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# Synthesis and Characterisation of 2,2-Dinitro-1,3-propanediol-based Plasticisers

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**Abstract:** In this paper, the synthesis of two energetic plasticisers (2,2-dinitro-1,3-bis(2-azido acetoxy) propane and 2,2-dinitro-1,3-bis(formyloxy) propane is outlined. The attempted syntheses of even further derivatives are described. The prepared compounds were characterised and evaluated as plasticisers. Their glass transition temperatures are acceptable to excellent, but both of them are thermally unstable.

**Keywords**: energetic material, energetic plasticiser, synthesis, characterisation, thermal stability

## Introduction

One of the key steps in the improvement of explosive charges and propellants is the development of new energetic ingredients. The aim of such additives is to enhance the performance as well as the mechanical properties of propellants and plastic bonded explosives (PBX), in comparison with the current binders and/or plasticisers. The reason for our interest in energetic plasticisers is the dissatisfactory mechanical properties of commercially available, energetic binders. The polar groups in the molecular structure of these compounds render them increasingly viscous and elevate their glass transition temperatures. The rise in glass transition temperature downgrades the low temperature properties, which are especially important for missile propellants. The higher viscosity can result in processibility problems.

The inert binders currently in use have excellent mechanical properties. However, they contain little energy and require high solids loading to have a sufficient performance. The disadvantages of available energetic polymers are mentioned above. Hitherto, the known energetic plasticisers have inconveniences such as low thermal stability, low energy content, high migratory ability and sometimes, they dissolve the filler. The low thermal stability can be remedied with stabilisers, but finding a molecule that is stable as such is a very interesting area of research.

Recently, attention has been directed towards *gem*-dinitro-based plasticisers [1]. Great effort has been put into industrial-scale production of BDNPF/A [2, 3] and to develop similar mixtures containing formals of other *gem*-dinitro alcohols [4, 5]. The research of the last decade has been focused mostly on azido-plasticisers [1]. These considerations focused our efforts on structures with energetically derivatised *gem*-dinitro compounds. Our earlier preparation of the interesting, but thermally labile energetic plasticiser 2,2-dinitro-1,3-bis-nitrooxy-propane [6] (NPN) and its properties prompted us to prepare other 2,2-dinitro-1,3-propanediol-based compounds.

# Calculations

Our first criterion in the selection of new molecules to synthesise was the result from the calculations of their heat of formation, density and performance. The heat of formation in the gaseous state was quantum mechanically calculated by the use of Gaussian (G98) [7]. The heat of formation in the solid state was then calculated by the method of Rice [8] and Politzer [9], with a code (hs95fo) developed by professor Tore Brinck at the Royal Institute of Technology in Stockholm. Molpak [10] was used to estimate the density. This approach was presented in a recent paper [11]. Cheetah 2.0 [12] was used to estimate the performance of the new molecules. The results were promising for the selected substances, as shown in Table 1. Our previously published [6] plasticiser NPN and butyl-NENA are shown in the table for comparison.

Structure	ΔH <sup>0</sup> f [kcal mol <sup>-1</sup> ]	ρ [g cm <sup>-3]</sup>	D <sub>CJ</sub> [km s <sup>-1</sup> ]	P <sub>CJ</sub> [GPa]	ISP [s]	OB [%]
	-75	1.90	8.7	31.7	248	+12.5
$H \xrightarrow{O}_{O_2N} \xrightarrow{O}_{NO_2} H$	-183	1.66	6.9	18.4	200	-36.0
$N_3$ $O$ $O$ $N_3$ $O$ $O$ $N_3$ $N_2$ $N_3$	-68	1.46	6.6	15.0	201	-48.2
$NO_2$ $N_3$ $NO_2$ $NO_2$	111	1.62	8.3	27.8	265	-29.6
$F_3C$ $O$ $O$ $CF_3$ $O$ $O$ $CF_3$	-371	1.73	6.1	16.0	211	-22.3
	-71	1.42	6.4	13.8	205	-104.2

 Table 1.
 Calculated properties of the energetic plasticisers

To calculate the enthalpy of formation of fluorine-containing compounds, the calculation code had to be slightly modified, since the work of Rice [8] and Politzer [9] does not include any other elements than carbon, hydrogen, nitrogen and oxygen.

