Characterization of the Hexanitrate Esters of Sugar Alcohols


Abstract: The hexanitrates of the six-carbon sugars mannitol and sorbitol were prepared and studied to gain insight in their relative stabilities. Synthesis and characterization of these materials resulted in the identification of two new crystalline polymorphs, one for each hexanitrate. Mannitol hexanitrate (MHN) exposed to elevated temperatures exhibited a different structure when measured by x-ray diffraction (XRD) and Raman spectroscopy; however, no differences were observed in the thermal behavior. Sorbitol hexanitrate (SHN) has two distinct crystalline polymorphs that result in different melting behavior and differences in Raman and XRD. Thermal stability of these hexanitrates was also examined; despite being isomers, SHN and MHN differ in their long-term thermal stability.

Keywords: Polymorphs · Nitrate ester · Sugar nitrates · thermal stability

1 Introduction

Nitrate esters are formed from materials containing hydroxyl groups. Materials with multiple hydroxyl groups, polyols, have been nitrated to produce explosive compounds, which are used in both the commercial and military sectors. Some examples of common nitrate esters include pentaerythritol tetranitrate (PETN), ethylene glycol dinitrate (EGDN), and nitroglycerin (NG) [1]. PETN is used in detonators, detonating cord, sheet explosives, and boosters and is even found in medicinal devices. EGDN and NG found immediate use in dynamite formulations and remain in many propellants, smokeless powders, and medicinal devices. Other polyols have also been subject to nitration, but due to certain undesirable properties, have not found military use. Polyols, such as erythritol, mannitol, and sorbitol, are referred to as sugar alcohols. They are available in the food industry as alternative low-calorie sweeteners. Originally inaccessible because their isolation from natural sources was expensive, bioengineering found means to produce these sugars on a large, efficient scale, making them accessible to the general public [2]. Unfortunately, their widespread availability, combined with the ease of nitration makes these potential precursors for terrorist exploitation.

The discovery of nitrate esters shown in Figure 1 dates to the mid- to late-1800’s. Recently erythritol tetranitrate (ETN) has received considerable attention [3–11]. ETN has a similar explosive performance to PETN; albeit at the cost of increased sensitivity [12]. It melts significantly lower than PETN (ETN, m.p. = 61 °C, PETN m.p. = 141 °C, dec). This melt is not accompanied by apparent decomposition, suggesting it might be melt castable. The wide commercial availability of erythritol and the low melting point of its nitrate ester explains its use as a homemade explosive (HME) [13].

The nitrate esters derived from xylitol, mannitol, and sorbitol have not received as much recent attention as ETN. Although its crystal structure was recently reported, xylitol pentanitrate (XPN) is notoriously difficult to isolate as a solid [14–16]. Mannitol hexanitrate (MHN) was first prepared in 1847 by Italian scientist Ascanoio Sobrero, who had isolated NG a year earlier. Since it was solid at room temperature, Sobrero was initially more interested in the potential of MHN rather than NG; however, following the accidental explosion in his lab of 400 grams of MHN, his interest waned. [17] MHN was used in detonators and even explosive rivet composition during World War II, before being replaced by more stable compositions [18]. Like NG and PETN, MHN acts as a vasodilator and in the past has been used in the treatment of angina pectoris [19]. Recently, a co-crystal of MHN with 1-nitronaphthalene was reported; it had slightly decreased sensitivity but also poorer performance [20]. Sorbitol hexanitrate (SHN) was reported in a 1930 patent as oil that when purified, resulted in a solid (m.p. 54–55 °C) [21]. Like EGDN, SHN was considered for use in non-freezing dynamites [17]. Recent nitrate ester studies have examined the stereoisomers of ETN (L-ETN and D-ETN, comparing them to diastereomeric ETN) and the hexanitrates SHN and MHN to determine if overall sensitivity (as judged by drop weight impact) varied among otherwise identical molecules [22].

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Nitrate esters as a class of improvised explosives is not new, but rather its popularity is driven by the availability of the precursor sugar alcohols. In the United States, the wide availability of erythritol combined with the favorable properties of ETN has directed nitrate ester research. Xylitol, mannitol, and sorbitol are less common but can be easily purchased online in powder form. While there has been researching into the mass spectrometry and thermal analysis of these compounds, there is still a lack of characterization of these compounds. This work aims to bridge that gap with material characterization on both an experimental and theoretical scale.

