

# The Nitrocarbamate Moiety for Safer Energetic Materials

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***Abstract:** The combination of chemical functional groups makes chemistry to a never ending story. As a matter of course, this concept could also be used in the topic of energetic materials. However, in the field of developing new energetic materials it is indispensable, that the manipulation of this energetic materials is safe. Nitrocarbamates are not widely used in the field of energetic materials. The principle of the synthesis of nitrocarbamates is demonstrated on the polyvalent alcohol pentaerythritol. First the pentaerythritol tetracarbamate was prepared from the alcohol with the reagent chlorosulfonyl isocyanate (CSI). At the second step the nitration was used to get the energetic material pentaerythritol tetra-nitrocarbamate (PETNC). This material is thermally more stable and shows a lower sensitivity against friction and impact compared to the well-known pentaerythritol tetranitrate (PETN) The thermal stabilities, the sensitivity and the energetic properties are discussed and compared to well known PETN.*

***Keywords:** energetic material, nitrocarbamates, nitrates, energetic properties, pentaerythritol tetranitrocarbamate.*

## 1. Introduction

The chemistry of high energetic materials is still a very active research topic. An interesting but meagerly investigated energetic functionality which emerged, are primary nitrocarbamates.[1] The pentaerythritol tetranitrate  $C(CH_2ONO_2)_4$  PETN (Nitropenta) is based on the neopentane derivate pentaerythritol and is a popular and well known explosive. The precursor for

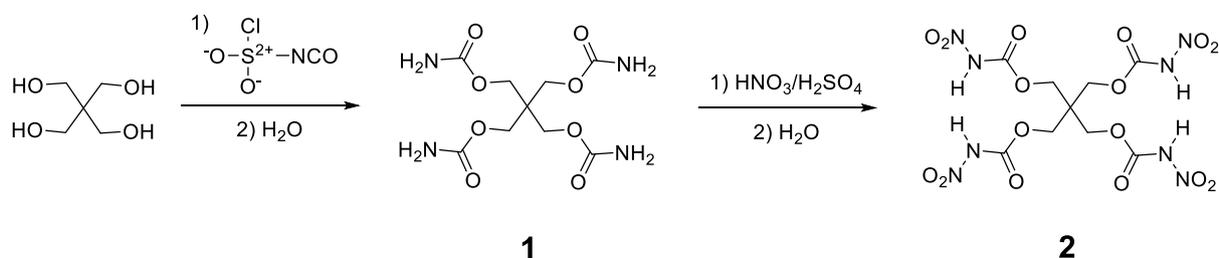
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PETN and for the here presented compound pentaerythritol tetranitrocarbamate (**2**) is the common and commercially available pentaerythritol.[2]

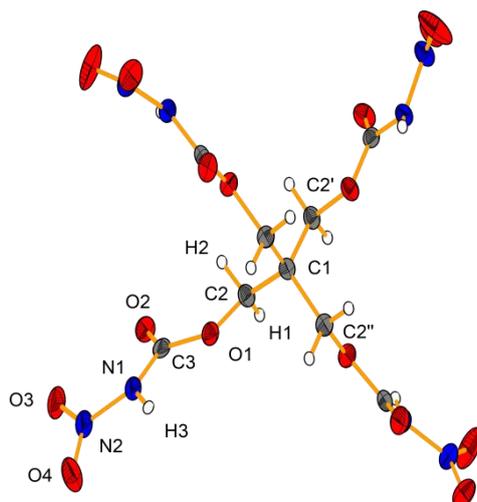
## 2. Synthesis and Discussion

Primary carbamates were synthesized by default in a two step synthesis. First the corresponding alcohol were reacted with an excess of phosgene and in the second step the carbamate is formed by the action of ammonia.[3] A much more economic way is the addition of alcohols to urethanes or the nucleophilic attack to *in situ* prepared isocyanic acid.[4] However the latter route is problematic with polyvalent alcohols. Some reasons for this are the general less reactivity of the reagent and potential of multiple additions. An alternative facile route is the reaction of the alcohol with the reagent chlorosulfonyl isocyanate (CSI).[5] CSI, is a commercially available reagent. It was discovered in Germany in 1956 and is one of the most reactive isocyanates. The reaction with CSI and alcohols are very fast and already proceeds at low temperatures. Also possible multi-addition is prevented by the formation of an chlorosulfonylamide intermediate. This SO<sub>2</sub>Cl group could be removed by simple aqueous work-up, leaving the pure carbamate.[6] The advantages of CSI are monosubstitution, fast reaction times, simple isolation and nearly quantitative yields. This facile reagent was also adopted for the synthesis of pentaerythritol tetracarbamate (**1**) and could be synthesized in a one step synthesis with a very high yield of 99 %.[1]



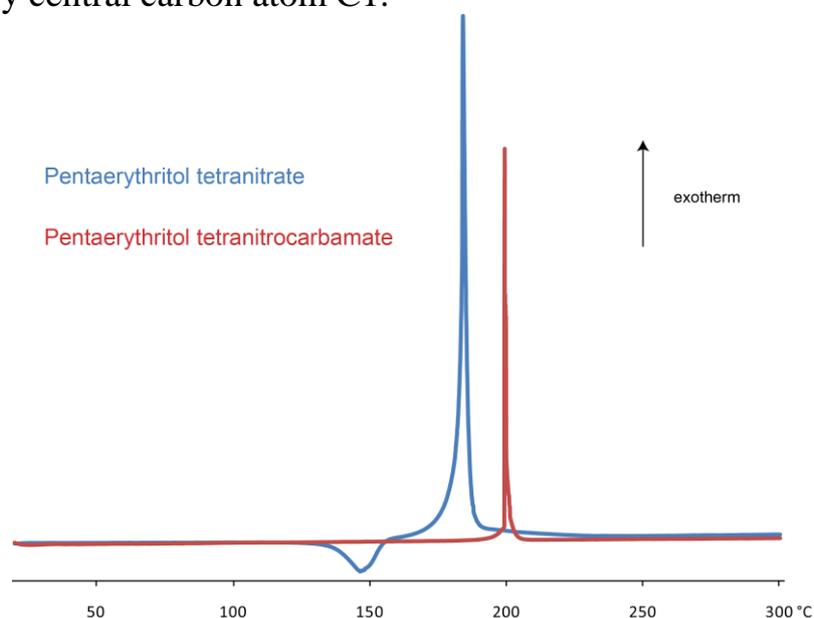
**Scheme 1.** Synthesis of pentaerythritol tetracarbamate (**1**) and pentaerythritol tetranitrocarbamate (**2**).

