Computational studies of impact sensitivity in energetic plasticizers

– using DFT on BuNENA, MeNENA and DINA

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Summary

Energetic materials are key constituents in rocket propellants. Modern solid rocket propellants contain energetic plasticizers, whose purpose is to adjust propellant properties such as thermal stability, energy content, mechanical properties, oxygen balance and burning behavior. We studied the impact sensitivity of three such energetic plasticizers.

In this project, we studied the energetic plasticizers 2-[butyl(nitro)amino]ethyl nitrate (BuNENA), 2-[methyl(nitro)amino]ethyl nitrate (MeNENA) and (nitroazanediyl)bis(ethane-2,1-diyl) dinitrate (DINA). We tried to predict their impact sensitivity based on molecular bonding energies using density functional theory with the exchange-correlation functional M06-2X and the TZVP basis set. We studied two different elimination reactions: homolytical dissociation of nitro groups and elimination of nitrous acid.

Based on these calculations, the $O-NO_2$ bond is the one that breaks the easiest, which is consistent with the literature. We also showed that these bonds are stronger in BuNENA than in MeNENA and DINA, and that the latter two have similar bond strengths. This finding is not consistent with experimentally measured sensitivity. Therefore, the difference in impact sensitivity indicated in the literature cannot be explained solely by the dissociation energy of the nitro group. The elimination of nitrous acid should be studied more thoroughly to gain an improved understanding.

We also performed a comparison of some different exchange-correlation functionals with coupled-cluster singles and doubles with perturbed triples. Our results showed that the bond dissociation energy calculated with a CAM-B3LYP functional was closest to the coupled-cluster result.

Finally, we carried out a fallhammer experiment on BuNENA. Our experiment showed significantly lower impact sensitivity than reported in the literature. This may be due to variations in the experimental method. Further investigations should therefore be conducted.

Sammendrag

Energetiske materialer er nøkkelingredienser i rakettdrivstoff. Moderne faste rakettdrivstoffer inneholder energetiske myknere, som forbedrer parametere som termisk stabilitet, energiinnhold, mekaniske egenskaper, oksygenbalanse og forbrenningsegenskaper. Vi har undersøkt slagfølsomheten til tre slike energetiske myknere.

I dette prosjektet har vi sett på 2-[butyl(nitro)amino]etyl nitrate (BuNENA), 2-[metyl(nitro)amino]etyl nitrate (MeNENA) og (nitroazandiyl)bis(etan-2,1-diyl) dinitrat (DINA). Vi forsøkte å forutsi slagfølsomheten basert på molekylære bindingsenergier ved å bruke tetthetsfunksjonalteori med exchange-korrelasjonsfunksjonalen M06-2X og basissettet TZVP. Vi har undersøkt to ulike eliminasjonsreaksjoner: homolytisk dissosiasjon av nitrogrupper og eliminering av salpetersyrling.

Basert på disse beregningene er det $O-NO_2$-bindingen som lettest brytes, noe som stemmer overens med litteraturen. Vi viste også at disse bindingene er sterkere i BuNENA enn i MeNENA og DINA, og at de to sistnevnte har lignende bindingsstyrker. Dette stemmer ikke overens med eksperimentelt målte slagfølsomheter. Derfor kan ikke forskjellen i slagfølsomhet angitt i litteraturen forklares av dissosiasjonsenergien til nitrogruppen alene. Eliminering av salpetersyrling bør undersøkes grundigere for å få resultater som gir mer innsikt om dette.

Vi sammenlignet ulike exchange-korrelasjonsfunksjonaler med coupled-cluster singles og doubles med perturberte triples. Det viste seg at bindingsdissosiasjonsenergien beregnet med CAM-B3LYP-funksjonalen var nærmest coupled-clusterresultatet.

Til slutt utførte vi et eksperiment med fallhammer på BuNENA. Dette viste betydelig lavere følsomhet enn det som er rapportert i litteraturen. Dette kan skyldes variasjoner i de eksperimentelle metodene. Det bør derfor utføres ytterligere undersøkelser.

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Preface

This report is based on the work I did at FFI during the summer of 2023, under the supervision of Erik Unneberg. The testing of impact sensitivity of BuNENA was performed by Tomas Lunde Jensen. I would like to thank both Erik and Tomas for their theoretical guidance and patience regarding computational and software challenges.

Ylva Os
9 August 2023, Kjeller.

Nomenclature

Abbreviations

h_{50}	Impact energy level at which there is a 50% probability of ignition occurring
T_g	Glass transition temperature
BDE	Bond Dissociation Energy
CAM	Coulomb Attenuating Method
EM	Energetic Material
ESP	Electrostatic Potential
HBDE	Heterolytic Bond Dissociation Energy
IS	Impact Sensitivity
IUPAC	International Union of Pure and Applied Chemistry
mp	Melting point
xc	Exchange correlation

Chemical Compounds

Alkyl-NENA	Alkyl-nitratoethylnitramine
BuNEȦ	n-Butyl-nitroxyethylamino radical
BuNEȮ	n-Butyl-nitramineethyloxidanyl radical
BuNENA	2-[Butyl(nitro)amino]ethyl nitrate
DEP	Diethyl phthalate
DINA	(Nitroazanediyl)bis(ethane-2,1-diyl) dinitrate
HONO	Nitrous acid
MeNENA	2-[Methyl(nitro)amino]ethyl nitrate

Mathematical Symbols

ΔE	Difference in Energy [kJ/mol]
$\mathcal{H}$	Molecular Hamiltonian
Ψ	Quantum state function / wave function
E	Energy [kJ/mol]

Quantum Chemical Methods

CCSD(T)	Coupled Cluster Singles and Doubles with perturbed Triples
DFT	Density Functional Theory

MP2   Second-order Møller-Plesset Perturbation Theory

MS-CASPT2   Multistate Complete-Active-Space Second-order Perturbation Theory

ROHF   Restricted Open-Shell Hartree Fock

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1 Introduction

Development of rocket propellants is an interesting subject for many scientific fields, and perhaps especially chemistry. Some rocket propellants can be as simple as liquid hydrogen[6] evaporating and exiting the nozzle, whereas other propellants, and more specifically solid propellants, are much more complicated in their chemical composition. When deciding on the different ingredients it is important to have as much available information as possible regarding the different compounds, to be able to create the most effective and suitable propellant for their area of use. The most essential group of chemicals when working with rocket propellant components are energetic materials.

