



Computational study of imidazole derivative as high energetic materials

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ABSTRACT

Density functional theory (DFT) calculations were performed for a series of imidazole derivatives. B3LYP and B3P86 functionals with 6-31G** basis set were used. Heats of formation (HOFs) were predicted through designed isodesmic reactions. Calculated results show that the HOFs relate to the number and the position of nitro groups. The HOFs increase with the augment of the number of the NO₂ group for the direct imidazole derivatives and decrease with the augment of the number of the NO₂ group for 1-picrylimidazole derivatives. Thermal stabilities were evaluated via bond dissociation energies (BDEs). The result shows that the increase of nitro group number on imidazole ring reduces the stability of the molecule. Further, the correlation was developed between impact sensitivity h_{50} and the ratio (BDE/E) of the weakest bond BDE to the total energy E . The detonation performance data were also calculated.

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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]. The nitro is an important group for energetic materials [3]. Through increasing numbers of the group, the compounds' density and the number of mole gaseous combustion products formed per gram of material can be increased, thereby enhancing propellant performance.

Imidazole derivatives with more than two nitro groups are expected to be potential energetic ingredients for insensitive explosive formulations [4–11]. Various nitroimidazole derivatives including 2,4-dinitroimidazole, 4,5-dinitroimidazole, 2,4,5-trinitroimidazole, 1,2,4,5-tetranitroimidazole have been investigated experimentally and theoretically [6–8,10]. 4,4',5,5'-Tetranitro-2,2'-bi-1H-imidazole (TNBI) has been synthesized by treating 2,2'-bi-1H-imidazole with an excess of sodium nitrate [12]. Cho et al.'s study [13] also reported that 1-methyl-2,4,5-trinitroimidazole was a promising candidate as an insensitive high

explosive, with explosive performance comparable to that of Hexo-geon (RDX). Unfortunately, despite their important value, few studies are found in literature concerning the thermodynamic properties of the imidazole derivatives in detail.

As is well known, the bond strength of the weakest bond for an explosive molecule, which may be obtained by calculating the bond dissociation energy (BDE), is of considerable importance in the area of energetic materials, since the rupture of this linkage is believed to be a key factor in many decomposition processes. Research shows that the bond R–NO₂ (R=C, N or O) is the weakest one in energetic ring molecules and the rupture of the bond is the first step in decomposition process [14–17]. Further, the stabilities and impact/shock sensitivities of energetic materials have also frequently been related to the strengths of bond R–NO₂ [18–21]. Besides, heat of formation (HOF) is crucial thermodynamic quantity. It is required to assess the stability of a molecule, and to calculate other thermodynamic functions. What is more important, the heat of formation is frequently taken to be indicative of the “energy content” of a high energy density material (HEDM). However, to the best of our knowledge, less experimental BDE values are available, and the weakest bond has not been identified and studied for the imidazole derivatives. For HOFs, owing to the sparsity of experimental data and the lack of a systematic theoretical study, values for the title compounds are at present uncertain. Further, because less than 0.02% of known organic species have had their heats of formation measured [22], the application of quantum methods is both inevitable and desirable, provided that reasonable accuracy can be obtained.

In this paper, the HOFs have been calculated for the imidazole derivatives using density functional theory (DFT) B3LYP and B3P86 methods with 6-31G** basis set via designed isodesmic reactions.

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Results from the different methods were compared. The BDEs of the weakest bond (C–NO₂) for the imidazole derivatives are evaluated. The detonation performance data are also calculated for the studied compounds. These results provide useful information for the molecular design of novel high energetic density materials.

2. Theory and computational details

The density functional theory (DFT) [23,24] has emerged as a very reliable theoretical method. Hence, it has been used to

evaluate BDEs and HOFs of interested molecules. Geometry optimizations, energy and frequency calculations were performed for imidazole derivatives using the Gaussian03 package [25]. In this work, seven high explosive molecules were studied. All calculations of molecular geometry and energy were performed using DFT method, Becke 3 parameters exchange and Lee, Yang and Parr correlation functionals [26,27] and Perdew's 86(P86) [28], with the default Gaussian convergence criteria for the seven molecules in this work. The choice of the two methods is not only because B3LYP and B3P86 methods can precisely predict heats of formation [29,30]

