About the Azido Derivatives of Pentaerythritol Tetranitrate
Tobias Lenz,[a] Thomas M. Klapötke,[a] Moritz Mühlemann,[b] and Jörg Stierstorfer[a]

Dedicated to Professor Dr. Peter Klüfers on the occasion of his 70th birthday.

Abstract: With the first ever synthesis of monoazidopentaerythritol trinitrate, a comparative study of the properties of all azidonitrate derivatives from pentaerythritol tetranitrate (PETN) to tetraazidopentaerythritol (TAPE) was possible. The azides were prepared by halogen azide exchange and the remaining alcohols were then converted into the organic nitrate esters using acetyl nitrate. The resulting compounds pentaerythritol tetranitrate (PETN), monoazidopentaerythritol mononitrate (MAPETN), diazidopentaerythritol dinitrate (DAPEDN), triazidopentaerythritol mononitrate (TAPEMN), tetraazidopentaerythritol (TAPE) were analyzed for their chemical (XRD, NMR, EA, IR) and energetic properties (DTA/DSC, impact and friction sensitivity) and presented for comparison. An interesting trend of decreasing melting points from PETN to the triazide was observed, with the monoazide found to meet the thermal requirements for a melt-castable explosive. The mechanical sensitivities were successfully explained by Hirshfeld analysis. The energetic properties were calculated with the EXPLO5 code and show a decreasing performance towards the highly sensitive tetraazido derivative. Furthermore, PETN was successfully initiated with its tetraazido derivative TAPE.

Keywords: energetic materials · nitrate esters · azides · PETN · sensitivities

1 Introduction

Since 1867 when Alfred Nobel invented dynamite, organic nitrates are ubiquitous in the field of energetic materials. While nitroglycerine, contained in dynamite and propellants, has been replaced in many fields, due to its headache causing properties and high sensitivity, the tetranitrate of pentaerythritol finds a wide range of applications. It is characterized by a favorable one-step synthesis, low toxicity, and high performance. The explosive, shortened PETN, is used in both the military and civilian sectors. The nitrate can be found as the main charge in grenades and shaped charges or as a booster charge in detonators. PETN is also available as detonating cord, in which tubes are filled with PETN, which can then be flexibly wrapped around trees or inserted into boreholes. Furthermore PETN is used in Semtex or sheet explosives. In mixtures with TNT, PETN is known as pentolite for mining operations. A pentolite booster is needed to transfer the energy from the detonator to the more insensitive, often ammonium nitrate-based main charge. This is one of the reasons why PETN is often referred to as the boundary between primary and secondary explosives [1].

Because PETN is such a well-known explosive, several attempts have been made to modify it. Functionalities like polynitramino [2], nitrate salts [3], amine [4] or nitrocarbamate [5] were introduced. Furthermore, silica [6] and oxophosphine [4] derivatives are known. Herein we report the synthesis of all azido derivatives from pentaerythritol tetranitrate to tetraazidopentaerythritol. In Figure 1 the molecular structures of Pentaerythritol tetranitrate (PETN), Monoazidopentaerythritol trinitrate (MAPETN), Dia-
2 Experimental Section

CAUTION! All investigated azidonitrates are explosive and sensitive materials. Although no incidents were observed during preparation and handling of these compounds, safety precautions (such as wearing a leather coat, face shield, Kevlar sleeves, Kevlar gloves, earthed equipment, and earplugs) should be drawn especially when manipulating dry materials.