1.1 Energetic materials and sensitivity

Energetic materials (EMs) is a class of compounds that can release a high amount of chemical energy. Their application areas are many and include fuels, propellants, pyrotechnic compositions and explosives. When handling such chemicals, it is important to ensure safety, as mishandling can trigger the energy release and have hazardous consequences[16]. To avoid this, it is crucial to have knowledge of the materials' sensitivity. The sensitivity of an EM is a chemical property and refers to its susceptibility to ignition or detonation from various stimuli such as impact, friction, heat, or electrostatic discharge. There are many factors that contribute to the sensitivity of a material, and numerous studies have been performed to reveal them[16].

One of the most studied aspects of sensitivity is the effect of physical impact (impact sensitivity, IS)[34]. This is often measured by a fallhammer experiment, where a prescribed weight is repeatedly dropped onto the sample, and the height at which there is a 50% chance of ignition (h_{50}) is estimated.[17]. A problem is that there are several ways to define whether or not a compound has ignited. The most common being the detection of sound or first reaction of decomposition, which can lead to different results[34].

The IS is closely related to molecular stability. When looking at the molecular properties, electronic structure and quantum chemical calculations may give good insight. For example, calculations can be performed to determine the electron density, atomic and molecular charges, electronegativity, electrostatic potential (ESP), bond orders and energies, and molecular orbitals, to name some.

This can be useful as a high electron density, or more localized electrons, imply a stronger bond and thus a lower IS, as more force must be applied to break the bond. Atomic charges are also shown to be linked to the sensitivity[16]. A higher ESP implies fewer electrons, and following the previous logic, results in a weaker bond and a higher sensitivity. Furthermore, a highly conjugated system may have more stable bonds, and thus a lower sensitivity[16]. Another way to look at the sensitivity is in terms of activation energy and rate constants. If the activation energy is high, the probability of breaking a bond is much lower, and so the sensitivity increases.

From this, one of the simplest models for theoretically predicting the impact sensitivity is to calculate the bond strength of the designated reaction pathway.

1.2 Alkyl-NENAs as plasticizers

Nitratoethylnitramine (NENA) and its derivatives are commonly used energetic plasticizers. The molecule includes both a nitrate ester and a nitroamine group, in addition to having very flexible bonds[30]. The purpose of the plasticizers is to increase thermal stability, energy content, adjustment of oxygen balance in the formulation, reduce the glass transition temperature (T_g) and the britle-ductile transition temperature, improving the mechanical properties of the propellant matrix, and adjust the burning behavior[15].

In this project we have looked at three molecules, 2-[butyl(nitro)amino]ethyl nitrate (BuNENA), 2-[methyl(nitro)amino]ethyl nitrate (MeNENA) and (nitroazanediyl)bis(ethane-2,1-diyl) dinitrate (DINA), whose structures are shown in Figure 1.1.

2-(Butyl(nitro)amino)ethyl nitrate (**1**)

BuNENA

2-(Methyl(nitro)amino)ethyl nitrate (**2**)

MeNENA

(Nitroazanediyl)bis(ethane-2,1-diyl) dinitrate (**3**)
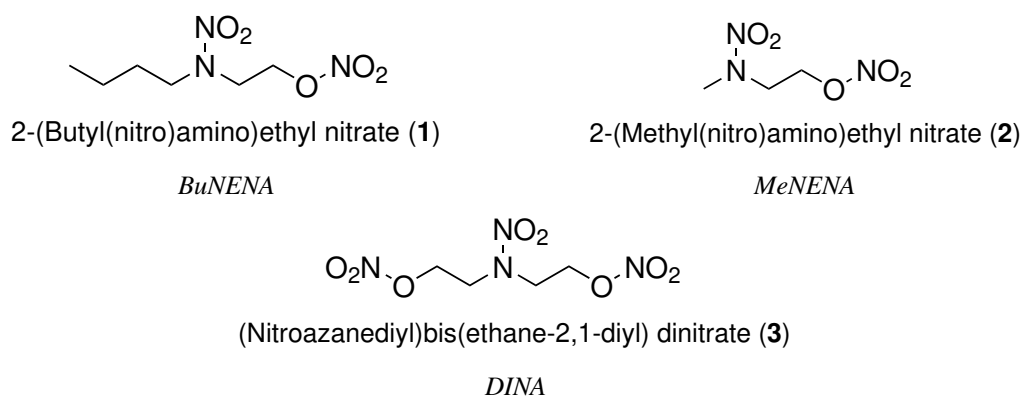
DINA

*Figure 1.1   Structure of BuNENA (**1**), MeNENA (**2**) and DINA (**3**)*

1 is often used as a plasticizer due to its low IS[12,22,23]. It has shown to lower the T_g with 20 °C, when in a mixture composed of 20 % of the plasticizer, improved mechanical properties and burning rate[25], in addition to reducing the sensitivity of the propellant[5]. When compared to diethyl phthalate (DEP) based propellant systems, using **1** results in lower hazards and a higher thermal stability[22].

