

Quantum chemical study on nitroimidazole, polynitroimidazole and their methyl derivatives

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ABSTRACT

The insensitive explosive candidates, nitroimidazoles, polynitroimidazoles and their methyl derivatives, are investigated using density functional theory (DFT). The homolytic bond dissociation energies (BDEs) corresponding to $-\text{NO}_2$ group removal from carbon or nitrogen site on imidazole ring were calculated at B3P86/6-311G** level, and the weakest bond has been determined. Further, a correlation is developed between impact sensitivity h_{50} and the ratio (BDE/ E) of the weakest bond BDE to the total energy E , and we extrapolate this relationship to predict the impact sensitivities for compounds where experiments are not available. It is found that most of the title compounds are insensitive towards impact stimuli with their h_{50} larger than 60.0 cm. Heats of formation (HOFs) for the 21 title compounds at 298 K in gas are also determined both at B3LYP/6-311G** and B3P86/6-311G** levels using isodesmic work reactions. The calculated BDEs and HOFs consistently indicate that C-nitro-substituted imidazole is more stable than the corresponding N-substituted one, and the introduction of methyl on C increases the stability whereas the methyl attached to N atom decreases the stability.

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1. Introduction

Energetic materials (explosives, propellants and pyrotechnics) are used extensively both for civil and military applications. Recently, because of many catastrophic explosions resulting from unintentional initiation of munitions by aboard ships, aircraft carriers, munitions trains, impact or shock, continuous strong efforts have been made to develop new materials having good thermal stability, impact and shock insensitivity, better performance, economic and environmentally friendly syntheses in order to meet the requirements of future military and space applications [1,2]. One of the promising potential candidates emerging from this effort is imidazole derivatives with more than two nitro groups [3–5], specifically 2,4-dinitroimidazole (2,4-DNI). Attractive features of 2,4-DNI are its much less sensitivity and its moderate performance, expected to be 60% greater than 2,4,6-trinitrotoluene (TNT). Its sensitivity is less than current explosives cyclo-1,3,5-trimethylene-2,4,6-trinitramine (RDX) and octahydro-1,3,5,7-tetranitro-1,3,5,7-tetrazocine (HMX), the highly powerful explosives which are widely used in current military technologies. Moreover, it can be prepared from the inexpensive starting materials [6]. Besides 2,4-DNI, other polynitro-substituted imidazole

derivatives, such as 4,5-dinitroimidazole, 2,4,5-trinitroimidazole, 1-methyl-2,4,5-trinitroimidazole and 4,4',5,5'-tetranitro-2,2'-bi-1H-imidazole (TNBI), have also been synthesized and tested as insensitive high energy materials [4,7–11]. Theorists suggest that the explosive performance of trinitro-substituted imidazoles should be almost close to that of RDX [12]. Drop weight impact tests show that 2,4,5-trinitroimidazole has a much higher impact sensitivity (h_{50}) value (68 cm) than RDX (28 cm), HMX (32 cm), and even higher than 2,4,6-trinitrophenol (picric acid, 64 cm)[13]. Cho et al.'s preliminary sensitivity tests reveal that 1-methyl-2,4,5-trinitroimidazole is a promising candidate as an insensitive high explosive, with its explosive performances comparable to RDX and with its sensitivity intermediate between RDX and TNT [9,14]. In addition, owing to its low melting point (82 °C), 1-methyl-2,4,5-trinitroimidazole is believed to be an excellent candidate for inclusion in melt-castable explosives, and may lead to increased explosive power. Cho et al.'s theoretical results also show that 1,2,4,5-tetranitroimidazole is more powerful than HMX [12,15].

It is well known that the dissociation of the weakest bond of an explosive molecule plays an important role in the initiation of detonation. In unsaturated systems, including polynitroimidazoles, an interesting feature of many C–NO₂ bonds is the presence of a buildup of positive electrostatic potential above and below the bond region, and these positive buildups can serve as initial sites for nucleophilic attack [16,17]. Researchers' study showed that R–NO₂ (R=C, N or O) bond is the weakest bond in energetic ring molecules

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and the rupture of this bond is the first step in decomposition process [18,19]. In addition, the chemistry stabilities and impact/shock sensitivities of energetic materials have frequently been related to the strengths of the weakest bond R–NO₂, which may be obtained by calculating the bond dissociation energy (BDE) [18–24]. Rice et al. [21] showed that there is a rough correlation between the logarithm of the impact sensitivity values h_{50} and the weakest BDE. Fried et al. [25] reported that the ratio (BDE/Ed) of the weakest bond BDE to the explosive decomposition energy (Ed) is a nearly linear function of the logarithm of the impact sensitivity values h_{50} . Recently Song et al.'s [26,27] research further substantiates that there is a nearly linear correlation between the ratio of the weakest BDE to the molecular total energy and the impact sensitivity value h_{50} in a certain class of explosives. All these further indicate that the BDE of the weakest bond of the explosive molecule plays a key role in the initiation event. As for heat of formation (HOF), it is one of the most crucial thermodynamic quantities. It is required to estimate the amount of energy released or absorbed in a chemical reaction, to calculate other thermodynamic functions and, what is more important, to assess the stability of a molecule.

