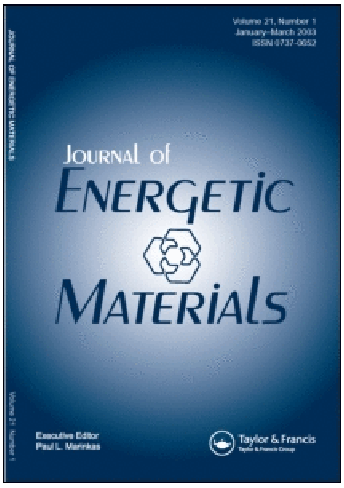

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Density Functional Theory Study of Several Nitrotriazole Derivatives

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Quantum chemical calculations at B3LYP/6-31G and B3P86/6-31G* levels are used to predict the bond dissociation energies (BDEs) of seven nitrotriazole derivatives. It is noted that the BDEs of the initial scission step are between 44 and 70 kcal/mol, which are larger than those of piperidine and diazocine compounds and polynitro benzoate molecules. In addition, substituent groups greatly affect the bond dissociation energies of the title compounds. The heats of formation (HOFs) for seven energetic materials are also calculated via designed isodesmic reactions. From computational results it is noted that substituent groups strongly affect the HOFs. The research demonstrated that the HOF of the compound substituted by a five-membered ring is larger than those substituted by a six-membered ring for 1,2,4-triazole. The detonation performance data of the title compounds are also calculated according to the HOFs calculated by B3LYP/6-31G* level.*

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Keywords: bond dissociation energy, density functional theory, heat of formation, nitrotriazole derivatives

Introduction

Energetic materials play an important role in aeronautics, the weapons industry, and other high-tech fields at present [1,2]. Development of new energetic materials and improvement of existing energetic materials have become topics of interest for experimentalists and theoreticians. The nitro group 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. The nitrotriazole derivatives are interesting energetic compounds [4]. The synthesis of nitrotriazole derivatives as energetic materials and as intermediates to energetic materials has received a great deal of attention in the past 10 years [5]. Baryshnikov et al. [6] have synthesized several 4-nitro-1,2,3 triazoles by reacting sodium azide with a variety of 1,1-dinitroethylene synthons. They also reported the synthesis of 5,5′-dinitro-4,4′-bi-1,2,3-triazole [7]. Wartenberg et al. [8] reported nitrotriazole explosive, 4,6-bis(5-amino-3-nitro-1,2,4-triazolyl)-5-nitropyrimidine (DANTNP). Prabhakaran et al. [9] have evaluated the kinetic parameters of 3-nitro-1,2,4-triazole-5-one (NTO) using various kinetic models. The $C{-}NO_2$ bond cleavage, with rupture of the adjacent C−N bond, has been suggested as the rate-determining step. Nitrotriazole derivatives represent a new generation of energetic materials, which are of interest because of their potential high density, energy, and properties as solid propellant oxidizers [10].

The dissociation energy of the weakest bond of an explosive molecule has been expected to play an important role in the initiation of detonation. Politzer and Murray calculated $C{-}NO_2$ and $N{-}NO_2$ bond dissociation energy in several small and moderately sized high explosives [11]. Murray et al. [12] obtained the links between surface electrostatic potentials of energetic molecules, impact sensitivities, and C−NO_2/N−NO_2 bond dissociation energies. Storm et al. [13] reported the impact sensitivities of 1-picryl-1,2,3-triazole, 2-picryl-1,2,3-triazole, 4-nitro-1-picryl-1,2,3-triazole, and 4-nitro-2-picryl-1,2,3-triazole. Politzer et al. [14] showed the decomposition of 4-nitro-1,2,3-triazole through the evolution of N_2 by using density functional analysis. Rice et al. [15] calculated C−NO_2 bond dissociation energies of some nitroaromatic molecules. Recently, Wu et al. [16] studied the binary collisions of pentaerythritol tetranitrate (PETN) and the correlation to shock sensitivity. They concluded that the dissociation mechanism of PETN remains unimolecular, and the dominant reaction channel is the breaking of the O−NO_2 bond. For a compound containing several nitro groups, it is necessary to determine which bond is the weakest bond.