Documented and relevant physical properties are presented in Table 1.1.

Table 1.1   Impact sensitivity (IS) and melting point (mp) of the relevant compounds.

Compound	IS [J]	mp [°C]
1	1[13]	−9[2,13,23]
	6[2,23,24]	−(27 − 24)[18]
	40[9]	
2	35[11]	37 − 40[3,18]
3	6[23]	49.5 − 52.5[13,23,35]
	7.5[13]	

1.3 Elimination of NO$_2$

As the initial energetic decomposition of the alkyl-NENA molecules is the elimination of the NO$_2$ groups, we will in this report consider two of the most probable mechanisms for this bond cleaving. In a report by Shim *et al.*[26] it is concluded that the decomposition of **1** may follow two competing pathways. The first being a homolytic dissociation, and the second dissociation of nitrous acid as a result of hydrogen rearrangement.

1.3.1 Homolytical dissociation of the nitro groups

When a covalent bond breaks, the bonded electron pair can either go to one of the atoms, or be split into two radicals. The latter is called homolytical dissociation and is shown in Equation 1.1.

$$A - B \rightarrow A \cdot + B \cdot \tag{1.1}$$

According to the official IUPAC definition, it is this reaction, at 298 K, that allows us to calculate the bond dissociation energy (BDE)[19]. The BDE is a state function, meaning that the result does not depend on the reaction path.

When calculating the BDE, we do so by comparing the energy difference between the total molecule (A - B) and the two fragments which are dissociated (A and B radicals):

$$\text{BDE}_{A-B} = E_{A\cdot} + E_{B\cdot} - E_{A-B} \, . \tag{1.2}$$

For the NENAs there are two reaction paths for the dissociation of the first nitro group, shown in Figure 1.2.
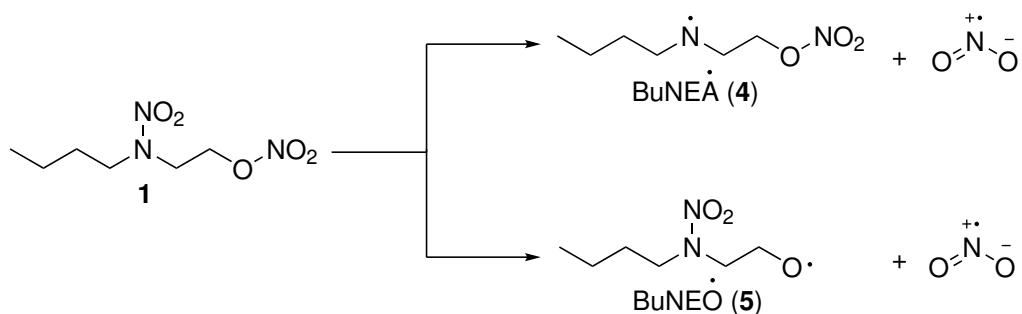
*Figure 1.2   Homolytical dissociation paths for elimination of NO$_2$ in **1***

1.3.2 Elimination of nitrous acid

Even though calculating the BDE for the homolytical dissociation of a nitro group can give us a lot of information regarding the system, there are additional ways to eliminate a NO$_2$ group. When looking at a chemical system, we must remember that the molecule is dynamic, and so are the bonds. For example, it is very common for organic mechanisms to be initiated by hydroxy protonation, to make it a better leaving group[28]. This can be done by an outside hydrogen source or within the
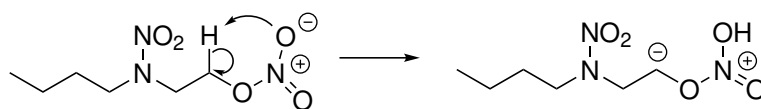
*Figure 1.3   Rearrangement of hydrogen in **1** to one of the primary oxygen on the nitrato group.*

molecule itself, creating nitrous acid (HONO). The hydrogen rearrangement prior to this is shown in Figure 1.3.

In this case, we have two charged atoms, and a contribution of electrostatic interactions, instead of a pure covalent bond. This means that in addition to the homolytic dissociation, it is also likely we get a heterolytic dissociation, resulting in two neutral molecules.

2   Computational chemistry

Due to the technological advancements of the past decades, chemical simulations and calculations on computers have become more accessible and popular. This allows us to compare experimental results with theoretical models or predict reaction outcomes, resulting in a broader understanding of chemistry and allows us to experiment without the cost of chemicals and laboratory health, safety and environment risks.

2.1   Quantum chemistry

When working with particles on the molecular scale, classical physical properties do not hold and we must therefore use molecular quantum mechanics to describe our systems. In this case we use a quantum state, often denoted as Ψ, to describe our system. Mathematically, this is a wave function that describes the probability amplitude of finding a particle in a particular state. The function is complex-valued and depends both on the spatial coordinates of the particle's position and time.

Given the wave function, you can apply an arbitrary quantum operator, whose eigenvalues correspond to all possible measurable results for the given state. One such operator is the energy operator, more often known as the *Hamiltonian*, $\mathcal{H}$. This gives rise to the time-dependent Schrödinger equation,

$$\mathcal{H}\Psi(x,t) = E\Psi(x,t), \tag{2.1}$$

where x being the position of the particle at a given time t and E is the energy. Unfortunately, this equation can only be solved analytically for one-electron systems, and it has therefore become a goal for quantum chemists to develop accurate and applicable methods that can approximate solutions to this problem.

