Identifying the Molecular Properties that Drive Explosive Sensitivity in a Series of Nitrate Esters

Nicholas Lease,a Lisa M. Klamborowski,a Romain Perriot,b Marc J. Cawkwell,*b Virginia W. Manner*a

[a] High Explosives Science & Technology, Los Alamos National Laboratory, Los Alamos, NM 87545
[b] Theoretical Division, Los Alamos National Laboratory, Los Alamos, NM 87545

Supporting Information Table of Contents

I. Synthesis of PETN-OH Derivatives.................................................S2
II. Drop-Weight Impact Testing Data...........................................S4
III. Neyer Analysis Data for Drop Weight Impact Tests..............S6
IV. Impact Testing Sound Levels...............................................S9
V. Friction and ESD Sensitivity Data........................................S13
VI. Density Functional Tight Binding Calculations......................S15
VII. Calculated Charges ..........................................................S24

email: vwmanner@lanl.gov; cawkwell@lanl.gov
Synthesis of PETN Derivatives:

**CAUTION**: The molecules synthesized in this paper are sensitive energetic materials and react to stimuli such as impact, spark and friction and should only be handled by trained explosives handlers with the proper safety precautions.

The hydroxyl derivatives PETriN, PEDN, and PEMN (Scheme S1) were all synthesized following known literature procedures. These are known compounds that have been of interest in pharmaceutical research as potential vasodilators.

**Materials and Methods.** Nitric acid (fuming), sulfuric acid, ethanol, and pentaerythritol were purchased from Fisher Scientific and used as received. Dichloromethane, 1,4 Dioxane, and silver nitrate were purchased from Acros Chemical and used as received. 2-(bromomethyl)-2-(hydroxymethyl)propane-1,3-diol was purchased from TCI America and used as received. Deuterated solvents (chloroform d, D$_2$O) were purchased from Acros chemical and Sigma Aldrich and used as received. 1H-NMR and 13C-NMR were recorded on a 400-MHz Bruker spectrometer. NMR signals were referenced to residual solvent signals in the deuterated solvents.

2-(hydroxymethyl)-2-((nitrooxy)methyl)propane-1,3-diyl dinitrate (PETriN): PETriN was prepared following literature procedures.$^1$ 1H-NMR (400 MHz, CDCl$_3$) δ 3.78 (s, 2H, CH$_2$-OH), 4.57 (s, 6H, CH$_2$-ONO$_2$). 13C($^1$H)-NMR (100 MHz, CDCl$_3$) δ 43.4, 60.5, 69.6

2,2-bis(hydroxymethyl)propane-1,3-diyl dinitrate (PEDN): PEDN was prepared following literature following literature procedures.$^2$ 1H-NMR (400 MHz, (CD$_3$)$_2$CO) δ 3.68 (s, 4H, CH$_2$-OH), 4.57 (s, 4H, CH$_2$-ONO$_2$). 13C($^1$H)-NMR (100 MHz, (CD$_3$)$_2$CO) δ 45.5, 61.1, 72.5

3-hydroxy-2,2-bis(hydroxymethyl)propyl nitrate (PEMN): PEMN was synthesized using a modified literature procedure.$^2$ To a 100 mL round bottom flask 2-(bromomethyl)-2-(hydroxymethyl)propane-1,3-diol (1.0 g, 5.0 mmol) and silver nitrate (2.6 g, 15.3 mmol) are added and the flask is wrapped in aluminum foil. Acetonitrile (21 mL) is added to the round bottom flask and the solution is then heated to 70°C for 24 hours.

---

$^1$ Rolewicz, H.A.; Grimes Jr., C.D.; Stevenson Jr., K. “Preparation of Pentaerythritol Trinitrate”. Patent Number 3,408,383. Oct 29, 1968

$^2$ Lange, K.; Koenigh, A.; Roegler, C.; Seeling, A.; Lehmann, J. “NO donors. Part 18: Bioactive metabolites of GTN and PETN-Synthesis and vasorelaxant properties”. *Bioorg. Med. Chem. Lett.* 19, 2009, 3141-3144.
while being protected from any light. After 24 hours, green precipitate can be seen in the solution. The solution is cooled to room temperature, the solution is filtered, and the solvent is removed under reduced pressure leaving a crude white powder. One to two drops of water is added to the white solid followed by 25 mL of ethyl acetate. The solid is sonicated to suspend the solid in solution, the filtrate is collected, and the solid is washed with ethyl acetate. The filtrate is dried on MgSO₄, filtered and the solvent is removed leaving a light yellow oil. Upon sufficient drying, the oil will solidify to an off-white powder. NMR shows pure PEMN with many small impurities in the baseline of the spectra (Figure S1; for purification see below).

Figure S1. Synthesis methods for PETN Derivatives.

Purification of PEMN:

In order to purify the PEMN the three alcohol groups are protected with tert-Butyldimethysilyl chloride (Figure S2). To a 50 mL round bottom flask, PEMN (0.5 g, 2.8 mmol), tert-Butyldimethysilyl chloride (1.73 g, 11.5 mmol), DMAP (0.03 g, 0.25 mmol) and pyrazole (1.56 g, 22.8 mmol). Next 8 mL of THF is added and the solution is stirred overnight. The next day saturated sodium bicarbonate solution is added and the solution is extracted with hexanes (3x). The organic layer is dried on MgSO₄, filtered and the solvent is removed. Tert-Butyldimethyisilyl protected PEMN (0.5 g, 0.96 mmol) is dissolved in a THF/Water mix (12.5 mL: 2.5 mL) and cooled to 0°C. To this chilled solution trifluoroacetic acid is added (1.0 mL). Solution is stirred at 0°C for 30 minutes followed by 3 hours at room temperature. The solvent is removed under reduced pressure giving pure PEMN. ¹H-NMR (400 MHz, D₂O) δ 3.57 (s, 6H, CH₂-OH), 4.52 (s, 2H, CH₂-ONO₂). ¹³C{¹H}-NMR (100 MHz, D₂O) δ 44.9, 60.3, 71.9.
Drop Weight Impact Sensitivity Data:

Impact Testing was conducted using a ERL Type 12 drop hammer equipment using a 2.5-kilogram weight, a 0.8-kilogram striker and sound detection equipment. In all tests, the striker is made of steel with a smooth, polished finish. Each run of material consisted of at least 15 test runs, with each run using approximately 40 milligrams of material placed on the steel anvil with or without the presence of grit paper. The striker is gently placed just touching the material and the 2.5-kilogram weight is dropped from various heights. A Go was defined as a 117 average decibel level between the two sound detectors (one behind and one to the side of the apparatus). The parameter reported is the DH50, which is defined as the height from which 50% of the drops are expected to be Go’s. A series of at least 15 drops from various heights is performed, and the DH50 values are calculated using the Neyer D-optimal method (Figures S3 – S7).