2.1 Tetraazidopentaerythritol (TAPE)

1,3-Dibromo-2,2-bis(bromomethyl)propane (0.50 g, 1.4 mmol) was dissolved in DMF (10 mL) and sodium azide (1.02 g, 15.7 mmol) was added. The mixture was heated 10 h at 100 °C. The completion of the reaction was checked by TLC. Then the solvent was evaporated under reduced pressure. Water was added to the residue and the mixture was extracted with ethyl acetate (×3). The solvent was dried over MgSO₄ filtrated and evaporated to dryness, yielding TAPE (0.19 g, 0.8 mmol, 60%) as a colorless crystalline solid. DTA (5 K min⁻¹): 44 °C (endo), 218 °C (dec.). ¹H NMR (DMSO-d₆, 400 MHz, ppm): δ = 3.40 (s, 8H). ¹³C NMR (DMSO-d₆, 100 MHz, ppm): δ = 51.7, 43.6. ¹⁴N NMR (DMSO-d₆, 29 MHz, ppm): δ = −133, −175. FT-IR (ATR): ν = 2956 (w), 2929 (m), 2868 (w), 2221 (w), 2175 (w), 2087 (vs), 1444 (s), 1352 (m), 1287 (s), 1269 (vs), 1153 (m), 1123 (m), 945 (m), 908 (m), 895 (s), 653 (m), 634 (m), 599 (m), 556 (m), 463 (s) cm⁻¹. EA calcd. for C₅H₄N₃O₃ (236.20 g mol⁻¹): C 25.43, N 71.16, H 3.41%; found: C 25.75, N 70.36, H 3.43%. IS: < 1 J; FS: 1 N.

2.2 General Procedure for Organic Nitrate Formation

To a solution of acetic acid anhydride (5 parts) and glacial acetic acid (1 part), nitric acid (1 part) was added dropwise at 5–10 °C under stirring. After the solution was cooled down to 5 °C, the azido compound (0.4 M for MAPE, 0.3 M for DAPE, 0.2 M for TriAPE) was added carefully in portions and the reaction is stirred 20 min at 5 °C. After completion, the solution is poured on ice water (20 parts).

2.3 Monoazidopentaerythritol Trinitrate (MAPETN)

Following the general procedure, 2-(azidomethyl)-2-(hydroxymethyl)propane-1,3-diol (0.50 g, 3.6 mmol), acetic acid anhydride (7.5 mL), glacial acetic acid (1.5 mL), nitric acid (1.5 mL) were used. After addition to water the precipitating solid was extracted with ethyl acetate (×3) and residues of acid were neutralized with sodium bicarbonate. The solvent was dried over MgSO₄ filtrated and evaporated to dryness, yielding MAPETN (0.79 g, 2.7 mmol, 86%) as a colorless crystalline solid. DTA (5 K min⁻¹): 82 °C (endo), 180 °C (dec.). ¹H NMR (DMSO-d₆, 400 MHz, ppm): δ = 4.63 (s, 6H), 3.69 (s, 2H). ¹³C NMR (DMSO-d₆, 100 MHz, ppm): δ = 71.1, 50.1, 41.5. ¹⁴N NMR (DMSO-d₆, 29 MHz, ppm): δ = −46, −137. ¹⁵N NMR (DMSO-d₆, 41 MHz, ppm): δ = −43.8, −134.5, −172.0, −317.1. FT-IR (ATR): ν = 2111 (m), 1635 (vs), 1467 (w), 1304 (m), 1273 (vs), 1027 (m), 999 (m), 846 (s), 754 (s), 737 (m), 707 (m), 690 (m), 643 (w), 621 (m) cm⁻¹. EA calcd. for C₅H₄N₄O₆ (296.15 g mol⁻¹): C 20.28, N 28.38, H 2.72%; found: C 20.33, N 28.14, H 2.72%; IS: 2 J; FS: 36 N.

2.4 Diazidopentaerythritol Dinitrate (DAPE)
2.5 Triazidopentaerythritol Mononitrate (TAPEMN)

Following the general procedure, 3-azido-2,2-bis (azidomethyl)propan-1-ol (0.50 g, 2.4 mmol), acetic acid anhydride (7.5 mL), glacial acetic acid (1.5 mL), nitric acid (1.5 mL) were used. After addition to water the precipitating solid was extracted with dichloromethane (× 3) and residues of acid were neutralized with sodium bicarbonate. The solvent was dried over MgSO₄, filtered and evaporated to dryness, yielding TAPETN (0.5 g, 1.9 mmol, 82%) as a yellowish liquid. DTA (5 K min⁻¹): −24 °C (endotherm), 180 °C (decomposition).

1H NMR (DMSO-d₆, 400 MHz, ppm): δ = 4.49 (s, 2H), 3.50 (s, 6H). 13C NMR (DMSO-d₆, 100 MHz, ppm): δ = 72.2, 51.3, 42.9. 15N NMR (DMSO-d₆, 29 MHz, ppm): δ = −42, −134, −173.

