TRIGGER BOND ANALYSIS OF ENERGETIC MATERIALS

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Abstract

High energy density materials are challenging to analyze due to their sensitivity to impact, friction, and other stimuli. Computational chemistry techniques allow for these materials to be studied without hazard to equipment or personnel. In this study, density functional theory is used to predict molecular properties for comparison with experimental data. Specifically, we have used Wilberg bond index (WBI) analysis to identify the bonds that are likely to break to initiate detonation. In this study, trends in the trigger bond strength are examined for a series of catenated nitrogen compounds. Comparison of the WBIs for the bonds with these molecules allow the weakest bonds to be determined as a hint to the mechanism for triggering explosive decomposition.

Introduction

Hypergolic propellants such as hydrazine are also used in rocket fuel due to the nature of the hypergolic propellants. Hypergolic propellants are very toxic liquids that react violently when they encounter one another.[1] These toxic liquids are the same fluids that are used in rockets and military weapons. These dangerous and highly toxic fluids have caused several incidents as there were many documented reports of unintentional spills of the hypergolic propellants from 1968 to 2009.[1] Propellants such as hydrazine (N_2H_4) is a very common rocket fuel propeller however by using this dangerous chemical comes with repercussions. Over the decades there have been unintentional spills of these hypergolic propellants as well as explosions such as the incidents at Wallops Island and the Kenedy Center in 2014 and 2015.[2] This led the surrounding areas of both to be severely affected due to the contamination of the fuels used as the rocket fuel. Though liquid hydrogen (LH_2) and oxygen are safer for the environment and the workers who load them onto the rockets than that of hypergolic propellants, they still pose a risk however due to them not being very energy efficient.

Propellants are categorized as part of a class of compounds, known as High Energy Density Materials (HEDMS), also including explosives. Such materials are used for space flight, mining, and military aircrafts.[3,4] Some commonly used HEDMs include triaminotrinitrobenzene (TATB), octogen (HMX), nitroglycerin, trinitrotoluene (TNT), and hexahydro-1,3,5-triazine (RDX) all contain nitro functional groups. These nitro functional groups are thought to be the explosophores in the compounds that break off creating a domino effect of reactions that make up an explosion. Other explosophores are azo groups, nitric esters, and nitramines. These explosophores are found on the trigger bond, the bond that first breaks that starts the decomposition on a compound.[3] The decomposition of a compound allows for the study of why some compounds are more effective as HEDMs while others are not. By looking at the decomposition of HEDMs new HEDMs can be developed that don't release toxic gases into the atmosphere or the environment.[4] With these new HEDMs new fuels and explosives can be made to help explore new and even further planets or moons and help collecting samples of compounds found in mines.

Factors such as impact, friction, and shock can affect HEDMs in a multitude of different ways. By studying the sensitivity of a compound can help in understanding how to handle it safely and how reliable the energetic material is.[5] Due to the nature of HEDMs, who reacts violently as well as produces lots of gases and heat, studying such materials

experimentally is difficult.[4] Due to how dangerous HEDMs they could easily damaged equipment in a laboratory, harm individuals conducting research on them and even damage the building in which they are being conducted in. Computational method such as density functional theory (DFT) are used to provide a safer and more cost-effective way to study the HEDM compounds. By using computational methods properties of the molecules allow for the prediction of trigger bonds. The Wiberg Bond Index (WBI) is a measure of the electron density in a bond.[6] Wiberg Bond Index (WBI) has also been used to identify trigger bonds in HEDMs. The WBI is calculated through equation 1.

$$WBI_{AB} = \sum_{p\epsilon A}\sum_{p\epsilon B}(D_{pq})^2 \qquad (1)$$

By using the one-step equation WBIs can be determine for a molecule or compound to determine what bond(s) are more likely to be the trigger bond.