Materials with higher DH50 values are more insensitive to initiation than those with lower DH50 values.

For solid materials the striker is gently placed on the top of the sample. For liquid or oil samples, an approximately 1-millimeter gap is imposed between the anvil and the striker, in this situation the striker is held loosely in place with magnets). The gap between the striker and liquid sample is to prevent dispersion of the liquid between the sticker and the anvil. All liquid samples are inspected for the presence of bubbles prior to placing the striker above the sample, as bubbles can facilitate hot spot formation, due to adiabatic compression of trapped air.

In drop-weight impact sensitivity tests, solid samples are typically run using standard grit paper, in order to add high-melting point grit as a consistent source of ignition in the system. Grit paper can also influence sound levels, so control experiments were performed with grit paper when possible. It is important to note that the physical phases were not consistent among all the derivatives. While PETN is a crystalline white solid material, PETriN was only isolated as a clear oil, and all attempts to solidify the material were unsuccessful. Both PEDN and PEMN were initially isolated as clear oils, however over time the materials...
would sometimes (inconsistently) solidify as amorphous waxy solids. NMR analysis indicated that both the solids and oils were of similar purity. Table S1 shows that samples prepared in different configurations and phases gave very similar sound level and impact sensitivity results.

Though drop-weight impact testing allows for rapid identification of preliminary explosive safety properties, the primary diagnostic for determining if a reaction occurred is often determined through sound levels.\textsuperscript{3,4} Well-behaved explosives (i.e. those which do not undergo partial reactivity) exhibit an “S” shaped curve in a plot of drop height vs. sound level.\textsuperscript{5} Generally, less sensitive materials such as trinitrotoluene (TNT) exhibit more scatter than a more sensitive explosive like PETN. Figures S8 and S9 show the sound levels for the PETN derivatives in this system, and Tables S2 – S6 list the raw collected data.

Table S1: Sensitivity Data and Sound Levels for PETN and hydroxyl PETN derivatives at room temperature.

| Material | Impact DH\textsubscript{50} (cm)\textsuperscript{a} | Average dB level for “Go” | Average dB level for “No Go” | Friction DH\textsubscript{50} (N) | Electrostatic Discharge (J) | DSC (°C) melt / decomp onset |
|----------|-----------------------------------|--------------------------|-----------------------------|-----------------------------|-----------------------------|-----------------------------|
| PETN     | 10.7 ± 1.3 (grit) (s)             | 129 ± 2                  | 98 ± 6                      | 56.0 ± 2.2                  | 0.0625                      | 140.87 / 165.26             |
|          | 20.8 ± 4.3 (bare) (s)             | 130 ± 3                  | 100 ± 5                     |                            |                            |                             |
| PET\textsubscript{n}N | 27.0 ± 2.2 (bare) (l) | 134 ± 3                  | 99 ± 1                      | > 360                      | 0.0625                      | -- / 163.95                 |
| PEDN     | 120.5 ± 3.4 (bare) (l)            | 121 ± 2                  | 108 ± 7                     | > 360                      | 0.0625                      | -- / 166.4                  |
|          | 114.1 ± 7.1 (grit) (s)            | 124 ± 1                  | 108 ± 7                     |                            |                            |                             |
| PEMN     | ~ 320 (grit) (s)                  | 118 ± 1                  | 110 ± 6                     | > 360                      | 0.0625                      | 57.7 / 162.4                |
|          | > 320 (bare) (s)                  | --                      | 111 ± 5                     |                            |                            |                             |

\textsuperscript{a}For each derivative, it is specified whether grit (grit) or no grit (bare) was used on the steel anvil. The phase of the material is designated as liquid (l) or solid (s).

\textsuperscript{3} P. J. Rae and P. M. Dickson, Some Observations About the Drop-weight Explosive Sensitivity Test, \textit{J. Dyn. Behav. Mater.}, \textbf{2020}, 7, 414-424.

\textsuperscript{4} Lease, N.; Holmes, M.D.; Englert-Erickson, M.A.; Kay, L.M.; Francois, E.G.; Manner, V.W. “Analysis of Ignition Sites for the Explosives 3,3’-diamino-4,4’-azoxyfurazan (DAAF) and 1,3,5,7-Tetranitro-1,3,5,7-tetrazoctane (HMX) Using Crush Gun Impact Testing”. \textit{ACS Mater. Au.} \textbf{2021}, 1, 2, 116-129.

\textsuperscript{5} Marrs, F.W.; Manner, V.W.; Burch, A.C.; Yeager, J.D.; Brown, G.W.; Kay, L.M.; Buckley, R.T.; Anderson-Cook, C.M.; Cawkwell, M.J. “Sources of Variation in Drop-Weight Impact Sensitivity Testing of the Explosive Pentaerythritol Tetranitrate”. \textit{Ind. Eng. Chem. Res.} 2021, 60, 13, 5024-5033.
**Neyer Analysis Data for Drop Weight Impact Tests:**

![Graph showing raw data used in Neyer analysis for PETriN tested on bare anvil.](image)

**Figure S3.** Raw data used in Neyer analysis for PETriN tested on bare anvil.
**Figure S4.** Raw data used in Neyer analysis for PEDN tested with grit on anvil.

**Figure S5.** Raw data used in Neyer analysis for PEDN tested on bare anvil.
**Figure S6.** Raw data used in Neyer analysis for PEMN tested with grit on anvil.

**Figure S7.** Raw data used in Neyer analysis for PEMN tested on bare anvil.
**Impact Testing Sound Levels:**

![Graph](image)

**Figure S8.** Sound level vs. drop height plots for PETN, PETriN, PEDN and PEMN. Three of the materials demonstrate an “S” shaped curve seen when analyzing sound level data from drop hammer testing. Sensitive explosives that undergo a complete reaction on the time scale of the drop hammer test exhibit more of a step function where there is clear delineation between a “Go” and “No Go” (PETriN and PETN in this case). Less sensitive materials (PEDN) generally have a more traditional “S” shaped curve most likely due to increased prevalence of partial reactions on the drop hammer time scale.