In this article, the bond dissociation energies (BDEs) and heats of formation (HOFs) of several nitrotriazole derivatives are calculated. The HOFs are well known to evaluate the explosive performances of energetic materials. Computational approaches have shown their advantages and been employed to obtain HOFs of those demanding materials [17–21]. Thermal stability was evaluated via BDE [22].

Theory and Computational Details

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 and energy and frequency calculations were performed for nitrotriazole derivatives using the *Gaussian 03* package [25]. In this work, seven high explosive molecules were studied. All calculations of molecular geometry and energy were performed using DFT method; Becke three-parameters exchange; Lee, Yang, and Parr correlation functionals [26,27]; and Perdew 1986 gradient corrected correlation functional [28], with the default Gaussian convergence criteria for the seven molecules of this work.

The seven nitrotriazole derivatives are 1-(3′,4′dinitro pheny)-4-nitro-1,2,3-triazole ($C_8H_4N_6O_6$), 1-picryl-1,2,3-triazole

($C_8H_4N_6O_6$), 3-amino-5-picrylamino-1,2,4-triazole ($C_8H_6N_8O_6$), 3-nitro-1-picryl-1,2,4-triazole ($C_8H_3N_7O_8$), 4-nitro-1,2,3-triazole ($C_2H_2N_4O_2$), 4-nitro-1-picryl-1,2,3-triazole ($C_8H_3N_7O_8$), and 5,5′-dinitro-3,3′-bi-1,2,4-triazole ($C_4H_2N_8O_4$).

Here, because we assume a homolytic cleavage of the $C{-}NO_2$ bond while calculating BDEs, the fragments are radical species. The calculations of geometry and energy for all fragments were performed using the spin-unrestricted method with the same basis set 6-31G*. Vibrational analyses show 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. For every molecule, we optimized several possible stereoisomers and selected the structure with the lowest energy as the most stable structure.

The $R{-}NO_2$ 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 NO_2 group is removed [29]. For example, for 1-picryl-1,2,3-triazole($C_8H_4N_6O_6$), the BDE is

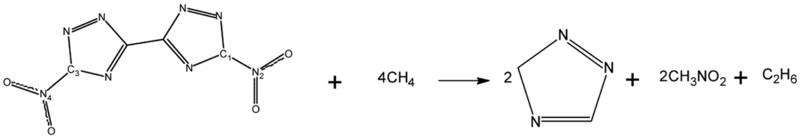
$$BDE = E(C_8H_4N_5O_4) + E(NO_2) - E(C_8H_4N_6O_6) \qquad (1)$$

The bond dissociation energy with ZPE correction is

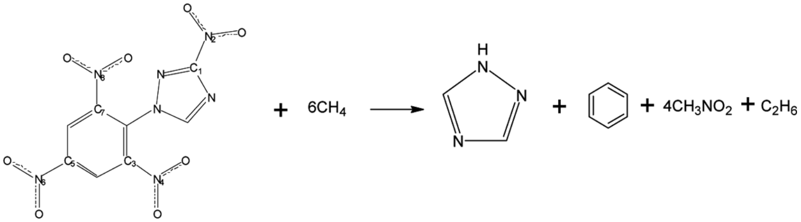
$$BDE_{ZPE} = BDE + \Delta ZPE \qquad (2)$$

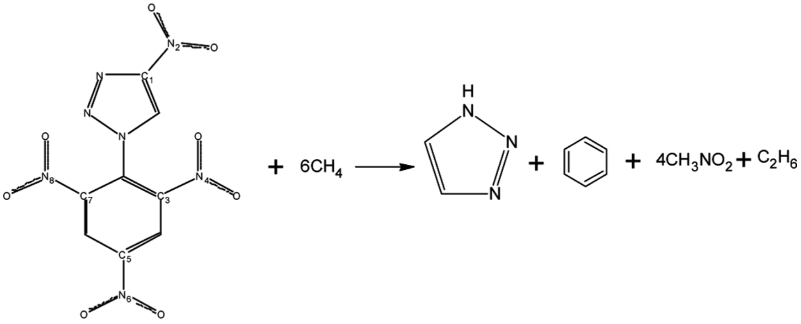
where ΔZPE is the difference between the zero-point energies (ZPE) of the products and the reactants.

