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# Understanding Trigger Linkage Dynamics in Energetic Materials Using Mixed Picramide Nitrate Ester Explosives

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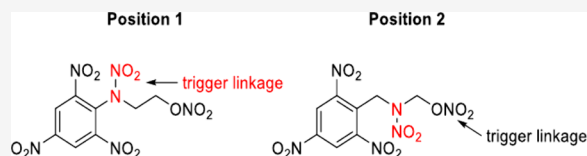


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**ABSTRACT:** The ability to predict the handling sensitivity of new organic energetic materials has been a longstanding goal. We report the synthesis and characterization of six new nitropicramide energetic materials with mixed functional groups that mimic known explosives such as nitroglycerin, erythritol tetranitrate (ETN), and pentaerythritol tetranitrate (PETN). The molecules have been studied theoretically using quantum molecular dynamics (QMD) simulations and density functional theory (DFT) calculations to identify the weakest bond in the reactants - the trigger-linkages - which control handling sensitivity, and to quantify their specific enthalpies of explosion. In good accord with the drop weight impact sensitivity data, our calculations predict that the sensitivities of the molecules are very similar owing to the small variations of the energy output and rates of trigger linkage rupture. In addition, both the QMD and DFT calculations point to the nitropicramide N–NO<sub>2</sub> bonds as the trigger linkages rather than the more typical O–NO<sub>2</sub> bonds. We propose that the switch of the trigger linkage from the nitrate esters to the nitramine groups arises from the strongly electron withdrawing character of the adjacent trinitrobenzene groups.



Location of Nitramine effects trigger linkage position

Explosives are able to rapidly release stored energy from their chemical bonds as large amounts of gaseous products, heat, and light. Common insults that can cause an energetic material to react include impact, friction, heat, electrostatic discharge, or shock compression. All of these stimuli ultimately lead to localized high temperature conditions within the materials that initiate a cascade of exothermic reactions. Chemical properties that appear to be correlated with sensitivity include crystal structure/crystal packing,<sup>1–7</sup> electrostatic effects,<sup>7–12</sup> inter/intramolecular bonding (hydrogen bonding),<sup>13–17</sup> thermodynamic and chemical properties.<sup>18–22</sup> However, the most reliable physically motivated models for explosive sensitivity are based implicitly or explicitly on the Arrhenius reaction kinetics of bonds breaking in energetic materials in either the gas- or condensed phase.<sup>23–29</sup> The success of these models indicate that the sensitivity of energetic materials is governed primarily by their high temperature thermal stability, that is, sensitive energetic materials have smaller kinetic barriers to reaction than insensitive materials.

Common functional groups in energetic materials include nitrate esters (–ONO<sub>2</sub>), nitros (–NO<sub>2</sub>), nitramines (–NNO<sub>2</sub>), peroxides (–O–O–), and azides (–N<sub>3</sub>). In addition to these energetic groups, nitrogen-containing heterocycles are commonly used in explosives due to the large amounts of energy stored in their ring structures.<sup>30</sup> Combining different functional groups can enable the tuning of the properties of energetic materials,<sup>31–33</sup> since molecular structure can influence multiple properties such as thermal stability, shock sensitivity, and safety, to name a few.

The first few reactions that occur during explosive decomposition are thought to be particularly important for determining the overall reaction rate and sensitivity because they generate highly reactive intermediate species that initiate the cascade of additional reactions. This effect was illustrated clearly by recent quantum molecular dynamics simulations, which identified long incubation times prior to the first reaction. However, once that reaction had occurred, the thousands of reactions leading to the exothermic runaway followed promptly.<sup>28,34</sup> The weakest bonds in the reactant molecules—the so-called “trigger linkages”<sup>35</sup>—are therefore a useful indicator of the overall sensitivity of an explosive. Systematic studies of the trigger linkage strengths of a set of energetic molecules, which were inferred by bond-dissociation energies calculated by density functional theory (DFT), confirmed the expected correlation with impact sensitivity whereby molecules with small bond dissociation energies were relatively sensitive.<sup>20,36</sup> Our team has extended this framework by using gas-phase quantum molecular dynamics simulations to identify first reactions that pass through a transition state in addition to simple homolytic bond scissions.<sup>27</sup> We have used this approach to understand the chemical origins of trends in

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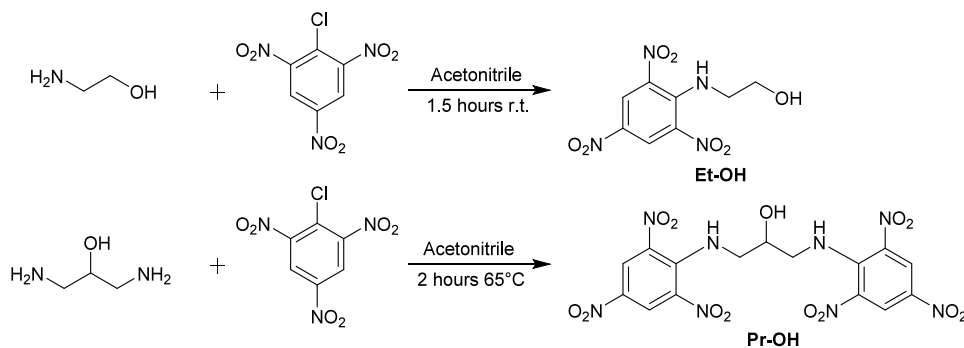
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## Scheme 1. Synthesis of Compounds Et-OH and Pr-OH



