

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

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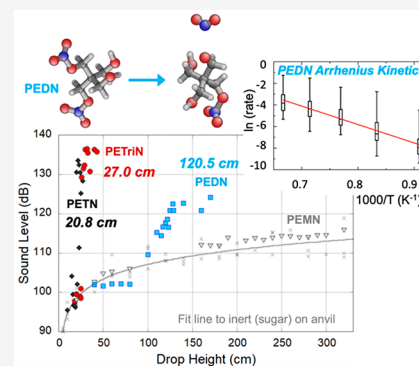
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**ABSTRACT:** Energetic materials undergo hundreds of chemical reactions during exothermic runaway, generally beginning with the breaking of the weakest chemical bond, the “trigger linkage.” Herein we report the syntheses of a series of pentaerythritol tetranitrate (PETN) derivatives in which the energetic nitrate ester groups are systematically substituted by hydroxyl groups. Because all the PETN derivatives have the same nitrate ester-based trigger linkages, quantum molecular dynamics (QMD) simulations show very similar Arrhenius kinetics for the first reactions. However, handling sensitivity testing conducted using drop weight impact indicates that sensitivity decreases precipitously as nitrate esters are replaced by hydroxyl groups. These experimental results are supported by QMD simulations that show systematic decreases in the final temperatures of the products and the energy release as the nitrate ester functional groups are removed. To better interpret these results, we derive a simple model based only on the specific enthalpy of explosion and the kinetics of trigger linkage rupture that accounts qualitatively for the decrease in sensitivity as nitrate ester groups are removed.



The initiation of runaway exothermic reactions in an energetic material involves a spectrum of complex phenomena that generally begins with the temperature input, often via hot spots,<sup>1</sup> required to break the weakest intramolecular bonds, or “trigger linkages”. Those reactions can either quench or propagate to a self-sustaining deflagration depending on the interplay between the reaction rates, the energy release from the reactions, and dissipation to the environment.<sup>2–5</sup> Hence, explosive sensitivity depends, in part, on the rates of the first reactions and the performance of the explosive. In order to understand the relative importance of these factors, we have designed and synthesized a molecular system based on pentaerythritol tetranitrate (PETN) where the underlying chemistry, via the trigger linkages, was held constant, while we systematically varied the explosive performance via the heat of explosion,  $Q$ .

The drop-weight impact test is the most widely utilized small-scale test to evaluate explosive safety during the initial design stage. Although there is a high degree of variability in the results of the impact test,<sup>6</sup> in practice, general trends in the sensitivity of energetic materials have emerged from large-scale studies. These include the importance of oxygen balance, heat of explosion, and the type of energetic functional group, all of which can be connected to trigger linkage strength and/or explosive performance.<sup>7–14</sup> More recently, our group and others have investigated systematic changes to molecular structure, hydrogen and intermolecular bonding, and physical properties in order to modify explosive sensitivity.<sup>15–21</sup>

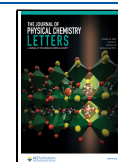
Specifically, we have investigated how changes to the PETN backbone correlate with handling sensitivity.<sup>19,22,23</sup>

Hundreds or thousands of unique reactions can occur in explosives on the time scale of the impact test. Nevertheless, reliable single-step Arrhenius kinetics,  $\kappa = A \exp(-E_a/k_B T)$ , where  $\kappa$  is a rate,  $A$  the pre-exponential factor,  $E_a$  the activation enthalpy,  $k_B$  the Boltzmann constant, and  $T$  the temperature, which collate all of the reaction steps leading up to an explosion into a single pre-exponential factor and activation enthalpy, have been obtained from both experiment and simulation.<sup>24–26</sup> The single-step time-to-explosion kinetics measured by Wenograd in the 1960s<sup>27</sup> and subsequent studies at Los Alamos by Storm et al. using Rogers’ single-step kinetics showed that the impact sensitivity of an energetic material depends partly on the critical temperature that is required to start a detectable deflagration on the 250  $\mu$ s duration of the drop weight test.<sup>7,28</sup> These results were confirmed theoretically using Arrhenius kinetics for the time-to-explosion as a function of temperature obtained from condensed-phase quantum molecular dynamics (QMD) simulations.<sup>29</sup> We have also employed ensembles of reactive gas-phase QMD simulations

