

ASSIGNING TRIGGER BONDS IN NOVEL HIGH ENERGY DENSITY MATERIALS USING DFT AND WIBERG BOND INDICIES

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Development of high energy density materials (HEDMs) which are more stable less toxic are of interest for military and aerospace applications. Density Functional Theory (DFT) calculations on 26 azo-linked, high-nitrogen HEDMs were used to determine trigger bonds and potential pathways for explosive decomposition. The challenge to studying energetic materials is the instantaneous reaction upon detonation which makes computational methods ideal for interpreting decomposition mechanisms. Trigger bonds are expected to have lower electron density and break to initiate decomposition. In azo-bridged HEDMs, the trigger bond to the azo is expected to break to form nitrogen gas and two azole-based radicals. To predict trigger bonds, Wiberg bond indices (WBIs) are used to provide a relative scale of comparison to a reference molecule (% Δ WBIs) with shared bond type, hybridization, and explosophore. % Δ WBIs are compared to experimental impact sensitivities and theoretical estimates determined from the electrostatic potential surfaces.

INTRODUCTION

Conventional explosives (i.e. 2,4,6-trinitrotolulene (TNT), 1,3,5-trinitro-1,3,5-triazacyclohexane (RDX), etc.) used in military, aeronautics, and mining applications have effective detonation properties, but produce many hazardous products such as CO, NO, and NO₂ gases.¹⁻³ In addition, propellants, such as hydrazine, are harmful to the health of those handling the material.^{2,3} Designing HEDMs for improved detonation properties in conjunction with 'greener' detonation products is a difficult task involving trial and error.⁴ Experimentalists are restricted in their ability to determine instantaneous mechanisms of decomposition.⁵ Computational methods can serve to reduce material waste by predicting decomposition properties through density functional theory (DFT) and Natural Bond Order (NBO) analysis.⁶⁻⁹ Conventional explosives typically consist of carbon backbones and hydrogen. -NO₂ groups or other sources of oxygen are necessary additives to these compounds to fully oxidize hydrogens and carbons.⁴ However, excessive amounts of this explosophore needed to fully oxidize the atoms destabilizes the molecule.

Lowering the carbon and hydrogen content within the backbone of the HEDMs will reduce the necessity of -NO₂ to oxidize these atoms.⁴ Compounds that have increased nitrogen content within the backbone can stabilize the molecule, produce non-toxic N₂ gas, and increase the heat of formation for gaseous production, oxygen balance, and density of the HEDM.^{2-5,10} In this study, we investigate the bonds within azo-bridged, high-nitrogen containing HEDMs.

Initiation of decomposition of HEDMs is characterized as the trigger bond, the bond that breaks to initiate detonation.^{5,9} Theoretical predictions in determining the trigger bond have been calculated using bond dissociation energies (BDEs)¹¹ but have resulted in

inaccurate results; A better means of predicting the trigger bonds, due to a more simplistic calculation, uses a measure of the electron density within the bond using the Wiberg bond index (WBI).^{5,9} The WBI is characterized as the sum of the off-diagonal square of the density matrix, P (**Equation 1**).¹²

$$WBI_{AB} = \sum_{p \in A} \sum_{q \in B} (D_{pq})^2$$

This value itself is not effective alone in correctly assigning the trigger bond. The WBI must be compared to a reference molecule. A relative scale of comparison with a bond that shares the same atom linkage, bond type, and hybridization is applied. The % Δ WBI is a calculation of the change in electron density from the addition of various explosophores (-NO₂, -N₃, etc.). (**Equation 2**). Greater negative values reflect a decrease in the electron density within the bond when compared to the reference molecule.^{5,9}

$$\% \Delta WBI_{AB} = \frac{WBI_{AB}(\text{HEDM}) - WBI_{AB}(\text{reference})}{WBI_{AB}(\text{reference})} \times 100$$

The goal of energetic material research is to design HEDMs with a trigger bond longer and less dense than in the conventional explosives. An example of this calculation is provided (**Figure 1**).⁵

Experimental methods to determine the relative sensitivity of HEDMs include electrical spark and impact sensitivity tests. Impact sensitivity tests are performed with a 2.5 or 5 kg weight dropped in small increments on the material.⁵ The height (in cm.) in which it detonates is characterized as the impact sensitivity.