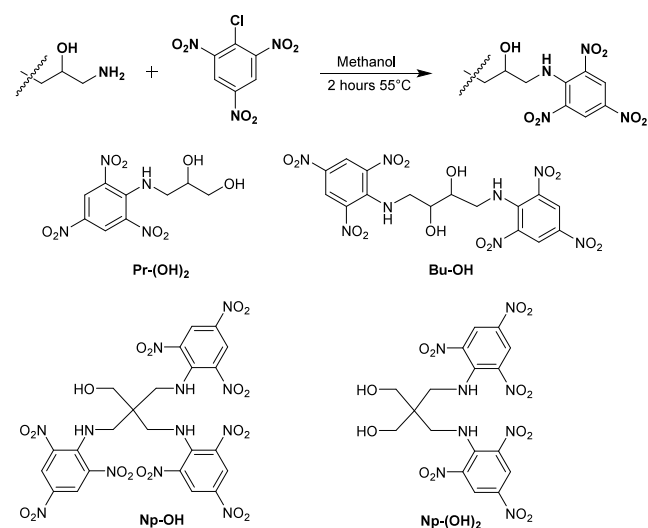
the impact sensitivity of a series of nitrate ester explosives in which systematic changes to their structure were made.<sup>37,38</sup> Additionally, this model has been shown to be effective when analyzing less common explosive functional groups such as picrates, picramides and nitropicramides.<sup>39</sup>

Herein we report the synthesis of six new energetic materials with a mix of nitrate ester and nitropicramide functional groups. These molecules are based on aliphatic chains (ethane (Et), propane (Pr), butane (Bu), and neopentane (Np)) analogous to known explosives such as EGDN (ethylene glycol dinitrate), nitroglycerin, ETN (erythritol tetranitrate) and PETN (pentaerythritol tetranitrate). Explosive sensitivity analysis (impact, spark, friction, and thermal) has been conducted on the novel explosives. With the exception of a neopentane derivative that was less sensitive than expected, the impact sensitivities of the new materials are comparable. These results are consistent with a series of gas-phase QMD simulations that show that all six molecules have the same trigger linkages - the N-NO<sub>2</sub> bonds in the nitropicramide groups - and very similar reaction rates.

Synthesis of the mixed aliphatic nitrate ester/nitropicramide derivatives was focused on four aliphatic backbones: ethane, propane, butane and neopentane. The first step for the synthesis of all of the derivatives was the reaction of picryl chloride with the corresponding aliphatic amine. Starting materials for the ethane and propane series were purchased commercially. The amine starting materials for the butane and neopentane series were synthesized following literature reports.<sup>33,31</sup> Slightly different conditions were used for different starting amines. The ethane-based compound Et-OH was synthesized following a literature procedure, generating an off yellow solid.<sup>40</sup> Following a slightly modified procedure compound Pr-OH was synthesized (Scheme 1).

Starting materials with more than one hydroxyl group showed poor solubility in acetonitrile resulting in large amounts of unreacted starting material when treated with picryl chloride. The remaining propane, butane and neopentane compounds used methanol as a solvent resulting in the desired products. (Scheme 2). Isolation of the product through crash precipitation into ice water was effective for Bu-OH and Np-OH while Pr-(OH)<sub>2</sub> and Np-(OH)<sub>2</sub> had to be extracted from the ice water using diethyl ether.

Nitrations of the six mixed alcohol/picramide derivatives were performed using nitric acid and trifluoroacetic anhydride. The reagent was added at 0 °C and held at that temperature for 1 h and then stirred at room temperature for 3 h (Scheme 3). Attempts to add the solid starting materials to the nitric acid/TFAA mixture resulted in incomplete reactions with

Scheme 2. Synthesis of Compounds Pr-(OH)<sub>2</sub>, Bu-OH, Np-OH, and Np-(OH)<sub>2</sub>

multiple nitrated products. Adding the starting material dissolved in a small amount of acetonitrile enabled full nitration of the starting alcohol/picramide. Once fully reacted the suspensions were poured into ice water, crash precipitating the product which was then washed with water and sodium bicarbonate solution to remove any residual acid. We attempted to grow crystals of the novel nitropicramide/nitrate ester derivatives, however only crystals for Et-ONO<sub>2</sub> and Pr-ONO<sub>2</sub> were successfully grown. Full synthetic procedures and crystallographic data are provided in the Supporting Information.