However, to the best of our knowledge, for polynitroimidazoles and their methyl derivatives less experimental BDE values is available and the weakest bond has not been identified and studied. Due to the problems of safety, difficulty in purifying and the lack of a systematic theoretical study, the HOF values for the title compounds are also at present uncertain. Thus, theoretically studying the geometry and the property such as the weakest R–NO₂ BDE, HOF of polynitroimidazoles and their derivatives, is of importance.

The aim of the present work is to use density functional theory (DFT) to estimate the weakest R–NO₂ BDE, the impact sensitivity, and the HOFs for the mono-, polynitroimidazoles and their methyl derivatives for which less value is found in the literature. Furthermore, it is known that for ring molecules such as nitroaromatics, the increasing number of NO₂ groups reduces the stability of the molecule. In this study, the stability caused by the insertion of group –NO₂ and –CH₃ is also investigated for title compounds.

2. Theory and computational details

All calculations were carried out with the Gaussian 03 program package [28]. The hybrid density functionals B3LYP [29,30] and B3P86 [29,31] in conjunction with Pople basis set 6-311G** are used to calculate HOFs, and B3P86/6-311G** is used to calculate BDEs. The geometries of molecules, including the title compounds and the reference species mentioned below to calculate HOFs, the NO₂ group and their NO₂ loss fragments for the title compounds are optimized without any constraints. Vibrational analysis has also been performed for each stationary point to verify a minimum energy structure and to provide zero-point energies (ZPEs) and thermal correction (H_T). The $\langle S^2 \rangle$ values are all very close to 0.75,

which shows negligible spin contamination of pure doublets states for fragment open-shell systems.

The choice of the two methods is not only because B3LYP/6-311G** and B3P86/6-311G** can precisely predict heats of formations [32], and the latter produces accurate bond dissociation energies [33] for various aromatic nitro compounds, but also because they require less time and computer resources such as disk and memory space. While high-quality levels of theory, such as G2, G2(MP2), G2(MP2, SVP), G3, G3B3, CBS, and CCSD(T), have been developed to give accurate results, the impractical problem is that the sophisticated methods require far too much computational time and disk space to treat electron correlation.

The homolytic bond dissociation enthalpy (DH) is defined as the reaction enthalpy, which is required to break the R–NO₂ bond to form two radicals at 298 K and 1 atm pressure.

$$\begin{aligned} \text{DH}(\text{R}-\text{NO}_2) &= \Delta H_f^0(\text{R}) + \Delta H_f^0(\text{NO}_2) - \Delta H_f^0(\text{RNO}_2) \\ &= H(\text{R}) + H(\text{NO}_2) - H(\text{RNO}_2) \end{aligned} \quad (1)$$

where RNO₂ is the parent molecule, R, NO₂ are the two radicals, and $\Delta H_f^0(\text{R})$ and $H(\text{R})$ are the heats of formation and enthalpy for R, respectively.

For many organic molecules, BDE and DH are almost numerically equivalent, and as a result the terms “bond dissociation energy” and “bond dissociation enthalpy” (DH) often appear interchangeably in literature [34]. Therefore, at 0 K, the homolytic bond dissociation energy can be given in terms of Eq. (2) [34]

$$\text{BDE}(\text{R}-\text{NO}_2) = E(\text{R}) + E(\text{NO}_2) - E(\text{RNO}_2) \quad (2)$$

The total energy E of each species includes electronic energy (E_e) and zero-point correction (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 the atomization reaction or isodesmic reaction methods, and in this paper the latter is employed. Isodesmic reaction, where the numbers of bonds and bond types are preserved on both sides of the reaction, often leads to cancellation of systematic errors resulting from the bond environments, spin contamination, basis set superposition and other nonrandom factors [35]. Further, the use of the same number internal rotors on both sides of the reaction can make the thermodynamic contributions from hindered rotors, which can be difficult to compute, fortuitously cancel out. The accuracy of HOF obtained theoretically is conditioned by the reliability of HOF of the reference compounds and the choice of the working chemical reaction used in the evaluation.

We selected reference compounds displayed in Table 1 and designed the isodesmic work reactions. For the isodesmic reactions, the heats of reaction $\Delta H_{298.15\text{K}}$ at 298.15 K can be calculated through the reaction enthalpies:

Table 1
Calculated electronic energies (E_e /hartree) and experimental heats of formation for reference species (ΔH_f^0 /kcal mol⁻¹)