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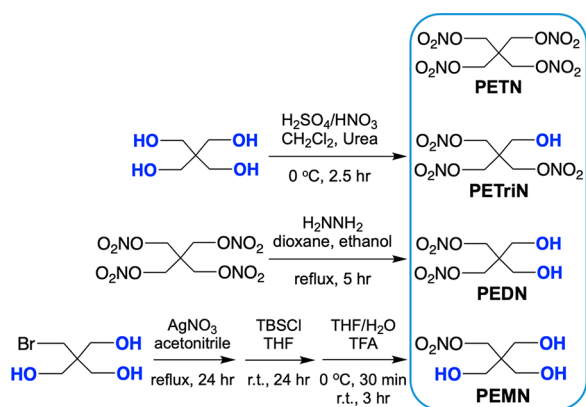
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to evaluate directly the kinetics of trigger linkage rupture, which showed a similar strong correlation with experimental impact sensitivity. These results imply that the relatively simple kinetics of trigger linkage rupture, which are based only on the first reactions, are a good surrogate for the kinetics of an explosive to undergo thermal runaway.

The correlation between explosive performance and sensitivity is well-known since, in general, the most powerful explosives are also the most sensitive. Both the body of work from Zeman<sup>12,30,31</sup> and recent studies by our team<sup>32</sup> find that the Bell-Evans–Polanyi principle<sup>33,34</sup> provides the best description of the dependence between sensitivity and performance, through the specific heat of explosion,  $Q$ . Understanding sensitivity trends in an explosive system in which the energy release is changed while maintaining the trigger linkage chemistry is difficult, because modifications to molecular structure often change a range of physical properties, such as melting point, density, and crystal packing, all of which are thought play a role in determining handling sensitivity. In this work we investigate the explosive PETN and its hydroxyl-based analogs, namely, PETriN, PEDN, and PEMN (Scheme 1). Modification of PETN in this manner allows for

**Scheme 1. Chemical Structures and Syntheses of PETriN, PEDN, and PEMN**



preservation of the  $-ONO_2$  trigger linkage chemistry while systematically altering the heat of explosion. We evaluate their experimental drop-weight impact sensitivity values,  $H_{50}$ , as we replace the energetic nitrate ester functional group with inert hydroxyl groups, and we calculate reaction rates and heats of explosion in order to probe the importance of trigger linkage/functional group versus overall energy output. Finally, we derive a simple model that accounts for the precipitous decrease in sensitivity as nitrate ester groups are substituted. To our knowledge, this is the first example of the analysis of an explosive system where the trigger linkage is held constant with systematic changes in energy release. This study is particularly

timely, considering the recent interest in explosive design in numerous seemingly disparate fields of study, from the synthesis of new energetics,<sup>35–37</sup> the computational design of new explosives,<sup>38</sup> to the machine learning-based evaluation of large historical data sets for the importance of various molecular descriptors in influencing impact sensitivity.<sup>39–44</sup>

The following synthesized energetic molecules react to stimuli such as impact, spark, and friction and should only be prepared by trained explosives handlers with the proper safety precautions. The hydroxyl derivatives of PETN (Scheme 1) are commonly made either through a reduction of PETN or a nitration of pentaerythritol. In addition to their potential medicinal properties,<sup>45</sup> PETriN and PEDN are known thermal, radiation, and biological decomposition products of PETN.<sup>46</sup> PETriN was synthesized following a patent procedure<sup>47</sup> in which pentaerythritol was nitrated using a mixed acid synthesis in the presence of dichloromethane. The use of dichloromethane prevents full nitration of the pentaerythritol to PETN. PEDN was synthesized through a hydrazine reduction of PETN<sup>48</sup> in which two of the nitrate esters are reduced to the alcohol. Finally, PEMN was synthesized using a modified procedure<sup>48</sup> where a bromide-substituted pentaerythritol substrate is reacted with silver nitrate in acetonitrile (Scheme 1). Purification of PEMN is difficult using common chromatography practices due to the highly polar nature of the material. We developed a procedure to purify PEMN through protection of the alcohol groups with *tert*-butyldimethylsilyl chloride, followed by removal of the protecting groups in an acid-based workup.