FT-IR (ATR): ν = 2938 (w), 2874 (vw), 2094 (vs), 1635 (s), 1543 (w), 1451 (m), 1365 (w), 1273 (vs), 1009 (m), 847 (s), 754 (m), 708 (w), 644 (m), 601 (w), 552 (m), 45 ppm. The FT-IR of TAPETN in DMSO-d₆ shows a single strong peak at 134.5 cm⁻¹.

N3 is identified through 1H NMR of MAPETN in DMSO-d₆. The chemical shift of protons next to the nitrate is decreasing stepwise from PETN with 4.70 ppm to TAPEMN with 4.49 ppm. The shifts of the protons next to azide are decreasing from MAPETN 3.69 ppm to TAPEMN 3.40 ppm. The 15N shifts of the nitrates can be observed in the range of −45 ppm. The β nitrogen of the azide was observed at about −135 ppm and in some cases the γ nitrogen shows in the range of −175 ppm. The 15N NMR of MAPETN in DMSO-d₆ shows four resonances for nitrogen, one of the nitrates and three of the azide. The chemical shift for nitrate is observed at −43.8 ppm, which is typical for primary organic nitrates. The nitrogen of the azide can be found at −134.5, −172.0, and −317.1 ppm, typical shifts for azide.

3 Results and Discussion

3.1 Synthesis

An overview of the synthesis is given in Scheme 1. On an industrial scale, PETN is synthesized from the corresponding alcohol by nitration with white fuming nitric acid. The pentaerythritol scaffold can be brominated with hydrogen bromide to the solid mono (MBPE) [10], di (DBPE) [11], and tri (TriBPE) [12] or by treatment with phenyl chloride and sodium bromide to the tetrabromide (TBPE) [13]. In this work, the bromide functionality was replaced by an azide functionality through exchange with sodium azide to prepare MAPETN and DAPEDN in good yields. The resulting azido alcohols were then converted to the corresponding nitrate esters. It was observed, that for the synthesis of MAPETN with nitric acid, mixtures of PETN and the desired azido nitrate were yielded. A more selective nitrate formation with acetyl nitrate leads the wanted azido nitrates MAPETN, DAPEDN, and TAPEMN in good yields.

All azido nitrates were analyzed by 1H, 13C, and 15N NMR in DMSO-d₆. The chemical shift of protons next to the nitrate is decreasing stepwise from PETN with 4.70 ppm to TAPEMN with 4.49 ppm. The shifts of the protons next to azide are decreasing from MAPETN 3.69 ppm to TAPE 3.40 ppm. In the carbon NMR increasing shifts for the centered carbon from PETN 40.8 ppm to TAPE 43.6 ppm are observed. The nitrate bound carbons show the same trend from PETN 70.3 ppm to TAPEMN 72.2 ppm. This is also the case for shifts of azide bound carbons from MAPETN 50.1 to 51.7 ppm for TAPE.

The 15N shifts of the nitrates can be observed in the range of −45 ppm. The β nitrogen of the azide was observed at about −135 ppm and in some cases the γ nitrogen shows in the range of −175 ppm. The 15N NMR of MAPETN in DMSO-d₆ shows four resonances for nitrogen, one of the nitrates and three of the azide. The chemical shift for nitrate is observed at −43.8 ppm, which is typical for primary organic nitrates. The nitrogen of the azide can be found at −134.5, −172.0, and −317.1 ppm, typical shifts for azide.

3.2 Crystallographic Data

The crystal structures of PETN and TAPE are known to literature. Crystals of MAPETN and DAPEDN and TAPE were obtained by evaporation of the extraction solvent. On the crystals of MAPETN and DAPEDN and TAPE, low-temperature single-crystal X-ray diffraction experiments were performed. TAPE was measured at low temperature to decrease the rotation of the azide functionality. TAPEMN shows to be solid below −24 °C but all efforts to obtain a crystal structure failed. Both highly symmetric molecules, PETN with P42₁c and TAPE with I4₁a crystallize in tetragonal space groups. The azido-nitrates MAPETN and DAPEDN crystallize in the orthorhombic space group Pbcn. The room

![Scheme 1. Synthesis of azido and nitrate derivatives of pentaerythritol (PE).](image)

![Figure 2. 15N NMR of MAPETN in DMSO-d₆. N3 is identified through 15N NMR in advance.](image)
temperature densities were calculated from the crystal structure densities and it shows, that a linear decrease in density is taking place. (Figure 3) PETN shows the highest density with 1.778 g cm\(^{-3}\) followed by MAPETN with 1.667 g cm\(^{-3}\). DAPEDN shows a slightly lower density of 1.586 g cm\(^{-3}\) and the TAPE has the lowest density with 1.480 g cm\(^{-3}\). The density of TAPEMN is estimated to follow the trend and should therefore be in the area of 1.53 g cm\(^{-3}\).