![Graph](image)

**Figure S9.** Sound levels (in dB) for PETN and all hydroxyl derivatives, vs. drop height (in cm). The phase of the material is specified as s (solid) or l (liquid), along with the presence of grit or bare anvil.
**Impact Testing Sound Level Data:**

Table S2. PETriN (oil, bare)

| Drop # | Height | Go/No go | Left dB | Back dB | Conditions after drop |
|--------|--------|----------|---------|---------|-----------------------|
| 1      | 30cm   | 1        | 136.4   | 136.1   | no HE remained         |
| 2      | 20cm   | 0        | 97.8    | 101.5   | all HE remained        |
| 3      | 25cm   | 0        | 100.1   | 101.9   | all HE remained        |
| 4      | 28cm   | 1        | 131.3   | 131.7   | no HE remained         |
| 5      | 26cm   | 1        | 129.1   | 129.5   | no HE remained         |
| 6      | 24cm   | 0        | 97.7    | 100.1   | all HE remained        |
| 7      | 32cm   | 1        | 136.3   | 136.7   | no HE remained         |
| 8      | 29cm   | 1        | 132.1   | 132.5   | no HE remained         |
| 9      | 25cm   | 0        | 98.4    | 98.8    | all HE remained        |
| 10     | 40cm   | 1        | 136.1   | 136.4   | no HE remained         |
| 11     | 20cm   | 0        | 98.7    | 100.3   | all HE remained        |
| 12     | 35cm   | 1        | 130.1   | 131.4   | no HE remained         |
| 13     | 18cm   | 0        | 97.3    | 98.3    | all HE remained        |
| 14     | 43cm   | 1        | 135.1   | 136.4   | no HE remained         |
| 15     | 33cm   | 1        | 135.3   | 135.7   | all HE remained        |

Table S3. PEDN (oil, bare)

| Drop # | Height | Go/No go | Left dB | Back dB | Conditions after drop |
|--------|--------|----------|---------|---------|-----------------------|
| 1      | 110cm  | 0        | 113.7   | 116.8   | all HE remained       |
| 2      | 125cm  | 1        | 119.8   | 121.9   | all HE remained       |
| 3      | 120cm  | 1        | 117.3   | 118.1   | all HE remained       |
| 4      | 115cm  | 0        | 114.1   | 114.7   | all HE remained       |
| 5      | 123cm  | 0        | 116.5   | 116.6   | all HE remained       |
| 6      | 128cm  | 1        | 121.4   | 123.5   | all HE remained       |
| 7      | 122cm  | 1        | 118.1   | 119.2   | all HE remained       |
| 8      | 117cm  | 0        | 115.6   | 117.8   | all HE remained       |
| 9      | 129cm  | 1        | 120.4   | 121.3   | all HE remained       |
| 10     | 100cm  | 0        | 109.1   | 110.1   | all HE remained       |
| 11     | 80cm   | 0        | 101.2   | 103.1   | all HE remained       |
| 12     | 70cm   | 0        | 101.1   | 103.3   | all HE remained       |
| 13     | 140cm  | 1        | 121.6   | 123.7   | all HE retained       |
| 14     | 160cm  | 1        | 120.4   | 121.4   | all HE remained       |
| 15     | 170cm  | 1        | 123.1   | 125.1   | all HE remained       |
| 16     | 60cm   | 0        | 101.2   | 103.2   | all HE remained       |
| 17     | 50cm   | 0        | 101.1   | 102.1   | all HE remained       |
| 18     | 40cm   | 0        | 101.2   | 102.7   | all HE remained       |
### Table S4. PEDN (solid, grit)

| Drop # | Height | Go/No go | Left dB | Back dB | Conditions after drop |
|--------|--------|----------|---------|---------|-----------------------|
| 1      | 100cm  | 0        | 107.3   | 108.7   | all HE remained        |
| 2      | 120cm  | 1        | 124.8   | 126.8   | all HE remained        |
| 3      | 110cm  | 1        | 122.1   | 122.1   | all HE remained        |
| 4      | 105cm  | 0        | 114.4   | 114.5   | all HE remained        |
| 5      | 115cm  | 0        | 115.1   | 116.1   | all HE remained        |
| 6      | 125cm  | 1        | 123.5   | 122.6   | all HE remained        |
| 7      | 118cm  | 0        | 113.7   | 115.4   | all HE remained        |
| 8      | 122cm  | 1        | 123.1   | 123.4   | all HE remained        |
| 9      | 120cm  | 1        | 123.9   | 124.1   | all HE remained        |
| 10     | 80cm   | 0        | 103.8   | 106.8   | all HE remained        |
| 11     | 70cm   | 0        | 100.1   | 101.4   | all HE remained        |
| 12     | 50cm   | 0        | 100.1   | 100.7   | all HE remained        |

### Table S5. PEMN (solid, grit)

| Drop # | Height | Go/No go | Left dB | Back dB | Conditions after drop |
|--------|--------|----------|---------|---------|-----------------------|
| 1      | 320cm  | 1        | 116.8   | 119.1   | all HE remained        |
| 2      | 300cm  | 0        | 115.3   | 116.1   | all HE remained        |
| 3      | 315cm  | 0        | 116.1   | 117.1   | all HE remained        |
| 4      | 320cm  | 0        | 116.4   | 116.7   | all HE remained        |
| 5      | 310cm  | 0        | 115.7   | 116.4   | all HE remained        |
| 6      | 320cm  | 1        | 116.7   | 119.3   | all HE remained        |
| 7      | 320cm  | 0        | 116.3   | 116.6   | all HE remained        |
| 8      | 320cm  | 1        | 116.9   | 118.9   | all HE remained        |
| 9      | 315cm  | 0        | 115.4   | 116.3   | all HE remained        |
| 10     | 320cm  | 0        | 116.1   | 116.4   | all HE remained        |
| 11     | 285cm  | 0        | 109.1   | 110.1   | all HE remained        |
| 12     | 275cm  | 0        | 107.3   | 108.9   | all HE remained        |
| 13     | 270cm  | 0        | 107.4   | 108.7   | all HE remained        |
| 14     | 260cm  | 0        | 105.1   | 106.1   | all HE remained        |
| 15     | 240cm  | 0        | 101.4   | 102.7   | all HE remained        |
| 16     | 220cm  | 0        | 101.2   | 103.1   | all HE remained        |
| 17     | 200cm  | 0        | 101.4   | 102.7   | all HE remained        |
| 18     | 180cm  | 0        | 102.1   | 103.4   | all HE remained        |
| 19     | 170cm  | 0        | 101.1   | 102.3   | all HE remained        |
Table S5 (Continued). Extra run (with grit) with separately prepared sample of PEMN