Methods

DFT Study

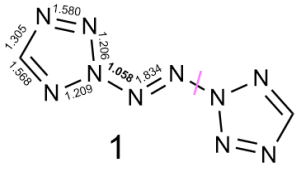
The optimization of 23 different HEDMs was done using $Gaussian09$[7] and M06-2X[8] functional and triple-ζ basis set augmented with polar functions (TZVP).[9] TZVP method was picked due to the basis set dependence that WBI calculations have when diffuse functions are included.[10] The WBI calculations on the optimized catenated nitrogen structures were done through NBO analysis Version 3.1.[11] The dataset of the 23 molecules was selected from three papers. The dataset contains 23 catenated nitrogen compounds.[4,12, 13]

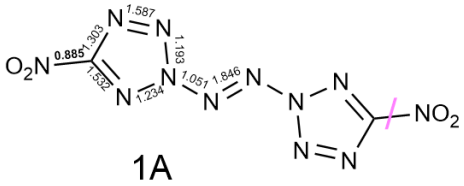
Results and Discussion

DFT Study

23 HEDMs were DFT(M06-2x/TZVP) optimized and were consistent with available DFT calculations. The set was chosen to determine whether WBI can identify the bonds that are likely to break to initiate detonation. The molecules contain all catenated nitrogen compounds containing 10 parent skeletons ranging with N4, N6, N8, N10 and N12 nitrogen bridges.

For each of the catenated nitrogen compounds, the WBI is strongly correlated with the predicted trigger bond (Figure 1). WBI demonstrates the weakening on a bond found in a compound or molecule. A low WBI indicates a loss of electron density and therefore a weakening of the bond. As two atoms are pulled farther apart, the electron density decreases. With the WBI's present on the catenated nitrogen compounds by observing and reviewing the pink line, indicating the predicted breakage of a bond found on the molecule, the bond more likely to be the trigger bond is the bond with the weakest/lowest WBI on each given molecule (Figure 1). Though the parent skeleton compound did not have any functional groups; the addition of nitro functional groups can affect what assignment of the trigger bond (Figure 1).





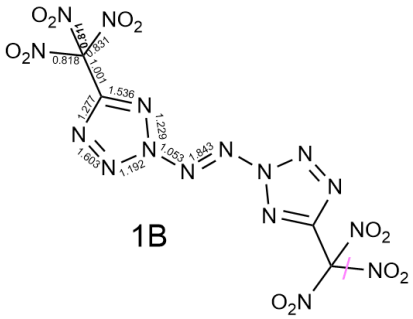
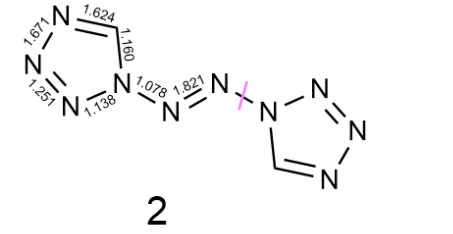
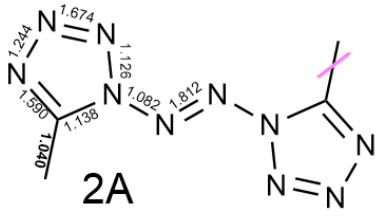


Figure 1. Three 10-nitrogen ringed compounds with the WBIs calculated along the catenated compound. The pink line indicates the predicted trigger bond.

For the 10-nitrogen bridged compounds, the parent skeleton molecule **2** shows that the predicted trigger bond is more likely to break along the azo bridge between the two rings (Figure 2). However, when looking at the other two molecules where a functional group was added to the parent skeleton, the predicted trigger bond is the functional groups nitro found in molecules **2B** (Figure 2). Molecule **2A** would not have a trigger bond located where the pink line indicates on the methyl group due to the stability of the functional group.