Compound	E_e			Compound	E_e		
	B3LYP/6-311G**	B3P86/6-311G**	ΔH_f^0		B3LYP/6-311G**	B3P86/6-311G**	ΔH_f^0
Imidazole	-226.27691	-226.92257	31.8 ± 0.1 ^a	CH ₃ NNO ₂ CH ₃	-339.75336	-340.61254	-1.2 ± 0.3 ^a
NH ₃	-56.57604	-56.75630	-11.0 ^a	CH ₃ NHCH ₃	-135.20542	-135.67602	-4.7 ± 0.5 ^a
CH ₄	-40.53375	-40.71398	-17.9 ± 0.1 ^a	NH ₂ NO ₂	-261.11379	-261.68165	-0.8 ^b
CH ₃ NO ₂	-245.08169	-245.64918	-19.3 ± 0.3 ^a	CH ₃ NH ₂	-95.88844	-96.21372	-5.4 ± 0.2 ^a
CH ₂ =CH ₂	-78.61398	-78.89799	12.5 ^a	CH ₂ CHNO ₂	-283.16957	-283.84103	9 ± 2 ^c
CH ₃ CH ₃	-79.85626	-80.18234	-20.0 ± 0.1 ^a				

^a ref. [36].

^b ref. [37].

^c ref. [38].

$$\Delta H_{298.15\text{K}} = \sum_{\text{product}} \Delta H_f^0 - \sum_{\text{reactant}} \Delta H_f^0 \quad (3)$$

where $\sum_{\text{product}} \Delta H_f^0$ and $\sum_{\text{reactant}} \Delta H_f^0$ are the sums of the heats of formation for products and reactants in gas at 298.15 K, respectively. Since the HOFs of reference compounds are available from experiment, the HOFs of the title compounds can be obtained if the heats of reaction $\Delta H_{298.15\text{K}}$ are known. The $\Delta H_{298.15\text{K}}$ can be calculated from the following equations:

$$\Delta H_{298.15\text{K}} = \Delta E_{298.15\text{K}} + \Delta(PV) = \Delta E_e + \Delta ZPE + \Delta H_T + \Delta nRT \quad (4)$$

where ΔE_e and ΔZPE are the electronic energy difference and the zero-point energy difference between products and reactants at 0 K, respectively; ΔH_T is the changes in thermal correction to enthalpies between products and reactants; $\Delta(PV)$ equals ΔnRT for reaction in gas phase. For isodesmic reactions, $\Delta n = 0$.

3. Results and discussion

3.1. Molecular geometry

Fig. 1 shows the molecular frameworks of the 21 mono- and polynitroimidazoles and their methyl derivative compounds.