# **Experiments**

### Synthesis

2,2-Dinitropropanediol and dinitromethane salts

The parent compound of the above-mentioned energetic plasticiser is 2,2-dinitro-1,3-propanediol (1). This is synthesised by a so-called Henry reaction between an alkali metal salt of dinitromethane and formaldehyde [13], cf. Scheme 1.





This compound (1) can also be synthesised by the Henry reaction between nitromethane and formaldehyde, followed by oxidation of the product with sodium persulphate [14]. Our reason to choose the synthesis shown above, Scheme 1, was our experience in the area of *gem*-dinitro chemistry. There were two main sources of dinitromethane salts: nitration of barbituric acids [15] (2) and hydrolysis of 1,1-diamino-2,2-dinitroethylene [16] (FOX-7, 3), cf. Scheme 2. The experimental section [16] of the paper describing the hydrolysis of FOX-7 claims that the hydrolysis is complete in three hours. Further studies have shown that twelve to sixteen hours are required for the reaction to reach completion.



Scheme 2. Synthesis of dinitromethane salts.

#### 2,2-Dinitro-1,3-bis(formyloxy)propane

2,2-Dinitro-1,3-bis(formyloxy)propane (4) was synthesised as described in the literature [17], cf. Scheme 3. 2,2-Dinitro-1,3-propanediol (1) is reacted with formic acetic anhydride in a basic, organic solution. One inconvenience of this synthesis is that the anhydride must be freshly prepared.



Scheme 3. Synthesis of 2,2-dinitro-1,3-bis(formyloxy)propane.

### 2,2-Dinitro-1,3-bis(2-azidoacetoxy)propane

The hitherto unpublished 2,2-dinitro-1,3-bis(2-azidoacetoxy)propane (6) was synthesised according to the procedure described in Scheme 4. 2,2-dinitro1,3-propanediol (1) is treated with chloroacetyl chloride to yield 2,2-dinitro-1,3-bis(2-chloroacetoxy)propane (5). Chloroacetic anhydride can also be used. Substitution of the chlorines with sodium azide produces the desired product (6).



Scheme 4. Synthesis of 2,2-dinitro-1,3-bis(2-azidoacetoxy)propane.

## Attempted synthesis of 2,2-dinitro-1,3-bis(trifluoroacetoxy)propane

When 2,2-dinitro-1,3-propanediol (1) was treated with triflic anhydride, under the same reaction conditions as with formic acetic anhydride, no reaction occurred. No product (7) was obtained, Scheme 5, despite various attempts.



Scheme 5. Attempted synthesis of 2,2-dinitro-1,3-bis(trifluoroacetoxy)propane

Attempted synthesis of 2,2-dinitro-1,3-diazidopropane

The synthesis of 2,2-dinitro-1,3-diazidopropane (10) was attempted in two different ways, cf. Scheme 6. In the first 2,2-dinitro-1,3-propanediol (1)is transformed into 2,2-dinitro-1,3-dichloropropane (8), by the use of thionyl chloride and pyridine. The second way is the nitration of the same parent compound (1) in mixed acids into 2,2-dinitro-1,3-bis(nitrooxy)propane [6] (10). Experience in our group prompted us to try nitrate esters as leaving groups. The two strategies share the same problem. Both intermediates are decomposed, presumably by proton abstraction by the azide ion, the nitrate ester faster (9)than the chloride (8).



Scheme 6. Attempted syntheses of 2,2-dinitro-1,3-diazopropane.

It later became known to us that 2,2-dinitro-1,3-diazidopropane (10) has been synthesised [18]. It is very sensitive to impact and friction and has been tested as a primary explosive [19, 20], a fact that dissuaded us from further attempts of preparation.

## Characterisation

Our group has selected two criteria to evaluate potential plasticisers. The first is the glass transition temperature of the pure compound, which was measured using a Mettler DSC 30, differential scanning calorimeter, equipped with a ceramic sensor. Every test as well as the calibration was performed in a nitrogen atmosphere (50 mL/min) at a heating rate of 10 °C/min. The samples were put in 40  $\mu$ L aluminium cups with a pierced lid. The sample weight was between 10 and 20 mg. Calibration was made with indium (Mettler-Toledo,

Sweden) ( $T_m$ = 156.6 °C) and anhydrous *n*-octane (Sigma-Aldrich, Sweden) ( $T_m$ = -57 °C). All tests were performed in duplicate.