Drop-weight impact sensitivity testing was conducted by placing a 40 mg sample of material between a steel anvil and 0.8 kg striker. A 2.5 kg weight was adjusted to different heights and dropped on the material. When the material generated an average sound reading of higher than 117 dB on the two sound meters, an energetic event was determined to have occurred, and the drop was considered a “Go.”<sup>49</sup> The higher the drop height needed to cause a go, the less sensitive the material is determined to be. A series of at least 15 drops from various heights was performed and then analyzed using the Neyer statistical method to determine the height (and therefore energy) at which 50% of the samples react ( $H_{50}$ ).<sup>50</sup>

Drop heights from impact testing are given in Table 1, along with friction, electrostatic discharge, and calorimetry data. For consistency, all of the impact data presented in Table 1 were collected using the Type 12B tool on a bare anvil with a polished steel striker, though tests run with standard grit paper (Type 12) gave similar results for the PETN derivatives (Supporting Information). In this system of PETN derivatives, the loss of each nitrate ester functional group led to a decrease in the impact sensitivity of the material (i.e., an increase in  $H_{50}$ ). Consistent with literature data,<sup>6</sup> PETN (s) has a drop height of  $20.8 \pm 4.3$  cm when collected on a bare anvil. The

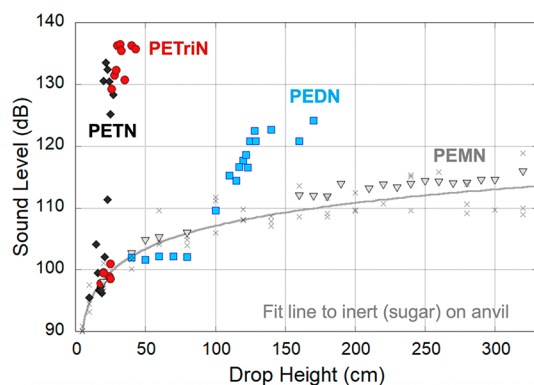
**Table 1. Sensitivity Data and Sound Levels for PETN and Hydroxyl PETN Derivatives at Room Temperature**

material <sup>a</sup>	impact $DH_{50}$ (cm)	average sound level (dB) for “Go” <sup>b</sup>	average sound level (dB) for “No Go”	friction $DH_{50}$ (N)	electrostatic discharge (J)	DSC (°C) melt/decomp onset <sup>b</sup>
PETN (s)	$20.8 \pm 4.3$	$130 \pm 3$	$100 \pm 5$	$56.0 \pm 2.2$	0.0625	140.87/165.26
PETriN (l)	$27.0 \pm 2.2$	$134 \pm 3$	$99 \pm 1$	> 360	0.0625	--/163.95
PEDN (l)	$120.5 \pm 3.4$	$121 \pm 2$	$108 \pm 7$	> 360	0.0625	--/166.4
PEMN (s)	>320	--	$111 \pm 5$	> 360	0.0625	57.7/162.4

<sup>a</sup>Solids are designated as (s), and liquids are designated as (l). <sup>b</sup>The use of “--” indicates that no data is available.

drop height of PETriN (1) was found to be higher, at  $27.0 \pm 2.0$  cm, indicating a less-sensitive explosive. In general, liquids typically exhibit smaller drop heights than solids for a given material<sup>16</sup> because they have different mechanisms for ignition under impact testing conditions.<sup>51</sup> PEDN was generally isolated as an oil, though it could sometimes be purified as a solid. Both phases of the material were tested for impact sensitivity, with similar values of  $\sim 120$  cm, even with differences in phase and grit paper (Supporting Information). PEMN was also isolated as an oil or waxy solid and only exhibited borderline Go reactions at the maximum height of the impact drop tower (320 cm).

Recent analyses of drop-weight impact test decibel levels indicated that well-behaved explosives (i.e., those that do not undergo partial reactions with unreacted material left on the anvil after a go) exhibit an “S”-shaped curve in a plot of drop height versus sound level.<sup>52,53</sup> We hypothesized that, in the drop weight impact test, explosives with more energetic groups would generate larger decibel readings during reaction due to their larger specific heat of explosion and gas releases and that the sound levels would decrease systematically as explosive groups were sequentially removed. Figure 1 gives the sound



**Figure 1.** Sound levels in dB for PETN and all hydroxyl derivatives, vs drop height (in cm) on a bare anvil, showing PETN (black diamonds), PETriN (red circles), PEDN (blue squares), PEMN (gray triangles), and inert sugar (small gray  $\times$ ). A best-fit line is given for the sugar, in order to show where sound levels should generally be for inert materials. The S-shaped curve is most clearly visible in the PEDN sound levels.