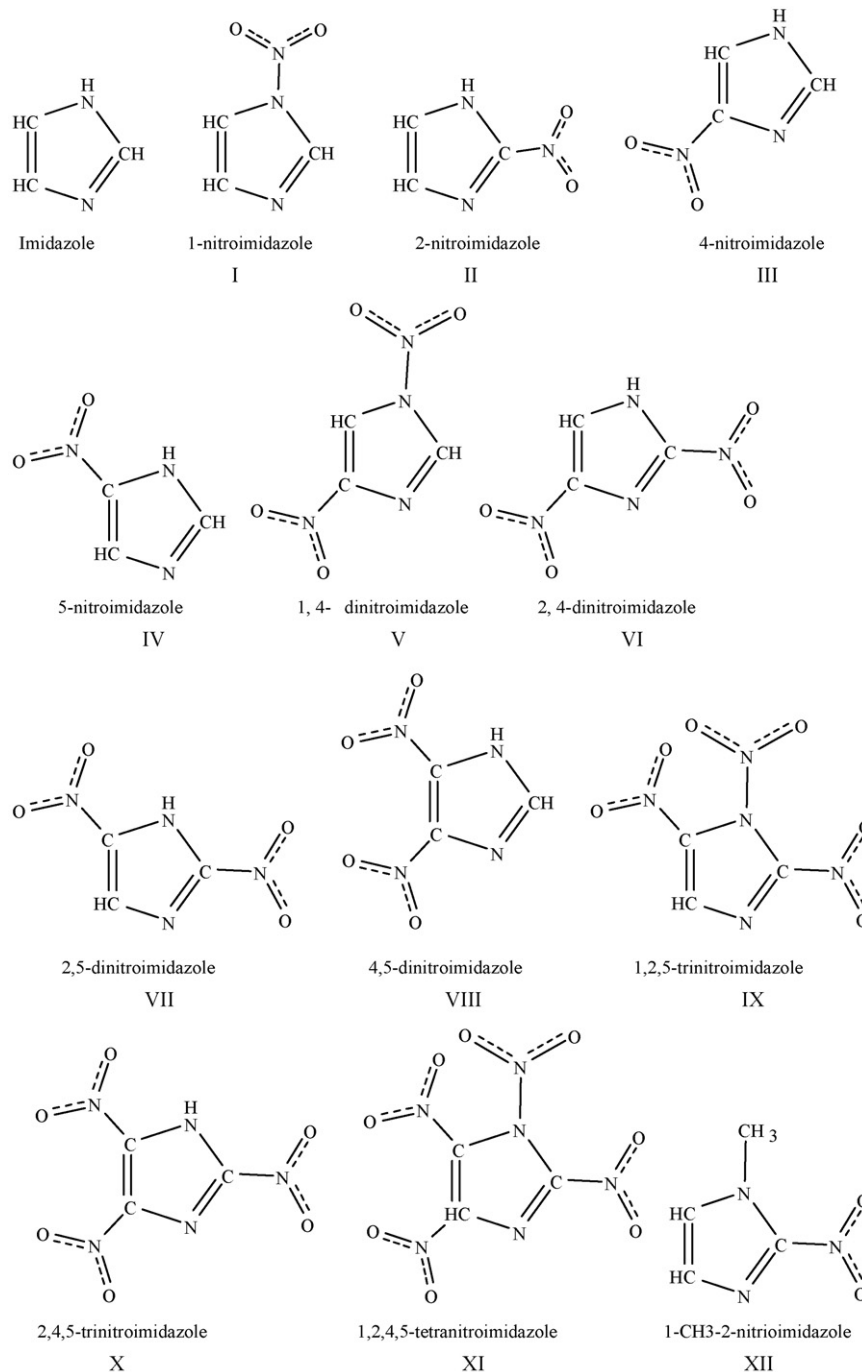


Fig. 1. Polynitroimidazole and their methyl derivatives considered in this study.

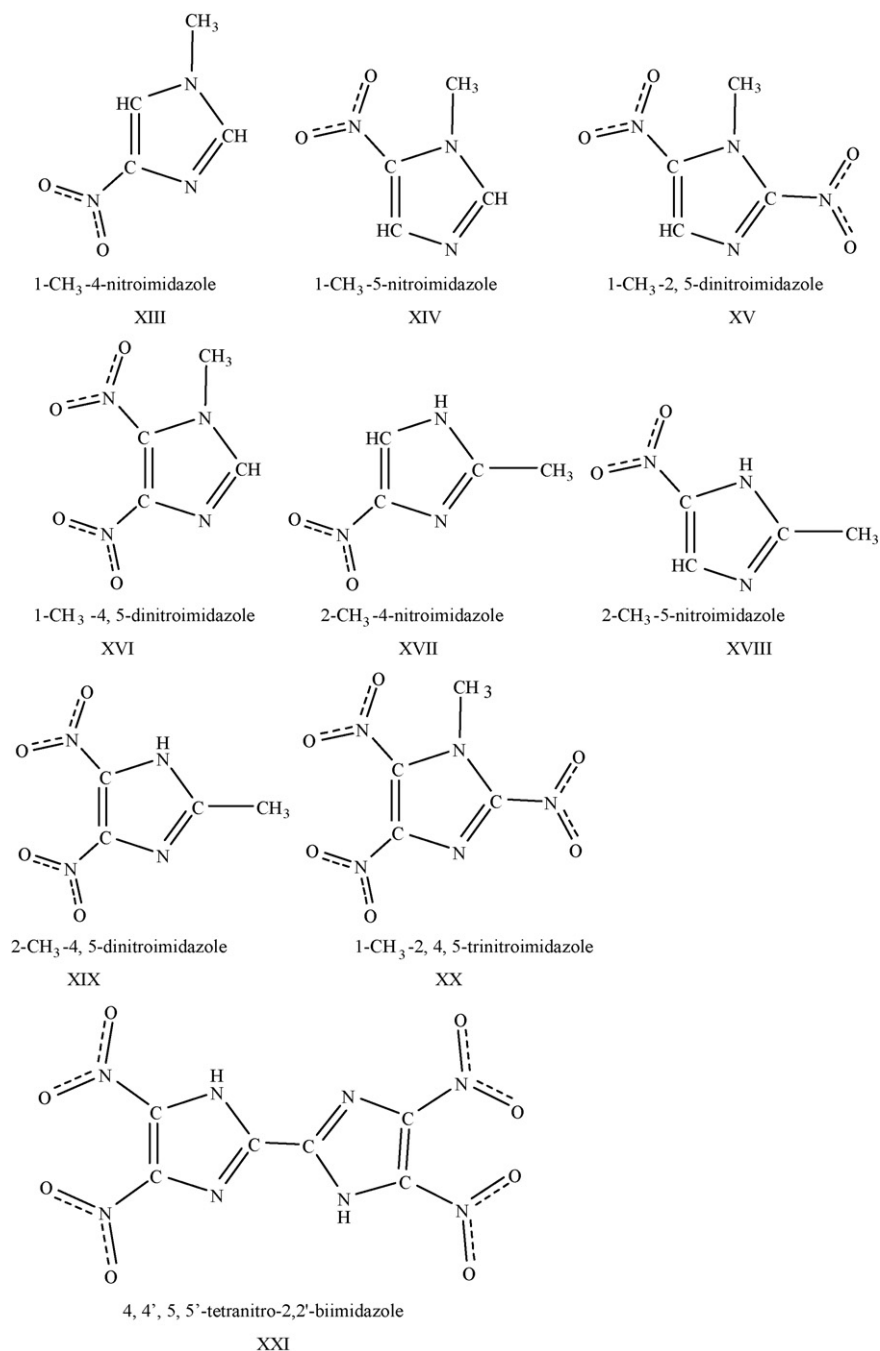


Fig. 1. (Continued).

