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Synthesis and Sensitivity Studies of ETN and PETN Derivatives

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Abstract. Understanding the factors that contribute to explosive sensitivity is key to developing new explosives. Explosive sensitivity is controlled by multiple factors some of which include crystal packing, hydrogen bonding and co-crystallization. Explosive functional groups impart a chemical effect towards explosive sensitivity due to different functional groups having different thermodynamic stabilities and decomposition methods. Herein we report the synthesis of erythritol and pentaerythritol complexes functionalized with nitrate esters, nitramines and azides. Six molecules were synthesized (two literature reported, four new complexes) and their explosive sensitivity was compared to ETN and PETN using impact, spark and friction sensitivity measurements. The molecules synthesized were a mixture of solids and liquids leading to questions about the effects of physical state on explosive sensitivity. These molecules were compared to our recent study on the impact sensitivity of molten ETN. Stereoisomers of ETN were synthesized to compare with liquid samples at room temperature. We observed that by mixing functional groups of varying sensitivity we were able to tune the explosive sensitivity of the molecule. Additionally, we observed liquid explosives with higher sensitivities than solid explosives, as to be expected due to their differing modes of initiation for liquid vs. solid explosives. These results suggest functionalization of known explosive frameworks can be used to tune explosive sensitivity due to changes in both chemical and physical properties of the molecules.

INTRODUCTION

Understanding the multiple factors that influence the sensitivity of explosives is paramount for both the development of new explosives as well as the safe handling of currently used explosives. Recent research has pinpointed certain molecular properties that influence explosive sensitivity, including crystal packing of the explosive [1], intermolecular hydrogen bonding [2,3], co-crystallization [4], and electrostatic effects [5] to name a few.

In addition to structural and intermolecular effects, chemical interactions of explosive functional groups can influence explosive sensitivity. Some common explosive functional groups include nitrate esters, nitramines, nitro, peroxides and perchlorates [6]. Functional groups have distinct reactivity, which are determined by thermodynamic stability, bond dissociation energies and decomposition pathways [2]. However, we propose that by combining different energetic functional groups with different explosive sensitivities we can tune the sensitivity of a molecule. In order to monitor the effects of the functional groups, the central framework of the molecule must stay the same. Observing the effects of these functional group changes can help us identify factors influencing stability, melting point, density and crystal packing. This information can then be applied to the design of new potential explosives. Changing even a single functional group can have an effect on many unexpected properties, such as decomposition rate and temperature, melting and vaporization temperatures. These properties can influence how these explosives are used and handled. Finally synthesizing core molecules with various functional groups can be useful to validate computational models, which can then potentially be used to predict new explosives with selected features.

RESULTS AND DISCUSSION

The two central frameworks chosen were pentaerythritol and erythritol, both used in the well-known explosives pentaerythritol tetranitrate (PETN) and erythritol tetranitrate (ETN). PETN is a prevalent explosive used commonly in military stockpiles and ETN is an emerging explosive, which has seen use in recent homemade explosive incidents [7,8]. ETN and PETN derivatives containing nitramines, azides and nitrate esters in various configurations were synthesized [9] (Fig.1).

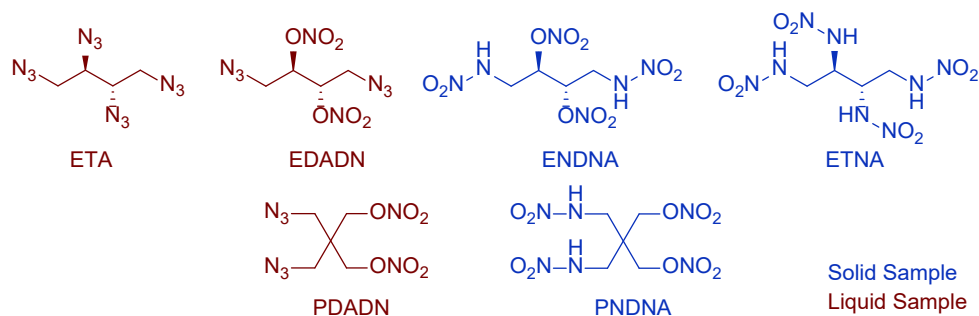


FIGURE 1. Literature reported (ETA, PDADN) and newly synthesized PETN and ETN derivatives

