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Sensitivity and Performance of Azole-Based Energetic Materials

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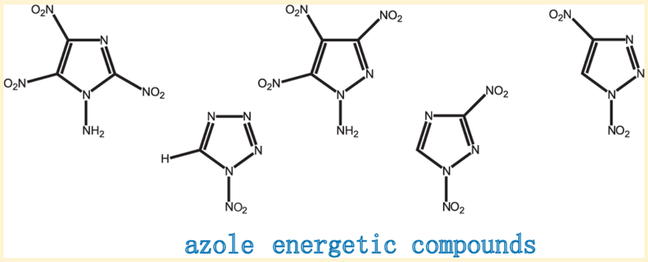

ABSTRACT: Imidazole, pyrazole, 1,2,3-triazole-, 1,2,4-triazole-, and tetrazole-based energetic materials are theoretically investigated by employing density functional theory (DFT). Heats of formation ($\Delta_f H^0$'s) for the studied compounds (298 K) in the gas phase are determined at the B3P86/6-311G (d, p) theory level through isodesmic reactions. The bond dissociation energies (BDEs) corresponding to NO_2, NH_2, CH_3, and Cl removal from carbon or nitrogen positions of the azole ring are also calculated at the B3P86/6-311G (d, p) theory level. The substituent effect of electron-withdrawing (NO_2, Cl) and electron-donating (NH_2, CH_3) groups on the $\Delta_f H^0$s and BDEs is discussed. Both electron-withdrawing groups and electron-donating groups (except the CH_3 group) dramatically increase the $\Delta_f H^0$s of these energetic materials when the substituent is at an N position on the azole ring. For substitution at a C atom on the azole ring, electron-withdrawing and electron-donating groups have different effects on the $\Delta_f H^0$s for different azole compounds. A correlation is developed for this series of energetics between impact sensitivity $h_{50\%}$ and the defined sensitivity index (SI): based on this empirical relationship and its extrapolation, the impact sensitivities of compounds for which experiments are not available are provided. The promising energetic compounds in each groups, which have potentially good energetic performance and low sensitivity, are 1-amino-2,4,5-trinitroimidazole, 1-amino-3,4,5-trinitropyrazole, 1,4-dinitro-1,2,3-triazole, 1,3-dinitro-1,2,4-triazole, and 1-nitrotetrazole.

I. INTRODUCTION

Energetic materials, including explosives and propellants that are useful for a variety of military purposes and industrial applications, have been studied for decades.[1−7] In order to meet future civilian and military safety and environmental requirements, research efforts have been undertaken to develop new energetic materials.[8−12] Among these new molecules, imidazole, pyrazole, triazole, and tetrazole based energetic species have drawn particular attention due to their high heats of formation, favorable detonation performance, good thermal stabilities, and impact and shock insensitivity.[11−14]

The heat of formation ($\Delta_f H^0$) is a crucial thermodynamic quantity. It is required to assess the stability of a molecule, and to calculate other thermodynamic functions. Detonation velocity (D) and pressure (P) are also important characteristics for scaling and relating the detonation performance of energetic materials. They can be calculated by using the Kamlet−Jacobs equation:[15]

$$P = K\rho^2\varphi, \quad K = 15.58, \quad \varphi = NM^{1/2}Q^{1/2} \tag{1}$$

$$D = A\varphi^{1/2}(1 + B\rho), \quad A = 1.01, \quad B = 1.30 \tag{2}$$

in which ρ is the density, N is the moles of gas produced by per gram of explosive, M is the average molar weight of detonation products, and Q is the estimated heat of detonation.

According to above equations, both velocity (D) and pressure (P) are related to the heat of detonation (Q). Q can be obtained from the heat of formation of the explosive, defined as[7,15]

$$Q \cong \frac{\Delta_d H}{\text{formula weight of explosive}} = \frac{\Delta_f H^0(\text{explosive}) - \Delta_f H^0(\text{products})}{\text{formula weight of explosive}} \tag{3}$$

The heat of detonation Q is frequently taken to be indicative of the "energy content/gram" of a high energy density material. Surprisingly, few bond dissociation energies (BDEs) and $\Delta_f H^0$ values are available, and systematic studies for the azole series are not reported for either quantity. Further, because less than 0.02% of known organic species have their heats of formation measured,[16] the application of quantum chemical methods is both inevitable and desirable, provided that reasonable accuracy can be obtained.

Dissociation of the weakest bond of an explosive molecule can play a relatively important role in the initiation of detonation, since rupture of this linkage is believed to be a key factor in many decomposition processes. In aromatic systems, including azole-based compounds, an interesting feature of many $C-NO_2$ bonds is the presence of a buildup of positive electrostatic potential above and below the bond region: these positive buildups can serve as initial sites for nucleophilic attack.[17,18] Typically, the $R-NO_2$ (R = C, N, or O) bond is the weakest bond in energetic ring molecules, and

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rupture of this bond on the ground state potential energy surface can be a first step in the decomposition process.[19,20] In addition, the chemical stabilities and impact/shock sensitivities of energetic materials are frequently related to the strength of the weakest bond R−NO_2: this bond energy can be obtained by calculating the BDEs for specific molecules.[20−27]

In addition, the impact sensitivity,[7,28,29] most often characterized by the height $h_{50\%}$ (in cm) that a given weight (most often 2.5 kg) must be dropped onto the sample to trigger an observable decomposition with a 50% probability, is an important and useful empirical parameter for determination of mechanical sensitivities of new energetic compounds. A general procedure to evaluate $h_{50\%}$ from molecular structure would therefore be of interest as a guide for the design and synthesis of new explosives.[30,31]

Considerable effort has been devoted to the development of such structure-sensitivity relationships.[7,26,29−48] Electronic band gap,[35,36] electronic shakeup promotion energies,[37] molecular electronegativity,[38] X-NO_2 bond lengths[39] and BDE,[25,33] total energy content per unit volume,[40] Mulliken net charges of the nitro group,[44,49] etc. have been all suggested as potential measures of energetic material structure/sensitivity relationships. Recently Mathieu[50] predicted the impact sensitivity for 156 compounds by using the relationship between impact sensitivity ($h_{50\%}$) and sensitivity index (SI): he relates the SI to the weakest bond in a given molecule and in general to X-NO_2. Mathieu's work suggests that the prediction of impact sensitivity is feasible for restricted classes of energetic materials (such as nitroaromatics) by finding the correlation between impact sensitivity ($h_{50\%}$) and SI. Due to this apparent success of ref 50, we also try to predict the impact sensitivity for our studied azole based compounds employing the SI concept and relationship.

In this work, imidazole, pyrazole, 1,2,3-triazole-, 1,2,4-triazole-, and tetrazole-based energetic compounds are investigated by using density functional theory (DFT) calculations for the ground state. Even though excited states are typically involved as well in the decomposition of energetic compounds, to initiate a chain reaction that results in the final explosion, reactions related to the ground state potential energy surface also play an important role in the whole explosive process. Thus the thermal reaction kinetics of energetic compounds on the ground state is also worthy of investigation and can be used to determine series characteristics, such as impact sensitivity. Heats of formation ($\Delta_f H^0$'s) for these studied compounds at 298 K in the gas phase are determined at the B3P86/6-311G (d, p) theory level using isodesmic reactions. The BDEs corresponding to NO_2, NH_2, CH_3, and Cl removal from carbon or nitrogen positions on the azole ring are also calculated at the B3P86/6-311G (d, p) theory level. The substitution effect of electron-withdrawing (NO_2, Cl) and electron-donating (NH_2, CH_3) groups on the $\Delta_f H^0$s and BDEs are determined and discussed. An empirical correlation is developed between impact sensitivity $h_{50\%}$ and the sensitivity index (SI); based on the generalization and extrapolation of this relationship, one can predict the impact sensitivities for compounds for which experiments are not available. Combining all the related factors, the most promising general energetic compounds from each azole ring group, which have potentially good energetic performance and low sensitivity, are propounded to be 1-amino-2,4,5-trinitroimidazole (compound 8), 1-amino-3,4,5-trinitroimidazole (compound 21), 1,4-dinitro-1,2,3-triazole (compound 29), 1,3-dinitro-1,2,4-triazole (compound 39), and 1-nitrotetrazole (compound 49).

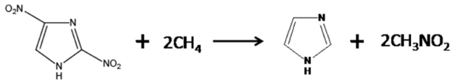
II. COMPUTATIONAL METHODS

All calculations are carried out with the Gaussian 09 program package.[51] The hybrid density functional B3P86 in conjunction with Pople basis set 6-311G (d, p) is used to calculate the heats of formations ($\Delta_f H^0$s), the BDEs, and geometries of molecules, including the title compounds and the reference species mentioned below to calculate $\Delta_f H^0$s.[26,27,33,52−54] Vibrational analysis is also performed for each stationary point to verify a minimum energy structure and to provide zero-point energies (ZPEs) and thermal corrections (H_T). The choice of these methods predicts $\Delta_f H^0$s and BDEs for various aromatic nitro compounds both efficiently and accurately. The homolytic BDE can be given in terms of[55]

$$\mathrm{BDE(R{-}NO_2)} = E(\mathrm{R}) + E(\mathrm{NO_2}) - E(\mathrm{RNO_2}) \tag{4}$$

in which the total energy E of each species includes the electronic energy (E_e) and the ZPE generated from a vibrational frequency calculation.

With respect to the computation of the standard heats of formation at 298.15 K, one can use either the atomization or isodesmic reaction method. In this work, the isodesmic reaction method is employed. Isodesmic reactions, for which the numbers of bonds and bond types are preserved on both sides of the reaction equation, often lead to cancellation of systematic errors resulting from the bond environments, spin contamination, basis set superposition errors, and other nonrandom factors.[56] The accuracy of $\Delta_f H^0$ obtained theoretically is conditioned by the reliability of $\Delta_f H^0$ of the reference compounds. The enthalpies of formation for the studied compounds are derived from isodesmic reactions: some examples of isodesmic reactions for imidazole-based compounds are given below:



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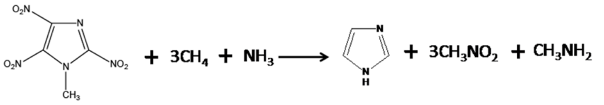

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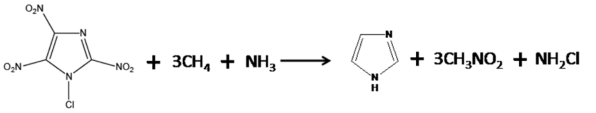

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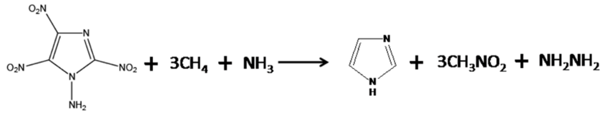


(8)