The optimized geometry parameters of compounds imidazole, III, VI, VIII, XX, and XXI at two difference calculation levels along with the experiments [39–41] are provided in [Supplementary Material](#). It can be seen that for all compounds where literature bond parameters exist, there is a good agreement between calculated and experimental equilibrium geometry, with average absolute error for bond lengths ranging from 0.003 to 0.041 Å, and for bond angles from 0.2° to 0.7°. Further, there exists relatively little variation between B3LYP/6-311G** and B3P86/6-311G** levels. All these indicate that our optimized geometries are reliable in predicting the properties such as C–NO₂ BDEs and HOFs.

3.2. Determination of the weakest bonds, the corresponding BDEs and the sensitivity

As reported by Owens [20] that the initial breakdown bond, for a number of different chemical families of energetic molecules including nitroimidazole type, is the bond R–NO₂. Thus, we have calculated the BDEs corresponding to homolytic C–NO₂ and N–NO₂ bond cleavage in the 21 title compounds. Table 2 provides the computed homolytic BDEs for each of the molecules with B3P86/6-311G** method, which is found to give best experimental C–NO₂ BDE data for nitro aromatic molecules with an average absolute deviation 1.16 kcal mol⁻¹ in Shao's study [33].

Table 2
Calculated N (or C)–NO₂ bond dissociation energies^a (BDEs) for the title compounds

Compound	Bond	BDE ^b (kcal mol ⁻¹)	Compound	Bond	BDE ^b (kcal mol ⁻¹)
I	N1–NO ₂	33.3	XI	C2–NO ₂	60.6
II	C2–NO ₂	72.2		C4–NO ₂	60.5
III	C4–NO ₂	73.5		C5–NO ₂	61.1
IV	C5–NO ₂	77.0	XII	C2–NO ₂	70.3
V	N1–NO₂	34.5	XIII	C4–NO ₂	73.9
	C4–NO ₂	70.0	XIV	C5–NO ₂	75.7
VI	C2–NO₂	69.1	XV	C2–NO₂	64.1
	C4–NO ₂	70.1		C5–NO ₂	68.5
VII	C2–NO₂	67.5	XVI	C4–NO₂	63.1
	C5–NO ₂	72.1		C5–NO ₂	66.1
VIII	C4–NO₂	63.3	XVII	C4–NO ₂	74.4
	C5–NO ₂	67.9	XVIII	C5–NO ₂	78.1
IX	N1–NO₂	22.2	XIX	C4–NO₂	63.7
	C2–NO ₂	62.3		C5–NO ₂	68.6
	C5–NO ₂	67.3	XX	C2–NO ₂	63.3
X	C2–NO ₂	66.0		C4–NO ₂	61.7
	C4–NO₂	61.4		C5–NO₂	61.1
	C5–NO ₂	64.2	XXI	C4–NO₂	62.4
XI	N1–NO₂	20.5		C5–NO ₂	78.7

^a The boldface indicates the weakest bond and corresponding BDE value.

^b BDEs are calculated by B3P86/6-311G**.

As has been suggested by Chung et al. [42], a molecule should have more than a 20 kcal mol⁻¹ barrier to dissociate in order to be considered as a viable candidate for new high energy density materials. Inspecting Table 2, we can conclude that all the molecules investigated are all viable candidates for new high energy density materials.

It is known that the initial stages in thermal decompositions of energetic materials can be deduced on the basis of the BDEs. As seen from Table 2, N–NO₂ bond strength is between 20 and 35 kcal mol⁻¹, making this the weakest bond for mono- or polynitroimidazole containing N–NO₂ linkage (such as compounds I, V, IX, and XI). This indicates that the rupture of N–NO₂ bond is the initial site in the decomposition process. For molecules with all nitro groups attached to C atoms, the position of nitro group also has an important effect on the BDE. For example, the BDE of C–NO₂ on C2 site is 4.6 kcal mol⁻¹ lower than BDE of C–NO₂ on C5 site for compound VII, and is 1.0 kcal mol⁻¹ lower than that in C4 site for compound VI. But compound X is an exception to this observation, with the C–NO₂ BDEs on C4 and C5 sites both lower than that on 2 site, and with the value on 4 site the lowest. A possible explanation for this behavior in compound X is that the presence of the strong repulsive interactions between O atoms in adjacent nitro groups attached to C4 and C5 sites on the imidazole ring, weaken the C–NO₂ bond strength each other. Table 2 also shows that the increase of NO₂ group number on imidazole ring reduces the stability of the molecule, which is characterized by the decrease of the weakest C–NO₂ bond energy. With respect to methyl nitroimidazole derivatives, the issues discussed above are also found. It should be noted that the insertion of electron donating group –CH₃ attached to N atom decreases the corresponding C–NO₂ BDE, while the insertion increases the C–NO₂ BDE values when –CH₃ is attached to C atom.