The carbamate **1** were converted into the pentaerythritol tetranitrocarbamate (**2**) by a mixture of concentrated sulfuric (96 %) and fuming nitric acid (100 %) (1:1). The reaction was quenched in ice-water and the pure product can filter off.[1]



**Figure 1.** Molecular structure of pentaerythritol tetranitrocarbamate (**2**) with ellipsoids at the 50 % probability level.

Single crystals of the pentaerythritol tetranitrocarbamate (**2**) were obtained from acetone at ambient temperature. It crystallizes in the tetragonal space group  $P-42_1c$  with two formula units per unit cell. The density is  $1.77 \text{ g cm}^{-3}$  at  $-173 \text{ }^\circ\text{C}$ . The asymmetric unit consists only of one arm and the quaternary carbon (Figure 1). This is due to the tetragonal space group which has a 4-fold rotoinversion axis with two glide planes perpendicular to one another through the quaternary central carbon atom C1.



**Figure 2.** DTA of pentaerythritol tetranitrocarbamate (**2**) (red) and pentaerythritol tetranitrate (PETN) (blue), heating rate of  $5 \text{ }^\circ\text{C/min}$ .

The tetranitrocarbamate **2** has no melting point and decompose up to a temperature of  $196 \text{ }^\circ\text{C}$  (onset) (Figure 3). Therefore, the thermal stability of **2** is higher than that of PETN which melts and begins to decompose at  $165 \text{ }^\circ\text{C}$  or lower.[3] The nitrocarbamate **2** has also a lower sensitivity towards impact with

a value of 8 J and no sensitivity to friction. The nitrogen content is 23 % and is more than 5 % higher compared to that of PETN, however the oxygen balance  $\Omega$  and the detonation velocity is lower compared to those of PETN (Table 2).

**Table 1.**  
Physical and energetic properties of **2** and pentaerythritol tetranitrate (PETN).

	PETN	PETNC
Formula	$C_5H_8N_4O_{12}$	$C_9H_{12}N_8O_{16}$
MW / $g\ mol^{-1}$	316.13	488.23
$IS / J$ [a]	3	8
$FS / N$ [b]	60	360
$ESD / J$ [c]	0.50	0.75
$N / \%$	17.7	23.0
$\Omega_{CO} / \%$ [d]	+15.2	+3.28
$\Omega_{CO_2} / \%$ [d]	-10.1	-26.2
$T_{Melt.} / ^\circ C$	138	-
$T_{Dec.} / ^\circ C$	165	196
$\rho / g\ cm^{-3}$ (RT)	1.78	1.76
$\Delta_f H_m^\circ / kJ\ mol^{-1}$ [e]	-480	-1311
$\Delta_f U_m^\circ / kJ\ kg^{-1}$ [e]	-1423	-2594
$\Delta_{Ex} U^\circ / kJ\ kg^{-1}$ [f]	-6140	-3928
$T_{Ex} / K$ [g]	4083	2951
$P_{CJ} / kbar$ [h]	314	258
$V_{Det.} / m\ s^{-1}$ [i]	8448	7743
$V_o / L\ kg^{-1}$ [j]	752	728

[a] impact sensitivity, [b] friction sensitivity, [c] sensitivity towards electrostatic discharge, [d] oxygen balance assuming the formation CO/CO<sub>2</sub>, [e] enthalpy and energy of formation calculated with the CBS-4M method with Gaussian09, [f] predicted heat of combustion, [g] temperature of gaseous products, [h] detonation pressure, [i] detonation velocity and [j] volume of gaseous products calculated with the program package EXPLO5 Version 6.02 [7].



**Figure 3.** Small scale reactivity test SSRT of **2**. a) Schematic set-up b) Aluminum block after the test c) Measuring the volume with sand.

In order to assess the explosive performance of **2** on a small laboratory scale, a SSRT (small scale reactivity test) was performed. For this test a defined volume of the explosive is pressed into a perforated steel block, which is topped with a commercially available detonator (Orica-DYNADET-C2-0ms).[8] Initiation of the tested explosive results in denting a separate aluminum block, which is placed right underneath the steel block (Figure 3). From measuring the volumes of the dent, it can be concluded that the small scale explosive performance of **2** (605 mg sand) is slightly lower than the performance of PETN (917 mg sand), thus also confirming the calculated values with EXPLO5 [8]. However, the test indicated that the nitrocarbamate **2** can be detonated.

### 3. Conclusion

The best synthesis for pentaerythritol tetracarbamate (**1**) is the one step synthesis from pentaerythritol, which is inexpensive and commercially available. The synthesis has compared to previously known routes several advantages, like fast reaction time and high yield and pure product. The nitration to the new energetic material pentaerythritol tetranitrocarbamate (**2**) proceeds in high yields. **2** is thermally stable and decompose at 196 °C. It shows a higher heat stability and lower sensitivity against friction and impact compared to the well-known pentaerythritol tetranitrate (PETN).

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