2.2   Density functional theory

A usual problem in computational quantum chemistry is the cost of running calculations. In wave function theory, each electron in the system is described with three coordinates, which results in a brutal scaling of the calculations. In contrast, density functional theory (DFT) approximates the wave function as one three-dimensional function, drastically reducing the computational cost of the calculations.

According to the Hohenberg-Kohn theorems[10], the ground state energy of a many-electron system may be uniquely described by an electron density, which only depends on three spatial coordinates, where the energy is expressed as a functional of the density, $E_{DFT} = E[\rho]$. The problem is that this is only theoretical. In practice, there are parts of the total functional, specifically the exchange-correlation (xc) term, which is unknown and must be estimated. This can be done in several ways, and often one approximation can create a functional that works well for one system, but not for another. Another common problem is overfitting of a functional. The lack of generality is a problem currently worked on by many researchers[32]. Nevertheless, the method has proven to give very accurate results, even outperforming MP2[1] in some cases, and is widely used, due to its high accuracy relative to its computational cost.

2.2.1 Functionals

Choosing the correct functional for your system is essential for the success of a DFT calculation. In Section 3.5 we compare the effect of different functionals on the BDE and energy levels, and here we will discuss some of the theoretical background of the used functionals.

M06-2x is a hybrid meta xc functional developed by Zhao and Truhlar[36], and it is an extension to the M06 functional, with an additional double nonlocal exchange term. The functional has shown great performance in calculating BDEs, outperforming other functionals such as B3LYP, VSXC, B97-3 and M06[36]. In addition it does well on the HC7 database, which tests medium-ranged correlation energy in medium sized hydrocarbons[21].

B97D includes an empiric correction for dispersion interactions, compared to the B97 xc functional. B97D is thus particularly well-suited for calculating long-range interactions, including weak van der Waals forces, which can be challenging for traditional DFT functionals to capture accurately. Therefore, B97D is commonly used to study molecular complexes and non-covalent interactions in biochemical systems[14].

ωB97-XD uses a weighted combination of exact Hartree-Fock exchange and DFT exchange. It also includes an dispersion correction, making it suitable for non-covalent interactions. This combination makes the ωB97-XD functional a good choice for systems such as those involving long-range interactions, van der Waals forces, and hydrogen bonding[4].

The Coulomb attenuating method (CAM-B3LYP) is an extended version of the commonly used B3LYP functional with a correction to long range interactions using the Coulomb-attenuating method. It is commonly used in computational chemistry for systems with heavy atoms, transition metals, and long-range electronic interactions. The CAM modification attenuates long-range electron-electron interactions, making it suitable for describing charge transfer and dispersion forces. Its accuracy benefits various applications, including excited states, non-covalent interactions and reaction mechanisms[33].

2.2.2 Basis functions

In quantum chemical methods, it is common to pick a certain number of basis functions, which will be combined in linear combinations to create our wave function. The description of the wave function then gets more accurate the more basis functions you include. There have been developed numerous basis sets, with a hierarchy of accuracy, where more functions are added and the convergence point of infinite functions is considered the exact solution for the given quantum method, called the complete basis set limit. One must therefore take into account what functions are important to include, for example how important it is to have additional polarized and diffuse functions. Indeed, this depends on the specific properties of interest.

In this project we decided to use the basis set TZVP, which we show to have minimal changes on the expansion to aug-ccpvtz, with a systematic shift of 0.11 eV on average for medium sized singlet state molecules using MS-CASPT2 calculations. Similar results have been achieved when doing the same calculations using DFT[27].

3   Results and discussion

BDEs for dissociation of HONO and NO_2 were calculated for **1**, **2** and **3**, using DFT with the M06-2X/TZVP functional and basis. BDEs for dissociation of NO_2 were also calculated using different xc functionals and CCSD(T) for comparison.

3.1   Configuration evaluation

Due to the many possible structural configurations of the alkyl-NENAs, a configuration study was performed on six arbitrary structures for each molecule. The total molecular energy was calculated. The largest energy difference between the **1** geometries was around 20 kJ/mol and did not have a significant impact on the BDEs. It is therefore only the structures with the lowest energy (shown in Figure 3.1) which are considered further in this report.