Intramolecular distances and torsion angles are given underneath the Figures 4–6. Bond length and torsion angles of all compounds are similar to the already discussed and reported PETN [14] or TAPE [15]. For MAPETN a disorder in the structure is observed. For every other molecule the azide and nitrate functionality at C3 changes position. Therefore, an azide and nitrate are bound to the C3 and C3\(^{i}\) at 50% each. For simplicity, only the nitrato group at C3 and the azide group at C3 is represented in Figure 4.

MAPETN shows stabilizing intermolecular interactions of O2–H 2.51 Å, O6–H 2.45 Å and O5–H 2.48 Å. Furthermore,
the N11···H interaction with 2.46 Å is stabilizing intermolecular.

For DAPEDN the nitrate oxygen O2 shows attractive interactions with distances of O2···H 2.45 Å. The O3···H distance with 2.75 Å is much less attractive. The nitrogen N4 is interacting with hydrogen bound at C2. These N···H interactions with 2.65 Å are in the area of the added van der Waals radii (VdW\(_{\text{N}+\text{H}}\) = 2.65 Å).

In the structure of the tetraazide TAPE interactions of the two polarized azide nitrogen atoms, N1 and N3 with hydrogen are observed. The distance N···H 2.86 Å is longer than the sum of the van der Waals radii of N···H and longer than in DAPEDN.

### 3.3 Hirshfeld Analysis

Hirshfeld surfaces of PETN, DAPEDN, and TAPE were generated and their Fingerprint plots were calculated (Figure 7). The distance of interactions can be calculated by the addition of the distance \(d_e\) and \(d_i\). Therefore, points in the lower left region represent close interactions. The percentage of the different interactions is visualized in the bar diagram below [16]. MAPETN shows a disorder of the nitrate and azide positions, so a Hirshfeld analysis could not be performed.

PETN shows the most stabilizing and relatively close attractive O···H interactions. These stabilizing interactions are decreasing in number for the higher nitrogen content derivatives, up to an extreme for TAPE where no O···H interactions are possible. The decrease of O···H interactions goes along with an increase in less attractive N···H interactions. These interactions are stabilizing for DAPEDN because of their relatively short distance. For TAPE the distance of N···H interactions increases and the stabilization is therefore less. The decrease of stabilizing interaction agrees with the increasing sensitivity. Attractive interactions are decreasing from PETN to DAPEDN to TAPE.

Destabilizing effects in the crystal structure are O···O, N···N, O···N, or H···H repulsive interactions. PETN shows a high amount of relatively close O···O repulsion. For DAPEDN relatively close O···O and O···N repulsions are found. TAPE shows weaker repulsive N···N interactions but very strong H···H repulsion. The hydrogen repulsion is very close and therefore very destabilizing. The repulsive effects are in-

![Figure 7](image-url)
increasing from PETN to DAPEDN to TAPE, which is also associated with the increasing sensitivity.

Hirshfeld analysis clearly shows that the derivatives containing nitrates show very stabilizing O···H interactions that compensate for the repulsive O···O, O···N interactions. For the high nitrogen-containing derivatives, O···H is replaced by weaker N···H stabilization, and repulsion is caused by close H···H contacts. The Hirshfeld analysis agrees with the increasing sensitivity towards TAPE.