The experimental $\Delta_f H^0$s for reference compounds chosen for the isodesmic reations are listed in Table 1. For the isodesmic reactions, heats of reaction ΔH_{298} at 298 K can be calculated as

$$\Delta H_{298} = \Sigma \Delta_f H_p^0 - \Sigma \Delta_f H_R^0 \tag{9}$$

in which $\Delta_f H_p^0$ and $\Delta_f H_R^0$ are the heats of formation of products and reactants at 298 K, respectively. The $\Delta_f H^0$ of the studied compounds can be figured out when the heat of reaction ΔH_{298} is known. Based on calculation, the ΔH_{298} can be calculated from the following equation:

$$\begin{aligned}\Delta H_{298} &= \Delta E_{298} + \Delta(PV)\\ &= \Delta E^0 + \Delta \mathrm{ZPE} + \Delta H_\mathrm{T} + \Delta nRT\end{aligned} \tag{10}$$

Table 1. The Experimental Heat of Formation[a] ($\Delta_f H^0$/kcal·mol^{-1}) for Reference Compounds Chosen for the Isodesmic Reactions

compound	$\Delta_f H^0$	compound	$\Delta_f H^0$
CH_4[a]	−17.9	NH_2NO_2[d]	−6.2
NH_3[a]	−10.97	imidazole[a]	31.76
CH_3NO_2[b]	−17.8	pyrazole[a]	42.88
NH_2Cl[c]	16	1H-1,2,3-triazole[a]	43.19
NH_2CH_3[a]	−5.4	1H-1,2,4-triazole[a]	46.06
NH_2NH_2[a]	22.8	tetrazole[a]	76.48
CH_3Cl[a]	−20		

[a] NIST Chemistry WebBook, http://webbook.nist.gov/chemistry [b] Reference 57. [c] Reference 58. [d] Reference 59.

in which ΔE^0 and ΔZPE are the total electronic energy difference and the zero point energy difference between products and reactants at 0 K, respectively, ΔH_T is the change in thermal correction to enthalpies between products and reactants, and $\Delta(PV)$ equals ΔnRT for reaction in gas phase. For isodesmic reactions, $\Delta n = 0$. Combing these two equations, the $\Delta_f H^0$ of the studied compounds can be obtained.

III. RESULTS AND DISCUSSION

3.1. Heats of Formation. Fifty-five compounds including imidazoles, pyrazoles, 1,2,3-triazoles, 1,2,4-triazoles, and tetrazoles, as shown in Figures 1−5, have been calculated at the B3P86/6-31G (d, p) theory level and evaluated with respect to heats of formation and BDEs. Tables 2−5 present the $\Delta_f H^0$s and BDEs for these compounds. The calculated $\Delta_f H^0$s for the investigated molecules are all endothermic (see Tables 2−5), as is desirable for high energy density materials. Figure 6 presents the plot of heat of formation versus number of NO_2 groups on the ring; the numbers on the plots refer to the compound numbers given in Figures 1−5. The black squares denote compounds that only contain C-NO_2 groups; the red circles denote the compounds that have one N-NO_2 and all other ring attached NO_2 groups are C-NO_2 groups. The heats of formation increase with the number of nitro groups on the ring, as is clearly shown in Figure 6. With all available N and C positions substituted by NO_2 groups (compounds 5, 18, 30, 40, 50), $\Delta_f H^0$ increases dramatically. Even though only several samples are chosen for the study of the effect of increasing NO_2 groups on the azole ring, the general trend that $\Delta_f H^0$ for azole molecules increases as more NO_2 groups are substituted on the azole ring is clear. A large positive $\Delta_f H^0$ is found for these azole energetic molecules. Thus the more nitro groups substituted on the azole ring, the better the potential energetic performance.

In addition, compounds that have one N−NO_2 group have a higher $\Delta_f H^0$ than those that have only C−NO_2 groups, even if the number of NO_2 groups are the same; for example, compare compounds 1 and 2, 15 and 16, 28 and 29, 38 and 39, and 48 and 49 (using Figure 5). A similar trend has also been characterized for imidazole by others.[60,61] They suggest that the

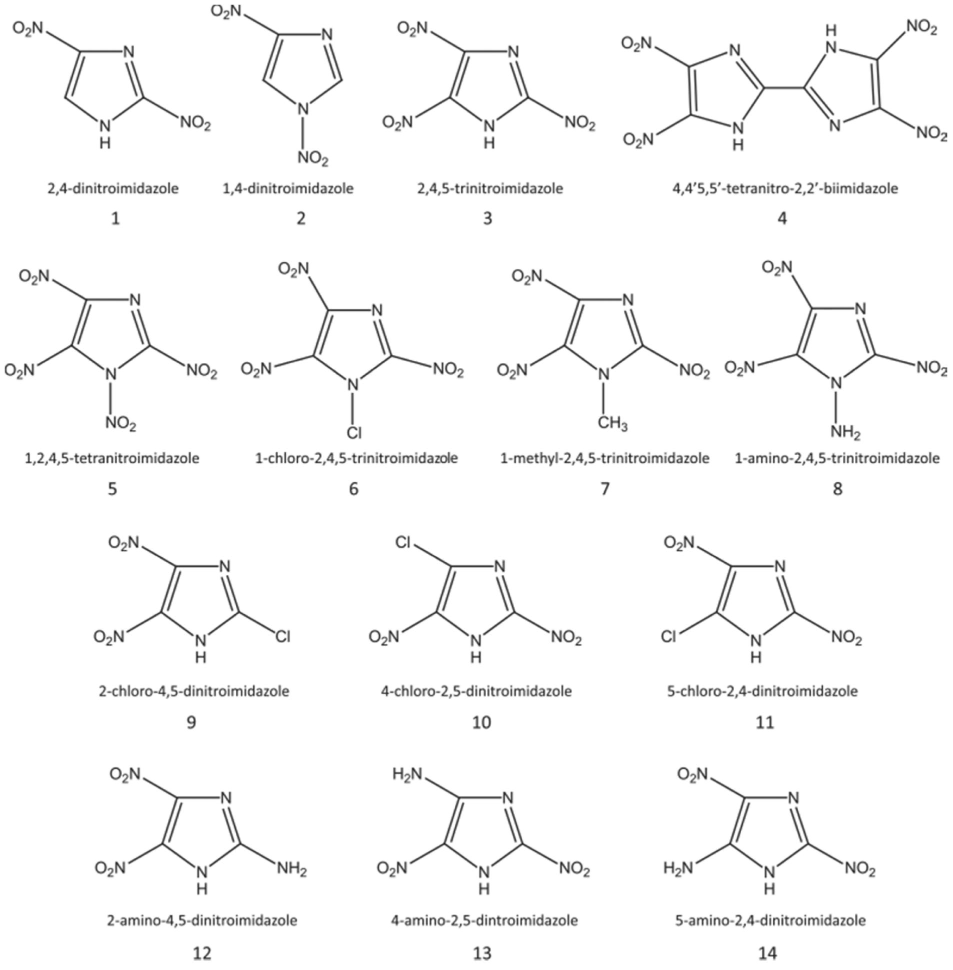


Figure 1. Structures of imidazole-based energetic materials.

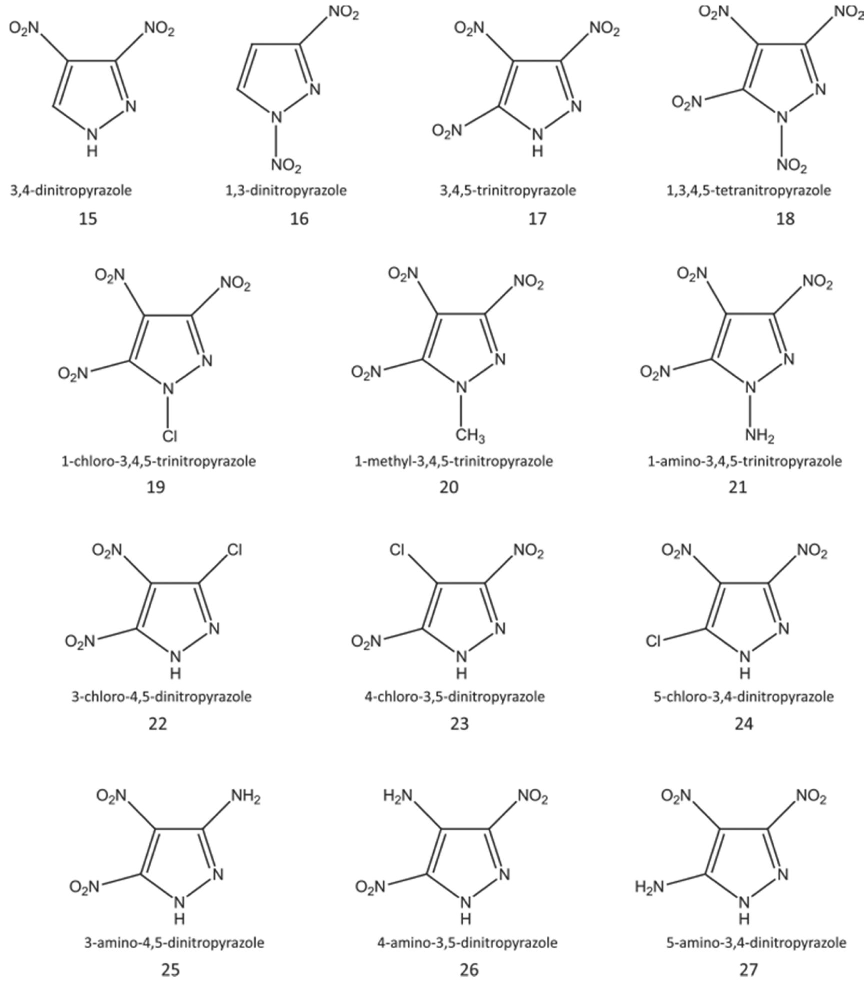


Figure 2. Structures of pyrazole-based energetic materials.

$\Delta_f H^0$ difference for *N*-nitro- and *C*-nitro-substituted imidazoles is due to the difference of bond energy between the $N-NO_2$ and $C-NO_2$ moieties. As the BDE of $N-NO_2$ is smaller than that of $C-NO_2$, according to the definition of heat of formation, the $N-NO_2$ systems consume less energy than the $C-NO_2$ systems during the process of decomposition into its constituent elements at standard states. Therefore, $N-NO_2$ substituted compounds have higher $\Delta_f H^0$ than corresponding $C-NO_2$ substituted compounds.[60,61] Based on this idea, the N-NO_2 BDE in compounds 2, 16, 29, 39, and 49 is on average 23.8 kcal/mol lower than the weakest $C-NO_2$ BDE in compounds 1, 15, 28, 38, and 48, and the $\Delta_f H^0$s of compounds 2, 16, 29, 39, and 49 are on average 12.2 kcal/mol higher than those of compounds 1, 15, 28, 38, and 48. This correlation shows that the weaker $N-NO_2$ bonds indeed increase the $\Delta_f H^0$s of $N-NO_2$ systems. Based on the above discussion and the general trend for all azoles, one can conclude that NO_2 substituted azoles at an N ring position usually are less stable than those substituted at a C ring position due to the weaker $N-NO_2$ bond and the higher heat of formation.