Previous theoretical calculations have suggested that impact sensitivities heights (H_{50%}) can be predicted using DFT methods.¹³ H_{50%} refers to the height from which 50% of the drops result in the reaction of the sample.^{13,14}

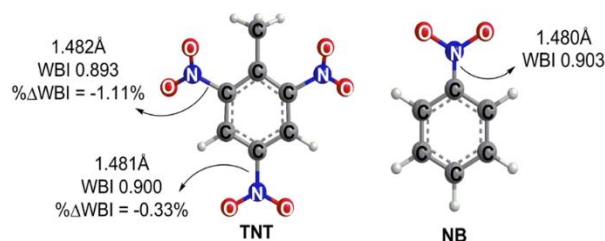


Figure 1. Example calculation % Δ WBI analysis for TNT with reference nitrobenzene

$$h_{50\%} = 9.2_{(cm)} + 8.034464 \times 10^2_{(cm)} \times \exp\left[-(0.3663 \frac{kcal}{mol}) |\bar{v}_s^+ |\bar{v}_s^-|\right]$$

Where $|\bar{v}_s^+ |\bar{v}_s^-|$ is the electrostatic potential

In this study, several novel HEDMs (**Figure 2**) were tested in the gas phase and condensed phase to trigger bonds to determine how intermolecular interactions could affect their detonation properties. In addition, the results will show that % Δ WBIs can be used to understand how intermolecular interactions influence the sensitivity of HEDMs. The results could be used as a screening method to guide the synthesis of more efficient energetic materials, thus decreasing hazardous waste and improving energetic properties.

COMPUTATIONAL METHODS

All HEDMs were DFT-optimized through the Gaussian09 software package¹⁵ with the hybrid function 'M06-2X'¹⁶ and triple- ζ basis set (TZVP)¹⁷ with no imaginary frequencies. WBI calculations were determined through Natural Bond Orbital (NBO) analysis version 3.1.¹⁸ Reference molecules for every HEDM contained the same hybridization, bond type, and linkage and are provided in **Data table 1**. Reference molecules were optimized using the same method and basis set for a more direct comparison. Dihedral angles were determined from optimized structures using Gaussian09 as well.

Electrostatic potentials were calculated using the Multiwfn software package¹⁹ and accomplished using the electrostatic potential surface (ESP) data, the average positive and negative potential values for each HEDM.¹³ The positive and negative average values were provided in the calculation for electrostatic potential.