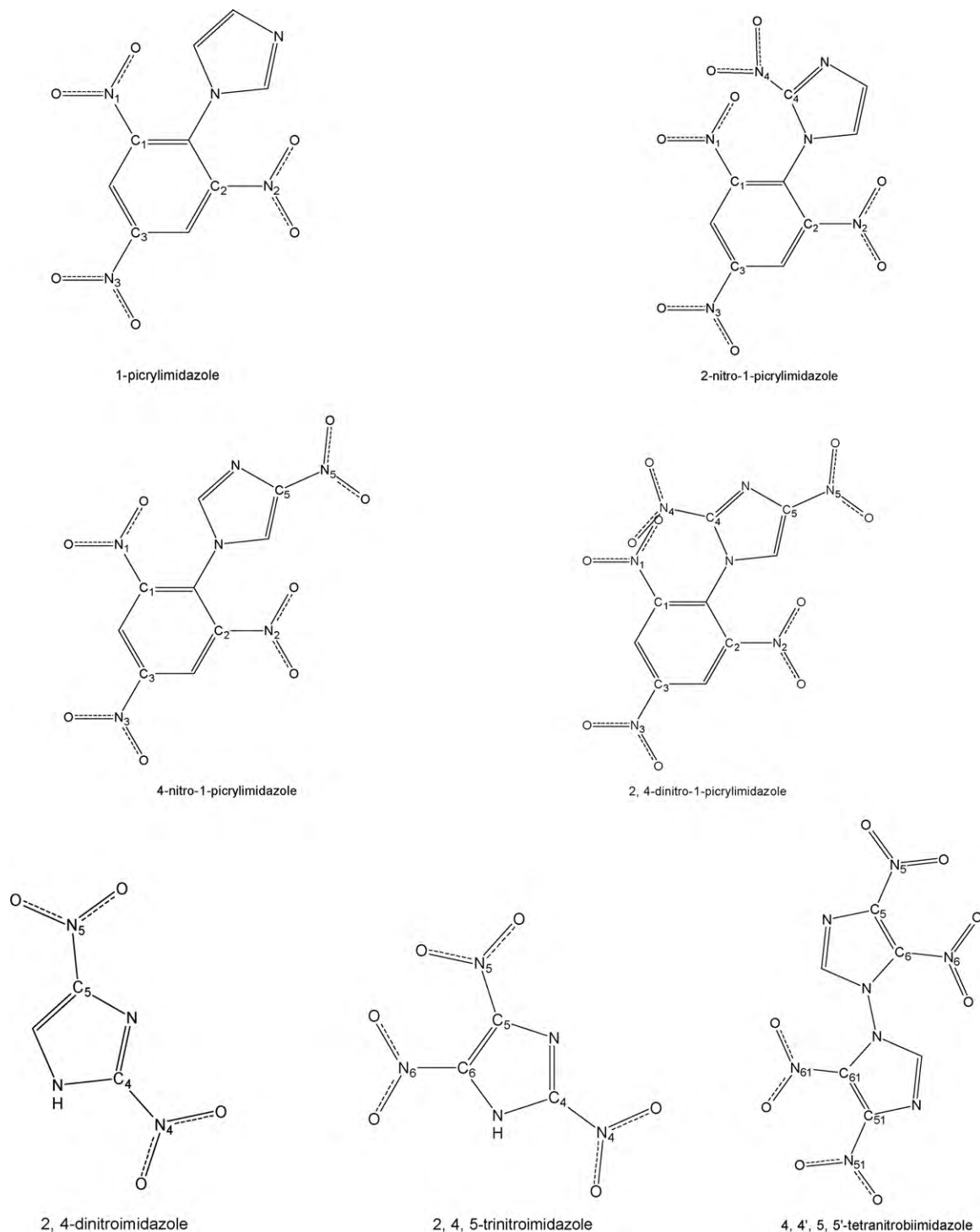


Fig. 1. Molecular frameworks and chemical names of seven title compounds.

and the latter can produce accurate bond dissociation energies [31] for various aromatic nitro compounds, but also because they require less time and computer resources such as disk and memory space. The seven imidazole derivatives are 1-picrylimidazole ($C_9H_5N_5O_6$), 2-nitro-1-picrylimidazole ($C_9H_4N_6O_8$), 4-nitro-1-picrylimidazole ($C_9H_4N_6O_8$), 2,4-dinitroimidazole ($C_3H_2N_4O_4$), 2,4,5-trinitroimidazole ($C_3HN_5O_6$), 4,4',5,5'-tetranitroimidazole ($C_6H_2N_8O_8$), 2,4-dinitro-1-picrylimidazole ($C_9H_3N_7O_{10}$). The molecular frameworks of seven title compounds are listed in Fig. 1.

Here, because we assume a homolytic cleavage of C–NO₂ bond while calculating BDEs, the fragments are radical species. The calculations of geometry and energy for all fragments were performed with the Pople basis set 6-31G**. Vibrational analysis shows that the optimized structures have no imaginary frequencies. This indicates that the structure of each molecule corresponds to a local minimum on the potential energy surface. 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 R–NO₂ bond strength, where R denotes the remainder of the molecule, is obtained by calculating the BDE, defined here as the difference between the total energy of the parent molecule and the energies of the products of the unimolecular dissociation in which an NO₂ group is removed [16]. For example, for 2,4,5-

trinitroimidazole ($C_3HN_5O_6$), the BDE is:

$$BDE = E(C_3HN_4O_4) + E(NO_2) - E(C_3HN_5O_6) \quad (1)$$

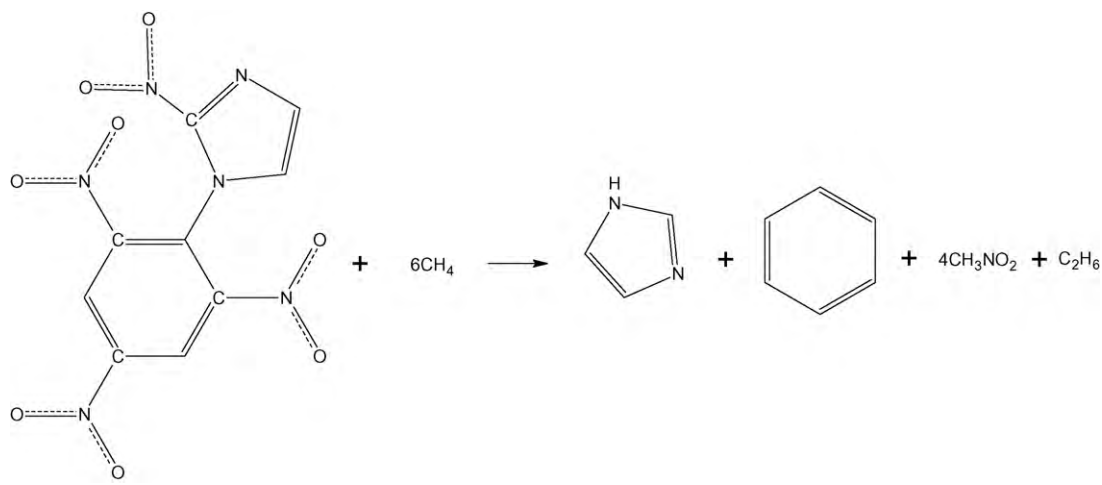
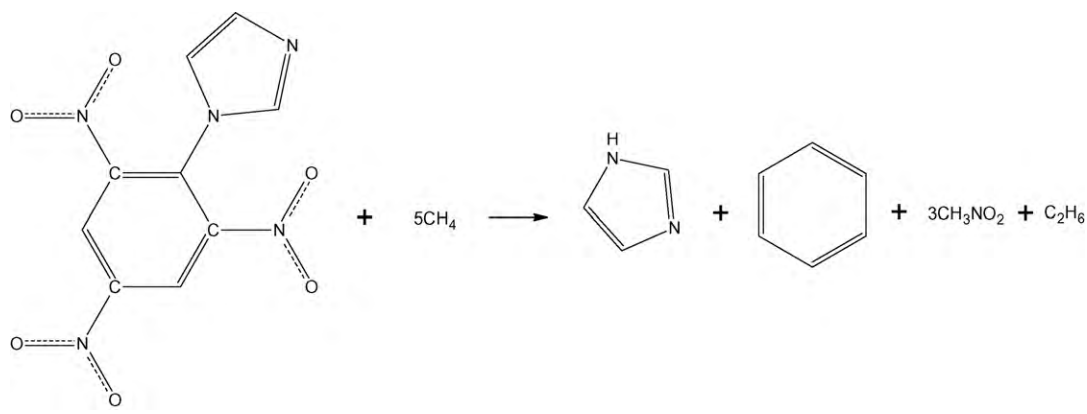
The bond dissociation energy with ZPE correction:

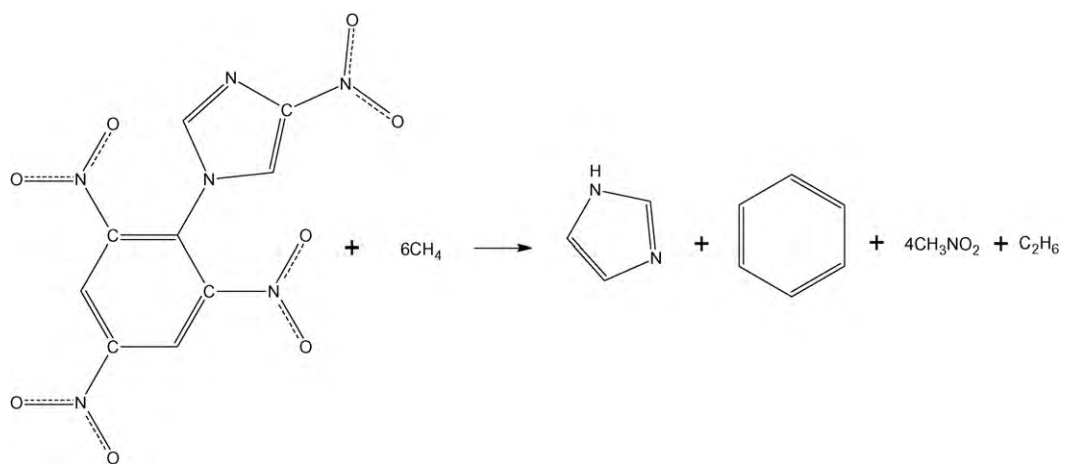
$$BDE_{ZPE} = BDE + \Delta ZPE \quad (2)$$

where ΔZPE is the difference between the zero-point energies (ZPE) of the products and the reactants.

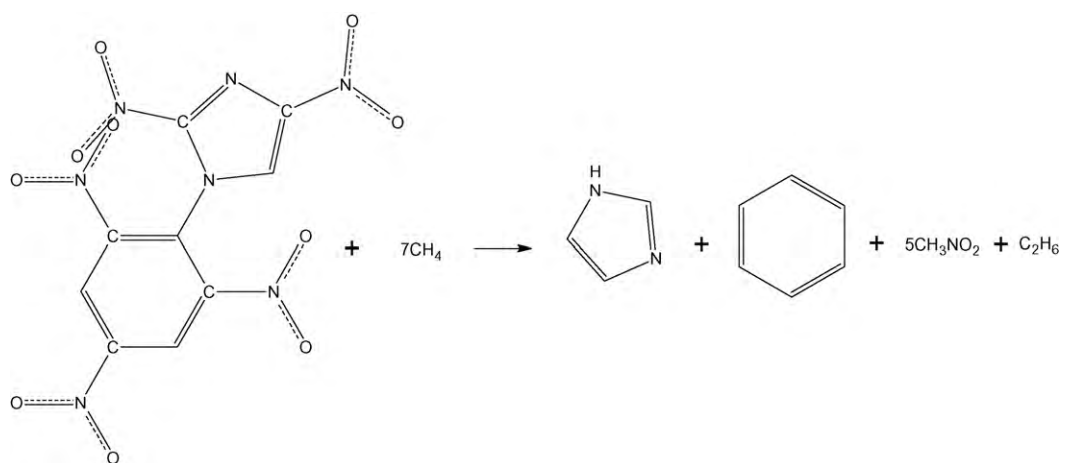
With respect to the computation of the standard heats of formation at 298.15 K, one can use the atomization reaction or isodesmic reaction method. In this paper isodesmic reaction method is employed. Isodesmic reaction, where the numbers of bonds and bond types are preserved on both sides of the reaction, often leads to cancellation of systematic errors resulting from the bond environments, spin contamination, basis set superposition and other non-random factors [32]. The accuracy of HOF obtained theoretically is conditioned by the reliability of HOF of the reference compounds.

The enthalpy of formation for the title compounds were derived from the following isodesmic reactions:

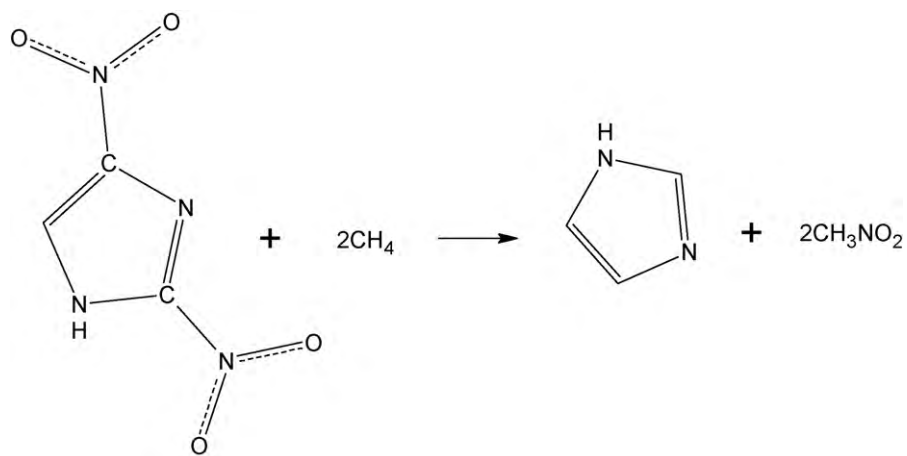




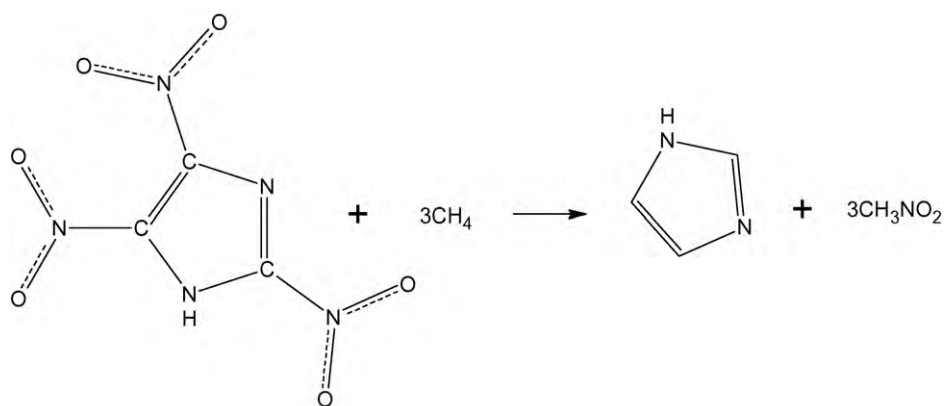
(5)