The effect of electron-donating and electron-withdrawing groups substituted at N or C positions can also be investigated. As shown in Figure 7, the heat of formation versus different electron-donating and electron-withdrawing groups at the N-position can be also explored: the trends for all substituted azoles are similar. Electron-withdrawing groups NO_2 and Cl increase the $\Delta_f H^0$ dramatically after substituting for the H atom at the N position. Even though the NO_2 group is a stronger electron-withdrawing group than Cl, its influence on the $\Delta_f H^0$ is similar to that of Cl substitution at the N position. On the other hand, the electron-donating groups CH_3 and NH_2 present quite different results. The stronger electron-donating group NH_2 (compounds 8, 21, 35, 45, and 53) raises the $\Delta_f H^0$ dramatically, compared with CH_3 substitution (compounds 7, 20, 31, 41, and 55) at N position. Thus we can conclude that for substitution at the N position, electron-withdrawing groups induce a comparable effect on the $\Delta_f H^0$, regardless of the strength of the group, but the stronger the electron-donating group is, the more the $\Delta_f H^0$ increases.

Through comparisons of imidazoles, pyrazoles, 1,2,3-triazoles, 1,2,4-triazoles, and tetrazoles, in vertical columns in Figure 7, one can study the effect of increasing the number of N atoms in the ring on the heats of formation for azoles compounds. As shown in Figure 7, the imidazole compounds, which contain two separated N atoms in the imidazole ring, have much lower $\Delta_f H^0$'s than the pyrazole compounds, which contain two neighboring N atoms in the azole ring. Adding another separated N atom in the azole ring, however, (pyrazole to 1,2,4-triazole) has only a small affect on the $\Delta_f H^0$'s: compare pyrazole, 1,2,3-triazole, and 1,2,4-triazole compounds. This result implies that the neighboring N atoms in the azole ring play a more important role for the $\Delta_f H^0$s than the separated N atoms do. The trend of $\Delta_f H^0$s for all azole compounds is imidazole < pyrazole ≈ 1,2,3-triazole ≈ 1,2,4-triazole < tetrazole.

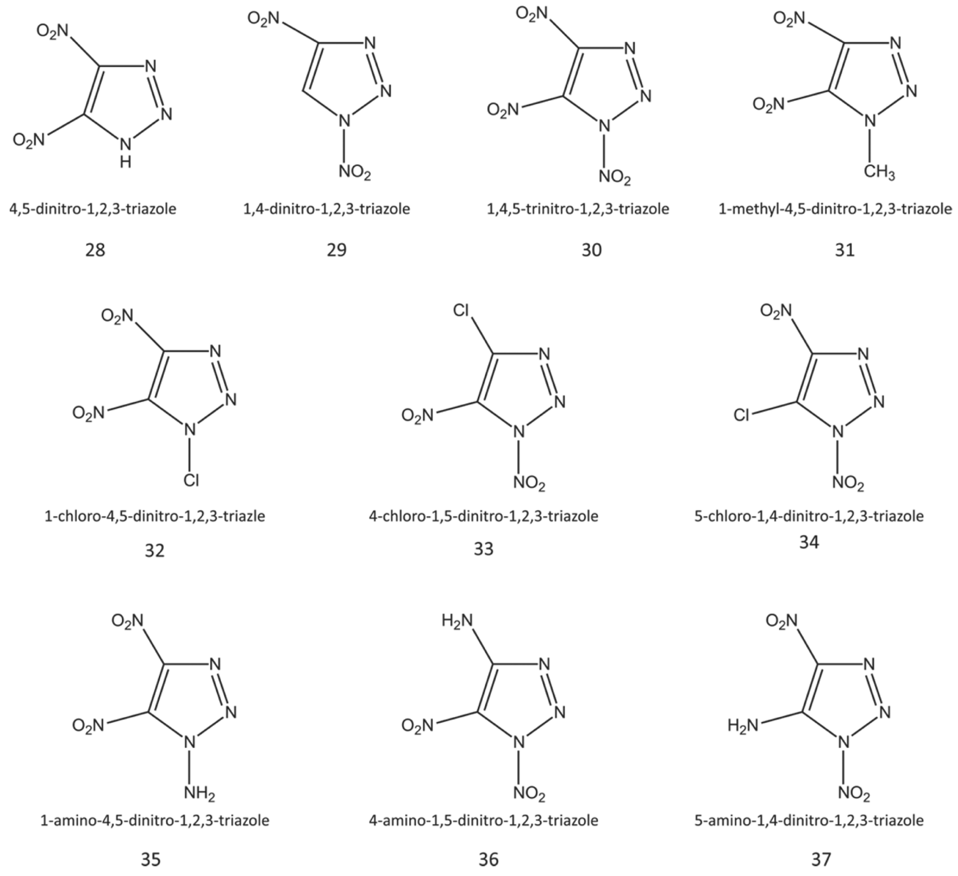


Figure 3. Structures of 1,2,3-triazole-based energetic materials.

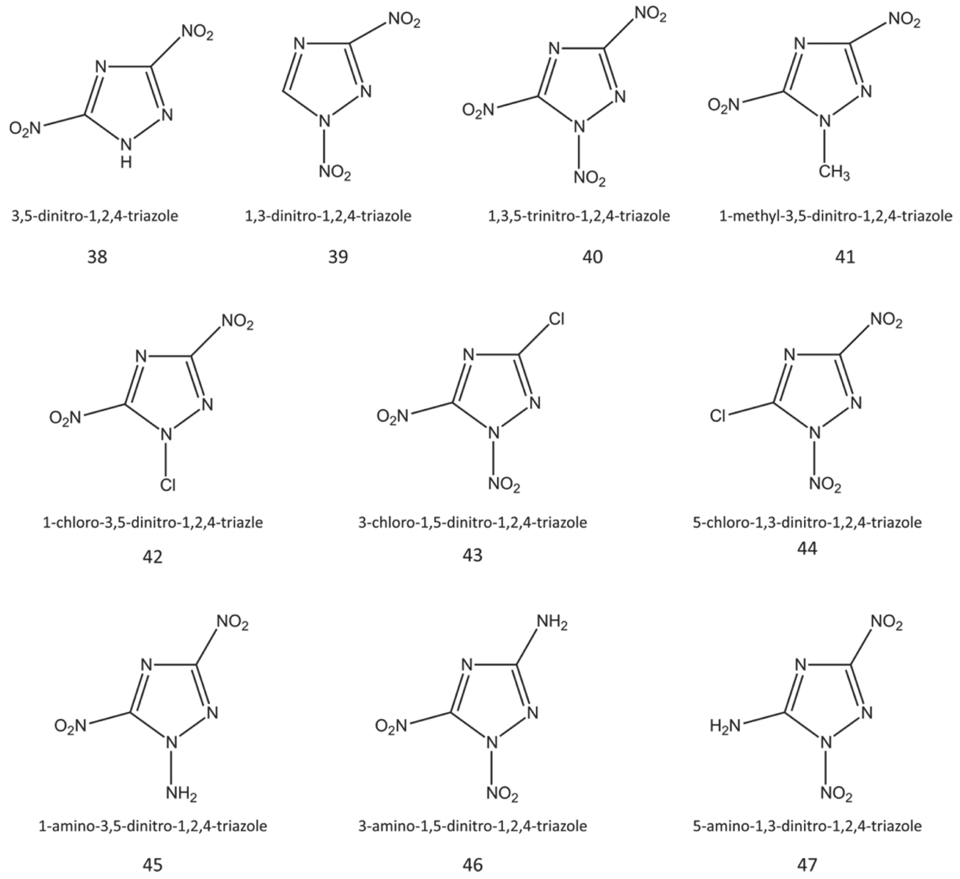
To investigate the position effect of electron-withdrawing and electron-donating groups on the ring, a plot of heats of formation of compounds versus electron-withdrawing Cl (red) and electron-donating NH_2 (black) groups is illustrated in Figure 8. In general, no matter which group (electron-withdrawing or electron-donating) is chosen for substitution at the N position, the $\Delta_f H^0$ increases dramatically. With regard to C position substitution, different azole compounds display different phenomena. For imidazole and pyrazole compounds, no matter at which C position the substitution occurs, the electron-withdrawing group Cl has little effect on the $\Delta_f H^0$s. The electron-donating group NH_2, however, reduces the $\Delta_f H^0$'s for all imidazole and pyrazole compounds. For 1,2,3-triazole, 1,2,4-triazole, and tetrazole compounds, a different trend is apparent for C substitution on the ring: the electron-withdrawing group Cl increases the $\Delta_f H^0$'s, and the electron-donating group NH_2 does not change the $\Delta_f H^0$s significantly.

On the basis of the above results and discussion, we reach several conclusions: (1) $\Delta_f H^0$'s relate to the number of nitro groups attached to the ring and increase with the addition of NO_2 groups, thereby increasing the number of NO_2 groups in the molecule will improve the potential energetic performance; (2) $\Delta_f H^0$s for N−NO_2 substituted energetic materials are typically much higher than those for C−NO_2 substituted energetic materials, and thus, in order to obtain better potential energetic performance, NO_2 substitution should be on the N atom of the five-member ring; (3) increased N atoms of the five member ring also have an effect on the $\Delta_f H^0$s of energetic materials (tetrazole > triazole ≈ pyrazole > imidazole); (4) if substitution occurs on the N atom of the five-member ring, both electron-withdrawing and electron-donating groups (except the CH_3 group) will dramatically increase the $\Delta_f H^0$s of these energetic materials; (5) if substitution occurs on the C atom of the five-member ring for imidazole and pyrazole compounds, the electron-withdrawing group Cl has little effect on the $\Delta_f H^0$s and the electron-donating group NH_2 reduces the $\Delta_f H^0$s; and (6) if the substitution occurs on the C atom of the five member ring for 1,2,3-triazole, 1,2,4-triazole, and tetrazole compounds, the electron-withdrawing group Cl increases the $\Delta_f H^0$s and the electron-donating group NH_2 does not change the $\Delta_f H^0$s significantly.