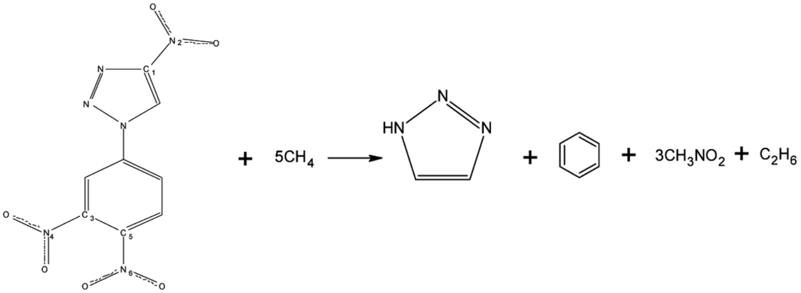
The predictions of HOFs adopt the hybrid DFT B3LYP and B3P86 methods with 6-31G* basis set via designed isodesmic reactions [30]. An isodesmic reaction is a kind of process in which the number of each kind of formal bond is conserved. Calculation errors inherent in the individual reactant and product molecules in the reactions are largely reduced. Thus, the calculated deviation of HOF will be small. The method of isodesmic reactions has been employed very successfully to calculate HOFs [31–33]. The enthalpy of formation for the title compounds was derived from the following isodesmic reactions:

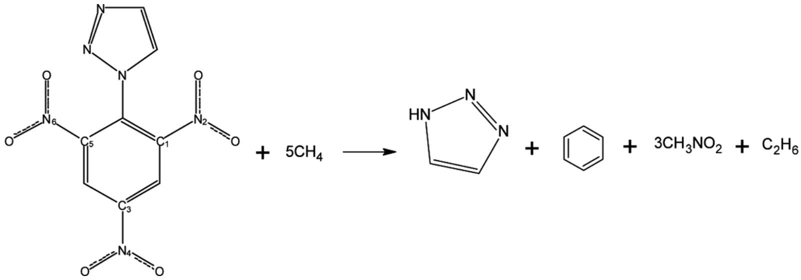


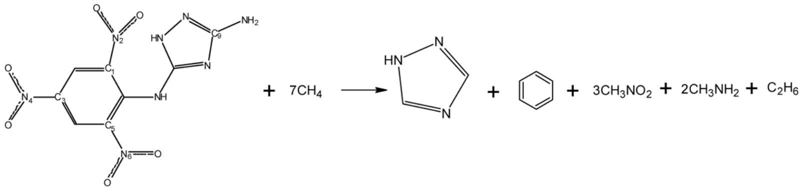
5, 5'-Dinitro-3, 3'-bi-1, 2, 4-triazole ($C_4H_2N_8O_4$)

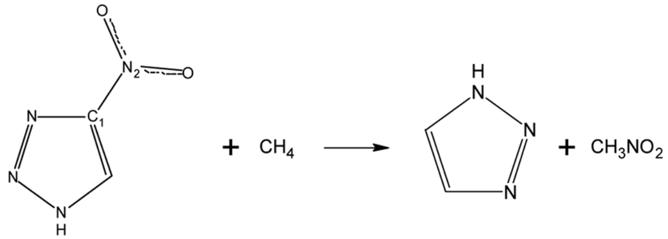












4-nitro-1, 2, 3-triazole ($C_2H_2N_4O_2$)

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

$$\Delta H_{298} = \sum \Delta H_{f,P} - \sum \Delta H_{f,R} \tag{10}$$

where $\Delta H_{f,P}$ and $\Delta H_{f,R}$ are the HOFs of reactants and products 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:

$$\begin{aligned}\Delta H_{298.15K} &= \Delta E_{298.15K} + \Delta(PV) = \Delta E_0 + \Delta ZPE + \Delta H_T + \Delta nRT\\ &= \sum_{product} \Delta H_f^0 - \sum_{reac\tan t} \Delta H_f^0 \end{aligned} \tag{11}$$

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 change in thermal correction to enthalpies between products and reactants; and $\Sigma_{product}\Delta H_f^0$ and $\Sigma_{reactant}\Delta H_f^0$ 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 the gas phase. For isodemic reactions, $\Delta n = 0$. Here, we should notice that what is really relevant to energetic materials is the solid-state value, but according to Hess's law, the solid-phase HOF can be obtained by using the gas HOF.