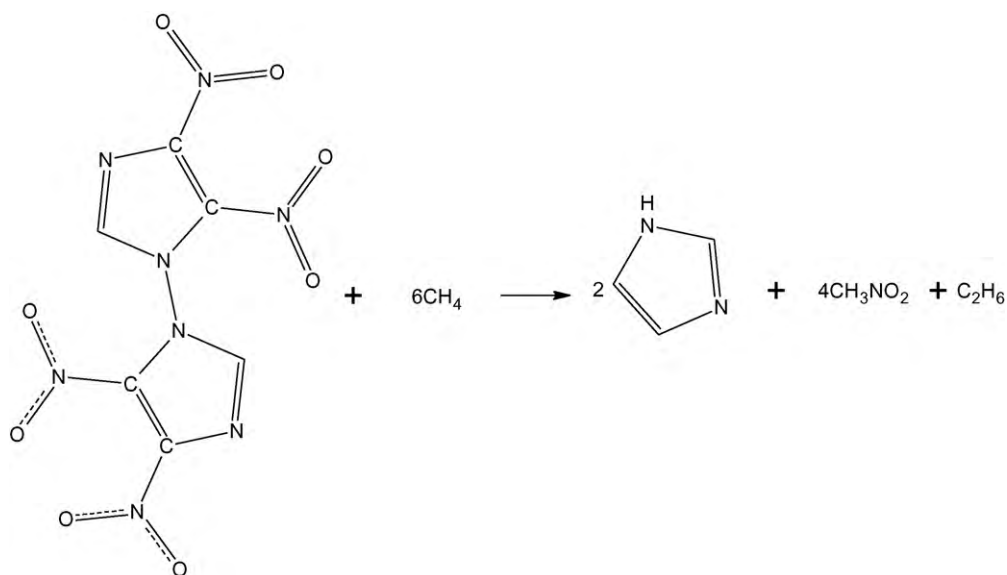
(6)



(7)



(8)



For the isodesmic reactions (3)–(9), heat of reaction ΔH_{298} at 298 K can be calculated from the following equation:

$$\Delta H_{298} = \sum \Delta H_{f,P} - \sum \Delta H_{f,R} \quad (10)$$

where $\Delta H_{f,P}$ and $\Delta H_{f,R}$ are the HOFs of products and reactants at 298 K, respectively. The HOFs of the title compounds can be figured out when the heat of reaction ΔH_{298} is known. The HOFs at 298.15 K can be calculated from the following equation:

$$\begin{aligned} \Delta H_{298.15\text{K}} &= \Delta E_{298.15\text{K}} + \Delta(PV) = \Delta E_0 + \Delta ZPE + \Delta H_T + \Delta nRT \\ &= \sum_{\text{product}} \Delta H_f^\circ - \sum_{\text{reactant}} \Delta H_f^\circ \end{aligned} \quad (11)$$

where ΔE_0 and ΔZPE are the total 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; $\sum_{\text{product}} \Delta H_f^\circ$ and $\sum_{\text{reactant}} \Delta H_f^\circ$ are sums of the heats of formation for products and reactants in gas at 298.15 K, respectively. $\Delta(PV)$ equals ΔnRT for reaction in gas phase. For isodesmic reactions, $\Delta n = 0$.

3. Results and discussion

3.1. Heats of formation

Table 1 lists the total energies, zero-point energies at B3LYP/6-31G** and B3P86/6-31G** methods for several reference compounds involved in the isodesmic reactions (3)–(9). Experimental HOFs are also included. Thermodynamic information was obtained from scaled vibrational frequencies with scaling factors taken from Scott and Radom [33]. The experimental HOFs of refer-

ence compounds CH_4 , C_2H_6 , CH_3NO_2 , $\text{C}_3\text{H}_4\text{N}_2$, C_6H_6 are taken from Refs. [34,35]. Table 2 shows the total energies, zero-point energies, and the HOFs obtained via Eq. (11).

It is noted from Table 2 that the HOFs calculated by B3LYP/6-31G** and B3P86/6-31G** methods are similar and the HOFs calculated by B3P86/6-31G** method are slightly smaller than those by B3LYP/6-31G** method. Table 2 also shows that the calculated heats of formation for the investigated molecules are all endothermic which is desirable for high energy density materials. In addition, from Table 2, the studied compounds can be divided into two categories, one is called direct imidazole derivatives (2,4-dinitroimidazole, 2,4,5-trinitroimidazole, 4,4',5,5',-tetranitroimidazole) and the other is 1-picrylimidazole derivatives (1-picrylimidazole, 2-nitro-1-picrylimidazole, 4-nitro-1-picrylimidazole, 2,4-dinitro-1-picrylimidazole).

From the calculated results, we can see that substituent groups greatly affect the HOFs of the 1-picrylimidazole derivatives. The HOFs of 1-picrylimidazole, 2-nitro-1-picrylimidazole, 4-nitro-1-picrylimidazole and 2,4-nitro-1-picrylimidazole are 55.4, 53.0, 50.6 and 50.4 kcal/mol at B3LYP/6-31G** level, respectively. This shows the value of HOF relates to the number of nitro groups and decreases with the augment of the number of the NO_2 group for the substituted 1-picrylimidazole. We think this is because the benzene ring shows the strong negative inductive effect and negative conjugative effect, when the nitro group is connected with the benzene ring, which makes the density of electric cloud decrease greatly and has effect on the properties of the substituted 1-picrylimidazole.

When the H atom on the C atom was replaced by the NO_2 group for 1-picrylimidazole, the HOFs of 2-nitro-1-picrylimidazole, 4-nitro-1-picrylimidazole and 2,4-nitro-1-picrylimidazole are all smaller than that of 1-picrylimidazole. In addition, we investigated the effect of NO_2 group substituted in different position. It is noted from Table 2 that when the nitro group being attached to the

Table 1
Calculated total energy (E_0), zero-point energy (ZPE) and experimental heats of formation (HOF) of the reference compounds at the B3LYP and B3P86 levels with 6-31G** basis set. E_0 is in a.u., ZPE and HOF are in kcal/mol.