3.2. Determination of the Weakest Bond.

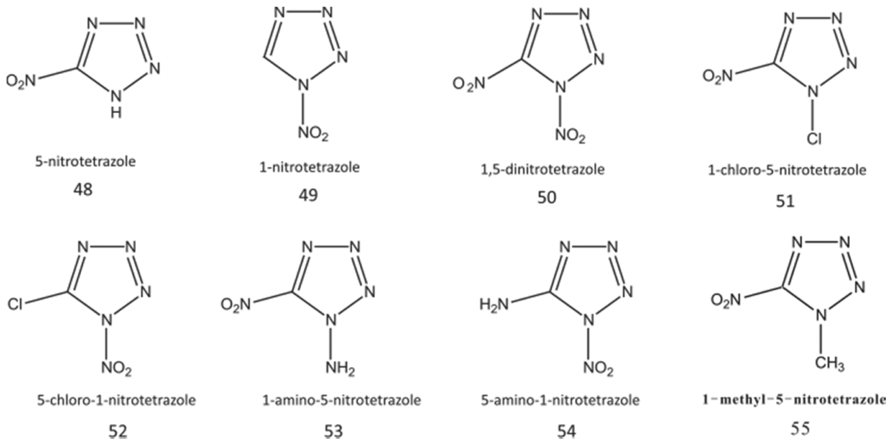
The bond strength of the weakest bond for an energetic molecule is of considerable importance, since the rupture of this linkage can be a key factor in many thermal and other decomposition processes. Research shows that the bond R−NO_2 (R = C, N or O) is the typically weakest one for the ground state of energetic ring molecules, and this bond rupture can be involved in the decomposition and energy release process.[21,62,63] Further, the stabilities and impact/shock sensitivities of energetic materials have also frequently been related to the strengths of bond R−NO_2.[22,26,33,39,42,49,64,65]

To elucidate this, the BDE for each compound is calculated at the B3P86/6-31G** level and listed in Tables 2−6. With the increase of the number of NO_2 groups on the C atom, the BDE of the weakest bond C−NO_2 slightly decreases, but the change is almost negligible. For example, BDE for 2,4-dinitroimidazole (C2−NO_2, 69.1 kcal/mol) > 2,4,5-trinitroimidazole (C4−NO_2, 61.4 kcal/mol) and 3,4-dinitropyrazole (C3−NO_2, 63.4 kcal/mol) > 3,4,5-trinitropyrazole (C4−NO_2, 62.7 kcal/mol). The BDE for N−NO_2 (average 35 kcal/mol) is much smaller than that of C−NO_2 (average 65 kcal/mol) for all these five-member



3,5-dinitro-1,2,4-triazole 38
1,3-dinitro-1,2,4-triazole 39
1,3,5-trinitro-1,2,4-triazole 40
1-methyl-3,5-dinitro-1,2,4-triazole 41
1-chloro-3,5-dinitro-1,2,4-triazle 42
3-chloro-1,5-dinitro-1,2,4-triazole 43
5-chloro-1,3-dinitro-1,2,4-triazole 44
1-amino-3,5-dinitro-1,2,4-triazole 45
3-amino-1,5-dinitro-1,2,4-triazole 46
5-amino-1,3-dinitro-1,2,4-triazole 47

Figure 4. Structures of 1,2,4-triazole-based energetic materials.



5-nitrotetrazole 48
1-nitrotetrazole 49
1,5-dinitrotetrazole 50
1-chloro-5-nitrotetrazole 51
5-chloro-1-nitrotetrazole 52
1-amino-5-nitrotetrazole 53
5-amino-1-nitrotetrazole 54
1-methyl-5-nitrotetrazole 55

Figure 5. Structures of tetrazole-based energetic materials.

ring compounds. This result is in agreement with that of the non-aromatic energetic materials, for which nitramine type ($N-NO_2$) energetic materials (RDX, HMX) are usually more sensitive than $C-NO_2$ type energetic materials (FOX-7) due to the weaker $N-NO_2$ bond. The energy difference between the $N-NO_2$ and $C-NO_2$ BDEs also partly explains the $\Delta_f H^0$ difference for *N*-nitro-substituted and *C*-nitro-substituted compounds as discussed in section 3.1. Therefore the $N-NO_2$-substituted energetic materials usually have higher $\Delta_f H^0$'s and better potential energetic performance but are more sensitive due to the weaker $N-NO_2$ bond.

If an electron-withdrawing group (NO_2 or Cl) substitutes for the H atom at an N position of the five-member ring, the $N-NO_2$ or N−Cl bond usually is the weakest bond: the average BDEs in this instance are 35 and 55 kcal/mol, respectively. If an electron-donating group (NH_2 or CH_3) substitutes for the H atom at an N position of the five-member ring; however, the weakest bond is always a $C-NO_2$ bond with average 65 kcal/mol dissociation energy. Thus, the electron-donating group substitution at an N position can improve the stability of energetic materials.

If substitution of the electron-withdrawing group Cl and the electron-donating group NH_2 occurs at a C position, the BDEs of the $C-NO_2$ bond do not change significantly. The average BDE of the $C-NO_2$ bond is still about 65 kcal/mol. Even though the average change of BDE of the $C-NO_2$ bond is small, the electron-withdrawing group Cl and the electron-donating

Table 2. Calculated N (or C)−NO_2 (or NH_2, Cl) BDE[a] and Heat of Formation ($\Delta_f H^0$) for Imidazole-Based Energetic Materials at the B3P86/6-311G (d, p) Theory Level[b]

compound	bond	BDE	$\Delta_f H^0$	compound	bond	BDE	$\Delta_f H^0$
1	**C2−NO_2**	**69.1**	29.7	8	N1−NH_2	69.1	66.2
	C4−NO_2	70.1			C2−NO_2	68.0	
2	**N1−NO_2**	**34.5**	45.4		**C4−NO_2**	**61.3**	
	C4−NO_2	70.0			C5−NO_2	64.4	
3	C2−NO_2	66.0	41.5	9	C2−Cl	95.6	32.4
	C4−NO_2	**61.4**			C4−NO_2	67.0	
	C5−NO_2	64.2			**C5−NO_2**	**62.6**	
4	**C4−NO_2**	**62.4**	73.3	10	**C2−NO_2**	**66.9**	27.9
	C5−NO_2	65.7			C4−Cl	95.3	
5	**N1−NO_2**	**20.4**	76.4		C5−NO_2	71.0	
	C2−NO_2	60.1		11	C2−NO_2	68.1	29.4
	C4−NO_2	60.5			**C4−NO_2**	**67.8**	
	C5−NO_2	61.2			C5−Cl	96.7	
6	**N1−Cl**	**40.5**	84.5	12	C2−NH_2	116.1	27.0
	C2−NO_2	61.3			C4−NO_2	70.1	
	C4−NO_2	61.6			**C5−NO_2**	**64.0**	
	C5−NO_2	59.6		13	**C2−NO_2**	**67.8**	17.7
7	N1−CH_3	84.2	43.0		C4−NH_2	120.7	
	C2−NO_2	63.3			C5−NO_2	74.8	
	C4−NO_2	61.7		14	**C2−NO_2**	**71.5**	19.5
	C5−NO_2	**61.0**			C4−NO_2	77.9	
					C5−NH_2	121.6	

[a]Boldface entries indicate the weakest bond. [b]Heats of sublimation are neglected. Units are kcal/mol and compound numbers are given in Figure 1.

Table 3. Calculated N (or C)−NO_2 (or NH_2, Cl) BDE[a] and Heat of Formation ($\Delta_f H^0$) for Pyrazole-Based Energetic Materials at the B3P86/6-311G (d, p) Theory Level[b]

compound	bond	BDE	$\Delta_f H^0$	compound	bond	BDE	$\Delta_f H^0$
15	**C3−NO_2**	**63.4**	49.0		**C4−NO_2**	**62.5**	
	C4−NO_2	68.1			C5−NO_2	64.3	
16	**N1−NO_2**	**46.8**	58.1	22	C3−Cl	91.5	51.5
	C3−NO_2	68.1			C4−NO_2	61.2	
17	C3−NO_2	64.6	58.4		**C5−NO_2**	**60.4**	
	C4−NO_2	**62.7**		23	**C3−NO_2**	**66.1**	45.7
	C5−NO_2	66.1			C4−Cl	95.8	
18	**N1−NO_2**	**36.8**	89.1		C5−NO_2	69.7	
	C3−NO_2	60.0		24	**C3−NO_2**	**62.4**	48.4
	C4−NO_2	61.4			C4−NO_2	66.1	
	C5−NO_2	57.7			C5−Cl	96.5	
19	**N1−Cl**	**57.6**	96.1	25	C3−NH_2	118.3	29.0
	C3−NO_2	62.6			C4−NO_2	72.2	
	C4−NO_2	61.2			**C5−NO_2**	**65.5**	
	C5−NO_2	61.7		26	**C3−NO_2**	**74.4**	32.2
20	N1−CH_3	101.1	55.0		C4−NH_2	124.2	
	C3−NO_2	65.0			C5−NO_2	76.5	
	C4−NO_2	**62.6**		27	**C3−NO_2**	**63.6**	39.6
	C5−NO_2	64.4			C4−NO_2	75.6	
21	N1−NH_2	83.6	80.4		C5−NH_2	120.3	
	C3−NO_2	63.8					

[a]Boldface entries indicate the weakest bond. [b]Heats of sublimation are neglected. Units are kcal/mol and compound numbers are given in Figure 2.

group NH_2 still have a positional effect on the BDE of the C−NO_2 bond. For imidazole-based compounds, the weakest C−NO_2 bond reaches the max (67.8 kcal/mol in compound 11 and 71.5 kcal/mol in compound 14), as the electron-withdrawing group Cl or the electron-donating group NH_2 substitutes at the C5 position. For pyrazole-based compounds, the weakest C−NO_2 bond reaches a maximum value (66.1 kcal/mol in compound 23 and 74.4 kcal/mol in compound 26), if the electron-withdrawing group Cl or the electron-donating group NH_2 substitutes at the C4 position.

Both the electron-withdrawing group Cl and the electron-donating group NH_2 weaken the N−NO_2 bond, especially if the substitution occurs at a C position. For example, the BDE of the N−NO_2 bond reaches a minimum value of 29.7 (compound 33) and 18.4 (compound 36) kcal/mol, for the Cl and NH_2 substitution at the C4 of 1,2,3-triazole based compounds,

Table 4. Calculated N (or C)−NO_2 (or NH_2, Cl) BDE[a] and Heat of Formation ($\Delta_f H^0$) for 1,2,3-Triazole-Based Energetic Materials at the B3P86/6-311G (d, p) Theory Level[b]

compound	bond	BDE	$\Delta_f H^0$	compound	bond	BDE	$\Delta_f H^0$
28	**C4−NO_2**	**63.1**	56.5	33	**N1−NO_2**	**29.7**	72.1
	C5−NO_2	64.3			C4−Cl	96.5	
29	**N1−NO_2**	**41.7**	65.4		C5−NO_2	62.2	
	C4−NO_2	68.9		34	**N1−NO_2**	**40.8**	69.5
30	**N1−NO_2**	**34.8**	85.1		C4−NO_2	67.0	
	C4−NO_2	64.2			C5−Cl	93.9	
	C5−NO_2	58.9		35	N1−NH_2	86.0	77.5
31	N1−CH_3	103.7	51.6		**C4−NO_2**	**62.7**	
	C4−NO_2	**63.2**			C5−NO_2	65.7	
	C5−NO_2	63.7		36	**N1−NO_2**	**18.4**	60.7
32	N1−Cl	61.3	91.7		C4−NH_2	122.9	
	C4−NO_2	62.8			C5−NO_2	63.9	
	C5−NO_2	**61.1**		37	**N1−NO_2**	**27.6**	51.3
					C4−NO_2	77.4	
					C5−NH_2	126.8	

[a]Boldface entries indicate the weakest bond. [b]Heats of sublimation are neglected. Units are kcal/mol and compound numbers are given in Figure 3.