2 Experimental Methods

2.1 Synthesis of MHN Via Mixed Acid Method

MHN was prepared via mixed acid nitration according to published literature procedures [23, 24]. Fuming nitric acid was chilled in an ice bath and mannitol was slowly added, maintaining a temperature less than 10°C. The resultant yellowish slurry was warmed to between 10–15°C and sulfuric acid was slowly added. The mixture became a nearly solid slurry and manual stirring was used to mix the reaction. After an hour, the reaction was poured onto ice water, and the product recovered by vacuum filtration. The solid was rinsed with water, saturated sodium bicarbonate, and additional water to remove leftover acid impurities. The solid dried on a vacuum for a minimum of 30 minutes and then at room temperature overnight.

2.2 Synthesis of Hexanitrate Esters Via Acetyl Nitrate Method

Acetic acid (21 mL, 0.367 mol) and acid anhydride (21 mL, 0.222 mol) were placed in a 100 mL round bottom flask and chilled to 0°C. White fuming nitric acid (10.6 mL, 0.254 mol) was slowly added so that the temperature did not rise above 10°C. The mixture was stirred for 30 minutes before the polyol (2 g, 0.011 mol) was added. The addition of polyol caused a slight temperature increase before the temperature re-equilibrated to 0°C. The reaction mixture was stirred at 0°C for 2 hours and then at room temperature for another 2 hours. The reaction mixture was then poured into 400 mL of rapidly stirring ice water to recover the product. In the case of MHN, and sometimes with SHN, a solid precipitate formed directly from the reaction mixture. This solid was recovered via vacuum filtration and rinsed with water, saturated aqueous sodium bicarbonate, and again with water to remove any excess acid. The solid was dried under vacuum for 30 minutes and then at room temperature overnight.

2.3 Purification and Crystallization of SHN

SHN did not always crystallize out when the crude reaction was poured into water. When SHN formed oily masses which hardened rather than forming a suspended solid in the water, it was recovered via a modified literature procedure [25]. The SHN was dissolved in methylene chloride and transferred to a separatory funnel where it was washed three times with water, followed by three times with saturated sodium bicarbonate solution. The product solution was dried over anhydrous sodium sulfate and the methylene chloride was evaporated under reduced pressure. The SHN was collected as a clear oil that was re-dissolved in minimal methylene chloride and chilled in an ice bath. Hexane was added slowly which resulted in a white precipitate. The SHN was collected by vacuum filtration, rinsed with a small amount of cold hexane, and dried on a vacuum for 20 minutes. The final product collected was a fluffy white solid (m.p. 53–55°C).

Figure 1. Nitrate ester explosives and their melting points.
2.4 Synthesis of Mannitol Pentanitrate (MPN)

MPN was synthesized via a slightly modified literature procedure [26]. Mannitol hexanitrate was dissolved in acetone and 0.5 mL of aqueous ammonium carbonate (0.2 g/mL) solution was added. Almost immediately the solution turned orange. The solution was allowed to stand at room temperature overnight before the solvent was removed at reduced pressure. The resulting dark orange oil was reconstituted in ethanol. Water was added, and the resultant tan-orange MPN precipitate was removed by filtration and rinsed with cold ethanol.

2.5 Analysis Methods

A TA Q100 differential scanning calorimeter (DSC), calibrated against indium, was used to examine the thermal response of the samples (typically 0.15–0.25 mg) at a ramp rate of 10 °C min⁻¹. Raman spectra were collected using an Ondax 785 nm 225 mW laser and an Andor Shamrock 500i-D2-R spectrometer. For hot-stage experiments, a Mettler Toledo FP900 Thermosystem with FP82HT hot stage was used. Some samples were also monitored during separate runs for their thermal behavior on a Nikon Eclipse E400 POL polarized light microscope. A Nicolet 6700 FT-IR Spectrometer was used to collect infrared spectra. For both Raman and FT-IR spectra, Spectragryph Software for Optical Spectroscopy was used to generate plots [27]. Powder x-ray diffraction (XRD) spectra were collected on a Rigaku MiniFlex600 benchtop powder X-ray diffractometer. 1H NMR spectra were collected in CDCl₃ using a Bruker Advance 300 Hz spectrometer.