TABLE I. Drop-weight impact test results for solid and liquid ETN and PETN derivatives

Material (conditions)	Impact D_{H50} (cm)	Material (conditions)	Impact D_{H50} (cm)
ETN (s)	14.7 ± 3.4	ENDNA (s)	26.7 ± 4.4
PETN (s)	20.8 ± 4.0	ETNA (s)	52.5 ± 4.2
ETA (liq)	0.8 ± 0.7	PDADN (liq)	2.5 ± 0.56
EDADN (liq)	1.5 ± 1.7	PNDNA (s)	54.6 ± 13.9

Impact sensitivity measurements were conducted using a standard ERL type 12-drop hammer equipment using a 2.5-kilogram weight. A 0.8-kilogram striker is struck onto an anvil and reaction is monitored using sound detection equipment [10]. In all of these studies, no grit paper was used for impact testing (Type 12B), in order to keep measurements consistent between liquids and solids. Impact sensitivities of ETN and PETN were measured on the bare anvil resulting in impact values of 14.7 ± 3.4 and 20.8 ± 4.0 cm respectively. Azide derivatives behaved as to be expected samples functionalized with azides showed increased sensitivity. Complex ETA (Fig. 1) showed a large increase in impact sensitivity with a DH_{50} value of 0.8 ± 0.7 , which is among the most sensitive molecule ever tested on our apparatus. When analyzing the mixed erythritol derivative EDADN (1.5 ± 1.7 cm) we observed sensitivity in between ETN and ETA, with the sample being much closer to ETA in sensitivity. Nitroamine derivatives of erythritol showed the opposite trend. ETNA showed a large decrease in impact sensitivity to 52.5 ± 4.2 cm while the half nitroamine/ half nitrate ester ENDNA exhibits intermediate sensitivity 26.7 ± 4.4 cm, a value right between ETN and ETNA. Similar results were observed using the PETN derivatives with the azide substituted molecules showing an increase in sensitivity while the nitroamine functionalized derivative decreased in sensitivity.

TABLE II. Friction and Spark sensitivity for solid and liquid ETN and PETN derivatives.

Material	Friction D_{H50} (N)	ESD (J)	Material	Friction D_{H50} (N)	ESD (J)
ETN (s)	54.0	0.0625	ENDNA (s)	>360	0.25
PETN (s)	59.5	0.0625	ETNA (s)	>360	0.25
ETA (liq)	5.0	0.125	PDADN (liq)	31	0.125
EDADN (liq)	53.2	0.0625	PNDNA (s)	>360	0.25

Spark and friction sensitivities were studied and as with the impact testing showed some interesting results. Spark sensitivity measurements of erythritol and pentaerythritol derivatives showed the addition of nitramines reduced the spark sensitivity, while the addition of azides showed only a small decrease or no change in sensitivity. For friction

sensitivity measurements, the addition of any nitroamine substituent drastically decreased the sensitivity to the point that no reaction could be observed on our apparatus. Azides on the other hand had mixed results affecting the friction sensitivity. ETA (5.0 N) showed a dramatic increase in friction sensitivity compared to ETN (54.0 N) despite being a liquid sample. PDADN (31 N) showed two fold increase in friction sensitivity compared to the un-functionalized PETN (59.5 N). The most interesting result was that of the mixed erythritol azide nitrate EDADN. While impact sensitivity of this molecule was increased compared to ETN, the friction sensitivity was comparable to ETN.

It should be noted that during our studies we observed in many cases a higher sensitivity with our liquid samples. Liquid explosives are known to be more sensitive due to different initiation mechanisms such as cavitation [11,12]. We previously reported the increased sensitivity of molten ETN, wherein we discussed heated impact tests [13]. We observed a marked increase in sensitivity of this molten ETN which suggested to us that the physical state of the explosive can be a factor toward explosive sensitivity.