Table 5. Calculated N (or C)−NO_2 (or NH_2, Cl) BDE[a] and Heat of Formation ($\Delta_f H^0$) for 1,2,4-Triazole-Based Energetic Materials at the B3P86/6-311G (d, p) Theory Level[b]

compound	bond	BDE	$\Delta_f H^0$	compound	bond	BDE	$\Delta_f H^0$
38	C3−NO_2	65.9	55.3	43	**N1−NO_2**	**30.1**	73.0
	C5−NO_2	**65.8**			C3−Cl	96.6	
39	**N1−NO_2**	**43.8**	69.5		C5−NO_2	58.1	
	C3−NO_2	65.6		44	**N1−NO_2**	**33.7**	69.3
40	**N1−NO_2**	**36.2**	85.9		C3−NO_2	65.2	
	C3−NO_2	64.4			C5−Cl	93.4	
	C5−NO_2	57.2		45	N1−NH_2	84.3	76.4
41	N1−CH_3	105.0	51.3		C3−NO_2	66.8	
	C3−NO_2	66.6			**C5−NO_2**	**64.8**	
	C5−NO_2	**64.8**		46	**N1−NO_2**	**18.2**	66.0
42	N1−Cl	62.0	92.0		C3−NH_2	118.7	
	C3−NO_2	70.1			C5−NO_2	59.2	
	C5−NO_2	**61.6**		47	**N1−NO_2**	**28.7**	55.4
					C3−NO_2	65.9	
					C5−NH_2	122.3	

[a]Boldface entries indicate the weakest bond. [b]Heats of sublimation are neglected. Units are kcal/mol and compound numbers are given in Figure 4.

respectively. The BDE of the N−NO_2 bond reaches a minimum value of 30.1 (compound 43) and 18.2 (compound 46) kcal/mol for substitution of the Cl and NH_2 at the C3 atom of 1,2,4-triazole based compounds, respectively.

Based on above discussion, we can reach several conclusions: (1) substitution of an electron-withdrawing group at the N position of these five-member ring compounds will make the compound more sensitive due to the generation of a weaker N−NO_2 or N−Cl bond; (2) substitution of an electron-donating group at the N position of the five-member ring compound will maintain the stability of these species; (3) substitution of an electron-withdrawing or an electron-donating group at a C position of the five-member ring weakens the N−NO_2 bond, but does not have a significant influence on a C−NO_2 bond.

3.3. Prediction of Impact Sensitivity.

We have discussed the $\Delta_f H^0$'s, which are related to the energetic performance, and the weakest bond, which is related with the stability of the compounds above. To obtain an excellent energetic material that has good energetic content and low sensitivity, one should consider a number of factors. Impact sensitivity (defined below) is a direct way to exhibit the stability of the compounds. Thus, we try to predict the impact sensitivity for these azole energetic materials. As introduced above, all kinds of methods have been used to build up a relationship between the sensitivity and parameters related to the molecular structure.[29−48] Rice et al.[21] have made a plot of $\ln(h_{50\%})$ versus calculated BDE, which presents a linear correlation between them. We also tried to make a plot between $\ln(h_{50\%})$ and BDE for the compounds in Table 7; however, the result did not present a linear relationship between $\ln(h_{50\%})$ and BDE. The possible reason is that all the samples they chose are benzene-based compounds, so they may present similar thermodynamics and reaction activity. When coming to more complicated compounds that are not related through a simple and direct common chemistry, this kind of linear correlation between $\ln(h_{50\%})$ and BDE usually will not exist. Thus, in our work, the experimental correlation between impact sensitivity ($h_{50\%}$) and SI is applied to predict the stability of azole based compounds.[20,50]

Based on the experimental sensitivity $h_{50\%}$ available and the calculated SI values, a plot of $h_{50\%}$ versus SI is illustrated in Figure 9. Here SI is defined as follows:[50]

$$\mathrm{SI} = ND_{\min}/\Delta_d H \qquad (11)$$

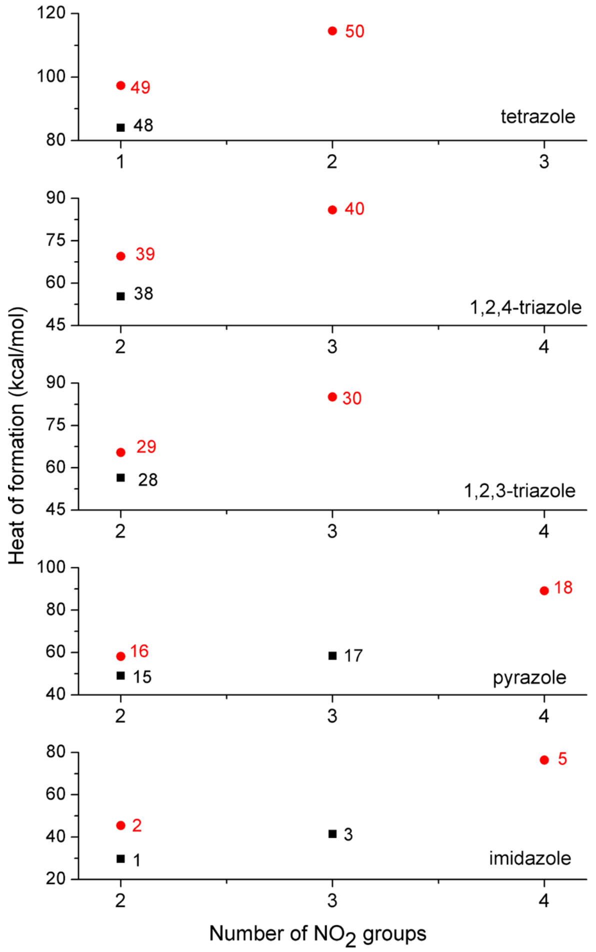


Figure 6. A plot of heat of formation ($\Delta_f H^0$) versus number of NO_2 groups on the ring. Note that the heats of formation ($\Delta_f H^0$'s) generally increase with the number of NO_2 groups attached to the ring. Black squares ■ denote compounds that contain only C-NO_2 groups. Red circles ● denote compounds that have one N-NO_2 group and all other NO_2 groups are C-NO_2 groups. Numbers on the plot refer to the compound numbers given in Figures 1−5

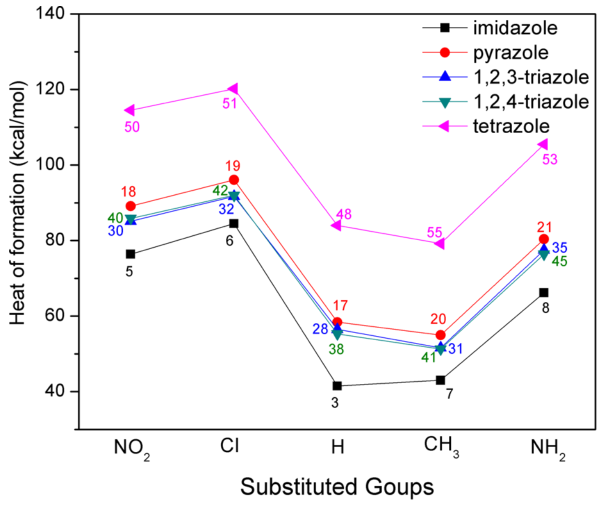


Figure 7. Plot of heat of formation ($\Delta_f H^0$) versus different electron-donating and electron-withdrawing groups at an N ring position. The horizontal axis is the different substituent groups and electron donating capacity increases from left to right. The color coded numbers on the plot are the compound numbers given in Figures 1−5

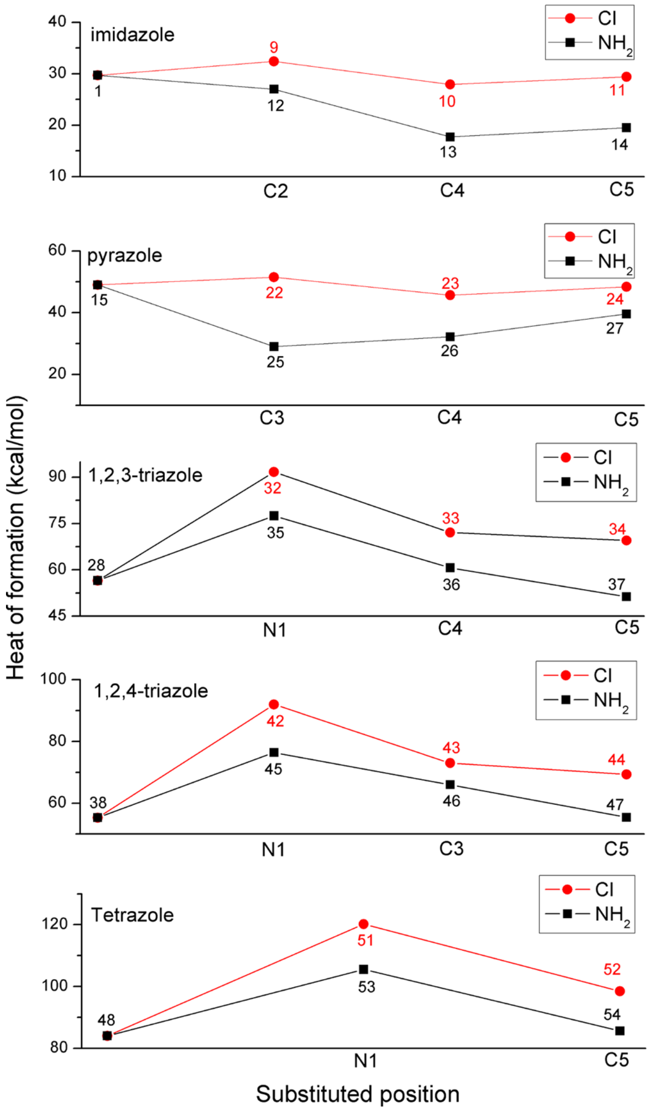


Figure 8. Plot of heat of formation ($\Delta_f H^0$) versus electron-withdrawing Cl (red) and electron-donating NH_2 (black) group. The horizontal axis is the substitution position on the ring for Cl and NH_2 groups, and "no sub" (at the left) stands for no Cl or NH_2 on the ring. The color coded numbers on the plot are the compound numbers given in Figures 1−5

in which N is the corresponding number of atoms, D_{min} is the weakest BDE, and $\Delta_d H$ is obtained as the difference between the formation enthalpy $\Delta_f H^0$ of the explosive compound and corresponding enthalpies for the decomposition products. The products are estimated with the help of the "H_2O-CO_2 arbitrary"[7,15] as previously reported. The equation below is commonly referred to as "H_2O-CO_2 arbitrary":

$$C_aH_bN_cO_d \rightarrow \frac{1}{2}cN_2 + \frac{1}{2}bH_2O + \left(\frac{1}{2}d - \frac{1}{4}b\right)CO_2 + \left(a - \frac{1}{2}d + \frac{1}{4}b\right)C \quad (12)$$

As shown in Figure 9, a linear correlation is found for the impact sensitivity ($h_{50\%}$) and SI for these five-member aromatic ring explosives, as shown below:

$$h_{50\%} = -76.47408 + 855.42521*\mathrm{SI} \quad (13)$$

Table 6. Calculated N (or C)−NO_2 (or NH_2, Cl) BDE[a] and Heat of Formation ($\Delta_f H^0$) for Tetrazole-Based Energetic Materials at the B3P86/6-311G (d, p) Theory Level[b]

compound	bond	BDE	$\Delta_f H^0$	compound	bond	BDE	$\Delta_f H^0$
48	**C5−NO_2**	**66.5**	84.0	52	**N1−NO_2**	**32.0**	98.4
49	**N1−NO_2**	**42.2**	97.3		C5−Cl	94.0	
50	**N1−NO_2**	**18.7**	114.5	53	N1−NH_2	84.3	105.5
	C5−NO_2	58.7			**C5−NO_2**	**65.7**	
51	**N1−Cl**	**59.0**	120.2	54	**N1−NO_2**	**26.8**	85.6
	C5−NO_2	62.5			C5−NH_2	122.0	
				55	**C5−NO_2**	66.4	79.2

[a]Boldface entries indicate the weakest bond. [b]Heats of sublimation are neglected. Units are kcal/mol and compound numbers are given in Figure 5.