A Thermal Activity Monitor III (TAM III; TA Instruments, New Castle, DE, USA) was employed to investigate thermal stability. Synthesized hexanitrate ester samples (5–6 mg) were run in triplicate isothermally between 80–125 °C until samples fully decomposed. Total decomposition was verified using the LCMS method below. Samples were run against permanently affixed TAM III reference insert, and heat flow verification was performed using 99% pure biphenyl (Acros Organics, New Jersey, USA).

LC-Exactive-MS analysis were analyzed using a Thermo Scientific Accela pump (Waltham, MA, USA) coupled to a Thermo Scientific Exactive Orbitrap mass spectrometer. The chromatographic separation was performed using Thermo Scientific Accelain™ Polar Advantage II C18 analytical column (3 μm dₚ, 2.1 × 50 mm). Samples injection volume was 20 μL. The mobile phase comprised of aqueous buffer (A −200 μM ammonium acetate, 200 μM ammonium chloride, 0.1% formic acid) and acetonitrile (B) with a flow rate of 300 μL/min. The following gradient was used for chromatographic separation: initial −95% A/5% B was held for 60 s, followed by a gradient ramp to 95% B over 120 s with 60 s hold, after which it was reverted back to initial condition over 110 s and held for re-equilibration for additional 70 s for a total run time of 7 min. Electrospray (ESI) in negative ionization mode was used for all MHN and SHN adducts detections; all relevant Exactive Orbitrap conditions are provided in Table 1.

Of the expected ions ([M−H]⁻, [M+Cl]⁺, [M+CHOO]⁻ and [M+CH₂COO]⁻) the chloride and formate adducts were the predominate ones found in the analysis of MHN/SHN and their lesser nitrated counterparts (i.e. mannitol pentanitrate and sorbitol pentanitrate, MPN and SPN, and the corresponding tetrinitrates MTN/STN and trinitrates MTriN/STriN). Although formate adducts were present for all lesser nitrated species, they were not observed for the hexanitrites MHN and SHN; in contrast, chloride adducts were detected with all species. Interestingly, acetates were not observed in experiments, even though the ions were available for adduct formation as a part of the mobile phase. The di- and mono-nitro mannitols, mannitol, and sorbitol were never detected although they were sought. The dimer of MHN/SHN [dimer+Cl]⁻ was observed in significant amounts, it was less pronounced for MPN/SPN [dimer+Cl]⁻ species; MTN/STN [dimer+Cl]⁻ was observed only once in an extremely crude sample. It is worth noting that we did not observe deprotonated species for any MHN/SHN and lesser nitrated counterparts, with one notable exception of an extremely crude sample in which [M−H]⁻ of MTN/STN and MTriN/STriN were observed, but no other species.

2.6 Theoretical Methods

The quantum chemical calculations were carried out using the Gaussian-09 package. The ωB3LYP hybrid density functional was used in conjunction with the Pople triple-ζ augmented diffuse functions (6-311G+(d,p)) basis set. All the calculated frequencies correspond to harmonic approximation. The calculations of intrinsic reaction coordinates (IRC) using internal coordinates were performed in order to examine whether the transition states under consideration connect the expected reactants and products.

| Table 1. Specifications for the Exactive Orbitrap. |
|-----------------|-----|
| **Source**      | ESI-|
| Spray voltage (kV) | 3.5 |
| Capillary temperature (°C) | 215 |
| Capillary voltage (V) | −25 |
| Corona discharge current (μA) | 20 |
| Sheath gas (arb) | 30 |
| Auxiliary gas (arb) | 15 |
| Tube lens (V) | −75 |
| Skimmer voltage (V) | −20 |
| Mass resolution | 25,000 |
| Scan ranges | m/z 100.0–800.0 |
3 Results and Discussion

Nitrate esters are usually prepared through nitration of the relevant alcohol using acetyl nitrate or mixed nitrate/sulfuric acids. Care must be taken to remove acid during purification since residual acid can lead to decomposition. Most nitrate esters are readily soluble in organic solvents but have low water solubility. Despite variations in their melting temperatures, their onset of thermal decomposition is remarkably close; many nitrate esters exhibit decomposition when heated above 70 °C. As a class, their first step in decomposition is the loss of an NO$_2$ group, which is believed to catalyze further decomposition. Decomposition may be visible as an accumulation of orange-brown gas in the headspace above a sample. Since nitrate ester decomposition begins with NO$_2$ group loss, it is not surprising that the larger, more nitrated species are generally less stable.