*BuNENA (**1**).*   *MeNENA (**2**).*

*DINA (**3**). The nitrate ester groups are labeled with L and R to distinguish between them.*
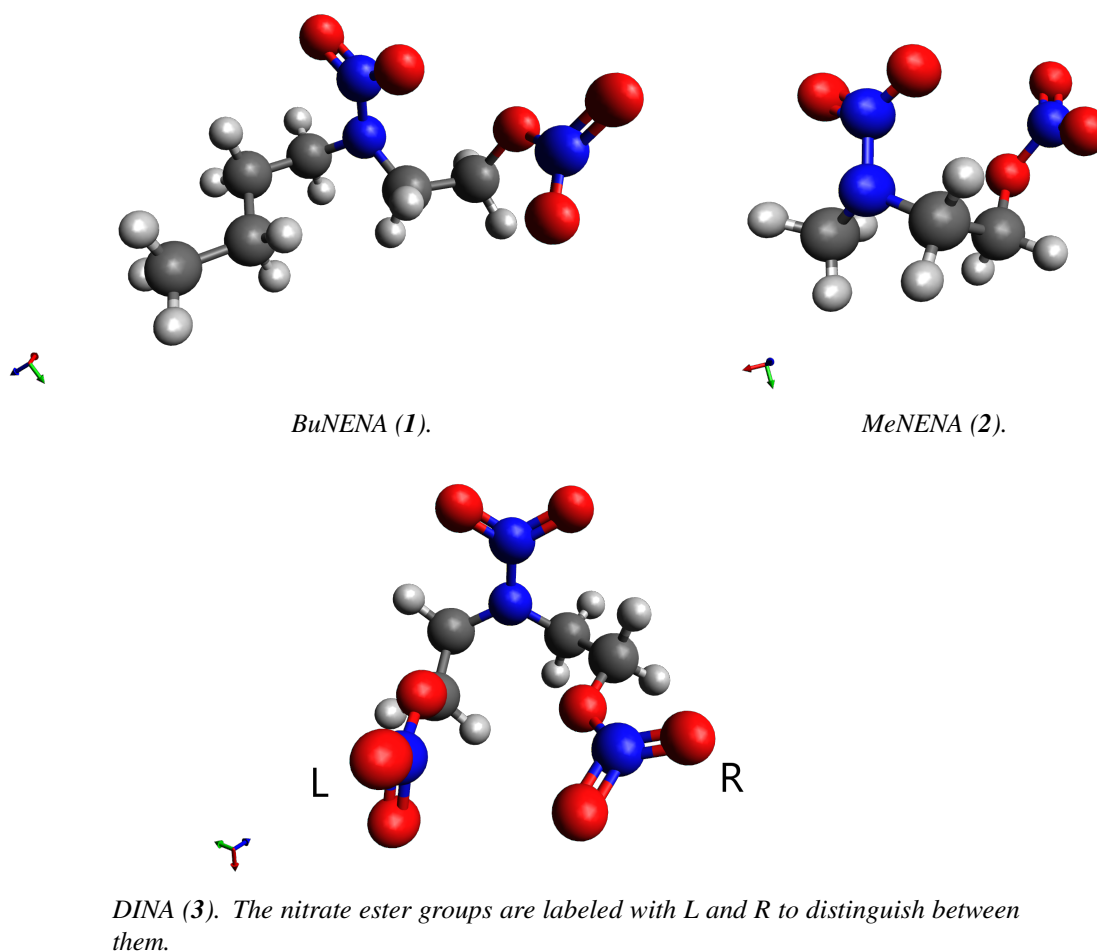
*Figure 3.1   Optimized geometry for **1**, **2** and **3**.*

3.2   Determination of BDE of BuNENA (1) from homolytical dissociation

Table 3.1 shows the calculated BDEs for **1** at different temperatures. It is unclear in the literature whether or not the radicalized fragments should be individually geometry optimized, and we have therefore decided to compare the results. Figure 3.2 compares the structure of **4** before and after geometry optimization. As we can see in the optimized geometry, we have a twist around the central amine nitrogen. This has an effect on the energy, which is larger than that obtained by varying the configuration. We have therefore decided to continue with calculating the remaining BDEs without geometry optimizing the fragments, to keep things simple.
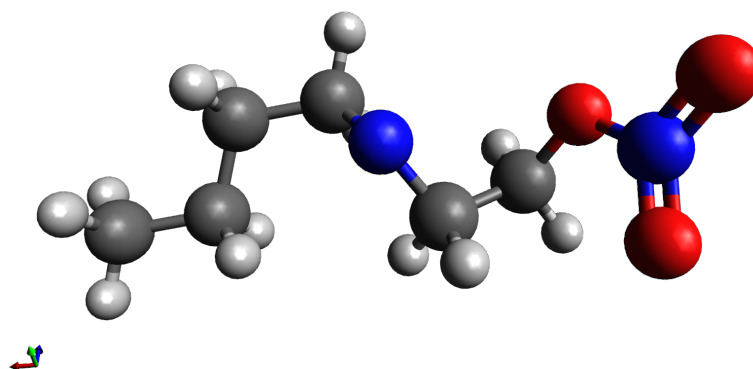
(a) Before optimization
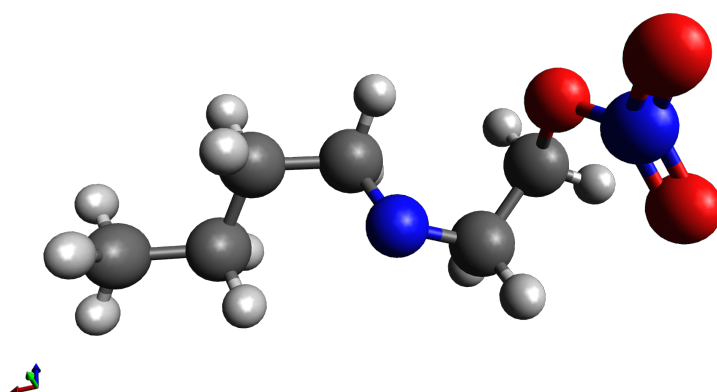
(b) After optimization

*Figure 3.2   Visualization of BuNEÀ (**4**) before and after geometry optimization.*

For both temperatures the $O-NO_2$ bond has a lower BDE than the $N-NO_2$ bond, meaning that the decomposition of **1** to **5** and NO_2 is the most kinetically favorable. This result is consistent with the work of Shim *et al.*[26].

*Table 3.1   Calculated BDEs for **1** with and without geometry optimizing the radical fragments.
ΔE refers to the deviation from the non-optimized **1** BDE.*

	Bond	BDE [kJ/mol]		ΔE_{BDE} [kJ/mol]	
		0 K	298 K	0 K	298 K
1	$N-NO_2$	251.717	250.751		
	$O-NO_2$	183.213	185.352		
1 opt[1]	$N-NO_2$	214.401	216.501	37.316	34.250

[1] *In this calculation the radical fragments were geometry optimized, resulting in a twist around the central amine nitrogen, see Figure 3.2.*

3.3   Comparison of BDEs with MeNENA (2) and DINA (3)

The reported ISs of **1**, **2** and **3** (Table 1.1) vary a lot, even though their structures are quite similar. Comparing the BDEs of the molecules might thus give useful information about the sensitivities of the compounds.