The second is the thermal stability as measured by heat flow calorimetry. STANAG 4582 describes the NATO requirements on the stability of explosives and nitrocellulose-based propellants [21]. This procedure specifies that a sample should not at any time have a higher heat-flow than 63.1  $\mu$ W/g, being kept at 75 °C for 19 days, or higher than 114  $\mu$ W/g at 80 °C for 11 days to be considered as stable. Approximately 0.5 grams of each sample was used. The measurements were done isothermally in a Thermal Activity Monitor, TAM 2277, heat flow (micro) calorimeter. The samples were put in 3 mL glass ampoules and hermetically sealed with aluminium caps. If a new product is stable, according to these conditions, further evaluation of its compatibility with different fillers and binders are performed.

A first test of the thermal stability is a so-called block test, which is a measure of precaution to avoid damaged microcalorimeter cells. The sample is stored in an ordinary, metal heating block for 11 days at 80 °C. If no change in colour and/or gas evolution is observed, a new sample will be put into the heat flow calorimeter for a more thorough measurement.

## 2,2-Dinitro-1,3-bis(formyloxy)propane

This compound (4, Scheme 3) is an excellent plasticiser in terms of its glass transition temperature, which is -77 °C, cf. Figure 1. A sample of this product turned black without any larger gas evolution in a block test, *vide supra*. Therefore, no further heat flow calorimetric evaluation of this molecule was performed. Since the product was thermally unstable, the unidentified peaks in the thermogram were not further investigated. The exothermal peak at -20 °C remains unexplained. The endothermal peak between 0 °C and 5 °C is believed to be due to moisture in the product.



Figure 1. Glass transition temperature measurement of 2,2-dinitro-1,3-bis(formyloxy)propane.

### 2,2-Dinitro-1,3-bis(2-azidoacetoxy)propane

This compound (6, Scheme 4) has an acceptable glass transition temperature of -49 °C, cf. Figure 2. Though, it has low thermal stability, as shown in Figure 3. The heat-flow peaks at approximately 3300  $\mu$ W/g, which is more than fifty times higher than the acceptance limit of STANAG 4582 [21] (63  $\mu$ W/g).



**Figure 2.** Glass transition temperature measurement of 2,2-dinitro-1,3-bis(2-azidoacetoxy)propane.



**Figure 3.** Heat flow produced by 2,2-dinitro-1,3-bis(2-azidoacetoxy)propane at 75 °C, measured by calorimetry.

# Discussion

### Calculation vs. observed values

There are discrepancies between the calculated and the observed properties of the plasticisers, as shown in Table 2. A major problem when performing calculations on potential plasticisers is that they generally are liquids. Our codes are adapted to estimate the properties of gases and solids.

The heat of formation is first calculated in the gas phase. The heat of sublimation is then calculated to enable the conversion from  $\Delta H^{0}_{f}(g)$  to  $\Delta H^{0}_{f}(s)$ . To obtain the heat of formation of a liquid, the heat of evaporation is needed, instead of the heat of sublimation. This can explain the discrepancies in this area. The enthalpy of formation has not been measured for any of the new products. Therefore, butyl-NENA is added for comparison.

A similar problem is encountered when calculating the density. Molpak [10] assumes that the substance is crystalline to be able to calculate the best packing of the molecules.

Table 2.	The calcul	ated and	observed	heats	of formation	and	densities
	of some pl	asticisers					

	$\Delta H^{0}_{f}$		ρ	
Structure	[ксаг	mol ·]	[g cm <sup>-5</sup> ]	
	Calc.	Obs.	Calc.	Obs.
	-75	n.m.	1.90	1.66 [1]
	-183	n.m.	1.66	1.47
$N_3$ $O$ $O$ $N_3$ $N_3$ $N_3$ $N_3$ $N_3$ $N_3$	-68	n.m.	1.46	1.50
	-71	-46 [22]	1.42	1.22

#### **Synthesis**

It is noteworthy that 2,2-dinitro-1,3-propanediol (1) is stable to pyridine in dichloromethane, whereas it decomposes into 2,2-dinitroethanol (11) and formaldehyde in basic, aqueous solutions [13], cf. Scheme 7.



Scheme 7. Decomposition of 2,2-dinitro-1,3-propanediol (1) in basic, aqueous solution.

The reaction of the diol with chloroacetyl chloride, formic acetic anhydride and chloro acetic anhydride in the presence of pyridine was successful. In the case of trifluoroacetic anhydride no product was obtained. Our hypothesis is that the equilibrium in basic, organic solution is unfavourable for the product.