3.1 Structure of Hexanitrate Esters

Some nitrate esters exhibit polymorphism. Changes in the crystal structure of an energetic material have performance implications due to density changes that usually accompany these transitions. Such solid-state changes may result from altering the temperature or recrystallization process or a change in pressure, such as achieved in diamond anvil cells. PETN has two known polymorphs that depend on the crystallization technique [28]. Researchers have examined the crystallization of ETN, but to date, no other phases have been observed [9, 11].

3.1.1 Mannitol Hexanitrate (MHN)

Urbanski, in reporting the IR spectra of various nitrate esters, noted that MHN had two interconvertible crystalline forms that differed in IR and XRD spectra but not in melting point (reported as 112–113 °C); no evidence beyond IR was offered [29]. Based on Urbanski’s note, we expected a single endotherm (108–112 °C); however, two endotherms were often observed. Sometimes these were sharp (105 °C, 110 °C); and sometimes, broad (Figure 2). We were hesitant to attribute these observations simply to impurities because they were frequently seen in MHN samples that had been recrystallized. The identity of these endothermic events was explored using thermal and spectroscopic techniques.

Raman spectroscopy coupled with a hot stage microscope allowed examination of the temperature effects on MHN structure. This method allowed the use of larger samples that could be subsequently tested via DSC, XRD, and FT-IR. On the hot stage, MHN was heated to 105 °C and held at temperature for 5 minutes before cooling. During the heating and cooling period, Raman spectra were actively collected. To screen for structural differences, the focus was on the low wavenumber region, the THz region. The vibrations and librations in this region are associated with the movement of entire crystal lattices. Even though there may be no major differences in the fingerprint region, when combined with XRD, minor variations can provide clear evidence of different crystal structures [30, 31]. When heated to 105 °C, MHN did not melt, but changes were observed in the Raman spectrum as the solid sat at that temperature (Figure 3 with a full spectrum of MHN in Figure S1 of supplementary information). The changes in the Raman spectrum correlate to a change in the MHN crystal structure.
and are corroborated by XRD patterns (Figure 4). This structural change upon heating was observed in numerous MHN samples when the sample had not been previously exposed to elevated temperatures (such as during recrystallization). This behavior was also observed in crude samples of MHN that were sufficiently pure not to melt or decompose before 105°C was reached.

Figure 3 reveals that once MHN is heated to 105°C the Raman spectrum alters. The change in the crystal structure is identified by multiple peak shifts in the MHN Raman spectrum. At 105°C two peaks, originally at 225 and 230 cm⁻¹, shift to 235 and 240 cm⁻¹, respectively. These shifts indicate a structural transition to a different form of MHN.

Figure 4. Powder XRD of neat, recrystallized MHN (1), MHN heated to 105°C (2), and MHN that had melted and solidified (3); all measurements collected on room temperature solid.
250 cm\(^{-1}\) undergo a change; the intensity of 225 cm\(^{-1}\) is drastically reduced, and the peak at 250 cm\(^{-1}\) shifts to a lower frequency, 240 cm\(^{-1}\). The peaks originally at 311 and 327 cm\(^{-1}\) appear to coalesce into a single peak at 316 cm\(^{-1}\). There are slight shifts in the fingerprint region, upwards of a few wavenumbers. Based on DFT calculations, the assignment of vibrational frequencies for MHN and SHN were made (Table S1, Figures S2–S3). The small wavenumbers shifts are related to ONO\(_2\) groups, in various regions: 600–700 cm\(^{-1}\) (O–NO\(_2\) bond stretching) and 800–900 cm\(^{-1}\) (O–NO\(_2\) bond stretching/O=N=O scissoring). The 1300 cm\(^{-1}\) region was assigned to joint O=N=O symmetric stretching; however, there was little change observed. There was a large change in the 1600–1700 cm\(^{-1}\) with the MHN transition, which is the NO\(_2\) asymmetric stretching region (though assigned to 1700–1800 cm\(^{-1}\) by DFT).