Compound	B3LYP/6-31G**		B3P86/6-31G**		HOF	Ref.
	E_0	ZPE	E_0	ZPE		
CH_4	-40.478949	28.27885	-40.660240	28.31788	-17.8	[32]
C_2H_6	-79.763803	47.02293	-80.091342	47.14823	-20.1	[32]
CH_3NO_2	-244.963419	31.34752	-245.533251	31.58915	-19.3	[32]
$\text{C}_3\text{H}_4\text{N}_2$	-226.151837	44.71635	-226.799987	45.01910	31.8	[33]
C_6H_6	-232.157595	63.13859	-232.912464	63.36007	16.2	[33]

Table 2

Calculated total energy (E_0), zero-point energy (ZPE) and heats of formation (HOF) of the title compounds at the B3LYP/6-31G** and B3P86/6-31G** levels. E_0 is in a.u., ZPE and HOF are in kcal/mol.

Compound	B3LYP/6-31G**			B3P86/6-31G**		
	E_0	ZPE	HOF	E_0	ZPE	HOF
1-Picrylimidazole	-1070.574596	99.22	55.4	-1073.109383	100.12	54.6
2-Nitro-1-picrylimidazole	-1275.060554	100.67	53.0	-1277.985823	101.80	51.0
4-nitro-1-picrylimidazole	-1275.064334	100.80	50.6	-1277.988000	101.84	49.6
2,4-Nitro-1-picrylimidazole	-1479.546677	102.19	50.4	-1482.859564	103.37	49.0
2,4-Dinitroimidazole	-635.131726	48.03	21.9	-636.557927	48.60	21.3
2,4,5-Trinitroimidazole	-839.601279	49.22	31.0	-841.416087	49.92	29.1
4,4',5,5',-Tetranitroimidazole	-1268.991258	82.24	108.9	-1271.806501	83.33	108.5

2-position of imidazole, the HOF of the 2-nitro-1-picrylimidazole is 53.0 kcal/mol, whereas the HOF changes to 50.6 kcal/mol when the nitro group being attached to the 4-position of imidazole.

For the direct imidazole derivatives, substituent groups greatly affect the HOFs of substituted imidazole. 2,4-dinitroimidazole has two nitro groups and its HOF is 21.9 kcal/mol at B3LYP/6-31G** level. When another NO₂ group is attached to the 5-position of 2,4-dinitroimidazole, the HOF of 2,4,5-trinitroimidazole increases and is equal to 31.0 kcal/mol. If the H atom of 4,5-dinitroimidazole at 1-position is replaced by 4,5-dinitroimidazole, the HOF of 4,4',5,5',-tetranitroimidazole dramatically increases and its value is 108.9 kcal/mol. From above analysis, we can conclude that the value of HOF relates to the number and the position of nitro groups and increases with the augment of the number of the NO₂ group for the direct imidazole derivatives, which is contrary to the conclusion obtained for 1-picrylimidazole derivatives.

In view of these theoretical results, it is advisable for us to select the direct imidazole derivatives with more nitro groups or the substituted 1-picrylimidazole derivatives with less nitro groups in order to obtain the desirable energetic materials possessing high explosive performance.

Comparing the calculated HOFs by B3LYP/6-31G** and B3P86/6-31G** methods, one can obtain that the discrepancy of the two levels is very small, with deviations ranging from 0.1 to 1.9 kcal/mol, and with an average value of 1.0 kcal/mol. Further, the effects of the number and position of nitro groups on HOFs for the two levels are consistent with each other. The linear relationship between the HOFs from B3LYP/6-31G** and B3P86/6-31G** is very good:

$$\Delta H_f^\circ(\text{B3P86}) = -1.8826 + 1.0155 \times \Delta H_f^\circ(\text{B3LYP}) \quad (12)$$

with $R^2 = 0.9995$. The coherency obtained from the two levels demonstrates precision and suggests reasonable accuracy.

3.2. Molecular stability

As a high energetic explosive, the thermal stability of title compounds should be emphasized. The bond dissociation energy could evaluate the strength of bonding that is fundamental to understanding chemical processes [36], and provide useful information for understanding the stability of the substituted imidazole compounds. Owens [14] reported that the initial breakdown bond, for a number of different families of energetic molecules including imidazole derivatives, was the bond R–NO₂. To elucidate this, we calculated the dissociation energies for the possible initial steps in the pyrolysis route. It should be pointed out that we select the C–NO₂ bond as the possible breaking bond at the B3LYP/6-31G** and B3P86/6-31G** levels. The values of bond dissociation energies (BDE) and the experimental $h_{50\%}$ [37] are listed in Table 3. The calculated data by Jane Murray et al. [38] are also included. It is noted from Table 3 that our computational results are good agreement

with those calculated by Jane Murray, which shows the accuracy of our computation.

The BDE calculated by B3P86 functional is about 3.8 kcal/mol bigger than the result calculated by B3LYP functional, which is consistent with the result calculated before [39]. Chung et al. [40] concluded that a molecule should have more than a 20 kcal/mol barrier to dissociate in order to be considered as a viable candidate for new high energy density materials. From the calculated results in Table 3, it is noted that all the molecules investigated in this paper are all viable candidates for new high energy density materials.

For 1-picrylimidazole, we can notice that the C₁–N₁ and C₂–N₂ bonds are equivalent; the BDE of the C₁–N₂ bond is 59.2 kcal/mol for B3LYP method, which is smaller than that of the C₃–N₃ bond. This indicates that the rupture of C₁–N₂ or C₂–N₂ bond is the initial site in the decomposition process. Similarly, for 2-nitro-1-picrylimidazole, 4-nitro-1-picrylimidazole, 2,4-nitro-1-picrylimidazole, the C₁–N₁ and C₂–N₂ bonds are the weakest bonds and may be the initial scission step. 2-Nitro-1-picrylimidazole and 4-nitro-1-picrylimidazole are isomeric compounds. It is noted that the BDE of the C₁–N₁ bond for 2-nitro-1-picrylimidazole is 57.0 kcal/mol, which is slightly smaller than that of 4-nitro-1-picrylimidazole. This indicates that the position of substituent group slightly effects the BDE and 4-nitro-1-picrylimidazole is more stable than 2-nitro-1-picrylimidazole. The BDE of the C₁–N₁ bond for 2,4-nitro-1-picrylimidazole is bigger than that of 2-nitro-1-picrylimidazole, but smaller than that of 4-nitro-1-picrylimidazole.