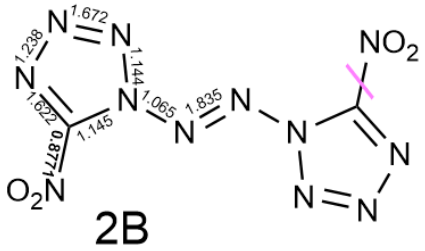
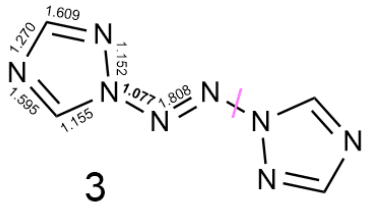
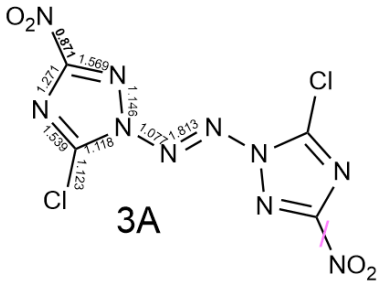
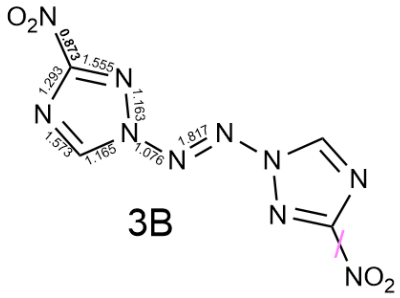


Figure 2. Three 10-nitrogen bridged compounds with the WBI's calculated. The pink line indicates the predicted trigger bond.

For the parent N6 skeleton, the predicted trigger bond is the nitrogen bridge linkage between the two rings (Figure 3). The functional groups on this set of compounds however are very different. Besides the consistent functional group added to the parent skeleton structure chlorine was added as well. By looking at the WBI's calculated however the nitro group remained to be where the predicted trigger bond would be found.







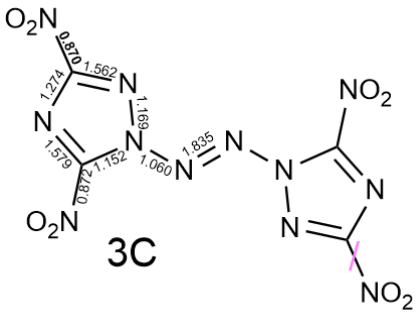


Figure 3. Four 6-nitrogen bridged compounds with the WBI's calculated. The pink line indicates the predicted trigger bond.

The N8 compounds functional groups added to the parent skeleton structure are more likely to break due to the high stability and easily breakable nitro groups are on molecules **5A** and **5B** (Figure 4).

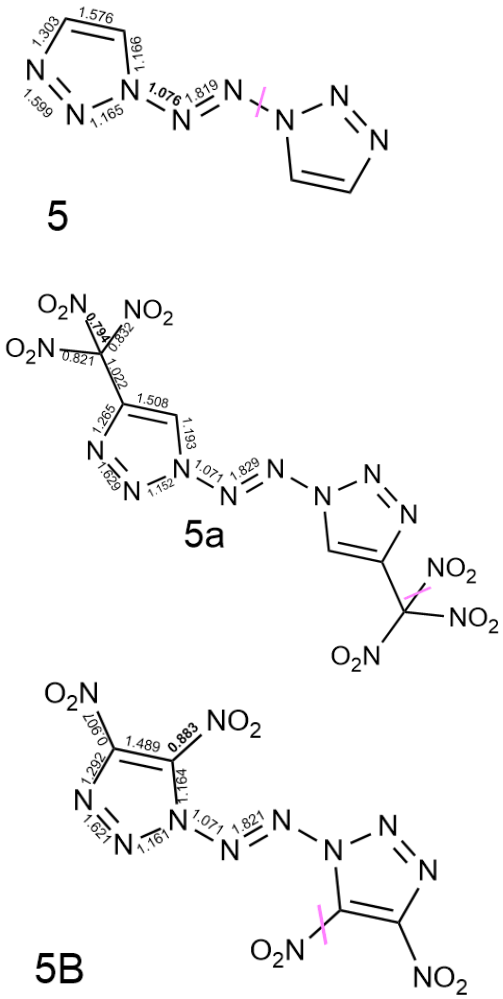


Figure 4. Three 8-nitrogen bridged compounds with the WBI's calculated. The pink line indicates the predicted trigger bond.