The effect of heat on MHN was further examined. By DSC, nascent MHN exhibited two endotherms (Figure 5). This MHN was heated to 105 °C, held for 5 minutes, and returned to room temperature. The DSC trace of this MHN showed only a single endotherm (Heat 1) and combined with the spectroscopy data, supported the idea that the 105 °C endotherm was a solid-solid phase transition. If so, then both polymorphs of MHN have the same melting point (110–112 °C). MHN was then heated to melting and allowed to crystallize. The DSC again showed two endotherms (Heat 2), suggesting that this transition is reversible.

MHN is often recrystallized at elevated temperatures; therefore, we looked for possible temperature and solvent effects. MHN recrystallized in hot ethanol (~ 80 °C) exhibited an XRD spectrum similar to MHN that had been previously melted (Figure 6). These XRD were different from those of MHN that was recrystallized at room temperature (through solvent/antisolvent methods) or in warm ethanol (55 °C). Ethanol was chosen as the solvent for MHN recrystallization based on historical usage [21, 24]. After noting that heat facilitated differences in XRD, we examined the effect of other solvents on recrystallization of MHN (Raman (Figure S4) and XRD (Figure S5) appear in supplemental); only ethyl acetate appeared to affect the spectra.

The concept of heat facilitating the transition is of interest since it has been reported that unless MHN has been purified through multiple recrystallization steps, decomposition will begin at temperatures greater than 70 °C [32]. Lesser nitrated species are often contaminants remaining in the hexanitrates, either as remnants of incomplete nitration during synthesis or a sign of denitration and the beginning of decomposition. Removal of the lesser nitrated species is difficult due to similar solubilities, though removal can be achieved through complex solvent systems and chromatographic methods.

LC/MS analysis was performed to establish the amount of MHN and MPN in the samples, specifically those samples that had been melted. MHN often had some MPN impurity present from incomplete nitration during synthesis; despite recrystallization, complete removal of the lesser nitrated species proved difficult. As Urbanski noted: “… a product crystallized only once or twice withstands heating at 75 °C for only a few hours, after which brown fumes start to develop [32].” Acknowledging the lack of standards which would allow quantification and the tendency of the lesser nitrated species to be more sensitive to ionization in the MS, we used the ratio of MPN to MHN to evaluate the effects of recrystallization and melting. As Table 2 shows, recrystalliza-

![Figure 5](https://example.com/figure5.png)

Figure 5. MHN was heated offline and sampled for DSC, which supported that the endotherm at 105 °C was a solid-solid transition and that the two MHN forms have the same melting point. The middle DSC trace is of MHN II, while the other two are of MHN I.
tion in alcohol reduced the amount of MPN present in MHN but melting promoted MHN decomposition to MPN.

Returning to the report of Urbanski and Witanowski, the authors recognized two polymorphs by slight differences in the infrared spectra, a few wavenumbers. They labeled these MHN A and MHN B [29]. We identified two MHN polymorphs by Raman and XRD, the initially formed MHN I and that formed after heating to 105°C (MHN II). To compare to the report of Urbanski and Witanowski we also collected IR spectra (Figure 7) and determined that MHN I is likely their MHN B and their MHN A is our MHN II.

### 3.1.2 Sorbitol Hexanitrate (SHN)

In the SHN patent from 1930, Bergeim reported the isolation of nitrated sorbitols that exhibited two different melting points [21]. He recovered an oil, that when crystallized had a melting point of 53–55°C and a nitrogen content (% N) of 18.48% (theoretical %N: 18.59%). He also reported that when larger volumes of water were used to precipitate the product from alcoholic solution, a product with 17%N and melting point of 44°C was recovered. The lower measured %N and the melting point would suggest that Ber-
geim isolated sorbitol pentanitrate (SPN); however, we suspect that Bergeim may have observed two different crystal structures of SHN.