For 2,4-dinitroimidazole, the BDE of the C₄–N₄ bond is 66.0 kcal/mol, which is smaller than that of the C₅–N₅ bond. This shows that the C₄–N₄ bond is the initial scission step. The 2,3-dinitroimidazole is the isomer of 2,4-dinitroimidazole. We computed the C₄–N₄ and N–N bond dissociation energies for 2,3-dinitroimidazole. The results show that the BDE of the C₄–N₄ bond is 57.3 kcal/mol, which is smaller than that of 2,4-dinitroimidazole, while the BDE of the N–N is only 20.2 kcal/mol. This shows that the position of the substituent group has great effect on the BDE of the imidazole derivatives. When one NO₂ group is at 3-position instead of 4-position, the N–N bond may be the initial site in the decomposition process because the nitro groups are in distinctively different electronic and steric effects.

While the BDE of the C₄–N₄ bond for 2,4,5-trinitroimidazole is 62.5 kcal/mol, which is larger than the BDEs of C₅–N₅ and C₆–N₆ bonds. A possible explanation for this behavior is the different electronic and steric effects for the nitro groups. The weakest bond for 2,4,5-trinitroimidazole is the C₅–N₅ bond and its BDE is 58.9 kcal/mol. For 4,4',5,5',-tetranitroimidazole which has four nitro groups, the C₅–N₅ bond is the weakest bond and the initial site in the decomposition process. Table 3 also shows that the increase of nitro group number on imidazole ring reduces the stability of the molecule, which is characterized by the decrease of the weakest C–NO₂ bond energy.

For the studied imidazole derivatives, the BDE values of the initial scission step are between 57 and 73 kcal/mol, which are bigger

Table 3
Bond dissociation energies (BDE, kcal/mol) for seven title compounds at B3LYP/6-31G** and B3P86/6-31G** levels.

Compound	B3LYP/6-31G**						B3P86/6-31G**						$H_{50\%}^a$
	C ₁ -N ₁	C ₂ -N ₂	C ₃ -N ₃	C ₄ -N ₄	C ₅ -N ₅	C ₆ -N ₆	C ₁ -N ₁	C ₂ -N ₂	C ₃ -N ₃	C ₄ -N ₄	C ₅ -N ₅	C ₆ -N ₆	
1-Picrylimidazole	59.2	59.2	63.6	-	-	-	62.8	62.8	67.5	-	-	-	314
2-Nitro-1-picrylimidazole	57.0	57.0	62.8	66.3	-	-	61.8	61.8	67.5	71.6	-	-	312
4-Nitro-1-picrylimidazole	59.5	59.5	62.5	-	68.9	-	63.1	63.1	66.4	-	-	-	161
2,4-Nitro-1-picrylimidazole	57.4	57.4	62.7	64.8	66.9	-	61.4	61.4	66.3	70.8	-	-	46
2,4-Dinitroimidazole	-	-	-	66.0	68.1 (68.5) ^b	-	-	-	-	70.3	72.0	-	105
2,4,5-Trinitroimidazole	-	-	-	62.5 (64.7)	58.9 (59.6)	60.8 (62.5)	-	-	-	63.0	65.9	-	68
4,4',5,5'-Tetranitroimidazole	-	-	-	-	58.2	61.0	-	-	-	62.2	64.9	-	37

The bold-faced number means that the corresponding bond is most reactive in the studied compound.

^a Data from Ref. [37].

^b The data in the bracket is taken from the Ref. [38].

than those of piperidine and diazocine compound [41] and polynitro benzoate molecules [42].

In the NBO analysis [43], the donor–acceptor (bond–antibond) interactions are taken into consideration by examining possible interactions between ‘filled’ (donor) Lewis-type NBOs and ‘empty’ (acceptor) non-Lewis NBOs and then estimating their energies by second-order perturbation theory. These interactions (or energetic stabilizations) are referred to as ‘delocalization’ corrections to the zeroth-order natural Lewis structure. The most important interaction between “filled” (donor) Lewis-type NBOs and “empty” (acceptor) non-Lewis NBOs is reported in Table 4.

It is noted from Table 4 that the second-order perturbation energies are smallest for $lp(O_2)$ participate as donors and the $BD^*(N_2-C_2)$ antibond as acceptors [$lp(O_2) \rightarrow BD^*(N_2-C_2)$] for 1-picrylimidazole derivatives. The charge transfer energy values are 4.00, 4.02, 3.98, 3.95 kcal/mol for 1-picrylimidazole, 2-nitro-1-picrylimidazole, 4-nitro-1-picrylimidazole, 2,4-dinitro-1-picrylimidazole at B3LYP level, respectively. The BDEs of the N_2-C_2 bond are the smallest for 1-picrylimidazole derivatives through the above analysis, which may be the initial site in the decomposition process. This shows that the smaller the second-order perturbation energies are, the smaller the bond dissociation energies are for 1-picrylimidazole derivatives.

The second-order perturbation energies for $lp(O_5)$ participating as donors and the $BD^*(N_5-C_5)$ antibond as acceptors [$lp(O_5) \rightarrow BD^*(N_5-C_5)$] are 4.30 and 4.38 kcal/mol for 2,4,5-trinitroimidazole and 4,4',5,5',-tetranitroimidazole respectively, which is the largest in the two compounds. While the second-order perturbation energy for $lp(O_4)$ participating as donors and the $BD^*(N_4-C_4)$ antibond as acceptors [$lp(O_4) \rightarrow BD^*(N_4-C_4)$] is 4.36 kcal/mol for 2,4-trinitroimidazole, which is largest in the compound. For the direct imidazole derivatives, the N_4-C_4 bond may be the initial site in the decomposition process for 2,4-dinitroimidazole and the N_5-C_5 bond may be the weakest bond for 2,4,5-trinitroimidazole and 4,4',5,5',-tetranitroimidazole. This shows that the bigger the second-order perturbation energies are, the smaller the bond dissociation energies are for the direct imidazole derivatives, which is contrary to the conclusion of 1-picrylimidazole derivatives.