| Drop # | Height | Go/No go | Left dB | Back dB | Conditions after drop |
|--------|--------|----------|---------|---------|-----------------------|
| 1      | 320cm  | 0        | 110.7   | 113.1   | all HE remained        |
| 2      | 320cm  | 0        | 109.8   | 112.3   | all HE remained        |
| 3      | 320cm  | 0        | 110.8   | 112.9   | all HE remained        |
| 4      | 320cm  | 0        | 109.8   | 112.1   | all HE remained        |
| 5      | 320cm  | 0        | 110.7   | 112.9   | all HE remained        |
| 6      | 320cm  | 0        | 111.5   | 112.7   | all HE remained        |
| 7      | 320cm  | 0        | 109.3   | 110.7   | all HE remained        |
| 8      | 320cm  | 0        | 110.1   | 111.8   | all HE remained        |
| 9      | 320cm  | 0        | 109.8   | 111.8   | all HE remained        |
| 10     | 320cm  | 0        | 110.4   | 112.1   | all HE remained        |
| 11     | 320cm  | 0        | 109.7   | 111.3   | all HE remained        |
| 12     | 320cm  | 0        | 110.5   | 112.3   | all HE remained        |
| 13     | 320cm  | 0        | 110.1   | 112.7   | all HE remained        |
| 14     | 320cm  | 0        | 109.8   | 111.8   | all HE remained        |
| 15     | 320cm  | 0        | 109.9   | 112.1   | all HE remained        |

Table S6. PEMN (solid, bare)

| Drop # | Height | Go/No go | Left dB | Back dB | Conditions after drop |
|--------|--------|----------|---------|---------|-----------------------|
| 1      | 320cm  | 0        | 114.1   | 117.6   | all HE remained        |
| 2      | 300cm  | 0        | 113.1   | 115.9   | all HE remained        |
| 3      | 290cm  | 0        | 113.1   | 115.7   | all HE remained        |
| 4      | 280cm  | 0        | 112.9   | 115.1   | all HE remained        |
| 5      | 270cm  | 0        | 112.8   | 114.9   | all HE remained        |
| 6      | 260cm  | 0        | 113.1   | 115.3   | all HE remained        |
| 7      | 250cm  | 0        | 113.4   | 115.1   | all HE remained        |
| 8      | 240cm  | 0        | 112.9   | 114.7   | all HE remained        |
| 9      | 230cm  | 0        | 111.4   | 115.1   | all HE remained        |
| 10     | 220cm  | 0        | 112.1   | 115.3   | all HE remained        |
| 11     | 210cm  | 0        | 111.4   | 114.7   | all HE remained        |
| 12     | 190cm  | 0        | 112.9   | 114.6   | all HE remained        |
| 13     | 180cm  | 0        | 111.4   | 112.1   | all HE remained        |
| 14     | 170cm  | 0        | 111.4   | 112.3   | all HE remained        |
| 15     | 160cm  | 0        | 111.4   | 112.6   | all HE remained        |
Friction and Electrostatic Discharge (ESD) Sensitivity Data:

Friction Sensitivity Data. Friction and electrostatic discharge sensitivity (ESD) are typically measured for all explosives in the novel design stage in order to more broadly examine handling safety characteristics. All hydroxyl derivatives of PETN exhibited no indication of reaction at the highest setting on the apparatus (360 N), which is not unusual for liquid nitrate ester explosives. ESD analysis of the hydroxy derivatives of PETN indicated that all the derivatives had the same sensitivity as the parent PETN molecule despite the differences observed in the impact and friction sensitives.

Friction sensitivity measurements were conducted using a BAM friction sensitivity test machine. Friction sensitivity on this machine is performed using a fixed porcelain pin and a movable porcelain plate that executes a reciprocating motion at a rate of 141 rpm with a stroke length of 10 millimeter with an applied force varying from 5 to 360 N.

Electrostatic Discharge (ESD). Electrostatic discharge sensitivity testing is conducted on a SMS ABL electrostatic discharge machine. To perform the test a sample of about 5 to 10 mg is placed onto the sample holder and is positioned onto a grounded pedestal. To confine the sample slightly the material on the pedestal is covered with Scotch tape. During the test, if the material generates enough gas to tear the Scotch tape confining the material the test is considered a Go. High voltage is applied and discharged into the material through an approaching needle. Capacitance values are adjusted in order to attain the desired stimulus levels. Results of the electrostatic discharge testing are given in threshold stimulus level (TIL). A TIL corresponds to the highest spark energy at which 20 consecutive tests produced a no Go with at least one recorded reaction out of the 20 at the next highest voltage level (Table S7 – S9).

---

6 G. B. Storm, J. R. Stine, J. F. Kramer, “Sensitivity relationships in energetic materials,” Los Alamos National Laboratory, LA-UR-89-2936.
Table S7. PETriN ESD data.

| Discharge Level | 1  | 2  | 3  | 4  | 5  | 6  | 7  | 8  | 9  | 10 |
|-----------------|----|----|----|----|----|----|----|----|----|----|
| 0.25 Joules     | E  |    |    |    |    |    |    |    |    |    |
| 0.125 Joules    | N  | E  |    |    |    |    |    |    |    |    |
| 0.0625 Joules   | N  | N  | N  | N  | N  | N  | N  | N  | N  | N  |
| 0.025 Joules    | N  | N  | N  | N  | N  | N  | N  | N  | N  | N  |

Table S8. PEDN ESD data.

| Discharge Level | 1  | 2  | 3  | 4  | 5  | 6  | 7  | 8  | 9  | 10 |
|-----------------|----|----|----|----|----|----|----|----|----|----|
| 0.25 Joules     | N  | E  |    |    |    |    |    |    |    |    |
| 0.125 Joules    | N  | N  | N  | E  |    |    |    |    |    |    |
| 0.0625 Joules   | N  | N  | N  | N  | N  | N  | N  | N  | N  | N  |
| 0.025 Joules    | N  | N  | N  | N  | N  | N  | N  | N  | N  | N  |