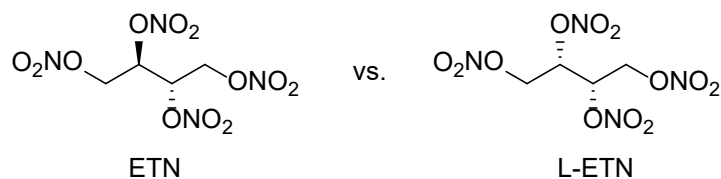


FIGURE 2. ETN and its diastereomer L-ETN

In order to investigate molten ETN sensitivity at room temperature we synthesized a stereoisomer of ETN, which we refer to as L-ETN [14]. These molecules are identical except for the spatial arrangement of the nitrate esters in the secondary carbon positions. Unlike ETN, L-ETN is a liquid at room temperature and all attempts to crystallize the product were unsuccessful. The inability of L-ETN to crystallize was attributed to increased steric hindrance of the secondary nitrate esters. Impact sensitivity results show an increase in sensitivity of L-ETN when compared to room temperature ETN, but slightly lower sensitivity when compared to molten ETN at 65 °C. We attribute the difference between L-ETN and ETN at room temperature to the physical state change of the matter.

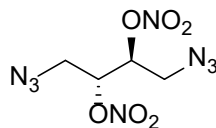
TABLE III. Drop-weight impact test results for diastereomers ETN, L-ETN,

Material (conditions)	Impact D_{H50} (cm)
ETN (24 °C, bare)	14.7 ± 3.4
Molten ETN (65 °C, bare)	1.0 ± 0.6
L-ETN(24 °C, bare)	3.0 ± 0.2

EXPERIMENTAL

Synthesis of PETN and ETN derivatives

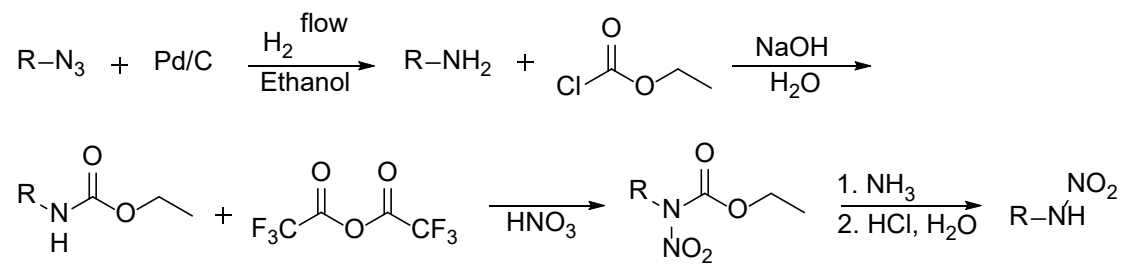
EDADN: (2R,3S)-1,4-diazidobutane-2,3-diyl dinitrate



Fuming nitric acid (90%) (1.0 mL) is added to a round bottom flask and then cooled to 0°C with an ice bath. Next, acetic anhydride (0.83 g, 0.77 mL) is added dropwise to the cooled nitric acid. 1,4-diazido-2,3 butanediol (0.35 g) is added slowly. The solution is stirred for 5 hours upon which the solution turned from golden yellow to clear. The solution was then poured into ice water. An oil was observed in the water and was extracted using diethyl ether. The diethyl ether solution was then washed with aqueous sodium bicarbonate solution. The solvent was then removed

leaving a pale yellow oil. $^1\text{H-NMR}$ (400 MHz, CD_3Cl) δ 3.68-3.78 (m, 4H, CH_2), 5.41 (t, $J = 3.1$ Hz, 2H, CH). $^{13}\text{C-NMR}$ (100 MHz, CD_3Cl) δ 49.5, 77.41.

General nitro amine synthesis:



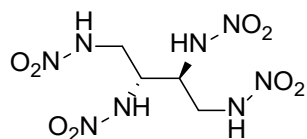
Alkyl azide is dissolved in 95% ethanol. Palladium on carbon (10 wt%) is then added to the solution. The suspension is then bubbled with argon gas for 10 minutes. Next, hydrogen gas is bubbled into the vigorously stirring suspension for 5 hours. The suspension is then filtered to give a pale yellow solution. The solvent is removed leaving a yellow oil/solid.