The linear correlation coefficient R^2 is 0.82. Table 7 lists the data (the weakest BDE, the heat of formation, and the experimental impact sensitivity $h_{50\%}$) of energetics used in Figure 9.

From the correlation found for the impact sensitivity and sensitivity index, one can predict the impact sensitivity for the rest of compounds based on eqs 11−13. These results are listed in Table 8. Basically, the $h_{50\%}$ decreases with the number of the NO_2 groups on the five-member ring: this means the compounds become more sensitive as the number of NO_2 groups on a ring increases. Concurrently, the $\Delta_f H^0$ of the compounds increases with the number of NO_2 groups, as discussed in section 3.1. Consider imidazole-based energetic materials as an example. The order of the $h_{50\%}$ is 2,4-dinitroimidazole (182 cm) > 2,4,5-trinitroimidazole (83 cm) > 4,4′5,5′-tetranitro-2,2′-biimidazole (39 cm). *N*-substituted compounds are usually more sensitive than *C*-substituted compounds due to the weaker N−NO_2 bond; e.g., 2,4-dinitroimidazole (182 cm) > 1,4-dinitroimidazole (44 cm), which is in agreement with the discussion about the weakest bond in section 3.2; however, also noted is that *N*-substituted compounds have higher $\Delta_f H^0$s than *C*-substituted compounds, which means that *N*-substituted compounds have potentially better energetic performance. Thus, a conflict between energetic performance and sensitivity arises.

If an electron-withdrawing group (NO_2 or Cl) replaces an H atom of the five-member ring on the N position, the $h_{50\%}$ dramatically drops. The stronger the electron-withdrawing group is, the more sensitive the energetic compound is: i.e., NO_2 reduces $h_{50\%}$ more than Cl. On the other hand, an electron-donating group (NH_2 or CH_3) does not change the $h_{50\%}$ as much as an electron-withdrawing group, and this maintains the stability of energetic compounds. For example, 2,4,5-trinitroimidazole (83 cm) > 1-amino-2,4,5-trinitroimidazole (70 cm) ≈ 1-methyl-2,4,5-trinitroimidazole (76 cm) ≫ 1-chloro-2,4,5-trinitroimidazole (18 cm) > 1,2,4,5-tetranitroimidazole (0.28 cm).

The substitution position of the electron-withdrawing group or the electron-donating group also influences the impact sensitivity. If the electron-withdrawing group (Cl) or the electron-donating (NH_2) group replaces the H atom on C4, rather than C5, of 1,2,3-triazole based compounds, the $h_{50\%}$ reaches its minimum. If the electron-withdrawing group (Cl) or the electron-donating (NH_2) group substitutes for the H atom on C3, rather than C5, of 1,2,4-triazole based compounds, the $h_{50\%}$ also reaches its minimum.

3.4. Performance versus Sensitivity.

The choice of energetic material for a given task will of course depend upon the situational details: that is, in one instance highest stability might be the major concern, while in another maximum stored energy might be the major concern. Additionally, issues dealing with environment and health can become important under certain conditions. In this work, we plot the 55 compounds in 2D planes based on their heats of detonation versus impact sensitivity, as shown in Figure 10, in order to compare, contrast, and analyze the differences between these energetic compounds. Several criteria can be used to choose the most appropriate energetic compounds, depending on the most important situational issues. (1) If stability is the most

Table 7. Calculated[b] Weakest BDE, Heat of Formation ($\Delta_f H^0$), and Experimental Impact Sensitivity ($h_{50\%}$) for Energetics in Figure 9[a]

compound	weakest bond	BDE (kcal/mol)	$\Delta_f H^0$ (kcal/mol)	$h_{50\%}$ (cm)
1,4-dinitroimidazole	N1−NO_2	34.5	45.4	55[c]
2,4-dinitroimidazole	C2−NO_2	69.1	29.7	105[d]
2,4,5-trinitroimidazole	C4−NO_2	61.4	41.5	68[d]
1-methyl-2,4,5-trinitroimidazole	C5−NO_2	61.0	43.0	49[e]
4,4′,5,5′-tetranitro-2,2-biimidazole	C4−NO_2	62.4	73.3	37[d]
1-amino-3,5-dinitropyrazole	C5−NO_2	69.2	65.1	158[d]
3-nitro-1,2,4-triazole	C3−NO_2	68.4	49.1	320[d]
1-methyl-3,5-dinitro-1,2,4-triazole	C5−NO_2	64.8	51.3	155[d]
4-methyl-3,5-dinitro-1,2,4-triazole	C3−NO2	63.5	62.2	155[c]
5,5′-dinitro-3,3′-bi-1,2,4-triazole	C5−NO_2	67.7	104.0	153[d]

[a]Heats of sublimation are neglected. [b]Calculated by B3P86/6-311G(d,p). [c]Reference 7. [d]Reference 20. [e]Reference 61.

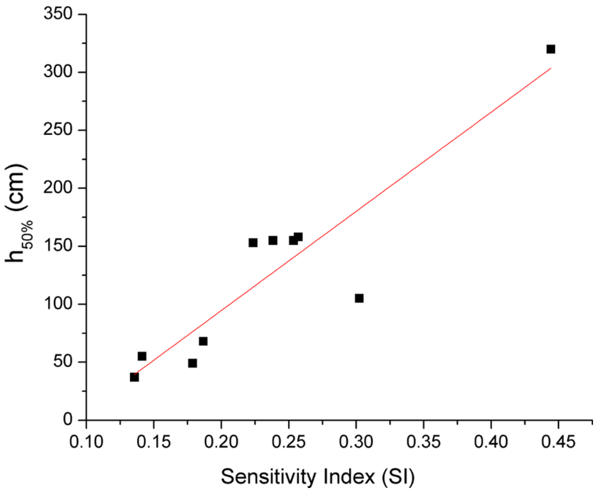


Figure 9. The relationship between $h_{50\%}$ and SI for energetic materials.

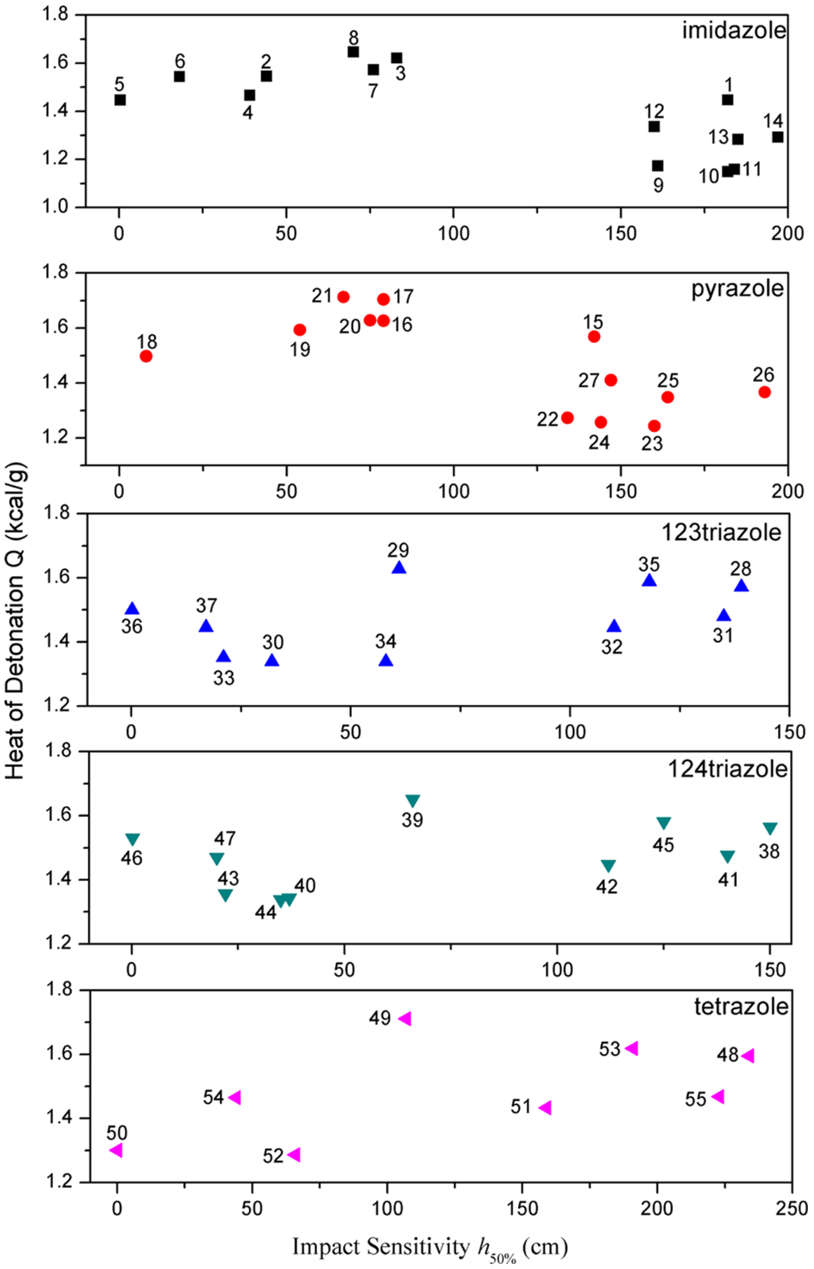


Figure 10. Plot of 55 compounds (imidazole, pyrazole, 1,2,3-triazole, 1,2,4-triazole, and tetrazole) in the 2D plane based on impact sensitivity ($h_{50\%}$) and heat of detonation (Q). Numbers stand for the compound number defined in Figures 1− 5

important issue, compounds 14 (5-amino-2,4-dinitroimidazole), 26 (4-amino-3,5-dinitropyrazole), 28 (4,5-dinitro-1,2,3-triazole), 38 (3,5-dinitro-1,2,4-triazole), and 48 (5-nitrotetrazole) are the optimal energetic materials that have maximum impact sensitivity values for their respective series. (2) If heat of detonation (Q) is the most important issue, compounds 8 (1-amino-2,4,5-trinitroimidazole), 21 (1-amino-3,4,5-trinitropyrazole), 29 (1,4-dinitro-1,2,3-triazole), 39 (1,3-dinitro-1,2,4-triazole), and 49 (1-nitrotetrazole) are the matched energetic materials that have maximum heat of detonation (Q) among their respective series, as shown in Figure 10.