Rice et al. [16] calculated the C–NO₂ BDEs of some nitroaromatic molecules. They concluded that there was a rough correlation between the logarithm of the impact sensitivity values $h_{50\%}$ and the BDE for rupture of the weakest bond in these molecules. Considering the complexity of detonation mechanism of high explosives, Fried et al. [44] believed that BDE was not the only factor influencing sensitivity, and the relationship involved other factors, as well. Their studies showed that the BDE scaled by energy content was a promising indicator for predicting high explosive sensitivity. So we examined the relationship between BDE/E and impact sensitivity. For the studied imidazole derivatives, a good linear relationship is observed in Fig. 2. The function relationship for the direct imidazole derivatives is given by Eq. (12) and the linear correlation coefficient is 0.999.

$$h_{50} = 15.5255 - 7.32 \times \left(\frac{BDE}{E} \right) \quad (13)$$

For 1-picrylimidazole derivatives, we also obtained the linear relationship. For 1-picrylimidazole, 4-nitro-1-picrylimidazole and 2,4-nitro-1-picrylimidazole, it is noted that the relationship between BDE/E and impact sensitivity is linear. The function relationship is $h_{50} = 589.3373 - 102.05136 \times (BDE/E)$, with the linear correlation coefficient R is 0.998. It is surprised to notice that 2-nitro-1-picrylimidazole is an exception. The relationship between BDE/E and impact sensitivity for 2-nitro-1-picrylimidazole deviates the straight line enormously. We think it is because that the 2-position nitro group at the imidazole is a withdrawing group and

Table 4

The second-order perturbation energies $E^{(2)}$ (kcal/mol) corresponding to the most important charge transfer interactions (donor → acceptor) in the compounds studied by using B3LYP method.

	Don.NBO	Acc.NBO	$E^{(2)}$		Don.NBO	Acc.NBO	$E^{(2)}$
2-nitro-1-Picrylimidazole	lpO ₁	BD ^a (N ₁ -C ₁)	4.04	4-Nitro-1-picrylimidazole	lpO ₁	BD ^a (N ₁ -C ₁)	4.04
	lpO ₂	BD ^a (N ₂ -C ₂)	4.02		lpO ₂	BD ^a (N ₂ -C ₂)	3.98
	lpO ₃	BD ^a (N ₃ -C ₃)	4.16		lpO ₃	BD ^a (N ₃ -C ₃)	4.14
	lpO ₄	BD ^a (N ₄ -C ₄)	4.43		lpO ₄	BD ^a (N ₄ -C ₄)	4.31
2,4-Dinitro-1-picrylimidazole	lpO ₁	BD ^a (N ₁ -C ₁)	3.96	1-Picrylimidazole	lpO ₁	BD ^a (N ₁ -C ₁)	4.01
	lpO ₂	BD ^a (N ₂ -C ₂)	3.95		lpO ₂	BD ^a (N ₂ -C ₂)	4.00
	lpO ₃	BD ^a (N ₃ -C ₃)	4.14		lpO ₃	BD ^a (N ₃ -C ₃)	4.18
	lpO ₄	BD ^a (N ₄ -C ₄)	4.39				
	lpO ₅	BD ^a (N ₅ -C ₅)	4.25				
2,4-Dinitroimidazole	lpO ₄	BD ^a (N ₄ -C ₄)	4.36	2,4,5-Trinitroimidazole	lpO ₄	BD ^a (N ₄ -C ₄)	4.09
	lpO ₅	BD ^a (N ₅ -C ₅)	4.28		lpO ₅	BD ^a (N ₅ -C ₅)	4.30
					lpO ₆	BD ^a (N ₆ -C ₆)	4.02
4,4',5,5',-Tetranitroimidazole	lpO ₅	BD ^a (N ₅ -C ₅)	4.38				
	lpO ₆	BD ^a (N ₆ -C ₆)	3.97				
	lpO ₅₁	BD ^a (N ₅₁ -C ₅₁)	4.39				
	lpO ₆₁	BD ^a (N ₆₁ -C ₆₁)	3.97				

^a lp stands for lone-pair.

makes the density of positive charge at the imidazole ring larger because of its negative inductive effect, which makes the BDE of 2-nitro-1-picrylimidazole decrease; when the nitro group is substituted at 4-position of imidazole, the density of electric cloud

on benzene ring decreases, which makes the BDE of 4-nitro-1-picrylimidazole bigger than that of 2-nitro-1-picrylimidazole.

3.3. The condensed phase heats of formation of imidazole derivatives studied

For assessment of the potential performance of the energetic material of interest, the desired quantity is usually the condensed phase ΔH_f° . In order to accommodate this need, we compute the condensed phase heat of formation of all mentioned energetic compounds through the same method of Byrd and Rice. According to Hess's law, the condensed phase heat of formation ($\Delta H_{f(s)}^\circ$) can be obtained by

$$\Delta H_{f(c)}^\circ = \Delta H_{f(g)}^\circ - \Delta H_{\text{sub}} \quad (14)$$

where $\Delta H_{f(g)}^\circ$ is the predicted gas-phase heat of formation, ΔH_{sub} is the heat of sublimation. The heat of sublimation can be represented as

$$\Delta H_{\text{sub}} = a(\text{SA})^2 + b\sqrt{(\sigma_{\text{tot}}^2 \nu)} + c \quad (15)$$

where the constants a , b , and c are determined through a least-squares fit of Eq. (15) with experimental values for ΔH_{sub} . SA is

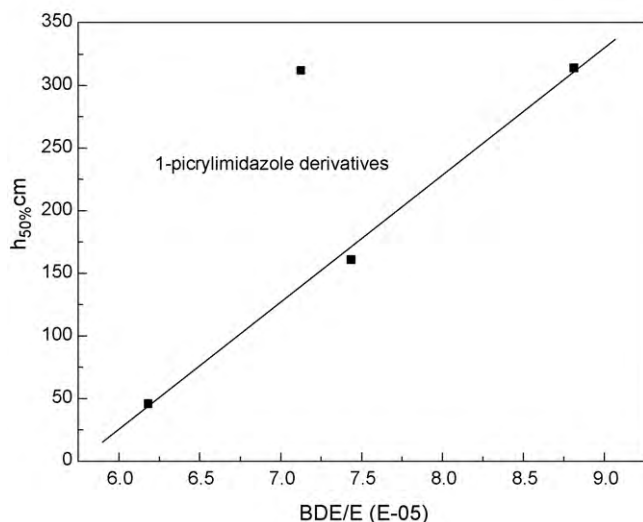
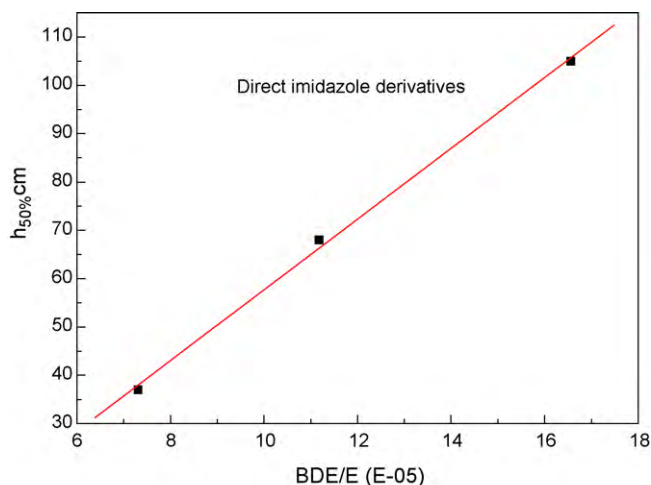


Fig. 2. The relationship between h_{50} and BDE/E for direct imidazole and 1-picrylimidazole derivatives.