The problems encountered in the attempted syntheses of 2,2-dinitro-1,3diazidopropane can be explained by the instability of the intermediates in even slightly basic conditions. 2,2-Dinitro-1,3-dichloropropane can undergo a retroHenry reaction, by loosing formaldehyde and hydrochloric acid. 2,2-Dinitro-1,3-bis(nitrooxy)propane is very sensitive to bases. Its protons are supposed to be easily abstracted, despite the lack of  $pK_a$  measurements. This assumption is based on the observation of oligomerisation in basic media. The formation of oligomers was observed by mass spectrometry (not shown in this paper), but their structures were not determined.

Analogous results from these two compounds and NPN indicate that 2,2-dinitro-1,3-diol-based compounds have low glass transition temperatures, but they seem to be thermally unstable. The close proximity of the electron withdrawing groups in these structures might be a reason for their low stabilities. These results made us discard 2,2-dinitro-1,3-propanediol as a core for energetic plasticisers. The effects of extended carbon chains on the glass transition temperature and thermal stability are under current investigation.

### Experimental

All solvents were used as purchased. Dinitromethane salts were prepared in two ways; the first was developed by Langlet *et al.* [15] and the second was the hydrolysis of FOX-7, *vide infra.* 2,2-Dinitro-1,3-propanediol [11] and 2,2-dinitro-1,3-bis(formyloxy)propane [17] were synthesised as described in the literature.

<u>Potassium dinitromethane:</u> KOH (26.4 g, 0.4 mol, 85%, 2 eq) was dissolved in 150 mL water. FOX-7 (29.6 g, 0.2 mol, 1 eq) was added and the mixture was left refluxing overnight. Yellow crystals form on cooling. The crystals were filtered off, washed with 10 mL cold water, 50 mL anhydrous ethanol and 50 mL diethyl ether and dried at 40 °C. This procedure yielded 26.3 g (91.3%). T<sub>m</sub> (dec): 221 °C, <sup>1</sup>H NMR (DMSO-d<sub>6</sub>,  $\delta$ , ppm): 8.19 (s, 1H). It should be noted that a white solid, consisting of ammonium carbonate, forms in the reflux condenser.

<u>2,2-Dinitro-1,3-bis(2-chloroacetoxy)propane</u>: A solution of chloroacetic chloride (2.83 g, 25 mmol, 2.5 eq) in CH<sub>2</sub>Cl<sub>2</sub> (4 mL) was added dropwise to a mixture of 2,2-dinitro-1,3-propane diol (1.66 g, 10 mmol, 1 eq) and pyridine (2.4 g, 30 mmol, 3 eq) in CH<sub>2</sub>Cl<sub>2</sub> (20 mL) at 0 °C. The temperature of the mixture was kept below 5 °C. The cooling was removed after the addition and the reaction was left for 4 h at ambient temperature. Water (20 mL) was added to the dark brown reaction mixture, which was stirred for 30 min. The organic layer from the mixture was separated, washed with aqueous HCl (2 M, 2×20 mL), water (3×20 mL), dried over Na<sub>2</sub>SO<sub>4</sub> and concentrated *in vacuo* to produce a lightbrown, oily product in quantitative yield. T<sub>m</sub> 63 °C, 1H NMR (CDCl3,  $\delta$ , ppm): 4.10 (s, 4 H), 5.10 (s, 4 H).

<u>2,2-Dinitro-1,3-bis(2-azidoacetoxy)propane</u>: Sodium azide (1.3 g, 20 mmol) and sodium iodide (1.5 g, 10 mmol) were added to a solution of 2,2-dinitro-1,3-bis(2-chloroacetoxy)propane (1.6 g, 5 mmol) in acetone (40 mL). The reaction mixture was stirred at room temperature overnight. This resulted in a yellow solution. Water (40 mL) was added to dissolve the salt residues. The mixture was extracted with diisopropyl ether (20 mL x 3). The combined organic phases were washed with water (10 mL x 3), dried over Na<sub>2</sub>SO<sub>4</sub>, purified by flash chromatography on silica gel and evaporated to produce a light yellow, oily product. The yield was 1.55 g (93.4%),  $T_g = -48.8$  °C, <sup>1</sup>H NMR (CDCl3,  $\delta$ , ppm): 3.97 (s, 4 H), 5.12 (s, 4 H); elemental analysis: calculated for C7H8N8O8: C 25.31, H 2.43, N 33.73 found: C 25.46, H 2.39, N, 33.77.

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