Small-scale sensitivity measurements were conducted on all six of the nitrate ester/nitropicramide derivatives and the results are presented in Table 1. Impact sensitivity data was collected on an ERL Type 12 drop hammer apparatus,<sup>41</sup> the friction sensitivity was tested on a BAM friction apparatus<sup>42</sup> and the electrostatic discharge data was collected on a SMS ABL electrostatic discharge machine.<sup>43</sup> A Neyer analysis was used to determine the DH<sub>50</sub> value in friction and impact testing, which is the value at which a reaction is expected to occur in 50 percent of trials.<sup>44</sup> For the ESD measurements a sample is placed between two pieces of tape and a discharge of varying energy is applied to the sample. A go is determined to have occurred if a popping sound is heard, or the tape has broken. Once a no-go value is established it is repeated 15 times to ensure no reaction occurs at that discharge level. Differential scanning calorimetry (DSC) was used to measure

## Scheme 3. Synthesis of Mixed Nitrate Ester/Nitropicramide Derivatives

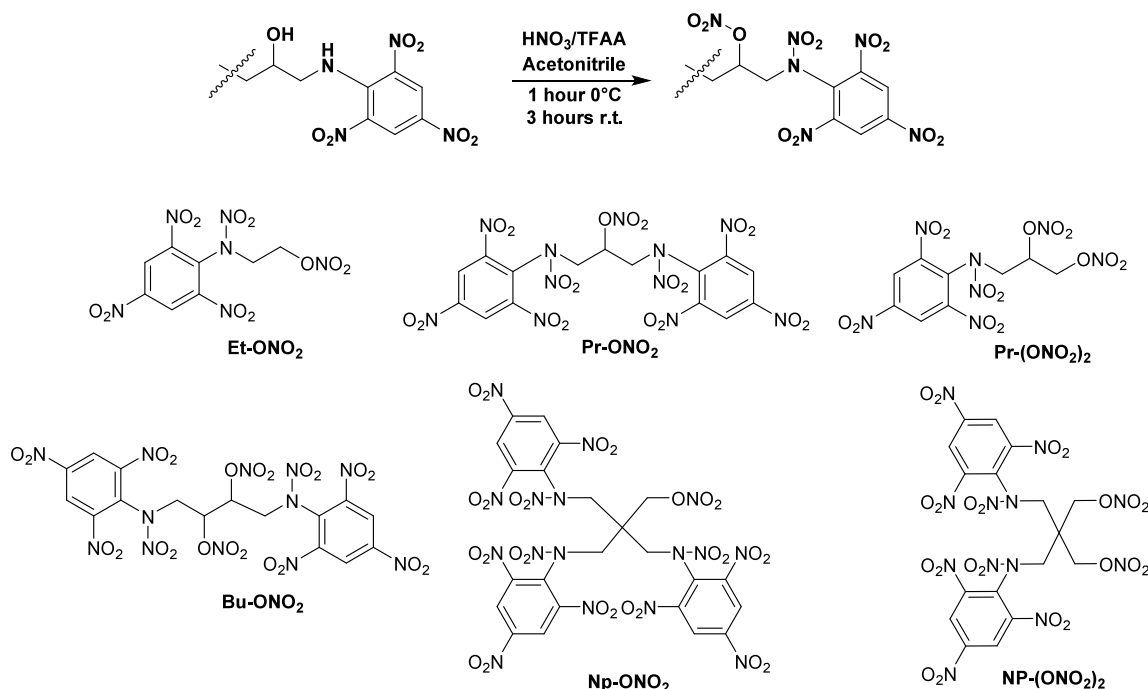


Table 1. Impact, Friction, Electrostatic Spark, and Thermal Sensitivity Data

material	impact DH <sub>50</sub> (cm)	friction DH <sub>50</sub> (N)	electrostatic discharge DH <sub>50</sub> (J)	DSC ( $^\circ\text{C}$ ) melt/decomp. onset
Et-ONO <sub>2</sub>	44.9 ± 38.4	>360	0.0625	126.0/161.1
Pr-ONO <sub>2</sub>	40.5 ± 6.40	339.1 ± 57.5	0.0250	N.A./151.2
Pr-(ONO <sub>2</sub> ) <sub>2</sub>	18.8 ± 3.20	202.1 ± 42.6	0.0625	N.A./155.4
Bu-ONO <sub>2</sub>	36.1 ± 8.70	>360	0.0250	N.A./158.2
Np-ONO <sub>2</sub> <sup>a</sup>	91.4 ± 14.5	N/A	N/A	N.A./130.1
Np-(ONO <sub>2</sub> ) <sub>2</sub>	29.3 ± 18.7	>360	0.1250	N.A./154.6

<sup>a</sup>Pure sample could only be prepared in sufficient quantity for impact and thermal analysis.

melting points and onset of decomposition temperatures for the six explosive derivatives.