In 2017, Gribanov et al. reported the crystal structure of SHN along with its melting point (53°C) and 1H and 13C NMR spectra [25]. Gribanov synthesized SHN using the acetyl nitrate method, a method that often produces high yields of nitrated product [33]. This method was used by our lab to prepare SHN, but the recovered product SHN often melted between 44–55°C, rather than the expected 55°C. Initially, this was thought to be the result of impurities in the product such as the penta- or lower nitrated species, which has been reported with other nitrate esters [11]. Varying synthesis conditions to include different nitration times (4 to 18 hours), reaction temperatures, and recrystallization procedures did not improve the melting point. Subsequent analysis suggested that the lower melting material may be a different crystal structure rather than the presence of impurities.

The preparation of SHN differs little from that of MHN or other nitrate esters, but precipitation/crystallization yielded visible differences. While MHN exclusively formed a solid when poured on ice water, SHN behavior varied; sometimes SHN formed a solid that remained suspended in the stirring ice water, and sometimes it formed an oil. This crude SHN oil was dissolved in methylene chloride, washed with water and saturated aqueous sodium bicarbonate solution, and the solvent removed under reduced pressure [25]. Crystallization of the oil from methylene chloride and hexane formed SHN (designated SHN I) that melted at 53–55°C.

The crude solid that initially precipitated when the reaction mixture was poured onto ice water was identified by 1H NMR to be SHN (Figure 8); however, the batch to batch melting point was found to vary depending on conditions, e.g. length of time the SHN was left in the water. Analysis by Raman and XRD indicated that there were variations in the overall structure of the product; thus, it was labeled SHN II. When the melting point of the product was greater than 50°C, the crude SHN was structurally similar to that of the SHN I (Figure 9). When the melting point was less than 50°C, the product was SHN II. In some cases, both polymorphs were observed. Thermograms that showed two endothermic events had Raman and XRD exhibiting characteristics of both SHN I and SHN II.

When preparing nitrate esters two serious concerns are residual acid destroying long-term stability and the presence of lower nitrates resulting from incomplete nitration or subsequent decomposition, where the loss of nitro groups is often the first step. Between the two forms of SHN, the greatest difference was noted in the Raman spectra. Unlike MHN, where the differences were seen in the THz region of the Raman spectrum, there are numerous differences in the fingerprint region of the two forms of SHN (Figure 10). Most of the differences in the middle wavenumber region (500–1750 cm⁻¹) occur with modes that DFT calculations associated with O-NO₂ motions. A table of Raman shifts, both calculated and experimental, can be found in the supplemental data (Table S2). XRD distinguished between the two forms of SHN as seen in Figure 11, although the differences between the two forms are not dramatic and occur mostly in the low 2Θ region.

Factors which governed the formation of SHN I vs SHN II were difficult to isolate. Preliminary data suggest that acidity is a factor and that crystallizing from acidic solution is
more likely to result in the recovery of SHN II. There was no evidence of spontaneous transformation from SHN II to SHN I over time; however, extended storage at ambient conditions often led to the decomposition of SHN, regardless of the structure. Figure 12 shows the physical appearance of the two SHN polymorphs.
3.2 Thermal Stability of Nitrate Esters

Thermal stability as a function of carbon chain length, degree of nitration, and isomeric structures are of interest. The stability of nitrate esters is not a new question and has been addressed by those with commercial or military applications [34]. Using a combination of data derived from thermal gravimetric (TGA) and DSC techniques, Yan et al. ordered the thermal stability of ten nitrate esters of varying chain lengths with least stable being MHN: MHN < XPN < TMPTN < SHN < NIBGT < ETN < PETN < DiPEHN [35]. Our experience has been that purified SHN left standing at room

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Figure 11. XRD of SHN polymorphs compared to crude and crystallized SHN (note the large peak in SHN I is thought to be an artifact).

Figure 12. Physical appearance of the two SHN polymorphs.
temperature will evolve orange-brown fumes in less than a week and eventually turn into a viscous, acidic oil. The oil takes on a yellow color and sometimes a green layer appears at the interface. Extreme decomposition results in dark brown oil. In contrast, MHN can stand at room temperature for over a year without apparent signs of decomposition.