Table 3.2 presents the calculated BDEs of **1**, **2** and **3**. Table 3.3 shows the difference in energy between **1** and **2/3**. We see that the difference in BDEs of **2** and **3** are almost within chemical accuracy of each other, and can be considered equal by these calculations, despite having very different reported sensitivities.

The BDEs of the $N-NO_2$ bonds of **2** and **3** deviate from **1** with a little more that 10 kJ/mol, and the $O-NO_2$ bonds with a little wider range of between 3 and 9 kJ/mol. Even though this is above chemical accuracy and can indicate that the IS of **1** is lower, it is not sufficient to conclude that the BDEs are the sole reason for the difference in sensitivity. This may indicate that homolytical dissociation is not a representative mechanism, or that we have other properties that can not be obtained by a single molecule in gas phase. This can for example be intermolecular forces, macroscopic properties or some intramolecular interactions that are not taken into account by this method.

*Table 3.2   Calculated BDEs for **1**, **2** and **3**.*

Molecule	Bond	BDE [kJ/mol]	
		0 K	298 K
1	$N-NO_2$	251.717	250.751
	$O-NO_2$	183.213	185.352
2	$N-NO_2$	240.320	239.779
	$O-NO_2$	180.574	182.535
3	$N-NO_2$	238.729	238.745
	$O-NO_2L$ [1]	178.896	179.177
	$O-NO_2R$ [1]	175.908	176.373

[1] *The BDEs were calculated for both nitrate ester groups, see molecule **3** in Figure 3.1.*

*Table 3.3 Comparison of BDE compared to **1**. $\Delta E = E_1 - E_{2/3}$.*

		ΔE_{BDE} [kJ/mol]	
Molecule	Bond	0 K	298 K
2	$N-NO_2$	11.397	10.972
	$O-NO_2$	2.639	2.817
3	$N-NO_2$	12.988	12.006
	$O-NO_2L$	4.316	6.175
	$O-NO_2R$	7.304	8.979

3.4   Determination of BDE from HONO elimination

The BDE of the HONO elimination was calculated for **1** and **2**. The energies were surprisingly large (see Table 3.4). Interestingly **1** has the lowest energy bond, which is in contrast with the results for the homolysis. The difference between the O-HONO and N-HONO is also much smaller than that of $O-NO_2$ and $N-NO_2$ for **1**, whereas for **2** the difference is over 110 kJ/mol. For both molecules, it is the amine bond which is the weakest.

*Table 3.4   BDEs calculated for the HONO elimination of **1** and **2**.*

		BDE [kJ/mol]	
Molecule	Bond	0 K	298 K
1	N-HONO	541.725	549.830
	O-HONO	587.099	589.511
2	N-HONO	490.911	499.139
	O-HONO	606.362	603.306

It is important to note that due to complications with stability after the hydrogen rearrangement, the structure could only be geometry optimized by using a force field (MMFF94s), which might have resulted in some uncertainty in the BDEs. In more accurate geometry optimizations the hydrogen was placed back on the original carbon.

If we look at the last structure in Figure 1.3, we see that the bond between the oxygen and nitrogen is not a pure covalent bond, but also has the characteristics of a dative bond. Considering this, it might not be so surprising that the energy needed to split this bond into radicals is so large, due to the electrostatic attraction.

Table 3.5 shows the heterolytic bond dissociation energy (HBDE), which is the energy needed to do a bond cleavage via heterolysis. This energy is negative, meaning that we would gain energy by dissociation. Intuitively, this makes sense considering that dissociation would result in two stable neutral molecules. For **1**, the initial decomposition of the nitrate ester has the highest energy gain, similarly to the NO_2 elimination, making it the most likely to fracture first. For **2**, it is the opposite, and the O-HONO bond is a lot more stable than the others.

It is necessary to investigate the HONO elimination more thoroughly to be able to draw any useful conclusions based on the information from these calculations.

*Table 3.5   Heterolytical BDE calculated for **1** and **2**.*

Molecule	Bond	HBDE [kJ/mol]	
		0 K	298 K
1	N-HONO	-395.707	-390.764
	O-HONO	-545.371	-536.933
2	N-HONO	-435.397	-431.737
	O-HONO	-91.023	-88.366

3.5   Effect of different functionals on the BDE of BuNENA (1)

Lastly we look at some other xc functionals to see how this affects the BDEs of **1**. In Table 3.6 we see a large deviation in energies between the different functionals, shown more clearly in Table 3.7 and in Figure 3.3. Here we see that M06-2X have the largest BDE of all the functionals and B97D has the lowest. CAM-B3LYP and ωB97-XD have very similar energies. The deviation in energy between functionals seems to correspond to a shift of the BDE energies, and the difference between the two bonds do no change much. As a result this is not very severe to our proof of concept calculations.

*Table 3.6   BDEs of **1** calculated for different xc functionals.*

Functional	Bond	BDE [kJ/mol]	
		0 K	298 K
M06-2X	$N-NO_2$	251.717	250.751
	$O-NO_2$	183.213	185.352
B97D	$N-NO_2$	184.743	187.429
	$O-NO_2$	141.060	147.228
ωB97-XD	$N-NO_2$	222.839	224.123
	$O-NO_2$	160.547	165.191
CAM-B3LYP	$N-NO_2$	214.729	213.162
	$O-NO_2$	155.690	157.065

Table 3.7   Comparison of the BDE values of the different xc functionals in Table 3.6. $\Delta E = BDE_{M06-2X} - E_{functional}$.