Similar drop-weight impact sensitivities were observed with Et-ONO<sub>2</sub>, Pr-ONO<sub>2</sub>, Bu-ONO<sub>2</sub> and Np-(ONO<sub>2</sub>)<sub>2</sub>, with values of 44.9 ± 38.4, 40.5 ± 6.40, 36.1 ± 8.70 and 29.3 ± 18.7 cm, respectively. However, Pr-(ONO<sub>2</sub>)<sub>2</sub> was more sensitive to impact, at 18.8 ± 3.2 cm, and Np-ONO<sub>2</sub> was less sensitive, with a value of 91.4 ± 14.5 cm. In friction testing, Et-ONO<sub>2</sub>, Bu-ONO<sub>2</sub>, Np-ONO<sub>2</sub>, and Np-(ONO<sub>2</sub>)<sub>2</sub> did not react at the highest setting on our BAM friction apparatus. Pr-ONO<sub>2</sub> exhibited very little frictional sensitivity with a value of 339.1 ± 57.5 N. The most sensitive material in friction testing was Pr-(ONO<sub>2</sub>)<sub>2</sub>, however the value recorded 202.1 ± 42.6 N can still be considered on the lower end of sensitivity. For reference, pentaerythritol tetranitrate (PETN), a sensitive explosive used in detonators, has a frictional sensitivity of 59 N. Electrostatic discharge sensitivity values for all molecules fell between 0.025 and 0.125 J, which are typical values for nitramines and nitrate ester explosives. The onset of thermal decomposition for almost all the derivatives was between 151 and 161  $^\circ\text{C}$ . The only outlier was Np-ONO<sub>2</sub>, which had a thermal onset decomposition temperature of 130.1  $^\circ\text{C}$ , which is lower than other known nitrate ester explosives like PETN and erythritol tetranitrate (ETN).

Literature reports have shown that thermochemical properties such as heat of formation, heat of explosion and oxygen

balance can trend with impact sensitivity.<sup>35,45–49</sup> Calculated thermochemical properties for the mixed nitropicramide nitrate ester derivatives are listed in Table 2. The heat of

Table 2. Calculated Thermochemical Properties of Synthesized Explosives

material	$\Delta^\circ H_f$ (kcal/mol)	Q (kcal/g)	oxygen balance (%)
Et-ONO <sub>2</sub>	11.0	1.10	−35.34
Pr-ONO <sub>2</sub>	58.8	1.09	−38.31
Pr-(ONO <sub>2</sub> ) <sub>2</sub>	−11.2	1.22	−27.44
Bu-ONO <sub>2</sub>	33.9	1.13	−33.23
Np-ONO <sub>2</sub>	132	1.13	−43.95
Np-(ONO <sub>2</sub> ) <sub>2</sub>	33.6	1.10	−39.11

formation values,  $\Delta^\circ H_f$ , were calculated using the protocol based on DFT calculations developed by Byrd and Rice.<sup>50</sup> Only one explosive, Pr-(ONO<sub>2</sub>)<sub>2</sub>, had a negative heat of formation value while the other explosives ranged from 11 to 132 kcal/mol. The heat of explosion, Q, quantifies the change in enthalpy between the reactants and products, where the equilibrium product species are estimated from the stoichiometry, and the oxidation priority described in ref. 51. Molecules with a large specific heat of explosion tend to have good explosive performance because a large amount of energy can be liberated per unit mass. Table 2 shows that the heat of

explosion calculations for all the nitropicamide/nitrate ester derivatives are similar, ranging from 1.09 to 1.22 kcal/g. This is consistent with the similar impact sensitivities among all the derivatives. It should be noted that the most sensitive derivative Pr-(ONO<sub>2</sub>)<sub>2</sub>, as determined from the drop weight impact results, had the highest heat of explosion: 0.09 kcal/g higher than the next closest derivative.

Oxygen balance indicates whether a molecule contains enough oxygen to fully oxidize all the carbon and hydrogen in the molecule. A molecule with a positive oxygen balance has more oxygen than is needed while a molecule with a negative oxygen balance does not have enough oxygen to fully oxidize its components. The oxygen balance of an explosive provides a rapid estimate of its performance, since molecules with better oxygen balance are able to generate greater fractions of highly exothermic product species like CO, CO<sub>2</sub>, and H<sub>2</sub>O. The derivatives exhibited negative oxygen balance values ranging from -27.44% to -43.95%. The most sensitive explosive Pr-(ONO<sub>2</sub>)<sub>2</sub> had an oxygen balance closest to zero, while the most insensitive explosive Np-ONO<sub>2</sub> had the most negative value. The impact sensitivity of the derivatives was shown to correlate well with the heat of explosion and oxygen balance.

Our protocol for using quantum molecular dynamics (QMD) to automatically find the weakest bonds or first reactions in a molecule has been described in detail elsewhere, and only brief recap will be provided here.<sup>27,28,39</sup> The simulations use the semiempirical density functional tight binding formalism (DFTB)<sup>52,53</sup> including self-consistent charge transfer with the *lanl31* parameter set for C, H, N, and O.<sup>54</sup> The interatomic forces are computed on-the-fly from the ground state electronic structure at each time step. To obtain meaningful statistics for the distribution of the times for reaction, 100 independent trajectories are launched for each molecule at each temperature by changing the seed for the random number generators for the initial atomic velocity distributions and Langevin thermostat. Reactions are detected by monitoring the bond distances at regular intervals throughout the trajectories and their times,  $\tau$ , are used to compute the rates,  $\kappa = 1/\tau$ .