Results and Discussions

The Bond Dissociation Energies of Several Nitrotriazole Derivatives

The molecular structures are given in Eqs. (3)–(9). As a high energetic insensitive explosive, the thermal stability of title compounds should be emphasized. To elucidate this, we calculated the dissociation energies for the possible initial steps in the pyrolysis route. It should be pointed out that the $C{-}NO_2$ and $C{-}NH_2$ bonds on the ring were selected as the possible breaking bond at B3LYP/6-31G* and B3P86/6-31G* levels. The calculated BDEs are listed in Table 1. It is noted that the BDE calculated by B3P86 functional is by about 4.0 kcal/mol larger than the result calculated by B3LYP functional, which is consistent with the result calculated previously [34].

For compound (1), we can notice that the BDEs of the $C_1{-}N_2$ and $C_3{-}N_4$ bonds are equivalent. For compound (2), the BDEs of the $C_3{-}N_4$ and $C_7{-}N_8$ bonds are equivalent, so there are three possible breaking bonds, the $C_1{-}N_2$, $C_3{-}N_4$, and $C_5{-}N_6$ bonds. From Table 1, we can see that the BDE of the $C_3{-}N_4$ bond is the smallest and is equal to 44.91 kcal/mol for the B3LYP/6-31G* method. Compounds (2) and (3) are isomeric compounds, and it is noted that the BDE of the $C_5{-}N_6$ bond for compound (3) is the smallest and equal to 63.24 kcal/mol

Table 1

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

	B3LYP/6-31G*					B3P86/6-31G*				
Compound	C_1–N_2	C_3–N_4	C_5–N_6	C_7–N_8	C_9–NH_2	C_1–N_2	C_3–N_4	C_5–N_6	C_7–N_8	C_9–NH_2
(1)	**60.11**	60.11	—	—	—	64.32	64.32	—	—	—
(2)	55.50	**44.91**	52.74	44.91	—	58.71	49.50	56.77	49.50	—
(3)	85.58	65.86	**63.24**	65.86	—	89.28	69.59	66.56	69.59	—
(4)	68.20	**56.09**	56.52	—	—	72.02	59.98	60.40	—	—
(5)	**56.35**	63.28	56.35	—	—	60.21	67.67	60.21	—	—
(6)	**54.51**	67.28	54.51	—	110.18	58.69	71.35	58.69	—	115.31
(7)	**69.65**	—	—	—	—	73.52	—	—	—	—

Numbers in bold mean that the corresponding bond is most reactive in the studied compound.

for the B3LYP/6-31G* method; the BDE of the C_1-N_2 bond is the largest and equal to 85.58 kcal/mol. For compound (4), the BDE of the $C_5{-}N_6$ bond is slightly smaller than that of the $C_1{-}N_2$ bond and they are all larger than that of $C_3{-}N_4$ bond, which means that the $C_3{-}N_4$ bond is the initial scission step. For compounds (5) and (6), the BDEs of the $C_1{-}N_2$ and $C_5{-}N_6$ bonds are equivalent and smaller than that of the $C_3{-}N_4$ bond. The BDE of the C-NH_2 bond is much larger than that of the $C_3{-}N_4$ bond, so the $C_1{-}N_2$ or $C_5{-}N_6$ bond should be the initial scission step. It is noted that the BDE of the $C_1{-}N_2$ bond is 69.65 kcal/mol for compound (7).

For the title compounds, the BDEs of the initial scission step are between 44 and 70 kcal/mol, which are larger than those of piperidine and diazocine compounds [35] and polynitro benzoate molecules [36]. It is noted that substituted groups greatly affect the BDEs of title compounds. Compounds (1), (2), and (6) are 1,2,4-triazole derivatives, and from Table 1 it is noted that the BDE of the initial scission step is smaller if a six-membered ring (for example, a picryl group) is attached to 3-nitro-1,2,4-triazole compound. In addition, compound (7) is 4-nitro-1,2,3-triazole, whereas compounds (3), (4), and (5) are 4-nitro-1,2,3-triazole derivatives, so we can conclude that when a picryl group is attached to the 1 position of 4-nitro-1,2,3-triazole compound, the BDE of the initial scission bond decreases; when a 3′,4′dinitropheny group is attached to 4-nitro-1,2,3-triazole compound, the BDE of the initial scission bond also decreases. In addition, it is noted that the BDE of compound (4) is smaller than that of compound (3) for the initial scission bond.