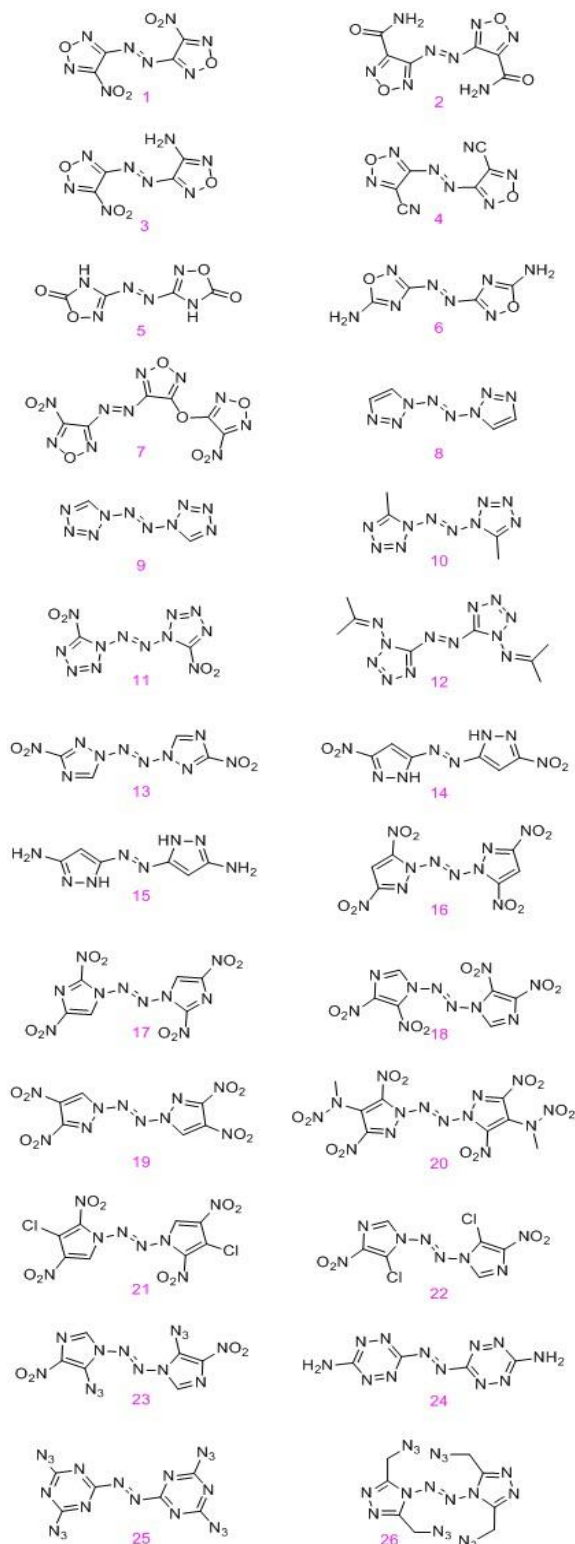


Figure 4. Azo-bridged HEDMs to be analyzed in this study

Table 1. Calculated WBIs and % Δ WBIs for DFT (M062X/TZVP) optimized geometries for 26 azo-bridged HEDMs with available experimental and theoretically calculated impact sensitivities. Dihedral angles were included for HEDMs with activation at the linkage.

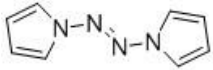
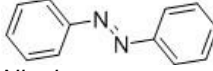
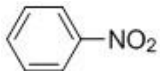
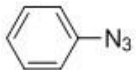
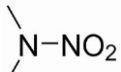
HEDM	WBI	Reference	% Δ WBI	IS (J)	H _{50%} (cm)	Dihedral Angle (°)
1-14	1.061	B	-1.431		49	39.73
2-37	1.075	B	-0.121		650	0.022
3-18	0.897	NB	-0.654		81	
4-38	1.078	B	0.0929		77	10.37
5-57	1.065	B	-1.078	>40	26	15.63
6-56	1.040	B	-3.409	>40	227	38.89
7-17	1.065	B	-1.076		39	26.44
8-72	1.076	A	-2.092		243	0.21
9-62	1.078	A	-1.965	<< 1	28	0.18
10-61	1.082	A	-1.583	S	531	0.32
11-64	1.065	A	-3.084	<< 1	16	12.07
12-63	1.095	B	1.756		109	7.43
13-73	0.873	NB	-3.280	10	48	
14-65	0.887	NB	-1.695	12.5	72	
15-66	1.104	B	2.564	7.4	717	0.10
16-81	1.063	A	-3.293	5	25	13.06
17-84	1.069	A	-2.774	15	13	15.52
18-85	1.081	A	-1.674	10	15	9.73
19-82	0.877	NB	-2.781	5	12	
20-83	0.954	DMNA	-9.047	2	27	
21-86	0.887	NB	-1.707	25	49	
22-87	0.902	NB	-0.0554	4	208	
23-88	1.371	Azidobenzene	-6.289	2	145	
24-117	1.045	B	-2.917	70 (cm)	472	28.53
25-115	1.005	B	-6.700	18.3 (cm)	554	58.03
26-75	1.399	Azidobenzene	-4.368	2	98	

RESULTS AND DISCUSSION

1. Characterization of Azo-Bridged HEDM Trigger Bonds

26 novel HEDMs were DFT (M06-2X)/TZVP optimized with C_i symmetry, if available. 19 of these HEDMs were predicted to detonate at the azo-bridge according to % Δ WBIs and electrostatic potential mapping of the optimized structures. In addition to the HEDMs, each reference molecules was DFT (M06-2X)/TZVP optimized. A common observation in our data was the decrease in density of electron surrounding the bridge linkage within our HEDMs. The addition of explosives

or additional electronegative atoms had a withdrawing effect on many azo-linkages. **Figure 5** shows the electrostatic potential surfaces (ESP) for a sampling of our molecules. For azo-bridged references, the linkage was near-planar with dihedral angles 0.002° and 0.798° for reference A and B respectively. For this study, we compared the two different azo-bridged references and their corresponding HEDMs to find trends between dihedral angles, impact sensitivity and % Δ WBIs.