Table 5

The predicted condensed phase heats of formation of the imidazole derivatives (kcal/mol).

Name	ΔH_f° (condensed)
1-Picrylimidazole (C ₉ H ₅ N ₅ O ₆)	70.8
2-Nitro-1-picrylimidazole (C ₉ H ₄ N ₆ O ₈)	70.4
4-Nitro-1-picrylimidazole (C ₉ H ₄ N ₆ O ₈)	70.4
2,4-Nitro-1-picrylimidazole (C ₉ H ₃ N ₇ O ₁₀)	70.0
2,4-Dinitroimidazole (C ₃ H ₂ N ₄ O ₄)	59.0
2,4,5-Trinitroimidazole (C ₃ HN ₅ O ₆)	58.6
4,4',5,5'-Tetranitroimidazole (C ₆ H ₂ N ₈ O ₈)	133.3

Table 6

Method for calculating the N , \bar{M} , and Q parameters of the C_aH_bO_cN_d explosives.

Parameters	Stoichiometric ratio		
N (mol/g)	$c \geq 2a + 0.5b$ $\frac{b+2c+2d}{4Mr}$	$2a + 0.5b > c > 0.5b$ $\frac{b+2c+2d}{4Mr}$	$0.5b > c$ $\frac{b+d}{2Mr}$
\bar{M} (g/mol)	$\frac{4Mr}{b+2c+2d}$	$\frac{56d+88c-8b}{b+2c+2d}$	$\frac{2d+28d+32c}{b+d}$
$Q \times 10^{-3}$ (J/g)	$\frac{120.9b+196.8a+\Delta H_f^\circ}{Mr}$	$\frac{120.9b+196.8(c-0.5b)+\Delta H_f^\circ}{Mr}$	$\frac{241.8c+\Delta H_f^\circ}{Mr}$

Table 7

The predicted densities and detonation properties of the title compounds.

Compounds	Q (kJ/g)	V (cm ³ /mol)	ρ (g/cm ³)	D (km/s)	P (GPa)
1-Picrylimidazole	5.466	147.22	1.90	10.78	53.64
2-Nitro-1-picrylimidazole	5.82	175.33	1.85	11.14	56.36
4-Nitro-1-picrylimidazole	5.82	175.33	1.85	11.14	56.36
2,4-Nitro-1-picrylimidazole	6.087	202.65	1.82	11.49	58.99
2,4-Dinitroimidazole	5.847	92.55	1.71	11.38	55.73
2,4,5-Trinitroimidazole	6.566	114.86	1.78	12.31	66.73
4,4',5,5'-Tetranitroimidazole	6.600	169.82	1.85	12.28	68.02

the surface area of the 0.001 electron/bohr³ isosurface of the electron density of the molecule, σ_{tot}^2 is a measure of the variability of electronic potential on the surface, and ν is the degree of balance between the positive and negative charges on the isosurface. The latter two quantities have been shown by Politzer et al. to be important in treating macroscopic properties that are dependent on noncovalent electrostatic interactions [45–47].

The B3LYP hybrid generalized-gradient approximation (GGA) density functional theory was used with 6-311++G(2df,2p) basis set to optimize geometries and determine the densities for generating the electrostatic potentials (ESPs) and the atom and group equivalents. The optimized structure is assumed to correspond to a local potential energy minimum. The computed condensed phase heats of formation are listed in Table 5.

3.4. Detonation performance data

Detonation velocity (D) and pressure (P) are the most important targets of scaling the detonation characteristics of energetic materials. For a series of the explosives with CHNO elements, detonation velocities and pressures can be calculated by using the Kamlet–Jacobs equation [48,49]:

$$D = 0.7062 \times \Phi^{0.5} (1.0 + 1.3\rho) \quad (16)$$

$$\Phi = N\bar{M}^{0.5}Q^{0.5}$$

$$P = 7.617 \times 10^8 \Phi \rho^2 \quad (17)$$

where each term in Eqs. (16) and (17) is defined as follows: P , detonation pressure (GPa); D , the detonation velocity (km/s); ρ , the packed density (g/cm³); Φ , the characteristics value of explosives; N , the moles of gas produced by per gram of explosives; \bar{M} , an average molar weight of detonation products; and Q , the estimated heat of detonation (kJ/g). Here, the parameters N , \bar{M} , and Q were calculated according to the chemical composition of each explosive as listed in Table 6. The HOFs calculated by B3LYP/6-31G** level are used. The density of each compound was predicted from the molecular volume divided by molecular mole mass, while the molecular volume of each molecule was calculated according to the method given by Politzer et al. [50].

Table 7 collects the predicted V , ρ , Q , D and P of the title compounds. Reviewing the direct imidazole and 1-picrylimidazole derivatives, it is noted that the values of D and P gradually increase when the number of –NO₂ group increases. For the isomeric compounds (4-nitro-1-picrylimidazole and 2-nitro-1-picrylimidazole) with the same number of –NO₂ groups, the difference between the values of D and P is very small. In a word, it shows that the introduction of nitro group can improve the detonation properties of the imidazole derivatives.

4. Conclusion

Based on the DFT computations for the imidazole derivatives, the following conclusions can be drawn:

- (1) The HOFs relates to the number and the position of nitro groups and increases with the augment of the number of the NO₂ group for the direct imidazole derivatives, while it decreases with the augment of the number of the NO₂ group for 1-picrylimidazole derivatives.
- (2) The position of nitro group slightly affects the BDE and the increase of nitro group number on imidazole ring reduces the stability of the molecule.
- (3) For the imidazole derivatives, the correlation is developed between impact sensitivity h_{50} and the ratio (BDE/E) of the weakest bond BDE to the total energy E , with the linear correlation coefficient R is larger than 0.99.
- (4) The detonation performance data are calculated according to the HOFs calculated by B3LYP/6-31G** level and the values of D and P gradually increase when the number of –NO₂ group increases.

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