Based on the experimental sensitivity h_{50} available and the calculated BDE/E values for the weakest bond, a plot of h_{50} versus BDE/E has been illustrated in Fig. 2. A good linear relationship is observed for our studied nitroimidazole type compounds. This result is also consistent with Song et al.'s study [26,27] in which a linear correlation is found for ester, nitroaromatic nitramine and polynitro benzoate molecules with nitro alkyl group. The function relationship is given by Eq. (5), and the linear correlation coefficient is 0.98.

$$h_{50} = -23.16597 + \left(73.60873 \times \frac{\text{BDE}}{E} \right) \times 10^4 \quad (5)$$

From the equation above, we predicted the impact sensitivities for the rest of molecules which have no experiment results and listed them in Table 3. Inspecting Table 3, it is clear that the relative stability order towards impact stimuli is in the following sequence: IV > III > II ≈ XVIII > XIV > XVII ≈ XIII > XII > VI > VII > VIII > XV ≈ XIX ≈ XVI > I > X > XX > V > XXI > IX > XI. As the same case in polynitro aliphatics [2], polynitro imidazoles containing at least one N–NO₂ (nitramine) linkage (compounds I, V, IX, and XI) are more sensitive than nitro imidazoles containing C–NO₂ linkage. Thus substitution on the ring C atoms is preferable to substitution on the N atoms based on the consideration of safety. Furthermore, like the general trend for benzene derivatives [2], the sensitivity increases with the increasing number of electron-drawing group –NO₂ for our studied family of molecules, i.e. the more impact sensitive explosives are those with the more nitro groups substituted on imidazole ring. In addition, the introduction of electron donating –CH₃ group increases sensitivity regardless of substituted on N atom or C atom. And the N-methyl-substituted nitroimidazoles are more sensitive

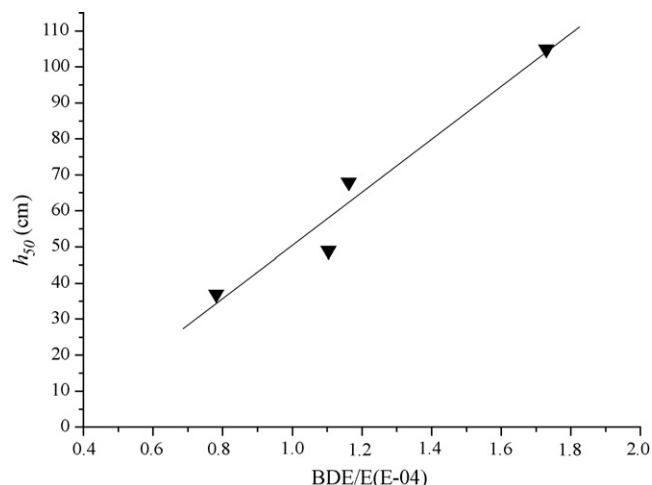


Fig. 2. The relationship between h_{50} and BDE/E for some title compounds.

Table 3
The electronic energies (E_e) calculated by B3LYP/6-311G** and B3P86/6-311G**, their symmetry point groups and predicted impact sensitivity for the title compounds

Compound	E_e (hartree)		Symmetry	h_{50} (cm)		Compound	E_e (hartree)		Symmetry	h_{50} (cm)		Experimental ^b
	B3LYP	B3P86		Calculated ^a	Experimental ^b		B3LYP	B3P86		Calculated ^a	Experimental ^b	
I	-430.79689	-431.82960	Cs	67		XII	-470.14552	-471.32428	Cs	152		
II	-430.82851	-431.86178	Cs	173		XIII	-470.15114	-471.32973	Cs	161		
III	-430.83031	-431.86350	Cs	176		XIV	-470.14939	-471.32797	Cs	165		
IV	-430.83095	-431.86407	Cs	186		XV	-674.68704	-676.25325	C1	88		
V	-635.34322	-636.76339	Cs	40		XVI	-674.68438	-676.25044	C1	86		
VI	-635.37472	-636.79547	Cs	104		XVII	-470.16435	-471.34381	Cs	162		
VII	-635.37345	-636.79404	Cs	101		XVIII	-470.16568	-471.34509	Cs	171		
VIII	-635.36518	-636.78572	C1	93		XIX	-674.70098	-676.26783	C1	87		
IX	-839.86067	-841.66772	Cs	8		XX	-879.21837	-881.17211	C1	58	49	
X	-839.90281	-841.71077	C1	62		XXI	-1269.53937	-1272.34604	C2	35	37	
XI	-1044.38951	-1046.58355	C1	1								

^a Predicted using Eq. (5).

^b Ref. [20].

than C-methyl-substituted nitroimidazoles. The reason for this phenomenon may be that the C–NO₂ BDE is lower in the former molecules than that in the latter ones.

Sensitivity data obtained also suggest that most of the nitroimidazoles and their methyl derivatives are insensitive towards impact stimuli with h_{50} larger than 60.0 cm and could be potential candidates for low vulnerable applications.