Table 2. Calculated WBIs for DFT (M062X/TZVP) optimized structures of reference molecules.		
Reference	Bond	WBI
Name here 	N(sp ²)-N(sp ²)	1.099
Name here 	C(sp ²)-N(sp ²)	1.077
Nitrobenzene 	C(sp ²)-N(sp ³)	0.902
Azidobenzene 	C(sp ²)-N(sp ²)	1.463
Dimethylnitro-aniline (DMNA) 	N(sp ³)-N(sp ³)	1.049

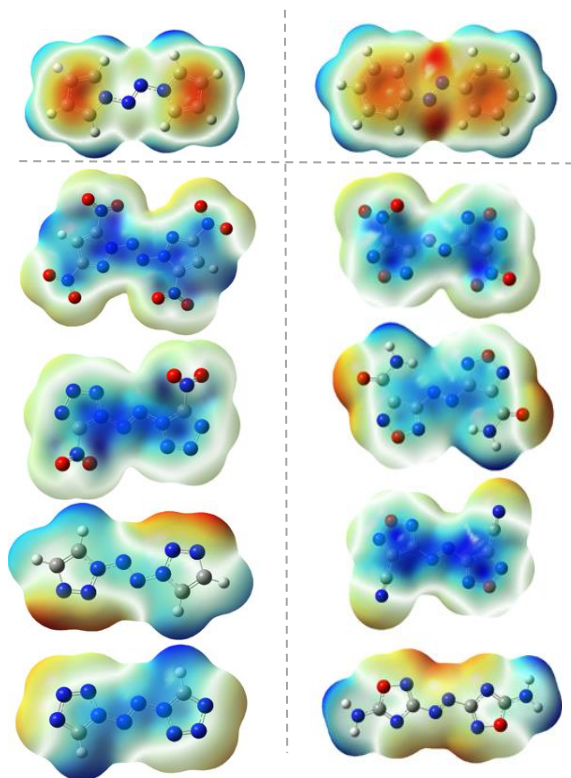


Figure (5). ESP map for a few molecules from data set **A** (left) and data set **B** (right) of order of increasing sensitivity from top to bottom. The blue regions depict a net positive region.

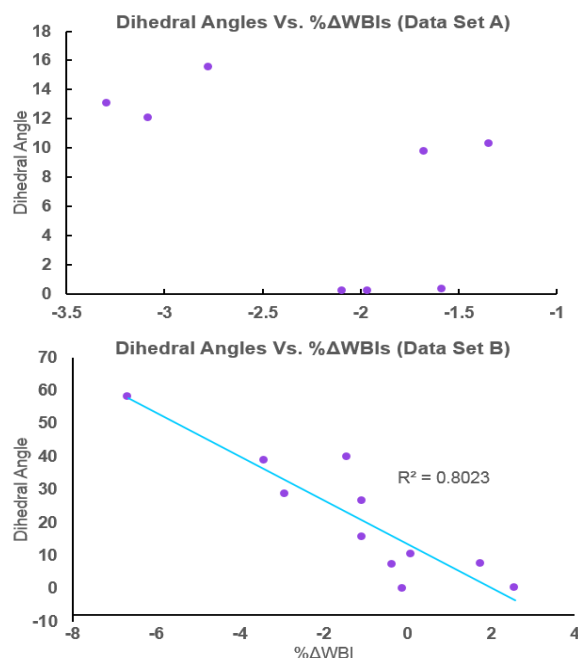


Figure 6. Dihedral angles vs % Δ WBIs for both data sets. Data set A did not have any correlation, thus no trend line was plotted.

From the optimized structures, WBIs were calculated for each of the references and HEDMs (**Tables 1 and 2**). For all HEDMs with the bridge consisting of 4 nitrogen atoms (N-N=N-N), the reference (name here, A). HEDMs with bridge linkage as C-N=N-C were compared to (name here B).

Dihedral angles of the bridge region can be attributed to the instability of the compound. We presume that increased activation may be a result of excess twist found within the bridge. An excess twist may cause interruption in p – orbital overlap. This data was anticipated to show a negative correlation of dihedral angle vs % Δ WBIs in which a greater dihedral angle within the bridge would produce a more activated trigger bond. Factors that could cause the dihedral angle to twist out of the plane of the molecule include steric effects between substituted groups and electron repulsion of the nonbonding orbitals of the azo group. For example, HEDM 1 has a dihedral twist of 39.73°. This molecule also has a –NO₂ substitution which sterically hinders the bridge atoms. The oxygen is in place of the empty p-orbital of the nitrogen in the azo-linkage. The bridge twists to avoid these effects. In addition, for molecules **24** and **25**, the same steric effects exist but are due to the orbitals of adjacent nitrogen atoms of the bridge and within the ring. These molecules experience the greatest twist compared to all other HEDMs (28.53° and 58.03° respectively). The % Δ WBIs calculated for these molecules predict that the trigger will lie within the bridge with relative decreases in density of -2.92% and -6.70% respectively. A full correlation of % Δ WBIs and dihedral angles is provided (**Figure 6**). As a general observation,