In order to examine the difference in thermal stability between the two hexanitrate esters, isothermal calorimetry in the TAM III was used. MHN, SHN, and ETN were analyzed at five temperatures (80, 90, 100, 110, and 120°C). Thermal stability can be evaluated from maximum heat flow or the induction time (time to maximum rate). A plot of time-to-maximum rate versus temperature (Figure 13) clearly indicates the superior stability of ETN, but the poorer stability of SHN relative to MHN is not dramatically illustrated. However, at all five temperatures examined, SHN was above its melting point, while MHN did not melt until 112°C. To fairly assess their relative stabilities an even wider range of temperatures needs to be examined. The Arrhenius parameters derived from this data (Table 3) are lower than those previously reported for experiments employing scanning techniques, i.e. DSC or TGA. This apparent discrepancy is also likely a result of the temperature range examined.

3.3 Theoretical Analysis

Density functional theory (DFT) calculations were performed to assess and compare potential first steps in breaking the CO–NO₂ bond. The bond dissociation energy in these cases correlates with the stabilization energy of the lone electron formed in the radical produced following the CO–NO₂ bond rupture. Among the four molecules examined (i.e. ETN, XPN, MHN, and SHN) only sorbitol hexanitrate exhibited spatial asymmetry which led to the observation of two different radical stabilization energies, seen in Figure 14 below.

The free energies (at 110°C) and enthalpy associated with rupture of the CO–NO₂ bond at the different sites of the four molecules examined are shown in Table 4. For

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**Table 3. Thermal decomposition parameters from this work and literature.**

<table>
<thead>
<tr>
<th>Compound</th>
<th>Method</th>
<th>Temp (°C)</th>
<th>( E_a ) (kJ mol(^{-1}))</th>
<th>( \log A ) (s(^{-1}))</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>MHN</td>
<td>isothermal (TAM)</td>
<td>80–120</td>
<td>83.3</td>
<td>6.5</td>
<td>this work</td>
</tr>
<tr>
<td></td>
<td>SMM</td>
<td>–</td>
<td>159.10</td>
<td>15.9</td>
<td>[36]</td>
</tr>
<tr>
<td></td>
<td>TGA</td>
<td>155–182</td>
<td>151.6</td>
<td>15.9</td>
<td>[35]</td>
</tr>
<tr>
<td></td>
<td>isothermal (TAM)</td>
<td>80–120</td>
<td>84.3</td>
<td>6.6</td>
<td>this work</td>
</tr>
<tr>
<td>SHN</td>
<td>TGA</td>
<td>131–213</td>
<td>147.8</td>
<td>15.49</td>
<td>[35]</td>
</tr>
<tr>
<td></td>
<td>SMM</td>
<td>100–145</td>
<td>168</td>
<td>15.8</td>
<td></td>
</tr>
<tr>
<td></td>
<td>isothermal (TAM)</td>
<td>90–120</td>
<td>96.3</td>
<td>8.0</td>
<td>this work</td>
</tr>
<tr>
<td></td>
<td>isothermal (LCMS)</td>
<td>60–140</td>
<td>104.3</td>
<td>9.57</td>
<td>[5]</td>
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<tr>
<td>ETN</td>
<td>DSC</td>
<td>–</td>
<td>95.0</td>
<td>10.37</td>
<td>[10]</td>
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<tr>
<td></td>
<td>TGA</td>
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<td>145.1</td>
<td>14.79</td>
<td>[35]</td>
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<td></td>
<td>manometric</td>
<td>70–140</td>
<td>159</td>
<td>15.7</td>
<td></td>
</tr>
</tbody>
</table>

SMM: Soviet Manometric Method, TGA: Thermogravimetric analysis
both free energy and enthalpy, the results in the top line that corresponds to SHN represents the data obtained for the left side of the molecule, while the bottom line are results obtained for the right side of the molecule. The free energy of CO–NO$_2$ dissociation associated with the “central” carbon in the molecular chain is the lowest value in all the nitrates examined, with SHN having the lowest free energy value calculated. It should be noted that the free energies required to start the decomposition process of MHN and SHN (bold values in Table 4) are in reasonable agreement with the values found in our isothermal studies (Table 3) and suggest that it is a loss of one of the “central” nitro groups that is the first step in decomposition.