In Figure 1 we present an Arrhenius plot for the reaction rates normalized by the number of trigger linkages in each molecule,  $\kappa/N_x$ . By analyzing the final snapshots from each trajectory, we found that the overwhelming majority of reactions are associated with the rupture of the N-NO<sub>2</sub> bonds in the nitramine groups immediately adjacent to the trinitrobenzene (TNB) groups. Hence,  $N_x$  was set equal to the

number of nitropicamide groups present in each molecule. For clarity, only the results of linear regressions to the sets of  $\ln(\kappa/N_x)$  versus inverse temperature data are presented. Figure 1 shows that the normalized reaction rates for the six materials are similar, that is, all undergo reactions within a few 100 ps at temperatures between 1100 and 1400 K. The corresponding activation energies,  $E_a$ , and pre-exponential factors,  $\ln(A)$ , for each molecule are provided in Table 3. Molecules with

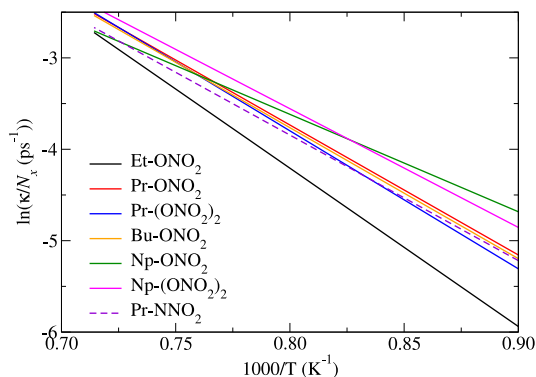
**Table 3. Best Fit Pre-Exponential Factors and Activation Energies for the Normalized Rates of Trigger Linkage Rupture from QMD**

	$\ln(A)$ (ps <sup>-1</sup> )	$E_a$ (eV)
Et-ONO <sub>2</sub>	9.64 ± 0.60	1.49 ± 0.06
Pr-ONO <sub>2</sub>	7.64 ± 0.53	1.23 ± 0.06
Pr-(ONO <sub>2</sub> ) <sub>2</sub>	8.27 ± 0.56	1.30 ± 0.06
Bu-ONO <sub>2</sub>	7.69 ± 0.60	1.24 ± 0.04
Np-ONO <sub>2</sub>	4.90 ± 0.47	0.92 ± 0.05
Np-(ONO <sub>2</sub> ) <sub>2</sub>	6.83 ± 0.35	1.12 ± 0.04
Pr-NNO <sub>2</sub>	7.14 ± 0.53	1.18 ± 0.06

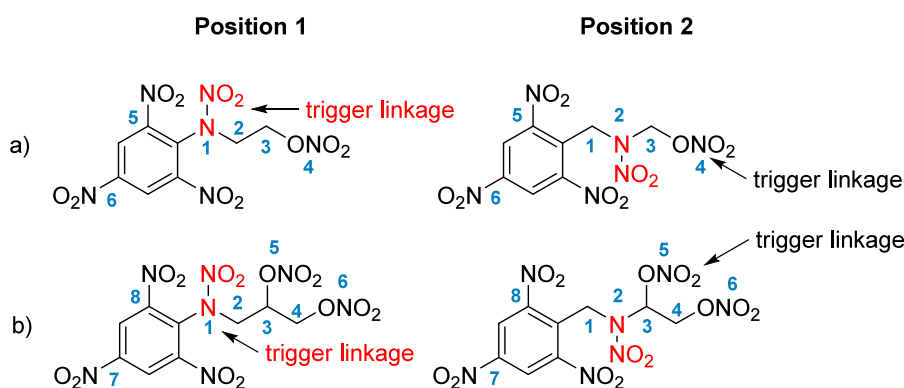
different chemistry and trigger linkages require significantly different temperatures than those used in this work for reaction on the same time scales (see, for example, refs. 27 and 53). In addition, Figure 1 shows that the rates for the two propane derivatives, Pr-ONO<sub>2</sub> and Pr-(ONO<sub>2</sub>)<sub>2</sub>, and two neopentane derivatives, Np-ONO<sub>2</sub> and Np-(ONO<sub>2</sub>)<sub>2</sub>, are practically indistinguishable. The activation energies and pre-exponential factors, Table 3, differ more notably owing to the kinetic compensation effect via the numerical uncertainties in the data. The normalized rate for the single butane derivative, Bu-ONO<sub>2</sub>, is similar to those of the two propane derivatives, while that of Et-ONO<sub>2</sub> is marginally slower than those of the other five molecules. Based on the common reaction mechanisms and trigger linkages it was expected that the six molecules would have broadly similar reaction rates when normalized by  $N_x$ , but it is also encouraging that our simulation methodology can also reliably distinguish between molecules by their unreactive aliphatic backbones, that is, Et-ONO<sub>2</sub> < Bu-ONO<sub>2</sub> ≈ Pr-ONO<sub>2</sub> ≈ Pr-(ONO<sub>2</sub>)<sub>2</sub> < Np-ONO<sub>2</sub> ≈ Np-(ONO<sub>2</sub>)<sub>2</sub>.