Table S9. PEMN ESD data.

| Discharge Level | 1  | 2  | 3  | 4  | 5  | 6  | 7  | 8  | 9  | 10 |
|-----------------|----|----|----|----|----|----|----|----|----|----|
| 0.25 Joules     | E  |    |    |    |    |    |    |    |    |    |
| 0.125 Joules    | E  |    |    |    |    |    |    |    |    |    |
| 0.0625 Joules   | N  | N  | N  | N  | N  | N  | N  | N  | N  | N  |
| 0.025 Joules    | N  | N  | N  | N  | N  | N  | N  | N  | N  | N  |
Density Functional Tight Binding Calculations

All of the atomic-scale calculations were performed using semi-empirical Density Functional Tight Binding (DFTB) theory.\textsuperscript{7,8} The lan31 parameterization\textsuperscript{9} for molecules containing C, H, N, and O developed by Cawkwell and Perriot was used exclusively because of its good accuracy and transferability versus density functional theory.

1.1 Heat of formation

The gas phase heat of formation of PETN, PETriN, PEDN, and PEMN were calculated via DFTB total energies, \( u \), with the set of atom-equivalent energies, \( \{\epsilon_l\} \), detailed in Ref. 10,

\[
\Delta H_f = u - \sum_l n_l \epsilon_l
\]  

where \( n_l \) are the number of atoms of type \( l \). The total energies were calculated in the gas phase at zero electronic temperature after the molecular geometries were optimized using the FIRE algorithm\textsuperscript{11} until the maximum force acting on any atom was less than 0.001 eV/Å. The Coulomb energies were calculated in real space and self-consistency with respect to the Mulliken charge distribution was enforced to a tolerance of \( 10^{-6} \) electrons using the DIIS algorithm.\textsuperscript{12} Counts of the C, N, and O atoms forming only single bonds versus those in resonant structures or double bonds were determined from the self-consistent density matrix as in Ref. 10.

\textsuperscript{7} Elstner, M.; Porezag, D.; Jungnickel, G.; Elsner, J.; Haugk, M.; Frauenheim, T.; Suhai, S.; Seifert, G., Self-Consistent-Charge Density-Functional Tight-Binding Method for Simulations of Complex Materials Properties. \textit{Phys. Rev. B} \textbf{1998}, \textit{58}, 7260-7268.
\textsuperscript{8} Frauenheim, T.; Seifert, G.; Elstner, M.; Hajnal, Z.; Jungnickel, G.; Porezag, D.; Suhai, S.; Scholz, R., A Self-Consistent Charge Density-Functional Based Tight-Binding Method for Predictive Materials Simulations in Physics, Chemistry and Biology. \textit{Phys. Status Solidi B} \textbf{2000}, \textit{217}, 41-62.
\textsuperscript{9} Cawkwell, M. J.; Perriot, R., Transferable Density Functional Tight Binding for Carbon, Hydrogen, Nitrogen, and Oxygen: Application to Shock Compression. \textit{J. Chem. Phys.} \textbf{2019}, \textit{150}, 024107.
\textsuperscript{10} Cawkwell, M. J.; Burch, A. C.; Ferreira, S. R.; Lease, N.; Manner, V. W., Atom Equivalent Energies for the Rapid Estimation of the Heat of Formation of Explosive Molecules from Density Functional Tight Binding Theory. \textit{J. Chem. Inf. Model} \textbf{2021}, \textit{61}, 3337-3347.
\textsuperscript{11} Bitzek, E.; Koskinen, P.; Gahler; Moseler, M.; Gumbsch, P., Structural Relaxation Made Simple. \textit{Phys. Rev. Lett.} \textbf{2006}, \textit{97}, 170201.
\textsuperscript{12} Pulay, P., Convergence Acceleration of Iterative Sequences: The Case of Scf Iteration. \textit{Chem. Phys. Lett.} \textbf{1980}, \textit{73}, 393-398.
The accuracy of the \( \Delta H_f \) estimated from the semi-empirical DFTB-\textit{lanl}31 parameterization was assessed by comparison to the results of the DFT-based formalism of Byrd and Rice at the B3LYP/6-311++G(2df,2p)//B3LYP/6-31G* level of theory (Table S10). The maximum discrepancy between the fast DFTB and first principles DFT calculations is about 10 kcal/mol for PEMN, which is consistent with the more detailed error analyses presented in Ref. 10.

**Table S10.** Comparison of the semi-empirical DFTB-\textit{lanl}31 parameterization to the DFT-based formalism of Byrd and Rice.

|                  | DFTB-\textit{lanl}31 | Byrd and Rice: B3LYP/6-311++G(2df,2p)//B3LYP/6-31G* |
|------------------|-----------------------|------------------------------------------------------|
|                  | \( \Delta H_f \) (kcal/mol) | \( Q_m \) (kcal/mol) | \( Q \) (kcal/g) | \( \Delta H_f \) (kcal/mol) | \( Q_m \) (kcal/mol) | \( Q \) (kcal/g) |
| PETN             | -106.1                | 463.8       | 1.47        | -102.3                | 467.6       | 1.48        |
| PETriN           | -121.8                | 308.2       | 1.14        | -122.4                | 307.6       | 1.13        |
| PEDN             | -134.0                | 238.7       | 1.06        | -139.3                | 233.4       | 1.03        |
| PEMN             | -148.1                | 188.0       | 1.04        | -158.0                | 178.0       | 0.98        |

**1.2 Gas-phase reactive MD**

Gas-phase DFTB-MD simulations were performed to evaluate the kinetics of trigger linkage rupture by determining the time for any covalent bond to break as a function of temperature.\textsuperscript{13,14} The simulations used a stochastic Langevin thermostat\textsuperscript{15} to control the temperature and to ensure that the thermal fluctuations

\textsuperscript{13} Cawkwell, M. J.; Ferriera, S. R.; Lease, N.; Manner, V. W., Ranking Explosive Sensitivity with Chemical Kinetics Derived from Molecular Dynamics Simulations. In Molecular Modeling of the Sensitivities of Energetic Materials, Mathieu, D., Ed. Elsevier: Amsterdam, 2021; Vol. 22, pp 347-367.