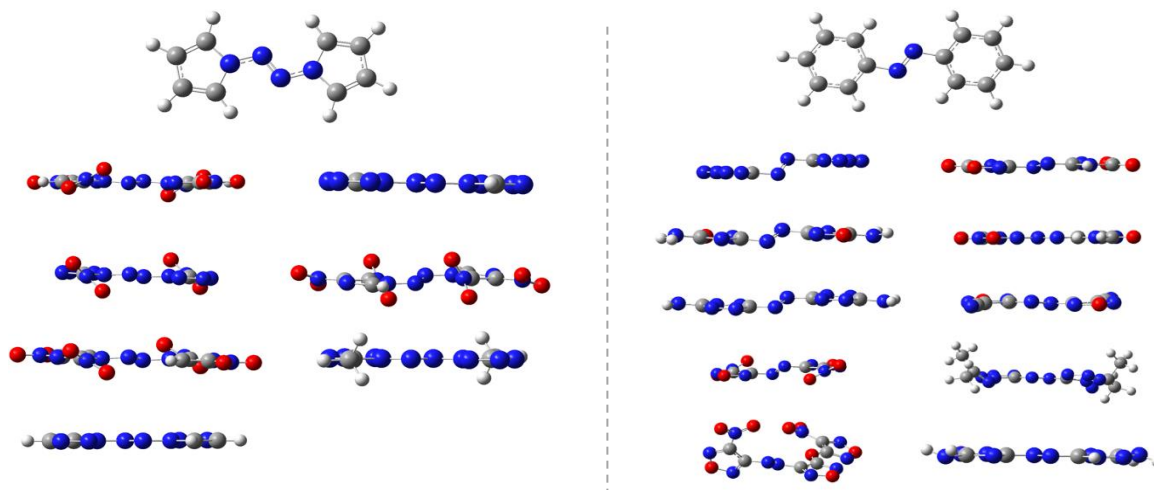


Figure 7. Side view of dihedral angles within the azo-bridge with data set **A** (left) and data set **B** (right). Order of increasing sensitivity moves from top to bottom, left to right.

we found that data set **A** showed no correlation with $\% \Delta \text{WBIs}$. Conversely, data set **B** correlated well adequately with an R^2 value of 0.8023. Currently, it is unknown why data set **A** did not fall within the trend. From observing structures, the twists within the bridge do not appear to be as extreme as data set **A** observations.

In addition to dihedral angles, another explosive property, impact sensitivity (IS), was compared with $\% \Delta \text{WBIs}$. Generally, impact sensitivities are performed experimentally by dropping 2.5 or 5 kg weights on the HEDM. The greater the IS, the greater the stability of the molecule. When theoretically determining the IS, there were not many consistencies with the experimental ISs. This method of calculating the IS was parameterized for a specific set of molecules in a previous study.¹³ Because this method was not parameterized for this specific set, there can arise some anomalies compared to the experimentally determined values. In addition, we speculate that molecules with very positive regions will increase the IS prediction. For the $-\text{NH}_2$ substituted HEDMs for data set **B**, these values were generally higher than HEDMs that did not contain $-\text{NH}_2$ substitutions.

To continue, the anticipated trend between IS and $\% \Delta \text{WBIs}$ should show positive correlation. For data set **A**, we observe poor correlation of IS and $\% \Delta \text{WBIs}$. Two values were considered outliers for our trend (molecules **9** and **18**). This is not fully understood considering the amount of $-\text{NO}_2$ substitution for **18**. Ordinarily, we expected this molecule to have a low impact sensitivity and high dihedral angle twist due to the steric hindrance, yet this was not observed. This molecule is still being tested and analyzed to learn the explanation for these anomalies. In contrast, data set **B** correlated acceptably. For this data, we found two different sets of data to exist, the original data and a smaller, subsection of HEDMs consisting of $-\text{NH}_2$