3.3. Heats of formation in the gas phase

The isodesmic work reactions used in this paper and the calculated heats of formation at the B3LYP/6-311G** and B3P86/6-311G** levels are listed in Table S2 in Supplementary Material. Table 1 gives the experimental heats of formation and calculated electronic energies for the reference species used in the isodesmic work reactions. For 1-NO₂, 4-NO₂ and 5-NO₂ substituents, two isodesmic work reactions were performed to calculate the heats of formation, respectively. The calculated HOFs errors from choice of reaction schemes are reduced by averaging the HOFs over the two reaction schemes. By Hess's law, the two reaction schemes could be added together to give a "master" reaction scheme, so averaging the calculated HOFs is equivalent to calculating the HOF from the "master" reaction scheme. As reported by Williams and Whitehead [43] and Bozzelli [44], this process can improve the results, presumably because it includes more molecules with known HOFs than a single isodesmic reaction scheme, and partially eliminates errors in HOFs caused by peculiarities of reference species in each reaction scheme.

Previous studies [32,37,43–46] have shown that the use of isodesmic work reactions by choosing appropriate reference compounds with accurate HOF values can result in considerable improvements in determining values of HOF. On the basis of these, data in Table S2 and Table 4 are supposed to be credible, although the experimental values of HOFs are unavailable for comparison.

As for the HOFs obtained from B3LYP/6-311G** level listed in Table 4, the NO₂-substituents on N-position have bigger HOFs than the corresponding NO₂-substituents on C-position, regardless mononitro-substituted imidazoles or polynitro-substituted imidazoles. The HOF of 1-nitroimidazole (I) is 53.6 kcal mol⁻¹, which is 26.2 kcal mol⁻¹ larger than 2-nitroimidazole (II, 27.1 kcal mol⁻¹), 4-nitroimidazole (III, 27.7 kcal mol⁻¹) and 5-nitroimidazole (IV, 27.3 kcal mol⁻¹) on average. For dinitroimidazoles and trinitroimidazoles, the same trend occurs: (1) the mean difference of HOF values between dinitroimidazoles with a –NO₂ group attached to N atom (compound V) and those with two –NO₂ groups attached to C atoms (compound VI–VIII) is 25.1 kcal mol⁻¹; (2) for trinitroimidazoles, the HOF of 1,2,5-trinitroimidazole (IX) is 32.6 kcal mol⁻¹ larger than 2,4,5-trinitroimidazole. In search of the reason, we can see from the molecular structure (see Fig. 1) that the HOF difference of N-nitro-substituted imidazoles and C-nitro-substituted imidazoles is mainly due to the difference of bond energy between N–NO₂ and C–NO₂. As the bond dissociation energy of N–NO₂ is smaller than that of C–NO₂, according to the definition of heat of formation, the former consumes less energy than the latter during process of its decomposition into its constituent elements in standard states. Therefore NO₂-substituted imidazoles in N-position have higher heats of formation than the corresponding ones in C-position. The predicted HOF discrepancy between the former and the latter is in good agreement with the corresponding BDE gap, which indicates that the calculated heats of formation are reliable. For instance, the BDE of N–NO₂ in 1-nitroimidazole (I) and 1,4-dinitroimidazole (V) is 24.4 kcal mol⁻¹ smaller averagely than that of C–NO₂ in compounds 2-nitroimidazole (II), 4-nitroimidazole (III), 5-nitroimidazole (IV), 2,4-dinitroimidazole (VI), 2, 5-dinitroimidazole (VII), and 4, 5-dinitroimidazole (VIII),

Table 4The calculated average heats of formation (ΔH_{avg}^0 /kcal mol⁻¹) for the title compounds

Compound	ΔH_{avg}^0 ^a		Compound	ΔH_{avg}^0 ^a	
	B3LYP/6-311G**	B3P86/6-311G**		B3LYP/6-311G**	B3P86/6-311G**
I	53.6	54.3	XII	29.4	28.8
II	27.1	26.8	XIII	27.5	27.1
III	27.7	27.6	XIV	28.7	28.3
IV	27.3	27.2	XV	32.6	32.0
V	55.3	55.4	XVI	36.0	35.5
VI	27.4	27.0	XVII	17.5	17.1
VII	28.1	27.9	XVIII	16.7	16.3
VIII	35.1	34.9	XIX	23.8	23.3
IX	71.4	71.9	XX	42.1	41.4
X	38.8	38.6	XXI	71.6	71.2
XI	82.4	83.1			

^a Average of the values of the two isodesmic reactions.

while the HOF discrepancy between the former and the latter is 25.3 kcal mol⁻¹ on average. The fact that the NO₂-substituted imidazoles in N-position is less stable than that in C-position may account for the phenomenon why 1,4-dinitroimidazole is easily isomerized to 2,4-dinitroimidazole even by heating at a modest temperature [6,16].