The QMD simulations of the six molecules showed consistently that the nitropicamide N-NO<sub>2</sub> bond ruptures first in the gas-phase under thermal activation. The O-NO<sub>2</sub> bonds are generally considered to be weaker than N-NO<sub>2</sub> bonds, which accounts for the relative impact sensitivities of nitramine and nitrate-ester-based explosives. To verify that the results obtained from the QMD simulations are not an artifact of the limited transferability of the *lanl31* DFTB parametrization, X-NO<sub>2</sub> and C-ONO<sub>2</sub> bond dissociation energies were computed for Et-ONO<sub>2</sub> and Pr-(ONO<sub>2</sub>)<sub>2</sub> using both DFTB-*lanl31* and more accurate and reliable DFT methods. For both Et-ONO<sub>2</sub> and Pr-(ONO<sub>2</sub>)<sub>2</sub> we have additionally studied how the N-NO<sub>2</sub> bond dissociation energy depends on the position of the nitramine group on the aliphatic chains, which are depicted in Figure 2. These results are presented in Tables 3 and 4 for the two isomers of Et-ONO<sub>2</sub> and Pr-(ONO<sub>2</sub>)<sub>2</sub>, respectively.

The DFT calculations of the bond dissociation energies used B3LYP/6-31G\* to perform geometry optimizations and B3LYP/cc-pVTZ to compute the total energies within the Gaussian16 package.<sup>55</sup> The DFTB calculations used the FIRE



**Figure 1.** Arrhenius plot for the reaction rates of the nitrate ester/nitropicamide derivatives.



**Figure 2.** Molecules used in bond dissociation energy calculations: (a) Et-ONO<sub>2</sub> and (b) Pr-(ONO<sub>2</sub>)<sub>2</sub>. The sets of X-NO<sub>2</sub> and C-ONO<sub>2</sub> bond dissociation energies are calculated with the nitramine, NNO<sub>2</sub>, groups at the 1 and 2 positions.

**Table 4. Bond Dissociation Energies Calculated for Et-ONO<sub>2</sub> Using DFT (B3LYP/cc-pVTZ//6-31G\*) and the *lanl31* DFTB Parameterization<sup>a</sup>**

Et-ONO <sub>2</sub>	NNO <sub>2</sub> position 1		NNO <sub>2</sub> position 2	
	B3LYP/cc-pVTZ//6-31G* (eV)	DFTB- <i>lanl31</i> (eV)	B3LYP/cc-pVTZ//6-31G* (eV)	DFTB- <i>lanl31</i> (eV)
C-NO <sub>2</sub> (6)	2.80	3.66	-	-
C-NO <sub>2</sub> (5)	2.60	3.31	-	-
N-NO <sub>2</sub>	<b>1.27</b>	<b>1.85</b>	1.71	2.39
O-NO <sub>2</sub> (4)	1.58	2.20	<b>1.46</b>	<b>1.77</b>
C-ONO <sub>2</sub> (3)	3.36	3.04	3.06	2.75

<sup>a</sup>The smallest dissociation energies for the molecule with the nitramine groups at the 1 and 2 positions are denoted by bold text.

**Table 5. Bond Dissociation Energies Calculated for Pr-(ONO<sub>2</sub>)<sub>2</sub> Using DFT (B3LYP/cc-pVTZ//6-31G\*) and the *lanl31* DFTB Parameterization<sup>a</sup>**

Pr-(ONO <sub>2</sub> ) <sub>2</sub>	NNO <sub>2</sub> position 1		NNO <sub>2</sub> position 2	
	B3LYP/cc-pVTZ//6-31G* (eV)	DFTB- <i>lanl31</i> (eV)	B3LYP/cc-pVTZ//6-31G* (eV)	DFTB- <i>lanl31</i> (eV)
C-NO <sub>2</sub> (7)	2.79	3.69	2.84	3.69
C-NO <sub>2</sub> (8)	2.50	3.35	2.32	3.40
N-NO <sub>2</sub>	<b>1.28</b>	<b>1.83</b>	1.41	2.18
O-NO <sub>2</sub> (5)	1.57	1.99	<b>1.16</b>	<b>1.81</b>
O-NO <sub>2</sub> (6)	1.56	2.24	1.57	-
C-ONO <sub>2</sub> (3)	3.18	2.80	2.54	2.47
C-ONO <sub>2</sub> (4)	3.32	3.21	3.22	3.01

<sup>a</sup>The smallest dissociation energies for the molecule with the nitramine groups at the 1 and 2 positions are denoted by bold text.

algorithm<sup>56</sup> to optimize the geometries of the molecules and fragments until the maximum force acting on any atom was less than 0.001 eV/Å. The Mulliken spin states of the fragments were calculated self-consistently using the formalism outlined in refs. 53 and 57 (Tables 4 and 5).