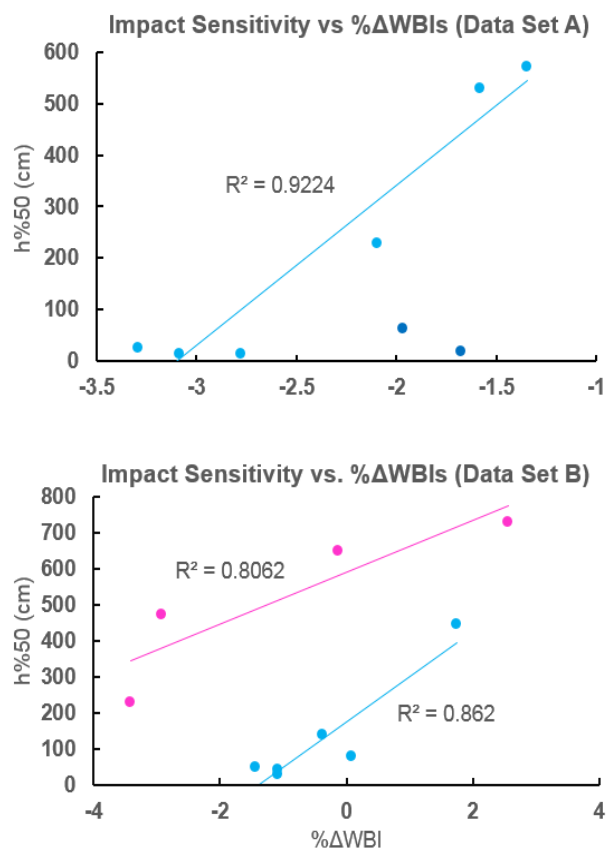


Figure 8. Impact sensitivities vs $\% \Delta \text{WBIs}$ for data sets **A** (top) and **B** (bottom). In pink is the trend line formed from the HEDMs with $-\text{NH}_2$ substitutions. In set **A**, in dark blue are the points that did not follow the trend and were considered outliers.

substitution. HEDMs **2**, **6**, **15**, and **24** all contained -NH_2 substitutions that seemed to cause the creation of a separate trend (**Figure 8**). While both sets are different, we observe the positive slope for both thus agreeing with our hypothesis that $\% \Delta \text{WBIs}$ and impact sensitivities can relate agreeably with one another.

From this research, no conclusions could be made from data set **A**. For both analyses, a trend line could not be generated from the raw data that represented the points. Using IS vs $\% \Delta \text{WBIs}$ two points were excluded from the analysis leading us to pursue a deeper analysis of this set of data. Conversely, data set **B** followed calculated trends suitably. On average, R^2 values for all of the correlations of energetic properties with $\% \Delta \text{WBIs}$ were ~ 0.82 . We expected that our $\% \Delta \text{WBIs}$ would show positive linear relation with our theoretical impact sensitivities. This reflects the prediction that the decrease in electron density of a bond will result in a molecule more susceptible to impact. Dihedral angles in comparison to $\% \Delta \text{WBIs}$ for this set showed a negative linear correlation. As a result, we can predict that increased twists within the azo-bridge can cause activation of the HEDM.

CONCLUSIONS

In this experiment, we tested 26 azo-bridged HEDMs to predict the most likely trigger bond for this class of energetics. $\% \Delta \text{WBIs}$ for these molecules predict that the most activated bond lies within the azo-bridge. Two data sets, A and B, were analyzed by comparing ESP mapping, dihedral angle, and impact sensitivity. We observed a relationship to exist between $\% \Delta \text{WBIs}$ with impact sensitivity and dihedral angle for data set B. Decreased impact sensitivity values were found to correlate with larger, more negative $\% \Delta \text{WBIs}$, resulting in a positive slope ($R^2 = \sim 0.81$). Dihedral angles for set B were found to share a negative, linear relationship with $\% \Delta \text{WBIs}$. Increased twist in the dihedral angle in the azo-bridge leads to activation of this bond. However, data set **A** has many uncertainties associated with its characteristics. Analysis of dihedral angle correlation with $\% \Delta \text{WBIs}$ led to no conclusions about their relationship. In addition, we found little connection between $\% \Delta \text{WBIs}$ and impact sensitivity. More calculations must be performed to better understand trends that lie within our data. We hope to find more azo-bridged HEDMs in the literature to add to our data set to achieve improved results. In all, $\% \Delta \text{WBIs}$ correlated well with properties for data set A and can serve to predict trigger bonds for this class of HEDMs

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