Functional	Bond	ΔE_{BDE} [kJ/mol]	
		0 K	298 K
B97D	$N-NO_2$	66.974	63.322
	$O-NO_2$	42.152	38.125
ωB97-XD	$N-NO_2$	28.878	26.628
	$O-NO_2$	22.666	20.161
CAM-B3LYP	$N-NO_2$	36.988	37.589
	$O-NO_2$	27.523	28.287

To be able to see which xc functionals are closer to the correct energy, a UCCSD(T) calculation on ROHF was preformed to find the total electronic energy. This was used to find an electronic BDE, which will deviate from the actual BDE by a constant, due to not including the nuclear vibrational
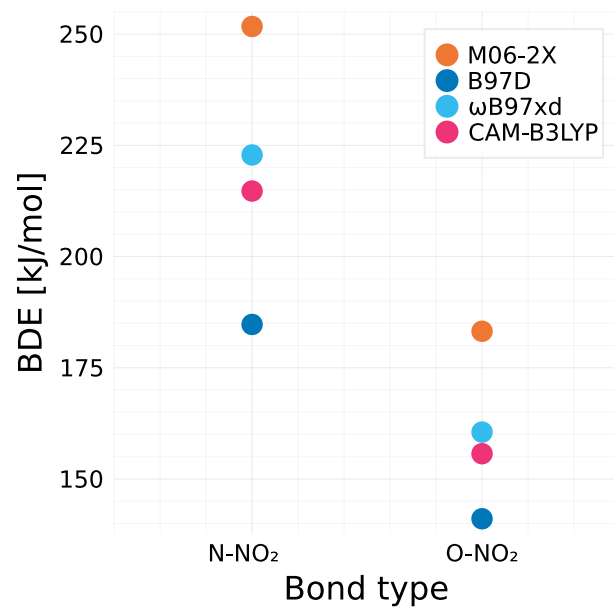
Figure 3.3   Plot of BDEs for the different functionals in Table 3.6 at 0 K.

energy. The use of spin-unrestricted methods will result in some spin contamination, but it is still more accurate than the DFT calculations. As we can see in Table 3.8, the functional closest to the CCSD(T) result is CAM-B3LYP, and surprisingly, M06-2X is overall preforming the worst.

Table 3.8   *BDEs calculated from the total electronic energy. CCSD(T) was calculated from ROHF.*

Method/functional	Bond	eBDE[1] [kJ/mol]	$\Delta E_{CCSD(T)}$ [kJ/mol]
CCSD(T)	$N-NO_2$	235.379	
	$O-NO_2$	185.449	
M06-2X	$N-NO_2$	278.929	-43.550
	$O-NO_2$	205.725	-20.276
ωB97-XD	$N-NO_2$	249.733	-14.354
	$O-NO_2$	184.038	1.412
B97D	$N-NO_2$	209.973	25.406
	$O-NO_2$	162.453	22.996
CAM-B3LYP	$N-NO_2$	240.658	-5.279
	$O-NO_2$	177.014	8.435

[1]*Due to the fact that only electronic properties being included this is not the actual BDE.*

3.6   Experimental testing of IS of BuNENA (1)

The main issue in the literature (Table 1.1) is the disagreement regarding the IS and mp of **1**. As **1** is known for having a low IS, it thus seems odd to report the IS as being 1 or 6 J. Previously, in Section 1.1, it is mentioned that there are several ways to measure the sensitivity, and some of these reported values might have been measured under different conditions.

ICT[24], one of the sources reporting an IS of 6 J, states that their measurements were performed in accordance with STANAG 4489[20]. However, these only explain how to measure solids, and as **1** has a mp well below room temperature, it is unclear whether these measurements have been carried out in a very cold environment, with added hardeners or on a liquid, all of which would likely give different results. For example, is it not surprising if a compound requires more energy to explode at a low temperature.

We also conducted our own fallhammer measurements for BuNENA, the full results of which are given in Table A.1 in the Appendix. These were done in accordance with the United Nations (UN) test procedure[31], along with some additional tests. As shown in Table A.1, we get soot as low as at 20 J, however, this only occurred twice out of 7 times.

Based on decomposition by gas production, the IS could be as low as less than 10 J, however, this must be investigated further by doing more measurements to get a conclusive result. Even though some reactions have occurred, the experiment did not have any explosions and all measurement is thus considered negative, and **1** has an IS larger than 50 J.

4 Method

4.1 Computational conditions and considerations

For this project we have used the Gaussian 09[7] quantum chemistry program. The calculations were carried out using DFT with the M06-2X[36] functional and TZVP basis set. Molecular structures are visualized using Avogadro[8].

For the calculations we considered six structural conformations of BuNENA. These were all geometry optimized and the BDE was calculated. As there was no large difference between the different confirmations, only the one with the lowest total energy was used further in the project. Six different confirmations of MeNENA and DINA were constructed, and the ones with the lowest energies were again used for the remaining calculations.

The BDE calculation was done according to Equation 1.2. A decision was made to not geometry optimize the individual fragments, as this resulted in a twisting around the main amine nitrogen.

We also made a comparison between additional xc functionals, those being B97D, ωB7-xd and CAM-B3LYP. For reference, a calculation using UCCSD(T) on ROHF was done using the computational program PySCF[29], all with the TZVP basis set. Due to computational cost, the compared energies were only calculated for the total electronic energies.