From the above analysis, it is noted that compound (7) is the least reactive compound, whereas compound (2) is the most reactive compound among the title compounds.

In addition, the position of the subtituent group has a great effect on the BDE. The seven nitrotriazole compounds have many isomeric compounds. Here, we calculated some isomeric structures of the compound 4 (1-(3′,4′dinitropheny)-4-nitro-1,2,3-triazole) with the B3LYP/6-31G* method and obtained the dissociation energies for the possible

Table 2

Bond dissociation energies (BDE, kcal/mol) of some isomeric structures of the compound 4 at B3LYP/6-31G* level

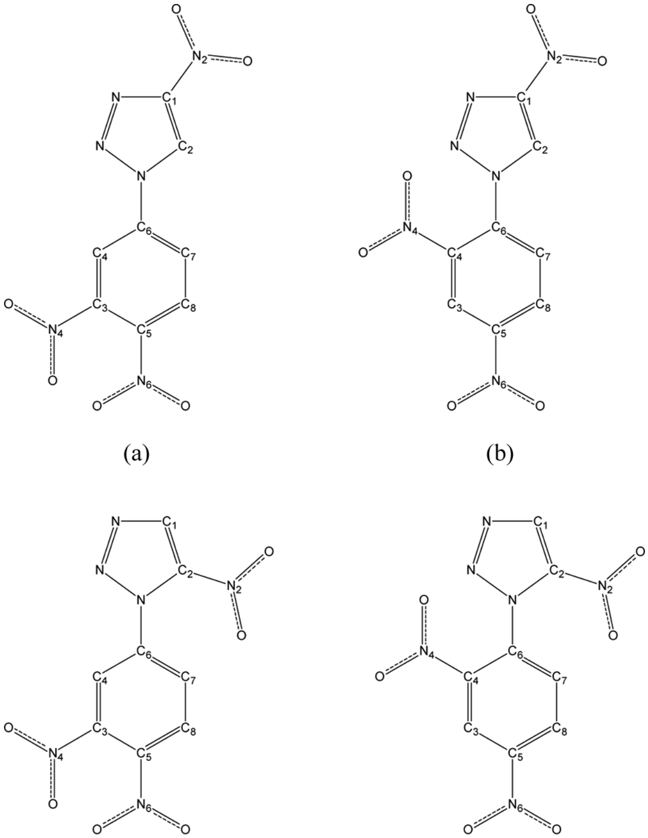
Compound	C_1–N_2	C_2–N_2	C_3–N_4	C_4–N_4	C_5–N_6
1-(3′,4′Dinitropheny)-4-nitro-1,2,3-triazole	68.20	—	**56.09**	—	56.52
1-(2′,4′Dinitropheny)-4-nitro-1,2,3-triazole	68.49	—	—	**58.30**	64.64
1-(3′,4′Dinitropheny)-5-nitro-1,2,3-triazole	—	73.72	**56.11**	—	56.39
1-(2′,4′Dinitropheny)-5-nitro-1,2,3-triazole	—	49.31	—	**33.30**	36.91

Numbers in bold mean that the corresponding bond is most reactive in the studied compound.

initial steps in the pyrolysis route. The results are listed in Table 2.

The molecular structures of four compounds are listed in Fig. 1. From Table 2, we can see that the BDEs of the C_2–N_2 bond are the largest for the four different compounds, whereas the BDE of the C_4–N_4 bond is the smallest, which shows that the cleavage of the C_4–N_4 bond may be the initial step in the pyrolysis route. In the four compounds, the BDE of the C_4–N_4 bond for 1-(2′,4′dinitropheny)-5-nitro-1,2,3--,2,3-triazole is the smallest, which shows that it is the most reactive compound.

The molecular structure of compound 6(a), the tautomeric structure of compound 6, is listed in Fig. 2. The result shows that the energy of compound 6(a) is −1197.26 a.u., which is slightly higher in energy than that of compound 6 (−1197.32 a.u.). The BDE of the C_1–N_2 bond is 64.0 kcal/mol, which is much larger than that of compound 6 (54.51 kcal/mol); the BDE of the C_3–N_4 bond is 66.53 kcal/mol, which is slightly smaller than that of compound 6 (67.28 kcal/mol). The above analysis shows that compound 6(a) is less reactive than compound 6.