level of each drop for each PETN derivative, and Table 1 shows the average sound levels collected for each PETN derivative during a Go as well as averages obtained for each “No Go” (partial or no reaction). PETN, PETriN, and PEDN generated the expected S-curve behavior (see Supporting Information for an expanded view of PETN and PETriN), with maximum sound levels for PEDN (121–124 dB) that were

significantly lower than those of PETN and PETriN (129–134 dB). Most sound levels for PEMN fell below the threshold to be considered a Go, at the approximate sound level expected for an inert material in this test.<sup>53</sup>

Static total energy and reactive gas-phase and condensed-phase QMD simulations have been performed for the PETN derivatives using density functional tight binding (DFTB) theory with the *lanl31* parametrization for molecules containing C, H, N, and O. Details on how the simulations were set up and performed are provided in the Supporting Information.

The energy release for the four molecules has been estimated by two methods. First, the gas-phase heat of formation,  $\Delta H_f$ , of the PETN derivatives was computed from the total DFTB energy,  $u$ , using the seven-parameter atom-equivalent energies developed for the *lanl31* parametrization in ref 54. The DFTB-predicted  $\Delta H_f$  presented in Table 2 are within a few kcal/mol of those obtained from the more computationally expensive density functional theory-based formalism of Byrd and Rice<sup>55</sup> (Supporting Information). The heat of explosion,  $Q$ , is obtained from the difference in the heat of formation between the reactants and products

$$Q = \frac{-1}{\text{Mol. Wt.}} \left( \sum_i n_i (\Delta H_f^p)_i - \Delta H_f^r \right) \quad (1)$$

where  $n_i$  is the number of moles of product species,  $i$ , with heat of formation  $(\Delta H_f^p)_i$  derived from one mole of reactants (Mol. Wt. indicates molecular weight).<sup>56</sup> The quantities and types of the product species are assumed to be fully determined by the stoichiometry of the reactants according to the oxidation priority established in ref 57, and the corresponding  $\Delta H_f^p$  values were obtained from the NIST Chemistry WebBook.<sup>58</sup> The molar and specific heats of explosion are given in Table 2, which clearly reflect the expected decrease in explosive performance when energetic nitrate ester groups are replaced by inert hydroxy groups.

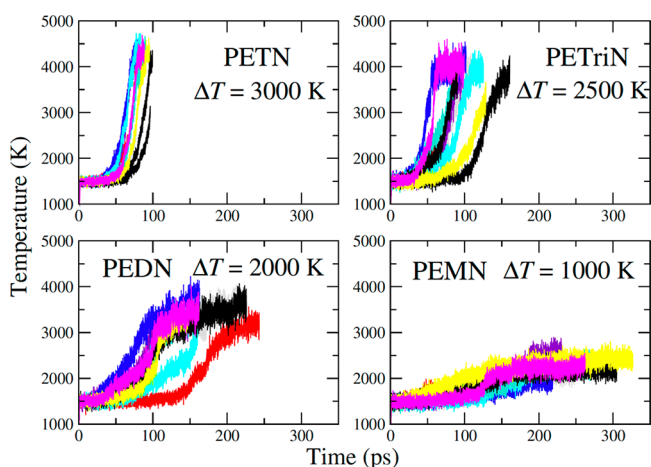
Our second approach to estimating the energy release from the derivatives during thermal explosion used a series of condensed-phase QMD simulations in the microcanonical ensemble. The extended Lagrangian Born–Oppenheimer MD formalism of Niklasson et al. was used to ensure the long-term stability of the trajectories and the precise conservation of the total energy during reactions.<sup>59–62</sup> As in refs 19, 29, and 65, the conservation of the total energy before, during, and after the thermal explosion leads to a precipitous increase in the kinetic temperature during the exothermic runaway stage. The simulations of crystalline PETN at its ambient density,  $\rho = 1.78$  g/cm<sup>3</sup>, used a  $2 \times 2 \times 2$  periodic supercell containing 16 molecules, while simulations of liquid PETriN, PEDN, and PEMN used periodic supercells containing eight molecules at