3.4 Physiochemical Properties

3.4.1 Thermal Analysis

The thermal behavior was investigated by differential thermal analysis (DTA), hotplate, and hot needle test. TAPEMN was also analyzed by low-temperature DSC as it shows a melting point of −24 °C. The DTA curves of the five investigated compounds are shown in Figure 8. The tetraazide is the most thermally stable compound with a decomposition at 218 °C. All compounds with a nitrate functionality decompose at about 180 °C like PETN. Remarkable is that, from PETN to TAPEMN, the melting point decreases gradually by 50–60 °C with each azide exchanged, starting from PETN with 143 °C to TAPEMN with −24 °C (Table 1). The asymmetric triazide shows the lowest melting point due to the disturbed crystal packing. The highly symmetric TAPE is melting at 44 °C and not following the trend. This stability is a consequence of the high symmetry within the crystal. With a melting point of 82 °C and a decomposition point of 180 °C, MAPETN is a melt cast explosive, melting in the area of TNT and decomposing about 100 °C earlier [1c].

Upon fast heating on a hot plate (HP), the nitrate rich PETN and MAPETN are deflagrating. The more nitrogen-rich compounds DAPEDN, TAPEMN, and TAPE are detonating violently on the hot plate.

Table 1. Physicochemical properties of PETN, MAPETN, DAPEDN, TAPEMN, TAPE, Pb(N₃)₂, RDX.

|          | PETN     | MAPETN   | DAPEDN   | TAPEMN   | TAPE     | Pb(N₃)₂ | RDX     |
|----------|----------|----------|----------|----------|----------|---------|---------|
| Formula  | C₅H₁₃N₆O₆| C₅H₁₃N₆O₅| C₅H₁₃N₆O₅| C₅H₁₃N₉O₁| C₅H₁₃N₁₂| PbN₃    | C₅H₁₃N₆O₆|
| M [g mol⁻¹] | 316.14   | 296.15   | 276.06   | 256.19   | 236.20   | 291.24  | 222.12  |
| IS [J g⁻¹]  | 3.5      | 2.0      | 3.0      | 1        | < 1      | 2.5–4   | 7.5     |
| FS [%]   | 54       | 36       | 15       | 80       | 1        | 0.1–1   | 120     |
| Ω [%]   | −10.1    | −27.0    | −46.4    | −68.7    | −94.8    | −        | −21.61  |
| Tₘelt [°C] | 143      | 82       | 32       | −24      | 44       | −       | −       |
| T dec [°C] | 180      | 180      | 182      | 175      | 218      | 320–360 | 210     |
| Density [298 K] [g cm⁻³] | 1.778 | 1.667 | 1.586 | 1.5³.vol | 1.480 | 4.71 | 1.800 |
| ΔHₘol [kJ mol⁻¹] | −484 | −59 | 362 | 795 | 1180 | − | 31 |
| Detonation parameters calculated with EXPLO5V6.05 |
| −Δ-ul [kJ kg⁻¹] | 6166 | 5702 | 5532 | 5427 | 5074 | 1639 | 5740 |
| Tₚ [K] | 4038 | 3849 | 3747 | 3588 | 3213 | − | 3745 |
| pₜₚ [GPa] | 31.3 | 27.8 | 24.2 | 21.2 | 20.5 | − | 33.6 |
| D [m s⁻¹] | 8471 | 8092 | 7842 | 7740 | 7819 | 5180 | 8801 |
| Gas vol. [L kg⁻¹] | 744 | 771 | 809 | 820 | 799 | 308 | 711 |

[a] Impact sensitivity (BAM Drophammer, 1 of 6), [b] Friction sensitivity (BAM friction tester, 1 of 6), [c] Nitrogen content, [d] Oxygen balance towards CO₂,
[e] Melting point from DTA (5 K min⁻¹, onset), [f] Decomposition temperature from DTA (5 K min⁻¹, onset), [g] Calculated density from low temperature X-ray diffraction,
[h] Calculated (CBS-4M) heat of formation, [i] Heat of explosion, [j] Explosion temperature, [k] Detonation pressure, [l] Detonation velocity,
[m] Volume of detonation gases (assuming only gaseous products).
As the hotplate test shows the reaction of an unconstrained sample against heating, the hot needle (HN) test is performed on substances fixed and confined with adhesive tape. The contact of a red glowing hot needle causes decomposition of PETN and MAPETN, whereas DAPEDN shows fast deflagration. TAPEMN and TAPE are violently detonating.