(a) (b)

(c) (d)

Figure 1. Molecular frameworks and chemical names of some isomeric structures of compound 4. (a) 1-(3′,4′Dinitropheny)-4-nitro-1,2,3-triazole, (b) 1-(2′,4′dinitropheny)-4-nitro-1,2,3-triazole, (c) 1-(3′,4′dinitropheny)-5-nitro-1,2,3-triazole, and (d) 1-(2′,4′dinitropheny)-5-nitro-1,2,3-triazole.

Heats of Formation

Table 3 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

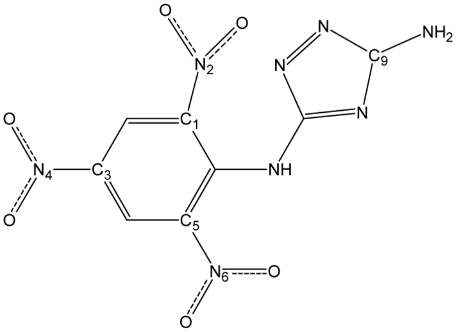


Figure 2. Tautomeric structure of compound 6.

obtained from scaled vibrational frequencies with scaling factors taken from Scott and Radom [37]. The experimental HOFs of reference compounds CH_4, C_2H_6, CH_3NO_2, CH_3NH_2, and C_6H_6 are taken from the literature [38–41]. Table 4 shows the total energies, zero-point energies, values of the thermal corrections for title compounds, and values of HOFs obtained via Eq. (11). Previous studies showed that theoretically predicted HOFs were in good agreement with experimental values by choosing appropriate reference compounds in the isodesmic reactions [23–33].

It is noted from Table 4 that the HOFs calculated by the B3LYP/6-31G* and B3P86/6-31G* methods are similar and the HOFs calculated by the B3P86/6-31G* method are slightly smaller than that by the B3LYP/6-31G* method. From the calculated results, we can see that substituent groups greatly affect the HOFs of the title compounds. The HOFs of compounds (1), (2), and (6) are 95.75, 70.84, and 50.48 kcal/mol at B3LYP/6-31G* level, respectively. The gas HOF for 1,2,4-triazole is 46.1 kcal/mol [42]. This shows that the HOF of the compound increases when an H group is substituted by a five-membered or six-membered ring for 1,2,4-triazole. In addition, the HOF of the compound substituted by a five-membered ring is larger than that substituted by a six-membered ring for 1,2,4-triazole.

Compounds (3) and (4) are 4-nitro-1,2,3-triazole derivatives. Their HOFs are 68.48 and 85.81 kcal/mol at the

Table 3

Calculated total energy (E_0), zero-point energy (ZPE), and experimental heats of formation (HOF) of the reference compounds at the B3LYP/6-31G* and B3P86/6-31G* levels

	B3LYP/6-31G*		B3P86/6-31G*			
Compound	E_0 (a.u.)	ZPE (kcal/mol)	E_0 (a.u.)	ZPE (kcal/mol)	HOF (kcal/mol)	Ref.
CH_4	−40.473159	28.38	−40.650837	28.45	−17.8	[35]
C_2H_6	−79.755178	47.21	−80.078714	47.35	−20.05	[35]
CH_3NO_2	−244.959157	31.49	−245.523957	31.73	−19.3	[35]
CH_3NH_2	−95.788776	40.43	−96.111192	40.63	−5.4	[36,37]
C_6H_6	−232.147908	63.22	−232.897882	63.45	16.2	[38]
1,2,3-Triazole	−242.163213	37.09	−242.805384	37.42	65.07	[39]
1,2,4-Triazole	−242.189296	37.64	−242.831496	37.95	46.1	[40]

Table 4
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

	B3LYP/6-31G*			B3P86/6-31G*		
Compound	E_0 (a.u.)	ZPE (kcal/mol)	HOF (kcal/mol)	E_0 (a.u.)	ZPE (kcal/mol)	HOF (kcal/mol)
1	−892.164964	65.65	95.75	−894.201185	66.60	95.37
2	−1291.095157	93.64	70.84	−1293.998034	94.70	70.39
3	−1291.072879	93.14	68.48	−1293.975345	94.23	68.24
4	−1086.593911	92.03	85.81	−1089.110295	92.95	85.65
5	−1086.588000	91.70	89.54	−1089.104478	92.64	89.34
6	−1197.318157	114.18	50.48	−1200.127128	115.28	47.48
7	−446.651596	38.78	63.22	−447.670507	39.26	63.17