From Table 4, it should be noted that the calculated heats of formation for our investigated molecules are all endothermic which is desirable for high energy density materials. Table 4 also shows that the value of HOF relates to the number of nitro groups among I–XI compounds. The general trend is that the HOF increases smoothly as more-NO₂ groups substituted in imidazole. The order of the HOFs is as follows: tetra-nitroimidazoles (XI) > tri-nitroimidazole (IX, X) > dinitro-imidazole (V, VI, VII, VIII) > mono-nitroimidazole (I, II, III, IV). It is well known that for an energetic compound it is desirable to have a high, positive HOF to exhibit good energetic performance. Thus the more nitro group substituted in the imidazole, the better energetic performance.

Comparing with the HOF of compounds I (53.6 kcal mol⁻¹), V (55.3 kcal mol⁻¹), IX (71.4 kcal mol⁻¹) and XI (82.4 kcal mol⁻¹), we can see that the increase of nitro group number for compounds including one N–NO₂ linkage raises the HOF dramatically.

In addition, we investigate the effect of –CH₃ group substituted in different position. As for the insertion of –CH₃ in N-position, we can see from Table 4 that the HOFs of three methyl mononitroimidazole compounds (XII–XIV) are larger than or equivalent to the corresponding nitroimidazoles (II–IV). The difference in HOF between the former and the latter is 2.3 kcal mol⁻¹, –0.2 kcal mol⁻¹ (the negative value expresses the former (XIII) have smaller HOF than the latter (III)) and 1.5 kcal mol⁻¹. Comparing the HOFs of compounds XV, XVI with those of VII, VIII, one can also find the methyl dinitroimidazole derivatives possess larger HOFs than dinitroimidazoles. For trinitroimidazole, the same trend described above has also been found. Therefore, one can say that the insertion of –CH₃ in N-position can increase the heats of formation for mono-nitroimidazoles or polynitroimidazoles. With respect to the case CH₃-substituents in C-position, the situation is different. The heats of formation of the methyl mono-nitroimidazoles (XVII, XVIII) and di-nitroimidazole (XIX) are smaller than the corresponding nitroimidazoles (III, IV, and VIII). This is not surprising because this phenomenon is in consistent with the effect methyl makes on C–NO₂ BDE caused by substitution in different position. So according to the definition of heats of formation, the decreasing HOF is attributed to the stronger C–NO₂ bond strength and the increasing HOF is due to the weaker C–NO₂ bond strength. In view of these theoretical results, it is advisable for us to select methyl nitroimidazoles derivatives with –CH₃ substituted in N-position not in C-position, in order to

obtain the desirable energetic materials possessing high explosive performance.

Since no experimental values are available, we have also calculated the HOFs at B3P86/6-311G** level. Comparing the calculated HOFs by the two different levels, one can obtain that the discrepancy of the two levels is very small, with deviations ranging from 0 to 0.9 kcal mol⁻¹, and with an average value of 0.4 kcal mol⁻¹. Further, the effects of the number and position of groups (–NO₂ and –CH₃) on HOFs from these two levels are consistent with each other. The linear relationship between the HOFs from B3LYP/6-311G** level and B3P86/6-311G** level is very good:

$$\Delta H_f^0(\text{B3P86}) = -0.8871 + 1.0189 \times \Delta H_f^0(\text{B3LYP}),$$

with $R = 0.9999$. The coherency obtained from the two B3LYP/6-311G** and B3P86/6-311G** calculation levels demonstrates precision and suggests reasonable accuracy.

4. Summary and conclusions

We have used density functional theory methods to study the structure and thermochemistry properties such as bond dissociation energies, heats of formation and impact sensitivity (h_{50}) for mono-, polynitroimidazoles and their methyl derivatives. The trends we found in the behavior of these compounds are summarized below:

- (1) BDEs for C–NO₂ and N–NO₂ are calculated, and the weakest bond, referred to as the “trigger linkage” in the process of detonation is determined. In all cases containing N–NO₂ linkage, N–NO₂ is the weakest bond, suggesting that it can be the trigger linkage in detonation. For the rest of compounds, C–NO₂ BDE is the weakest and the value is weakened with the increasing number of nitro groups on imidazole ring. The insertion of –CH₃ on N atom decreases the BDEs whereas on C atom increases the BDEs.
- (2) A relationship is developed between the impact sensitivity h_{50} and the weakest bond BDE, and this relationship is extrapolated to predict h_{50} of the compounds without experiment results. The predicted values demonstrate that most of the title compounds are insensitive to impact stimuli with h_{50} larger than 60.0 cm, and they could be potential candidates for low vulnerable applications.
- (3) HOFs at 298 K in gas are calculated via isodesmic work reactions at two different calculation levels B3LYP/6-311G** and B3P86/6-311G**, and coherent results are obtained. The accuracy of the calculated HOFs is assured by increasing the number of isodesmic reactions and averaging the calculated values. Our

results indicate that HOFs of $-\text{NO}_2$ and $-\text{CH}_3$ substitution compounds on C atom are smaller than corresponding ones on N atom. This trend is consistent with that of BDE, which suggests the precision of our calculation.

These trends are obtained from the 21 nitroimidazole derivatives but they can be applicable not limited to the 21 molecules.

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.jhazmat.2008.03.135.

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