Each selection standard above can be the right way to choose an energetic compound for different demands. Nonetheless, for a more general determination of "optimal energetic compounds", one can consider the following compromise approach. A good energetic compound should have excellent potential energetic performance and acceptable sensitivity, so all the related factors, such as heat of detonation (Q), impact sensitivity, etc. should be taken into account. Impact sensitivities for the currently employed, applied energetic materials HMX, RDX, and PETN are 32, 28, and 16 cm, respectively; the heats of detonation (Q) for HMX, RDX, and PETN are 1.235, 1.243, and 1.223 kcal/g, respectively.[7] Thus a value of impact sensitivity (60 cm) is set as the limit for the sensitivity of energetic materials and all the compounds with the $h_{50\%}$ larger than 60 cm are considered as generally insensitive (~ safe) energetic materials. Compounds with this minimum value of impact sensitivity and a maximum heat of detonation (Q) will be the generally most promising energetic compounds. In this way, compounds 8 (1-amino-2,4,5-trinitroimidazole), 21 (1-amino-3,4,5-trinitropyrazole), 29 (1,4-dinitro-1,2,3-triazole), 39 (1,3-dinitro-1,2,4-triazole), 49

Table 8. Heat of Formation $\Delta_f H^0$, Predicted Impact Sensitivity $h_{50\%}$, and Heat of Detonation (Q) for Azole-Based Energetic Compounds[a]

compound	$\Delta_f H^0$ (kcal/mol)	$h_{50\%}$ (cm)	Q (kcal/g)	compound	$\Delta_f H^0$ (kcal/mol)	$h_{50\%}$ (cm)	Q (kcal/g)
1	29.7	182	1.447	28	56.5	139	1.572
2	45.4	44	1.546	29	65.4	61	1.628
3	41.5	83	1.621	30	85.1	32	1.339
4	73.3	39	1.466	31	51.6	135	1.479
5	76.4	0.28	1.446	32	91.7	110	1.446
6	84.5	18	1.544	33	72.1	21	1.352
7	43.0	76	1.573	34	69.5	58	1.339
8	66.2	70	1.647	35	77.5	118	1.588
9	32.4	161	1.173	36	60.7	0.16	1.500
10	27.9	182	1.150	37	51.3	17	1.446
11	29.4	184	1.158	38	55.3	150	1.565
12	27.0	160	1.337	39	69.0	66	1.651
13	17.7	185	1.283	40	85.9	37	1.343
14	19.5	197	1.293	41	51.3	140	1.477
15	49.0	142	1.569	42	92.0	112	1.448
16	58.1	79	1.626	43	73.0	22	1.357
17	58.4	79	1.704	44	69.3	35	1.338
18	89.1	8	1.497	45	76.4	125	1.582
19	96.1	54	1.593	46	66.0	0.18	1.531
20	55.0	75	1.628	47	55.4	20	1.470
21	80.4	67	1.713	48	84.0	234	1.595
22	51.5	134	1.273	49	97.3	107	1.711
23	45.7	160	1.243	50	114.5	0.1	1.301
24	48.4	144	1.257	51	120.2	159	1.433
25	29.0	164	1.348	52	98.4	66	1.287
26	32.2	193	1.367	53	105.5	191	1.618
27	39.6	147	1.410	54	85.6	44	1.465
				55	79.2	223	1.468

[a] Heats of sublimation are neglected.

(1-nitrotetrazole) are the selected, general purpose energetic compounds for the azole grouping.

IV. CONCLUSIONS

The azole-based compounds, imidazole, pyrazole, 1,2,3-triazole, 1,2,4-triazole, and tetrazole, are studied in this work. The BDE and the heat of formation ($\Delta_f H^0$) for all these compounds are obtained by calculation at the B3P86/6-311G (d, p) level of theory. The relationship between the impact sensitivity and the sensitivity index is built based on Mathieu's work.[50] The impact sensitivity of compounds without experimental data is predicted in this work.

According to the results and discussion above, we can reach several conclusions listed as below:

(1) The heats of formation ($\Delta_f H^0$s) increase with the increase of the number of the NO_2 groups on the ring: increasing the number of the NO_2 groups will improve the potential energetic performance, but the increasing number of the NO_2 groups will reduce the BDEs of C−NO_2 bonds and thereby reduce the stability of energetic compounds.

(2) The nitramine type compounds (N−NO_2) have potentially better energetic performance than C−NO_2 type compounds; however, the N−NO_2 bond is much weaker than the C−NO_2 bond, and thus nitramine type compounds are usually more sensitive.

(3) The heats of formation ($\Delta_f H^0$s) relate to the number of nitrogen atoms in the five-member ring. The heat of formation order generally is therefore tetrazole > triazole ≈ pyrazole > imidazole.

(4) If substitution occurs on an N atom of the five-member ring, both electron-withdrawing groups and electron-donating groups (except the CH_3 group) will dramatically increase the $\Delta_f H^0$s of energetic materials. If substitution occurs on a C atom of the five member ring for imidazole and pyrazole compounds, however, the electron-withdrawing group Cl has little effect on the $\Delta_f H^0$s and the electron-donating group NH_2 reduces the $\Delta_f H^0$s. If substitution occurs on a C atom of the five member ring for 1,2,3-triazole, 1,2,4-triazole, and tetrazole compounds, the electron-withdrawing group Cl increases the $\Delta_f H^0$s and the electron-donating group NH_2 does not significantly change the $\Delta_f H^0$s.

(5) For the C-NO_2 bond, neither electron-withdrawing nor electron-donating groups change the BDE significantly, independent of substitution at the C or N position on the ring. For N−NO_2 bond, both the electron-withdrawing and electron-donating groups reduce the BDE significantly, independent of substitution at the C or N position on the ring.

(6) For substitution on C atoms of the five-member ring, both the electron-withdrawing and electron-donating groups will dramatically reduce the impact sensitivity of energetic compounds when an N−NO_2 bond is present, and the impact sensitivity of energetic compounds does not change significantly when an N−NO_2 bond is not present.

(7) For substitution on N atoms of the five-member ring, the electron-withdrawing groups will reduce the impact sensitivity of energetic compounds more than the electron-donating groups do.

(8) The most promising energetic compounds from each azole group, which have both potentially good energetic performance and low sensitivity, are compounds 8 (1-amino-2,4,5-trinitroimidazole), 21 (1-amino-3,4,5-trinitropyrazole), 29 (1,4-dinitro-1,2,3-triazole), 39 (1,3-dinitro-1,2,4-triazole), 49 (1-nitrotetrazole).

Even though our results are based on calculation and an empirical relation between impact sensitivity and sensitivity index defined above, they are useful for those energetic compounds without experimental data. The predictions of course need more experiments to prove them, but these predictions are still helpful for design and synthesis of new energetic materials.

■ AUTHOR INFORMATION

Notes

The authors declare no competing financial interest.

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■ REFERENCES

(1) Williams, F. Electronic States of Solid Explosives and Their Probable Role in Detonations. *Adv. Chem. Phys.* **1971**, *21*, 289−302.

(2) Surber, E.; Lozano, A.; Lagutchev, A.; Kim, H.; Dlott, D. D. Surface Nonlinear Vibrational Spectroscopy of Energetic Materials: HMX. *J. Phys. Chem. C* **2007**, *111*, 2235−2241.

(3) Aluker, E. D.; Krechetov, A. G.; Mitrofanov, A. Y.; Nurmukhametov, D. R.; Kuklja, M. M. Laser Initiation of Energetic Materials: Selective Photoinitiation Regime in Pentaerythritol Tetranitrate. *J. Phys. Chem. C* **2011**, *115*, 6893−6901.

(4) Manaa, M. R.; Reed, E. J.; Fried, L. E.; Goldman, N. Nitrogen-Rich Heterocycles as Reactivity Retardants in Shocked Insensitive Explosives. *J. Am. Chem. Soc.* **2009**, *131*, 5483−5487.

(5) Manaa, M. R.; Schmidt, R. D.; Overturf, G. E.; Watkins, B. E.; Fried, L. E.; Kolb, J. R. Towards Unraveling the Photochemistry of TATB. *Thermochim. Acta* **2002**, *384*, 85−90.

(6) Reed, E. J. Electron-Ion Coupling in Shocked Energetic Materials. *J. Phys. Chem. C* **2012**, *116*, 2205−2211.

(7) Rice, B. M.; Hare, J. J. A Quantum Mechanical Investigation of the Relation between Impact Sensitivity and the Charge Distribution in Energetic Molecules. *J. Phys. Chem. A* **2002**, *106*, 1770−1783.

(8) Badgujar, D. M.; Talawar, M. B.; Asthana, S. N.; Mahulikar, P. P. Advances in Science and Technology of Modern Energetic Materials: An Overview. *J. Hazard. Mater.* **2008**, *151*, 289−305.

(9) Agrawal, J. P.; Hodgson, R. D. *Organic Chemistry of Explosives*; John Wiley & Sons: Chichester, U.K., 2007.

(10) Pagoria, P. F.; Lee, G. S.; Mitchell, A. R.; Schmidt, R. D. A Review of Energetic Materials Synthesis. *Thermochim. Acta* **2002**, *384*, 187−204.

(11) Fischer, N.; Gao, L.; Klapötke, T. M.; Stierstorfer, J. Energetic Salts of 5,5′-Bis(tetrazole-2-oxide) in a Comparison to 5,5′-Bis-(tetrazole-1-oxide) Derivatives. *Polyhedron* **2013**, *51*, 201−210.

(12) Fischer, D.; Klapötke, T. M.; Piercey, D. G.; Stierstorfer, J. Synthesis of 5-Aminotetrazole-1 *N*-oxide and Its Azo Derivative: A Key Step in the Development of New Energetic Materials. *Chem.—Eur. J.* **2013**, *19*, 4602−4613.

(13) Gutowski, K. E.; Rogers, R. D.; Dixon, D. A. Accurate Thermochemical Properties for Energetic Materials Applications. I. Heats of Formation of Nitrogen-Containing Heterocycles and Energetic Precursor Molecules from Electronic Structure Theory. *J. Phys. Chem. A* **2006**, *110*, 11890−11897.

(14) Gutowski, K. E.; Rogers, R. D.; Dixon, D. A. Accurate Thermochemical Properties for Energetic Materials Applications. II. Heats of Formation of Imidazolium-, 1,2,4-Triazolium-, and Tetrazolium-Based Energetic Salts from Isodesmic and Lattice Energy Calculations. *J. Phys. Chem. B* **2007**, *111*, 4788−4800.

(15) Kamlet, M. J.; Jacobs, S. J. Chemistry of Detonations. I. A Simple Method for Calculating Detonation Properties of CHNO Explosives. *J. Chem. Phys.* **1968**, *48*, 23−35.

(16) Luo, Y. R. *Handbook of Bond Dissociation Energies in Organic Compounds*; CRC Press: Boca Raton, FL, 2003.

(17) Murray, J. S.; Lane, P.; Politzer, P. Electrostatic Potential Analysis of the π Regions of Some Naphthalene Derivatives. *J. Mol. Struct.(THEOCHEM)* **1990**, *209*, 163−175.