B3LYP/6-31G* level, respectively. The gas HOF for 4-nitro-1,2,3-triazole is 63.22 kcal/mol [43]. This shows that that the HOFs of compounds increase when an H group is substituted by a six-membered ring for 4-nitro-1,2,3-triazole. The structural comparison between compounds (3) and (4) shows that the nitro group can decrease the HOF of title compounds. Compound (5) is a 1,2,3-triazole derivative; it is noted that the HOF increases when an H group is substituted by a picryl group. In addition, the investigation shows that the HOFs of compounds 6 and 6(a) are same.

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 [44,45]:

$$D = 0.7062 \times \Phi^{0.5}(1.0 + 1.3\rho) \tag{12}$$

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

$$P = 7.617 \times 10^{8}\Phi\rho^{2} \tag{13}$$

where each term in Eqs. (12) and (13) is defined as follows: P is detonation pressure (GPa); D is the detonation velocity (km/s); ρ is the packed density (g/cm^3); Φ is the characteristics value of explosives; N is the moles of gas produced by per gram of explosives; $\bar{M}$ is an average molar weight of detonation products; and Q is 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 5 [44,45]. The HOFs calculated by B3LYP/6-31G* level are used. The density of each compound was predicted from the molecular volume divided by molecular weight, and the molecular volume of each molecule was yielded from the statistical average of 100 single-point molar volume calculations for each

Table 5
Method for calculating the N, $\bar{M}$, and Q parameters of the $C_aH_bO_cN_d$ explosives

	Stoichiometric ratio		
Parameters	$c \geq 2a + 0.5b$	$2a + 0.5b > c > 0.5b$	$0.5b > c$
N (mol/g)	$\frac{b+2c+2d}{4Mr}$	$\frac{b+2c+2d}{4Mr}$	$\frac{b+d}{2Mr}$
$\bar{M}$ (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)	$\frac{120.9b+196.8a+\Delta H_f^o}{Mr}$	$\frac{120.9b+196.8(c-0.5b)+\Delta H_f^o}{Mr}$	$\frac{241.8c+\Delta H_f^o}{Mr}$

optimized structure. The molar volume was defined as inside a contour of 0.001 electrons/Bohr^3 density that was evaluated using a Monte Carlo integration implemented in the *Gaussian 03* [25] program. This method has accurately predicts the densities, detonation velocities, and detonation pressures of the explosives [46–50].

Table 6 reports the predicted V, ρ, Q, D, and P of the title compounds. Reviewing the compounds from 1 to 7, the values of D and P dramatically increase when the number of –NO_2

Table 6
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)	5.45	79.0	2.86	7.86	26.7
(2)	5.96	145.0	2.24	9.17	42.0
(3)	5.96	146.0	2.22	9.06	41.2
(4)	5.82	140.7	1.99	8.16	31.3
(5)	5.82	140.7	1.99	8.16	31.3
(6)	4.93	158.0	1.96	7.87	29.0
(7)	6.17	66.0	1.73	8.18	28.9

group is equal to, or larger than, 3. However, the values of D and P decrease a bit if there are other substituted groups in the molecule. For the isomeric compounds (2 and 3, 4 and 5) with the same number of $-NO_2$ groups, the difference between the values of D and P is small.

Conclusion

Through DFT study of the BDEs for seven compounds, it is noted that substituted groups affect the BDEs of title compounds and the BDEs of the initial scission step are between 44 and 70 kcal/mol. Through analyzing the computational results, we think that compound (7) is the least reactive compound, whereas compound (2) is the most reactive compound among the title compounds. The calculations of HOF suggest that the substituted groups affect the HOF values of title compounds. The HOF of the compound increases when an H group is substituted by a five-membered or six-membered ring for 1,2,4-triazole, and this conclusion is the same for 4-nitro-1,2,3-triazole. The detonation performance data of the title compounds are also calculated according to the HOFs calculated by B3LYP/6-31G* level.

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