\textsuperscript{14} Cawkwell, M. J.; Davis, J. V.; Lease, N.; Marrs, F. W.; Burch, A. C.; Ferreira, S. R.; Manner, V. W., Understanding Explosive Sensitivity with Effective Trigger Linkage Kinetics. ACS Phys. Chem. Au 2022, in press.

\textsuperscript{15} Martinez, E.; Cawkwell, M. J.; Voter, A. F.; Niklasson, A. M. N., Thermostatting Extended Lagrangian Born-Oppenheimer Molecular Dynamics. J. Chem. Phys. 2015, 142.
are consistent with the canonical ensemble. A finite electronic temperature corresponding to 0.2 eV was used to smear the occupancies in the vicinity of the chemical potential to help with energy conservation during bond breaking events. All simulations used a time step for the integration of equations of motion of 0.25 fs. A geometry optimization was performed on the molecules until the magnitude of the maximum force acting on any atom was less that 0.001 eV/Å was performed prior to the simulations to mitigate the possibility of reactions occurring before the molecules had reached thermal equilibrium because of ‘hot atoms’. The adaptive SCF scheme described in Ref. 14 was used to reduce the computational time required for each trajectory, where i) one SCF cycle with linear mixing was used when the HOMO-LUMO gap was greater than 1 eV, and ii) the SCF was converged fully (tolerance of $10^{-4}$ electrons on Mulliken charges) using the DIIS algorithm when the HOMO-LUMO gap was less than 1 eV. This adaptive scheme, which is used in conjunction with the extended Lagrangian Born-Oppenheimer molecular dynamics formalism of Niklasson et al.,$^{16-18}$ minimized the number of density matrix builds in the long intervals prior to the first reactions, and also ensures that the self-consistent ground state can be calculated accurately when bonds are severely stretched or distorted, as denoted by the narrowing of the HOMO-LUMO gap.

Two hundred independent trajectories were launched at each temperature for each molecule by assigning a different seed for the random number generators for the assignment of the initial velocities and the Langevin thermostat. Reactions were detected by post-processing the trajectories to find when more than one molecular fragment was present based on the analysis of atomic connectivity via pre-defined bond cut-off distances. We did not use the HOMO-LUMO gap itself to signal that a reaction had occurred because transient closures of the gap without reactions are common throughout the trajectories.

$^{16}$ Niklasson, A. M. N.; Tymczak, C. J.; Challacombe, M., Time-Reversible Born-Oppenheimer Molecular Dynamics. Phys. Rev. Lett. 2006, 97.
$^{17}$ Niklasson, A. M. N.; Tymczak, C. J.; Challacombe, M., Time-Reversible Ab Initio Molecular Dynamics. J. Chem. Phys. 2007, 126.
$^{18}$ Niklasson, A. M. N., Extended Born-Oppenheimer Molecular Dynamics. Phys. Rev. Lett. 2008, 100, 123004.
Supporting Information: Identifying Molecular Properties that Drive Explosive Sensitivity

Figure S10. Gas phase data collected for each derivative. Each vertical line represents 200 trajectories calculations for each molecule. The fit line is to all raw, normalized rate data rather than taking an average of each point and then fitting.

1.3 Condensed-phase reactive MD

Time-to-explosion and the change in temperature during thermal explosion for PETN, PETriN, PEDN, and PEMN were determined through a series of independent MD simulations in the microcanonical (constant NVE) ensemble on small simulation cells under three-dimensional periodic boundary conditions. The simulations for PETN were performed on a $2 \times 2 \times 2$ supercell containing 16 molecules (464 atoms) at the experimental, room temperature density of 1.778 g/cm$^3$. The simulations on PETriN, PEDN, and PEMN were performed on liquid-like samples generated by initially placing molecules at random positions (but avoiding close contacts or overlapping molecules) within the simulation cell followed by a molecular statics relaxation (maximum force < 0.01 eV/Å) and thermalization to 300 K. The simulations of liquid PETriN, PEDN, and PEMN each contained 8 molecules. Their mass densities at room temperature and pressure were estimated by through a series of dispersion-corrected DFTB-MD simulations with a volume-rescaling barostat. The barostat was used to update the volume of the simulation cell to drive the average pressure, $P = (1/3)\text{Tr}(\sigma)$, where $\sigma$ is the stress tensor computed from the DFTB forces and velocities, toward a target value.

Like regular Kohn-Sham DFT, DFTB theory tends to underestimate the magnitude of intermolecular
forces arising from London dispersion. The poor description of London dispersion forces in regular DFT and DFTB theory leads to a systematic underestimation of the density of organic molecular crystals and liquids, such as those under consideration in this work.\textsuperscript{19} The so-called dispersion corrections in DFT and DFTB theory are an empirical correction to the total energy and forces that provide additional intermolecular interactions at long range.\textsuperscript{20,21} We have parameterized the dispersion correction proposed by Wu and Yang,\textsuperscript{22} and Grimme\textsuperscript{21} for the lanl31 DFTB model to a subset of the S66x8 dataset developed by Rezac \textit{et al.}\textsuperscript{23} The dispersion correction takes the form

\begin{equation}
E_D = -\frac{s_6}{2} \sum_{i,j=1\atop i\neq j}^{N} \frac{C_6^{(i,j)}}{R_{ij}^6} f_d(R_{ij})
\end{equation}

where $s_6$ is an adjustable parameter that uniformly rescales the strength of the dispersion forces between all pairs of atoms, $C_6^{(i,j)}$ are parameters that set the strength of the interactions between the elements at sites $i$ and $j$, $R_{ij}$ is the distance between atoms $i$ and $j$, $N$ the total number of atoms, and $f_d$ is a damping function that removes the singularity in the forces at small $R$, which takes the form,

\begin{equation}
f_d(R) = \frac{1}{1 + \exp(-\alpha(\frac{R}{R_0}-1))}
\end{equation}

Here, $R_0$ and $\alpha$ set the radial distance of the onset of the damping function and its steepness, respectively.

In Grimme’s formulation, $R_0$ is equal to the sum of van der Waals radii of the species at $i$ and $j$, $R_0 = R_{vdW}^{(i)} + R_{vdW}^{(j)}$, and $\alpha$ is a constant that is typically taken to be equal to 23.