(18) Politzer, P.; Laurence, P. R.; Abrahmsen, L.; Zilles, B. A.; Sjoberg, P. The Aromatic C−NO_2 Bond as a Aite for Nucleophilic Attack. *Chem. Phys. Lett.* **1984**, *111*, 75−78.

(19) Zhang, S.; Truong, T. N. Thermal Rate Constants of the NO_2 Fission Reaction of Gas Phase α-HMX: A Direct Ab Initio Dynamics Study. *J. Phys. Chem. A* **2000**, *104*, 7304−7307.

(20) Bulusu, S. N. *Chemistry and Physics of Energetic Materials*; Kluwer Academic, Boston: Norwell, MA, 1990.

(21) Rice, B. M.; Sahu, S.; Owens, F. J. Density Functional Calculations of Bond Dissociation Energies for NO_2 Scission in Some Nitroaromatic Molecules. *J. Mol. Struct. (THEOCHEM)* **2002**, *583*, 69−72.

(22) Atalar, T.; Jungová, M.; Zeman, S. A New View of Relationships of the N−N Bond Dissociation Energies of Cyclic Nitramines. Part II. Relationships with Impact Sensitivity. *J. Energ. Mater.* **2009**, *27*, 200−216.

(23) Zhang, R.-Z.; Li, X.-H.; Zhang, X.-Z. Theoretical Studies on a Series of 1,2,4-Triazoles Derivatives as Potential High Energy Density Compounds. *J. Chem. Sci.* **2012**, *124*, 995−1006.

(24) Zhao, J.; Xu, D.; Cheng, X. Investigation of Correlation between Impact Sensitivities and Bond Dissociation Energies in Some Triazole Energetic Compounds. *Struct. Chem.* **2010**, *21*, 1235−1240.

(25) Li, J. Relationships for the Impact Sensitivities of Energetic C-Nitro Compounds Based on Bond Dissociation Energy. *J. Phys. Chem. B* **2010**, *114*, 2198−2202.

(26) Murray, J. S.; Concha, M. C.; Politzer, P. Links between Surface Electrostatic Potentials of Energetic Molecules, Impact Sensitivities and C−NO_2/N−NO_2 Bond Dissociation Energies. *Mol. Phys.* **2009**, *107*, 89−97.

(27) Wu, C. J.; Fried, L. E. Detonation. *Proc. 11th Symp. (Int.) Detonation, CO* **1998**, 490−497.

(28) Akhavan, J. *The Chemistry of Explosives*; Royal Society of Chemistry: Cambridge, U.K., 2011.

(29) Fried, L. E.; Manaa, M. R.; Pagoria, P. F.; Simpson, R. L. Design and Synthesis of Energetic Materials. *Annu. Rev. Mater. Res.* **2001**, *31*, 291−321.

(30) Rice, B. M.; Byrd, E. F. C. Theoretical Chemical Characterization of Energetic Materials. *J. Mater. Res.* **2006**, *21*, 2444−2452.

(31) Zeman, S. *High Energy Density Materials: Structure and Bonding*; Springer-Verlag: Heidelberg, Germany, 2007, *125*, 195−271.

(32) Anders, G.; Borges, I. Topological Analysis of the Molecular Charge Density and Impact Sensitivity Models of Energetic Molecules. *J. Phys. Chem. A* **2011**, *115*, 9055−9068.

(33) Song, X.-S.; Cheng, X.-L.; Yang, X.-D.; He, B. Relationship between the Bond Dissociation Energies and Impact Sensitivities of Some Nitro-Explosives. *Propellants, Explos., Pyrotech.* **2006**, *31*, 306−310.

(34) Kamlet, M. J.; Adolph, H. G. Relationship of Impact Sensitivity with Structure of Organic High Explosives 0.2. Polynitroaromatic Explosives. *Propellants Explos.* **1979**, *4*, 30−34.

(35) Zhu, W.; Xiao, H. First-Principles Band Gap Criterion for Impact Sensitivity of Energetic Crystals: A Review. *Struct. Chem.* **2010**, *21*, 657−665.

(36) Zhang, H.; Cheung, F.; Zhao, F.; Cheng, X.-L. Band Gaps and the Possible Effect on Impact Sensitivity for Some Nitro Aromatic Explosive Materials. *Int. J. Quantum Chem.* **2009**, *109*, 1547−1552.

(37) Sharma, J.; Beard, B. C.; Chaykovsky, M. Correlation of Impact Sensitivity with Electronic Levels and Structure of Molecules. *J. Phys. Chem.* **1991**, *95*, 1209−1213.

(38) Sharma, J.; Beard, B. C.; Chaykovsky, M. Correlation of Impact Sensitivity with Electronic Levels and Structure of Molecules. *J. Phys. Chem.* **1991**, *95*, 1209−1213.

(39) Politzer, P.; Murray, J. S.; Lane, P.; Sjoberg, P.; Adolph, H. G. Shock-Sensitivity Relationships for Nitramines and Nitroaliphatics. *Chem. Phys. Lett.* **1991**, *181*, 78−82.

(40) Pepekin, V. I.; Korsunskii, B. L.; Denisaev, A. A. Initiation of Solid Explosives by Mechanical Impact. *Combust., Explos., Shock Waves* **2008**, *44*, 586−590.

(41) Koch, E.-C. Acid−Base Interactions in Energetic Materials: I. The Hard and Soft Acids and Bases (HSAB) Principle − Insights to Reactivity and Sensitivity of Energetic Materials. *Propellants, Explos., Pyrotech.* **2005**, *30*, 5−16.

(42) Murray, J. S.; Lane, P.; Politzer, P.; Bolduc, P. R. A Relationship between Impact Sensitivity and the Electrostatic Potentials at the Midpoints of C−NO_2 Bonds in Nitroaromatics. *Chem. Phys. Lett.* **1990**, *168*, 135−139.

(43) Zhang, C. Review of the Establishment of Nitro Group Charge Method and Its Applications. *J. Hazard. Mater.* **2009**, *161*, 21−28.

(44) Zhang, C.; Shu, Y.; Huang, Y.; Zhao, X.; Dong, H. Investigation of Correlation between Impact Sensitivities and Nitro Group Charges in Nitro Compounds. *J. Phys. Chem. B* **2005**, *109*, 8978−8982.

(45) McNesby, K. L.; Coffey, C. S. Spectroscopic Determination of Impact Sensitivities of Explosives. *J. Phys. Chem. B* **1997**, *101*, 3097−3104.

(46) Ge, S.-H.; Cheng, X.-L.; Wu, L.-S.; Yang, X.-D. Correlation between Normal Mode Vibrations and Impact Sensitivities of Some Secondary Explosives. *J. Mol. Struct. (THEOCHEM)* **2007**, *809*, 55−60.

(47) Yan, Q.-L.; Zeman, S. Theoretical Evaluation of Sensitivity and Thermal Stability for High Explosives Based on Quantum Chemistry Methods: A Brief Review. *Int. J. Quantum Chem.* **2013**, *113*, 1049−1061.

(48) Rice, B. M.; Byrd, E. F. C.; Mattson, W. D. Computational Aspects of Nitrogen-Rich HEDMs. In *High Energy Density Materials*; Klapötke, T. M., Ed.; Springer: Berlin/Heidelberg, 2007; Vol. *125*, pp 153−194.

(49) Tan, B. S.; Long, X. P.; Peng, R. F.; Li, H. B.; Jin, B.; Chu, S. J.; Dong, H. S. Two Important Factors Influencing Shock Sensitivity of Nitro Compounds: Bond Dissociation Energy of X−NO_2 (X = C, N, O) and Mulliken Charges of Nitro Group. *J. Hazard. Mater.* **2010**, *183*, 908−912.

(50) Mathieu, D. A. Toward a Physically Based Quantitative Modeling of Impact Sensitivities. *J. Phys. Chem. A* **2013**, *117*, 2253−2259.

(51) Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Scalmani, G.; Barone, V.; Mennucci, B.; Petersson, G. A. et al. *Gaussian 09*, revision A.1; Gaussian, Inc.: Wallingford, CT, 2009.

(52) Li, J.; Zhao, F.; Jing, F. An Ab Initio Study of Intermolecular Interactions of Nitromethane Dimer and Nitromethane Trimer. *J. Comput. Chem.* **2003**, *24*, 345−352.

(53) Shao, J. X.; Cheng, X. L.; Yang, X. D. Density Functional Calculations of Bond Dissociation Energies for Removal of the Nitrogen Dioxide Moiety in Some Nitroaromatic Molecules. *J. Mol. Struct.* **2005**, *755*, 127−130.

(54) Li, J. An Evaluation of Nitro Derivatives of Cubane Using Ab Initio and Density Functional Theories. *Theo. Chem. Acc.* **2009**, *122*, 101−106.

(55) Blanksby, S. J.; Ellison, G. B. Bond Dissociation Energies of Organic Molecules. *Acc. Chem. Res.* **2003**, *36*, 255−263.

(56) Hehre, W. J. Ab Initio Molecular Orbital Theory. *Acc. Chem. Res.* **1976**, *9*, 399−406.

(57) Dorofeeva, O. V.; Suntsova, M. A. Enthalpies of Formation of Nitromethane and Nitrobenzene: Theory vs Experiment. *J. Chem. Thermodyn.* **2013**, *58*, 221−225.

(58) Livett, M. K.; Nagy-Felsobuki, E.; Peel, J. B.; Willett, G. D. Photoelectron Spectra of Chloramine and Dichloramine. *Inorg. Chem.* **1978**, *17*, 1608−1612.

(59) Gurvich, L. V.; Veyts, I. V.; Alcock, C. B. *Thermodynamic Properties of Individual Substances*, 4th ed.; Hemisphere Publishing Corp.: New York, 1991; Vol. 2.

(60) Li, X. H.; Zhang, R. Z.; Zhang, X. Z. Computational Study of Imidazole Derivative as High Energetic Materials. *J. Hazard. Mater.* **2010**, *183*, 622−631.

(61) Su, X. F.; Cheng, X. L.; Meng, C. M.; Yuan, X. L. Quantum Chemical Study on Nitroimidazole, Polynitroimidazole and Their Methyl Derivatives. *J. Hazard. Mater.* **2009**, *161*, 551−558.

(62) Sharia, O.; Kuklja, M. M. Ab Initio Kinetics of Gas Phase Decomposition Reactions. *J. Phys. Chem. A* **2010**, *114*, 12656−12661.

(63) Manaa, M. R.; Fried, L. E. Intersystem Crossings in Model Energetic Materials. *J. Phys. Chem. A* **1999**, *103*, 9349−9354.

(64) Brill, T. B.; James, K. J. Kinetics and Mechanisms of Thermal Decomposition of Nitroaromatic Explosives. *Chem. Rev.* **1993**, *93*, 2667−2692.

(65) Politzer, P.; Murray, J. S. C−NO_2 Dissociation Energies and Surface Electrostatic Potential Maxima in Relation to the Impact Sensitivities of Some Nitroheterocyclic Molecules. *Mol. Phys.* **1995**, *86*, 251−255.