Both the DFT and DFTB-calculations show that the N-NO<sub>2</sub> bond has the lowest bond dissociation energy—lower than those of the O-NO<sub>2</sub> and C-NO<sub>2</sub> bonds - when the nitramine groups are in the '1' position immediately adjacent to the TNB group (Figure 2). The corresponding N-NO<sub>2</sub> bond dissociation energies are 1.27 and 1.85 eV from DFT and DFTB, respectively for Et-ONO<sub>2</sub> and 1.28 and 1.83 eV from DFT and DFTB, respectively, for Pr-(ONO<sub>2</sub>)<sub>2</sub>. Furthermore, both methods show that if the nitramine group is instead in the '2' position, the O-NO<sub>2</sub> bond has the smallest dissociation energy. To confirm the switch of the trigger linkage from the nitramine to the nitrate ester when the nitramine is in position '2', a set of QMD simulations on the isomer of Et-ONO<sub>2</sub> (Figure 2(a)) were performed, in which the first reactions occurred overwhelmingly via the rupture of the O-NO<sub>2</sub> bond.

The C-NO<sub>2</sub> and C-ONO<sub>2</sub> bond dissociation energies calculated by DFT and DFTB were found to be significantly larger than those of either the N-NO<sub>2</sub> or O-NO<sub>2</sub> dissociation energies, which accounts for why those reactions were never seen in the QMD calculations.

We postulate that the strongly electron withdrawing character of the TNB group is responsible for weakening the N-NO<sub>2</sub> bond in the '1' position such that it becomes the trigger linkage. To confirm this interpretation, we performed DFT and DFTB calculations of N-NO<sub>2</sub> bond dissociation energies in two series of nitropicramides where we (i) varied the electronegativity of the neighboring nitrobenzene group through adding or subtracting nitro groups and (ii) increased the separation of the N-NO<sub>2</sub> from the TNB functional group (Supporting Information). These calculations showed that the N-NO<sub>2</sub> bond is longer and weaker (smaller dissociation energy) when electrons are withdrawn from it via increasing electronegativity of the adjacent group and that the strength of the N-NO<sub>2</sub> bond increases systematically as the number of C-C bonds between the TNB and NNO<sub>2</sub> increases. This picture

is consistent with recent theoretical work that indicated that X-NO<sub>2</sub> bonds can be considered to be charge shift bonds whose strength is affected by the electronegativity of adjacent groups.<sup>58</sup>

Previous studies have shown that the accuracy of the binding energies obtained from the *lanl31* DFTB parametrization with respect to DFT is about 10 kcal/mol, or 0.5 eV.<sup>59</sup> The bond dissociation energies presented in Tables 4,5, and the Supporting Information are consistent with errors in the DFTB total energies of this magnitude. Nevertheless, the DFTB calculations accurately capture the major trends seen in the DFT calculations and the dependences of the dissociation energies on the relative positions of the energetic groups within the molecules.

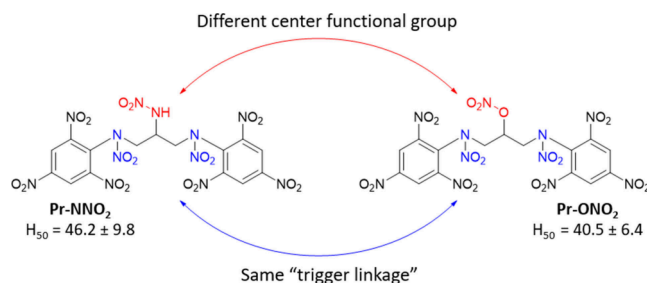
The drop weight impact sensitivities of the set of six nitropicramide/nitrate ester explosives, with the exceptions of Pr-(ONO<sub>2</sub>)<sub>2</sub> and Np-ONO<sub>2</sub>, are in the vicinity  $H_{50} \approx 40 \pm 10$  cm. The similarities between the impact sensitivities can be explained theoretically by QMD and DFT simulations that indicate that all the molecules have (i) the same N-NO<sub>2</sub> trigger linkage, (ii) similar specific enthalpies of explosion,  $Q$ , and (iii) similar reaction rates in the gas phase. The impact sensitivity of Pr-(ONO<sub>2</sub>)<sub>2</sub> is marginally higher than those of the other molecules,  $H_{50} = 19 \pm 3$  cm, which can be explained by its relatively large specific enthalpy of explosion,  $Q = 1.22$  kcal/g, that arises from its additional nitrate ester group. A large specific enthalpy of explosion can increase sensitivity by promoting exothermic runaway via the classic Frank-Kamenetskii model of the adiabatic induction time,

$$\frac{1}{t_{\text{adb}}} = \frac{QAE_a}{C_V k_B T^2} \exp\left(\frac{-E_a}{k_B T}\right) \quad (1)$$

where  $A$  and  $E_a$  are the pre-exponential factor and activation enthalpy for the Arrhenius reaction kinetics of the explosive,  $C_V$  the heat capacity at constant volume,  $T$  the temperature, and  $k_B$  the Boltzmann constant.<sup>60</sup> Here, a large enthalpy of explosion increases the rate of self-heating that precedes a thermal explosion. Empirical results also suggest a more sensitive connection between the enthalpy of explosion and  $H_{50}$  where the effective activation energy for the onset of a thermal explosion is reduced via the Bell-Evans-Polanyi principle, that is,  $E'_a = E_a - \alpha Q$ , where  $\alpha$  is a small positive constant.<sup>27,47–49</sup>

