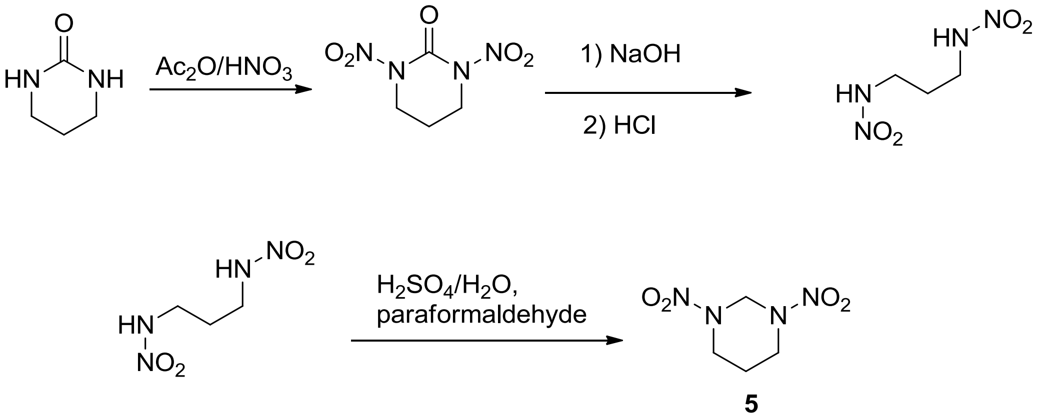


Fig. 9 Classic synthesis of DHP

The classic synthesis has a low overall yield and requires a very large amount of sulfuric acid, generating excess acidic waste. The synthesis of **1** as a precursor to DHP is much higher yielding and allows a substantial reduction in the amount of sulfuric acid used. Compound **1** undergoes thermal ring contraction with extrusion of a molecule of formaldehyde to efficiently form DHP.

Compound **2** also undergoes thermal-ring contraction with extrusion of formaldehyde to form Compound **7** but does not contract down to the 5-membered nitramine **8** (Scheme 5), as depicted in Fig. 10.

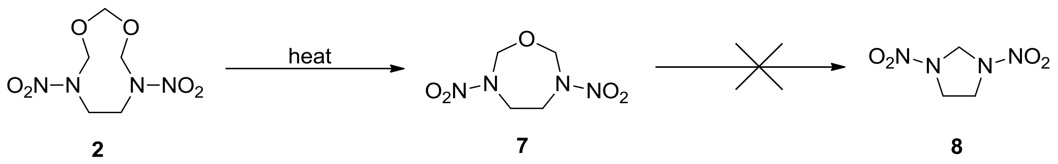


Fig. 10 Ring contraction of 2

It is speculated that ring strain may account for the failure to undergo thermally induced ring contraction from the **7** to **8**, while the 8-membered ring readily undergoes this transformation (Fig. 11).

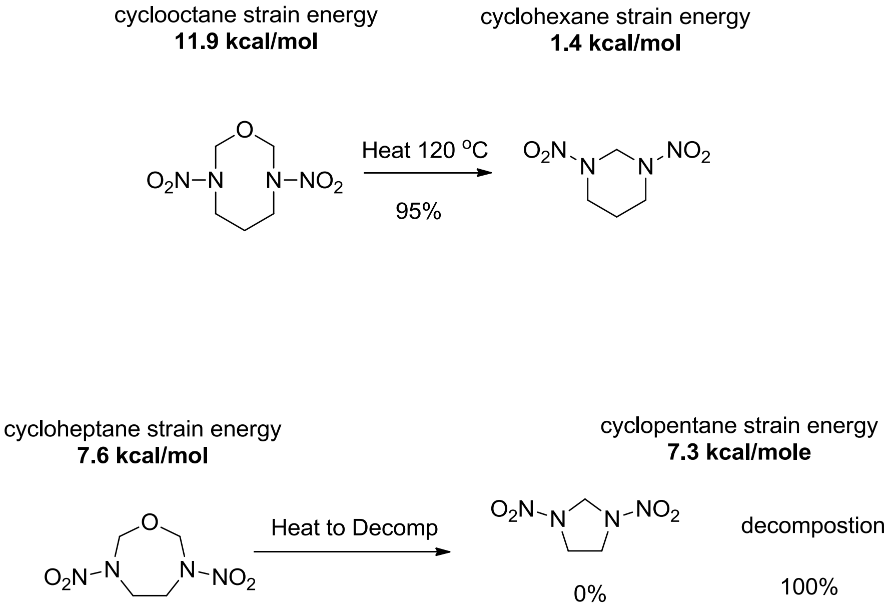
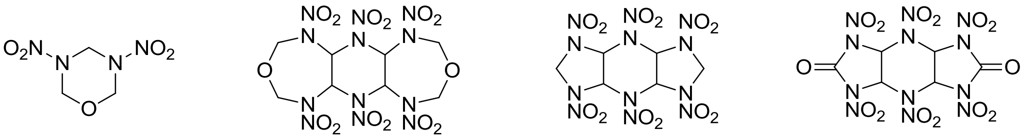


Fig. 11 Ring strain

6. Conclusions

Further development will be focused on increasing the scope of the ring contraction by screening solvents and various acid catalysts to promote the described transformation. Preliminary results suggest this will be possible because traces of **8** have been detected by gas chromatography–mass spectrometry in small-scale screening reactions which utilizing nitromethane as a solvent and catalyst, which cause **7** to undergo reactions. While mostly decomposition has been observed, it is thought that with more screening, the reaction can be driven to a more productive pathway.

Other ether-linked nitramines (depicted in Fig. 12) are being targeted for synthesis.



9 **10** **11** **12**

Fig. 12 Future targets

Compound **9** has been published in the Russian literature as having a melting point of 100 °C, but the synthesis has been unreproducible. Compound **10** is a potential precursor to **11,** which is a more stable analog of **12**, a very powerful but moisture-sensitive explosive. However, **11**, lacking carbonyl groups, is expected not to exhibit moisture sensitivity but retain much of the performance of **12**. It is thought that through careful screening of conditions, **10** can be synthesized and forced to undergo ring contraction to form **11**.

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List of Symbols, Abbreviations, and Acronyms

ATR	attenuated total reflectance
cm	centimeter
CO_2	carbon dioxide
DATR	diamond-attenuated total-reflectance
DHP	1,3-dinitrohexahydropyrimidine
D_v	detonation velocity
ESD	electrostatic discharge
FTIR	Fourier transform infrared spectroscopy
g	gram
GPa	gigapascal
ΔH_d	heat of detonation
ΔH_f	heat of formation
HCl	hydrochloric acid
HNO_3	nitric acid
H_2SO_4	sulfuric acid
H_{50}	50% initiation height
IMX	insensitive munitions explosive
J	joule
kJ	kilojoule
MHz	megahertz
min	minute
mL	milliliter
mmole	millimole
mol	mole
N	newton
N_2	nitrogen
NaOH	sodium hydroxide
NMR	nuclear magnetic resonance

OB	oxygen balance
PBX	plastic-bonded explosive
P_{cj}	Chapman–Jouguet pressure
ρ	density
s	second
TNT	trinitrotoluene
ZnSe	Zinc Selenide

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