4.2 Fallhammer experiment of IS of BuNENA

A fallhammer experiment was performed by Tomas Lunde Jensen with a BAM (BFH-12) fallhammer according to the UN test procedure[31].

5   Further work

There are still many more possibilities for further computational studies on the alkyl-NENAs. Most importantly, we should study the effect of intermolecular forces, either in a crystal or liquid. This can be very expensive using normal quantum mechanics, however, force field molecular dynamics might give us some interesting results. One could for example simulate how the compound responds to outside effects such as pressure or temperature, and study shock induced decomposition.

Some sources also state that both the compactness and density have an effect on the BDE. This may also be easier to calculate using molecular dynamics, or other methods designed for larger systems.

It would also be interesting to see if one could look more accurately at the HONO elimination, or other decomposition mechanisms. The main problem here is that the rearrangement of the hydrogen atom does not have a local energy minimum, making it hard to optimize the correct geometry.

Activation energy is also a key point when looking at chemical reactions. For a homolytical dissociation this is not very relevant, but when studying hydrogen rearrangement for the HONO elimination, this can perhaps help give a better understanding of the mechanism and how important it is for the sensitivity of the alkyl-NENAs.

6   Conclusion

It is consistent with most of our calculations that the $O-NO_2$ bond is most sensitive to dissociation of the studied alkyl-NENAs. According to the bond dissociation energies, BuNENA seems to be less sensitive than MeNENA and DINA, with about 10 kJ/mol. The bond dissociation energies for DINA and MeNENA are almost identical. The latter deviates the most from the literature and it is clear that there are additional parameters determining the impact sensitivity rather than just the molecular bond strengths.

According to the fallhammer experiment the sensitivity of BuNENA is larger than 50 J by UN-standards and thus higher than those reported in the literature. As there are many ways to define a positive result of the fallhammer experiments, further investigations should be conducted to find a conclusive result of the impact sensitivity.

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A   Fallhammer sensitivity test of BuNENA

Table A.1   Experimental results of the fallhammer test of BuNENA.

BuNENA	Lot: 14D0063			Date: 03.08.2023				
	Humidity: 63 % rF, Temp.: 21C							

Test no.	Weight [kg]	Height [cm]	Energy [J]	Flame/ explosion	NO [ppm]	CO [ppm]	Soot	Sound
1	5	20	10	-	0	0	-	
2	5	30	15	-	0	0	-	
3	5	40	20	-	0	0	-	
4	5	50	25	-	0	0	-	
5	5	60	30	-	0.5	0	-	
6	10	35	35	-	1.0	0	+	
7	10	40	40	-	0	0	+	
8	10	50	50	-	0.5	0	+	
9	10	70	70	-	0.5	0	+	
10	10	100	100	-	0.5	0	+	
11	10	50	50	-	0	0	-	
12	10	50	50	-	0	0	-	
13	10	50	50	-	0	0	-	
14	10	50	50	-	0	0	-	
15	10	50	50	-	0	0	+	(+)
16	10	50	50	-	0	0	-	
17	2	100	20	-	0.5	0	+	
18	2	100	20	-	0	0	-	
19	2	100	20	-	0	0	-	
20	2	100	20	-	0	0	-	
21	2	100	20	-	0	0	-	
22	2	100	20	-	1.0	0	+	
23	2	50	10	-	1.0	0	-	
24	2	50	10	-	1.0	0	-	
25	2	50	10	-	0.0	0	-	
26	2	50	10	-	0.5	0	-	
27	2	50	10	-	0.5	0	-	(+)
28	2	50	10	-	0.0	0	-	

About FFI

The Norwegian Defence Research Establishment (FFI) was founded 11th of April 1946. It is organised as an administrative agency subordinate to the Ministry of Defence.
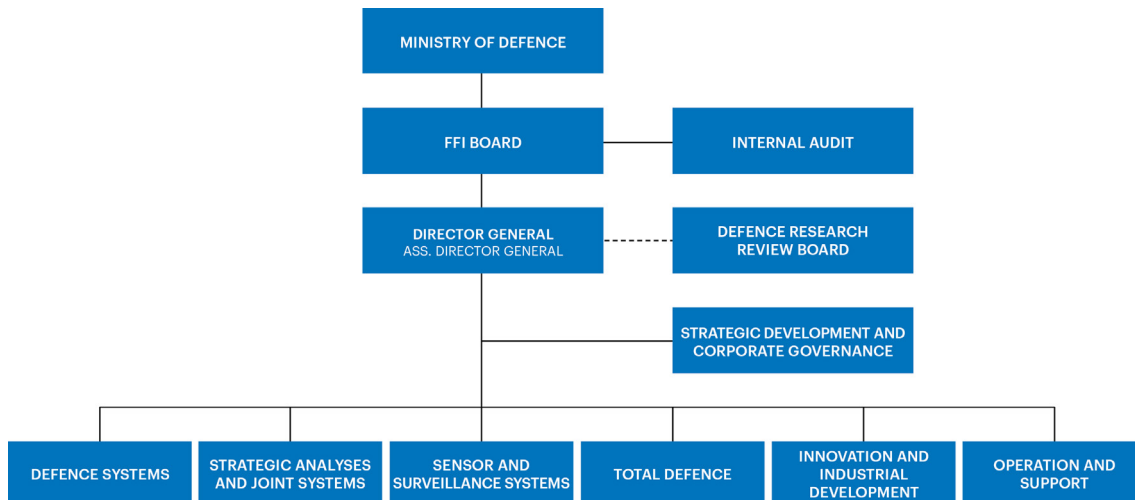
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FFI's vision

FFI turns knowledge and ideas into an efficient defence.

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