The dispersion corrections for the lanl31 DFTB model were parameterized to the interaction

\textsuperscript{19} Sorescu, D. C.; Rice, B. M., Theoretical Predictions of Energetic Molecular Crystals at Ambient and Hydrostatic Compression Conditions Using Dispersion Corrections to Conventional Density Functionals (Dft-D). \textit{J. Phys. Chem. C} \textbf{2010}, \textit{114}, 6734-6748.

\textsuperscript{20} Brandenburg, J. G.; Grimme, S., Accurate Modeling of Organic Molecular Crystals by Dispersion-Corrected Density Functional Tight Binding (DFTB). \textit{J. Phys. Chem. Lett.} \textbf{2014}, \textit{5}, 1785-1789.

\textsuperscript{21} Grimme, S., Accurate Description of Van Der Waals Complexes by Density Functional Theory Including Empirical Corrections. \textit{Journal of Computational Chemistry} \textbf{2004}, \textit{25}, 1464-1474

\textsuperscript{22} Wu, Q.; Yang, W., Empirical Correction to Density Functional Theory for Van Der Waals Interactions. \textit{J. Chem. Phys.} \textbf{2002}, \textit{116}, 515.

\textsuperscript{23} Rezac, J.; Riley, K. E.; Hobza, P., S66: A Well-Balanced Database of Benchmark Interaction Energies Relevant to Biomolecular Structures. \textit{J. Chem. Theory Comput.} \textbf{2011}, \textit{7}, 2427-2438.
energies between non-hydrogen bonded dimers from the S66x8 dataset as a function of their separation distance, \( r \),

\[
E_D(r) = E_{S66x8}(r) - (u(r) - u_A - u_B)
\]  \( \text{(S.4)} \)

where \( E_{S66x8} \) is the S66 reference energy, and \( u(r) \), \( u_A \), and \( u_B \) are the DFTB energies of the dimer and the two molecules forming the dimer, respectively. To avoid overfitting Eqs. 2 and 3 to the relatively small sub-set of non-hydrogen bonded dimers in S66x8, we used the \( C_6 \) coefficients for C, H, N, and O from Ref. 21 without modification and optimized the scaling parameter, \( s_6 \), for our system. Similarly, we used as an initial guess the set of van der Waals radii, \( R_{vdW} \), from Mantina et al.\(^{24} \) (C: 1.70, H: 1.10, N: 1.55, and O: 1.52 Å) and introduced an adjustable parameter, \( \omega \), to uniformly scale the radii, \( \{R'_{vdW}\} = \omega \{R_{vdW}\} \), which, like \( s_6 \), was optimized to minimize the root mean square difference between the reference data from S66x8 and the dispersion corrected \textit{lanl31} model. We kept the value of \( \alpha \) fixed at 23, and assumed that the \( C_6 \) coefficients between different elements were equal to the geometric mean of the two, that is,

\[
C_6^{(i,j)} = (C_6^{(i,i)}C_6^{(j,j)})^{1/2}
\]  \( \text{(S.5)} \)

The values of \( s_6 \) and \( \omega \) were optimized by steepest descent. The optimized value of \( s_6 \) was nearly unity, 1.0384, while the optimal van der Waals radii for the damping function, \( f_d(R) \), were increased by about 17\%, \( \omega = 1.166 \). The optimized terms for the dispersion corrections for C, H, N, and O are given in Table S11. In our condensed phase calculations, the dispersion corrections were computed within a cut-off radius of 12 Å from each atom.

\(^{24}\) Mantina, M.; Chamberlin, A. C.; Valero, R.; Cramer, C. J.; Truhlar, D. G., Consistent Van Der Waals Radii for the Whole Main Group. \textit{J. Phys. Chem. A} \textbf{2009}, \textit{113}, 5806-5812.
Table S11. Dispersion parameters, $C_6$, and optimized van der Waals radii, $R_{vdW}$, for the dispersion correction for lanl31.

|   | $C_6$ (eVÅ$^6$) | $R_{vdW}$ (Å) |
|---|---------------|---------------|
| C | 17.1          | 1.982         |
| H | 1.66          | 1.282         |
| N | 11.5          | 1.807         |
| O | 7.2           | 1.772         |

In order to estimate the expected errors in the predicted densities of liquid PETriN, PEDN, and PEMN from our dispersion-corrected DFTB-MD simulations, we computed the densities of ten well-characterized molecular crystals and liquids at room temperature and ambient pressure by running isothermal-isobaric MD trajectories (constant $NPT$) using a volume-rescaling barostat. The lengths of the three principal lattice vectors for the molecular crystals were allowed to vary independently so that the corresponding diagonal components of the stress tensor, $\sigma$, approached the target value. The unit cell angles were not allowed to vary during the simulations. The simulation cells for the liquid-like samples were rescaled isotropically.

The equilibrated lattice parameters and densities, $\rho$, from the constant-$NPT$ MD simulations are provided in Table S12 along with reference values from experiment. In Figure S11 we provide a correlation plot for the lanl31+D predicted densities versus those determined experimentally. The coefficient of determination is $R^2 = 0.80$, which indicates that the dispersion corrected MD simulations account for about 80% of the variation in the experimental data. The root mean square error in the predicted densities is about 0.1 g/cm$^3$, which indicates that our predicted densities for liquid PEMN, PEDN, and PETriN are expected to be accurate to ±0.1 g/cm$^3$. Finally, the predicted densities of the three liquids, which were calculated using periodic simulation cells each containing eight molecules in the isothermal-isobaric ensemble at 300 K and zero pressure, are given in Table S13.
Table S12. Equilibrium lattice parameters and densities at 300 K from constant NPT molecular dynamics simulations using lanl31 DFTB-D. Experimental data is provided in parentheses.