**Table 2.** DFTB-Calculated Heat of Formations,  $\Delta H_f$ , Enthalpies of Explosion,  $Q$ , Number of Nitrate Ester Groups,  $N_x$ , and the Pre-Exponential Factors,  $\hat{A}$ , Activation Enthalpies,  $E_a$ , for the Rates of Trigger Linkage Rupture for PETN, PETriN, PEDN, and PEMN from DFTB-MD<sup>a</sup>

material	$\Delta H_f$ (kcal/mol)	$Q_m$ (kcal/mol)	$Q$ (kcal/g)	$N_x$	$\hat{A}$ (ps <sup>-1</sup> )	$E_a$ (eV)
PETN	-106.1	463.8	1.47	4	$1196 \pm 414$	$1.40 \pm 0.04$
PETriN	-121.8	308.2	1.14	3	$1013 \pm 321$	$1.38 \pm 0.03$
PEDN	-134.0	238.7	1.06	2	$1318 \pm 443$	$1.39 \pm 0.04$
PEMN	-148.1	188.0	1.04	1	$3162 \pm 1092$	$1.47 \pm 0.04$

<sup>a</sup>The mean errors in the predicted  $\Delta H_f$  are estimated to be  $\pm 10.4$  kcal/mol.

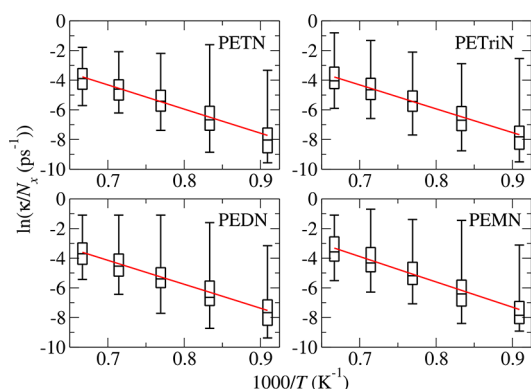
the mass densities estimated by dispersion-corrected DFTB simulations in the isothermal–isobaric ensemble (Supporting Information). The evolution of the temperature in 10 independent simulations of PETN, PETriN, PEDN, and PEMN after thermalization to an initial temperature of 1500 K are presented in Figure 2. These results illustrate clearly the



**Figure 2.** Evolution of the kinetic temperature in PETN, PETriN, PEDN, and PEMN during thermal explosions from DFTB MD simulations in the microcanonical ensemble.

decrease in the performance and energy output as nitrate ester groups are replaced by hydroxyl groups, as depicted by the systematic decreases in both the final temperature of the products and the rates of energy release.

The “strength” of the trigger linkages in the four molecules was estimated from the Arrhenius rates associated with thermally breaking any covalent bond within the molecules in the gas phase.<sup>29,54,63</sup> The rates were computed from gas-phase QMD simulations, which were performed in the canonical ensemble using a Langevin thermostat<sup>64</sup> to control the temperature (Supporting Information). Ensembles of 200 independent trajectories at temperatures from 1100 to 1500 K were analyzed to determine the time,  $\tau$ , required to break any covalent bond.<sup>29,65</sup> These results are presented in Arrhenius plots in Figure 3. Because we found that the first bonds to break in all four molecules are associated overwhelmingly with



**Figure 3.** Arrhenius plots derived from ensembles of normalized time-to-reaction data,  $\kappa/N_x$ , from gas-phase QMD simulations of PETN, PETriN, PEDN, and PEMN. The ranges of the rates of bond-breaking events obtained from our QMD simulations are depicted by the box-and-whisker symbols.

the  $-\text{ONO}_2$  groups, we have presented the rates,  $\kappa = 1/\tau$ , normalized by the number of nitrate ester groups per molecule,  $N_x$ . Linear regressions to the normalized rates as a function of inverse temperature show that the strengths of the trigger linkages are very similar, that is, the normalized rates are the same to within statistical uncertainties. The activation enthalpies,  $E_a$ , and pre-exponential factors,  $\hat{A}$ , presented in Table 2 are also very similar but exhibit greater variation between the molecules, which we attribute to the so-called kinetic compensation effect that arises from linear regressions to noisy data.<sup>66</sup>