Like the other figures the functional groups of molecules **6** and **6A** predict the trigger bond to be at the nitro groups (Figure 5). However, compared to other molecules there is no parent skeleton structure. Due to this there are only functional groups connected to the catenated nitrogen compounds. The three different types of functional groups are chlorine, methyl, and nitro groups. Due to the stability of nitro groups as well as the breakability the nitro group will more likely be the predicted trigger bond as the bond between the ring and the functional group is very weak. In molecule **6** however there will not be a trigger bond located where the pink line indicates on the methyl group due to the stability of the methyl group.

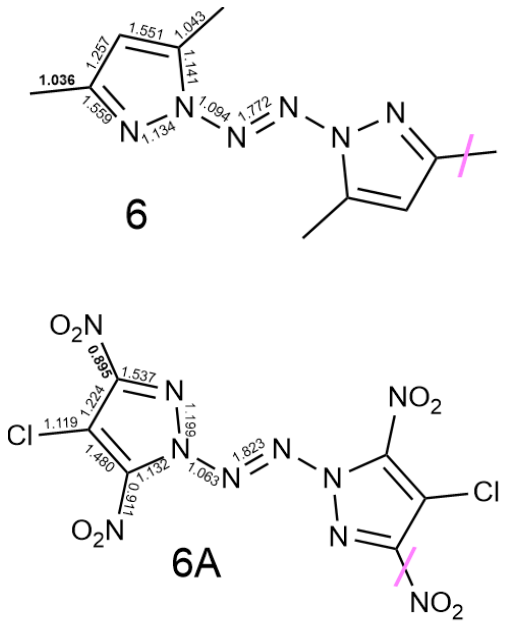


Figure 5. Two 6-nitrogen bridged compounds with WBIs calculated, both with functional groups. The pink line indicates the predicted trigger bond.

Though the two molecules do not have a parent skeleton, a structure with nothing attached to the ring itself, the two 4-nitrogen ringed compounds follow a trend with the other molecules found in Figures 1-5 as the functional groups, the nitro groups, are the predicted trigger bond in each of the compounds (Figure 6).

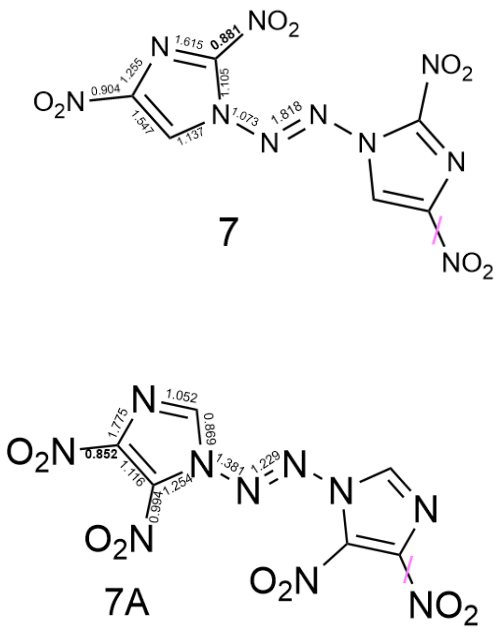
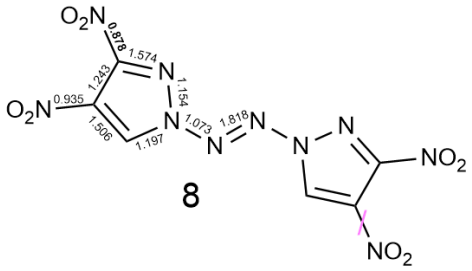


Figure 6. Two 4-nitrogen bridged compounds with WBIs calculated, both with functional groups. The pink line indicates the predicted trigger bond.

Though the molecule set does not have a parent skeleton the molecules do however display more functional groups added to the catenated nitrogen ring (Figure 7). Molecules **8**, **8A**, and **8B** all have functional groups attached to their rings. Similar to the other molecules found in this data set most compounds have a predicted trigger bond at the nitro group due to nitro group usually being the weakest bond. This is due to methyl groups strong stability as methyl groups consist of one carbon and three hydrogens.