As a result of NO$_2$ ejection, which initiates the decomposition reaction, two radicals are generated; one is NO$_2$, and second the remaining molecule. The decomposition reaction for all nitrate esters studied then proceeds via lower free energy barriers, in the range 23–44 kJ/mol at 110 °C (or enthalpy values in the range 28–49 kJ/mol) with high exothermicities in the range 295–348 kJ/mol at 110 °C (enthalpy in the range 160–206 kJ/mol), see Tables S3 and S4 in the supplementary material. The second step in the decomposition processes result in an ejection of an additional NO$_2$ radical and the formation of two aldehydes following a C–C bond rupture: CH$_2$O and CH$_2$(ONO)$_2$–(CHONO)$_2n$–CHO, (where n = 1–3 in the case of hexanitrates) (Tables S3 and S4). The decomposition process continues by similar steps: an endothermic NO$_2$ ejection and an exothermic event related to the rupture of another C–C bond in the molecular fragment radical produced in the previous step. These processes have similar energetic parameters until the formation of a CH$_2$O–CHO radical; this radical can participate in two different processes. The first is further decay into CH$_2$O and the stable formyl radical, HCO. This reaction has a free energy exothermicity of 50.3 kJ/mol at 110 °C (enthalpy endothermicity of 10.9 kJ/mol). The second possibility is a barrierless recombination of two of these radicals to yield hydroxy acetaldehyde (HOCH$_2$–CHO) and ethanedial (CHO–CHO). This reaction has a very high free energy exothermicity of 304.5 kJ/mol at 110 °C (307 kJ/mol in terms of enthalpy).

In addition to the decomposition process described above, another route is possible. This is HONO ejection from every one of the discussed nitrates. Such a reaction for ETN was previously reported [5]. However, due to the free energy barrier of HONO ejection being much higher (140–160 kJ/mol at 110 °C with 142–155 kJ/mol enthalpy barriers), such reactions are improbable as starting step in the decomposition process.

### Table 4. Free energy and enthalpy (at 110 °C) associated with CO–NO$_2$ bond rupture from optimized molecular structures.

<table>
<thead>
<tr>
<th></th>
<th>CH$_2$O-NO$_2$ bond breaking free energy, $\Delta G$ kJ/mol</th>
<th>CH$_2$O-NO$_2$ bond breaking energy, $\Delta E$ kJ/mol</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>External Internal Central</td>
<td>External Internal Central</td>
</tr>
<tr>
<td>Erythritol tetranitrate</td>
<td>48.8 31.5 -</td>
<td>121.3 109.2 -</td>
</tr>
<tr>
<td>Xylitol pentanitrate</td>
<td>67.5 57.4 39.0</td>
<td>123.4 117.2 99.2</td>
</tr>
<tr>
<td>Mannitol hexanitrate</td>
<td>56.0 55.1 45.4</td>
<td>124.7 121.8 111.4</td>
</tr>
<tr>
<td>Sorbitol hexanitrate</td>
<td>56.6 50.7 28.7</td>
<td>124.2 120.3 102.2</td>
</tr>
<tr>
<td></td>
<td>56.2 57.5 41.0</td>
<td>123.9 123.9 115.0</td>
</tr>
</tbody>
</table>

![Figure 14. Three-dimensional portrayal of SHN.](image)
Characterization of the Hexanitrate Esters of Sugar Alcohols

4 Conclusion

Even though the hexanitrate esters have not seen much use as explosives, legal or otherwise, they remain viable terrorist options considering the ease of obtaining the precursor sugar alcohol. Two polymorphs for the hexanitrate sugars MHN and SHN have been recognized and characterized. Typical synthetic routes appear to produce one polycrystal sugar alcohol. Two polymorphs for the hexanitrate of University Programs, under Grant 2013-ST-061-ED0001. Views on Homeland Security (DHS), Science & Technology Directorate, Office of Propellants Explos. Pyrotech.

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Data Availability Statement

Data available on request from the authors.

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