The sensitivity of Np-ONO<sub>2</sub>,  $H_{50} = 91 \pm 15$  cm, is an outlier with respect to the other five molecules and the three nitropicramides in ref. 39. Nevertheless, the drop weight impact test is relatively imprecise because the phenomena leading to ignition, which include fracture, plastic flow, melting, and viscous heating, are complex and the diagnostics for a “go” are just two microphones with an empirically established sound threshold. As a result, the uncertainty inherent to the drop weight test has been estimated to be a multiplicative factor of 1.5.<sup>61</sup> Hence, this outlier result could still be considered within the range of the other sensitivity measurements, but further studies will be required to establish the reproducibility of this result.

Further evidence for the N-NO<sub>2</sub> bond acting as the trigger linkage in the nitropicramide/nitrate ester derivatives can be seen through comparing Pr-ONO<sub>2</sub>, which is described in this work, with Pr-NNO<sub>2</sub> which was recently reported in ref.<sup>39</sup> The two molecules, which are depicted in Figure 3, are identical, with the only difference being the energetic functional group in



**Figure 3.** Impact sensitivity and highlighted trigger linkages for molecules Pr-NNO<sub>2</sub> and Pr-ONO<sub>2</sub>.

the center of the molecule: Pr-NNO<sub>2</sub> contains a central nitramine group, whereas Pr-ONO<sub>2</sub> has a nitrate ester. The drop weight impact sensitivities of the two molecules are identical to within the uncertainties of the measurements, with  $H_{50} = 46 \pm 10$  and  $41 \pm 6$  cm, for Pr-NNO<sub>2</sub> and Pr-ONO<sub>2</sub>, respectively. Hence the presence of the ONO<sub>2</sub> group on Pr-ONO<sub>2</sub> does not sensitize this molecule with respect to Pr-NNO<sub>2</sub>, which we propose is possible only if the nitropicramide groups, which are common to both molecules, dictate the overall sensitivity. Quantum molecular dynamics simulations of the rate of trigger linkage rupture in Pr-NNO<sub>2</sub> were performed (Figure 1 and Table 3), which seem confirm the validity of this model, that is, the first reactions in Pr-NNO<sub>2</sub> took place at the nitramines adjacent to the TNB groups and the resulting reaction rates for Pr-ONO<sub>2</sub> and Pr-NNO<sub>2</sub> are indistinguishable to within the uncertainty in the numerical data. This combined theoretical and experimental analysis gives an example of a unique, well-controlled molecular system where we have changed the trigger linkage from the typical nitrate ester to the nitramine through molecular design.

We have reported the synthesis and characterization of six new nitropicramide/nitrate ester derivatives. Impact sensitivity analysis showed that five of the six materials have very similar  $H_{50}$  values. Interestingly, QMD modeling and DFT calculations identified the trigger linkages in these molecules as the N-NO<sub>2</sub> bond adjacent to the trinitrobenzene rings, rather than the nitrate esters. When the N-NO<sub>2</sub> bond is directly adjacent to the trinitrobenzene ring, the trigger linkage shifts from the typically expected O-NO<sub>2</sub> bond to the N-NO<sub>2</sub> bond, which is weakened by its proximity to the strongly electron-withdrawing TNB group. This model is supported by previous measurements of the impact sensitivity of the related compound Pr-NNO<sub>2</sub>, which lacks a nitrate ester group. We also find that Pr-(ONO<sub>2</sub>)<sub>2</sub> is slightly more sensitive than the other five molecules because of its superior specific enthalpy of explosion. Therefore, the impact sensitivities of the six nitropicramide/nitrate esters can be rationalized by our chemical kinetics model by (i) identifying the nitropicramide N-NO<sub>2</sub> bond as the trigger linkage and (ii) assessing the enthalpies of explosion.

## ■ ASSOCIATED CONTENT

### Data Availability Statement

CIF files for crystal structures have been uploaded to the CCDC with the following deposition numbers: CCDC 2411065–2411066.

### Supporting Information

The Supporting Information is available free of charge at <https://pubs.acs.org/doi/10.1021/acs.jpcllett.4c03306>.

NMR spectra, synthetic procedures for novel materials, impact, friction, and spark sensitivity data for all energetic materials reported, DSC data for all energetic materials reported, crystal structures information, and computation analysis details (PDF)

Transparent Peer Review report available (PDF)

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### Notes

The authors declare no competing financial interest.

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