### 3.4.2 Sensitivities and Energetic Properties

Impact and friction sensitivities were determined according to the “UN declaration of dangerous goods” on a BAM Drophammer and a BAM Friction Tester (Figure 9). The basis for a positive test is at least one explosion in six tests. This result is additionally supported by six negative tests with lower energy [17].

A strong increase in the impact sensitivity is observed towards TAPE. The tetranitrate PETN shows an explosion when hit with 3.5 J energy. The monoazide MAPETN shows, as expected, an increased sensitivity of 2 J. Whereas DAPEDN, 3 J, shows a slightly lower impact sensitivity than PETN but higher sensitivity than MAPETN. This unexpected jump in sensitivity can be explained by morphology effects or a consequence of the measurement of probabilities. The liquid TAPEMN shows an impact sensitivity of < 1 J just like the solid TAPE. In short, the impact sensitivity increases with slight jumps from PETN to TAPE. As a liquid TAPEMN is like nitroglycerine highly sensitive to impact < 1 J.

The sensitivity to friction shows a continuous progression to TAPE, except for liquid TAPEMN. For PETN cracking can be observed at 54 N. For the solid azides, heavy detonations are observed at the lower detonation limit. The friction sensitivities are decreasing from 36 N for MAPETN to 15 N for DAPEDN to 1 N for TAPE. With 80 N explosion limit, TAPEMN is the least friction sensitive compound of all derivatives. In short, the friction sensitivity increases from PETN to TAPE, except for less sensitive TAPEMN. The melt-castable explosive MAPETN (2 J, 36 N) shows higher sensitivity than TNT (15 J, 360 N) [1c].

The heats of formation were calculated using the atomization method (using Gaussian CBS-4M electronic enthalpies) and the detonation parameters were calculated using the EXPLO5 V6.05 code [18]. (Details of the calculations can be found in the supporting information). For PETN a low heat of formation of $-484 \text{ kJ mol}^{-1}$ is calculated by this method. Exchange of nitrate with azide causes a stepwise increase in heat of formation (app. 425 kJ per $\text{-ONO}_2 / \text{-N}_3$ exchange) up to TAPE with $1180 \text{ kJ mol}^{-1}$.

PETN shows the best detonation parameters of all investigated compounds, with a detonation velocity of 8.5 km s$^{-1}$ and a pressure of 31.3 GPa. As the density decreases, velocity and pressure also decrease to TAPE with a velocity of 7.8 km s$^{-1}$ and a pressure of 20.5 GPa. The decrease in the performance can be explained due to the decrease in the density of the materials, but as the heat of formation goes up towards TAPE the negative effect of the lower densities is compensated to a certain degree.

As TAPE possesses high thermal stability and a sensitivity typical for primary explosives, classical initiation capability tests were performed. A 200 mg load of PETN was pressed into a copper shell and initiated by 50 mg of its tetraazide derivative TAPE. The result of the experiment is shown in Figure 10 where it is clearly visible that PETN was initiated. As TAPE is melting at 44°C it cannot be easily used as a replacement for the typical initiating primary explosive lead azide. Nevertheless, this experiment shows that organic azides are possible replacements for common initiating explosives. The test failed for the less sensitive DAPEDN therefore the less sensitive compounds were not tested. TAPEMN was not tested as it is a liquid at room temperature.

![Figure 9](image-url)  
**Figure 9.** Bar chart of the impact (grey) and friction (blue) sensitivities of the investigated compounds.

![Figure 10](image-url)  
**Figure 10.** Positive initiation capability test of TAPE on PETN.
4 Conclusion

Azide and nitrate derivatives of pentaerythritol were synthesized in good yields by azide exchange of the corresponding bromate derivatives, followed by nitration with in-situ generated acetyl nitrate. The properties of the pure compounds were investigated and compared (Figure 11). The mechanical sensitivities are increasing from PETN to TAPEMN. Every azide exchanged causes a drop of 50–60 °C which is observed from PETN to TAPEMN. Every azide exchanged causes a drop of 50–60 °C. The thermal stability of the organic nitrates is limited by 180 °C and a detonation velocity of 8.1 km s⁻¹ PETN, because of the lower densities and oxygen balance. However, the study shows that carbon bonded azides are possible candidates as new initiating or melt cast explosives, although in this case, the thermal or mechanical properties are not sufficient.

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Data Availability Statement

No data available.

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