The oil is dissolved in water. The solution is then cooled to 0 °C using an ice water bath. Once cooled, the ethylchloroformate (1 eq for di-nitroamine, 2 for tetra-nitroamine) is added dropwise. The remaining ethylchloroformate is added (1 eq for di-nitroamine, 2 for tetra-nitroamine) simultaneously with a KOH (aq) solution (2 eq for di-nitroamine, 4 for tetra-nitroamine). Once fully added, the solution is allowed to stir overnight. Solid is then filtered and washed with water. The solid is dissolved in ethyl acetate and washed with water 3x and the organic layer is dried with MgSO_4 . The solvent is removed leaving an off white powder.

Fuming nitric acid (100%) (1:2 ratio to TFAA) is added to a round bottom flask and cooled to 0°C with an ice bath. Next trifluoroacetic anhydride (2:1 ratio to HNO_3) is added dropwise to the cooled nitric acid. Carbamate is then added slowly to the stirring cooled solution. Once added the solution is allowed to stir for 3.5 hours at room temperature upon which the solution turns from golden yellow to clear. After stirring the solution is poured into ice water where a white sticky precipitate forms. The water layer is extracted with dichloromethane (DCM) and then washed with water, sodium bicarbonate solution (aq) 4x, and water again. The organic layer is dried on MgSO_4 , filtered and the solvent is removed.

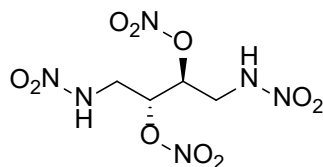
Nitrated carbamate is dissolved in DCM. Next gaseous ammonia is bubbled through the stirring solution for 5 min, upon which the solution becomes very cloudy. The cloudy solution is then extracted with water (2x) and poured into ice water. Next HCl(aq) is added dropwise until the solution is slightly acidic. The solution is then extracted with ethyl acetate (3x) and the combined organic layer is washed with water (3x). The organic layer is stirred on magnesium sulfate and filtered. The solvent is removed leaving a white solid.

ETNA: N,N',N'',N'''-((2R,3S)-butane-1,2,3,4-tetrayl)tetranitramide



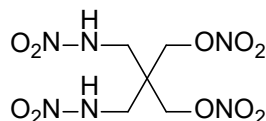
$^1\text{H-NMR}$ (400 MHz, DMSO-d_6) δ 3.48 (dd, $J = 14.6, 8.3$ Hz, 2H, CH_2), 3.77 (dd, $J = 14.8, 2.8$ Hz, 2H, CH_2), 4.57 (m, 2H, CH), 12.32 (s, 4H, NH). $^{13}\text{C-NMR}$ (100 MHz, DMSO-d_6) δ 43.2, 52.8.

ENDNA: (2R,3S)-1,4-bis(nitroamino)butane-2,3-diyl dinitrate



$^1\text{H-NMR}$ (400 MHz, DMSO- d_6) δ 3.91 (ddd, J = 83.7, 15.5, 5.2 Hz, 4H, CH_2), 5.64 (t, J = 4.6 Hz, 2H, CH), 12.35 (s, 2H, NH). $^{13}\text{C-NMR}$ (100 MHz, DMSO- d_6) δ 43.6, 77.22.

PNDNA: 2,2-bis((nitroamino)methyl)propane-1,3-diyl dinitrate



$^1\text{H-NMR}$ (400 MHz, DMSO- d_6) δ 3.7 (s, 4H, CH_2), 4.52 (s, 4H, CH_2), 12.26 (s, 2H, NH). $^{13}\text{C-NMR}$ (100 MHz, DMSO- d_6) δ 42.8, 45.0, 71.6.

CONCLUSIONS

Herein we reported the synthesis of PETN and ETN derivatives with azides, nitrate esters and nitramines. Sensitivity testing showed, as expected, that the more reactive the functional group the more reactive the molecule. However, testing also showed that by mixing functional groups we were able to tune the sensitivity of the molecule. Additionally, altering the functional groups on erythritol or pentaerythritol framework lead to alterations in physical state, with some derivatives as liquids and others as solids. This change in physical state appears to play a factor in explosive sensitivity. This point was further observed when studying the impact sensitivity of molten ETN and comparing it to its more sensitive liquid diastereomer L-ETN.

ACKNOWLEDGMENTS

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