While the chemistry and trigger linkage kinetics of the four PETN derivatives are clearly very similar, our drop weight impact testing reveals a precipitous increase in  $H_{50}$  when nitrate esters are replaced by hydroxyl groups. In a recent publication,<sup>32</sup> we proposed that drop weight impact sensitivity depends jointly on the kinetics of trigger linkage rupture and the enthalpy of explosion via

$$H_{50} \propto \frac{1}{A \exp(-(E_a - \alpha Q)/k_B T)} \quad (2)$$

where  $\alpha$  is a positive constant. It follows from eq 2 and the observation that this set of derivatives have similar normalized rates, activation enthalpies,  $E_a$ , and pre-exponential factors,  $\hat{A}$ , that the variation of  $H_{50}$  across the series should follow

$$H_{50} \approx H_{50}^0 \left( \frac{N_x^0}{N_x} \right) \exp(\gamma(Q^0 - Q)) \quad (3)$$

where the superscript “0” denotes those parameters for a reference molecule in the series of derivatives, and  $\gamma$  is a constant. Equation 3 indicates that  $H_{50}$  should increase relative to that of PETN as nitrate ester groups are removed through two routes: the first is connected to the slower rates of trigger linkage rupture, in an absolute sense when  $N_x$  decreases, while the second and dominant term is the predicted exponential dependence of  $H_{50}$  on the decrease of the heat of explosion,  $Q^0 - Q$ , when  $\text{ONO}_2$  groups are lost. The parameter  $\gamma$  was fitted to drop weight impact data<sup>7</sup> on small sets of nitrotoluene, nitroaniline, and nitrobenzene explosives that have different numbers of  $\text{NO}_2$  groups, plus the set of PETN derivatives described here (see Supporting Information). We obtained a value of about  $\gamma \approx 1.6$  g/kcal, but we found that  $\gamma$  is somewhat system-dependent. Equation 3, which depends only on gas-phase thermochemistry, accounts for at best 70% of the variation in  $\ln(H_{50})$ , and we attribute the remaining 30% of the variation to condensed phase properties and chemistry that are not captured by the model.<sup>32</sup> The intrinsic limitations associated with eq 3 and the small numbers of families of explosive molecules that are suitable for parametrization of  $\gamma$  lead inevitably to significant uncertainties in the values of  $\gamma$ . Nevertheless, eq 3, which is a physically transparent model for explosive chemical kinetics, accounts naturally for the precipitous increase in  $H_{50}$  observed experimentally for both the PETN derivatives studied here and historic data<sup>7</sup> obtained for several sets of nitrobenzene derivatives. These results are also consistent with the trends predicted for  $H_{50}$  across the same sets of nitrobenzene derivatives by other rate-based models of impact sensitivity.<sup>67</sup>

Using this system of PETN derivatives, we were able to systematically evaluate—both experimentally and computationally—the influence on explosive kinetics and energy release as we replaced energetic functional groups with inert hydroxyl

groups. As shown in Table 2 and Figure 3, the trigger linkage kinetics of the PETN derivatives are very similar because all have nitrate ester functional groups. However, experimental results from drop weight impact testing indicate lower generated sound levels (Figure 1) and sensitivities as nitrate esters are replaced by hydroxyl groups, which are consistent with a decrease in the heat of explosion. Our condensed-phase QMD simulations of the four molecules emphasize the critical role played by the heat of explosion in determining the sensitivity in molecules with otherwise identical trigger linkages. Figure 2 shows that, with the exception of a few trajectories, all of the simulations started reacting within the first 50 ps, which is consistent with identical trigger linkage strength and the different numbers of trigger linkages within each simulation, but we see systematically longer times to the completion of the reactions, from about 75 to 200 ps for PETN and PEMN, respectively, as  $Q$  decreases because the smaller energy release hinders the acceleration of the reactions toward a thermal explosion.

This study directly validates previous models that emphasize the importance of both functional group and heat of explosion in predicting energetic sensitivity. Critically, in addition to guiding future explosives design, these results will direct the rapidly emerging fields of explosive synthesis, computational chemistry, and use of machine-learning approaches to understand the wealth of existing impact test data results in the literature.

## ■ ASSOCIATED CONTENT

### SI Supporting Information

The Supporting Information is available free of charge at <https://pubs.acs.org/doi/10.1021/acs.jpcllett.2c02701>.

Synthesis, testing, and QMD information (PDF)

Transparent Peer Review report available (PDF)

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### Author Contributions

All authors have given approval to the final version of the manuscript.

## Notes

The authors declare no competing financial interest.

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