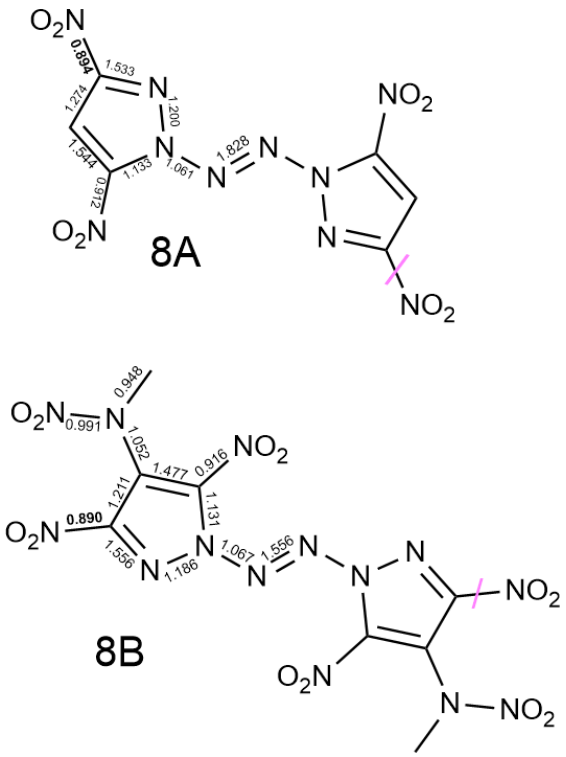


Figure 7. Three 6-nitrogen bridged compounds with WBIs calculated, both with functional groups. The pink line indicates the predicted trigger bond.

Molecules **4**, **9** and **10** are all the single paired molecules with no other molecules like one another (Figure 8). As in previous figures in the dataset molecules **4** and **9** both display the predicted trigger bond of a compound following the same trend among the data set where molecule **4**, a parent skeleton, predicted trigger bond is found along the nitrogen chain and in molecule **9** the functional group, a nitro group, is the predicted trigger bond for that given molecule. However, molecule **10** is a 12-nitrogen ringed compound whose WBI's are all over 1.0. This means that molecule **10** is not only very stable, but the trigger bond will be a lot harder to be trigger due to the stability of all the bonds found in this compound. Though a 12-nitrogen ring compound has not been synthesized yet looking into these types of structure can help when determining where a

molecule would most likely as well has looking into greener fuel alternatives.

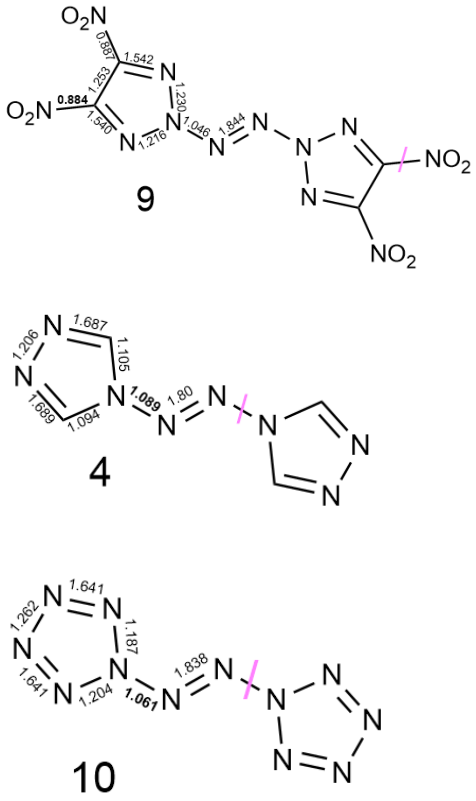


Figure 8. One 8-nitrogen, one 4-nitrogen, and one12-nitrogen bridged compounds with WBIs calculated, both with functional groups. The pink line indicates the predicted trigger bond.

Conclusion

Traditional HEDMs have been difficult to study experimentally due to their violent reactions, but DFT studies can help show their sensitives. By using Wiberg Bond Index (WBI), a tool used to look at the electron density of a bond in a compound, things such as identifying and predicting trigger bonds can help better understand and safely use these compounds. By identifying and predicting the trigger bonds in compound more compounds can be handle/stored safer as well as used as an alternative when it come to things such as rocket fuel, explosives, and military aircrafts.

Acknowledgements

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