| Compound   | \(a\) (Å)     | \(b\) (Å)   | \(c\) (Å)   | \(\rho\) (g/cm\(^3\)) |
|------------|----------------|-------------|-------------|-------------------------|
| CL20 \(^a\) | 8.9 (8.9)      | 12.8 (12.6) | 13.4 (13.4) | 2.00 (2.04)             |
| DAAF \(^b\) | 9.3 (9.3)      | 10.1 (9.6)  | 9.2 (8.9)   | 1.63 (1.74)             |
| HMX \(^c\)  | 6.4 (6.5)      | 10.7 (11.0) | 7.6 (7.4)   | 1.94 (1.91)             |
| Liquid     | -              | -           | -           | 1.22 (1.14)             |
| nitromethane \(^d\) | 6.1 (6.1) | 6.0 (6.1)   | 8.5 (8.7)   | 1.46 (1.40)             |
| Pentaerythritol \(^e\) | 9.3 (9.3) | 9.3 (9.3)   | 7.0 (6.6)   | 1.75 (1.77)             |
| PETN \(^f\) | 14.1 (13.1)    | 11.5 (11.6)| 10.8 (10.7)| 1.69 (1.81)             |
| Mono-TNT \(^g\) | 14.8 (14.9) | 6.2 (6.0)   | 20.7 (20.9)| 1.69 (1.71)             |
| ETN \(^i\)  | 16.0 (15.9)    | 6.1 (5.2)   | 14.0 (14.7)| 1.63 (1.85)             |
| Liquid ETN \(^j\) | -         | -           | -           | 1.49 (1.56)             |

a. Ref. 25  b. CSD entry KANQAR01, Ref. 26  c. Ref. 27  d. PubChem CID 6375  e. CSD entry PERYTO03, Ref. 28  f. CSD entry PERTYN11  g. Ref. 29  h. CSD entry ZZZMUC08.  i. Ref. 30  j. Ref. 31

Table S13. Predicted densities for liquid PEMN, PEDN, and PETriN at 300 K from constant NPT molecular dynamics simulations using lanl31 DFTB+D.

| Compound | \(\rho\) (g/cm\(^3\)) |
|----------|-----------------------|
| PEMN     | 1.46                  |
| PEDN     | 1.48                  |
| PETriN   | 1.49                  |

Bolotina, N. B.; Hardie, M. J.; Speer, R. L.; Pinkerton, A. A., Energetic Materials: Variable-Temperature Crystal Structures of Gamma- and Epsilon-HNIW Polymorphs. *J. Appl. Crystallogr.* 2004, 37, 808-814.
Beal, R. W.; Incarvito, C. D.; Rhatigan, B. J.; Rheingold, A. L.; Brill, T. B., X-Ray Crystal Structures of Five Nitrogen-Bridged Bifurazan Compounds. *Propellants Explos. Pyrotech.* 2000, 25, 277-283.
Deschamps, J. R.; Frisch, M.; Parrish, D., Thermal Expansion of HMX. *J. Chem. Crystallogr.* 2011, 41, 966-970.
Ladd, M. F. C., On the Structure of Pentaerythritol. *Acta Cryst.* 1979, B35, 2375-2377.
Choi, C. S.; Prince, E., The Crystal Structure of Cyclotrimethylene Trinitramine Acta Crystallographica 1972, B28, 2857.
Manner, V. W.; Tappan, B. C.; Scott, B. L.; Preston, D. N.; Brown, G. W., Crystal Structure, Packing Analysis, and Structural-Sensitivity Correlations of Erythritol Tetranitrate. *Cryst. Growth Des.* 2014, 14, 6154-6160.
Pure, recrystallized erythritol tetranitrate (ETN) powder was placed in a glass beaker and melted inside a water bath set to 70 °C. Once the ETN was fully molten, it was pipetted into a volumetric flask (heated in the same bath) until the liquid reached the volume line, and the apparatus was weighed. This process was repeated three times in separate 1 – 4 mL volumetric flasks, resulting in three calculated densities which averaged to 1.557 ± 0.032 g mL\(^{-1}\).
Our MD simulations of high temperature chemistry in PETN, PETriN, PEDN, and PEMN were all initialized at a temperature of 1500 K, which we found to be sufficient to cause a transition to a thermal explosion within the sub-ns time scales accessible to our DFTB-MD code. The simulations used a time step of 0.25 fs, the extended Lagrangian Born-Oppenheimer MD scheme to propagate the electronic degrees of freedom, the adaptive SCF framework described in Section 1.2, and a finite electronic temperature corresponding to 0.25 eV. In order to obtain better statistics of the time to explosion, we ran 10 independent trajectories for each material by using a different seed for the random number generator for the assignment of the initial atomic velocities. Each system was then thermalized using a velocity rescaling thermostat for 5 ps until the temperatures reached the target values of 1500 K. Following thermalization, the trajectories were continued in the microcanonical ensemble (constant $NVE$) in order to conserve the total energy and observe the precipitous increase in the kinetic temperature associated with exothermic runaway.

---

32 Cawkwell, M. J.; Manner, V. W., Ranking the Drop-Weight Impact Sensitivity of Common Explosives Using Arrhenius Chemical Rates Computed from Quantum Molecular Dynamics Simulations. J. Phys. Chem. A 2020, 124, 74-81.
Calculated Charges

Our gas-phase QMD simulations indicate that i) the trigger linkages across the set of PETN-OH derivatives are associated with the nitrate ester groups, and ii) the strengths of the trigger linkages are essentially independent of the number of hydroxyl groups in the molecule. We have analyzed the simplified DFTB electronic structure of the molecules to assess to what extent substituting ONO₂ groups for OH groups affects the bond strengths within the remaining CH₂ONO₂ groups by computing the self-consistent Mulliken partial charges on the quaternary C atom (C1), the bridging C atom (C2) and the ester bond oxygen (O1), which are depicted schematically in Fig. S12. The Mulliken charges, which are presented in Table S14, were computed following a geometry optimization of the molecules in the gas phase using the FIRE algorithm that was terminated when the maximum force on any atom was less than 0.001 eV/Å. The Mulliken charges on C1, C2, and O1 exhibit small but systematic changes across the series, where the magnitudes of the charges on C1 and O1 decrease from -0.06 to -0.03 e and -0.34 to -0.31 e, respectively from PETN to PEMN. The Mulliken charges on the C2 atoms remain constant across the series. These small differences in the charge distribution and electronic structure of the CH₂ONO₂ groups as a function of the number of OH groups are consistent with the observation that the bond strengths, as characterized by the pre-exponential factors and activation enthalpies reported in the manuscript, remain unchanged.

![Calculated charges on atoms C1, C2, and O1 for PETN.](image.png)

**Table S14.** Mulliken partial charges for each PETN derivative.

| Material | C1   | C2  | O1   |
|----------|------|-----|------|
| PETN     | -0.06| 0.26| -0.34|
| PETriN   | -0.05| 0.26| -0.33|
| PEDN     | -0.04| 0.26| -0.32|
| PEMN     | -0.03| 0.26| -0.31|